

REACTIONS OF PHENYL(TRIHALOMETHYL)MERCURIALS WITH OLEFINS

by

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Richard Joseph Minasz

Submitted to the Department of Chemistry in September, 1964 in partial fulfillment of the requirements for the degree of Master of Science.

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## ABSTRACT

Pure phenyl(bromodihalomethyl)mercurials have been prepared from phenylmercuric bromide by the haloform-potassium tert-butoxide procedure. Phenyl(trichloromethyl)mercury has been prepared by the reaction between phenylmercuric chloride and potassium trichloroacetate. When the preparation of phenyl(tribromomethyl)mercury by the same procedure is attempted, only a very low yield of the desired product is obtained.

The reaction of the phenyl(trihalomethyl)mercurials with cyclohexene has been shown to be a good preparative method for dihalonorcaranes. The reactions of these mercurials with olefins of low reactivity and easily polymerizable olefins are good synthetic routes to otherwise inaccessible or difficultly-prepared gem-dihalocyclopropanes. With olefins containing two reactive sites, the trihalomethylmercurials react in the same manner as does sodium trichloroacetate. All structural assignments were made on the basis of their infrared and nuclear magnetic resonance spectra.

The phenyl(trihalomethyl)mercurial-olefin reaction in benzene at reflux has been shown to proceed with complete stereospecificity. The reaction of phenyl(bromodichloromethyl)mercury with cis- and trans-propenyltrimethylsilane yielded only the cis- and trans-dihalocyclopropane, respectively. The structure of the cis isomer was established by its nuclear magnetic resonance spectrum.

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Center of Justice

To my future wife,  
whoever she may be

### General Introduction

Previous studies have shown that phenyl(trihalomethyl)mercury compounds react with olefins to give gem-dihalocyclopropanes in good yield<sup>1,2</sup> and that these reactions appear to involve dihalocarbenes as intermediates.<sup>1,3</sup> For example, phenyl(tribromomethyl)mercury reacted with a benzene solution of cyclohexene to give 7,7-dibromobicyclo[4.1.0]heptane in 88% yield and an essentially quantitative yield of phenylmercuric bromide.<sup>1</sup>

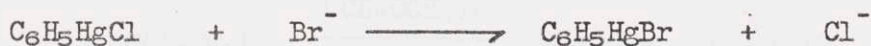
Of great interest in connection with this problem was the scope of the reaction of these trihalomethyl-substituted mercurials with various types of olefins, i.e., olefins of low reactivity toward dihalocarbenes, easily polymerizable olefins, olefins containing activated carbon-hydrogen bonds, etc. The stereochemistry of the reaction with geometric isomers was also of considerable importance.

Bromodihalomethyl-substituted mercurials were employed as the main starting materials for the work in this thesis due to their relatively short reaction time in comparison with the trichloromethyl-substituted mercurial (1 to 4 hr. vs. 48 hr.).<sup>1</sup> Although a complete survey of the mercurial-olefin reaction was not undertaken, the reaction appears to be of general synthetic usefulness in the preparation of gem-dihalocyclopropanes.



### Results and Discussion

Previous work<sup>2</sup> has shown that the preparation of phenyl-(trihalomethyl)mercury compounds from phenylmercuric halide, a trihalomethane, and potassium tert-butoxide proceeds by simple nucleophilic displacement of the halide ion by the trihalomethyl anion, the intermediacy of which has been demonstrated by Hine.<sup>4</sup> When bromine-containing haloforms were employed in this reaction with phenylmercuric chloride, the products were those expected, viz., phenyl(bromodihalomethyl)mercury, but the mechanistic interpretation of these reactions were complicated by the fact that exchange between bromide ion (generated from the haloform-base reagent mixture, which was used in twofold excess) and phenylmercuric chloride occurred. In an attempt to

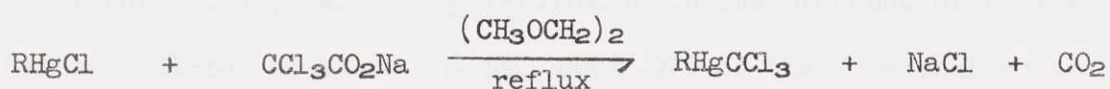


determine the extent of halide exchange, phenylmercuric chloride was treated with potassium bromide in a solvent-mixture consisting of tert-butyl alcohol and benzene at 0° with high-speed stirring. The analysis of the isolated product by thin-layer chromatography indicated that a mixture of phenylmercuric bromide and chloride was present; no satisfactory bromine-chlorine analysis, however, could be obtained. In a separate experiment in which phenylmercuric

chloride was treated with potassium bromide in acetone at room temperature, complete conversion to phenylmercuric bromide was attained.

The reaction of phenylmercuric bromide with bromodichloro-, chlorodibromomethane, or bromoform and solid potassium tert-butoxide, used as the 1:1 alkoxide-alcohol adduct,<sup>5</sup> in benzene with high-speed stirring at 0°, as described by Reutov and Lovstova,<sup>6</sup> yielded the corresponding phenyl(trihalomethyl)mercurials in 60, 78, and 87% yields, respectively. The attractiveness of the use of the solid alkoxide over a tert-butyl alcohol solution of the alkoxide was noticed when a yield of only 38% of the phenyl(tribromomethyl)-mercurial was obtained by the latter procedure.

Razuvaev and co-workers<sup>7</sup> and also Logan<sup>8</sup> have reported the preparation of trichloromethylmercury compounds by the general reaction:



The convenience and simplicity of this procedure compared with the haloform-base procedure inspired an investigation of the sodium trihaloacetate procedure for use in the preparation of the relatively unstable bromodihalomethyl-substituted mercurials. However, although phenyl(trichloromethyl)mercury was obtained in 63% yield by the thermal decomposition of potassium trichloroacetate (prepared by the neutralization of trichloroacetic acid with potassium

hydroxide) in the presence of phenylmercuric chloride in 1,2-dimethoxyethane, only a 7% yield of the tribromomethyl-substituted mercury compound could be obtained by the similar thermal decomposition of sodium tribromoacetate. It is believed that the tribromomethylmercurial was formed in a greater yield, but, due to its relatively thermal instability, decomposed partially under the reaction conditions (30 to 40°). In support of this hypothesis, 7,7-dibromobicyclo[4.1.0]heptane, identified by comparison of its infrared spectrum with that of an authentic sample, was obtained in a moderate (56%) yield by the thermal decomposition (in refluxing 1,2-dimethoxyethane) of sodium tribromoacetate in the presence of cyclohexene and phenylmercuric bromide.

Doering and Hoffmann<sup>9</sup> have reported the preparation of 7,7-dichlorobicyclo[4.1.0]heptane in 59% yield by the treatment of chloroform with potassium tert-butoxide in the presence of cyclohexene. Yields of 43-88, 34-59, and 8-91% of the 7,7-dichlorononcarane have also been obtained by the ethyl trichloroacetate-base,<sup>10</sup> hexachloroacetone-base,<sup>11</sup> and bromotrichloromethane-lithium reagent<sup>12</sup> procedures, respectively. In comparison with the above results, the reaction of phenyl(trichloromethyl)mercury with cyclohexene afforded 7,7-dichlorobicyclo[4.1.0]heptane in 89% yield. The use of phenyl(chlorodibromomethyl)mercury in this reaction gave 7-bromo-7-chlorobicyclo[4.1.0]heptane in a similar yield.

It has been established that dihalocarbenes behave as electrophilic reagents<sup>13,14</sup> and, therefore, a highly negatively-substituted olefin, such as tetrachloroethylene, would not be very reactive toward these species. Accordingly, dichlorocarbene, generated in the presence of tetrachloroethylene by thermal decomposition of sodium trichloroacetate<sup>15,16</sup> and by treatment of chloroform with strong bases,<sup>15,17</sup> has resulted in the formation of hexachlorocyclopropane, but in low yields (0.2 - 10%). In contrast, phenyl(bromodichloromethyl)mercury [and also phenyl(trichloromethyl)mercury] reacted with a large excess of tetrachloroethylene at 90° to give hexachlorocyclopropane in 74% yield. The marked difference between the above results can be traced to the method of dihalocarbene generation. Whereas, in the trihalomethylmercurial-tetrachloroethylene reaction, dichlorocarbene is generated in a neutral medium using the olefin as the solvent, the chloroform-base and sodium trichloroacetate procedures are complicated by competing side-reactions (e.g., reaction of the dichlorocarbene with the base and/or solvent) and result in lowered yields of the perchlorocyclopropane.

Similar reactions of phenyl(chlorodibromomethyl)- and phenyl-(tribromomethyl)mercury with tetrachloroethylene at 80° afforded bromopentachlorocyclopropane and 1,1-dibromotetrachlorocyclopropane in 48 and 28% yields, respectively. (Tobey and West<sup>17b</sup> have

reported the formation of the latter compound by the reaction of tetrachloroethylene and the bromoform-base reagent mixture, but only in 0.33% yield.) Steric hindrance in the formation of bromopentachloro- and gem-dibromotetrachlorocyclopropane or the thermal instability of these compounds could explain the sharp decrease in their yields. However, since no difference in the respective infrared spectra of these compounds, before and after melting, is observed, the former reason is favored. The mass spectra of these two compounds, like that of hexachlorocyclopropane,<sup>15</sup> showed no molecular ion peak.

In each of the reactions with tetrachloroethylene, several minor side-products were detected by vapor-phase chromatographic analysis. These may have arisen from some decomposition of the perhalocyclopropanes during the work-up of the reaction and have not been identified.

The reaction of acrylonitrile, a very easily polymerizable olefin, and phenyl(bromodichloromethyl)mercury yielded a single product, the structure of which was established, on the basis of its infrared, n.m.r., and mass spectra, as 1-cyano-2,2-dichlorocyclopropane. The infrared spectrum of the product showed a strong band at  $2250\text{ cm.}^{-1}$  and none in the  $1600\text{-}1650\text{ cm.}^{-1}$  region; absorption in the former region is known to be highly characteristic of nitrile groups.<sup>18</sup> In the n.m.r. spectrum, all the protons appeared as a multiplet, centered at 2.25 p.p.m. The mass spectrum,

showing a molecular ion at mass 135  $[(C_4H_3Cl_2N)^+]$ , confirmed the structural assignment of the product. The phenylmercuric bromide, as isolated from the reaction mixture, was, as could be seen from its melting point (275.0 - 286.5°) and its color (light brown), contaminated with small amounts of acrylonitrile polymer.

Roberts and Mazur<sup>19</sup> have reported the formation of chloromethylcyclopropane by the photoinitiated chlorination of methylcyclopropane. Attempts to isolate bromomethylcyclopropane by the reaction of cyclopropylcarbinol with phosphorus tribromide, however, led only to a mixture of bromides. In contrast, phenyl(bromodichloromethyl)mercury reacted with allyl bromide to yield, as the major product, 1-(bromomethyl)-2,2-dichlorocyclopropane. In the n.m.r. spectrum, two protons, assigned to the bromomethyl group, appeared as a quartet at 3.5 p.p.m.; a multiplet, centered at 1.9 p.p.m., two protons, and a triplet at 1.3 p.p.m., one proton, were attributed to the three cyclopropyl hydrogens. Trace amounts of eight high-boiling side-products (ca. < 1 to 2% each) were also detected in the reaction mixture but were not identified.

The reaction of mesityl oxide with the bromodichloromethyl-substituted mercurial furnished a product which was established, on the basis of its infrared and n.m.r. spectra, as 1-acetyl-2,2-dichloro-3,3-dimethylcyclopropane. The infrared spectrum showed a strong carbonyl band at  $1720\text{ cm.}^{-1}$ , with no band being observed

in the olefinic region, 1600-1650  $\text{cm}^{-1}$ . In the n.m.r. spectrum, the acetyl substituent appeared as a singlet at 2.25 p.p.m.; the two gem-dimethyl groups appeared as a doublet at 1.42 p.p.m. ( $J = 1.9$  c.p.s.); the cyclopropyl hydrogen appeared as a multiplet at 2.2 p.p.m. Although there are no protons alpha to the ring proton, a splitting pattern, such as that observed, would be expected due to its close proximity to the gem-dimethyl group; a doublet, such as that observed, would also be expected for the gem-dimethyl group.

The instability of the mesityl oxide-mercurial adduct under the conditions of analysis by vapor-phase chromatography ( $120^{\circ}$ ) led to an unsatisfactory elemental analysis; for this reason, the analysis was obtained for the 2,4-dinitrophenylhydrazone of the product. Analysis at lower temperatures, however, indicated that successful isolation of the adduct may be effected if the reaction and work-up temperatures do not exceed  $100^{\circ}$ .

Results of competition reactions between olefins and either phenyl(trihalomethyl)mercurials or sodium trichloroacetate as the dihalocarbene source have been reported.<sup>3</sup> The above results were based on the selectivity of the dihalocarbene toward various olefins using cyclohexene as a reference. In conjunction with this, two sets of reactions, involving the trihalomethyl-substituted mercurials and sodium trichloroacetate, were performed to measure the internal selectivity of the dihalocarbene. In the first series

of reactions, 2,5-dihydrofuran reacted with phenyl(bromodichloromethyl)mercury at  $80^{\circ}$  to give a product, **1**, arising from insertion into the  $C_2$  (or  $C_5$ ) carbon-hydrogen bond and another product, **2**, arising from addition of the dihalocarbene into the double bond, in a ratio of 1.18 to 1 (**1** to **2**). A similar reaction of the furan with sodium trichloroacetate at  $80^{\circ}$  in 1,2-dimethoxyethane resulted in the formation of **1** and **2** in a ratio of 1.23 to 1. The structures of the two products were established by comparison of their n.m.r. spectra with those reported by Anderson and Reese<sup>20</sup> (Figure I), and by comparison of their infrared spectra with those of authentic samples. A third reaction, using sodium trichloroacetate as the dihalocarbene source, in refluxing dioxane afforded **1** and **2** in a ratio of 1.30 to 1. The close agreement obtained

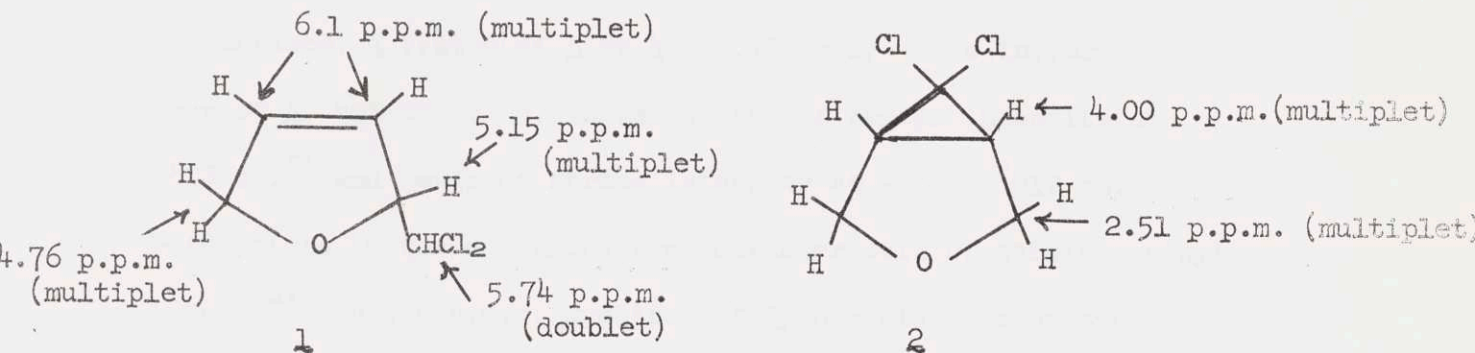


Figure I

in these results, although contradictory to those of Anderson and Reese, who reported the formation of **1** and **2** in ratios of 1 to 1.88 and 1 to 1.04 when using the ethyl trichloroacetate-base procedure



at 0° and the sodium trichloroacetate procedure at 110°, respectively, is to be expected since it has been shown that the phenyl(trihalomethyl)mercurial-olefin reaction, like that of the sodium trichloroacetate reaction, proceeds via free dihalocarbene.<sup>3</sup>

The reaction of 4-vinylcyclohexene with phenyl(bromodichloromethyl)mercury and with sodium trichloroacetate was also studied, Doering and Hoffmann<sup>9</sup> reported the addition of dichlorocarbene (via the haloform-base procedure) to 4-vinylcyclohexene to give a mixture of monoadducts, but were unable to separate the isomers. In contrast, phenyl(bromodichloromethyl)mercury and 4-vinylcyclohexene at 80° yielded a mixture of monoadducts which were separated by vapor-phase chromatography and identified as 3-vinyl-7,7-dichlorobicyclo[4.1.0]heptane, 3, and 4-(β,β-dichlorocyclopropyl)cyclohexene, 4 (ratio of 3 to 4 = 8.77 to 1). The infrared spectrum of 3, but not of 4, showed a band of medium intensity at 1825 cm.<sup>-1</sup> and bands of strong intensity at 988 and 912 cm.<sup>-1</sup>; absorptions in these regions are characteristic of terminal vinyl groups.<sup>21</sup> In the n.m.r. spectrum of 3, one olefinic proton occurred as a multiplet at 5.67 p.p.m., another as a multiplet at 5.0 p.p.m., and a third as a multiplet at 4.8 p.p.m.; in the spectrum of 4, both olefinic protons appeared as a triplet at 5.62 p.p.m. The use of sodium trichloroacetate as the dichlorocarbene source gave, under the same conditions, the same products

in a ratio of 8.46 to 1 (3 to 4). The close agreement between the results of the reactions of 4-vinylcyclohexene with the trihalomethylmercurial and with sodium trichloroacetate is again indicative of the dihalocarbene mechanism operative in both reactions.

Vapor-phase chromatographic analysis of the trihalomethylmercurial-vinylcyclohexene reaction mixture, using an XF 1150 column, showed four peaks, appearing as two sets of doublets. One doublet is believed to be due to the cis and trans isomers of the vinylnorcarane, 3 (Figure II). The cyclopropylcyclohexene, 4, contains two asymmetric carbon atoms and, thus, can exist in both threo and erythro forms (Figure II); the latter structures are believed to account for the second doublet.

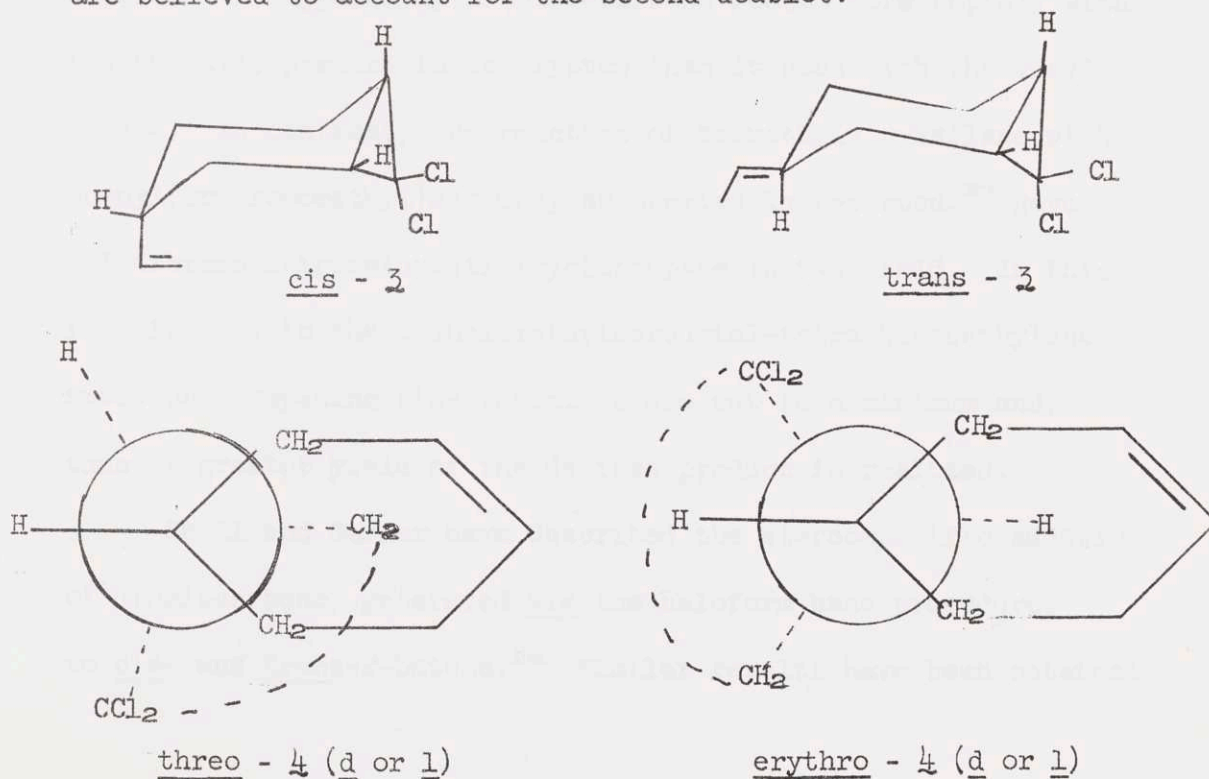


Figure II

The surprising results found in the case of the dihydrofuran-mercurial reaction, in which insertion of the dihalocarbene was favored over addition, suggested that the C<sub>2</sub> and C<sub>5</sub> protons may be greatly activated by the ether linkage. In confirmation of this, tetrahydrofuran and phenyl(bromodichloromethyl)mercury yielded a product identified, by comparison of its n.m.r. spectrum and refractive index with those of an authentic sample,<sup>20</sup> as 2-(dichloromethyl)tetrahydrofuran in 67% yield. A trace amount of tetrachloroethylene also was detected in the reaction mixture.

The formation of 1,1-dichloro-2-trimethylsilylcyclopropane in 0.2% yield by the reaction of trimethylvinylsilane with dichlorocarbene as generated by the chloroform-base method has been reported.<sup>22</sup> Apparently dichlorocarbene reacts more rapidly with the butoxide present in the system than it does with the vinylsilane. In contrast, the reaction of trimethylvinylsilane with phenyl(tribromomethyl)mercury, as previously reported,<sup>23</sup> gave 1,1-dibromo-2-trimethylsilylcyclopropane in 54% yield. In this reaction, as in the trihalomethylmercurial-tetrachloroethylene reaction, competing side-reactions are cut to a minimum and, thus, a greater yield of the desired product is realized.

Skell and Garner have described the stereospecific addition of dihalocarbene, generated via the haloform-base procedure, to cis- and trans-2-butene.<sup>24</sup> Similar results have been obtained

in the reaction of phenyl(trihalomethyl)mercurials with the cis and trans isomers of 2-butene and methyl crotonate.<sup>25</sup> Further investigation of the stereochemistry of the trihalomethylmercurial-olefin reaction has confirmed the latter results.

Separate reactions of phenyl(bromodichloromethyl)mercury with a benzene solution of cis- and trans-propenyltrimethylsilane at reflux gave cis- and trans-1-methyl-2-trimethylsilyl-3,3-dichlorocyclopropane, respectively. In the n.m.r. spectrum of the assumed cis isomer, the proton alpha to the methyl substituent appeared as an octet at 1.77 p.p.m., the proton alpha to the trimethylsilyl substituent as a doublet ( $J = 12.4$  c.p.s.) at 0.85 p.p.m., and the methyl group as a doublet ( $J = 6.2$  c.p.s.) at 1.35 p.p.m. The splitting constant obtained for the cis isomer ( $J_{\text{H-H}} = 12.4$  c.p.s.) was in favorable agreement with that reported by Williamson and co-workers for 1,1-dichloro-2-trimethylsilylcyclopropane ( $J_{\text{cis}} = 12.6$  c.p.s.),<sup>26</sup> and served as confirmation of the former's structure. The spectrum of the trans isomer was highly complicated - the proton alpha to the trimethylsilyl group was buried under the trimethylsilyl peak and the other ring proton was lost under the methyl absorption. As a result of this, no splitting constant could be obtained and the n.m.r. spectrum of the gem-dihalocyclopropane derived from the trans olefin could not be used as definitive evidence of its structure. The infrared spectra of the products

obtained in these reactions were fairly similar; some differences, however, were noted. Bands of strong intensity at 777, 801, and 1267  $\text{cm.}^{-1}$ , bands of medium intensity at 651 and 1100  $\text{cm.}^{-1}$ , and bands of weak intensity at 1940 and 2100  $\text{cm.}^{-1}$ , present in the infrared spectrum of the cis isomer, were absent in that of the assumed trans isomer; the spectrum of the latter showed bands of strong intensity at 795 and 1042  $\text{cm.}^{-1}$  and bands of weak intensity at 1202, 1310, and 1385  $\text{cm.}^{-1}$ , absent in the spectrum of the cis isomer. In addition, the refractive indices of the adducts obtained from the cis and trans olefins were 1.4614 and 1.4559 (taken at 25<sup>o</sup>), respectively. Furthermore, vapor-phase chromatographic analysis of the two propenylsilane adducts under the same conditions detected a marked difference in the two compounds - retention time of the cis adduct = 22.0 min.; of the trans adduct = 17.4 min. On the basis of these differences in the physical characteristics of the two adducts, the trans structure was assigned to the adduct obtained from trans-propenyltrimethylsilane.

## EXPERIMENTAL

### A. General Comments

Analyses were performed by Dr. S. M. Nagy (M.I.T.), by the Schwarzkopf Microanalytical Laboratory, Woodside 77, New York, and by the Galbraith Laboratories, Knoxville 21, Tennessee.

Melting points were taken using a Mel-Temp or Buchi melting point apparatus and are uncorrected.

Infrared spectra were taken by Mrs. Nancy Alvord (M.I.T.) using a Baird (Model B) infrared spectrophotometer and by the author using a Perkin-Elmer (Model 337) infrared spectrophotometer.

Nuclear magnetic resonance spectra were taken by Mr. Anthony Evinin (M.I.T.) with a Varian Associates A-60 high resolution spectrometer.

Refractive indices were measured with a Zeiss refractometer.

The columns used for vapor-phase chromatographic analyses were either a preparative column, 270 cm. in length, constructed of 10 mm. i. d. pyrex tubing, or an analytical column, 210 cm. in length, constructed of 6 mm. i. d. pyrex tubing. Helium was used as the carrier gas.

Area measurements of vapor-phase chromatographic peaks were made with an Ott planimeter.

Purification of solvents.- For all experiments in which benzene was used, Fisher reagent grade benzene was either distilled from calcium hydride or passed through Linde molecular sieves and Woelm alumina immediately before use.

Ansul 1,2-dimethoxyethane was either distilled from potassium or passed through Linde molecular sieves and Woelm alumina immediately before use.

tert-Butyl alcohol was stored over sodium and freshly distilled immediately before use.

All reactions involving organometallic reagents were carried out in an atmosphere of prepurified nitrogen.

#### B. Starting Materials

1. Phenylmercuric Bromide.\*- To a solution of 156 g. (0.37 mole) of tetraphenyltin (M. and T. Chemicals, Inc.) in 3 l. of boiling benzene was added, rapidly and with stirring, a hot solution of 360 g. (1.0 mole) of mercuric bromide (Mallinckrodt analytical reagent) in 350 ml. of tetrahydrofuran. The reaction mixture was stirred for an additional 5 min., cooled to room temperature, and filtered. The residue was washed with 150 ml. of cold benzene and dried in vacuo at 55°, giving 248 g. of pure phenylmercuric

bromide, m.p. 283.9-285.0° [Lit.<sup>27</sup> m.p. 280°]. A second crop of phenylmercuric bromide, 25 g., m.p. 284.8-286.2°, was obtained by evaporation of the filtrate to ca. one-fourth of its original volume. The total yield of phenylmercuric bromide was 76%.

\*Phenylmercuric chloride, m.p. 254.7-257.7°, <sup>28</sup> was prepared from mercuric chloride (Mallinckrodt) and tetraphenyltin in the same manner in 99% yield.

## 2. Conversion of Phenylmercuric Chloride to Phenylmercuric Bromide

by Potassium Bromide in tert-Butyl Alcohol and Benzene.- A solution of 15.7 g. (0.05 mole) of phenylmercuric chloride and 17.9 g. (0.15 mole) of potassium bromide in 200 ml. of anhydrous tert-butyl alcohol and 200 ml. of anhydrous benzene in a 1 l. Morton flask was stirred (high-speed stirring) at 0° for 2 hr., poured into 250 ml. of distilled water, and filtered. The residue was dried in vacuo at 55°, giving 16.5 g. of a white powder, I, m.p. 278-286°. The benzene phase of the filtrate was extracted with two 200 ml. portions of distilled water, dried, and evaporated at reduced pressure, giving a second crop of I, 1.0 g., m.p. 264-282°. Sublimation of a 2.00 g. sample of I at 150°/0.2 mm. afforded 1.87 g. of a white powder, m.p. 277.4-280.6°. Analysis of the sublimate by thin-layer chromatography indicated that it consisted of a mixture of phenylmercuric bromide and chloride. No satisfactory bromine-chlorine analysis for I was obtained.



3. Conversion of Phenylmercuric Chloride to Phenylmercuric Bromide by Potassium Bromide in Acetone.- A solution of 15.7 g. (0.05 mole) of phenylmercuric chloride and 29.8 g. (0.25 mole) of potassium bromide in 250 ml. of acetone in a 500 ml. Morton flask, equipped with a reflux condenser, was stirred (high-speed stirring) for 6 hr. at 25 to 35°. After filtration, the residue was washed with three 250 ml. portions of distilled water and dried in vacuo at 55°, giving 15.0 g. (84% crude yield) of a cream-colored solid, I, m.p. 285-286°. A second crop of I, 2.8 g., m.p. 270-280°, was obtained by evaporation of the solvent at reduced pressure and subsequent washing and drying of the residue. Sublimation of a 1.00 g. sample of I at 150°/0.1 mm. afforded 0.95 g. of a white powder, m.p. 285.2-287.6°. Analysis of the sublimate by thin-layer chromatography indicated that it consisted solely of phenylmercuric bromide. The yield of phenylmercuric bromide was 95%.

4. Sodium Tribromoacetate.\*- To a solution of 94.0 g. (0.317 mole) of tribromoacetic acid (Aldrich Chemicals) in 50 ml. of distilled water was added with stirring 317 ml. of a 1.000 N sodium hydroxide solution, and the resulting solution was stirred for an additional 15 min. After evaporation of the solvent under reduced pressure, the residue was dried in vacuo over phosphorus pentoxide at room temperature, giving 95.7 g. (95%) of sodium

tribromoacetate.

\*Potassium trichloroacetate was prepared in the same manner from trichloroacetic acid (Mallinckrodt analytical reagent).<sup>29</sup>

C. Preparation of Phenyl(trihalomethyl)mercurials

1. Phenyl(bromodichloromethyl)mercury.- Potassium, 19.6 g. (0.5 g. atom), was heated at reflux in 450 ml. of anhydrous tert-butyl alcohol for 15 hr. After complete solution of the potassium, the excess tert-butyl alcohol was removed by azeotropic distillation with ca. 1.2 l. of n-heptane. The remaining volatiles were removed under vacuum at room temperature yielding potassium tert-butoxide as white flakes of the 1:1 alkoxide-alcohol adduct.<sup>5</sup>

To a suspension of 89.4 g. (0.25 mole) of phenylmercuric bromide in 164 g. (1.0 mole) of bromodichloromethane (Dow Chemical Co.) and 1.2 l. of anhydrous benzene in a 2 l. Morton flask was added, with high-speed stirring at 0°, the solid potassium tert-butoxide over a 30 min. period. The reaction mixture was stirred for an additional hour at 0°, then poured into 1.5 l. of distilled water and filtered. The residue was washed with 200 ml. of benzene and dried in vacuo at 55°, giving 21.7 g. of unreacted phenylmercuric bromide. The aqueous phase of the filtrate was extracted with two 150 ml. portions of benzene and the benzene phase extracted with three 250 ml. portions of

distilled water. The benzene phase, extracts, and washings were combined, dried, filtered, and evaporated at reduced pressure, giving 82.4 g. (75% crude yield) of phenyl(bromodichloromethyl)mercury, m.p. 92.0-98.0°. Recrystallization of the crude product from a 20% solution of chloroform in n-hexane afforded 66.5 g. (60%) of pure phenyl(bromodichloromethyl)mercury, m.p. 108.0-110.0° (dec.) [Lit.<sup>2</sup> m.p. 110-111° (dec.)]. A small amount of unreacted phenylmercuric bromide, 3.3 g., was separated from the product during recrystallization. The total recovery of phenylmercuric bromide was 28%.

2. Phenyl(chlorodibromomethyl)mercury.- Solid potassium tert-butoxide was prepared on a 0.5 mole scale as in the above reaction.

To a suspension of 89.4 g. (0.25 mole) of phenylmercuric bromide in 208 g. (1.0 mole) of chlorodibromomethane (Eastman white label) and 1.2 l. of anhydrous benzene in a 2 l. Morton flask was added, with high-speed stirring at 0°, the solid potassium tert-butoxide over a 15 min. period. The reaction mixture was stirred for an additional 1.5 hr. at 0°, then poured into 1.5 l. of distilled water and filtered. The reaction mixture was worked up in the same manner as the previous reaction, giving 10.7 g. (12% recovery) of phenylmercuric bromide and 94.9 g. (78%) of pure phenyl(chlorodibromomethyl)mercury, m.p. 107.4 -

109.6° (dec.) [Lit.<sup>2</sup> m.p. 110-111° (dec.)].

3. Phenyl(tribromomethyl)mercury.- (a) Haloform-tert-butoxide procedure.- Solid potassium tert-butoxide was prepared on a 1.0 mole scale as in the above reaction.

To a suspension of 178.8 g. (0.50 mole) of phenylmercuric bromide in 379 g. (1.5 moles) of bromoform (Eastman white label) and 1.8 l. of anhydrous benzene in a 3 l. Morton flask was added, with high-speed stirring at 0°, the solid potassium tert-butoxide over a 45 min. period. The reaction mixture was stirred for an additional 1.5 hr. at 0°, then poured into 1.5 l. of distilled water and filtered. The reaction mixture was worked up in the same manner as the previous reaction, giving 10.2 g. (5% recovery) of unreacted phenylmercuric bromide and 230.7 g. (87%) of pure phenyl(tribromomethyl)mercury, m.p. 117.0-118.0° (dec.) [Lit.<sup>23</sup> m.p. 119° (dec.)].

(b) Sodium trihaloacetate procedure.- A suspension of 31.3 g. (0.10 mole) of phenylmercuric chloride and 47.8 g. (0.15 mole) of sodium tribromoacetate in 500 ml. of anhydrous 1,2-dimethoxyethane in a 1 l. Morton flask, equipped with a reflux condenser, was stirred (high-speed stirring) for 3 hr. at 30 to 40°. The reaction mixture was poured into 1.5 l. of distilled water and filtered. The residue was dried in vacuo over phosphorus pentoxide at room temperature, giving 42.0 g. of a light brown

powder, I, m.p. 136.2-139.8°. Recrystallization of I from a 20% solution of methylene chloride in n-hexane afforded 3.6 g. (7%) of pure phenyl(tribromomethyl)mercury, m.p. 117.0-117.8° (dec.). During recrystallization, 32.4 g. of a mixture of phenylmercuric bromide and chloride, as indicated by thin-layer chromatography, was separated.

4. Phenyl(trichloromethyl)mercury.- A suspension of 31.3 g. (0.10 mole) of phenylmercuric chloride and 40.3 g. (0.20 mole) of potassium trichloroacetate in 500 ml. of anhydrous 1,2-dimethoxyethane in a 1 l. Morton flask, equipped with a reflux condenser, was heated at reflux for 1 hr. with high-speed stirring. After cooling, the reaction mixture was poured into 1.5 l. of distilled water and filtered. The reaction mixture was worked up in the same manner as the previous reaction, giving 24.7 g. (63%) of pure phenyl(trichloromethyl)mercury, m.p. 116.2-117.5° [Lit.<sup>2</sup> m.p. 116.5-118°]. The unreacted phenylmercuric chloride was lost in activated charcoal during recrystallization.

D. Reactions of Phenyl(trihalomethyl)mercurials with Olefins

1. Reaction of Sodium Tribromoacetate with Cyclohexene in the Presence of Phenylmercuric Bromide.- A suspension of 31.9 g. (0.10 mole) of sodium tribromoacetate and 35.8 g. (0.10 mole) of phenylmercuric bromide in 49.3 g. (0.60 mole) of redistilled

(b.p. 82.8-84.2°) cyclohexene (Eastman white label) and 500 ml. of anhydrous 1,2-dimethoxyethane in a 1 l. Morton flask, equipped with a reflux condenser, was heated at reflux for 4 hr. with high-speed stirring. After filtration of the cooled reaction mixture, the residue was washed with 250 ml. of distilled water and dried in vacuo at 55°, giving 26.6 g. (75% recovery) of phenylmercuric bromide. A second crop of phenylmercuric bromide, 7.6 g., was obtained by removal of most of the solvent and excess olefin by distillation at atmospheric pressure. The remaining solvent and excess olefin were removed by distillation at reduced pressure (50-100 mm.). Fractional distillation of the remaining volatiles gave 14.3 g. (56%) of pure 7,7-dibromobicyclo[4.1.0]-heptane, b.p. 77.2-78.6°/0.5 mm.,  $n^{25}_D$  1.5568 [Lit.<sup>9</sup> b.p. 100°/8 mm.,  $n^{22}_D$  1.5578]. The purity of the product was established by vapor-phase chromatography (30% General Electric SE 30 Silicone Fluid on Chromosorb W, jacket temp. 160°, 15 p.s.i.); a small amount of bromoform also was detected in the solvent. The total recovery of phenylmercuric bromide was 96%.

2. Phenyl(trichloromethyl)mercury and Cyclohexene.- A solution of 79.2 g. (0.20 mole) of phenyl(trichloromethyl)mercury in 49.3 g. (0.60 mole) of redistilled cyclohexene and 150 ml. of anhydrous benzene in a 500 ml. three-neck flask, equipped with a reflux condenser, was heated at reflux with stirring for 48 hr.

After filtration of the cooled reaction mixture, the residue was dried in vacuo at 55°, giving 59.7 g. (95%) of phenylmercuric chloride, m.p. 257.3-258.4°. A second crop of phenylmercuric chloride, 1.3 g., m.p. 257.1-258.7°, was obtained by removal of most of the solvent and excess olefin by distillation at atmospheric pressure. The remaining volatiles were removed in a trap-to-trap distillation (-70 to 95°/0.2 mm.). Fractional distillation of the distillate gave 29.3 g. (89%) of pure 7,7-dichlorobicyclo[4.1.0]heptane, b.p. 73.5-75.0°/10 mm.,  $n^{25}_D$  1.5006 [Lit.<sup>9</sup> b.p. 78-79°/15 mm.,  $n^{23}_D$  1.5014]. The purity of the product was established by vapor-phase chromatography (30% General Electric SE 30 Silicone Fluid on Chromosorb W, jacket temp. 150°, 15 p.s.i.). The total yield of phenylmercuric chloride was 97%.

3. Phenyl(chlorodibromomethyl)mercury and Cyclohexene.- A solution of 48.5 g. (0.10 mole) of phenyl(chlorodibromomethyl)mercury in 24.6 g. (0.30 mole) of redistilled cyclohexene and 75 ml. of anhydrous benzene in a 200 ml. three-neck flask, equipped with a reflux condenser, was heated at reflux with stirring for 3 hr., then cooled and filtered. The reaction mixture was worked up in the same manner as the previous reaction, giving 35.3 g. (99%) of phenylmercuric bromide, m.p. 285.2-286.8°, and 17.8 g. (85%) of pure 7-bromo-7-chlorobicyclo[4.1.0]heptane, b.p. 42.8-44.7°/0.6 mm.,

$n^{25}_D$  1.5287 [Lit.<sup>30</sup>  $n^{25}_D$  1.5293]. The purity of the product was established by vapor-phase chromatography (30% General Electric SE 30 Silicone Fluid on Chromosorb W, jacket temp. 150°, 15 p.s.i.).

4. Phenyl(bromodichloromethyl)mercury and Tetrachloroethylene.-

A solution of 44.1 g. (0.10 mole) of phenyl(bromodichloromethyl)-mercury in 166 g. (1.0 mole) of redistilled (b.p. 120.0-120.5°) tetrachloroethylene (Eastman white label) in a 300 ml. three-neck flask, equipped with a reflux condenser, was slowly heated to 90° with stirring. After 3 min., light grey flakes began to precipitate from solution; the temperature (90°) was maintained for 1 hr. The reaction mixture was cooled and filtered. The residue was washed with ca. 25 ml. of tetrachloroethylene and dried in vacuo at 55°, giving 33.4 g. (93%) of phenylmercuric bromide as grey flakes, m.p. 285.0-287.0°. A second crop of phenylmercuric bromide, 0.6 g., m.p. 284.3-286.2°, was obtained by removal of some of the excess olefin by distillation at reduced pressure (170-180 mm.). The filtrate was concentrated twice by distillation at reduced pressure (170-180 mm.), cooled to 0°, and filtered. The residue was washed with a total of ca. 11 ml. of tetrachloroethylene, giving 20.6 g. (83% crude yield) of a white crystalline solid, I, m.p. 100-104°. Sublimation of I at 40°/0.1 mm. afforded 18.3 g. (74%) of pure hexachlorocyclopropane, m.p. 103.0-103.5° [Lit.<sup>15</sup> m.p. 104.0-104.5°]. A mixed melting



point of I with an authentic sample of hexachlorocyclopropane, supplied by Professor W. R. Moore<sup>15</sup> (M.I.T.), yielded no depression. Vapor-phase chromatographic analysis of the distillate indicated the presence of trace amounts (< 1%) of two high-boiling side-products. The total yield of phenylmercuric bromide was 95%.

Anal. Calcd. for  $C_3Cl_6$ : C, 14.49; Cl, 85.51. Found: C, 14.66; Cl, 85.21.

$\nu$  max (10% in carbon disulfide): 844(s), 903(m), 933(w),  $cm^{-1}$ .  
Comparison with an authentic sample:<sup>15</sup> 850(s), 905(m), 930(w),  $cm^{-1}$ .

5. Phenyl(trichloromethyl)mercury and Tetrachloroethylene.- A solution of 39.6 g. (0.10 mole) of phenyl(trichloromethyl)mercury in 166 g. (1.0 mole) of redistilled tetrachloroethylene in a 300 ml. three-neck flask, equipped with a reflux condenser, was slowly heated to 90° with stirring. After 50 min., white flakes began to precipitate from solution; the temperature (90°) was maintained for 48 hr. The reaction mixture was cooled and filtered. It was then worked up in the same manner as the previous reaction, giving 28.9 g. (92%) of phenylmercuric chloride, m.p. 255.8-257.9°. Sublimation of the crude product at 40°/0.05 mm. afforded 18.4 g. (74%) of pure hexachlorocyclopropane, m.p. 102.8-104.1°. Trace amounts of metallic mercury were dispersed in the phenylmercuric chloride; vapor-phase chromatographic analysis of the distillate indicated the presence of trace amounts (< 1%) of two high-boiling side-products.

6. Phenyl(chlorodibromomethyl)mercury and Tetrachloroethylene.- A solution of 48.5 g. (0.10 mole) of phenyl(chlorodibromomethyl)mercury in 180 g. (1.1 moles) of redistilled tetrachloroethylene in a 300 ml. three-neck flask, equipped with a reflux condenser, was slowly heated to 80° with stirring. After 1 min., light grey flakes began to precipitate from solution; the temperature (80°) was maintained for 1 hr. The reaction mixture was cooled and filtered. It was then worked up in the same manner as the previous reaction, giving 33.0 g. (92%) of phenylmercuric bromide, m.p. 284.0-286.5°. Sublimation of the crude product at 40°/0.3 mm. afforded 14.1 g. (48%) of pure bromopentachlorocyclopropane, m.p. 106.4-107.6°. Vapor-phase chromatographic analysis of the distillate indicated the presence of trace amounts (< 1%) of eleven high-boiling side-products.

Anal. Calcd. for C<sub>3</sub>BrCl<sub>5</sub>: C, 12.29; Br, 27.26; Cl, 60.45; mol. wt. 293. Found: C, 12.18; Br, 27.43; Cl, 60.20; mol. wt.<sup>31</sup> 290.

$\nu$  max (10% in carbon disulfide): 815(s), 833(s), 893(m), 908(m), 940(w), 956(shoulder), cm.<sup>-1</sup>.

Mass spectrum. Fragment, mass number (percentage): Cl, 35 (65.0); Cl, 37 (23.7); CCl, 47 (78.5); CCl, 49 (31.1); C<sub>2</sub>Cl, 59 (21.4); C<sub>2</sub>Cl, 61 (8.5); C<sub>3</sub>Cl, 71 (85.3); C<sub>3</sub>Cl, 73 (89.4); Br, 79 (16.4); Br, 81 (17.5); CCl<sub>2</sub>, 82 (27.5); CCl<sub>2</sub>, 84 (18.1); C<sub>2</sub>Cl<sub>2</sub>, 94 (23.7); C<sub>2</sub>Cl<sub>2</sub>, 96 (14.1); C<sub>3</sub>Cl<sub>2</sub>, 106 (36.2); C<sub>3</sub>Cl<sub>2</sub>, 108 (20.9); C<sub>3</sub>Cl<sub>2</sub>, 110

(5.6);  $\text{CCl}_3$ , 117 (32.8);  $\text{CCl}_3$ , 119 (24.3);  $\text{CCl}_3$ , 121 (11.3);  $\text{C}_3\text{Cl}_3$ , 141 (31.6);  $\text{C}_3\text{Cl}_3$ , 143 (28.2);  $\text{C}_3\text{Cl}_3$ , 145 (10.7);  $\text{C}_3\text{Cl}_5$ , 211 (45.2);  $\text{C}_3\text{Cl}_5$ , 213 (100);  $\text{C}_3\text{Cl}_5$ , 215 (42.4);  $\text{C}_3\text{Cl}_5$ , 217 (16.4);  $\text{C}_3\text{BrCl}_4$ , 255 (18.1);  $\text{C}_3\text{BrCl}_4$ , 257 (36.2);  $\text{C}_3\text{BrCl}_4$ , 259 (27.7);  $\text{C}_3\text{BrCl}_4$ , 261 (13.0).

7. Phenyl(tribromomethyl)mercury and Tetrachloroethylene.- A solution of 26.5 g. (0.05 mole) of phenyl(tribromomethyl)mercury in 166 g. (1.0 mole) of redistilled tetrachloroethylene in a 300 ml. three-neck flask, equipped with a reflux condenser, was slowly heated to  $80^\circ$  with stirring. After 4 min., light grey flakes began to precipitate from solution; the temperature ( $80^\circ$ ) was maintained for 2 hr. The reaction mixture was cooled and filtered. It was then worked up in the same manner as the previous reaction, giving 15.2 g. (81%) of phenylmercuric bromide, m.p.  $284.9-286.4^\circ$ . Sublimation of the crude product at  $25^\circ/0.05$  mm. afforded 4.7 g. (28%) of pure 1,1-dibromotetrachlorocyclopropane, m.p.  $115.0-116.0^\circ$  [Lit.<sup>17b</sup> m.p.  $115-116^\circ$ ]. Vapor-phase chromatographic analysis of the distillate indicated the presence of small amounts (ca. 1%) of three high-boiling side-products.

Anal. Calcd. for  $\text{C}_3\text{Br}_2\text{Cl}_4$ : C, 10.67; Br, 47.33; Cl, 42.00; mol. wt., 338. Found: C, 10.91; Br, 47.24; Cl, 42.24; mol. wt.,<sup>31</sup> 334.

$\nu$  max (10% in carbon disulfide): 781(s), 811(m), 877(w),

902(m), 919(m), 941(w),  $\text{cm.}^{-1}$ .

Mass spectrum. Fragment, mass number (percentage): Cl, 35 (60.0); Cl, 37 (25.8); CCl, 47 (60.8); CCl, 49 (27.5); C<sub>2</sub>Cl, 59 (19.1); C<sub>2</sub>Cl, 61 (10.8); C<sub>3</sub>Cl, 71 (100); C<sub>3</sub>Cl, 73 (54.1); Br, 79 (28.3); Br, 81 (25.0); CCl<sub>2</sub>, 82 (22.5); CBr, 91 (20.0); CBr, 93 (14.1); C<sub>2</sub>Cl<sub>2</sub>, 94 (20.0); C<sub>2</sub>Cl<sub>2</sub>, 96 (11.6); C<sub>3</sub>Cl<sub>2</sub>, 106 (46.7); C<sub>3</sub>Cl<sub>2</sub>, 108 (34.1); C<sub>3</sub>Cl<sub>2</sub>, 110 (20.0); CCl<sub>3</sub>, 117 (28.3); CCl<sub>3</sub>, 119 (26.7); CCl<sub>3</sub>, 121 (14.1); C<sub>3</sub>Cl<sub>3</sub>, 141 (39.1); C<sub>3</sub>Cl<sub>3</sub>, 143 (36.6); C<sub>3</sub>Cl<sub>3</sub>, 145 (18.3); C<sub>3</sub>Cl<sub>5</sub>, 211 (14.1); C<sub>3</sub>Cl<sub>5</sub>, 213 (19.1); C<sub>3</sub>Cl<sub>5</sub>, 215 (13.3); C<sub>3</sub>Cl<sub>5</sub>, 217 (6.7); C<sub>3</sub>BrCl<sub>4</sub>, 255 (33.3); C<sub>3</sub>BrCl<sub>4</sub>, 257 (68.3); C<sub>3</sub>BrCl<sub>4</sub>, 259 (61.7); C<sub>3</sub>BrCl<sub>4</sub>, 261 (26.7); C<sub>3</sub>BrCl<sub>4</sub>, 263 (8.3); C<sub>3</sub>Br<sub>2</sub>Cl<sub>3</sub>, 299 (15.0); C<sub>3</sub>Br<sub>2</sub>Cl<sub>3</sub>, 301 (27.5); C<sub>3</sub>Br<sub>2</sub>Cl<sub>3</sub>, 303 (25.0); C<sub>3</sub>Br<sub>2</sub>Cl<sub>3</sub>, 305 (20.0); C<sub>3</sub>Br<sub>2</sub>Cl<sub>3</sub>, 307 (6.7).

8. Phenyl(bromodichloromethyl)mercury and Acrylonitrile.- A solution of 22.0 g. (0.05 mole) of phenyl(bromodichloromethyl)mercury in 8.0 g. (0.15 mole) of redistilled (b.p. 76.9-77.1°) acrylonitrile (Eastman technical grade) and 75 ml. of anhydrous benzene in a 200 ml. three-neck flask, equipped with a reflux condenser, was heated at reflux with stirring for 2 hr. The reaction mixture was cooled and filtered. The residue, light brown powder, was washed with 50 ml. of benzene and dried in vacuo at 55°, giving 19.1 g. of phenylmercuric bromide, m.p. 275.0-286.5° (dec.), containing a small amount of polymer. Most of the solvent and excess olefin were removed in

a trap-to-trap distillation (-70 to 25°/0.5 mm.). The remaining volatiles were then removed in a trap-to-trap distillation (-70 to 65°/0.03 mm.) to give 45.0 g. of a clear, colorless liquid, F<sub>1</sub>. Fractional distillation of F<sub>1</sub> through a 3 in. unjacketed Vigreux column gave 5.3 g. (78%) of pure 1-cyano-2,2-dichlorocyclopropane, b.p. 78.0-79.0°/15 mm.,  $n_{25}^D$  1.4787. The purity of the product was established by vapor-phase chromatography (25% General Electric SE 30 Silicone Fluid on Chromosorb P, jacket temp. 140°, 15 p.s.i.):

Anal. Calcd. for C<sub>4</sub>H<sub>3</sub>Cl<sub>2</sub>N: C, 35.52; H, 2.21; Cl, 52.17; N, 10.30; mol. wt., 136. Found: C, 35.58; H, 2.44; Cl, 51.91; N, 10.10; mol. wt., <sup>32</sup> 135.

$\nu$  max (pure liquid): 587(w), 780(s), 879(m), 923(m), 1002(m), 1065(w), 1090(s), 1111(s), 1216(m), 1348(m), 1365(w), 1435(m), 2250 (s), 3045(m), 3100 (m), cm.<sup>-1</sup>.

N.m.r. spectrum (70 mg. in 200  $\mu$ l. of CCl<sub>4</sub>): 2.25 p.p.m., multiplet (3H).

9. Phenyl(bromodichloromethyl)mercury and Allyl Bromide.- A solution of 13.2 g. (0.03 mole) of phenyl(bromodichloromethyl)mercury in 10.9 g. (0.09 mole) of redistilled (b.p. 70.0-70.5°) allyl bromide (Eastman white label) and 50 ml. of anhydrous benzene in a 200 ml. three-neck flask, equipped with a reflux condenser, was heated at reflux with stirring for 2 hr. The reaction mixture was cooled and filtered. It was then worked up in the same manner as the

previous reaction, giving 10.3 g. (96%) of phenylmercuric bromide, m.p. 284.5-286.0°, and 4.7 g. (76%) of pure 1-(bromomethyl)-2,2-dichlorocyclopropane, b.p. 77.0-78.0°/23 mm.,  $n_D^{25}$  1.5150. The purity of the product was established by vapor-phase chromatography (25% General Electric SE 30 Silicone Fluid on Chromosorb P, jacket temp. 115°, 15 p.s.i.); trace amounts (< 1 to 2%) of eight high-boiling side-products were also detected in the reaction mixture.

Anal. Calcd. for  $C_4H_5BrCl_2$ : C, 23.56; H, 2.47; Br, 39.19; Cl, 34.78. Found: C, 23.62; H, 2.57; Br, 38.93; Cl, 35.03.

$\nu$  max (pure liquid): 620(m), 645(m), 750(s), 762(m), 806(m), 838(w), 855(m), 914(w), 944(m), 1020(m), 1085(w), 1116(s), 1195(m), 1218(s), 1234 (m), 1370(m), 1440(s), 2960(w), 3040(w), 3085(w),  $cm^{-1}$ .

N.m.r. spectrum (70 mg. in 200  $\mu$ l. of  $CCl_4$ ): 3.5 p.p.m., quartet (2H); 1.9 p.p.m., multiplet (2H); 1.3 p.p.m., triplet (1H).

10. Phenyl(bromodichloromethyl)mercury and Mesityl Oxide.- A solution of 4.41 g. (0.01 mole) of phenyl(bromodichloromethyl)mercury in 2.94 g. (0.03 mole) of redistilled (b.p. 129.0-129.5°) mesityl oxide (Eastman white label) and 25 ml. of anhydrous benzene in a 100 ml. three-neck flask, equipped with a reflux condenser, was heated at 80° with stirring for 2 hr., cooled, and filtered. The residue was washed with ca. 25 ml. of benzene and dried in vacuo at 55°, giving 3.44 g. (96%) of phenylmercuric bromide, m.p. 284.5-286.0°. The volatiles were then removed in a trap-to-trap

distillation (-70 to 60°/0.05 mm.) to give 55.8 g. of a clear, colorless liquid. Vapor-phase chromatographic analysis of the distillate indicated the presence of one product, identified by its n.m.r. spectrum as 1-acetyl-2,2-dichloro-3,3-dimethylcyclopropane,  $n_D^{25}$  1.4784. The yield of the volatile product, as determined by vapor-phase chromatography (25% General Electric SE 30 Silicone Fluid on Chromosorb P, jacket temp. 120°, 20 p.s.i.), using 7,7-dichlorobicyclo[4.1.0]heptane as an internal standard, was 83%. The product decomposed slowly under the conditions stated above. Thus, the 2,4-dinitrophenylhydrazone of the product, m.p. 155.0-156.0°, was prepared from the material obtained by preparative vapor-phase chromatography (jacket temp. 100°, 20 p.s.i.) by direct trapping in the 2,4-dinitrophenylhydrazine solution and subsequently recrystallized from ethyl alcohol.

Anal. Calcd. for  $C_{13}H_{14}Cl_2N_4O_4$ : C, 43.23; H, 3.91; Cl, 19.63; N, 15.51. Found: C, 43.21; H, 3.99; Cl, 19.70; N, 15.51.

1-acetyl-2,2-dichloro-3,3-dimethylcyclopropane:  $\nu$  max (6% in chloroform): 600(m), 830(m), 846(m), 900(m), 970(s), 1003(w), 1037(m), 1091(m), 1112(m), 1170(s), 1203(s), 1380(s), 1460(m), 1720(s), 2870(w), 2940(m), 2960(m), 3005(m), 3400(w),  $cm^{-1}$ .

N.m.r. spectrum (70 mg. in 200  $\mu$ l. of  $CCl_4$ ): 2.25 p.p.m., singlet (3H); 2.20 p.p.m., multiplet (1H); 1.42 p.p.m., doublet,  $J = 1.9$  c.p.s. (6H).

11. Phenyl(bromodichloromethyl)mercury and 2,5-Dihydrofuran.- A solution of 4.41 g. (0.01 mole) of phenyl(bromodichloromethyl)mercury in 2.10 g. (0.03 mole) of redistilled (b.p. 67.1-67.4°) 2,5-dihydrofuran (Antara Chemicals) and 25 ml. of anhydrous benzene in a 100 ml. three-neck flask, equipped with a reflux condenser, was heated at 80° with stirring for 1 hr., cooled, and filtered. The residue was washed with ca. 5 ml. of benzene and dried in vacuo at 55°, giving 3.50 g. (98%) of phenylmercuric bromide, m.p. 285.0-286.5°. The volatiles were then removed in a trap-to-trap distillation (-70 to 50°/0.05 mm.) to give 30.3 g. of a clear colorless liquid. Vapor-phase chromatographic analysis of the distillate indicated the presence of two products, identified by their n.m.r. spectra as 2-(dichloromethyl)-2,5-dihydrofuran, 1,  $n^{25D}$  1.4888 [Lit.<sup>20</sup>  $n^{19D}$  1.4933], and 3-oxa-6,6-dichlorobicyclo[3.1.0]hexane, 2,  $n^{25D}$  1.4957 [Lit.<sup>20</sup>  $n^{19D}$  1.4980]. The yields of 1 and 2, as determined by vapor-phase chromatography (25% General Electric SE 30 Silicone Fluid on Chromosorb P, jacket temp. 115°, 15 p.s.i.) using hexachloroethane as an internal standard, were 51.9 and 43.9%, respectively. (Ratio of 1 to 2 = 1.18 to 1.)

Anal. Calcd. for  $C_5H_6Cl_2O$ : C, 39.25; H, 3.95; Cl, 46.34.  
Found [1]: C, 39.37; H, 4.07; Cl, 46.32. Found [2]: C, 39.33;  
H, 4.15; Cl, 46.10.

$\nu$  max [1] (pure liquid): 678(s), 702(s), 728(s), 751(s),



771(s), 824(s), 895(w), 907(w), 917(m), 977(w), 991(w), 1019(m), 1085(s), 1110(w), 1226(m), 1315(w), 1350(s), 1465(m), 1615(m), 2860(s), 2950(m), 3000(w), 3080(w),  $\text{cm.}^{-1}$   $\nu$  max [2] (pure liquid): 718(s), 795(s), 830(m), 895(s), 960(w), 984(w), 1027(s), 1069(s), 1090(s), 1185(s), 1208(m), 1279(s), 1319(s), 1340(s), 1345(s), 1465(m), 1475(m), 1975(w), 2700(w), 2865(s), 2920(s), 2955(s), 3055(m),  $\text{cm.}^{-1}$ .

N.m.r. spectrum [1] (70 mg. in 200  $\mu\text{l.}$  of  $\text{CCl}_4$ ): 6.25 p.p.m., multiplet (1H); 5.95 p.p.m., multiplet (1H); 5.67 p.p.m., doublet,  $J = 4.8$  c.p.s. (1H); 5.07 p.p.m., multiplet (1H); 4.70 p.p.m., multiplet (2H). N.m.r. spectrum [2] (70 mg. in 200  $\mu\text{l.}$  of  $\text{CCl}_4$ ): 4.04 p.p.m., multiplet (2H); 2.45 p.p.m., multiplet (4H).

12. Sodium Trichloroacetate and 2,5-Dihydrofuran.- (a) in 1,2-Dimethoxyethane.- A solution of 1.85 g. (0.01 mole) of sodium trichloroacetate in 2.10 g. (0.03 mole) of redistilled 2,5-dihydrofuran and 25 ml. of anhydrous 1,2-dimethoxyethane in a 100 ml. three-neck flask, equipped with a reflux condenser, was heated at  $80^\circ$  with stirring for 5 hr., cooled, and filtered. The reaction mixture was worked up in the same manner as the previous reaction. The yields of 2-(dichloromethyl)-2,5-dihydrofuran, 1,  $n^{25\text{D}} 1.4891$ , and 3-oxa-6,6-dichlorobicyclo[3.1.0]hexane, 2,  $n^{25\text{D}} 1.4953$ , were 12.9 and 10.4, respectively. (Ratio of 1 and 2 = 1.23 to 1.). The infrared spectra of 1 and 2 were identical with those of the products of the above reaction.

(b) in Dioxane. - A solution of 1.85 g. (0.01 mole) of sodium trichloroacetate in 2.10 g. (0.03 mole) of redistilled 2,5-dihydrofuran and 25 ml. of anhydrous dioxane in a 100 ml. three-neck flask, equipped with a reflux condenser, was heated at reflux with stirring for 5 hr., cooled, and filtered. The reaction mixture was worked up in the same manner as the previous reaction. The yields of 1 and 2 were 28.6 and 22.0%, respectively. (Ratio of 1 to 2 = 1.30 to 1.).

13. Phenyl(bromodichloromethyl)mercury and 4-Vinylcyclohexene. - A solution of 4.41 g. (0.01 mole) of phenyl(bromodichloromethyl)mercury in 3.25 g. (0.03 mole) of redistilled (b.p. 128.5-128.9°) 4-vinylcyclohexene (Monomer Polymer Corp.) and 25 ml. of anhydrous benzene in a 100 ml. three-neck flask, equipped with a reflux condenser, was heated at 80° with stirring for 1 hr., cooled, and filtered. The residue was washed with ca. 15 ml. of benzene and dried in vacuo at 55°, giving 3.56 g. (99%) of phenylmercuric bromide, m.p. 285.0-287.0°. The volatiles were removed in a trap-to-trap distillation (-70 to 80°/0.03 mm.) to give 38.5 g. of a clear, colorless liquid. Vapor-phase chromatographic analysis of the distillate indicated the presence of two products, identified by their infrared and n.m.r. spectra as 3-vinyl-7,7-dichlorobicyclo-[4.1.0]heptane, 3,  $n_D^{25}$  1.5068, and 4-( $\beta,\beta$ -dichlorocyclopropyl)cyclohexene, 4,  $n_D^{25}$  1.4975. The yields of 3 and 4, as determined by

vapor-phase chromatography (25% Dow Corning Fluoropropyl Silicone Oil on Chromosorb P, jacket temp. 155°, 15 p.s.i.) using 7,7-dichlorobicyclo[4.1.0]heptane as an internal standard, were 82.5 and 9.4%, respectively. (Ratio of 3 to 4 = 8.77 to 1.). Vapor-phase chromatographic analysis of the reaction mixture (25% General Electric XF 1150 Silicone Fluid on Chromosorb P, jacket temp. 150°, 20 p.s.i.) showed four peaks, appearing as two sets of doublets.

Anal. Calcd. for  $C_9H_{12}Cl_2$ : C, 56.56; H, 6.41; Cl, 37.11.  
Found [3]: C, 56.66; H, 6.41; Cl, 37.28. Found [4]: C, 56.80; H, 6.44; Cl, 37.18.

$\nu$  max [3] (pure liquid): 607(w), 711(m), 786(w), 800(s), 844(w), 850(w), 860(w), 912(s), 988(s), 1026(w), 1070(w), 1115(w), 1179(w), 1225(m), 1345(m), 1385(w), 1420(m), 1450(s), 1460(m), 1645(s), 1825(m), 2850(s), 2940(s), 3010(shoulder), 3075(m),  $cm^{-1}$ .

$\nu$  max [4] (pure liquid): 555(w), 650(s), 723(w), 752(s), 793(w), 841(w), 872(m), 895(w), 910(m), 932(w), 957(m), 1008(m), 1042(s), 1109(s), 1123(m), 1139(m), 1190(w), 1211(m), 1227(m), 1248(w), 1271(w), 1292(w), 1340(w), 1390(m), 1440(s), 1450(m), 1605(shoulder), 1650(m), 2840(s), 2915(s), 3025(s),  $cm^{-1}$ .

N.m.r. spectrum [3] (60 mg. in 200  $\mu$ l. of  $CCl_4$ ): 5.67 p.p.m., multiplet (1H); 5.0 p.p.m., multiplet (1H); 4.8 p.p.m., multiplet (1H); 1.7 p.p.m., multiplet (9H). N.m.r. spectrum [4] (60 mg. in 200  $\mu$ l. of  $CCl_4$ ): 5.62 p.p.m., triplet (2H); 2.05 p.p.m., multiplet (6H); 1.5 p.p.m., multiplet (3H); 1.05 p.p.m., multiplet (1H).

14. Sodium Trichloroacetate and 4-Vinylcyclohexene.- A solution of 1.85 g. (0.01 mole) of sodium trichloroacetate in 3.25 g. (0.03 mole) of redistilled 4-vinylcyclohexene and 25 ml. of anhydrous 1,2-dimethoxyethane in a 100 ml. three-neck flask, equipped with a reflux condenser, was heated at 80° with stirring for 5 hr., cooled and filtered. The reaction mixture was worked up in the same manner as the previous reaction. The yields of 3-vinyl-7,7-dichlorobicyclo[4.1.0]heptane, 3,  $n^{25}_D$  1.5071, and 4-( $\beta,\beta$ -dichlorocyclopropyl)cyclohexene, 4,  $n^{25}_D$  1.4970, were 37.4 and 4.4%, respectively. (Ratio of 3 to 4 = 8.46 to 1.) The infrared spectra of 3 and 4 were identical with those of the products of the above reaction.

15. Phenyl(bromodichloromethyl)mercury and Tetrahydrofuran.- A solution of 4.41 g. (0.01 mole) of phenyl(bromodichloromethyl)mercury in 2.16 g. (0.03 mole) of redistilled (b.p. 65.0-65.6°) tetrahydrofuran (Fisher analytical reagent) and 25 ml. of anhydrous benzene in a 100 ml. three-neck flask, equipped with a reflux condenser, was heated at 80° with stirring for 4 hr., cooled, and filtered. The residue was washed with ca. 25 ml. of benzene and dried in vacuo at 55°, giving 3.30 g. (92%) of phenylmercuric bromide, m.p. 285.0-286.8°. The volatiles were removed in a trap-to-trap distillation (-70 to 45°/0.03 mm.) to give 56.2 g. of a clear, colorless liquid. Vapor-phase chromatographic analysis of the distillate indicated the presence of a small amount of tetrachloroethylene, identified by its

infrared spectrum, and of 2-(dichloromethyl)tetrahydrofuran, I,  $n_D^{25}$  1.4762 [Lit.<sup>20</sup>  $n_D^{21}$  1.4764], as identified by its n.m.r. spectrum. The yields of tetrachloroethylene and of I, as determined by vapor-phase chromatography (25% General Electric SE 30 Silicone Fluid on Chromosorb P, jacket temp. 120°, 20 p.s.i.) using hexachloroethane as an internal standard, were 2.5 and 67%, respectively.

Anal. Calcd. for  $C_5H_8Cl_2O$ : C, 38.74; H, 5.20; Cl, 45.74. Found: C, 38.96; H, 5.33; Cl, 45.56.

$\nu$  max (pure liquid): 660(w), 698(w), 769(s), 840(w), 870(w), 930(m), 1009(w), 1070(s), 1188(w), 1210(w), 1253(w), 1285(w), 1304(w), 1355(m), 1445(w), 1460(m), 1990(w), 2695(w), 2880(s), 2955(w), 2980(s),  $cm^{-1}$ .

N.m.r. spectrum (70 mg. in 200  $\mu$ l. of  $CCl_4$ ): 5.63 p.p.m., doublet,  $J = 4.9$  c.p.s. (1H); 4.2 p.p.m., multiplet (1H), 3.83 p.p.m., multiplet (2H); 2.0 p.p.m., multiplet (4H).

16. Phenyl(tribromomethyl)mercury and Trimethylvinylsilane.- A solution of 53.0 g. (0.10 mole) of phenyl(tribromomethyl)mercury in 30.1 g. (0.30 mole) of redistilled (b.p. 56.0-57.0°) trimethylvinylsilane and 150 ml. of anhydrous benzene in a 500 ml. three-neck flask, equipped with a reflux condenser, was heated at 60° with stirring. After 20 min., a white powder began to precipitate from solution; the temperature (60°) was maintained for 30 hr. The reaction mixture was cooled and filtered. The residue was washed with ca. 50 ml. of

benzene and dried in vacuo at 55°, giving 30.8 g. (86%) of phenylmercuric bromide, m.p. 286.0-287.0°. Most of the solvent and excess olefin were removed in a trap-to-trap distillation (-70 to 25°/0.1 mm.). The remaining volatiles were removed in a trap-to-trap distillation (-70 to 70°/0.1 mm.) to give 16.2 g. of a clear, colorless liquid, F<sub>1</sub>. Fractional distillation of F<sub>1</sub> through a 3 in. unjacketed Vigreux column gave 14.7 g. (54%) of ca. 98% pure 1,1-dibromo-2-trimethylsilylcyclopropane, b.p. 67.0-68.0°/6.5 mm., n<sup>25</sup><sub>D</sub> 1.5037 [Lit.<sup>23</sup> b.p. 84-86°/20 mm., n<sup>25</sup><sub>D</sub> 1.5032]. The purity of the product was established by vapor-phase chromatography (25% General Electric SE 30 Silicone Fluid on Chromosorb P, jacket temp. 115°, 15 p.s.i.); trace amounts (ca. < 1-2%) of three high-boiling side-products were also detected.

$\nu$  max (pure liquid): 657(s), 695(m), 757(s), 842(s), 905(s), 969(s), 1009(s), 1045(m), 1117(s), 1205(m), 1251(s), 1265(s), 1405(w), 1435(m), 2895(m), 2903(m), 2994(w), cm.<sup>-1</sup>.

N.m.r. spectrum (70 mg. in 200  $\mu$ l. of CCl<sub>4</sub>): 1.8 p.p.m., quartet (1H); 1.5 p.p.m., quartet (1H); 0.89 p.p.m., quartet (1H); 0.17 p.p.m., singlet (9H).

17. Phenyl(bromodichloromethyl)mercury and cis-Propenyltrimethylsilane.- A solution of 13.2 g. (0.03 mole) of phenyl(bromodichloromethyl)mercury in 10.3 g. (0.09 mole) of redistilled (b.p. 90.0-90.5°) cis-propenyltrimethylsilane (ca. 1% trans isomer) and 50 ml. of

anhydrous benzene in a 200 ml. three-neck flask, equipped with a reflux condenser, was slowly heated to reflux with stirring. When the bath temperature reached 55°, white flakes began to precipitate from solution; the reaction mixture was heated at reflux for 3 hr., cooled, and filtered. It was then worked up in the same manner as the previous reaction, giving 10.4 g. (97%) of phenylmercuric bromide, m.p. 284.8-286.0°, and 4.6 g. (78%) of pure cis-1-methyl-2-trimethylsilyl-3,3-dichlorocyclopropane, b.p. 89.0-90.0°/40 mm.,  $n_D^{25}$  1.4614. The purity (> 99%) of the product was established by vapor-phase chromatography (25% Dow Corning Silicone 710 Fluid on Chromosorb P, jacket temp. 175°, 15 p.s.i., retention time = 22.0 min.).

Anal. Calcd. for  $C_7H_{14}Cl_2Si$ : C, 42.63; H, 7.16; Cl, 35.96.

Found: C, 42.36; H, 7.36; Cl. . .

$\nu$  max (pure liquid): 602(w), 651(m), 694(m), 748(s), 762(m), 777(s), 801(s), 850(s), 917(s), 985(s), 1031(s), 1110(m), 1140(m), 1226(w), 1255(s), 1267(s), 1380(m), 1410(w), 1455(m), 1940(w), 2100(w), 2900(w), 2960(s), 3010(w),  $cm^{-1}$ .

N.m.r. spectrum (80 mg. in 200  $\mu$ l. of  $CCl_4$ ): 1.77 p.p.m., octet (1H); 1.35 p.p.m., doublet,  $J = 6.2$  c.p.s. (3H); 0.83 p.p.m., doublet,  $J = 12.4$  c.p.s. (1H); 0.19 p.p.m., singlet (9H).

18. Phenyl(bromodichloromethyl)mercury and trans-Propenyltrimethylsilane.- A solution of 13.2 g. (0.03 mole) of phenyl(bromodichloro-

methyl)mercury in 10.3 g. (0.09 mole) of redistilled (b.p. 84.5-85.5°) trans-propenyltrimethylsilane (ca. 1% cis isomer) and 50 ml. of anhydrous benzene in a 200 ml. three-neck flask, equipped with a reflux condenser, was slowly heated to reflux with stirring. When the bath temperature reached 55°, white flakes began to precipitate from solution; the reaction mixture was heated at reflux for 3 hr., cooled, and filtered. It was then worked up in the same manner as the previous reaction, giving 10.4 g. (97%) of phenylmercuric bromide, m.p. 284.2-285.6°, and 4.3 g. (73%) of pure trans-1-methyl-2-trimethylsilyl-3,3-dichlorocyclopropane, b.p. 86.5-88.0°/40 mm.,  $n_D^{25}$  1.4559. The purity (> 99%) of the product was established by vapor-phase chromatography (25% Dow Corning Silicone 710 Fluid on Chromosorb P, jacket temp. 175°, 15 p.s.i., retention time = 17.4 min.).

Anal. Calcd. for  $C_7H_{14}Cl_2Si$ : C, 42.63; H, 7.16; Cl, 35.96.

Found: C, 42.53; H, 7.00; Cl, 36.29.

$\nu$  max (pure liquid): 609(w), 694(m), 744(m), 758(w), 795(s), 844(s), 860(shoulder), 914(s), 976(s), 1027(w), 1042(s), 1141(m), 1202(w), 1252(s), 1310(w), 1380(m), 1385(w), 1410(w), 1455(m), 2870(w), 2895(w), 2930(w), 2955(s), 3000(w),  $cm^{-1}$ .

N.m.r. spectrum (80 mg. in 200  $\mu$ l. of  $CCl_4$ ): 1.36 p.p.m., multiplet (4H); 0.14 p.p.m., multiplet (10H).



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#### BIOGRAPHICAL NOTE

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