



ATTEMPTS TO GENERATE C_2 FROM ACETYLENE DERIVATIVES

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January, 1967

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ABSTRACT

Lithiobromoacetylide has been generated via (1) monobromination of lithium carbide, (2) halogen-metal exchange between dibromoacetylene and methyllithium, and (3) metallation of monobromoacetylene from dehydrohalogenation of 1,2-dibromoethylene. It could be trapped with cyclohexanone to give the expected 1-(bromoethynyl)cyclohexanol, but in the absence of such a substrate it was found to be extremely unstable, undergoing rapid disproportionation to C_2Br_2 and Li_2C_2 and/or polymerization, the preferred mode of decomposition being solvent-dependent. Under no circumstances could vicinal elimination of LiBr to produce C_2 be shown to have occurred nor was it necessary to invoke the intermediacy of C_2 to explain the products formed. Changing the cation of the metalbromoacetylide to potassium did not manifestly alter the results. Although the stepwise reaction of *n*-butyllithium with tetrabromoethylene did not lead to lithio-bromoacetylide, it exposed an interesting free-radical reaction between *n*-butyl bromide and *n*-butyllithium, the kinetics of which was briefly investigated.

Diiodoacetylene was found to undergo thermal decomposition at 150° by a first-order process in cumene, cyclooctane, and *n*-nonane as solvents. The rate of decomposition was solvent-dependent (ratios of rate constants = 1:0.3:0.06, resp.), and the nature of the products suggests that stepwise homolytic cleavage of the C-I bonds must be involved. No evidence supporting the intermediacy of a C_2 species was obtained. The stoichiometry of the reaction in cumene was determined, and a series of reaction steps, not involving a radical-chain process, is proposed to account for the observed products and stoichiometry. Triiodoethylene, a product of the decomposition in all three solvents, was synthesized by an independent route. Photolysis of diiodoacetylene in cyclohexene solution produced a significant yield of benzene (0.4 mmole/mole C_2I_2).

Lithioiodoacetylide, generated by reaction of C_2I_2 with one molar equivalent of methyllithium, was found to be a stable compound in cyclo-

hexene and ether solutions; its existence was established by deuteration and condensation with cyclohexanone. In THF solution, however, it was spontaneously alkylated by methyl iodide generated in situ to give 1-iodopropyne. When heated to 150° in cumene or when generated in THF in the absence of an alkylating agent, it polymerized readily. Photolysis of lithioiodoacetylide in cyclohexene solution led to moderate yields of 3,3'-bicyclohexenyl. This result implies the occurrence of a free-radical reaction which was shown to be characteristic of the photo-reaction between alkyl iodides and organolithium compounds in general. The addition of n-butyllithium to an alkyl iodide was found to greatly alter the course of the photodecomposition of the alkyl iodide and to result in a system which is an efficient source of free radicals. It is suggested that the organometallic reagent functions as a scavenger of iodine atoms and that the parallel results obtained in the photolysis of lithioiodoacetylide are a consequence of the latter's ability also to scavenge iodine atoms produced by homolytic photocleavage of the C-I bond. Thus, none of the pathways by which lithioiodoacetylide has been made to decompose requires the postulation of the intermediacy of a C₂ species.

Thesis Supervisor: William R. Moore
Title: Associate Professor of Chemistry

TO MY WIFE AND CHILDREN

ACKNOWLEDGEMENTS

The author wishes to thank Professor William R. Moore for imaginative guidance throughout the course of the work described and for discussions which led to a fuller and more meaningful interpretation of experimental results. No less helpful was his willingness to encourage and to stimulate when the occasion demanded, as it often did, and to provide respite by presiding over debates concerning matters more mundane than chemistry.

Special acknowledgement is made to the late Professor Arthur C. Cope for his generosity and understanding in permitting the author to return to his studies at M.I.T. after a prolonged absence, under conditions which reduced the burden which might have been imposed were he less concerned with the plight of the individual.

Thanks are due to the Department of Chemistry for financial assistance in the form of a Teaching Assistantship, to the National Institutes of Health for the granting of a Predoctoral Fellowship, and to George M. Rubottom and Stan S. Hall for help in obtaining spectral data.

Finally, special thanks for forbearance and the maintenance of a semblance of family life in the face of unimaginable odds must be awarded to my wife and children, without whose support and understanding this endeavor could not have succeeded.

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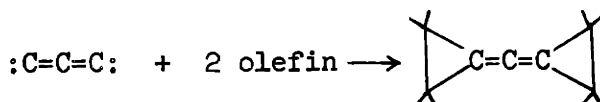
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INTRODUCTION

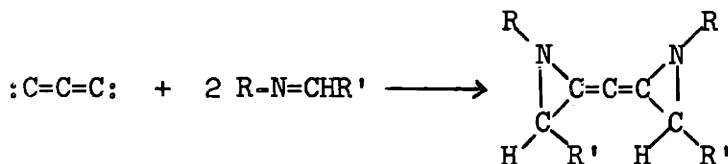
The existence of polyatomic carbon species from various high energy sources has been recognized for some time. Carbon vapor generated in a Knudsen cell was first reported to contain C, C₂, C₃, and possibly C₄ and C₅ by Chupka and Inghram.¹ These results were later extended by the use of mass spectroscopic experiments to measurements of the equilibrium composition of carbon vapor,² which showed the relative abundances of C, C₂, C₃, C₄, and C₅ to be 1, 2.8, 4.5, 0.35, and 0.5, respectively, at 4100°K.

Not until the pioneering trapping experiments of Skell³ were the chemical properties of any of the polyatomic species investigated. Utilizing carbon vapor generated from a carbon arc, he succeeded in trapping C₃ with olefins, the products being bisethanoallenes. C₃ was shown to be a nonselective dicarbene for olefin additions, but yet it did not show insertion properties. Its spectroscopically predicted singlet



ground state was confirmed by the stereospecificity of its addition to cis- and trans-2-butenes. C₃ has subsequently been added to imines using Skell's procedure.⁴

1. W. A. Chupka and M. G. Inghram, J. Phys. Chem., 59, 100 (1955) and earlier references therein.
2. J. Drowart, R. P. Burns, G. DeMaria, and M. G. Inghram, J. Chem. Phys., 31, 1131 (1959).
3. P. S. Skell and L. D. Wescott, J. Am. Chem. Soc., 85, 1023 (1963); P. S. Skell, L. D. Wescott, J. P. Golstein, and R. R. Engel, ibid., 87, 2829 (1965).
4. I. E. Den Besten and C. R. Wenger, ibid., 87, 5500 (1965).



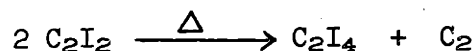
No comparable investigation has as yet been made of the chemical properties of C_2 . Using chiefly the spectroscopically observed Swan system of bands,⁵ C_2 has been reported from a number of other high energy sources, viz., the carbon tube furnace,⁶ hydrocarbon flames,⁷ the oxy-acetylene flame,⁸ the thermal decomposition of diacetylene,⁹ the explosive combustion of acetylene,¹⁰ and in high frequency electrical discharges in gases and flames.^{11,12} However, in no case were substrates introduced which might have acted as potential trapping agents for the C_2 species.

-
5. J. G. Phillips, *Astrophys. J.*, 108, 434 (1948).
 6. W. R. S. Garton, *Proc. Phys. Soc. (London)*, A66, 848 (1953).
 7. a) E. T. Child and K. Wohl, *Symposium Combustion, 7th, London and Oxford*, 215 (1958); *C.A.*, 54, 10271 (1960); b) R. Kushida and K. Wohl, *ibid.*, 221 (1958); *C.A.*, 54, 12537 (1960); c) U. Bonne, W. Jost, and H. G. Wagner, *Am. Chem. Soc., Div. Fuel Chem., Preprints*, 1, 6 (1961); *C.A.*, 58, 11162 (1963).
 8. a) G. V. Marr, *Can. J. Phys.*, 35, 1265, 1275 (1957); b) R. P. Broida and D. F. Heath, *J. Chem. Phys.*, 26, 223 (1957); c) N. A. Nesterko, *Nauch. Zapiski, Dnepropetrovskii Gosudarst. Univ.*, 72, 51 (1957); *C.A.*, 55, 1179 (1961); d) T. Takahishi, E. Yoshida, and A. Masuko, *Kogyo Kagaku Zasshi*, 63, 1364 (1960); *C.A.*, 56, 10442 (1962).
 9. J. H. Callomon and D. A. Ramsay, *Can. J. Phys.*, 35, 129 (1957).
 10. R. G. W. Norrish, G. Porter, and B. A. Thrush, *Proc. Roy. Soc. (London)*, A216, 165 (1953).
 11. a) V. S. Rossikhin and I. L. Tsikora, *Zhur. Fiz. Khim.*, 29, 1080 (1955); *C.A.*, 51, 817 (1957); b) V. S. Rossikhin and I. L. Tsikora, *ibid.*, 30, 453 (1956); *C.A.*, 51, 3271 (1957); c) V. S. Rossikhin, *Nauch. Zapiski, Dnepropetrovsk. Univ.*, 72, 33 (1957); *C.A.*, 55, 12027 (1961).
 12. M. McCarty and G. W. Robinson, *J. chim. phys.*, 56, 723 (1959).

Before considering the possible modes of reactivity of a C_2 species, a consideration of the allowable electronic configurations of the diatomic molecule may be pertinent. In carbon the π_u and σ_g' levels are so spaced that their energies are nearly the same, and we would expect the three configurations $(\sigma_g)^2(\sigma_u)^2(\pi_u)^4: {}^1\Sigma_g^+$, $(\sigma_g)^2(\sigma_u)^2(\pi_u)^3(\sigma_g'): {}^3\Pi_u$, and $(\sigma_g)^2(\sigma_u)^2(\pi_u)^2(\sigma_g')^2: {}^3\Sigma_g^-$ thus to have approximately the same energy.^{13a} Mulliken predicted^{13a,b} that the ${}^3\Pi_u$ configuration (lower state of the Swan bands) is probably of lowest energy, with ${}^3\Sigma_g^-$ a close second, and ${}^1\Sigma_g^+$ not very much higher. The appearance of both singlet (Mulliken) and triplet (Swan) absorption systems at equal intensity during the explosive combustion of acetylene¹⁰ did not allow a conclusion as to which was the ground state. However, experimental evidence that the ${}^3\Pi_u$ state is the ground state of C_2 has been presented.¹² It has been generally accepted that the ${}^3\Pi_u$ state is lowest with the ${}^3\Sigma_g^-$ state observed at 16.2 kcal/mole (0.70 e.v.) and the ${}^1\Sigma_g^+$ state at 8 ± 4 kcal/mole (0.35 e.v.).¹⁴ Nonetheless, the view has recently been expressed¹⁵ that the ${}^1\Sigma_g^+$ configuration is the ground state, albeit by less than 0.1 e.v. Clearly, then, the multiplicity of the C_2 molecule's ground state is a moot question, energy differences of very small magnitude obviously being involved.

-
13. a) R. S. Mulliken, Phys. Rev., 56, 778 (1939); b) R. S. Mulliken, Rev. Mod. Phys., 4, 65, 81 (1932).
14. K. S. Pitzer and E. Clementi, J. Am. Chem. Soc., 81, 4477 (1959).
15. H. B. Gray, "Electrons and Chemical Bonding," W. A. Benjamin, Inc., New York, 1965, p. 56.

Our own chief interest lay in the desire to generate C_2 at the laboratory bench and to attempt to trap it in a relatively unsophisticated manner. In this way we would hope to exploit quickly any reaction between C_2 and substrate which might lead to interesting and novel products and thus contribute a useful intermediate to the fields of both synthetic and mechanistic organic chemistry. In fact, as early as 1904 a claim was made for the generation of C_2 from the thermal decomposition of diiodoacetylene and from the treatment of the same



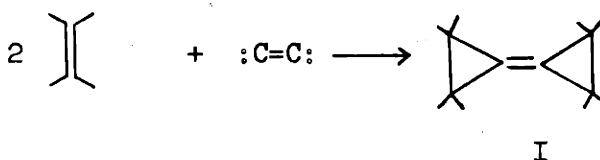
compound with alcoholic alkali.¹⁶ Carbon was reported to be a product of the former reaction, but no extensive exploration of the chemistry involved or of the C_2 species itself appears to have been undertaken. However, this claim prompted us to reinvestigate the reaction in question, and as a result we have been able to elucidate its course in some detail. Under the conditions which we employed, C_2 could not be shown to be an intermediate from the thermal decomposition of diiodoacetylene (see Results and Discussion).

The general approach which we chose for our attempts to generate C_2 was to induce the vicinal elimination of metal halide from metallohaloacetylides. Such an elimination is useful for introducing unsaturation into molecules, but in the case of metallohaloacetylides an electron-deficient C_2 species would result:



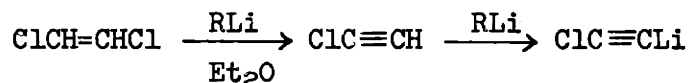
16. R. Schenck and J. Litzendorff, Chem. Ber., 37, 3453 (1904).

What electronic configuration the species might exhibit under the conditions used to generate it, i.e., whether singlet ("dicarbene") or triplet (diradical), would be difficult to predict. For synthetic purposes the dicarbene form was certainly of great interest for it would offer a route to the difficultly accessible system I. The substrate generally chosen for trapping C₂ in our experiments was cyclohexene, for not only would it be expected to undergo reaction with a dicarbene to give



a product of the type I, but it is also known to react with free radicals to give dehydrogenation (cyclohexadiene, benzene), coupling (3,3'-bicyclohexenyl), addition, or substitution products. Thus, the product(s) derived from cyclohexene would be expected to be an excellent indicator of the electronic state of the C₂ generated.

Lithiochloroacetylide had already been prepared and some of its chemical properties studied.¹⁷ It was generated by three routes and was found to be remarkably stable in the absence of reactive substrates. It



readily condensed with carbonyl compounds and was alkylated by alkyl

17. H. G. Viehe, ibid., 92, 1270, 1950, 3064 (1959).

halides. The corresponding sodium derivative was even isolated from the liquid ammonia system in a paraffin matrix and its infrared spectrum measured.

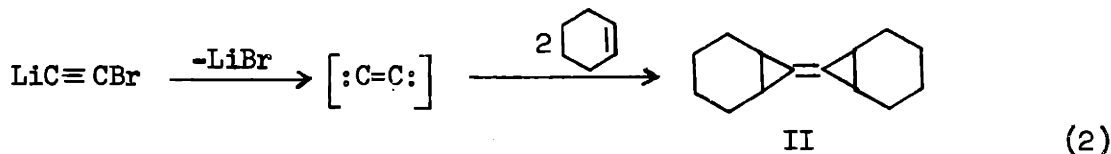
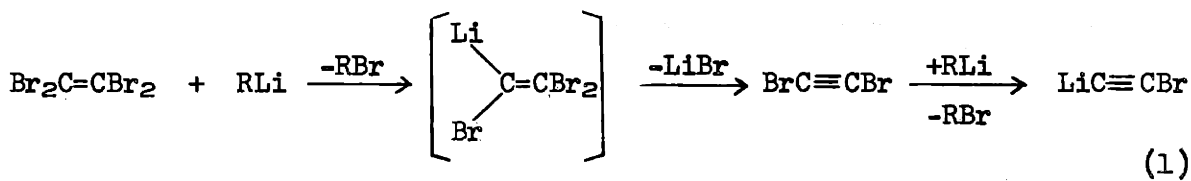
The high stability of the metallochloroacetylide series did not deter us, since we anticipated that the corresponding bromo and iodo compounds would exhibit a greater propensity for β -elimination of the metal halide, as is known to be the case for more highly saturated compounds. Thus, the investigations to be described are concerned chiefly with the generation and modes of decomposition of metallobromo- and -iodoacetylides and other chemistry related to findings which arose during the course of this study.

RESULTS AND DISCUSSION

A. Generation and Decomposition of Lithiobromoacetylide

1. The Reaction of Tetrabromoethylene with Alkyl lithium Reagents

It was anticipated that the sequence of reactions (1) involving two successive halogen-metal exchange processes would be a direct route to the desired metallohaloacetylide. Spontaneous elimination of LiBr hopefully would then occur generating the desired dicarbenic C₂ which in the presence of cyclohexene would lead to formation of the known¹⁸ product II (eq. 2).



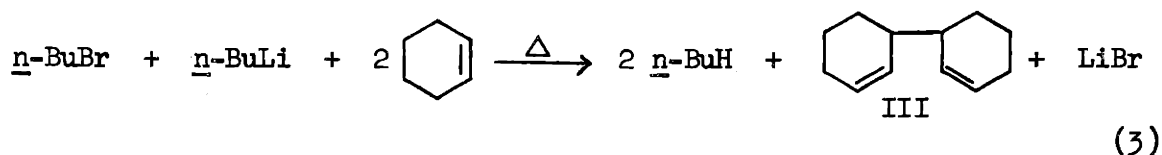
When tetrabromoethylene was treated with a 100% excess of methyl lithium in cyclohexene as solvent at 0° or at room temperature, the halide was rapidly consumed but g.l.c. analysis disclosed that no II was obtained, nor were any other products detected. (The g.l.c. conditions employed were such that a yield of II as low as 0.5% would have been detected). Slow treatment with excess *n*-butyllithium, however, in refluxing cyclohexene produced a single product, which upon isolation

18. H. R. Ward, Ph.D. Thesis, M.I.T., Nov. 1960.

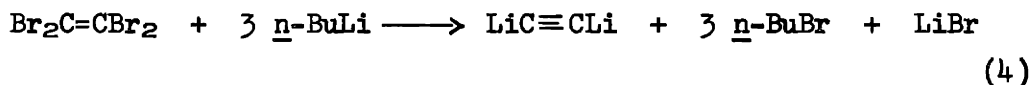
by preparative g.l.c. yielded spectral data consistent with its being 3,3'-bicyclohexenyl (III) (see Experimental). When the reaction was run at 0° only a trace of III was obtained, but in neither case was any II detected. Control experiments established that neither tetrabromoethylene nor n-butyllithium alone could give rise to III under the conditions employed.

The structural nature of the product III strongly suggested that either free radicals had been generated during the reaction (1) (R = n-butyl) or that a cyclohexene intermediate metallated in the 3-position might be involved in a coupling reaction. The intermediacy of any 3-lithiated cyclohexene as a precursor to III was ruled out, however, when it was found that cyclohexene was not metallated by n-butyllithium at the reflux temperature. Subsequently it was found that when only the "stoichiometric" amount of n-butyllithium (2 moles/mole C₂Br₄) was employed (eq. 1), no III was obtained and approximately one-third of the tetrabromoethylene remained. This result suggested that (a) the lithium reagent is consumed by a side reaction in addition to its reaction with tetrabromoethylene and (b) the formation of III requires the presence of excess n-butyllithium, either as a catalyst for the decomposition of lithiobromoacetylide to a radical species or as a reactant which itself is directly involved in the formation of free radicals. That the latter route to III was in fact operative was clearly shown by carrying out the thermal reaction between equimolar amounts of n-butyllithium and n-butyl bromide in refluxing cyclohexene and noting that the rate of formation and yield of III obtained corresponded closely to what was observed during the conduct of reaction (1). Thus, LiC≡CBr or a C₂ species were not necessary to explain the

production of III, but rather III arises from a free radical reaction between excess \underline{n} -BuLi and \underline{n} -BuBr generated in situ from reaction (1) (eq. 3). The concomitant production of \underline{n} -octane and possibly 3- \underline{n} -butylcyclohexene was further evidence for the generation of \underline{n} -butyl radicals in the system (3). (A brief study of the kinetics of reaction (3) is reported below).



Although the source of the 3,3'-bicyclohexenyl from reaction (1) in refluxing cyclohexene had been established, knowledge concerning the fate of the starting tetrabromoethylene was still lacking. If $\text{LiC}\equiv\text{CBr}$ had been generated and was stable under the conditions employed, we would have expected to be able to isolate monobromoacetylene as a gaseous product after quenching the reaction. In fact, the effluent gas evolved after quenching of reaction (1) with H_2O proved to be acetylene, trapped directly and as its mercury derivative.¹⁹ Thus, it appears that reaction (1) does not stop at the lithiobromoacetylide stage but that further lithium-halogen exchange occurs to produce ultimately lithium carbide. The overall reaction between tetrabromoethylene and \underline{n} -BuLi thus must be rewritten:



The stoichiometry of reaction (4) was corroborated by (a) determining

19. E. H. Keiser, *Am. Chem. J.*, 15, 535 (1893).

the quantity of C_2Br_4 remaining when less than 3 molar equivalents of n-BuLi was employed and (b) determining that the yield of n-butyl bromide corresponded to the quantity of n-butyllithium employed. This finding explains our previous observation that some tetrabromoethylene remained unconsumed upon reaction with two molar equivalents of n-BuLi and proves that lithiobromoacetylide must react faster with n-BuLi than does C_2Br_4 in an exchange reaction. This being the case, reaction (1) is unsuitable as a means of generating lithiobromoacetylide, and a new route had to be sought.

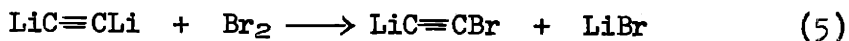
Before continuing the investigation, however, a brief study was undertaken of the interesting free radical reaction between n-butyl bromide and n-butyllithium mentioned earlier (eq. 3). Bryce-Smith^{20a} had previously studied the intermediacy of free radicals in butyllithium-butyl halide reactions employing cumene as a radical trap. He reported n-octane as the major product along with low yields of dicumyl, but no kinetic study was reported. We were chiefly interested in determining whether butyl radicals were being developed by reaction between the halide and organometallic directly or whether they arise from an induced decomposition of a previously formed complex between the reactants. We anticipated that the solvent employed for conducting the reaction might play a role if decomposition of a complex were important. Thus, we might have expected the reaction to be favorably influenced by a solvent like cyclohexene which is capable itself of forming an allylic radical, thereby perhaps providing a driving force for the decomposition of a

20. a) D. Bryce-Smith, J. Chem. Soc., 1603 (1956).

complex. On the other hand, cyclohexane would be expected to be inert in this respect and would not favorably influence the decomposition. We tested this argument by following the rate of loss of n-butyllithium in its reaction with n-butyl bromide in refluxing cyclohexene (b.p. 83°) and refluxing cyclohexane (b.p. 80°). The data in Table II (Experimental) show that n-butyllithium is consumed at roughly the same rate and to the same extent in both solvents, suggesting that the free-radical reaction does not involve a solvent-induced process. Direct production of butyl radicals from the reactants is thus indicated, and prior formation of a BuLi-BuBr complex need not be invoked. A second-order plot (Fig. 2, Experimental) of the admittedly crude g.l.c. data from the cyclohexene run yielded a rate constant for the second-order reaction of 4.4×10^{-4} l. mole⁻¹sec⁻¹ ($t_{1/2} = 3.7$ hrs.).^{20b}

2. Via Monobromination of Lithium Carbide

The availability of a facile route to lithium carbide via reaction (4) provided a possible route to lithiobromoacetylide (eq. 5). When Li₂C₂ was generated in ether solution and brominated, an infusible, polymeric, black-brown solid formed rapidly along with a volatile product



detected by g.l.c. Addition of cyclohexene immediately after the bromine treatment retarded formation of the polymer but resulted in the formation of no new products (specifically no II was produced). In pentane solution

20. b) For a detailed kinetic study of the reaction between n-butyllithium and 1-bromooctane in ether-hexane at 27°, see G. W. Gibson, Ph.D. Dissertation, University of Tennessee, June, 1963.

none of the polymer was formed, but the same volatile product detected in the ether system was now generated in increased yield. This product was not isolated, but its retention time was identical with that of an authentic sample of dibromoacetylene. This assignment was verified by its conversion to tetrabromoethylene upon further treatment with bromine (see below). The yields of C_2Br_2 were determined to be 14% in the ether system and 42% in the pentane system.

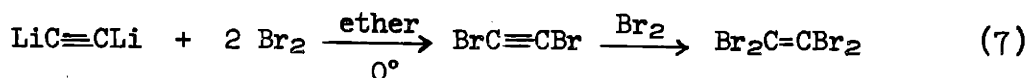
Employment of THF as solvent gave results qualitatively similar to those obtained in ether solution. Moreover, even at -78° in ether solution cyclohexene trapped no product of lithiobromoacetylide decomposition, the major product being dibromoacetylene in 60% yield.

Since the isolated infusible black solid from these reactions was found to contain approximately 20% bromine and cyclohexene was known not to be necessary for its formation, its most likely source is from polymerization of lithiobromoacetylide. This conclusion together with the finding of dibromoacetylene as a co-product suggests that lithiobromoacetylide, as soon as formed, undergoes spontaneous decomposition via two paths, viz., polymerization and/or disproportionation (eq. 6), the preferred path being solvent-dependent.



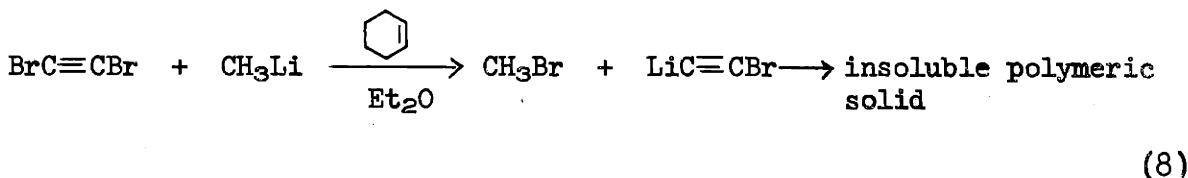
That lithiobromoacetylide is indeed the precursor to the polymeric solid was shown to be true by adding two molar equivalents of bromine rapidly to lithium carbide in ether solution. Formation of the polymer was completely suppressed and an 85-90% yield of C_2Br_2 (based on butyllithium) was obtained (eq. 7). Presumably under the conditions of the experiment lithiobromoacetylide was itself rapidly brominated before

it could decompose to the usual products. Addition of yet a third mole of bromine to the same system caused quantitative, rapid conversion of dibromoacetylene to tetrabromoethylene even at 0° (eq. 7). It was thus possible, using the sequence of reactions (4) and (7), to complete the cycle from C₂Br₄ starting material to C₂Br₄ product with an efficiency of approximately 85% in ether solution.



3. Via Halogen-Metal Exchange between Dibromoacetylene and Methyllithium

To determine if a slight variation in the method of generating lithiobromoacetylide might influence its mode of decomposition, we chose to treat dibromoacetylene generated by reaction (7) with one molar equivalent of methyllithium in ether solution in the presence of cyclohexene (eq. 8). The advantage of this method was that cyclohexene could be

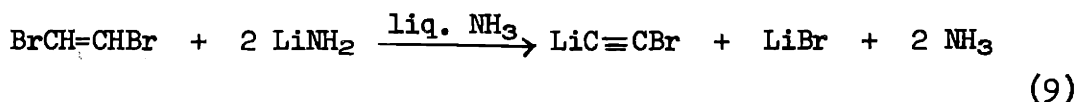


incorporated into the reaction system before generation of the lithio-bromoacetylide, a situation not possible when bromination of Li₂C₂ was employed. However, the results proved to be no different than had been observed in the latter case, insoluble polymeric solid again being the major product. No products which might have arisen from cyclohexene were detected by g.l.c.

4. Via Metallation of Monobromoacetylene from Dehydrohalogenation of 1,2-Dibromoethylene

Yet another route to the desired reactive intermediate was that

employed by Viehe¹⁷ for the generation of lithiochloroacetylide, viz., the metallation of monobromoacetylene produced by dehydrohalogenation of 1,2-dibromoethylene (eq. 9). This system provided us

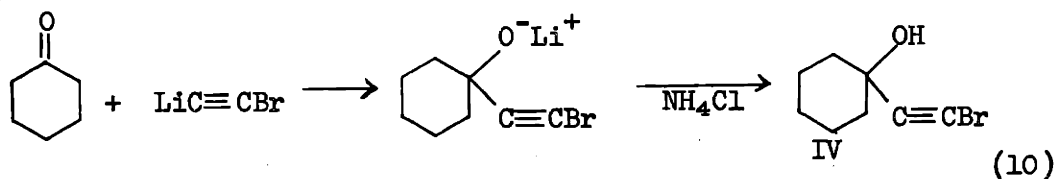


with an opportunity to test the stability and reactivity of lithio-bromoacetylide in an entirely different solvent and again afforded us the advantage of being able to incorporate cyclohexene before generation of the reactive intermediate. However, even under these conditions the lithio-bromoacetylide generated chose to polymerize and disproportionate in preference to eliminating LiBr. Polymer and dibromoacetylene again were the chief products, and no II or other products which could have arisen from cyclohexene were detected.

In an experiment in which all of the ammonia was displaced by cyclohexene after formation of the lithium amide, very little dehydrohalogenation of 1,2-dibromoethylene occurred after its addition to the suspension and no lithio-bromoacetylide was produced.

5. Trapping of the Reactive Intermediate

Thus far only indirect evidence for the successful production of lithio-bromoacetylide in various systems had been obtained. It was important that more direct proof of its intermediacy in the reactions discussed be procured. To do this we chose to trap it with cyclohexanone in a condensation reaction to be expected of nucleophilic reagents (eq. 10).



When lithiobromoacetylide was generated in liquid ammonia (eq. 9) and cyclohexanone was added rapidly, no polymeric black solid or dibromoacetylene resulted as products, as had been observed when only cyclohexene was present. Instead two products were discernible by g.l.c., which upon isolation proved to be 1-(bromoethynyl)cyclohexanol (IV) (major product) and 1-ethynylcyclohexanol (V) (incompletely characterized). Thus, we were successful in trapping the reactive intermediate before it could decompose.

When a similar experiment was performed but in which lithiobromoacetylide was generated by bromination of Li_2C_2 in ether solution (eq. 5), products IV and V again were formed (although as part of a more complex product mixture) and again the normal products of $\text{LiC}\equiv\text{CBr}$ decomposition were absent.

These experiments provided us with the first direct evidence for the generation of lithiobromoacetylide and confirmed the reactivity of this intermediate as a precursor to both C_2Br_2 and polymeric material in reactions where it is not scavenged by a suitable trapping agent. In this regard it is interesting to note that the decomposition of $\text{LiC}\equiv\text{CBr}$ must be so rapid that it fails to be alkylated by *n*-butyl bromide and methyl bromide, compounds which have been present in many of the reaction mixtures employed to generate the intermediate (cf. reactions (4) and (5) and reaction (8)).

6. Summary

Lithiobromoacetylide has been successfully generated in a number of systems but in no case has decomposition to a C_2 species, dicarbenic or otherwise, been established. Instead it decomposes spontaneously by

competing pathways of polymerization and disproportionation. This instability is in marked contrast to the high stability which Viehe noted for metallochloroacetylides.¹⁷ Although apparently inert to alkylation by alkyl bromides under the conditions employed, it readily condenses with cyclohexanone to give the expected tertiary alcohol IV.

B. Generation and Decomposition of Potassiobromoacetylde

A variable which had not yet been tested as possibly influencing the mode of decomposition of the metallochloroacetylde was the nature of the cation. To substitute potassium for lithium, potassium amide was substituted for lithium amide in the dehydrohalogenation-metallation reaction represented by eq. 9. Even in the presence of cyclohexene, the major product was dibromoacetylene with only a trace of polymeric solid. This result was different than that obtained with the lithio derivative in that a greater quantity of polymer was generated in the latter case. Nonetheless, no products which could have arisen from cyclohexene (such as II) were formed.

When the base employed for dehydrohalogenation of 1,2-dibromoethylene was potassium t-butoxide in DMSO, no dibromoacetylene was obtained. Instead, an intractable dense brown oil was formed.

Thus, although the nature of the cation and the reaction system itself can apparently influence the course of the decomposition of a metallochloroacetylde, they do not do so to the extent of inducing the formation of C₂. The next logical structural variation left to test was to change the halogen atom from bromine to iodine.

C. Thermal Decomposition of Diiodoacetylene

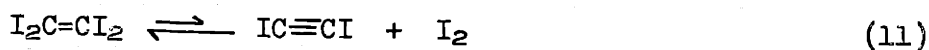
The route which we intended to use for the generation of lithio-iodoacetylide was to involve a halogen-metal exchange reaction on diiodoacetylene. However, in searching the literature for information concerning some of the properties of C_2I_2 , we uncovered an interesting reference¹⁶ in which its thermal decomposition in inert solvents at 138° was claimed to lead to carbon. It was suggested that C_2 might be an intermediate in the formation of this product (see Introduction). Encouraged by this possibility, we undertook a study of the thermal decomposition of C_2I_2 in solvents which would hopefully be potential trapping agents for a C_2 species.

The decomposition of diiodoacetylene in refluxing cyclohexene (b.p. 83°) proved to be extremely slow. After 26 hrs., starting material could still be isolated from a reaction aliquot. After 48 hrs. low yields of three products could be perceived by g.l.c., none of which was II. Addition of zinc metal to the reaction mixture did not appear manifestly to accelerate the decomposition, although the final product mixture was different than that obtained in the absence of zinc. The g.l.c. retention time of one of the major products corresponded to that of monoiodoacetylene, suggesting that some Zn-I exchange may have occurred to yield a zinc iodoacetylide. Very little carbonaceous matter was formed in either of the reactions.

After 2.5 hours in refluxing styrene (b.p. 145°), decomposition of diiodoacetylene led to very high molecular weight products, some I_2 , but no carbonaceous matter. No attempt was made to characterize any of the products formed.

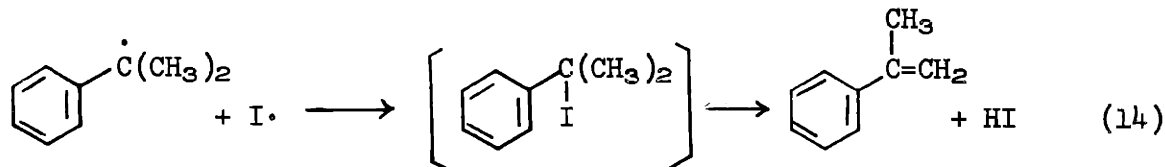
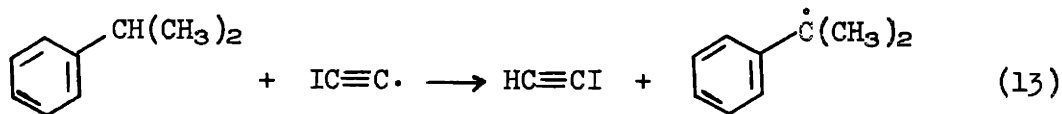
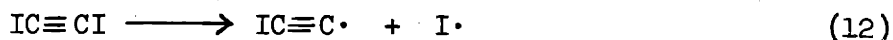
The use of refluxing cumene (b.p. 150°) as medium for the thermal decomposition of diiodoacetylene resulted in a reaction which was amenable to rather detailed product and kinetic studies.

The rapid coloration of refluxing cumene solutions of C_2I_2 revealed the liberation of I_2 . A product formed in significant yield proved to be α -methylstyrene (isolated by preparative g.l.c. and identified by infrared analysis and comparison of g.l.c. retention time with that of an authentic sample). A control experiment made it appear unlikely that free I_2 was the reagent causing the dehydrogenation of cumene. Moreover, titration of the free I_2 liberated revealed that less than 5% of the iodine in the starting material could be accounted for in this way. Based on the early work done on the decomposition of C_2I_2 (see Introduction), we looked for and succeeded in isolating tetraiodoethylene as another major product of the reaction. This product undoubtedly arises from addition of liberated I_2 (or 2 I.) to diiodoacetylene, and in fact the small amount of free I_2 found to be remaining in all reaction mixtures might arise from the equilibrium represented by eq. 11, since Schenck¹⁶ had shown this equilibrium to lie heavily to the left.

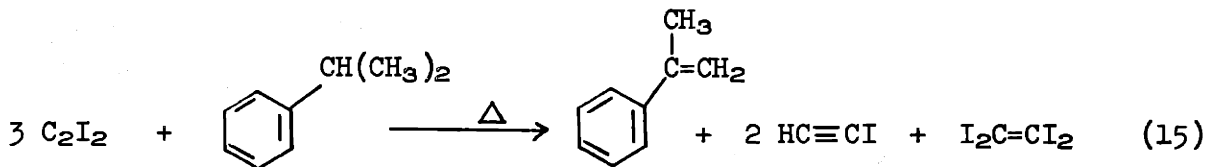


Since the quantity of C_2I_4 isolated did not account for all of the C_2 fragment and iodine in the starting material nor for the formation of the styrene, a search was made for volatile products of the reaction. It was attractive to consider the possibility that the agent responsible for dehydrogenating the cumene was C_2 , in which case acetylene would have been an expected product. When the decomposition of C_2I_2 was carried out with continuous nitrogen purging and direct cold-trapping

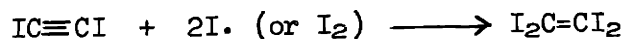
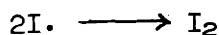
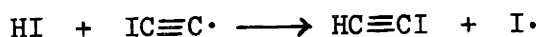
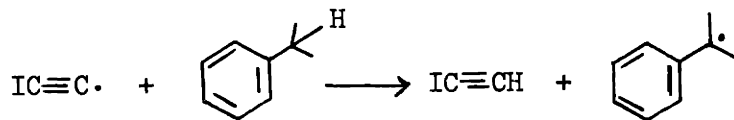
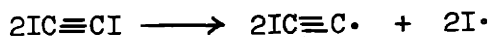
of the evolved gas, however, monoiodoacetylene not acetylene was isolated and identified. This result suggested that decomposition of diiodoacetylene must be occurring via a primary homolysis of a C-I bond (eq. 12), followed by attack of the resulting iodoacetylenic radical on solvent (activated H atom) to yield the cumyl radical (eq. 13), which through reaction with an iodine atom would lead to the observed product, α -methylstyrene (eq. 14). No more than a trace of free HI could be detected in the effluent gases from the reaction, but since HI is known to be an efficient scavenger of radicals, this result was not surprising.



Taking into account the known major products of the reaction, the following balanced equation can be written for the thermal decomposition of diiodoacetylene in refluxing cumene:



The following sequence of reactions is suggested as a possible means of accounting for the stoichiometry of eq. 15:



Careful attempts were made to obtain a material balance for the reaction based on this stoichiometry. The yield of α -methylstyrene was obtained by g.l.c. analysis utilizing an internal standard; monoiodoacetylene was isolated by continuous nitrogen purging and trapping in a cold trap, followed by estimation of the yield by a g.l.c. method; the C_2I_4 yield was obtained by isolation; iodine was determined by titration with $\text{Na}_2\text{S}_2\text{O}_3$. Table IV (Experimental) summarizes the yield data from the best run. It is clear that a poor material balance was obtained, since approximately 50% of the iodine and 65% of "C₂" from C_2I_2 remained unaccounted for, although the polymeric material undoubtedly accounts for some of this. Moreover, the 3.5-hour reaction period employed in this experiment proved to be longer than was necessary to decompose all of the starting material (see below), and secondary reactions involving the products could thus very well have contributed to the low material balance obtained.

The low material balance prompted a search for high molecular weight products of the reaction. The use of appropriate g.l.c. conditions revealed the presence of three high molecular weight products in low yield. The retention time of one of these corresponded to that for dicumyl. The other two products upon isolation by preparative g.l.c. proved to be unstable iodine-containing oils (see Experimental for spectral data). One of these (product A) was shown later to be triiodoethylene (see below).

The availability of g.l.c. methods for detecting diiodoacetylene, monoiodoacetylene, and α -methylstyrene suggested that the thermal decomposition of C_2I_2 in refluxing cumene might be amenable to a kinetic study. Figure 1 depicts graphically the behavior of these compounds (loss and/or formation) during the course of the heating period. It is significant that the yield of α -methylstyrene continues to increase even after decomposition of C_2I_2 is complete. This result can be accounted for by the thermal decomposition of monoiodoacetylene leading to the same product. Note also that the α -methylstyrene undergoes gradual consumption itself upon prolonged heating, possibly via a polymerization process.

Of some importance is the fact that the C_2I_2 data yielded a good first order plot (Fig. 3, Experimental). Two separate runs in which the loss of C_2I_2 was followed by g.l.c. yielded values of k_1 of 0.074 and 0.062 min^{-1} ($t_{1/2} = 9.4$ and 11.2 min., respectively), indicating a very rapid decomposition of C_2I_2 under the conditions employed. These results are similar to Schenck's findings for the first order decomposition of C_2I_2 in inert solvents at 138° ($k_1 = 0.0071 \text{ min}^{-1}$ in benzene),

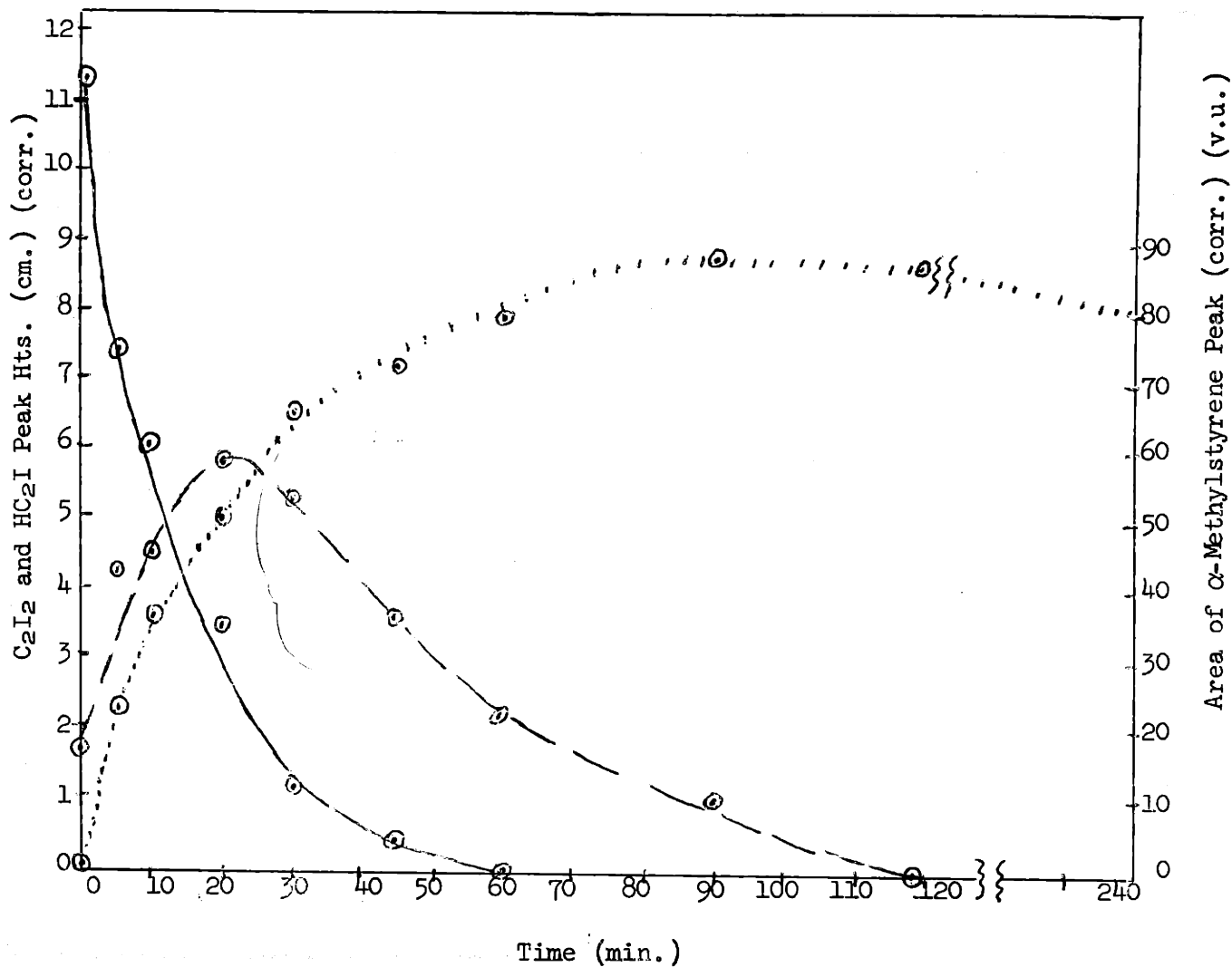


Fig. 1. Plot of quantities of reactant and products at various times during the thermal decomposition of C_2I_2 in cumene at 150° ; determined by g.l.c. analysis. — C_2I_2 peak hts.; — — HC_2I peak hts.; α -methylstyrene peak areas (right hand scale).

wherein rate of formation of "carbon" was followed.¹⁶ Moreover, the consumption of monoiodoacetylene from the 30 min. reaction mark (diiodoacetylene was largely consumed by this time) also was found to be a first order process with $k_1 = 0.028 \text{ min}^{-1}$, $t_{1/2} = 25 \text{ min.}$ (Fig. 4, Experimental) at 150° .

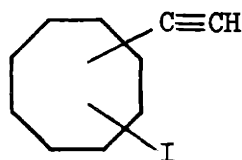
Support was obtained for the correctness of the stoichiometry of the decomposition of C_2I_2 represented by eq. 15 by following the rate of formation of α -methylstyrene. When that stoichiometry was assumed, the styrene data likewise corroborated the first-order process for consumption of C_2I_2 , with $k_1 = 0.067 \text{ min}^{-1}$ ($t_{1/2} = 10.3 \text{ min.}$) (Fig. 3, Experimental). The close agreement between the results obtained from the product data and that obtained directly from reactant data strongly favors the correctness of the indicated stoichiometry, at least for the early stages of the reaction.

The finding of smooth first order kinetics for the decomposition of C_2I_2 in refluxing cumene was unexpected in view of evidence that some C_2I_2 must be consumed by a competing reaction with I_2 (and possibly with HI; see below). This would indicate that any reactions involving C_2I_2 which are competing with the primary process of homolytic C-I cleavage (eq. 12) must be occurring rapidly and at a constant rate in order not to influence the kinetic order of the reaction.

It was desirable to conduct the thermal decomposition of diiodoacetylene in a solvent which contained hydrogen atoms less reactive than that present in cumene and hence which might be less amenable to attack by free radicals. Cyclooctane was chosen as just such a medium. However, the reaction proved to be even less clean than in cumene, a

much more complex product mixture resulting.

In refluxing cyclooctane (b.p. 149°) C_2I_2 was again found to decompose by a first-order process but with a half-life of 30 min. (Fig. 5, Experimental) roughly one-third the rate found in cumene. Of the several products of the reaction detected by g.l.c., moniodoacetylene could be isolated and cyclooctyl iodide was shown to be present by comparison of product peak retention time with that of an authentic sample. No dicyclooctyl, the radical coupling product of cyclooctane, was detected by g.l.c. One high molecular weight product (Product B), which proved to be unstable to the reaction conditions, was isolated by preparative g.l.c. from a short-term reaction as a red oil. Spectral data (see Experimental) suggest the gross structure VI. In addition, a second isolated red oil yielded infrared and n.m.r. spectral data identical with those of product A isolated from the cumene reaction system (see Experimental).



VI

In order to determine the source of the unexpectedly large number of products produced during the decomposition of C_2I_2 in cyclooctane, control experiments were performed in which first I_2 , then cyclooctyl iodide were subjected to decomposition under the same conditions. Iodine was completely absolved as a precursor to any of the products, and the decomposition of cyclooctyl iodide accounted for only two minor products. Thus the majority of the products formed in the C_2I_2 -

cyclooctane system must have arisen from reaction of C_2I_2 -derived radicals with solvent.

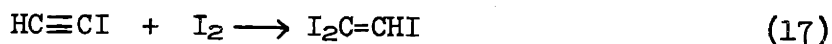
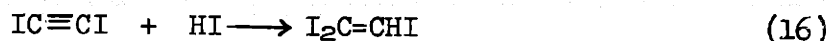
Even in refluxing n-nonane (b.p. 150°) the thermal decomposition of diiodoacetylene resulted in a product mixture every bit as complex as was the case with cyclooctane. The significant feature of this decomposition was the much decreased rate of consumption of C_2I_2 even though the temperature was the same as was employed in the previous two solvents. A six-hour reaction period proved to be insufficient to decompose all of the C_2I_2 , whereas in cumene and cyclooctane consumption was complete within 1-2 hours. The C_2I_2 g.l.c. data yielded less well defined first order kinetics showing a half-life of approximately 3 hrs. for the reaction (Fig. 6, Experimental). The ratios of half-lives of 1 : 3 : 18 for C_2I_2 decomposition in the three media cumene : cyclooctane : nonane are too large to be explained by the degree or two difference in the boiling points of the three solvents. Thus, the rate of C_2I_2 decomposition appears to exhibit a very definite solvent dependence.*

The highest molecular weight product detected by g.l.c. in this system had the same retention time as product A isolated from both cumene and cyclooctane systems. Clearly then, product A was not derived from the solvent. The infrared spectra (bands at 3050, 1190, 725, and 610 cm^{-1}) and n.m.r. spectra (one absorption, a singlet at 1.5τ) of the products

* In order to obtain the rate constants observed for the decomposition of C_2I_2 in cyclooctane and n-nonane assuming no solvent effect operative, that is assuming an activation energy ($E_a = 31\text{ kcal/mole}$) identical to that calculated for the decomposition in cumene (see below), temperatures of approx. 140° and 120° , resp., were calculated to be required. These values are obviously outside the limit of experimental error in conducting the decomposition in refluxing solvents and necessitate the operation of a solvent effect to explain the large rate differences observed.

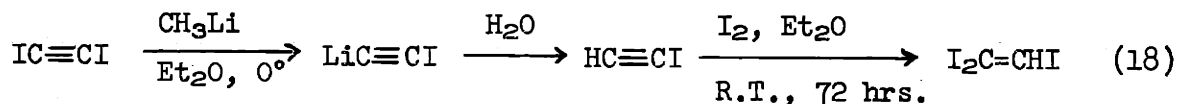
A isolated from the three systems were superimposable on each other. The mass spectral molecular weight of 406 together with the cracking pattern observed for the oil were consistent with its identification as triiodoethylene.

Triiodoethylene can be envisioned as arising during the thermal decomposition of C_2I_2 either from the addition of HI to diiodoacetylene (eq. 16) or by the addition of I_2 to monoiodoacetylene (eq. 17)



generated in situ. The fact that C_2I_2 reacts rapidly with HI was proven by following its rate of consumption in refluxing n-nonane with concurrent passage of HI gas through the reaction mixture. The bulk of the C_2I_2 was consumed within 15 min. with consumption complete within one hour, compared to its incomplete consumption even up to six hours in pure n-nonane.

Triiodoethylene has not been reported in the literature. As a further proof of structure for the product A isolated from the decomposition of diiodoacetylene, its synthesis was accomplished under mild conditions using the sequence of reactions (18). After stirring with I_2



in ether solution for 72 hours, practically all of the monoiodoacetylene was consumed. The product was isolated as a pale yellow oil, b.p. 40-60° (bath)/0.02 mm (satisfactory elemental analysis; see Experimental) in

an undetermined yield of not greater than 10% (tetraiodoethylene was a major by-product). Its infrared spectrum and g.l.c. retention time were identical to those for the products A isolated from the C_2I_2 decompositions described above.

Lacking experimental data, an estimate was made of the C-I bond dissociation energy in C_2I_2 using the absolute value of the first-order rate constant for its thermal decomposition in cumene, cyclooctane and n-nonane. It is assumed that the dissociation energy of the bond will be equal to the activation energy of the process (i.e., the reverse process, recombination of radicals, corresponds to zero activation energy). This being the case, then

$$D(C-I) = E_a = (\log A - \log k_1) 2.3 RT/1000 \text{ kcal/mole}$$

where A is the frequency factor for the reaction. Experimental evidence indicates²¹ that for a variety of unimolecular dissociations (caused by rupture of one bond only) the "true" values of A do not vary by more than a factor of 5 from 10^{13}sec^{-1} . Therefore, if we assume that C_2I_2 decomposition is truly unimolecular (though this point may require further elucidation),

$$E_a \approx (13 - \log k_1) 2.3 RT/1000 \text{ kcal/mole} .$$

Using values for k_1 of $1.23 \times 10^{-3} \text{sec}^{-1}$ from the decomposition of C_2I_2 in refluxing cumene, $3.83 \times 10^{-4} \text{sec}^{-1}$ for the decomposition in refluxing cyclooctane and $6.7 \times 10^{-5} \text{sec}^{-1}$ for decomposition in nonane, values of E_a of 31, 32, and 33 kcal/mole, respectively, are obtained.

21. M. Szwarc, Chem. Rev., 47, 75 (1950).

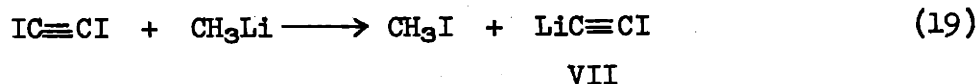
(Note that even if the chosen value of A were low by a factor of 10, the calculated values of E_a would be in error by only 2 kcal/mole). These rather low calculated values demand experimental verification. If true, they indicate that either (a) $IC\equiv C\cdot$ is an extremely favorable free radical or (b) iodine is bonded extremely weakly to an acetylenic (sp) carbon atom. Since iodine is known to be bonded very weakly to electronegative atoms such as oxygen, there may be an analogy for the possibility (b) if the grouping $C\equiv C$ can be considered to have electro-negative characteristics.

In summary, diiodoacetylene decomposes thermally at 150° in a first-order process whose rate is solvent-dependent. The primary process is clearly homolysis of the C-I bond, the radicals formed being sufficiently energetic to attack even secondary hydrogen atoms of hydrocarbon solvents. No evidence suggesting the intermediacy of a C_2 species was obtained. The decomposition in cumene is difficult to envision proceeding by a radical-chain process. A series of reaction steps have been proposed to account for the observed stoichiometry.

D. Generation and Decomposition of Lithiodoacetylide

It was anticipated that lithiodoacetylide should be even more unstable than the bromo analog and that the likelihood of LiI being eliminated leaving a reactive C_2 species was high.

The route chosen for generation of the intermediate was the reaction of diiodoacetylene with one molar equivalent of methyl lithium at 0° (eq. 19). When the reaction was conducted in cyclohexene as solvent

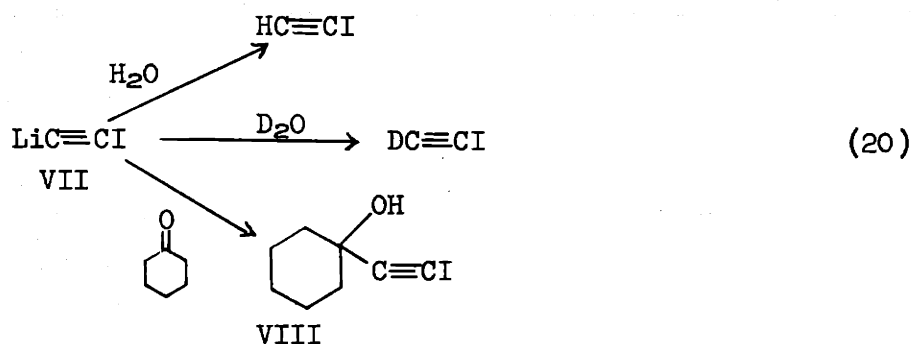


followed by stirring at room temperature for 4 hours, a single product was obtained after quenching with H_2O , which was not II. Rather, its volatility (it distilled between ether and cyclohexene) and g.l.c. behavior (eluted after cyclohexene on a Carbowax 20M column) indicated it was low-boiling and relatively polar. After isolation of the material by preparative g.l.c. (a macro-size collecting vessel had to be employed to trap it efficiently), it was found most convenient to handle it as a gas to obtain spectral data. The infrared and mass spectra ("cold" spectrometer) so obtained identified the product as moniodoacetylene (m/e 152, M^+ , 100%; m/e 127, I^+ , 30%), the product to be expected from simple halogen-metal exchange between the reactants. The n.m.r. spectrum of a neat liquid sample²² (sealed capillary) exhibited only singlet absorption at 7.22 τ , consistent with an uncoupled acetylenic proton.

This finding of moniodoacetylene as the only product of the described reaction was unexpected in that it suggested that lithioiodoacetylide must be stable in cyclohexene for 4 hours at room temperature. This was in sharp contrast with what had been observed with the corresponding bromoacetylide. To ensure that the iodoacetylide (VII) actually existed in the reaction mixture up to the time of quenching and was not abstracting a proton from the solvent to form moniodoacetylene, the reaction (19) was quenched with D_2O instead of H_2O after a 4-hour room-temperature reaction period. The gas-phase infrared spectrum of the isolated product did indeed show an acetylenic C-D bond as a doublet at 2580 cm^{-1} in place of the 3300 cm^{-1} doublet observed for $HC\equiv CI$. This lowering of

22. This liquid sample discolored rapidly even in the sealed tube at room temperature. After storage at -10° for 4 days, the tube containing the reddish-orange liquid detonated sharply while being handled at -20° . The moniodoacetylene was a solid at Dry Ice temperature and could be stored in this state safely for prolonged periods.

the absorption frequency by a factor of 1.28 indicated successful deuteration²³ and proved that lithioiodoacetylide was stable in the reaction mixture until the time of quenching. Corroboration of this result was obtained by trapping VII with cyclohexanone under similar reaction conditions. The melting point and spectral data of the isolated crystalline adduct were consistent with the expected structure VIII (see Experimental).



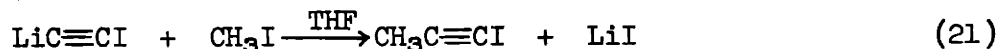
The stability of VII was tested even more rigorously by refluxing it in cyclohexene-ether solution. After 24 hours, monoiodoacetylene was found still to be the only product after quenching.²⁴ The low solubility of VII in the reaction medium might be a factor in explaining the unexpected stability of the intermediate. In refluxing cumene (b.p. 150°) or styrene (b.p. 145°) on the other hand, decomposition of VII did occur, more rapidly in the latter solvent than in the former. After 9 to 10 hours in refluxing cumene, lithioiodoacetylide was completely consumed and only a single volatile product was detected by g.l.c. in very low yield. The major product was an insoluble, brown, polymeric

23. K. Nakanishi, "Infrared Absorption Spectroscopy, Practical," Holden-Day, Inc., San Francisco, 1962, p. 134.

24. The source of the methyllithium employed for generation of VII, that is whether from CH₃I or CH₃Br, did not appear to influence the stability of the iodoacetylide.

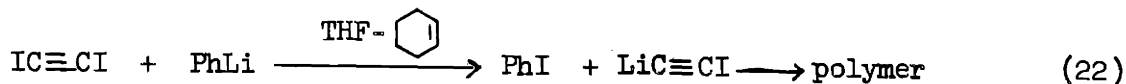
solid which contained 34% iodine. In refluxing styrene only 1.25 hours was required for virtually complete consumption of VII, but surprisingly no volatile products were detected by g.l.c. nor was any polymeric solid formed. The only manifestation of any reaction was a perceptible increase in viscosity of the medium, which occurred more rapidly than had been observed for the decomposition of C_2I_2 in styrene. This result is consistent with the hypothesis that lithio-iodoacetylide should behave as a scavenger of iodine atoms formed during the free-radical reaction and thus should permit a more rapid and extensive growth of solvent polymer chains by removing the potential chain-stopping atoms from the reaction medium. In the case of C_2I_2 , the iodine atoms generated are free to combine with growing polystyrene chains and thus to limit the size thereof, so that rate of viscosity increase would be expected to be slower, as was observed.

As another means of inducing the decomposition of lithioiodoacetylide, the effect of a drastic change in solvent was tested. When CH_3Li was added very slowly to C_2I_2 in THF solution or in THF containing 5% by volume cyclohexene, the lithioiodoacetylide initially formed (detected as $HC\equiv CI$ by g.l.c) was consumed rapidly even at 0° yielding a single product. Clearly, cyclohexene was not a precursor to this product. However, disappearance of CH_3I , formed in situ from the halogen-metal exchange reaction (eq. 19) concurrently with consumption of $LiC\equiv CI$ suggested that alkylation of the latter might be occurring to yield 1-iodopropyne (eq. 21). Isolation of the product by



preparative g.l.c showed it to be a colorless, strong-smelling liquid whose spectral data were consistent with this structure (see Experimental). Interestingly when instead of THF, pure diethyl ether was employed as the solvent for the halogen-metal exchange reaction (19), alkylation did not occur, CH_3I was not consumed, and VII was stable even at reflux. Thus, THF appears to be a specific solvent required for reaction (21) to occur.

If, as shown, lithioiodoacetylide exhibits enhanced reactivity in THF as solvent, a logical question to consider was how it might react in the absence of an alkylating agent. Specifically, might a C_2 species result by elimination of LiI with no other simple reaction pathway open to it? To help answer this question, phenyllithium was employed as the halogen-metal exchanging agent with C_2I_2 in THF solution and in 50% cyclohexene-50% THF (eq. 22). Iodobenzene, the



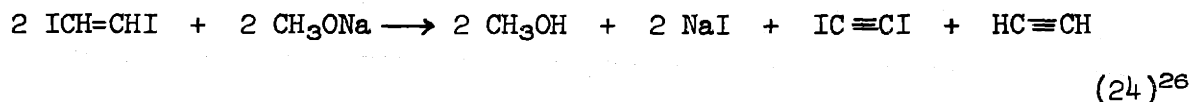
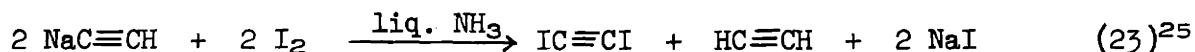
second product of the exchange reaction, would be expected to be unreactive as an alkylating (aryllating) agent toward lithioiodoacetylide. In both solvent systems a major product of the reaction proved to be a black, amorphous solid which contained 12.5% iodine. Iodobenzene, by the constancy of its g.l.c. peak area, was shown not to be involved in the formation of this polymer or of any other products. In addition, no II was detected by g.l.c. from the reaction incorporating cyclohexene. However, two other high molecular weight products were isolated from the reaction. One was an iodine-containing oil (preparative g.l.c.)

whose spectral data suggested an aromatic compound (see Experimental). The other, obtained in only trace yield, was a white crystalline solid which was insoluble in ether but sublimed readily. It was not possible (from combined runs) to obtain a sufficient quantity of this material to permit characterization.

Still another method employed to try to induce the decomposition of lithioiodoacetylide to the desired C_2 species was to influence its stability by introducing N,N,N',N'-tetramethylethylenediamine, a complexing agent sometimes used to modify the reactivity of alkyllithium compounds. Indeed, VII (generated by reaction (19)) proved to be stable at room temperature in the presence of 1 or 3 molar equivalents of the diamine (cyclohexene solvent), but after refluxing for 5 hours approximately 50% decomposition occurred. The products were 1-iodopropyne (from alkylation of VII by CH_3I produced in situ) and an insoluble residue. No II was produced. Moreover, the solubility of VII seemed to be increased by an excess of diamine, but very little difference in the total extent of reaction could be discerned between the two experiments.

Although attempts to induce vicinal lithium iodide elimination from VII to give the desired C_2 species had failed, a search of the literature indicated that changing of the cation of the metalloiodoacetylide would not achieve the desired result. In previously reported attempts to generate monoiodoacetylene under basic conditions (eq. 23 and 24) only diiodoacetylene (together with acetylene) resulted, indicating strongly that disproportionation of $HC\equiv CI$ occurs readily in the presence of bases, as we had observed in the metallobromoacetylide series. If this

is the case, then lithioiodoacetylide is unique in failing to undergo disproportionation.



Virtually the only path which yet lay open to us for effecting the decomposition of lithioiodoacetylide (VII) to a C₂ species was via photolysis. When VII was irradiated with 2537Å light for 24 hours in a quartz vessel in cyclohexene as solvent (eq. 19), none of the compound II was produced as determined by careful g.l.c. analysis. Rather 3,3'-bicyclohexenyl (III), the allylic radical coupling product of cyclohexene, was the major product (23% yield based on C₂), together with low yields of other products. The reaction appeared to be largely over by the 9-hour mark. The formation of III indicated that free radicals were being generated. Since the rate of consumption of VII was found to coincide closely with the rate of formation of III, it appeared that the (presumed) free radicals which were attacking the solvent arose from VII. However, the nature of the radical species involved was unclear.

The mode of generation of VII required that control experiments be conducted to ensure that the observed product III did not arise from the photolysis of CH₃I generated in situ or from residual C₂I₂. Photo-

25. T. H. Vaughn and J. A. Nieuwland, J. Am. Chem. Soc., 54, 787 (1932).

26. S. I. Miller and R. M. Noyes, ibid., 74, 629 (1952).

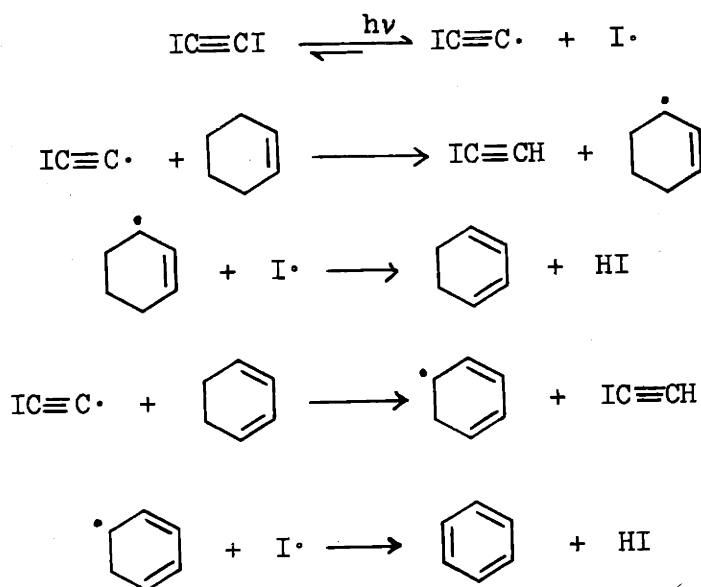
lysis of CH_3I in cyclohexene solution, with and without added LiI ,²⁷ under the conditions employed above failed to generate any III. The major solvent-derived products were benzene and a product whose g.l.c. retention time corresponded to that of 1,3-cyclohexadiene. (Benzene had been found to be a minor product from the photolysis of VII derived from reaction (19)).

Photolysis of a cyclohexene solution of diiodoacetylene²⁸ gave a complex product mixture but III was generated in only trace yield (less than one-tenth of the yield obtained from photolysis of VII). Benzene was the major product derived from solvent, occurring in 40% yield based on an assumed 1 : 1 stoichiometry of C_2I_2 to cyclohexene. Cyclohexadiene was not detected as a product of the reaction, even as an intermediate on the way to benzene. The vastly greater yield of benzene obtained here than from the photolysis of ordinary alkyl iodides remains unexplained. Monoiodoacetylene was seen to be an intermediate during the decomposition of C_2I_2 (g.l.c.), which subsequently was consumed. In fact, formation of benzene continued after loss of C_2I_2 was complete and ceased only after HC_2I was completely consumed. As expected, the C_2 fragment ultimately ended up as acetylene (20% based on C_2I_2) as determined by a gas-trapping experiment employing nitrogen as a purging

27. The CH_3Li employed for generation of VII had been prepared from CH_3I in ether solution and was found to contain a large quantity of LiI (see Experimental).

28. The only other study of the photolysis of diiodoacetylene was carried out in hexane solution, but it was cursory in nature and no extensive product study was made: J. W. Tamblin and G. S. Forbes, *J. Am. Chem. Soc.*, 62, 99 (1940).

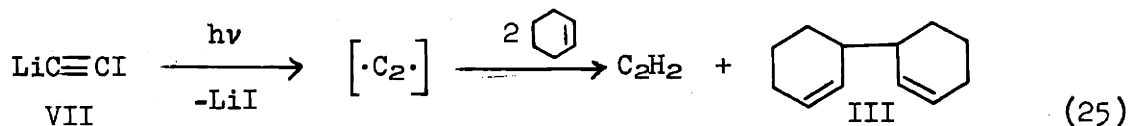
gas. In addition, monoiodoacetylene in 15% yield was trapped out from this experiment, corroborating its intermediacy in the photolytic decomposition of C_2I_2 . These results indicate that photodecomposition of C_2I_2 proceeds via step-wise cleavage of iodine atoms; the intermediate acetylenic radicals ($IC\equiv C\cdot$ and $HC\equiv C\cdot$) then abstract allylic hydrogen atoms from solvent to give the observed products, e.g.,



It is significant that the 3-cyclohexenyl radicals which must be produced on first attack undergo further dehydrogenation in this system in preference to coupling. This behavior is distinctly different from that observed during the photolysis of VII wherein the primary reaction of the 3-cyclohexenyl radicals is to couple.

The results of these control experiments strongly implicated lithioiodoacetylide as the direct precursor to the reactive radicals attacking solvent during photolysis, since only when this compound was present was 3,3'-bicyclohexenyl the major product. If photolytically induced β -elimination of LiI had occurred to yield C_2 , then clearly


its electronic configuration would best be represented as that of a triplet (diradical). Attack of this radical on solvent would be expected to yield acetylene in an amount at least equivalent to the bicyclohexenyl (eq. 25). In fact, when the photolysis of VII in cyclohexene was carried out with N₂-purging and cold-trapping, acetylene



gas was isolated in 55% yield (based on the stoichiometry of reaction (25)). However, an 8% yield of monoiodoacetylene isolated at the same time is difficult to explain on the basis of eq. 25. (Effluent gases swept from the reaction mixture after quenching with D₂O revealed only a trace of C₂D₂ and no C₂HD or CH₃D). Attempts were made to confirm quantitatively these results and to determine the effect of (a) the source of CH₃Li, (b) the composition of the solvent, and (c) N₂ sweeping on the yields of the three products from the photolysis. Table I summarizes the findings. It is clear that after the initial run (No. 2) with N₂ sweeping, the 55% yield of C₂H₂ and the 20% yield of III could not be reproduced (Runs No. 3-6). When VII was prepared from CH₃Li made from CH₃I somewhat higher yields of C₂H₂ and III were obtained than when CH₃Li from CH₃Br was employed (cf. Runs No. 3 and No. 6, No. 7 and No. 8). Thus, lithium iodide did seem to play a role as a complexing agent which might have enhanced the reactivity of lithioiodoacetylide in the desired direction (cf. Runs No. 3 and No. 5). Addition of ether to the solvent system did not appear manifestly to change the results (cf. Runs No. 3 and No. 4, No. 7 and No. 9). No explanation can be offered

Table I

Yields^a of Products from the Photolysis^b of Lithioiodoacetylide in Cyclohexene

<u>Run No.</u>	<u>Source of MeLi</u>	<u>Additives</u>	<u>% C₂H₂</u>	<u>% </u>	<u>% HC₂I</u>
1	CH ₃ Li	None	--	23	--
2	"	"	55	20	8
3	CH ₃ Br	"	10	7	11.5
4	"	15% Et ₂ O ^c	7	11	3.5
5	"	LiI/15% Et ₂ O ^c	18	12	13
6	CH ₃ I	None	18.5	11	13
7	"	"	--	27	--
8	CH ₃ Br	"	--	17	--
9	CH ₃ I	50% Et ₂ O ^c	--	21	--

^a Determined by g.l.c. using internal standards with appropriate response factors; percentages based on C₂ (stoichiometry of eq. 25).

^b Where only the yield of bicyclohexenyl is indicated a closed reaction system was employed; otherwise reaction mixtures were purged with N₂ and the evolved gases were condensed in appropriate cold traps during photolysis.

^c V/v percent in the solvent.

for the apparent irreproducibility of the photolyses conducted with N₂-purging or the lowered yields of III compared to those obtained in closed systems.

All of the photolyses of lithioiodoacetylide described thus far were carried out on heterogeneous systems because of the low solubility of the intermediate in cyclohexene. In order to ensure that the pro-

duction of III was not dependent upon any surface reactions, a homogeneous system was devised. Lithioiodoacetylde (1 mmole) was generated in 20 ml. of a 50-50 mixture of cyclohexene-ether in which it was found to be 90% solubilized. After centrifugation the clear supernatant was photolyzed giving a 13% yield of 3,3'-bicyclohexenyl. Moreover, decomposition was much more rapid than had been observed in the heterogeneous systems. This result assured us that surface effects were not important in influencing the mode of decomposition of VII. (The lowered yield of III may be due to loss of VII during transfer to the photochemical reactor).

Attempts were made to learn more about the composition of the product mixtures obtained from the photolyses, but the task was made difficult by the extremely low yields of the several products. Concentration of the reaction mixtures yielded only dark brown oils from which no solids could be induced to crystallize.

All of the studies reported thus far still had not allowed any conclusions regarding the nature of the radical species generated photolytically from lithioiodoacetylde and responsible for the production of 3,3'-bicyclohexenyl. The generation of the C_2 diradical (eq. 25) was still as good an explanation as any up to this point, but we desired information concerning the "freedom" of the free radicals formed, i.e., whether cage effects were important in leading to the observed products. To do this, a radical scavenger needed to be introduced into the reaction system, not an easy task considering the potential reactivity of the lithioiodoacetylde. Tri-n-butyltin hydride would have served the purpose well, but it was anticipated that its reducing properties would

be too strong to permit the survival of VII long enough for it to undergo photolytic decomposition. Contrary to expectations, however, a control experiment showed that VII was stable to the tin hydride in the dark at room temperature, although it reacted slowly in refluxing cyclohexene. Subsequent photolysis of VII in the presence of the hydride resulted in very rapid consumption of the iodoacetylde (the reaction was over after 30 min. irradiation) with production of a low yield of III. However, a control experiment in which CH_3I (also present in the previous reaction mixture) was photolyzed in the presence of the tin hydride likewise gave a low yield of III with very rapid consumption of the starting material. Since CH_3I alone had been shown to give no III, we had to conclude that the halogen compounds were undergoing rapid photoreduction in the presence of tri-*n*-butyltin hydride, which led to low yields of III (and formation of tri-*n*-butyltin iodide detected by g.l.c.). Thus, no new information could be obtained from these experiments concerning the nature of the radical species generated in the photolysis of VII.

In considering the effect of U.V. irradiation on ordinary alkyl iodides (and diiodoacetylene) the most likely primary process must be homolysis of the C-I bond. There is no reason to expect that a like process would not be operative for lithioiodoacetylde as well. Thus, in both cases a carbon radical and an iodine atom would be expected to be produced. Yet the work discussed above shows that different products are obtained in the two systems from the attack of radicals on the solvent (cyclohexene). Benzene is produced in the one case, 3,3'-bicyclohexenyl (III) in the second. One important difference in the two reaction systems can be pointed out, however, viz., that in the one an efficient scavenger

of iodine exists, lithioiodoacetylde. In the case of the alkyl iodides or C_2I_2 no such efficient scavenger is present. Before we could postulate the generation of C_2 from photolysis of lithioiodoacetylde we had to determine the effect of scavenging of iodine from systems in which alkyl iodides were being photolyzed. To do this the photodecomposition of n-butyl iodide was studied in cyclohexene solution, with and without added n-butyllithium, a potentially efficient scavenger of iodine.

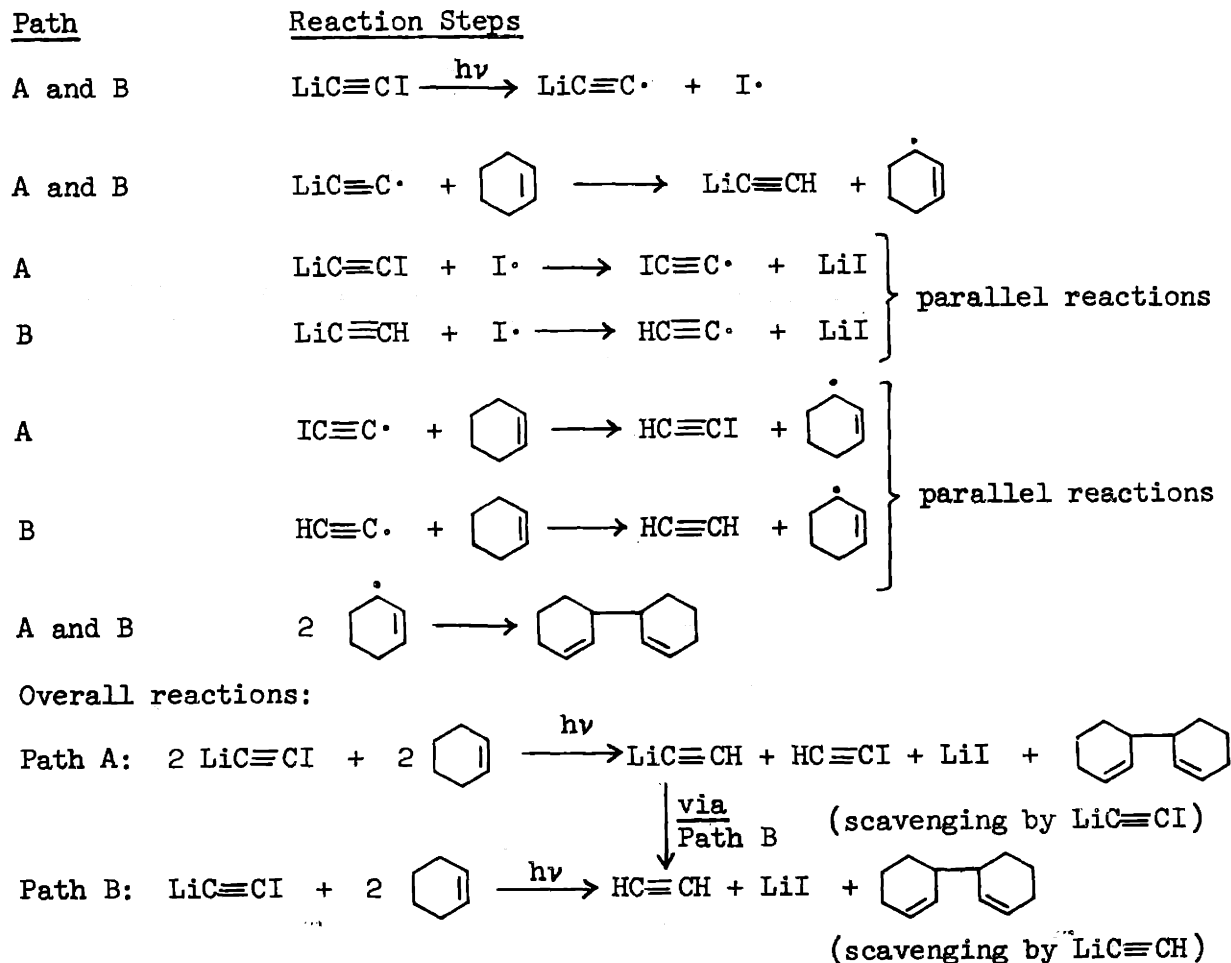
As expected, photolysis of n-butyl iodide in cyclohexene produced a low yield of benzene but no III. Addition of an equimolar amount or excess of n-butyllithium to the butyl iodide, however, resulted in a 60% yield of III (based on BuI consumed). Surprisingly, this same high yield was obtained also from a thermal reaction in the dark between BuI and BuLi at 40° (the temperature of the photolyzed reaction mixture). Subsequently, however, III was generated (33% yield) also from photolysis of BuI and BuLi at -10° to -20° , a temperature at which the "dark" reaction between the two reagents was shown not to occur.

These results provide clear evidence that addition of an iodine scavenger to an alkyl iodide being photolyzed will cause a drastic change in the nature of the product derived from the solvent. In particular, photolysis of alkyl iodides in the presence of alkyllithiums leads to high yields of 3,3'-bicyclohexenyl.²⁹ Thus, the genesis of III during

29. Apparently, in the absence of iodine 3-cyclohexenyl radicals couple in preference to undergoing dehydrogenation to benzene or reacting by other pathways. This suggests that the dehydrogenation process must be assisted by iodine atoms.

the photolysis of lithioiodoacetylide cannot be attributed to the generation of a C_2 radical species. Rather it is suggested that the primary process occurring, as with alkyl iodides, is cleavage of an iodine atom but that scavenging of these atoms (or of I_2) by lithioiodoacetylide (and/or lithium acetylide produced in situ) leads to the formation of the observed product, III. (At this time, it is not possible to prove which iodine species is being scavenged.)

The following scheme represents an attempt to describe a sequence of reaction steps which may account for the products obtained from the photolysis of lithioiodoacetylide in cyclohexene, assuming scavenging of iodine atoms:



EXPERIMENTAL

General.--All reactions involving organometallic reagents and thermolytic and photolytic reactions were carried out in an atmosphere of pre-purified nitrogen. Reaction vessels employed had side-arms which were fitted with No-Air stoppers to facilitate addition of reagents and withdrawal of reaction aliquots. All exploratory experiments were routinely monitored by analysis of reaction aliquots by gas-liquid chromatography (g.l.c.).

Cyclohexene (Eastman white label) was purified by passage through alumina and distillation from sodium and was stored over NaOH pellets; just prior to use it was again passed through a column of alumina. Cumene (Eastman white label) and cyclooctane (Cities Service Co.) were purified by sulfuric acid washing as described by Bartlett.^{30a} All other reagents were used as purchased unless otherwise indicated. *n*-Butyllithium was obtained from Foote Mineral Co., Exton, Pa.; methyl-lithium was prepared by standard procedures^{30b} from CH₃Br or CH₃I. The concentration of alkyllithium reagents were carefully determined and periodically checked using the double-titration method.^{30c}

G.l.c. analyses were performed using a Wilkens Aerograph Hy-Fi Model 600-B gas chromatograph. The following columns were employed: 5% Carbowax 20M on 80/100 mesh Chromosorb P (6 ft. x 1/8 in.) (20M-A); 1% Carbowax 20M on 80/100 mesh Chromosorb W (2 ft. x 1/8 in.) (20M-B); 20% Carbowax 20M on base-washed 80/100 mesh Chromosorb P (12 ft. x 1/8 in.) (20M-C); 20% LAC-1-R296 (Cambridge Industries Co.)- 3% H₃PO₄ on acid-washed 80/100 mesh Chromosorb W (4 ft. x 1/8 in.) (LAC); 10% 3-nitro-3-methylpimelonitrile on 80/100 mesh Chromosorb P (8 ft. x 1/8 in.) (NMPN);

5% SE-30 on 60/80 mesh Chromosorb W (5 ft. x 1/8 in.) (SE-A); 1% SE-30 on 80/100 mesh Chromosorb W (6 ft. x 1/8 in.) (SE-B). Peak areas were determined by planimetry or triangulation. G.l.c. response factors employed refer to the correction to be applied to convert relative peak areas of unknown and standard to mole or weight ratios, i.e., to satisfy the relationship

$$\frac{\text{Wt. or moles of X}}{\text{Wt. or moles of S}} = R_F \frac{A_X}{A_S}$$

For collection of products by preparative g.l.c. an F and M Model 810 flame-ionization unit fitted with a splitter was employed utilizing 1/4 in. versions of the appropriate columns listed above.

Photochemical reactions were conducted in 10- and 40-ml quartz vessels using a Rayonet Srinivasan-Griffin Photochemical Reactor fitted with a circular bank of 16 lamps (no. R.P.R.-2537A) emitting radiation at 2537Å (Southern N. E. Ultraviolet Corp., Middletown, Conn.).

Infrared spectra were determined in CCl₄ solution utilizing Perkin-Elmer Model 237 and 337 spectrometers. Nuclear magnetic resonance spectra (n.m.r.) were determined on neat liquid samples or in CCl₄ solution using tetramethylsilane as an internal standard, a Varian A-60 spectrometer being employed. Mass spectra were recorded by means of a Consolidated Electroynamics Model 21-130 mass spectrometer using an ionization potential of 70 volts. Elemental analyses were performed by Dr. S. M.

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30. a) P. D. Bartlett, E. P. Benzing, and R. E. Pincock, J. Am. Chem. Soc., 82, 1762 (1960). b) B. J. King, Ph.D. Thesis, MIT, August, 1965. c) H. Gilman and F. K. Cartledge, J. Organometal. Chem., 2, 447 (1964).

Nagy and associates of this institute. Melting points were determined on a Mel-Temp apparatus and are uncorrected.

Tetrabromoethylene.³¹--Pentabromoethane (Columbia Org. Chem. Co.) was recrystallized from ethanol to give white crystals, m.p. 53.5-55°. A solution of 64 g (0.15 mole) of pentabromoethane in 300 ml of an 80 : 20 EtOH-MeOH mixture to which 4 drops of phenolphthalein indicator had been added was heated to reflux, and 2N NaOH was added dropwise until a permanent pink color developed (77 ml, the theoretical amount). The pink solution was refluxed for 30 min. longer and excess base was neutralized by addition of a few drops of 1N HCl. Water was added until a permanent cloudiness developed, and after cooling the precipitated white plates were collected by filtration, washed with water, and dried. After recrystallization from dilute ethanol, 46.3 g (89.7%) of pure tetrabromoethylene was obtained, m.p. 55-56° (lit.³¹ 56°).

Anal. Calcd. for C₂Br₄: C, 6.99%; Br, 93.01%. Found: C, 7.10%; Br, 92.67%.

Reaction of Tetrabromoethylene with Methylithium in Cyclohexene.--A.

An ice-cold solution of C₂Br₄ (0.345 g, 1.0 mmole) in 10 ml of cyclohexene was treated rapidly with 2.5 ml of a 1.6 M solution of CH₃Li (4 mmoles CH₃Li), during which time a white ppt. formed. After a further 30 min. reaction period in the cold, the reaction was quenched by addition of 0.5 ml of CH₃OH. After washing with H₂O, the cyclohexene solution was analyzed by g.l.c. on 20M-A (150°) and 20M-C (80°). All of the starting

31. W. Taylor and A. M. Ward, J. Chem. Soc., 2006 (1934).

material was seen to have been consumed, but no II had been formed nor were any other products detected.

B. The above reaction was repeated at room temperature and with slower addition of CH_3Li (over a 2-hr. period). After work-up and g.l.c. analysis as above, the results proved to be identical.

Reaction of Tetrabromoethylene with n-Butyllithium in Cyclohexene.--

A. At 0° , slow addition of excess BuLi: An ice-cold solution of 0.345 g (1 mmole) of C_2Br_4 in 10 ml of cyclohexene was treated over a 4.5-hr. period with 2.7 ml of a 1.5 M solution of n-BuLi (4 mmoles). The white mixture was stirred for 20 min. longer at 0° , then was quenched by addition of 0.4 ml CH_3OH and 4 ml of H_2O . G.l.c. analysis of the cyclohexene solution (20M-A and 20M-C) showed that all of the C_2Br_4 had been consumed but that no II was formed. Instead a trace yield of a product later identified as III was detected (see below).

B. At reflux, slow addition of excess BuLi: A solution of 1 mmole of C_2Br_4 in 10 ml of cyclohexene was heated to reflux in an oil bath, then was treated with 4 mmoles of BuLi (2.7 ml, 1.5 M) over a 4.5-hr. period. After 20 min. longer at reflux, the reaction was quenched with CH_3OH and H_2O and the cyclohexene layer was analyzed by g.l.c. A single product was detected (20M-A, 150°) in significant yield. After isolation by preparative g.l.c., its infrared spectrum showed strong absorption at $3040\text{-}3010\text{ cm}^{-1}$ (olefinic C-H) and at 1640 cm^{-1} (C=C) and was qualitatively similar to that for cyclohexene in the fingerprint region. The n.m.r. spectrum consisted of a complex, broad pattern in the CH_2 region and a coarse triplet for vinyl protons centered at 4.38τ . The mass spectrum yielded peaks at m/e 162 (M^+) and m/e 81 ($\text{M}^+/2$, base peak).

On the basis of these data the product was identified as 3,3'-bicyclohexenyl (III).

C. At reflux, slow addition of the stoichiometric amount of BuLi: To a refluxing solution of 1 mmole C_2Br_4 in 10 ml of cyclohexene was added over a period of 3 hrs. 1.4 ml of a 1.4 M BuLi solution (2 mmoles). The mixture was refluxed for 30 min. longer and was then quenched as before. G.l.c. analysis (20M-A, 150°) revealed that only a trace of III had been formed (only 1% of that obtained from experiment B) and moreover that C_2Br_4 remained. Comparison with a standard solution indicated that only 70% of the starting material had undergone reaction.

D. At reflux, "rapid" addition of excess BuLi: A refluxing solution of 1 mmole C_2Br_4 in 10 ml of cyclohexene was treated with 4 mmoles BuLi (2.9 ml, 1.4 M) over a period of 20 min., and the reaction mixture was refluxed for 6 hrs. G.l.c. analysis of reaction aliquots (20M-A, 150°) revealed the rapid formation of III. The product still appeared to be being formed at the 6 hr. mark, when the reaction was quenched. Moreover, the final yield of III was approximately four times that obtained from the "slow" treatment with BuLi (see B above), as determined by comparison of peak areas.

Reaction of Cyclohexene with (a) Tetrabromoethylene and (b) n-Butyllithium.--Solutions of (a) 0.344 g (1 mmole) of C_2Br_4 in 10 ml of cyclohexene and (b) 4 mmoles of BuLi (2.7 ml, 1.5 M) in 10 ml of cyclohexene were refluxed side-by-side in an oil bath for 5 hrs. After cooling, the BuLi solution was quenched with CH_3OH and H_2O but the C_2Br_4 solution was not treated further. G.l.c. analysis of the two systems (20M-A, 150°) revealed that in neither case was any III produced.

Attempted Metalation of Cyclohexene by n-Butyllithium.--A solution of 2 mmoles BuLi (1.4 ml, 1.4 M) in 10 ml of cyclohexene was refluxed (oil bath) for a total period of 6 hrs. Reaction aliquots were withdrawn at various times and quenched in excess Dry Ice contained in 5-ml centrifuge tubes. After the Dry Ice had evaporated, each of the aliquots was treated with 0.25 ml of 1N HCl and solid NaCl was added to help salt out the organic acid. After removal of the aqueous layer with a syringe, the cyclohexene solution was dried over Na₂SO₄.

The main reaction mixture was cooled, poured into excess Dry Ice, and treated with 3 ml of 1N HCl. After salting out with NaCl, the cyclohexene layer was dried over Na₂SO₄.

G.l.c. analysis of the worked-up reaction aliquots (LAC, 150°) revealed the presence only of valeric acid, the product of n-BuLi carbonation. Moreover, the concentration of valeric acid from aliquot to aliquot remained constant throughout the entire course of the reaction. No product peak which could have been attributed to cyclohexene-3-carboxylic acid was detected.

Reaction of n-Butyl Bromide with n-Butyllithium in Cyclohexene.--A solution of 0.21 ml (0.27 g, 2 mmoles) of n-BuBr in 10 ml of cyclohexene was heated to reflux and was treated over 15 min. with 2 mmoles of BuLi (1.4 ml, 1.4 M). The mixture was allowed to reflux for 6 hrs., then was worked up in the usual manner. G.l.c. analysis of reaction aliquots (20M-A, 150°) disclosed the formation of III as a significant product. Moreover, its rate of formation closely paralleled that seen from reactions of C₂Br₄ with excess BuLi, and its final yield was comparable to yields obtained in the latter system.

Isolation of Acetylene from the Reaction of C_2Br_4 with $n-BuLi$.--

A mixture of 0.344 g (1 mmole) of C_2Br_4 and 4 mmoles (2.9 ml, 1.4 M) of $BuLi$ in 10 ml of cyclohexene was refluxed for 50 min. After cooling, the apparatus was arranged to allow sweeping of the reaction mixture with nitrogen. After quenching the reaction with 0.5 ml of CH_3OH , the mixture was swept with nitrogen, the effluent gas being conducted into 5 ml of an alkaline solution of $Hg(CN)_2$ (2.5 g $Hg(CN)_2$, 1.2 g KOH in 10 ml of water)³² contained in a test-tube. When precipitation of the white mercury derivative was complete, sweeping was stopped and the ppt. was washed with 5-6 portions of cold water by decantation until the washings were just barely alkaline.

A very small portion of the mercury derivative was suction filtered and dried to give a gray solid. An attempted m.p. determination resulted only in sintering to a black solid accompanied by formation of some free mercury.

The remainder of the moist solid was transferred to a small flask equipped with a side-arm and arranged for sweeping out with N_2 . The main neck of the flask was connected by silicone rubber tubing to a cooling train consisting of Dry Ice-ethanol and liq. N_2 traps. Decomposition of the mercury derivative was accomplished³³ by treating it with 10 ml of a 20% aq. KCN solution while the entire apparatus was being swept with N_2 . The derivative decomposed readily, and the evolved gas condensed as a white solid in the liq. N_2 trap. Infrared analysis of the contents of the latter produced a spectrum which matched Sadtler Standard Spectrum

32. K. A. Hofmann and H. Kirmreuther, Chem. Ber., 42, 4232 (1909).

33. N. A. Nesmeyanov and N. K. Kochetkov, Izvest. Akad. Nauk SSSR, Otdel Khim. Nauk, 587 (1949); C.A., 44, 7225 (1950).

No. 3961 for acetylene gas.

Determination of the Stoichiometry of the C_2Br_4 -BuLi Reaction.---

A. A mixture of 0.344 g (1 mmole) of C_2Br_4 and 2.7 mmoles of BuLi (1.5 ml, 1.8 M) in 10 ml of cyclohexene was stirred for one hour at room temperature. After arranging the apparatus for sweeping with N_2 , CH_3OH (0.2 ml) was added to quench the reaction and the mixture was swept with N_2 , the gas being passed into a cooling train of Dry Ice-ethanol and liq. N_2 traps. The contents of the two traps were subjected to infrared analysis. Acetylene was shown to be the major component of the liquid N_2 trap. The Dry Ice trap contained mostly cyclohexene and a little CH_3OH , but no bromoacetylene could be detected by comparison with a reference spectrum.³⁴

The quantity of C_2Br_4 remaining in the quenched reaction mixture was determined by g.l.c. by the method of standard addition (20M-A, 150°). It was found that 0.031 g. (0.09 mmole) of C_2Br_4 remained. Since 1 mmole had been introduced at the beginning of the reaction, 0.9 mmole had undergone reaction with 2.7 mmoles of n-BuLi, establishing the stoichiometry as 1 : 3 on a molar basis.

B. Lithium carbide was prepared in 3 ml of pentane by treatment of 1.10 mmoles C_2Br_4 with 2.90 mmoles n-BuLi. After quenching of the reaction the yield of n-butyl bromide was determined by g.l.c. by the method of standard addition (NMPN, 50°) to be 0.400 g (2.92 mmoles). Since this equals the number of mmoles of BuLi employed, the 1 : 1 stoichiometry of BuLi : BuBr is confirmed.

34. G. R. Hunt and M. K. Wilson, J. Chem. Phys., 34, 1301 (1961).

Determination of the Rate of Loss of n-Butyllithium in Its Reaction

with n-Butyl Bromide.--A. In cyclohexene solution: A solution of 0.21 ml (0.27 g, 2 mmoles) of n-BuBr in 10 ml of refluxing cyclohexene was treated with 2 mmoles of n-BuLi (1.4 ml, 1.4 M) over a period of 10 min. The mixture was refluxed with stirring for 6 hrs., 0.5-ml aliquots being removed at regular intervals. These aliquots were quenched in excess Dry Ice and worked up as described previously. The main reaction mixture was treated in a like fashion after completion of the reaction. G.l.c. analysis of the reaction aliquots (LAC, 150°) disclosed peaks for valeric acid and III. The consumption of BuLi and generation of III as the reaction progressed were clearly evident from the chromatograms. The percent BuLi remaining in each reaction aliquot, relative to the 30 min. aliquot, was determined from the ratio $\frac{\text{valeric acid peak ht.}}{30 \text{ min. valeric acid pk. ht.}}$, assuming a constant sample size analyzed for each aliquot. See Table II for tabulation of the results. Fig. 2 shows a second-order plot of the loss rate of BuLi.

B. In cyclohexane solution: The procedure employed for the cyclohexene reaction was used except that cyclohexene was replaced by 10 ml of cyclohexane. Total reaction time was 6 hrs. and aliquots were withdrawn, quenched, and worked up as above. G.l.c. analysis of the reaction aliquots (LAC, 150°) disclosed peaks for valeric acid and two unidentified products. The consumption of BuLi and build-up of products were clearly evident from the chromatograms. The percent BuLi remaining in each aliquot, relative to the 30 min. aliquot, was determined as above. See Table II for tabulation of results.

Table II

Reaction between n-BuLi and n-BuBr
(each initially 0.17M) in Refluxing Solvent

Reaction Time(hrs.)	% BuLi* Remaining Unreacted	
	In Cyclohexene (b.p. 83°)	In Cyclohexane (b.p. 81°)
0.5	100%	100%
1	91.5	83.5
1.5	72.2	68.4
2	71.0	59.3
3	57.6	53.1
4	50.0	47.2
5	47.5	--
6	43.7	41.8

* Determined by g.l.c. as n-valeric acid with the 30 min. reaction mark employed as reference point.

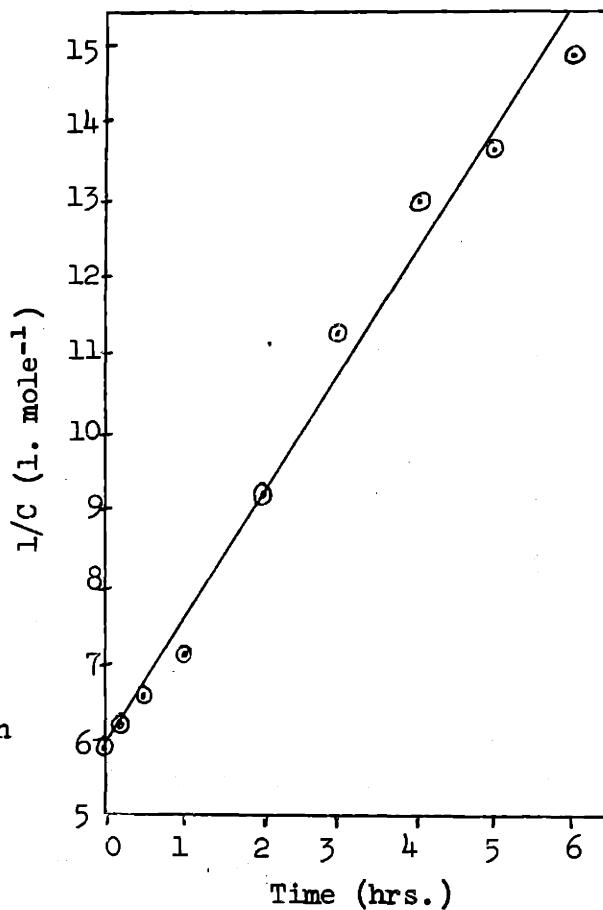


Fig. 2. Second-order plot of rate of BuLi loss in its reaction with BuBr at 83°; initial conc. of each reactant = 0.17 M; line fitted by least squares.

Monobromination of Lithium Carbide in Ether Solution and Decomposition of Lithiobromoacetylide.--A. To a solution of 0.363 g (1.05 mmoles) of C_2Br_4 in 3 ml of dry ether at 0° was added 2.90 mmoles (1.80 ml, 1.61 M) BuLi. After stirring the slurry for 15 min., 49.5 μ l (0.155 g, 0.97 mmole) of bromine was added neat over a 10 min. period. The mixture became gray, then red-brown in color, then deposited a black precipitate. After 15 min., 7 ml of cyclohexene was added and the mixture was stirred for 30 min. at 0° , for one hour at room temperature, and finally at reflux for 2 hrs. After quenching with water, the organic layer with suspended black solid was suction filtered. G.l.c. analysis of reaction aliquots (20M-A, etc., temp. up to 190°) revealed no high-boiling products. Analysis on NMPN (50°), however, disclosed a bromination product which appeared to be consumed during the course of the reaction but which initially represented 0.14 mmole of dibromoacetylene as determined by g.l.c.

The isolated black solid was washed with ether, several times with hot water and hot methanol, then with THF, then was dried in a vacuum at 55° . It did not melt up to 350° and gave the following elemental analysis: C, 64.56%; H, 3.29%; Br, 25.28%; Ash, 3.82%.

B. The above reaction was repeated except that Br_2 was added rapidly to the prepared Li_2C_2 , and after the bromine treatment, cyclohexene was added without delay. The mixture was then stirred for 30 min. at 0° , for 1.5 hrs. at room temp., and at reflux for 3 hrs. Although the reaction mixture gradually darkened, appearance of black-brown solid did not significantly occur until the reflux period. The cooled reaction mixture was quenched with 3 ml of H_2O and the layers separated. The black

solid recovered by filtration of the aqueous layer was much less in quantity than was obtained from A above.

G.l.c. analysis of reaction aliquots disclosed that after bromination, the only product discernible was dibromoacetylene (NMPN, 50°). No products which might have arisen by reaction of cyclohexene were detected.

Monobromination of Lithium Carbide in Pentane Solution and Decomposition of Lithiobromoacetylide.--Lithium carbide was prepared in 3 ml of pentane by reaction of 0.378 g (1.1 mmoles) of C_2Br_4 with 2.9 mmoles $n-BuLi$ at 0°. A solution of 49.5 μl (0.155 g, 0.97 mmole) of Br_2 in 1 ml of pentane was added dropwise, then 6 ml of cyclohexene was added rapidly at 0°. After 30 min. at 0°, the mixture was stirred at room temp. for 1 hr. and at reflux for 1.75 hrs. After cooling, the reaction mixture was quenched with 3 ml of water and the organic layer was washed with water and dried over Na_2SO_4 . No insoluble solid material was present after the water quench.

G.l.c. analysis of reaction aliquots disclosed that C_2Br_2 was produced to the extent of 0.41 mmole (g.l.c.; see below). However, no high molecular wt. products could be detected.

Dibromoacetylene.³⁵--A solution of 0.99 g of 86.4% KOH (0.855 g KOH, 0.015 mole) in 5 ml of 95% ethanol was kept under N_2 and cooled in an ice bath. Tribromoethylene (Columbia Organic Chem. Co.) (0.98 ml, 2.65 g, 0.01 mole) was added from a syringe, and the mixture was shaken and kept cool in an ice bath for 2 hrs. with occasional shaking. At the end of this time, 20 ml of pre-cooled, deaerated water was added,

35. J. W. Lawrie, Am. Chem. J., 36, 487 (1906).

whereupon a heavy, yellow-orange oil separated. The oil (0.6 ml) was transferred via syringe to 10 ml of dry ether under N_2 and dissolved therein. The ether solution was kept under N_2 until the dibromoacetylene could be destroyed by addition of iodine.

G.l.c. analysis of the ether solution (NMPN, 50°) yielded the major peak at the same retention time as the product peak obtained from the several decompositions of lithiobromoacetylide described previously.

Monobromination of Lithium Carbide in THF Solution and Decomposition of Lithiobromoacetylide.--A. At 0° : Lithium carbide was prepared from 1.2 mmoles of C_2Br_4 and 3.0 mmoles of n-BuLi in 5 ml of dry THF. This clear solution was treated rapidly with 1 mmole of Br_2 at 0° yielding a black mixture. Cyclohexene (5 ml) was added rapidly but formation of black solid was already well under way by this time. Further stirring at room temp. for 1.5 hrs. and at reflux for 2 hrs. resulted in no further physical changes. After cooling, the reaction was quenched with H_2O . The black solid-laden aqueous layer was separated, and the yellow organic phase was washed with H_2O and dried. Filtration of the aqueous layer yielded 25 mg of air-dried crude black solid.

G.l.c. analysis of the organic solution disclosed the presence of C_2Br_2 and two unidentified products in trace yields. No products attributable to cyclohexene as a precursor were discernible.

B. At Dry Ice temp.: Lithium carbide in THF was prepared as above and cooled in a Dry Ice-acetone bath. Br_2 and cyclohexene were added as before, whereupon the mixture became cloudy and dirty white. It was allowed to warm gradually to room temp. with stirring. After 15 min. the mixture was black with a suspended solid. After 3 hrs. no further change

had occurred and the reaction was quenched with 3 ml of H₂O. The organic layer was dried over Na₂SO₄. The black solid remaining in the reaction flask was collected by suction filtration, yielding 16 mg. after washing with H₂O and alcohol.

G.l.c. analysis disclosed C₂Br₂ again to be a product of the reaction together with a small amount of another bromination product. No product attributable to cyclohexene as a precursor was noted.

Monobromination of Lithium Carbide in Ether at -78° and Decomposition of Lithiobromoacetylide.--Lithium carbide was prepared from 2.90 mmoles BuLi and 1.08 mmoles C₂Br₄ in 3 ml of dry ether. After cooling in a Dry Ice-acetone bath, it was treated rapidly with 0.97 mmole of Br₂ followed by 7 ml. of cyclohexene. The still white mixture was allowed to warm gradually to room temp. After 3 hrs., the reaction was quenched, revealing that only a very small amount of brown solid material had formed.

G.l.c. analysis of reaction aliquots showed C₂Br₂ to be the only detectable product (0.58 mmole, g.l.c., NMPN). No high molecular wt. products could be detected even after analysis on a variety of columns.

Addition of Two and Three Molar Equivalents of Bromine to Lithium Carbide in Ether Solution.--A. Lithium carbide (0.97 mmole) was prepared from BuLi and C₂Br₄ in the usual manner in ether solution. After cooling in an ice bath, neat bromine was added in two portions, 49 μ l and 50 μ l (total 99 μ l, 0.309 g, 1.93 mmoles). The clear, orange solution was stirred for 75 min. at room temp., then was poured into water.

G.l.c. analysis of the ether solution confirmed that C₂Br₂ was the major product. Its yield was estimated by assuming that its molar response factor relative to n-BuBr is equal to that for C₂Br₄, viz., 2.25. Thus, knowing the yield of BuBr from the halogen-metal exchange reaction,

it was possible to determine the yield of C_2Br_2 to be 0.86 mmole or 89% based on BuLi.

B. The above experiment was repeated except that after the addition of 99 μ l of Br_2 , a third mmole (50 μ l) was added, with no further change in the appearance of the clear, orange solution. After further reaction at room temp. and refluxing for 1 hr., the reaction was quenched.

G.l.c. analysis of a reaction aliquot taken after 2 molar equivalents of Br_2 had been added disclosed that 0.81 mmole (83%) of C_2Br_2 had been formed. Chromatograms of aliquots taken after the addition of the third millimole of Br_2 disclosed the presence of no C_2Br_2 (NMPN, 50°) but showed the formation of C_2Br_4 (20M-A, 150°) as a major product, approx. 0.8 mmole calculated relative to BuBr.

Generation of Lithiobromoacetylide from Dibromoacetylene and Methyl-lithium.-- Lithium carbide was prepared from 1.2 mmoles of C_2Br_4 and 3.0 mmoles of BuLi in 3 ml of ether. The ice-cold slurry was then treated with 0.10 ml. (0.31 g, 1.95 mmoles) of neat Br_2 , giving a clear orange solution. After addition of 5 ml. of cyclohexene (withdrawal of a reaction aliquot at this point revealed that C_2Br_2 had been generated in 90% yield), the mixture was cooled to 0° and was treated with 0.99 mmole (0.9 ml., 1.1 M) of CH_3Li added over 30 min. The tan slurry was stirred at room temp. for 1 hr. and at reflux for 1.5 hrs., giving finally a black mixture. After quenching of the reaction, 16 mg. of brown insoluble solid was collected.

G.l.c. analysis revealed the presence only of some C_2Br_2 . No products attributable to cyclohexene were noted.

Reaction between LiNH_2 and 1,2-Dibromoethylene in Liq. NH_3 in the Presence of Cyclohexene.--Lithium metal 0.073 g (10.6 mmoles) was introduced into 10 ml of liquid NH_3 to which a couple of small crystals of $\text{Fe}(\text{NO}_3)_3$ had been added. The gray slurry was refluxed for 30 min. to complete the formation of LiNH_2 , then 5 ml (4 g, 50 mmoles) of cyclohexene in 5 ml of dry ether was added. After 10 min., a solution of 0.968 g (5.2 mmoles) of 1,2-dibromoethylene (Aldrich Chem. Co., a mixture of cis and trans) in 1 ml of dry ether was added over a period of 10 min. After refluxing for 2 hrs. the mixture had turned black and black solid had accumulated. The reaction was quenched by addition of 0.8 g of NH_4Cl , the NH_3 was allowed to evaporate, and the residual liquid was taken up in ether, washed, and dried. The recovered black solid amounted to 51 mg after purification by washing with ether, water, and methanol.

G.l.c. analysis of the ether solution disclosed no products which might have been attributable to a C_2 -cyclohexene adduct or any other high M.W. material. A very small amount of C_2Br_2 may have been formed.

Reaction between LiNH_2 and 1,2-Dibromoethylene in Neat Cyclohexene.--Lithium amide was prepared from 0.068 g (9.9 mmoles) of lithium and 10 ml of liq. NH_3 . The Dry Ice condenser was replaced by a water-cooled condenser fitted with a BaO drying tube and the ammonia was allowed to evaporate while 10 ml of cyclohexene was added. After cooling the amide suspension in an ice bath, a solution of 0.962 g (5.2 mmoles) of 1,2-dibromoethylene in 1 ml of cyclohexene was added. After a 45-min. room temp. reaction period, the mixture was refluxed for 2 hrs., cooled, and quenched with 5 ml of 1 N HCl . The organic layer was washed with HCl and H_2O and dried. The aqueous layer was suction filtered to recover 7 mg of a

crude black solid.

G.l.c. analysis of the reaction mixture disclosed that very little of the starting 1,2-dibromoethylene had undergone reaction. A small amount of dibromoacetylene may have been formed but no other products were discernible.

Trapping of Lithiobromoacetylide Generated from Reaction (9).--

Lithium amide (10 mmoles) was prepared from 0.071 g of lithium and 10 ml of liq. NH_3 . After cooling the gray slurry to -50° , a solution of 0.4 ml (0.909 g, 4.9 mmoles) of 1,2-dibromoethylene in 1 ml of ether was added rapidly. The cooling bath was removed and a solution of 0.52 ml (0.492 g, 5 mmoles) of cyclohexanone in 1 ml of ether was added rapidly to the refluxing mixture. After refluxing with stirring for 2 hrs., the reaction was quenched by addition of 0.8 g of NH_4Cl . Ether (5 ml) was added and the NH_3 was allowed to evaporate. An additional 5 ml of ether was added during the evaporation process. After adding 5 ml of H_2O (all solids dissolved), the ether layer was washed with H_2O and dried. A very small amount of black solid was obtained which was discarded. G.l.c. analysis (20M-A, 150°) of the ether solution disclosed two product peaks in addition to one for unreacted cyclohexanone. No dibromoacetylene proved to be present (NMPN, 50°).

Ether was stripped from the product solution and the residual orange oil was stored under petroleum ether in the ice-chest for 1.5 days; no crystallization occurred. After stripping off petroleum ether the orange oil was distilled in a Hickman still at 0.4 mm pressure, bath temp. $90-100^\circ$. G.l.c. analysis of the colorless distillate again disclosed the presence of two products plus some cyclohexanone. The two products were

finally isolated by preparative g.l.c., one being a liquid, the other a white solid. After recrystallization from petroleum ether, the solid (0.030 g) had m.p. 55-56° (lit.³⁶ 55.5-56.5° for 1-(bromoethynyl)-cyclohexanol); p-nitrobenzoate derivative m.p. 91-92° (lit.³⁶ 90.5-91°). Its infrared spectrum was consistent with that for 1-(bromoethynyl)-cyclohexanol (IV).

The infrared spectrum of the isolated liquid product showed bands characteristic of aliphatic C-H, a broad -OH band with a sharp spike at 3300 cm^{-1} ($\equiv\text{C-H}$), and a weak acetylene band at 2100 cm^{-1} . The compound is tentatively identified as 1-ethynylcyclohexanol (V) on this basis.

Trapping of Lithiobromoacetylide Generated from Reaction (5).--

Lithium carbide was generated from reaction of 0.420 g (1.2 mmoles) of C_2Br_4 and 3.0 mmoles (2.1 ml, 1.45 M) of *n*-BuLi in 3 ml of ether. After cooling to 0°, 51 μl (0.159 g, 1 mmole) of neat Br_2 was added rapidly. The slurry darkened immediately. It was treated without delay with a solution of 0.11 ml (0.10 g, 1.1 mmoles) of cyclohexanone in 0.1 ml of ether, the mixture becoming clearer. Stirring was continued at room temp. for 1 hr. and at reflux for 2 hrs., at which time there was no sign of black solid. After cooling in an ice-bath, the reaction was quenched with 2 ml of satd. NH_4Cl solution; the organic layer was washed with H_2O and dried.

G.l.c. analysis of the reaction mixture disclosed a total of six products including C_2Br_2 . The retention times (20M-A, 150°) of two of the products corresponded to those for IV and V obtained in the previous experiment.

Reaction between KNH_2 and 1,2-Dibromoethylene in Liq. NH_3 in the

36. F. Straus, L. Kollek, and W. Heyn, Chem. Ber., 63, 1881 (1930).

Presence of Cyclohexene.-- Potassium amide (10 mmoles) was prepared from 0.4 g of potassium and 10 ml of liq. NH_3 . A solution of 5 ml (4 g, 50 mmoles) of cyclohexene in 5 ml of ether was added, followed by a solution of 0.4 ml (0.91 g, 4.9 mmoles) of 1,2-dibromoethylene in 1 ml of ether over a period of 20 min. Stirring at reflux was continued for 2 hrs., at which time the mixture still contained no black solid. After quenching the reaction with 0.8 g of NH_4Cl , the mixture was worked up in the usual way.

G.l.c. analysis of the reaction mixture disclosed C_2Br_2 to be the major product. No products attributable to cyclohexene as precursor could be detected.

Generation of Potassiobromoacetylide from 1,2-Dibromoethylene and KOBu-t/DMSO in the Presence of Cyclohexene.--Cyclohexene (10 ml) was added to a solution of 2.48 g (0.022 mole) of potassium *t*-butoxide (MSA Corp.) in 20 ml of dry DMSO. After stirring for several minutes, a solution of 0.4 ml (0.91 g, 4.9 mmoles) of 1,2-dibromoethylene in 1 ml of cyclohexene was added over a 10 min. period, the mixture becoming opaque brown. It was stirred at room temp. for 2.5 hrs. and at 50-55° for 1.5 hrs., then was quenched by addition of 20 ml of H_2O .

G.l.c. analysis of reaction aliquots disclosed that no C_2Br_2 had been formed or other products attributable to reaction of cyclohexene. A brown, oily material, homogeneous with the aqueous phase of quenched aliquots appeared to be the chief product of the reaction.

Diiodoacetylene.³⁷--A 1-l., 3-neck, r.b. flask was fitted with a dropping funnel, mechanical stirrer, and a cork carrying an inlet tube

37. W. H. Dehn, J. Am. Chem. Soc., 33, 1598 (1911).

reaching into the reaction mixture and a gas exit tube. A second (200-ml, r.b.) flask fitted with a dropping funnel and a gas exit tube was filled with CaC_2 and served as a generator of acetylene gas. Acetylene flow was regulated by rate of addition of H_2O to the CaC_2 .

The reaction flask was charged with a solution of 50 g (0.3 mole) of KI in 100 ml of H_2O and flow of acetylene through the solution was commenced. A 1.1 M solution of NaOCl (0.5 M in NaOH)³⁸ was added dropwise to the stirred KI solution concomitantly with acetylene purging, at such a rate that the yellow color of NaOI which formed did not accumulate. The mixture first became cloudy, then deposited a flocculent white ppt. as NaOCl addition and acetylene passage were continued. NaOCl addition was stopped (0.35 mole) when it no longer caused discoloration of the KI solution, indicating that all of the latter had been consumed. After cooling the reaction flask in an ice bath, the heavy, white ppt. was collected by suction filtration and washed by decantation and on the filter with cold water. Yield of moist C_2I_2 was 38.0 g. The crystals were dried by dissolving in 150 ml of hot petroleum ether and letting this pink solution stand over 13 g of CaCl_2 overnight. After decanting from the drying agent, cooling of the solution to -20° caused deposition of snow-white crystals which, after collection by filtration, washing with cold petroleum ether, and air-drying, amounted to 23.4 g (56% based on KI), m.p. $75.5-76.5^\circ$ (lit.²⁵ $78.5-78.9^\circ$). The product was stored in the dark in the ice-chest.

38. Inorg. Synth., 1, 90 (1939).

Thermal Decomposition of Diiodoacetylene.--A. In Refluxing

Cyclohexene. A solution of 1.0 mmole of C_2I_2 in 7 ml of cyclohexene was heated to reflux (oil bath temp. $96-98^\circ$) with stirring. Withdrawal of a 0.5 ml aliquot after 26 hrs. and stripping of solvent therefrom under vacuum resulted in recovery of dark yellow needles soluble in ether and benzene, less soluble in petroleum ether. Presumably this material was C_2I_2 . The mixture was finally heated for a total period of 48 hrs. The clear, yellow solution was cooled, washed once with $NaHSO_3$ solution and with H_2O , and was dried.

G.l.c. analysis of reaction aliquots disclosed the formation of 3 products in very low yield; none were isolated.

B. In Refluxing Cyclohexene with Added Zinc Metal. The above experiment was repeated with addition of 0.08 g (1.2 mg-atoms) of zinc dust. The stirred suspension was heated to reflux for 30 hrs. The clear, yellow solution was cooled, poured into water, and dried.

G.l.c. analysis of reaction aliquots disclosed the formation of several products. A major product appeared to be moniodoacetylene based on its retention time (20M-A, 80°). Other products were not identified.

C. In Refluxing Styrene. A solution of 1.0 mmole of C_2I_2 in 7 ml of styrene was heated at reflux (bath temp. 155°) for 2.5 hrs. The mixture was wine-red in color. A marked increase in the viscosity of the mixture appeared to have occurred at the 1.75 hr. reaction mark. The final mixture was worked up as in A above.

G.l.c. analysis of reaction aliquots showed that only very high M.W. material had been formed. No products close to styrene in volatility or lower in volatility were discerned. The high M.W. material was not characterized.

D. In Refluxing Cumene. A solution of 1.0 mmole of C_2I_2 in 7 ml of cumene was heated at reflux (bath temp. 165°) for 6 hrs., during which time the mixture became wine-red in color, indicating liberation of I_2 . After cooling, the dark red mixture was worked up as in A above.

G.l.c. analysis of reaction aliquots disclosed that in addition to some apparently high M.W. material, a single significant product, which eluted just after cumene (20M-A, 120°), had formed. Formation of this product appeared to be complete after 1-2 hrs. of heating with some loss thereof occurring thereafter. Isolation of the material by preparative g.l.c. yielded a colorless liquid, the infrared spectrum of which matched that for α -methylstyrene in every respect.

Reaction between Iodine and Cumene at Reflux.--A wine-red solution of 0.251 g (0.99 mmole) of I_2 in 7 ml of cumene was heated to reflux. After 3.5 hrs. the reflux condensate had lost most of its purple color. Reaction aliquots withdrawn after 4 hrs. at reflux were black rather than red in color. After 6 hrs. the reaction was cooled to room temp. When the reaction flask was opened, white noxious fumes were evolved, indicating that HI had probably been formed. The blackish reaction mixture was washed with $NaHSO_3$, H_2O , and brine and dried (Na_2SO_4).

G.l.c. analysis of reaction aliquots (20M-A, 120°) disclosed that α -methylstyrene had in fact been formed, but its maximum yield after 1-hr. reaction was but a fraction of that obtained from reaction of cumene with C_2I_2 . Moreover, α -methylstyrene, once formed, was consumed at a faster rate than noted in the C_2I_2 -cumene experiment. The major products of the reaction were two high-boiling materials which were not identified.

Determination of Yield of Free I₂ from Thermal Decomposition of C₂I₂ in Cumene.--Several experiments were run in which 1 mmole of C₂I₂ was heated in 7 ml of refluxing cumene for various periods of time followed by either slow cooling to room temp. or rapid cooling by immersion of the still hot reaction flask in an ice-salt bath. After rinsing the condenser down with 1 ml of ether, 5 ml of an aqueous solution containing 1.5 g of KI was added to the reaction mixture with vigorous stirring, and the free I₂ was titrated using std. Na₂S₂O₃. The results are tabulated in Table III.

Table III

Yield of I₂ from Thermal Decomposition of C₂I₂ in Refluxing Cumene

<u>Mmoles C₂I₂</u>	<u>Reaction Time (hrs.)</u>	<u>Rate of Cooling</u>	<u>Mls. 0.1008N Na₂S₂O₃ Req'd.</u>	<u>Yield I₂ (g.)</u>	<u>% I₂ (Based on C₂I₂)</u>
1.02	1.33	slow	0.45	0.0058	2.2
1.01	1.75	slow	0.45	0.0058	2.3
1.00	1.75	rapid	0.25	0.0032	1.3
1.00	6.0	slow	0.80	0.0102	4.0
1.00	6.0	rapid	0.45	0.0058	2.3

Isolation and Identification of Tetraiodoethylene from Decomposition of C₂I₂ in Refluxing Cumene.-- The following procedure was carried out on one of the short and one of the long reactions reported in Table III. The dried reaction mixture, after titration for I₂ was distilled at the water pump to concentrate the product sought. The dark residue remaining was taken up in hot ether, filtered, and concentrated again under vacuum. The dark residual solid was recrystallized twice from benzene-ethanol

to give glistening, dark-yellow crystals of tetraiodoethylene, m.p. 190-191° (decomp.) lit.²⁵ 188-189°); mixed m.p. 188.5-191.5° with authentic C₂I₄.

Tetraiodoethylene.^{25,28}--A mixture of 3.00 g (10.8 mmoles) of C₂I₂ and 2.75 g (10.8 mmoles) of I₂ in 20 ml of toluene was refluxed for 3 hrs. The still red, clear solution was cooled to room temperature and allowed to stand overnight protected from light. After cooling in an ice-bath, a crop of lemon-yellow crystals was collected by suction filtration and combined with a second crop obtained by concentration of the mother liquor. After washing with cold ethanol and air-drying, yield of C₂I₄ was 5.36 g (93.2%). After twice recrystallizing from toluene, it had m.p. 191-192.5° (lit.²⁵ 188-189°).

Anal. Calcd. for C₂I₄: C, 4.52%; I, 95.48%. Found: C, 4.49%; I, 95.30%.

Isolation and Identification of Monoiodoacetylene from Decomposition of C₂I₂ in Refluxing Cumene.--The top of the condenser of the reaction apparatus was arranged to lead to a gas-trapping train consisting of traps immersed in Dry Ice-acetone and liq. N₂ in series. The reaction flask was charged with a solution of 0.558 g (2.0 mmoles) of C₂I₂ in 10 ml of cumene and a 20 gauge needle was inserted in the septum of the side-arm to allow continuous purging of the reaction mixture with N₂. The solution was heated at reflux (bath temp. 165°) for a total period of 3.5 hrs. with continuous nitrogen sweeping. At the end of this time the mixture was cooled and the cold traps were isolated.

The contents of each of the traps were transferred to a gas infrared cell and the spectra recorded. The liq. N₂ trap was found to be essentially

devoid of material except for the presence of weak bands found also in the spectrum of the Dry Ice trap contents. No bands attributable to acetylene could be discerned. The spectrum of the contents of the Dry Ice trap, however, showed acetylenic C-H absorption at 3300 cm^{-1} and a band at 2050 cm^{-1} . It was identical to the gas-phase spectrum for authentic monoiodoacetylene (see below).

Determination of Yield of HI from Decomposition of C_2I_2 in Refluxing Cumene.--The top of the reflux condenser of the reaction apparatus was connected by means of silicone rubber tubing to a finely drawn capillary tube which dipped to the bottom of a test tube containing 15 ml of H_2O . The reaction flask was charged with a solution of 0.559 g (2.0 mmoles) of C_2I_2 in 10 ml of cumene and nitrogen purging of the system was begun, the effluent gases being allowed to pass through the water trap. The solution was heated at reflux for 3.5 hrs. with continuous N_2 sweeping. At the end of this time, the water trap was disconnected, its contents were transferred to a 50 ml Erlenmeyer flask, and trapped acid was titrated with standard NaOH. The volume of 0.096 N base required was 1.25 ml, representing only 0.12 meq. of HI liberated from the reaction.

The anion of the trapped acid was proven to be iodide by precipitation of yellow AgI , which on reduction with $\text{Zn-H}_2\text{SO}_4$ and subsequent treatment with H_2O_2 gave a purple color in CCl_4 .³⁹

Determination of Yields of Five Products from the Thermal Decomposition of C_2I_2 in Refluxing Cumene.--The top of the reflux condenser of the reaction apparatus was connected by means of silicone

39. L. J. Curtman, "Introduction to Qualitative Chemical Analysis," MacMillan, New York, 1947, p. 320.

rubber tubing to a macro-size g.l.c. collector, which was immersed in a Dry Ice-acetone bath. The trap was charged with a solution of 45 μ l (57.6 mg., 0.42 mmole) of n-butyl bromide in 4 ml of ether, which was to act as an internal standard for estimation of yield of monoiodoacetylene which was to be trapped in the apparatus. The trap outlet was connected to a Nujol bubbler to facilitate control of N_2 flow.

A solution of 0.555 g (2.0 mmoles) of C_2I_2 in 10 ml of cumene was charged into the reaction flask, and the entire system was flushed with N_2 through a 20 gauge needle inserted through a septum in the flask side-arm. The mixture was heated to reflux and heating and sweeping of the mixture with N_2 were maintained for 3.5 hrs. At the end of this time, the mixture was cooled and the cold trap containing solid monoiodoacetylene was disconnected. While the trap was still cold, the product was carefully washed into the ether contained in the trap by tilting and gently agitating the latter. In this way, a solution of monoiodoacetylene in 4 ml of ether containing n-BuBr as an internal standard was obtained.

A. Yield of Free I_2 .--The reflux condenser of the reaction apparatus was rinsed down with 1-2 ml of ether, and a solution of 1.5 g KI in 5 ml of H_2O was added to the reaction flask. Free I_2 was titrated with 0.1008 N $Na_2S_2O_3$ to a starch end-point, 2.20 ml being required. This corresponds to 0.11 mmole I_2 .

B. Yield of Monoiodoacetylene.--The ether solution of $HC\equiv CI$ containing the internal standard was analyzed by g.l.c. on Cols. 20M-A (80°) and NMPN (50°). The response factor of monoiodoacetylene relative to n-BuBr could not be measured, but it was assumed to be equal to that

for C_2Br_4 determined previously, viz., 2.25 on a molar basis. Using this value and the relative peak areas for the product and standard peaks, the calculated yield of $HC\equiv CI$ was 0.42 mmole.

C. Yield of α -Methylstyrene.--Just prior to iodine titration, 50 μ l (38 mg) of n-tridecane was added to the cooled reaction mixture as an internal standard for α -methylstyrene (response factor 0.93). G.l.c. analysis of the reaction mixture (20M-A, 100°) (after titration for I_2) and determination of relative peak areas yielded a value of 0.54 mmole for the yield of α -methylstyrene.

D. Isolated Yield of Insoluble Polymeric Solid.-- After the yield of α -methylstyrene had been determined, the reaction mixture was suction-filtered to collect insoluble dark solid. Total yield of air-dried product was 15 mg.

E. Isolated Yield of Tetraiodoethylene.--The filtered, dark reaction mixture was concentrated carefully at the water pump, resulting in a two-phase mixture of a yellow solid and a dark brown liquid. After separation of the liquid, the solid was suspended in cold ethanol and collected by suction filtration. Yield of crude C_2I_4 was 0.177 g (0.33 mmole). After two recrystallizations from toluene, the yellow solid melted at $188-189^\circ$ (lit.²⁵ $188-189^\circ$).

Table IV

Yields of Products from Decomposition of 2.0 Mmoles of C_2I_2 in Cumene at 150°

Product	Yield (Mmoles)	% Yield*	I Content (Mg-atoms)	% I Acctd. For	"C ₂ " Content (Mmoles)	% "C ₂ " Acctd. For
$HC\equiv CI$	0.42	31.6	0.42	10.5	0.42	21.0
$I_2C=CI_2$	0.33	49.3	1.32	33.0	0.33	16.5
α -Methylstyrene	0.54	80.6	--	--	--	--

Table IV continued--

Product	Yield (Mmoles)	% Yield*	I Content (Mg-atoms)	% I Acctd. For	"C ₂ " Content (Mmoles)	% "C ₂ " Acctd. For
Free I ₂	0.11	--	0.22	5.5	--	--
HI	0.12	--	0.12	3.0	--	--
Polymeric solid	15 mg.	--	?	--	?	--
Totals			2.08	52.0	0.75	37.5

* Based on stoichiometry of eq. 15

Dicumyl.⁴⁰--A solution of 12.2 g (0.084 mole) of di-t-butyl peroxide in 33 ml (28.4 g, 0.24 mole) of cumene was heated in an oil bath at 140° in a N₂ atmosphere under an efficient reflux condenser. Heating was maintained for 48 hrs., at the end of which time the solution was still clear and colorless. Volatile material and solvent were distilled at atmospheric pressure through a Vigreux column leaving a cloudy white pot residue which on cooling solidified into a white, crystalline mass, yield 9.26 g (46%). Recrystallization from ethanol yielded 7.00 g of pure dicumyl, m.p. 115-117° (lit.⁴⁰ 118-119°).

Anal. Calcd. for C₁₈H₂₂: C, 90.70%; H, 9.30%. Found: C, 90.74%; H, 9.13%.

Detection and Isolation of High-Boiling Products from the Thermal Decomposition of C₂I₂ in Refluxing Cumene.--Using Col. 20M-B (100°) and high-sensitivity settings on the gas chromatograph, it was possible to detect three apparently high M.W. products of the reaction in low yield. The middle peak of the three corresponded in retention time to dicumyl.

40. E. H. Farmer and C. G. Moore, J. Chem. Soc., 131 (1951).

The other two products were isolated in low yield by preparative g.l.c. as dark red-brown liquids. Infrared analysis yielded for the first product (Product A) a single band at 3050 cm^{-1} , very weak bands at $3000\text{-}2580\text{ cm}^{-1}$ and at 1500 and 1450 cm^{-1} , and strong bands at 1185 , 695 , and 600 cm^{-1} . For the second product, typically aromatic absorptions were obtained with other significant bands at 1130 and 700 cm^{-1} . Due to the small amounts of materials collected, the n.m.r. spectra were weak. However, the first product showed a sharp singlet at very low field, 1.5τ , with other much weaker absorption characteristic of cumene (indicating the lack of purity of the sample isolated). The second product showed some aromatic absorption. These data were insufficient to permit characterization of the compounds.

Kinetic Analysis of the Thermal Decomposition of C_2I_2 in Refluxing Cumene.---Kinetic runs were performed in the following manner. n-Tridecane ($45\text{ }\mu\text{l}$, 34.4 mg) was added to 6 ml of cumene as an internal standard. The solution was heated to reflux (bath temp. 165°) and a solution of 1 mmole of C_2I_2 in 1 ml of cumene was then added rapidly. A 0.1 ml aliquot of the mixture was withdrawn immediately and served as the zero-time aliquot. Aliquots of the refluxing mixture were then taken at intervals up to 6 hrs. for run No. 1, up to 2 hrs. for run No. 2. Aliquots were quenched by squirting them into vials which were cooled in an ice bath. The formation of α -methylstyrene and the formation and decomposition of monoiodoacetylene could be followed by g.l.c. using Col. 20M-A (100°). Col. 20M-B (100°) was employed to follow loss of C_2I_2 . The raw data are depicted in Fig. 1, all peak hts. having been normalized to the n-tridecane peak. The first order plots of the kinetic data are shown

in Figs. 3 and 4. Run No. 2 differed from No. 1 only in that reaction aliquots were withdrawn at 5 min. intervals over the first 60 min. of the reaction to provide more points in the critical area of the kinetic plot.

Thermal Decomposition of C_2I_2 in Refluxing Cyclooctane.--A solution of 0.280 g (1.0 mmole) of C_2I_2 in 7 ml of cyclooctane was heated at reflux (bath temp. 165°) for 6 hrs. During this time it became dark violet in color. After the mixture had cooled, the condenser was rinsed down with 1 ml of ether, a solution of 1.5 g KI in 5 ml of H_2O was added to the reaction flask, and the free I_2 was titrated with 0.1008 N $Na_2S_2O_3$, 0.4 ml being required. This represents 0.02 mmole I_2 (2.0% based on C_2I_2). The organic layer was washed with H_2O and dried.

G.l.c. analysis of reaction aliquots (20M-B, 100°) disclosed that C_2I_2 was completely consumed by the 2-hr. reaction mark. (See Fig. 5 for the first-order plot depicting the rate of loss of C_2I_2 from this experiment.) A product (Product B) eluting with twice the retention time of C_2I_2 was found to start to undergo decomposition after 1.5 hrs. heating. The highest M.W. product formed had the same retention time as Product A obtained from the decomposition of C_2I_2 in cumene. A product eluting from Col. 20M-A (150°) had the same retention time as cyclooctyl iodide and was itself somewhat unstable under the reaction conditions. In addition to the products mentioned, several others were detected in lower yields.

When the main reaction mixture was stripped of solvent by distillation through a Holtzmann spiral-wire column, a clear, dark yellow-green oil was left, but no solid separated even upon cooling. Analysis of this

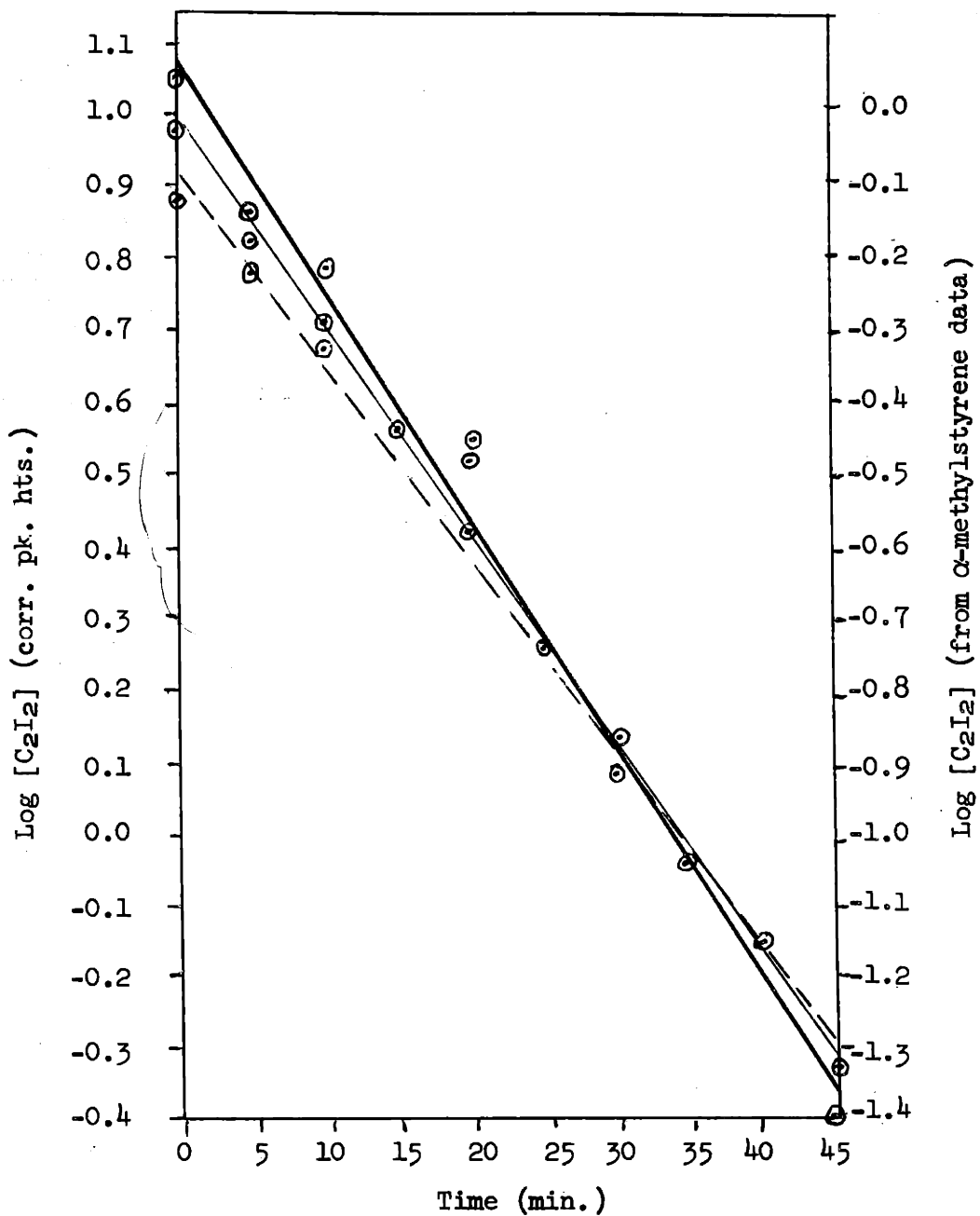


Fig. 3. First-order plot for decomposition of C_2I_2 in cumene at 150° .
From C_2I_2 peak ht. data: — Run 1; --- Run 2; — from α -methylstyrene
peak area data (from Run 1) (right hand scale). Lines fitted by least squares.

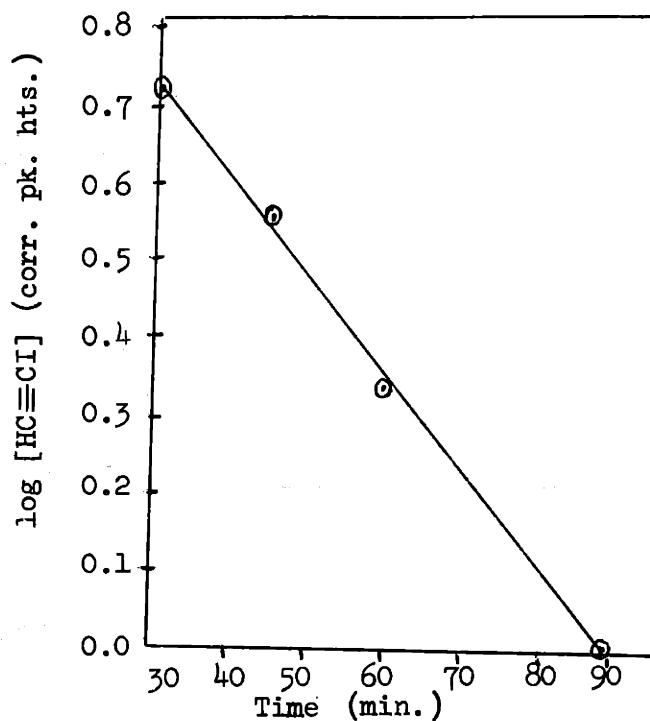


Fig. 4. First-order plot for decomposition of HC≡CI (g.l.c.) in cumene at 150°; (from Run No. 1); $k_1 = 0.028 \text{ min.}^{-1}$

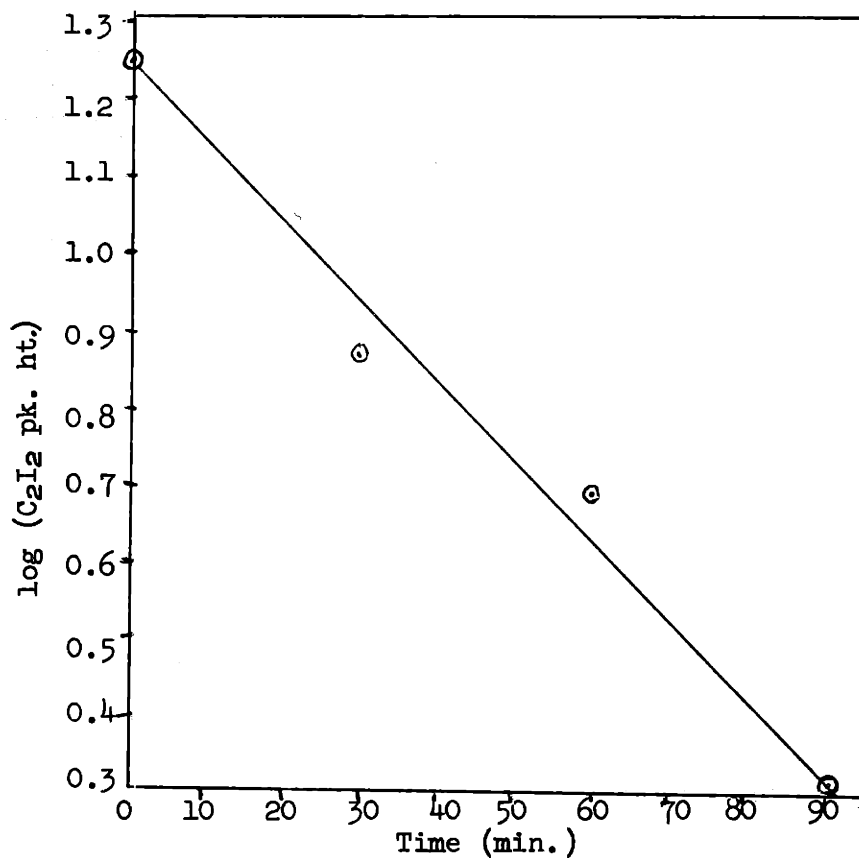


Fig. 5. First-order plot of kinetic data (g.l.c.) for thermal decomposition of C₂I₂ in refluxing cyclooctane; $k_1 = 0.023 \text{ min.}^{-1}$

residual oil by g.l.c. (SE-B) and by t.l.c. failed to reveal the presence of any C_2I_4 .

The high M.W. product mentioned above was isolated by preparative g.l.c. It proved to be a reddish-brown oil which exhibited infrared bands at 3060 (w), 1600 (w), 1540 (w), 1510 (w), 1450 (w), 1190 (s), and 610 (s) cm^{-1} . Its n.m.r. spectrum showed only singlet absorption at 1.5 τ with much weaker broad absorption at higher field due to cyclooctane impurity. In these respects the product was identical to Product A isolated from the cumene system.

Isolation of Monoiodoacetylene from Thermal Decomposition of C_2I_2 in Cyclooctane.--A gas-trapping train consisting of traps immersed successively in Dry Ice-acetone and liq. N_2 was filled with N_2 and connected to the top of the reflux condenser attached to the reaction flask. The latter was charged with a solution of 0.554g (2.0 mmoles) of C_2I_2 in 10 ml of cyclooctane, a N_2 -inlet tube was introduced via the no-air stopper in the flask side-arm, and N_2 flow through the entire apparatus was started. The reaction mixture was heated at reflux with continuous N_2 sweeping for 3.25 hrs. At the end of this time the reaction mixture was cooled and the cold traps were isolated.

The contents of the Dry Ice trap were transferred to a gas IR cell and the spectrum recorded: bands at 3350-3300 (doublet), 2050 ($C\equiv C$), 1240, and 630 cm^{-1} ; superimposable on the spectrum of a known sample of monoiodoacetylene. Several bands were also present which could not be accounted for. The IR spectrum of the contents of the liq. N_2 trap was merely a much weaker version of the above spectrum.

The recondensed contents of the Dry Ice trap were taken up in

ether and analyzed by g.l.c. using Cols. 20M-A (80°) and NMPN (50°). Two trace products in addition to $\text{HC}\equiv\text{CI}$ were detected and probably account for the extra peaks noted in the IR spectrum above. These products are unidentified.

Analysis of the main reaction mixture (20M-B, 100°; 20M-A, 150°) confirmed the formation of all of the products seen previously without N_2 sweeping. Moreover, the compound dicyclooctyl was shown not to be a product of the reaction by g.l.c. by comparison with a known sample.

Cyclooctyl Iodide.⁴¹--A mixture of 8.0 g (0.0625 mole) of cyclooctanol and 36.0 g of 55% HI solution (20.0 g, 0.155 mole HI) was heated on a steam bath with occasional shaking for 6.75 hrs. After cooling, the mixture was poured onto 30 g of ice and the organic layer was taken up in ether and combined with several ether extracts of the aqueous layer. The combined organic solutions were washed with H_2O , NaHCO_3 , and $\text{Na}_2\text{S}_2\text{O}_3$ solution and were dried over CaCl_2 . After filtering, ether was evaporated at the water pump, leaving 9.3 g of dark brown residue. Distillation of the latter through a spiral-wire Holtzmann column at the water pump yielded a forerun (0.13 g), b.p. 27-28°/8 mm, followed by the main product at 106-107°/8 mm. The latter appeared to undergo partial decomposition at the head of the distilling column so that the product collected was a clear, red-brown oil. A center cut amounting to 3.6 g was collected and used for subsequent purposes.

G.l.c. analysis of the distilled product (20M-B, 90°; SE-A, 130°) disclosed the presence of a single impurity besides cyclooctyl iodide. This impurity is most likely cyclooctene.

Anal. Calcd. for $\text{C}_8\text{H}_{15}\text{I}$: C, 40.37%; H, 6.30%; I, 53.33%. Found:

41. L. Ruzicka, R. A. Plattner, and H. Wild, *Helv. Chim. Acta*, 28, 395 (1945).

C, 43.11%; H, 6.51%; I, 52.74%.

Isolation of Unstable Product (Product B) from Shorter-Term Decomposition of C_2I_2 in Refluxing Cyclooctane.--A solution of 0.558 g (2.0 mmoles) of C_2I_2 in 10 ml of cyclooctane was heated at reflux with stirring for 3.25 hrs. After cooling, the clear, reddish-brown mixture was decanted from a blackish insoluble solid. G.l.c. analysis (20M-B, 100°) showed that the Product B was present in significant yield. The reaction mixture was concentrated at the water pump, and this product was isolated by preparative g.l.c. The dark red oil exhibited IR bands at 3310 ($\equiv CH$) and 2110 ($C\equiv C$) cm^{-1} plus absorption in the regions 3000-2700 and 1500-1300 cm^{-1} . The fingerprint region was quite similar to that in the spectra of cyclooctane and cyclooctyl iodide. The n.m.r. spectrum failed to show the acetylenic proton (apparently buried in the broad peak at δ 2.23) but rather was identical to the spectrum of cyclooctyl iodide: δ 1.60 (10 H) (broadened singlet), δ 2.23 (4 H) (broad multiplet), and δ 4.52 (1 H) (quintet). The mass spectrum gave a base peak at m/e 110 ($C_8H_{14}^+$), with other strong peaks at m/e 95, 97, and 109. A trace peak was also present at m/e 262, which is consistent with the gross structure VI for product B.

Prolonged Refluxing of Iodine in Cyclooctane: a Control Experiment.--

A mixture of 0.254 g (1.0 mmole) of I_2 in 7 ml of cyclooctane was refluxed for 6 hrs. (The iodine was only partially soluble in cold cyclooctane.) By the 4.5 hr. reaction mark the initially wine-red reflux condensate had completely lost the iodine color. At the end of the reflux period, the black mixture was cooled. When the reaction flask was opened, a small amount of white fumes was emitted.

Before g.l.c. analysis, each of the reaction aliquots was treated with $\text{Na}_2\text{S}_2\text{O}_3$ solution to remove I_2 . Analysis on Cols. 20M-B (100°) and 20M-A (150°) disclosed that no products were formed at any time during the heating period that could be detected by this method of analysis.

Thermal Decomposition of Cyclooctyl Iodide in Refluxing Cyclooctane.--

A solution of 0.18 ml (0.264 g, 1.1 mmoles) of cyclooctyl iodide in 7 ml of cyclooctane was refluxed with stirring for 6 hrs. On opening the cooled apparatus, white smoke was emitted. G.l.c. analysis of reaction aliquots (20M-B, 100° ; 20M-A, 150°) disclosed that cyclooctyl iodide was completely consumed after 2-3 hrs. at reflux. Only two products of the decomposition were discernible on each of the columns but only one of these on each column coincided in retention time with products obtained from decomposition of C_2I_2 in cyclooctane.

Thermal Decomposition of C_2I_2 in Refluxing n-Nonane.--A solution of 0.279 g (1.0 mmole) of C_2I_2 in 7 ml of n-nonane (Aldrich Chem. Co.) was heated at reflux with stirring for 6 hrs. The reflux condensate did not discolor due to the appearance of free I_2 until 3-3.5 hrs. at reflux. The final reaction mixture was a clear, reddish-orange with some suspended black solid. Very little free I_2 appeared to be present so no titration of the latter was attempted. After decantation from the insoluble solid, the reaction solution was not treated further. Yield of crude, ether-washed polymeric solid was 14 mg.

G.l.c. analysis of reaction aliquots disclosed the formation of at least 6 products. C_2I_2 could be seen to undergo gradual decomposition (20M-B, 100°), but a small amount was still present

after the 6 hr. reflux period. A product eluted from Col. 20M-B (100°) whose retention time was identical to that of the Product A obtained in the cumene and cyclooctane systems. None of the other products were identified.

The C_2I_2 peak ht. data obtained from 10 aliquots withdrawn at various time intervals were translated into data suitable for a first-order kinetic plot (see Fig. 6).

After the above analyses, the reaction mixture was concentrated and the product A was isolated by preparative g.l.c. It was red-brown in color and gave infrared and n.m.r. spectra identical to the products A isolated from the cyclooctane and cumene systems. In addition, mass spectral analysis afforded peaks at m/e 127 (100%, I^+), 152 (27%, $HC\equiv CI^+$), 254 (22%, I_2^+), 279 (20%, $ICH=CI^+$), and 406 (9%, M^+). These results are consistent with identification of Product A as triiodoethylene.

The oil remaining from the preparative g.l.c. work yielded by suction filtration 6 mg of glistening yellow-green crystals. After one recrystallization from toluene the solid had m.p. 188-190° (decomp.), identifying it as tetraiodoethylene.

Thermolysis of C_2I_2 in n-Nonane with Concurrent Passage of Gaseous HI.--Gaseous HI was generated by dropping a saturated solution of I_2 in 57% aq. HI (prepared from 100 g of I_2 and 50 g of HI solution) onto 50 g of red phosphorus, according to the method of Vogel.⁴² The

42. A. I. Vogel, "Practical Organic Chemistry," Longmans, Green, and Co., 3rd Ed., 1956, p. 182.

gas so generated was passed into a solution of 0.278 g (1.0 mmole) of C_2I_2 in 7 ml. of n-nonane, which was gradually heated to reflux with stirring. The mixture was heated thus with continued passage of HI for a period of 4 hrs. Soon after starting reflux, the reflux condensate became purple in color; later a purplish-brown solid accumulated in the reflux condenser. After completion of the reaction, HI flow was stopped and the cooled purple reaction mixture was treated with dil. $Na_2S_2O_3$ solution, H_2O , saturated $NaHCO_3$, and water again and was dried over Na_2SO_4 . The reflux condenser appeared to contain black crystals of I_2 .

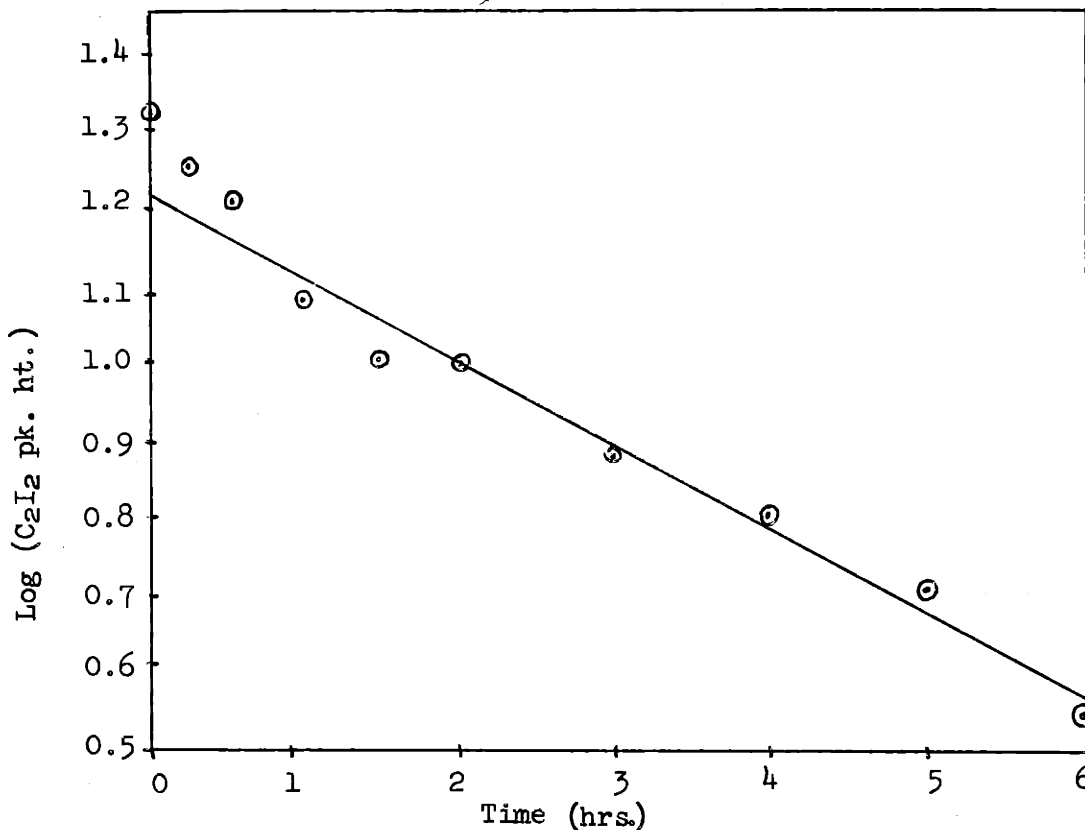


Fig. 6. First-order plot of kinetic data (g.l.c.) for thermal decomposition of C_2I_2 in refluxing n-nonane; $k_1 = 0.24 \text{ hr.}^{-1}$

G.l.c. analysis of reaction aliquots (20M-B, 100°) revealed that C_2I_2 had been completely consumed by the 1-hr. reflux mark. Triiodoethylene first increased in yield, then gradually itself appeared to undergo consumption. Several other products of the reaction also were detected but none was identified.

Triiodoethylene.--An ice-cold solution of 0.280 g (1.0 mmole) of C_2I_2 in 7 ml of dry ether was treated dropwise with 1.8 ml of an 0.55 M solution of CH_3Li in ether (0.99 mmole CH_3Li) over a period of 2 hrs. After stirring for 30 min. at room temp., the reaction was quenched by addition of 2 ml. of water. After drying over Na_2SO_4 for 1.5 hrs., the ether solution was analyzed by g.l.c. (20M-A, 80°) revealing the presence of $HC\equiv CI$ and CH_3I in good yield.

To the dried ether solution of monoiodoacetylene was added a solution of 0.258 g (1.0 mmole) of I_2 in 2 ml of ether. The flask was wrapped in aluminum foil and the contents were stirred at room temp. Since g.l.c. analysis of reaction aliquots indicated that consumption of $HC\equiv CI$ was very slow, the reaction was allowed to proceed for 72 hrs. At the end of this time the reaction was quenched by addition of 2 ml of $Na_2S_2O_3$ solution. The ether layer was washed with H_2O and dried (Na_2SO_4). G.l.c. analysis (20M-B, 100°) revealed the successful synthesis of triiodoethylene.

Upon evaporation of solvent at the water pump, the residual brownish oil contained suspended yellow solid. After cooling in a methanol-ice bath, the bulk of the crystals were removed mechanically with a spatula and that remaining in the reaction flask (suspended in the oil) was recrystallized from 95% ethanol, the mother liquor being carefully

retained. Recrystallization of the combined yellow solids from ethanol yielded 20 mg, m.p. 189-192° (decomp.), identifying the material as tetraiodoethylene.

G.l.c. analysis of the ethanolic mother liquor obtained above proved the presence of triiodoethylene therein. After evaporation of solvent in a stream of N₂, the residual yellow oil was distilled rapidly in a small Hickman still at 0.02 mm pressure at an air bath temp. of 40-60°. Infrared analysis of the yellow product showed bands at 3050, 1190, 720, and 605 cm⁻¹, identical to the spectra of triiodoethylene obtained from the decompositions of C₂I₂. Moreover, its g.l.c. retention time (20M-B, 100°) matched that for triiodoethylene obtained from the same decompositions. The remainder of the product (25 mg, 6%) was submitted for elemental analysis.

Anal. Calcd. for C₂HI₃: I, 93.83%. Found: I, 94.17%.

Generation of Lithioiodoacetylide in Cyclohexene Solution.--To a solution of 0.283 g (1.0 mmole) of C₂I₂ in 10 ml of cyclohexene kept at 0° was added 1.3 mmoles (1.3 ml, 1.0 M) of CH₃Li over a 1.5 hr. period. The mixture was then stirred at room temperature for 4 hrs., after which it was quenched with 3 ml of H₂O and the organic layer was washed with H₂O and dried over Na₂SO₄.

G.l.c. analysis of the cyclohexene solution (20M-A, 100° and 150°; NMPN, 50°) disclosed a single reaction product discernible on both columns. An attempt to collect the material from the dilute solution by preparative g.l.c. using a variety of small collectors and cooling baths was not successful. Therefore, the solution was concentrated by distillation through a spiral-wire Holtzmann column, where it was found

that all of the desired product distilled over in an early fraction between ether and cyclohexene (over the range 40-79°). The product was finally isolated from this enriched fraction by preparative g.l.c. employing a large-volume collector. It proved to be a solid at Dry Ice temp. A gas phase sample of the product was drawn into an evacuated gas IR cell and the IR spectrum measured. Characteristic absorptions were obtained at 3300 cm^{-1} (sharp doublet), 2050 cm^{-1} and 628 cm^{-1} . Monoiodoacetylene has been reported⁴³ to exhibit bands at 3320, 2075, and 629 cm^{-1} .

After recovery of the product from the gas IR cell, all of the monoiodoacetylene was distilled into a capillary tube suitable for the n.m.r. measurement of neat liquid samples and the top of the tube was sealed. Thawing of the frozen sample yielded a colorless liquid which gradually turned pink. The n.m.r. spectrum of the neat sample (no internal std.) showed only a single absorption at 7.22 τ .

In order to measure the mass spectrum of the compound, a fresh sample had to be prepared and isolated by repetition of the above experiment. The spectrum was obtained from a gas-phase sample of the compound using a cold inlet system: m/e 152 (100%, M^+), m/e 127 (30%, I^+). Thus, the identity of the product of the reaction as monoiodoacetylene is confirmed.

Deuteration of Lithioiodoacetylde.--To an ice cold solution of 0.280 g (1.0 mmole) of C_2I_2 in 10 ml of cyclohexene was added over a period of 1.5 hrs. 1.2 mmoles (1.2 ml., 1.0 M) of CH_3Li . The slurry was stirred at room temp. for 4.5 hrs., then the reaction was quenched

43. J. K. Brown and J. K. Tyler, Proc. Chem. Soc., 13 (1961).

by addition of 3 ml of D₂O. The colorless organic layer was washed with D₂O and dried over Na₂SO₄. The g.l.c. retention time (20M-A, 80°; NMPN, 50°) of the single product produced was identical to that for monoiodoacetylene on both columns. The product was concentrated and isolated by preparative g.l.c. using the procedure described above. Gas-phase infrared analysis yielded a spectrum with a strong band at 2580 cm⁻¹ (doublet), a very much weaker doublet at 3300 cm⁻¹ and other bands also present in the spectrum of HC≡CI. The 2580 cm⁻¹ band for the ≡C-D stretch represents a lowering of the normal ≡C-H stretching frequency by a factor of 1.28. These results are consonant with the formation of monoiodoacetylene-d by the reaction of lithioiodoacetylide with D₂O.

Trapping of Lithioiodoacetylide with Cyclohexanone.-- Lithioiodoacetylide was prepared by treating 0.557 g (2.0 mmoles) of C₂I₂ in 10 ml of cyclohexene at 0° slowly with 2.1 mmoles (2.1 ml, 1.0 M) of CH₃Li. After stirring the white slurry for 4 hrs. at room temp., a solution of 0.21 ml (0.196 g, 2 mmoles) of cyclohexanone in 0.5 ml of Et₂O was added over a 10 min. period at room temp. After stirring for one hr. longer, the reaction was quenched with 3 ml of satd. NH₄Cl solution, and the organic layer was washed with H₂O and dried (Na₂SO₄).

G.l.c. analysis of the reaction mixture (20M-A, 80°) disclosed that all of the lithioiodoacetylide had been consumed and that 1-ethynylcyclohexanol and 1,1'-ethynylene-bis-cyclohexanol were probable reaction products (20M-A, 150°; SE-A, 150°). Although no peak was obtained for 1-(iodoethynyl)cyclohexanol, deterioration of the base line of the gas chromatogram indicated that it might be present and decomposing on the column.

The yellow reaction solution was stripped of solvent at the water pump, and the oil which resulted was caused to solidify by standing in the ice-chest overnight. After recrystallization four times from ligroin, 0.135 g (27%) of pale yellow crystals were obtained, m.p. 84-86° (lit.⁴⁴ 88-89° for 1-(iodoethynyl)cyclohexanol). Infrared analysis disclosed bands at 3600, 3500-3300 (broad), and 2160 cm^{-1} , and the fingerprint region was very similar to that of 1-(bromoethynyl)cyclohexanol (IV) reported previously. The n.m.r. spectrum showed a broad complex band centered at 8.25 τ and a singlet at 7.32 τ in the area ratio 10 : 1, expected for 1-(iodoethynyl)cyclohexanol (VIII).

Stability of Lithioiodoacetylide in Refluxing Cyclohexene.--

Lithioiodoacetylide was prepared from 1.0 mmole of C_2I_2 and 1.1 mmoles (2.2 ml., 0.5 M) of CH_3Li (prepared from CH_3Br instead of CH_3I) in 10 ml of cyclohexene as previously described. The white slurry was stirred at room temp. for 2 hrs., then at reflux in an oil bath (bath temp. 76-78°) for a total of 24 hrs. G.l.c. analysis of quenched reaction aliquots (20M-A, 80°) taken at various times during the reflux period indicated that the quantity of $\text{LiC}\equiv\text{CI}$ was remaining unchanged. No new products were being formed, $\text{HC}\equiv\text{CI}$ being the only peak discernible.

After the 24-hr. reflux period, the heating bath was removed, stirring was stopped, and insoluble material was allowed to settle out over a 1.5-hr. period. G.l.c. analysis of an aliquot withdrawn from the clear, water-white supernatant disclosed a much reduced peak area for monoiodoacetylene compared to an aliquot taken from the hetero-

44. P. L. Southwick and J. R. Kirchner, J. Org. Chem., 27, 3305 (1962).

geneous, stirred reaction mixture, indicating a low solubility of $\text{LiC}\equiv\text{CI}$ in cyclohexene-ether.

After work-up of the reaction mixture in the usual manner, g.l.c. analysis under various conditions corroborated the absence of any products except monoiodoacetylene.

Thermal Decomposition of Lithioiodoacetylide.--A. In Refluxing Cumene. Lithioiodoacetylide was generated in 10 ml of cumene by reaction of 1.0 mmole C_2I_2 with 1.1 mmoles (1.05 ml, 1.1 M in Et_2O) of CH_3Li carried out in the usual manner. The milky white mixture was held at room temperature for 1 hr., then was heated at reflux (bath temp. $140-145^\circ$) for 10 hrs. with stirring. The opaque, dark brown mixture was quenched with 3 ml of H_2O , filtered from suspended dark solid, washed with H_2O and dried (Na_2SO_4).

G.l.c. analysis of reaction aliquots (20M-A, 80°) disclosed that the decomposition of $\text{LiC}\equiv\text{CI}$ was complete by the tenth hour at reflux. Only a trace amount of a single high M.W. product could be detected (20M-A, 150°), whose identity is unknown.

The recovered dark solid was thoroughly washed with ether, hot water, hot methanol, and again with ether; yield 11 mg.

Anal. Found: C, 52.91%; H, 2.50%; I, 33.95%.

B. In Refluxing Styrene. The above experiment was repeated using purified styrene⁴⁵ as solvent in place of cumene. After 1 hr. at room temp., the opaque white slurry of lithioiodoacetylide in styrene was heated at reflux (oil bath temp. 125°) for a total period of 1.25 hrs. This short reaction period was employed since g.l.c.

45. R. H. Boundy, R. F. Boyer, and S. M. Stoesser, "Styrene," Reinhold, New York, 1952, p. 208.

analysis of a 1-hr. reaction aliquot (20M-A, 80°) disclosed $\text{LiC}\equiv\text{CI}$ to be practically completely consumed and the mixture was increasing noticeably in viscosity. The homogeneous, orange-brown solution was quenched with H_2O , and the organic layer was washed with brine and dried. Upon g.l.c. analysis of reaction aliquots under various conditions, no products of the reaction (other than CH_3I) could be detected, high or low molecular weight.

Stability of Lithioiodoacetylide in THF as Solvent.--A solution of 0.280 g (1.0 mmole) of C_2I_2 in either 10 ml of dry THF or in a mixture of 9.5 ml of dry THF and 0.5 ml of cyclohexene was treated over a period of 1.5 hrs. with 1.2 mmoles (1.2 ml, 1.0 M) of CH_3Li at 0°. A white ppt. first formed then later dissolved, so that at the end of CH_3Li addition the reaction mixture was pale yellow and practically clear. The mixture was stirred for 2 hrs. at room temp., then was quenched with H_2O , and the organic layer was washed with satd. NaCl solution and dried over Na_2SO_4 .

G.l.c. analysis of quenched reaction aliquots (20M-A, 80°; NMPN, 50°) taken half-way through CH_3Li addition and at the end of CH_3Li addition and of the final reaction mixture showed clearly the production and consumption of $\text{LiC}\equiv\text{CI}$ (analyzed as $\text{HC}\equiv\text{CI}$) and the formation of a new product of higher retention time. In the reaction mixture not containing cyclohexene it was also possible to see by g.l.c. that CH_3I was not accumulating in the reaction mixture. By the end of the 2-hr. room temp. reaction period all of the lithioiodoacetylide had given way to the new product.

The product was concentrated by distilling off the solvent through a spiral-wire Holtzmann column, maximum distillate temp. being 63.5°. The product was isolated from the residue by preparative g.l.c. and was a colorless, strong-smelling liquid. Its infrared spectrum showed three bands between 3000 and 2850 cm^{-1} , weak absorptions at 2200 and 2050 cm^{-1} , and bands characteristic of the $-\text{CH}_3$ group at 1450 and 1370 cm^{-1} . The CH regions were virtually identical to those for 1-chloropropyne,⁴⁶ and the overall spectrum agreed closely with the Raman spectrum reported for 1-iodopropyne.⁴⁷ The n.m.r. spectrum showed only singlet absorption at 7.10 τ , while the mass spectrum showed a weak molecular ion peak at m/e 166, the base peak being m/e 39 (M-127). These results are consistent with identification of the product as 1-iodopropyne.

Stability of Lithioiodoacetylide in Diethyl Ether as Solvent.--

Lithioiodoacetylide was prepared from 1.0 mmole of C_2I_2 and 1.2 mmoles of CH_3Li in 10 ml of dry ether. After stirring for 2 hrs. at room temp., g.l.c. analysis of a quenched reaction aliquot showed that $\text{LiC}\equiv\text{CI}$ was still present in undiminished amount. The mixture was then refluxed for 2 hrs., cooled, and quenched with H_2O .

G.l.c. analysis of the final reaction mixture showed $\text{HC}\equiv\text{CI}$ to be the sole product. No 1-iodopropyne was present, and it was clear that CH_3I had not undergone reaction during the course of the experiment.

46. D. W. Davidson and H. J. Bernstein, *Can. J. Chem.*, 33, 1226 (1955).

47. A. G. Meister, *J. Chem. Phys.*, 16, 950 (1948).

Generation and Reaction of Lithioiodoacetylide in THF and THF-Cyclohexene Using Phenyllithium as Halogen-Metal Exchanging Agent.--

A. A solution of 0.280 g (1.0 mmole) of C_2I_2 in 10 ml of dry THF was treated at 0° with 1.3 ml of 0.79M PhLi (1.0 mmole) dropwise over a period of 2 hrs. During a 2 hr. room temp. stirring period, a black solid formed in significant amount. The reaction mixture was then heated at reflux for 3 hrs. with no further change in appearance occurring. After cooling, the reaction was quenched with H_2O , salt was added, and the layers were separated. (The bulk of the black solid matter was retained in the reaction flask.) The organic layer was washed with brine and dried. The yield of recovered black solid was 53 mg.

G.l.c. analysis of quenched reaction aliquots (20M-A, 80° and 150° ; 20M-B, 100°) disclosed peaks for $HC\equiv CI$ and iodobenzene. Not all of the $LiC\equiv CI$ was consumed during the reaction although some consumption took place during the reflux period. The only product of the reaction detected by g.l.c. eluted at 16 min. from Col. 20M-B at 100° , and its formation appeared to be complete upon completion of PhLi addition.

The crude black solid isolated above was purified by washing in the usual fashion.

Anal. Found: C, 56.92%; H, 3.43%; I, 12.68%; Ash, 1.71%.

The dried organic product solution was concentrated at the water pump, and the residual brown oil was diluted with ether. A ppt. of glistening white crystals formed which were collected and found to melt above 160° . They underwent facile sublimation during the m.p. determination. No further identification of this material was made.

B. The above experiment was repeated except using a mixture

of 5 ml of cyclohexene and 5 ml of THF as solvent. This time black solid ppt. did not form until the reflux period, however. The reaction mixture was worked up as above, 32 mg of crude black solid being collected.

G.l.c. analysis of reaction aliquots disclosed no difference from the reaction A above. Again only the one high M.W. product was formed, and no II could be detected.

When the main product solution was concentrated at the water pump and the residual oil was treated with ether, none of the white crystalline material observed above separated out. Therefore, the oil was used for the isolation of the high M.W. product by preparative g.l.c. It proved to be a red oil (3-4 mg) exhibiting IR bands at 3100-3000, 1950-1700, 1460, 1425, 1020, 1005, 700, 650, and 610 cm^{-1} . Its n.m.r. spectrum showed a single strong peak at approx. 2.5 τ with a slight upfield shoulder. No further identification of the product was made.

Attempt to Induce the Decomposition of Lithioiodoacetylide by Tetramethylethylenediamine.--A. One mmole of lithioiodoacetylide was generated in the usual manner by treating 1.0 mmole of C_2I_2 in 10 ml of cyclohexene with 1.0 mmole of CH_3Li (1.3 ml, 0.80 M). N,N,N',N'-tetramethylethylenediamine (0.102 g, 0.88 mmole) was added to the stirred mixture, and after 2 hrs. at room temp., although the mixture had discolored, g.l.c. analysis of a reaction aliquot (20M-A, 80°) disclosed that no $\text{LiC}\equiv\text{CI}$ had been consumed. The mixture was then heated at reflux for 5 hrs. during which time it became muddy brown. G.l.c. analysis indicated that now 50% of the lithioiodoacetylide had undergone decomposition, a single product being detected whose

retention time on two columns (20M-A, 80° and NMPN, 50°) identified it as 1-iodopropyne.

After the reflux period, the reaction mixture was allowed to cool unagitated for 15 min., and an aliquot was withdrawn from the clear, colorless supernatant above a settled brown solid. G.l.c. analysis showed a much reduced peak area for $\text{HC}\equiv\text{CI}$ compared to an aliquot taken while the mixture was being stirred, demonstrating the low solubility of $\text{LiC}\equiv\text{CI}$ in the reaction medium. After the cooled reaction mixture was quenched with water, a brown insoluble residue could be collected by filtration. No products other than 1-iodopropyne could be detected by g.l.c. (20M-A, 80° and 150°; NMPN, 50°).

B. The above experiment was repeated except that 0.319 g (2.75 mmole) of the diamine was added to the prepared lithioiodoacetylide. The overall results were little different than were obtained above except that decomposition of $\text{LiC}\equiv\text{CI}$ during reflux appeared to be a little slower and the yield of 1-iodopropyne a little lower. However, based on the relative peak areas of $\text{HC}\equiv\text{CI}$ from reaction aliquots taken before and after settling of solid material, it appeared that the $\text{LiC}\equiv\text{CI}$ had been completely solubilized by the excess diamine. Again, insoluble brown material was a product of the reaction. No other products other than 1-iodopropyne were detected by g.l.c.

Attempted Reaction between Diiodoacetylene and Lithium Metal.--

A. A solution of 0.280 g (1.0 mmole) of C_2I_2 in 10 ml of dry ether was stirred with a tiny piece of freshly cut lithium wire. After 2 hrs. at room temp., none of the lithium had reacted. More lithium was added (total 14 mg., 2.0 mmoles) and the mixture was refluxed for 5.25 hrs. In this time none of the lithium appeared to have reacted, and g.l.c.

analysis of the ether solution after quenching (20M-A, 80°) revealed (1) the absence of monoiodoacetylene and (2) C_2I_2 in undiminished quantity (20M-B, 100°). Thus, no lithioiodoacetylide had been generated.

B. A mixture of 0.281 g (1.0 mmole) of C_2I_2 , 39 μ l (85 mg, 0.45 mmole) of 1,2-dibromoethane, and 17 mg (2.45 mmoles) of freshly cut lithium wire in 10 ml of dry ether was stirred for one hr. at room temp., then for 5.5 hrs. at reflux. Little of the lithium appeared to have reacted even though shiny surfaces were present. G.l.c. analysis of the ether solution after quenching showed no $HC\equiv CI$ but did show that some 1,2-dibromoethane still remained. Thus, no lithioiodoacetylide had been generated.

Photolysis of Lithioiodoacetylide in Cyclohexene (Run No. 1, Table I).--

A solution of 0.281 g. (1.0 mmole) of C_2I_2 in 10 ml of N_2 -satd. cyclohexene was introduced via syringe into a N_2 -filled quartz reaction tube, stirring was started, and 1.95 ml of 0.51 M CH_3Li in Et_2O (1.0 mmole CH_3Li) was added dropwise over a period of 70 min. to the ice-cold solution. After stirring for one hr. at room temp., the reaction vessel was transferred to the photochemical reactor and irradiation with 2537 \AA light was carried out for 24 hrs. (During this time, the reaction vessel was cooled by a stream of air.) The clear, yellow-brown reaction mixture was then quenched with H_2O (2 ml) and dried over Na_2SO_4 .

G.l.c. analysis of reaction aliquots (20M-A, 80°) disclosed the slow disappearance of $LiC\equiv CI$, although a little was still left at the end of irradiation. The greater amount of starting material appeared to have been consumed by the 9-hr. mark. At least a dozen products could be detected, most in low yield (20M-A, 150°; SE-A, 150°;

SE-B, programming; 20M-B, 100°). By far the major product was found to be 3,3'-bicyclohexenyl (III) (retention time on two columns). Its maximum yield occurred at the 9-hr. mark and remained constant during the remainder of the photolysis. None of the compound II was detected even when high instrument sensitivity was employed. None of the other minor products of the reaction have been identified. Evaporation of solvent from the product solution gave a dark oil from which no solid separated even upon prolonged cooling.

Anhydrous Lithium Iodide.⁴⁸--An intimate mixture of 9.50 g (0.037 mole) of I₂ and 0.74 g (0.093 mole) of LiH was prepared in a 300-ml r.b., 3-neck flask which was fitted with reflux condenser, mechanical stirrer, and dropping funnel. Ether (125 ml) was added dropwise, cautiously at first because of the vigor of the reaction. Stirring was started when sufficient liquid was present in the flask. After ether addition was complete, the mixture was refluxed with stirring for 1.5 hrs., then was filtered from excess LiH. After distillation of ether at atmospheric pressure, the reddish-brown solid product was heated at 35-40° first under house vacuum, then for 1.75 hrs. at 1 mm pressure. The resulting light tan solid (9.43 g, 95% yield) was stored under N₂ in a desiccator protected from light.

Photolysis of CH₃I in Cyclohexene Solution: Control Experiments.---

A. A solution of 37 μl (84 mg, 0.59 mmole) of CH₃I in 6 ml of cyclohexene and 1.2 ml of ethyl ether was photolyzed with 2537Å light for 20 hrs. G.l.c. analysis of reaction aliquots (20M-A 150°; SE-A, 150°) disclosed that 3,3'-bicyclohexenyl (III) was not produced during the irradiation period. However, the presence of benzene and 1,3-cyclohexadiene as products was revealed (NMPN, 50°).

48. M. D. Taylor and L. R. Grant, J. Am. Chem. Soc., 77, 1507 (1955).

B. With Added Lithium Iodide. Anhyd. LiI (1.30 g, 9.7 mmoles) was cautiously dissolved in 4 ml of dry ether, 0.125 ml (0.285 g, 2.0 mmoles) of CH_3I was added, and the ether solution was added to 20 ml of cyclohexene contained in a quartz vessel. The stirred mixture was irradiated with 2537\AA light for 24 hrs., then was treated with 5 ml of H_2O and dried over Na_2SO_4 . G.l.c. analysis of quenched reaction aliquots revealed the absence of III as a product (20M-A, 150°). Both benzene and 1,3-cyclohexadiene were present (NMPN, 50°).

Photolysis of C_2I_2 in Cyclohexene Solution: Control Experiments.--

A. A solution of 0.222 g (0.8 mmole) of C_2I_2 in 8 ml of cyclohexene was irradiated with 2537\AA light for 7 hrs. G.l.c. analysis of reaction aliquots disclosed that all of the starting material had been consumed after 2 hrs. (20M-B, 110°) and that monoiodoacetylene was a primary product which underwent decomposition until gone upon cessation of irradiation (20M-A, 80° ; NMPN, 50°). 3,3'-Bicyclohexenyl proved to be formed in only very minor yield (10% or less of that obtained from the photolysis of $\text{LiC}\equiv\text{CI}$) (20M-A, 150° ; SE-A, 150°) as were several other products. Benzene was a major product of the reaction (20M-A, 80° ; NMPN, 50°), increasing in yield as the reaction progressed right up to the end of the 7-hr. irradiation period. Its final yield was determined by g.l.c. (20M-C, 105°) by the method of standard addition and was found to be 25.5 mg (0.3 mmole).

B. With Trapping of Evolved Gases. A gas-trapping train, consisting of traps immersed successively in Dry Ice-acetone and liq. N_2 , was connected by means of silicone rubber tubing to the top of the water-cooled condenser attached to the quartz photolysis tube. After charging

the vessel with a solution of 2.0 mmoles of C_2I_2 in 20 ml of cyclohexene, a flow of N_2 (dried by passage through a U-tube containing Linde 4A molecular sieve and cooled in Dry Ice-acetone) through the solution with stirring was commenced in such a way that evolved gases would be swept through the cold traps. The solution was irradiated with 2537Å light with continuous N_2 purging for 8 hrs., by which time g.l.c. analysis of a reaction aliquot showed that no more C_2I_2 (20M-B, 100°) or HC_2I (20M-A, 80°) remained.

Analysis of the contents of the two cold traps by gas-phase IR proved that acetylene and monoiodoacetylene had been generated from the photolytic reaction (comparison with spectra of authentic samples). The yield of acetylene was determined by addition of 2 ml of 1-butene to the liq. N_2 trap as an internal standard, followed by g.l.c. analysis of the gas on a 10% squalane column at -20°. Assuming a molar response factor of 2, a value of 0.39 mmole (19% based on C_2I_2) was obtained from the ratio of peak areas. Since the Dry Ice trap also contained condensed cyclohexene, its contents were taken up in ether, and the yield of HC_2I was determined by addition of n-BuBr as an internal standard followed by g.l.c. analysis of the liquid (NMPN, 50°), assuming a molar response factor of 2.25. Calculated yield of HC_2I was 0.29 mmole (14.5%).

Photolysis of Lithioiodoacetylide in Cyclohexene with Trapping of Evolved Gases.--General Procedure. Lithioiodoacetylide (2.0 mmoles) was generated in a quartz reaction tube by treating 2.0 mmoles of C_2I_2 in 20 ml of cyclohexene very slowly with 2.0 mmoles of CH_3Li (ether solution) at 0°. After a 1-hr. stirring period, the reaction vessel was

transferred to the photochemical reactor, and the top of the condenser was connected to a gas-trapping train consisting of traps immersed successively in Dry Ice-acetone and liq. N₂. The sweeping N₂ stream was dried by passage through a U-tube containing Linde 4A molecular sieve and immersed in a Dry Ice-acetone bath. It was conducted below the surface of the reaction mixture by means of a 15 gauge needle inserted through the no-air stopper in the vessel side-arm. After the flow of N₂ had been established, irradiation of the reaction mixture with 2537Å light was carried out for 10-11 hrs. with stirring, by which time analysis of a reaction aliquot (20M-A, 80°) indicated that only a small amount of starting material remained. An air stream was employed to help cool the reaction vessel. The rate of N₂ purging was monitored by means of a Nujol bubbler placed at the end of the gas-trapping train. Upon completion of photolysis the gas traps were isolated, the cooled reaction mixture was quenched by addition of 5 ml of D₂O or H₂O (see below), and the organic layer was washed with D₂O or H₂O, filtered if necessary, and dried over Na₂SO₄.

The yield of collected acetylene (identified by comparison of IR spectrum with that of an authentic sample) was determined by evacuating the frozen liq. N₂ trap and adding 2 or 3 ml of 1-butene as an internal standard. After warming to room temp., the trap was filled with N₂ and the contents were mixed thoroughly by pumping with a 20-ml syringe. By analyzing the gases by g.l.c. on 10% squalane at -15°, the ratio of product and standard peak areas was determined and the yield of acetylene was calculated by assuming a molar response factor of 2 for C₂H₂ vs. 1-butene.

Since the Dry Ice trap invariably contained approx. 5 ml of clear liquid (mostly cyclohexene and ether), the yield of HC_2I (identified by g.l.c. retention times on two columns) dissolved therein was determined simply by adding 25 mg of $n\text{-BuBr}$ as an internal standard, analyzing the solution by g.l.c. (NMPN, 50°), and determining the ratio of product and standard peak areas. A molar response factor of 2.25 for HC_2I vs. $n\text{-BuBr}$ was estimated from previous work.

Finally, the yield of 3,3'-bicyclohexenyl was determined by addition of 30 mg of $n\text{-tetradecane}$ as an internal standard to the final reaction mixture after work-up, followed by g.l.c. analysis (SE-A, 130°). A wt. response factor of 1.04, determined experimentally, was employed.

Using the above general procedure, the effect of each of the following experimental variables on the yields of products was determined (refer to Table I for tabulation of results):

A. Using CH_3Li from CH_3I (Run No. 2). In this run, before quenching of the photolyzed reaction mixture, the two cold traps were isolated and replaced in the gas-trapping train by a pair of empty ones. After re-establishing N_2 flow through the cooled reaction mixture, the latter was quenched with D_2O and gas purging was continued for 30 min. IR analysis of the contents of the liq. N_2 trap showed a trace of ether and possibly a trace of C_2D_2 (very weak bands at $2450\text{-}2400$ and 540 cm^{-1}).⁴⁹ The Dry Ice trap contents proved to be mostly cyclohexene with very weak doublets in the IR spectrum at 3300 and 2580 cm^{-1} , suggesting the presence of traces of $\text{HC}\equiv\text{CI}$ and $\text{DC}\equiv\text{CI}$.

49. G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., New York, 1945, pp. 288-293.

Since the photolysis vessel contained a good deal of water-soluble solid at the end of irradiation, the iodide present in the water washes of the reaction mixture and the vessel itself was determined by precipitation as AgI.⁵⁰ The wt. of AgI isolated was 2.28 g (9.7 mg-atoms of iodide ion). However, analysis for iodide ion of 4 ml of the CH₃Li solution employed for generation of starting material yielded an identical value, indicating that the CH₃Li solution was better than 2 M in LiI.

- B. Using CH₃Li from CH₃Br (Run No. 3).
- C. Using CH₃Li from CH₃Br and Incorporating 20% by Volume Ethyl Ether into the Solvent (Run No. 4).
- D. Using CH₃Li from CH₃Br and Adding Anhyd. LiI and Ether (Run No. 5).
- E. Using CH₃Li from CH₃I, a Repeat Experiment (Run No. 6).

Photolysis of Lithioiodoacetylide in Cyclohexene in a Closed N₂ Atmosphere.---General Procedure. Lithioiodoacetylide (1.0 mmole) was generated in the quartz reaction tube by treating 1.0 mmole of C₂I₂ in 10 ml of cyclohexene very slowly with 1.0 mmole of CH₃Li at 0°. After a 1-hr. stirring period at room temp., the reaction vessel was transferred to the photochemical reactor and irradiation with 2537Å light was carried out for 20 hrs. in a closed N₂ atmosphere with stirring. At the end of the irradiation period, g.l.c. analysis of a reaction aliquot (20M-A, 80°) showed that starting material was virtually entirely consumed. The cooled reaction mixture was quenched with 3 ml of H₂O,

50. H. H. Willard and N. H. Furman, "Elementary Quantitative Analysis," D. Van Nostrand Co., New York, 3rd Ed., 1940, p. 320.

and the organic layer was washed with H₂O and combined with ether washings of the aqueous phase and the reaction vessel. After the addition of 30 mg of n-tetradecane as an internal standard, the product solution was dried over Na₂SO₄. The yield of 3,3'-bicyclohexenyl was determined by g.l.c. by the method described in the preceding section.

Using the above general procedure, the effect of the following experimental variables on the yields of the bicyclohexenyl was determined (refer to Table I for tabulation of results):

- A. Using CH₃Li from CH₃I (Run No. 7).
- B. Using CH₃Li from CH₃Br (Run No. 8).
- C. Using CH₃Li from CH₃I and a 50 : 50 Cyclohexene-Ether Solvent Mixture (Run No. 9).

Photolysis of Lithioiodoacetylde in a Homogeneous System.--

Lithioiodoacetylde was generated in 20 ml of a 50 : 50 cyclohexene-ether mixture containing also 20 μ l of n-decane as an internal standard by treating 0.278 g (1.0 mmole) of C₂I₂ with 2.1 ml of 0.49 M CH₃Li (1.0 mmole CH₃Li) at 0°. This reaction was carried out in a 40-ml centrifuge tube equipped with magnetic stirrer and sealed with a no-air stopper. After stirring at room temperature for 1 hr., an aliquot of the stirred reaction mixture was withdrawn and the mixture was centrifuged until a clear supernatant liquid resulted. The clear, water-white supernatant liquid (17 ml, 75% of the total reaction mixture) was transferred via syringe to a quartz reaction tube and an aliquot of the supernatant liquid was withdrawn. G.l.c. analysis of the two aliquots (before and after centrifugation) (20M-A, 80°) revealed that

90% of the generated $\text{LiC}\equiv\text{CI}$ was in solution in the clear supernatant liquid (n-decane peak used as internal standard to normalize $\text{HC}\equiv\text{CI}$ peaks compared). Thus, the actual quantity of $\text{LiC}\equiv\text{CI}$ to be photolyzed was 0.68 mmole.

The clear solution of $\text{LiC}\equiv\text{CI}$ was photolyzed with 2537\AA light for 7 hrs. G.l.c. analysis of reaction aliquots disclosed that 92% of the starting material had already been decomposed by the 4-hr. reaction mark and little further reaction had occurred thereafter. After work-up in the usual manner, 23 mg of n-tetradecane was added as an internal standard. The yield of 3,3'-bicyclohexenyl determined by g.l.c. was 13% based on C_2 generated from 0.68 mmole $\text{LiC}\equiv\text{CI}$.

Attempted Hydrogenation of Photoproducts from Decomposition of $\text{LiC}\equiv\text{CI}$ in Cyclohexene.--A reaction mixture obtained from the photolysis of 1 mmole of $\text{LiC}\equiv\text{CI}$ in cyclohexene was stripped of solvent at the water pump (0.12 g of oil) and 3-4 ml of absolute ethanol was added. After introducing 0.012 g of 5% palladium-on-carbon catalyst, the product solution was hydrogenated at room temp. and 1 atmosphere pressure for 24 hrs. Although it had appeared that 5.8 ml (0.24 mmole) of H_2 had been taken up, g.l.c. analysis of the product solution (SE-A, 130° ; SE-B, programming) disclosed no change in the pattern of product peaks from what had been seen before hydrogenation. Even the 3,3'-bicyclohexenyl appeared to have resisted hydrogenation, suggesting the presence of a catalyst poison in the reaction mixture.

Thermal Decomposition of Lithioiodoacetylide in the Presence of Tri-n-butyltin Hydride.--Lithioiodoacetylide (1.0 mmole) in 10 ml of cyclohexene was prepared in the usual manner from C_2I_2 and CH_3Li . Tri-n-butyltin hydride (0.592 g, 2.0 mmoles) was added neat from a

syringe to the stirred suspension and stirring was continued at room temp. for 2 hrs. Since g.l.c. analysis (20M-A, 80°) indicated that none of the starting material had undergone reaction, the mixture was heated at reflux for 4 hrs., then was quenched with H₂O. G.l.c. analysis showed that 80% of the LiC≡CI had reacted after 4 hrs. at reflux. Tri-n-butyltin iodide was detected as a product of the reaction (SE-A, 50°), along with two other unidentified products in low yield.

Photolysis of Lithioiodoacetylide in the Presence of Tri-n-butyltin Hydride.--Lithioiodoacetylide (1.0 mmole) in 10 ml of cyclohexene was generated in the usual manner in a quartz reaction tube. Tri-n-butyltin hydride (2.2 mmoles) was added and the reaction mixture was irradiated with 2537Å light for a total of 4 hrs. An additional 0.9 mmole of the tin hydride was added after 30 min. irradiation to ensure an excess of hydride being present at all times during the irradiation period. The reaction mixture was quenched and worked up in the usual manner.

G.l.c. analysis of reaction aliquots (20M-A, 80°) disclosed that all of the starting LiC≡CI had been consumed by the 30 min. irradiation mark, that (Bu)₃SnH, although undergoing reaction, was present at all times during the entire irradiation period (SE-A, 150°), and that 3,3'-bicyclohexenyl was a product of the reaction. Its yield, determined by g.l.c. by the method of standard addition, was 11 mg (7% based on C₂).

Photolysis of CH₃I in the Presence of Tri-n-butyltin Hydride:
a Control Experiment.-- A solution of 0.634 g. (4.7 mmoles) of

anhydrous LiI and 62 μ l (0.142 g, 1.0 mmole) of CH_3I in 2.1 ml of ether was added to 10 ml of cyclohexene in a quartz reaction vessel. After addition of 2.2 mmoles of $(\text{Bu})_3\text{SnH}$, the mixture was irradiated for 4 hrs. and was quenched by addition of H_2O .

G.l.c. analysis of reaction aliquots disclosed that the tin hydride underwent partial consumption and that again the bicyclohexenyl was a product, this time in a yield of 5 mg (3% based on hypothetical C_2). As before, product formation appeared to be complete within 30 min. after irradiation was started.

Photolysis of n-Butyl Iodide in Cyclohexene Solution.--A solution of 92 μ l (0.15 g, 0.8 mmole) of n-butyl iodide (Eastman white label) in 8 ml of cyclohexene was irradiated with 2537 \AA light for 7 hrs. (The reaction vessel was cooled by a stream of cold air which had been passed through a column packed in ice). G.l.c. analysis of reaction aliquots (NMPN, 50 $^\circ$) disclosed that at the end of the reaction, 90% of the BuI had been consumed and a low yield of benzene had been obtained. 3,3'-Bicyclohexenyl was not a product of the reaction. Several other products were detected in low yield, however.

Photolysis of n-Butyl Iodide in the Presence of n-Butyllithium in Cyclohexene.--A. Equimolar Amounts. A solution of 0.17 ml (0.28 g, 1.5 mmoles) of BuI in 15 ml of cyclohexene was charged into a quartz tube and 1.0 ml of 1.5 M BuLi (1.5 mmoles) was added. The clear, colorless solution was irradiated with 2537 \AA light for 7 hrs. (cooling accomplished by stream of cold air), during which time a white ppt. formed. The reaction was quenched and worked up in the usual manner.

G.l.c. analysis of the reaction mixture (NMPN, 50 $^\circ$) disclosed

that 60-70% of the BuI had been consumed and that 3,3'-bicyclohexenyl was a major product. Its yield, determined by g.l.c. (SE-A, 130°; n-tetradecane as internal standard), was 87 mg (0.55 mmole) (60% based on BuI consumed).

B. Excess BuLi. The above reaction was repeated except that 3 ml of 1.52 M BuLi (4.6 mmoles) was employed. After the 7-hr. irradiation period, the inside walls of the reaction vessel were coated with black material which proved to be water-soluble and was probably lithium metal or LiH. G.l.c. analysis as above showed that 80% of the BuI had been consumed and that 119 mg (0.73 mmole) (61% based on BuI consumed) of 3,3'-bicyclohexenyl had been produced.

C. At -20°. For this experiment, an immersion type photochemical apparatus was employed which could be immersed in a methanol-ice bath to ensure thorough cooling of the reaction mixture during photolysis. A solution of 1.7 ml (2.8 g, 15 mmoles) of BuI in 150 ml of cyclohexene was placed in the outer chamber of the reactor, and the quartz immersion well containing a high-pressure Hanovia Hg arc lamp (450 watts, Type L) was put in place. Stirring was accomplished by a stream of N₂ bubbles from a fritted bubbler placed at the bottom of the reactor. The entire apparatus was lowered into a Dewar flask filled with a methanol-ice mixture, 10 ml of 1.52 M BuLi (15.2 mmoles) was added, and the clear reaction mixture was irradiated for 4 hrs. at -10° to -20°. At the end of this time, the reactor contained a large amount of a heavy white ppt. The reaction was quenched with 30 ml of H₂O and was worked up in the usual manner.

G.l.c. analysis of the reaction mixture disclosed that 65% of

the starting BuI had been consumed and that 3,3'-bicyclohexenyl again was a product of the reaction. However, its yield this time, determined as in A above, was 0.515 g (3.2 mmoles) (33% based on reacted BuI).

Thermal Reaction between n-Butyl Iodide and n-Butyllithium.-- A.

At 40°. The highest temperature attained during the photolytic reactions described above proved to be 40°. Therefore, as a control experiment a mixture of 1.5 mmoles of BuLi and 1.5 mmoles of BuI in 10 ml of cyclohexene was heated in the "dark" at 40° (oil bath) for 7 hrs. The opaque, white reaction mixture was cooled, quenched, and worked up in the usual manner. G.l.c. analysis of the reaction mixture (NMPN, 50°) disclosed that 50% of the starting BuI had been consumed. Moreover, 3,3'-bicyclohexenyl was a major product (SE-A, 130°), its yield (g.l.c., n-tetradecane as standard) being 77 mg (0.47 mmole) (64% based on reacted BuI).

B. At -20°. The above reaction was repeated except that the reaction mixture was kept at -20° by means of a Dry Ice-acetone bath for 4 hrs. The mixture remained clear during this period, no ppt. forming. It was quenched and worked up in the usual manner. G.l.c. analysis disclosed that none of the BuI had reacted and no 3,3'-bicyclohexenyl had been produced over the 4 hr. reaction period.

Photolysis of n-Propyl Iodide in the Presence of Excess n-

Butyllithium in Cyclohexene.--BuLi (3 ml of 1.52 M solution, 4.6 mmoles) was added to a solution of 0.15 ml (0.26 g, 1.5 mmoles) of n-PrI in 15 ml of cyclohexene contained in a quartz vessel. The clear, colorless mixture was irradiated with 2537Å light for 6 hrs., during which time

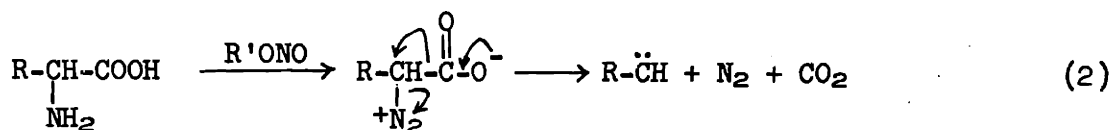
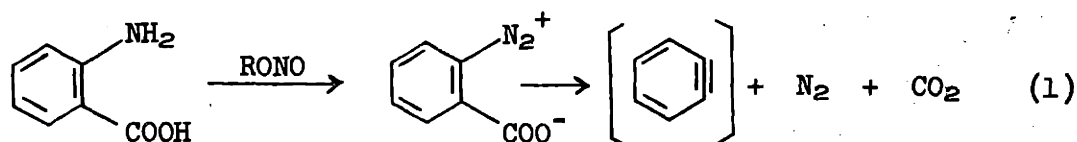
a white solid precipitated. As in the BuI system, toward the end of the reaction a gray water-soluble material coated the inside walls of the reaction vessel. The mixture was quenched and worked up in the usual manner.

G.l.c. analysis of reaction aliquots (NMPN, 50°) showed that some BuI had been produced even before irradiation of the reaction mixture had been begun. During the irradiation period, all of the PrI was finally consumed, and BuI was first formed, then underwent partial consumption, some still remaining at the end. 3,3'-Bicyclohexenyl was a major product of the reaction (SE-A, 130°), its yield (g.l.c., n-tetradecane as standard) being 113 mg (0.70 mmole) (47% based on n-PrI).

APPENDIX

I. Attempted Generation of Carbenes from α -Amino Acids

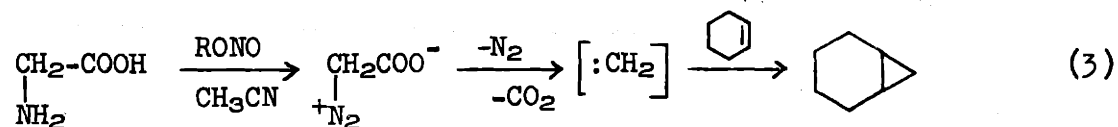
Diazotized anthranilic acid has been shown⁵¹ to be a benzyne precursor (eq. 1). The nature of the reaction is such that were it to be applied to an α -amino acid, the elimination of N_2 and CO_2 from the same carbon atom might be expected to lead to a carbene intermediate (eq. 2). If successful this reaction would represent a new route to these reactive species.



Attempts to diazotize glycine with isopentyl nitrite in aprotic solvents did not appear to be successful. The low solubility of the amino acid in solvents such as acetone, dioxane, THF, and DMF is undoubtedly the chief cause of this unreactivity. When the diazotization was carried out in acetonitrile containing cyclohexene, no evidence of reaction manifested itself and no norcaradiene, the product which would have been expected from trapping of methylene by cyclohexene, was obtained (eq. 3). Even when forcing conditions, such as heating in neat cyclohexene or addition of copper powder or cuprous chloride as catalysts, were employed or when dioxane was substituted for acetonitrile no significant reaction occurred. Moreover, under none of the conditions tested,

51. L. Friedman and F. M. Logullo, J. Am. Chem. Soc., 85, 1549 (1963).

even with the application of heat, could solubilization of glycine in the reaction mixtures be effected.



Use of a higher molecular weight amino acid, such as DL-valine, whose solubility in organic solvents hopefully would have been better than that of glycine, likewise failed to lead to significant reaction under the above conditions. Ethyl glycinate, another possible precursor to methylene, although apparently solubilized after long heating at 50-60° in dioxane-cyclohexene-isopentyl nitrite, gave no products which could be attributed to the generation of a carbene.

We must conclude, therefore, that under the conditions employed α -amino acids are not diazotized by isopentyl nitrite in aprotic solvents. We have thus not been able to show whether carbenes might result from spontaneous decomposition of diazotized amino acids in such solvents.

EXPERIMENTAL

Attempted Diazotization of Glycine.--A. In Acetonitrile-Cyclohexene. A suspension of 1.5 g (20 mmoles) of glycine in 60 ml of acetonitrile and 2.1 g (25 mmoles) of cyclohexene was stirred at room temp. while 3.0 g (25 mmoles) of isopentyl nitrite (Eastman practical grade) was added dropwise. No apparent reaction occurred (evolution of gas or liberation of heat). After a five-hour reflux period and standing overnight, g.l.c. analysis of the clear, orange solution (20M-C, 150°) revealed the absence of norcarane, and peaks only for starting materials

were obtained. Glycine remained undissolved at the end of the reaction.

B. In Dioxane-Cyclohexene. Glycine (0.38 g, 5 mmoles) was suspended in a mixture of 10 ml of dioxane and 10 ml of cyclohexene, 2 ml (1.74 g, 14.9 mmoles) of isopentyl nitrite was added at 50°, and the reaction mixture was stirred at 80° for 1.75 hrs. On cooling, unreacted glycine was still present. G.l.c. analysis of the clear, yellow liquid phase failed to yield any peak which could be attributed to norcarane.

C. In Neat Cyclohexene. A mixture of 0.5 g (7 mmoles) of glycine in 25 ml of cyclohexene was heated to reflux and 2.9 ml (2.5 g, 21 mmoles) of isopentyl nitrite was added dropwise over a 1 hr. period. After a further 1.5 hrs. at reflux, unreacted glycine still remained. G.l.c. analysis (20M-C, 150°) of the clear, orange supernatant liquid disclosed the presence only of starting material, no norcarane peak being detected.

D. In the Presence of Copper Powder. The above experiment (C) was repeated except that 0.125 g (2 mg-atoms) of copper powder was introduced into the reaction mixture before addition of isopentyl nitrite. G.l.c. analysis of the cooled reaction mixture again disclosed the absence of norcarane.

E. In the Presence of Cuprous Chloride. Experiment (B) above was repeated except that 0.20 g (2 mmoles) of cuprous chloride was added to the glycine suspension before isopentyl nitrite addition. After a 1.5-hr. reflux period, g.l.c. analysis of the reaction mixture disclosed only peaks for starting material, no norcarane being detected.

Attempted Diazotization of DL-Valine.--DL-Valine (0.6 g, 5.1 mmoles) was suspended in a mixture of 10 ml of dioxane and 10 ml of cyclohexene.

After warming to 50° in an oil bath, 2 ml (1.74 g, 14.9 mmoles) if isopentyl nitrite was added in portions over a period of 30 min., and the mixture was stirred at 90° for 1.5 hrs. At the end of this time considerable valine still remained undissolved. G.l.c. analysis of the clear, orange-red liquid phase disclosed the presence only of starting material. No significant peak was present which might have been assigned to a cyclohexene-isopropyl carbene adduct.

Attempted Diazotization of Ethyl Glycinate.-- A mixture of ethyl glycinate (0.515 g, 5 mmoles), 10 ml of cyclohexene and 10 ml of dioxane (the ester proved to be insoluble) was treated slowly at room temp. with 2 ml (1.74 g, 14.9 mmoles) of isopentyl nitrite. After heating for 2 hrs. at 50-60° and for 30 min. at 80°, the ester gradually dissolved until at the end, the mixture was practically completely homogeneous. However, g.l.c. analysis of the clear, orange-yellow solution again yielded no peak for norcarane.

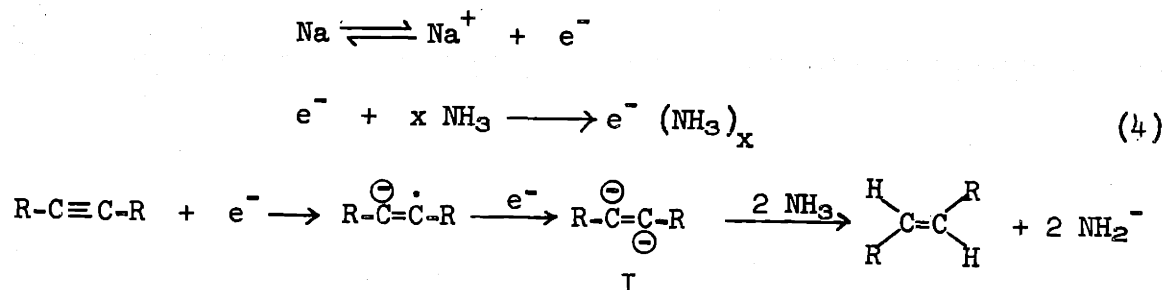
II. Studies Related to the Reduction and Isomerization of Dialkyl-
acetylenes in Liquid Ammonia.--A. Mechanism of the Na/Liq. NH₃

Reduction of 4-Octyne. The reduction of dialkylacetylenes by sodium in liquid ammonia is a very useful and specific method for preparing trans olefins to the exclusion of the cis isomers.⁵² A mechanism postulated for the reduction⁵³ proposes the intermediacy of a dianion (I) which, due to repulsion of charges, orients the electron pair trans to each other and helps to explain the stereospecificity of the reaction

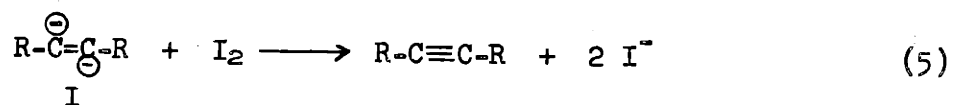
52. K. N. Campbell and L. T. Eby, J. Am. Chem. Soc., 63, 216, 2683 (1941).

53. K. W. Greenlee and W. C. Fernelius, ibid., 64, 2505 (1942).

(eq. 4). However, the character of the dianion, that is whether (1)



transient and reacting as rapidly as formed with ammonia to give product or (2) stable in the presence of excess ammonia and not forming olefin until addition of a proton source better than ammonia, has not been clarified. If ammonia is a strong enough acid to protonate the anion rapidly, then the reduction process would be expected to be as rapid as dianion formation and the latter would be difficult to detect. If, however, the dianion can exist finitely in the presence of excess sodium and is inert to ammonia, then it might be possible to alkylate it or to regenerate the starting acetylene in an electron-exchange reaction (eq. 5, e.g.) if a better electron acceptor were to be added to it. Thus, procedures exist for detecting the intermediacy of a stable dianion and for clarifying the mechanism of the reduction of acetylenes in the system in question.



We chose the electron-exchange process as the mode of detecting the dianion I during the Na/liq. NH₃ reduction of 4-octyne, since the recovery of starting acetylene would be the proof of existence of the dianion and hence the reaction could be easily monitored by gas-liquid chromatography. Likewise, if only trans olefin were to be obtained even

under electron-transfer conditions, then this also could be ascertained by g.l.c. and the presence of the dianion as a stable intermediate would be obviated.

4-Octyne was treated with excess sodium in refluxing liquid NH_3 . However, instead of quenching the reaction in the usual manner,^{52,54} methyl iodide, methyl bromide, or iodine (all acceptable electron-transfer reagents)⁵⁵ were added to attempt to "trap" the dianion I ($\text{R}=\underline{n}$ -propyl). In each case, trans-4-octene was obtained as the major product of the reaction and only a trace of starting acetylene could be detected. This failure to prevent the formation of the olefin by the procedure employed indicates strongly that if the dianion I is an intermediate in the reduction process, then it enjoys only transient existence, ammonia being sufficiently acidic to protonate it rapidly (eq. 4).

B. Isomerization of 4-Octyne by Sodium Amide in Liquid Ammonia.

Normally, internal acetylenes can be isomerized in good yield to terminal acetylenes by heating with sodium amide in a high-boiling, inert medium (mineral oil, toluene, etc.).⁵⁶ It has been shown in at least one case, however, (that of ethylamylacetylene)⁵⁷ that the isomerization is unsuccessful when carried out on a large scale in refluxing liquid ammonia (-33°) for several hours. On the other hand, the sodium amide isomerization of cyclic acetylenes to allenes has been accomplished when the acetylene is present in very dilute solution ($< 0.001 \text{ M}$) in refluxing

54. A. L. Henne and K. W. Greenlee, ibid., 65, 2020 (1943).

55. A. J. Birch, Quart. Rev. (London), 4, 69 (1950); W. Schlenk and E. Bergmann, Ann., 463, 1 (1928).

56. T. H. Vaughn, J. Am. Chem. Soc., 55, 3453 (1933).

57. T. H. Vaughn, R. R. Vogt, and J. A. Nieuwland, ibid., 56, 2120 (1934).

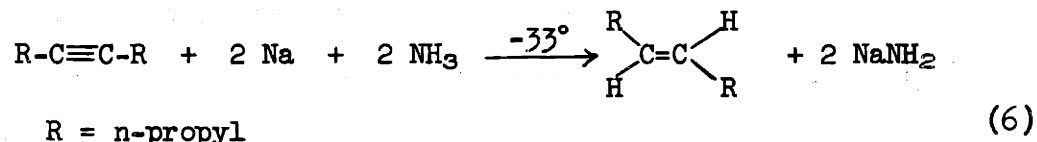
liquid ammonia.⁵⁸

In view of the success of the latter isomerization, a reinvestigation was made of the isomerizability of an acyclic acetylene, 4-octyne, but using a more dilute system than Vaughn⁵⁷ had employed. When a 0.0034M solution of 4-octyne in refluxing liquid ammonia was treated with sodium amide (0.7M) for 2.25 hrs., approximately 50-60% of the acetylene was converted to two products in equal amounts. Isolation by preparative g.l.c. disclosed these products to have infrared spectra very similar to that of 4-octyne, absorptions due to acetylenic linkages (3300 and 2200 cm^{-1}) being absent. They were thus assigned the identities 3- and 2-octyne. This result would corroborate Vaughn's failure⁵⁷ to obtain the terminal acetylene from ethylamylacetylene after several hours' reaction with NaNH_2 in liq. NH_3 .

The relatively slow rate of isomerization of 4-octyne under the conditions employed was not entirely expected in view of the rapid conversion found to take place between acetylenes and allenes in the cyclic series.⁵⁸ In fact, it had plausibly been postulated that in synthetic procedures involving both acetylenes and amide ion that acetylene isomerization might perhaps be a side reaction of consequence. However, it was found that when 4-octyne was reduced by sodium in liq. ammonia by adding sodium very slowly to the acetylene, in such a manner that unreacted 4-octyne was sure to come into contact with sodium amide produced in situ (eq. 6), only trans-4-octene was produced and no products of acetylene isomerization could be detected by g.l.c. (That

58. W. R. Moore and H. R. Ward, ibid., 85, 86 (1963).

sodium amide is in fact a product of the Na/liq. NH₃ reduction of



acetylenes was demonstrated by consecutively reducing and isomerizing 4-octyne in the same reaction mixture. Both trans-4-octene and the isomerization products reported above were obtained when 4-octyne was treated with only one-half the stoichiometric amount of sodium required for reduction, followed by a further 30 min. stirring period.) This result is consistent with the slow rate of acetylene isomerization noted previously and clearly shows that isomerization does not represent a serious side reaction during reduction of an acetylene in a Na/liq. NH₃ system.

Surmising that a low solubility of 4-octyne might be a factor in reducing its rate of isomerization by NaNH₂ in liq. NH₃, ether was employed as a cosolvent. However, no rate enhancement was observed. This result prompted us to investigate a method for determining the solubility of 4-octyne in liquid ammonia to determine if solubility was in fact influencing the results we had obtained. The procedure chosen for the determination relied on the concept that in a given solvent-liquid solute system, as the concentration of solute increases, the concentration of solute molecules in the vapor phase over the solution should increase until the limit of solubility of the solute is reached and a new liquid phase appears. At this point, the concentration of the solute molecules in the vapor phase should attain a maximum value and remain constant regardless of how much more of the

liquid solute is added to the system (assuming total pressure kept constant). Thus, by adding small increments of 4-octyne to refluxing liquid ammonia and analyzing vapor samples by g.l.c., it was possible to construct Fig. 1 (Experimental). The solute volume at which the curve levels off to zero slope (constant concentration of solute molecules in the vapor phase) represents the solubility of 4-octyne in 20 ml of liq. NH_3 . The value so obtained is 1 ml/20 ml of ammonia, a figure well above the 0.5 ml of 4-octyne added to 20 ml of NH_3 in the most concentrated reaction mixture employed in the work described previously. Hence, it is not possible to ascribe the slow isomerizability of 4-octyne by NaNH_2 in liquid ammonia to a lack of solubility in the solvent. (Employing the same procedure as described herein, the solubility of ether in refluxing liq. NH_3 was determined to be 35 ml/100 ml, Fig. 2, Experimental, and in liq. NH_3 0.7 M in NaNH_2 25 ml/100 ml, Fig. 3, Experimental.)

EXPERIMENTAL

Reduction of 4-Octyne by Sodium/Liq. Ammonia.--A. Quenching with CH_3I or CH_3Br . 4-Octyne (0.3 ml, 0.225 g, 2 mmoles) was added to a refluxing solution of 0.2 g (9 mmoles) of sodium in 20 ml of redistilled liquid ammonia, and the mixture was stirred for 30-40 min. under N_2 . The reaction was quenched by either injecting 0.56 ml (1.28 g, 9 mmoles) of CH_3I or by distilling in 0.5 ml (0.86 g, 9 mmoles) of CH_3Br . After addition of water and 10-20 ml of pentane, the ammonia was allowed to evaporate. The pentane layer was dried over CaCl_2 , concentrated, and analyzed by g.l.c. (20M-C, temp. progr. from 95°). A single product was obtained by both procedures, the retention time of which corresponded

to that for trans-4-octene. Only a trace of starting acetylene proved to be present.

B. Quenching with I₂. 4-Octyne (0.3 ml, 0.225 g, 2 mmoles) was added to a refluxing solution of 0.20 g (9 mmoles) of sodium in 20 ml of redistilled liq. NH₃, and the mixture was stirred under N₂ for 30-35 min. The reaction was quenched by addition of approx. 2 g of iodine crystals, whereupon the blue solution turned blackish in color. After addition of 10 ml of ether and a little water, the ammonia was evaporated and the dark brown mixture remaining was rinsed into a separatory funnel with 10 ml of ether. The liquid was separated from a brown sludge, and the orange-yellow ether layer was treated with 4 ml of saturated NaHSO₃ solution and 4 ml of H₂O. After drying over Na₂SO₄, g.l.c. analysis of the clear, colorless ether solution (20M-C, temp. progr. from 95°) showed trans-4-octene to be a product of the reaction with only a trace of 4-octyne still present.

Isomerization of 4-Octyne by Sodium Amide in Liquid Ammonia.--

A 0.7 M solution of NaNH₂ in liq. NH₃ was prepared by dissolving 0.32 g (14 mmoles) of sodium in 20 ml of liq. NH₃ and adding a crystal of ferric nitrate. After addition of 10 μ l (0.068 mmole) of 4-octyne, the mixture was stirred at reflux for 2.25 hrs. The reaction was quenched by addition of 0.8 g of solid NH₄Cl, 10 ml of ether was added, and the ammonia was evaporated. After concentration under vacuum, the ether solution was analyzed by g.l.c. (20M-C, temp. progr. from 95°) revealing the presence of unreacted 4-octyne and two products in the approx. ratio 4 : 3 : 3, resp. Isolation of the three materials by preparative g.l.c. and infrared analysis of the pure liquids corroborated the identity of

4-octyne and disclosed that the two product spectra were quite similar to that of 4-octyne, no new distinguishing absorptions being present.

Reduction of 4-Octyne in Liquid Ammonia by Very Slow Addition of Sodium.--Sodium was added in very small pieces to a stirred solution of 0.3 ml (0.225 g, 2 mmoles) of 4-octyne in 20 ml of liq. NH_3 in such a way that the blue color from each addition was discharged before the next piece was added. In this way slightly less than 0.2 g of sodium was added over a 3-hr. period. The final mixture was white and contained suspended solid. The reaction was quenched with 0.48 g of NH_4Cl , 12 ml of pentane was added, inorganic salts were dissolved by addition of H_2O , and the ammonia was allowed to evaporate. After washing, drying, and concentration, g.l.c. analysis of the pentane solution disclosed trans-4-octene to be the major product with only a trace of 4-octyne still present. Neither of the two products of isomerization of 4-octyne could be detected.

Concurrent Reduction and Isomerization of 4-Octyne.--To a solution of 0.5 ml (0.375 g, 3.4 mmoles) of 4-octyne in 20 ml of liq. NH_3 was added a single shiny piece of sodium (0.078 g, 3.4 mmoles). After 10 min. the blue color of the stirred solution was discharged leaving a white, opaque slurry. This was allowed to stir for 30 min. longer at reflux, and the reaction was quenched with 0.2 g of NH_4Cl . After addition of 20 ml of pentane and evaporation of ammonia, the concentrated pentane extract was analyzed by g.l.c. revealing major peaks for trans-4-octene and 4-octyne and two minor peaks, which corresponded to the products of isomerization of 4-octyne noted previously.

Sodium Amide Isomerization of 4-Octyne Using Ether as Cosolvent.--A solution of 10 μl of 4-octyne in 8 ml of dry ether was added to 20 ml

of a 0.7 M solution of NaNH_2 in liq. NH_3 prepared as described previously. The mixture was stirred under reflux for 2.25 hrs., then was quenched with 0.8 g NH_4Cl . After work-up in the usual manner, g.l.c. analysis of the concentrated ether solution disclosed 4-octyne as the major peak and two small peaks representing isomerization products of 4-octyne. However, the amounts of the two products were smaller relative to 4-octyne than was true for the same reaction without ether as cosolvent.

Determination of the Solubility of 4-Octyne in Liquid Ammonia.--

Liquid ammonia (20 ml) was distilled into a 50-ml, 3-neck, r.b. flask equipped with a Dry Ice condenser and magnetic stirrer and fitted with a rubber septum in one neck. Increments of 4-octyne varying from 3 μl at the beginning to 1 ml at the end (to a total volume of 3 ml) were added to the refluxing, stirred solvent, and after each addition a sample of the vapor phase was withdrawn employing a silicone-greased syringe. Duplicate vapor samples were analyzed by g.l.c. using a Silicone 710 column at 80° , and the heights of the octyne peaks were noted. The volume of vapor analyzed varied from 2 ml at the beginning of 4-octyne addition to 0.5 ml at the end. In this way a plot of volume of 4-octyne added to the ammonia vs. g.l.c. peak ht. of 4-octyne in the vapor phase was constructed and a break in the curve to zero slope noted at 1.0 ml of 4-octyne (Fig. 1). Thus, its solubility in liq. NH_3 is approx. 5 ml/100 ml.

Determination of the Solubility of Ether in Liquid Ammonia.--A.

The apparatus described above was employed. Anhydrous ether was added in increments of 0.5-3 ml (to 20 ml total volume) to 20 ml of refluxing

liq. NH_3 using a hypodermic syringe, and after each addition a 30 μl sample of the vapor phase was withdrawn with a 0.25-ml silicone-greased syringe. Duplicate vapor samples were analyzed on a 20% Carbowax 20M col. at 90° , and the heights of the ether peaks were noted. In this way a graph of ether volume added to the ammonia vs. g.l.c. peak ht. of ether in the vapor phase was plotted and a break in the curve noted at 7 ml of ether (Fig. 2). Thus, its solubility in liq. NH_3 is approx. 35 ml/100 ml.

B. The above experiment was repeated except that ether was added to 20 ml of a liq. NH_3 solution which was 0.7 M in NaNH_2 (prepared as described previously). The plot of added ether volume vs. ether peak hts. from the vapor phase showed a break to zero slope at 5 ml of ether, indicating its solubility in this medium to be 25 ml/100 ml (Fig. 3).

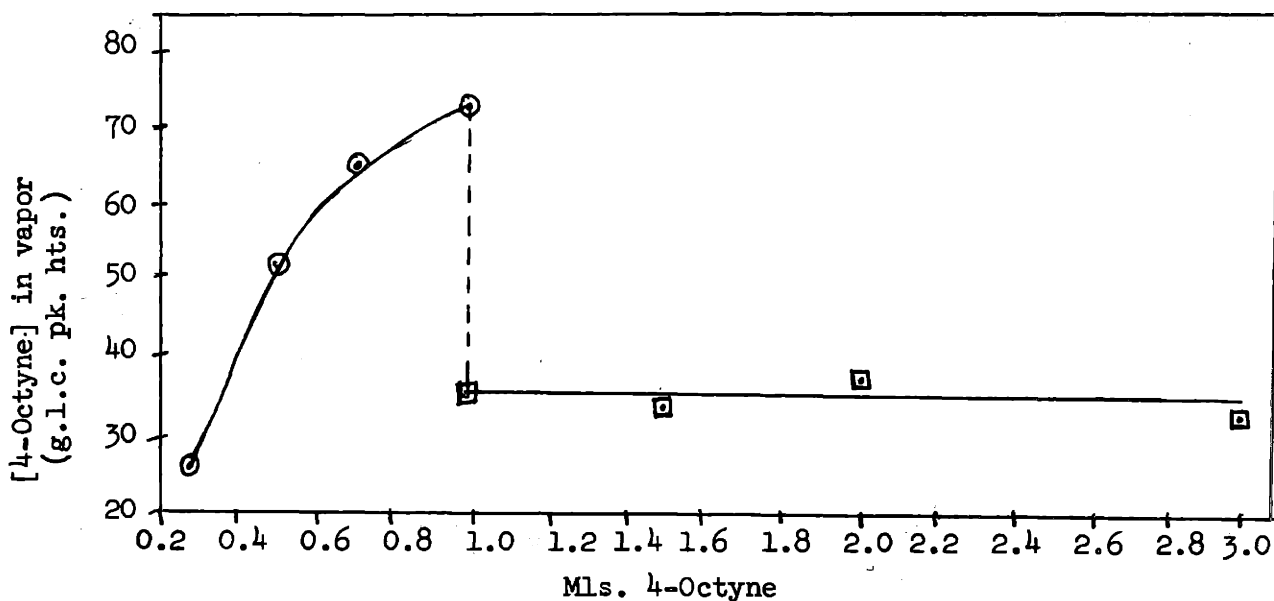


Fig. 1. Vapor phase concentration of 4-octyne as a function of volume of 4-octyne added to 20 ml of refluxing liquid ammonia; \odot 2 ml vapor sample analyzed, \square 0.5 ml vapor sample analyzed.

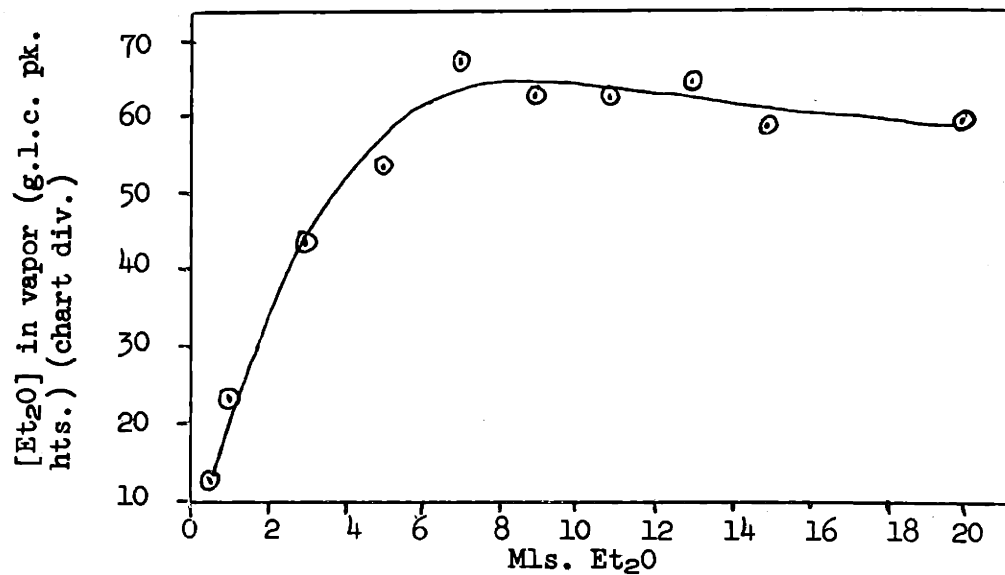


Fig. 2. Vapor phase concentration of diethyl ether as a function of volume of ether added to 20 ml. of refluxing liquid NH₃.

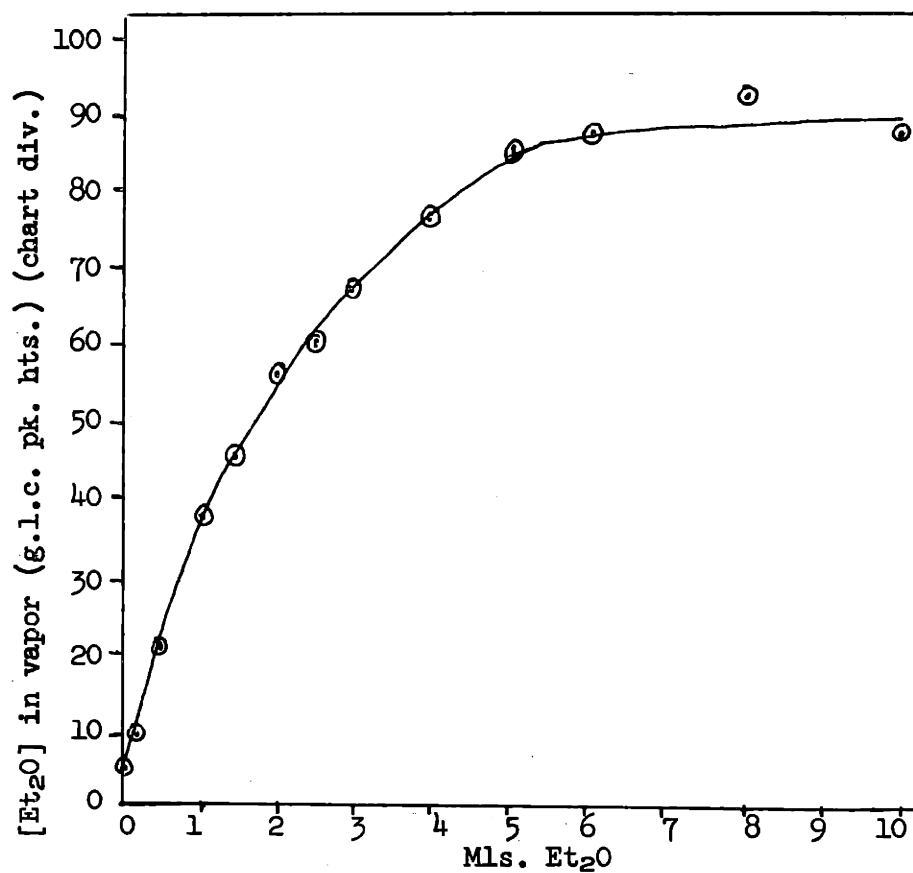


Fig. 3. Vapor phase concentration of diethyl ether as a function of volume of ether added to 20 ml. of refluxing liquid NH₃ 0.7 M in NaNH₂.

The Formation of Hexachlorocyclopropane by the Addition of Dichlorocarbene to Tetrachloroethylene

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The addition of dihalocarbenes to olefins discovered by Doering and Hoffmann¹ has provided an exceptionally useful and widely used synthesis of dihalocyclopropanes. Studies by Skell² and Doering³ have established that dibromocarbene and dichlorocarbene behave as electrophilic reagents since electron-donating groups on an olefin facilitate addition. Accordingly, a highly negatively substituted olefin would be expected to be quite unreactive³ toward dihalocarbenes. In particular, it appeared to be of interest to examine the addition of dichlorocarbene to tetrachloroethylene, an olefin which is resistant to electrophilic attack, since the potential adduct, hexachlorocyclopropane, which might prove to be of intrinsic interest, was reported by Stevens⁴ to be unavailable by way of chlorination of cyclopropane. To this end, dichlorocarbene was generated in the presence of tetrachloroethylene by treatment of chloroform with strong bases¹ and by the thermal decomposition of sodium trichloroacetate⁵ in 1,2-dimethoxyethane. Hexachlorocyclopropane was formed in these reactions, but in low yields (ca. 0.2–1%).⁶

The structure of the compound, a white crystalline solid, m.p. 104–104.5°, was established by elemental analysis, which gave an empirical formula of CCl₂, and the determination of the molecular weight cryoscopically and by mass spectrometry. The mass spectrum of C₃Cl₆ does not show any peak due to the molecular ion, but no fragments are formed which have more than three carbon atoms. The most abundant fragment is C₃Cl₅, corresponding to loss of a single chlorine atom. Inasmuch as there can be only two compounds with a molecular formula of C₃Cl₆, namely hexachlorocyclopropane and hexachloropropylene, and the latter is a well known commercially available liquid, it is clear that the solid referred to above is perchlorocyclopropane.

In retrospect, it appears likely that Stevens⁴ did prepare hexachlorocyclopropane. He reported that chlorination of 1,1,2,2-tetrachlorocyclopropane for seven days at 63° in the presence of ultraviolet light gave hepta- and octachloropropane as the main products, but also gave a very small amount of a white crystalline solid, m.p. 102–102.5°, which on the basis of elemental analysis he believed to be the then unknown 1,1,1,3,3,3-

hexachloropropane.⁷ Subsequently, Davis and Whaley⁸ have prepared 1,1,1,3,3,3-hexachloropropane by chlorination of 1,1,1,3,3-pentachloropropane followed by fractionation to separate the two hexachloropropanes which are formed and have reported that 1,1,1,3,3,3-hexachloropropane is a liquid, b.p. 205°, m.p. –27°. Since all four hexachloropropanes have Raman spectra⁹ which are consistent with the assigned structures, we believe that Stevens probably did succeed in preparing hexachlorocyclopropane.

The fact that perchlorocyclopropane was formed at all in the present study, albeit in very low yields, takes on greater significance when one considers that dichlorocarbene apparently fails to react with ethylene³ (in preference to reaction with *t*-butoxide). Tetrachloroethylene is far less reactive than ethylene in typical electrophilic reactions (*e.g.*, addition of bromine). Thus it is possible that in reacting with tetrachloroethylene, dichlorocarbene may be exhibiting either radical or nucleophilic character.

Experimental

Reaction of Chloroform with Potassium *t*-Butoxide.—Chloroform (36 g.) was added dropwise with stirring over a period of 1 hr. to a mixture of 50.5 g. of potassium *t*-butoxide (freed of alcohol by heating at 140° at 1 mm.) and 325 g. of freshly distilled tetrachloroethylene. The reaction mixture was cooled intermittently with an ice bath. The mixture was stirred at room temperature for an hour and then was poured into water. The organic layer was separated, dried, and the bulk of the tetrachloroethylene was removed by distillation at atmospheric pressure leaving a dark oil, a portion of which distilled at 70–120° (1–2 mm.) leaving a considerable quantity of residual tar. The distillate, shown by gas chromatography to be mainly tetrachloroethylene, was redistilled slowly under reduced pressure, leaving a solid residue. The latter was sublimed five times at 40–50° (0.5 mm.) giving 0.21 g. of hexachlorocyclopropane, m.p. 104.0–104.5°.

Anal. Calcd. for C₃Cl₆: C, 14.46; Cl, 85.54; mol. wt., 249. Found: C, 14.46; Cl, 85.69; mol. wt., 241.¹⁰

In solution (carbon disulfide and carbon tetrachloride), perchlorocyclopropane shows prominent bands in the infrared at 850 (s), 905 (m), and 930 (w) cm.⁻¹. Mass spectrum was measured on a Consolidated Electrodynamics Corporation Model 21–103C mass spectrometer with a heated inlet system (140°) at an ionizing potential of 70 v. The mass number of the largest isotopic peak of each monoisotopic carbon-containing fragment is given as a percentage of the largest peak in the spectrum. Normal isotopic distribution of Cl³⁵ and Cl³⁷ was observed within each fragment (thus all fragments listed contain only Cl³⁵ except the last three each of which contains one Cl³⁷).

Fragment, mass number (percentage): CCl, 47 (35.4); C₂Cl, 59 (6.4); C₃Cl, 71 (30.3); CCl₂, 82 (22.2); C₂Cl₂, 94 (12.2); C₃Cl₂, 106 (15.4); CCl₃, 117 (26.4); C₂Cl₃, 129 (4.4); C₃Cl₃, 141 (16.8); C₂Cl₄, 166 (12.8); C₃Cl₄, 178 (0.9); C₃Cl₅, 213 (100.0).

Use of Sodium Hydride.—Methyl alcohol (9.6 g., 0.30 mole) was added dropwise with stirring over a period of 9.5 hr. at room temperature to a mixture of 298 g. of tetrachloroethylene, 7.2 g. (0.30 mole) of sodium hydride, and 44.6 g. (0.37 mole) of chloroform. The mixture was processed as above to give 0.42 g. of hexachlorocyclopropane. When the methyl alcohol was omitted (reflux, 40 hr.) or replaced by *t*-butyl alcohol (60°, 11 hr.), only a trace of this product was isolated.

Use of Sodium Trichloroacetate.—A mixture of 18.5 g. of sodium trichloroacetate, 80 g. of tetrachloroethylene, and 150 ml. of 1,2-dimethoxyethane was refluxed 24 hr. After processing in the usual way, the mixture was concentrated by distillation and both distillate and residue were analyzed by gas chromatog-

(7) Analysis indicated 0.53% hydrogen, a value in between the required values of 0.00 for hexachlorocyclopropane and 0.80 for hexachloropropane.

(8) H. W. Davis and A. M. Whaley, *J. Am. Chem. Soc.*, **73**, 2361 (1951).

(9) H. Gerding and H. G. Haring, *Rec. trav. chim.*, **74**, 841 (1955).

(10) Determined by Dr. C. M. Starks by freezing point lowering of benzene solutions.

(1) W. von E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, **76**, 6162 (1954).

(2) P. S. Skell and A. Y. Garner, *ibid.*, **78**, 5430 (1956).

(3) W. von E. Doering and W. A. Henderson, Jr., *ibid.*, **80**, 5274 (1958).

(4) P. G. Stevens, *ibid.*, **68**, 620 (1946).

(5) W. M. Wagner, *Proc. Chem. Soc. (London)*, 229 (1959).

(6) (a) Since this work was completed, the formation of hexachlorocyclopropane by similar means (chloroform and fused potassium hydroxide at 105°), but in higher yields (5–10%), has been reported by S. W. Tobey and R. C. West, Abstracts of Papers presented at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., September 9–14, 1962, p. 95Q; (b) after submission of this manuscript we learned that E. K. Field and S. Meyerson have also prepared this compound and measured its mass spectrum.

raphy which indicated formation of *ca.* 1% of hexachlorocyclopropane ($t_R = 6.6$).¹¹ The chromatograms showed peaks due to several other minor components, one of which was collected ($t_R = 2.7$) and found to have a strong band at 1763 cm.^{-1} but which was not characterized further.

In a similar experiment, the gas evolved during the reflux period was collected and analyzed by infrared spectroscopy which indicated that the sample consisted of carbon dioxide that did

(11) Retention time relative to tetrachloroethylene, $t_R = 1.00$; 1,2-dimethoxyethane, $t_R = 0.33$ on silicone oil at 150° .

not contain more than a small amount ($< 5\%$) of carbon monoxide. This result apparently precludes significant reaction of dichlorocarbene with trichloroacetate ion to give, over-all, carbon monoxide, trichloroacetyl chloride, and chloride ion by a reaction path formally similar to that described¹² for the reaction of dichlorocarbene with alkoxide ions. In other control experiments it was found that the thermal decomposition of sodium trichloroacetate in 1,2-dimethoxyethane did not produce significant quantities of materials with retention times greater than that of the solvent.

(12) P. S. Skell and I. Starer, *J. Am. Chem. Soc.*, **81**, 4117 (1959).

BIOGRAPHICAL NOTE

The author was born on May 11, 1930 in Providence, Rhode Island. After attending secondary schools in that city, he graduated from Brown University magna cum laude and with Honors in Chemistry in June, 1951 and was at that time commissioned Ensign, USNR. There followed five years of active duty with the U.S. Navy, half of which time was spent aboard the USS Wright (CVL-49), the other half as an Instructor in Chemistry at the U.S. Naval Academy, Annapolis, Maryland. He was released from active duty in June, 1956 with the rank of Lieutenant, USNR and entered the graduate school of M.I.T. as a candidate for the Ph.D. degree in Organic Chemistry in September of that year. However, after one academic year, he suspended his studies and accepted a position with the Procter and Gamble Company, Cincinnati, Ohio as a development chemist. The development of improved stannous fluoride dentifrice formulations occupied his attention for three years, followed by three years of work in the field of flavor chemistry. In September, 1963 the author returned to M.I.T. to resume his graduate studies and to complete the work for the doctorate.