Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

HALOMETHYL–METAL COMPOUNDS
XLVII*. PHENYL(1,1-DICHLOROETHYL)MERCURY, A POTENTIAL CH_3CCl TRANSFER AGENT

DIETMAR SEYFERTH AND DAVID C. MUELLER**
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139 (U.S.A.)

(Received December 9th, 1970)

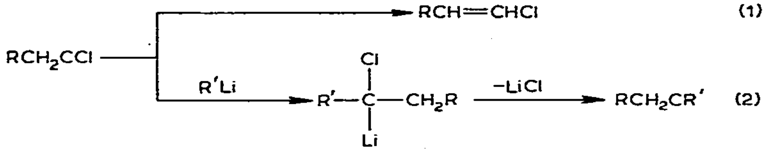
SUMMARY

Phenyl(1,1-dichloroethyl)mercury has been prepared via 1,1-dichloroethyllithium and evaluated as a potential CH_3CCl transfer agent. Although this mercurial reacted with triethylsilane to give $Et_3SiCHClCH_3$ (35%) and with allyltrimethylsilane to give 1-chloro-1-methyl-2-(trimethylsilylmethyl)cyclopropane (31%), its principal mode of reaction involved elimination of hydrogen chloride. The products resulting from this elimination were benzene (from HCl cleavage of Ph–Hg bonds) and redistributed mercury compounds containing the concomitantly formed $Hg{-}CCl{=}CH_2$ moiety. Possible reasons for this unexpected reaction are discussed.

INTRODUCTION

We have reported recently concerning our studies of the application of organomercury compounds of type $PhHgCX_2R$ [$R = Ph^2$, $CF_3{}^3$, $CR'(OR'')_2{}^4$] as RCX transfer agents. In view of the results obtained with $PhHgCX_2CF_3$ compounds, a study of analogous $PhHgCX_2CH_3$ systems was of interest, expecially since at the time this work was begun, no example of successful alkyl–C–X transfer to an olefin, to give a 1-alkyl-1-halocyclopropane, had been reported.

Although the chemistry of simple alkyl- and dialkylcarbenes is well understood[5], relatively little work has been devoted to alkylhalocarbenes. Alkylchlorocarbenes (or "carbenoids") have been generated by α-elimination of HCl (using an organolithium as base) from 1,1-dichloroalkanes or by the reaction of alkyllithium reagents with dichlorocarbene[6]. Such intermediates, once formed, either rearranged via hydrogen migration to give a 1-chloroalkene (eqn. 1) or reacted with RLi present to give a dialkylcarbene (eqn. 2). Methylchlorocarbene, generated by RLi attack on



---

* For Part XLVI see ref. 1.
** National Science Foundation Graduate Fellow, 1967–1970.

1,1-dichloroethane, was found to react exclusively in the sense of eqn. (2)[6]. However, methylchlorocarbene generated by photolysis of methylchlorodiazirine rearranged (eqn. 1) to give vinyl chloride as the only organic product[7,8]. Landgrebe and Mathis[9] attempted the addition of organomercury compound-derived alkylchlorocarbenes to olefins, but without success, rearrangement as in eqn. (1) being the only process observed (eqn. 3). Methylchlorocarbene was not included in their study although an

$$RR'CH{-}Hg{-}CCl_2CHRR'^{\star} \rightarrow RR'C{=}CHCl + RR'CH{-}HgCl \quad (3)$$

$$\begin{array}{ll} (a)\ R=R'=Me & (c)\ R=Pr;\ R'=H \\ (b)\ R=Et;\ R'=H & (d)\ R=Et;\ R'=Me \end{array}$$

appropriate precursor, $CH_3HgCCl_2CH_3$, had been prepared and had been reported in an accompanying publication[10]. In spite of these rather negative reports in the previous literature, we felt it would be worthwhile to prepare phenyl(1,1-dichloroethyl)mercury and to examine its potential application as a CH_3CCl transfer agent.

RESULTS AND DISCUSSION

Phenyl(1,1-dichloroethyl)mercury was prepared in good yield by the low temperature reaction of 1,1-dichloroethyllithium (a reagent which we had described in an earlier paper of this series[11]) with phenylmercuric chloride (eqn. 4). This mercurial, a white crystalline solid, appeared to be stable to air and moisture but decomposed slowly on storage at room temperature. It could be kept undecomposed indefinitely at 5°. Its reaction with anhydrous hydrogen chloride gave benzene and 1,1-dichloroethylmercuric chloride in high yield.

$$HCCl_2CH_3 \xrightarrow[THF/Me_2O]{BuLi/-100^\circ} LiCCl_2CH_3 \xrightarrow{PhHgCl} \underset{(67\%)}{PhHgCCl_2CH_3} \quad (4)$$

Thermal decomposition of phenyl(1,1-dichloroethyl)mercury occurred readily when it was heated in benzene at 80° for 53 h in the presence of an excess of cyclooctene. However, no 9-methyl-9-chlorobicyclo[6.1.0]nonane was formed in this reaction. Although phenylmercuric chloride, the expected product of α-elimination, was isolated in 23% yield, the major component of the nonvolatile reaction products was identified as 1-chlorovinylmercuric chloride, $CH_2{=}C(Cl)HgCl$. A minor contaminant, 1,1-dichloroethylmercuric chloride, also was present, and the combined yield of the latter two products was ca. 65%. When phenyl(1,1-dichloroethyl)mercury was decomposed by heating in chlorobenzene solution in the absence of an olefin, the same products were obtained: PhHgCl, 17%; $CH_2{=}C(Cl)HgCl$, 30%; CH_3CCl_2HgCl, 16%. Also present were benzene (67% based on starting mercurial) and two diorganomercury compounds, tentatively identified as $(CH_2{=}CCl)_2Hg$ and $CH_3CCl_2HgCCl{=}CH_2$ on the basis of their thin-layer chromatographic properties and their NMR spectra. The formation of these products can be rationalized in terms of processes

---

★ Prepared by CCl_2 insertion in the C–Hg bond of the respective $(RR'CH)_2Hg$ compounds, an interesting reaction but not one that appears to be of synthetic utility[10].

such as those shown in eqns. (5)–(12).

$$PhHgCCl_2CH_3 \rightarrow PhHgCCl{=}CH_2+HCl \quad (5)$$

$$PhHgCCl_2CH_3+HCl \rightarrow C_6H_6+ClHgCCl_2CH_3 \quad (6)$$

$$PhHgCCl{=}CH_2+HCl \rightarrow C_6H_6+ClHgCCl{=}CH_2 \quad (7)$$

$$PhHgCCl_2CH_3+ClHgCCl{=}CH_2 \rightarrow PhHgCl+CH_3CCl_2HgCCl{=}CH_2 \quad (8)$$

$$CH_3CCl_2HgCCl{=}CH_2 \rightarrow Hg(CCl{=}CH_2)_2+HCl \quad (9)$$

$$ClHgCCl_2CH_3 \rightarrow ClHgCCl{=}CH_2+HCl \quad (10)$$

$$2\ PhHgCCl_2CH_3 \rightarrow Ph_2Hg+Hg(CCl_2CH_3)_2 \quad (11)$$

$$(CH_3CCl_2)_2Hg \rightarrow CH_3CCl_2HgCCl{=}CH_2+HCl \quad (12)$$

The formation of benzene is a strong indication that hydrogen chloride elimination from a CH_3CCl_2–mercury compound has taken place, and the other reaction types shown above (substituent redistribution and electrophilic Hg–C cleavage) are known to occur readily in organomercury systems[12].

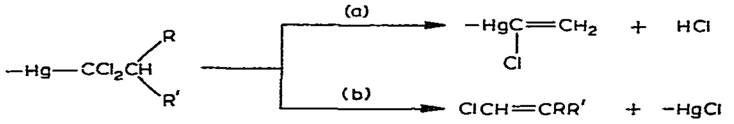
Some other experiments are pertinent to this discussion. Already mentioned has been the cleavage of $PhHgCCl_2CH_3$ by hydrogen chloride, and so the reactions in eqns. (6) and (7) most certainly will occur if HCl is generated. The HCl elimination reaction was examined more closely in the case of 1,1-dichloroethylmercuric chloride. When a solution of this compound in benzene was heated at reflux for 72 h, hydrogen chloride was detected in the vapor above the reaction mixture, but the starting mercury compound was recovered in 84% yield. However, when CH_3CCl_2HgCl was heated without solvent in a sublimator at 130–140°, hydrogen chloride was given off and 1-chlorovinylmercuric chloride (75–80% purity, as estimated by NMR) was obtained. These results suggest that the process in eqn. (10) [and, by inference, in eqn. (5)] can occur, but such a process would appear to be reversible, the equilibrium being driven to the right when the hydrogen chloride is efficiently removed from the system. This premise was tested by heating a chlorobenzene solution containing equimolar amounts of 1,1-dichloroethylmercuric chloride and diphenylmercury at 85–95°, the latter having been added as an HCl scavenger. The yield of benzene obtained in this reaction showed that at least 49% of the 1,1-dichloroethyl groups charged had eliminated HCl. The yield of phenylmercuric chloride was 35% in excess of that expected, an observation which is explicable in terms of substituent exchange reactions of the type shown in eqn. (13).

$$RHgCl+Ph_2Hg \rightarrow PhHgCl+PhHgR \quad (13)$$

$$R = CH_3CCl_2 \text{ and } CH_2{=}C(Cl){-}$$

The results described above are in contrast ot the work of Landgrebe and Mathis[9] [*i.e.*, eqn. (3)] who did not note hydrogen chloride elimination in analogous systems. However, the compounds they investigated did not contain phenyl–mercury linkages which would scavenge HCl much more effectively than alkyl–mercury bonds. To test the effect of this variable, isopropyl(α,α-dichloroisobutyl)mercury[10] was decomposed in solution, in the presence and in the absence of added diphenylmercury. When diphenylmercury was not present, the results of Landgrebe and Mathis were confirmed: isopropylmercuric chloride and 1-chloro-2-methylpropene were formed in nearly quantitative yield, 99% and 86%, respectively. Thus under these conditions only the α-elimination products are obtained. In the presence of diphenylmercury, however, the course of the reaction was altered markedly. Isopropylmercuric chloride and 1-chloro-2-methylpropene again were obtained, but the chloroolefin yield was only 50%. Benzene (21%, based on conversion of Ph_2Hg to $C_6H_6+PhHgCl$) and phenylmercuric chloride were produced, and so some HCl elimination must have taken place. The nonvolatile residue from the reaction mixture was examined by NMR spectroscopy. The presence of isopropylmercuric chloride was indicated, but additional signals, two overlapping singlets at δ 1.95 and 1.97 ppm, suggested the presence of the 1-chloro-2-methylpropenylmercury moiety, $Me_2C{=}C(Cl)Hg{-}$, with its nonequivalent methyl groups. (Note that the CH_3 signals of $Me_2C{=}CHCl$ appear as a broad singlet at 1.77 ppm.) It seems then that two reaction paths are available for thermal decomposition of 1,1-dichloroalkylmercury compounds: (*a*) HCl elimination which occurs readily when R and R′ in eqn. (14) are hydrogen and which occurs to some extent when R and R′ are methyl groups when an HCl scavenger is present; (*b*) α-elimination of Hg–Cl, which appears to be the exclusive process when the substituents R and R′ are a combination of H and alkyl in the absence of an effective HCl scavenger such as diphenylmercury. Path (*b*) also is the exclusive process occurring on thermolysis of phenyl(1,1-dichloro-2,2-dialkoxyethyl)mercury compounds[4] even in the presence of HCl-labile Ph–Hg bonds[*].

The apparent sensitivity of the reaction path (*a*) *vs.* (*b*) to substituents at the β-carbon atom provides the basis for a simple explanation of the above observations



(14)

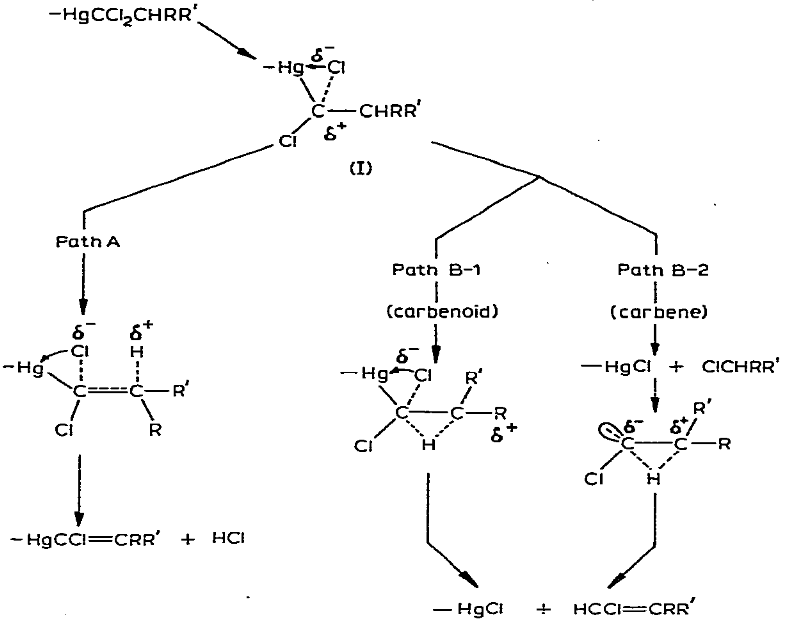
(Scheme 1). It is postulated that the α-elimination/hydrogen migration sequence proceeds by way of an initially polarized species, (I), which can rearrange, either directly (B-1), migration providing anchimeric assistance for the elimination, or through a free carbene intermediate (B-2), generated in a reversible, rate-determining step analogous to the generation of dichlorocarbene from $PhHgCCl_2Br$[13]. In either case, the partial positive charge at the α-carbon atom of (I) would be relieved, but a similar partial positive charge would be expected to develop at the β-carbon atom during the hydrogen migration[14]. The latter charge would be stabilized by alkyl or alkoxy substituents on the β carbon, and hence path (B) occurs readily when these substituents are present. In the case of $PhHgCCl_2CH_3$, a partial positive charge would not be stabilized effectively at the β-carbon atom and α-elimination/hydrogen migration are much slower. We suggest that hydrogen chloride elimination [path (A)] also proceeds *via* the species (I). Relief of the partial positive charge induced by

---

[*] An alternate explanation consistent with these observations and those of Landgrebe and Mathis is possible; namely that all $RHgCCl_2CHR'R''$ compounds decompose primarily via HCl elimination to give $RHgCCl{=}CR'R''$. The formation of the observed pyrolysis products, RHgCl and $CHCl{=}CR'R''$, then would result from HCl cleavage of the $Hg{-}CCl{=}CR'R''$ bond. When diphenylmercury is added to such a system, the Ph–Hg bond, of course, would compete for the HCl formed; benzene also would be formed and some $Hg{-}CCl{=}CR'R''$ moieties would remain. However, we prefer the explanation given above.

mercury at the α-carbon atom would be accomplished by a process analogous to hyperconjugation as outlined in Scheme 1.

Although cyclooctene has served very generally as a carbene "trap", we felt that the decomposition of phenyl(1,1-dichloroethyl)mercury in the presence of some other substrates which are known to be particularly effective reactants for divalent carbon transfer reagents (carbenes or carbenoids) might be worth investigating. Therefore the reactions of this mercurial with triethylsilane and allyltrimethylsilane were studied.

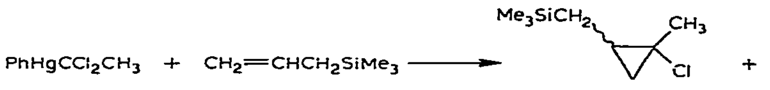


Reaction of phenyl(1,1-dichloroethyl)mercury with an excess of triethylsilane in the absence of solvent at 80–85° for 72 h gave the expected insertion product in 35% yield, together with products resulting from the reduction of phenylmercuric chloride by the excess of silicon hydride (eqns. 15 and 16). When the reaction was carried out in benzene solvent using a smaller excess of Et_3SiH, the Si–H insertion product yield was only 12% and products stemming from HCl elimination from the starting mercurial also were present.

$$PhHgCCl_2CH_3 + Et_3SiH \rightarrow Et_3SiCHClCH_3 + PhHgCl \qquad (15)$$

$$PhHgCl + Et_3SiH \rightarrow Et_3SiCl + Hg + C_6H_6 \qquad (16)$$

CH_3CCl transfer from phenyl(1,1-dichloroethyl)mercury to allyltrimethylsilane also was observed. A reaction carried out in carbon tetrachloride solution (so that if benzene was formed, it could be detected) at 80–85° for 69 h gave a mixture of both isomers of 1-chloro-1-methyl-2-(trimethyl-



(17)

silylmethyl)cyclopropane in about 31% yield (eqn. 17). Phenylmercuric chloride was isolated in 43% yield and benzene was present in 24% yield. The presence of benzene indicates that some HCl elimination had taken place. In another experiment infrared spectroscopy indicated the presence of a $CH_2=C(Cl)$–mercury compound.

Among the known and synthetically useful reactions of phenyl(halomethyl)-mercury compounds are "one-pot" Wittig reactions in which the mercurial, triphenylphosphine and an aldehyde or a ketone are heated in a solvent to give a haloolefin, triphenylphosphine oxide and phenylmercuric halide[3,15]. When such a reaction was attempted with $PhHgCCl_2CH_3$ using benzaldehyde as the carbonyl compound, only benzene and a solid, $(Ph_3P)_2HgCl_2$, were isolated. When the reaction between the mercurial and triphenylphosphine was carried out in the absence of benzaldehyde, the same products were observed. The brown oil obtained after evaporation of the volatiles from the filtered reaction mixture could not be distilled. When distillation was attempted, a solid sublimed which was identified as $Hg(CCl=CH_2)_2$. The formation of the latter can be rationalized in terms of the reaction sequence given by eqns. (5), (7) and (18). In support of eqn. (18), it is known that the action of triphenyl-

$$2\ ClHgCCl=CH_2 + 2\ Ph_3P \rightarrow Hg(CCl=CH_2)_2 + (Ph_3P)_2HgCl_2 \qquad (18)$$

phosphine on trichlorovinylmercuric chloride gives bis(trichlorovinyl)mercury and $(Ph_3P)_2HgCl_2$[16].

CONCLUSIONS

This study has shown that phenyl(1,1-dichloroethyl)mercury is capable of adding CH_3CCl to the C=C bond of allyltrimethylsilane and inserting CH_3CCl into the Si–H bond of triethylsilane, reactions characteristic of phenyl(halomethyl)-mercurials. However, the general applicability of such reactions remains to be investigated. It is clear, however, that the use of phenyl(1,1-dichloroethyl)mercury as a CH_3CCl transfer agent is complicated by and most likely will be severely limited by (*cf.* the case of the reaction with cyclooctene) the other thermolytic reaction it can undergo, hydrogen chloride elimination to give an α-chlorovinylmercury compound. This alternative method of decomposition is doubly troublesome when CH_3CCl transfer is being sought since the HCl generated can destroy starting material by cleavage of its Ph–Hg linkage. A rationalization of the two modes of $PhHgCCl_2CH_3$ reaction has been presented, but this is by no means proven. We hope that further work in these Laboratories will make available more useful and generally applicable organometal-based CH_3CCl transfer systems.

Very recently, it has been reported that the CH_3CCl generated by methylchlorodiazirine photolysis can be intercepted in part (before hydrogen migration to give vinyl chloride is complete) when olefins are present in the reaction mixture[17]. However, in only one example, that of isobutene, was a yield of cyclopropane given, and this was estimated to be 5–10%. In view of the low yield reported, this procedure does not appear to have much significance in terms of synthetic applications. Another reaction described only very recently is the thermolysis at 235° of $CH_3CCl_2SiF_2Cl$, which very likely proceeds via α-elimination of SiF_2Cl_2, giving CH_3CCl which rearranges to vinyl chloride, the observed product[18].

EXPERIMENTAL

General comments

All reactions were carried out in flame-dried glassware under an atmosphere of prepurified nitrogen using rigorously dried solvents. Dimethyl ether, a gas, was dried by passing it through a drying tower of magnesium sulfate/calcium chloride and condensing it directly into the precalibrated reaction vessel. n-Butyllithium was obtained from the Foote Mineral Co. as a hexane solution which was standardized prior to use. Infrared spectra were recorded using a Perkin–Elmer Model 337, 237B or 257 grating infrared spectrophotometer, NMR spectra using either a Varian Associates A-60 or T-60 spectrometer. Chemical shifts are expressed in δ units, using either tetramethylsilane (TMS) (0.00 ppm) or chloroform (7.27 ppm) as internal standards.

Gas–liquid partition chromatography (GLC) was used routinely for yield determinations and for collection of analytical samples. Commercial stainless steel columns were employed with either an F&M Model 700, 720, or 5754 gas chromatograph. Several different columns were used: (A) 6 ft × 0.25 in 10% DC-200 silicone oil (5754); (B) 4 ft × 0.25 in 10% UC-W98 silicone rubber (5754); (C) 6 ft × 0.25 in 10% Carbowax 20M (5754); (D) 6 ft × 0.25 in 20% DC-200 silicone oil (700 or 720); (E) 6 ft × 0.25 in 20% UC-W98 silicone rubber (700); (F) 6 ft × 0.25 in 20% XE-60 silicone gum nitrile (700 or 720); (G) 12 ft × 0.25 in 20% Carbowax 20M (700); (H) 6 ft × 0.25 in 20% polyphenyl ether (700); (I) 6 ft × 0.25 in 20% Carbowax 20M (700); (J) 6 ft × 0.25 in 20% Apiezon L (5754); (K) 6 ft × 0.25 in 20% Apiezon L (720); and (L) 4 ft × 0.25 in 20% LAC 728 (700). All columns were packed on acid-washed, dimethylchlorosilane-treated Chromosorb W; a helium carrier gas flow rate of 40–60 ml/min was commonly employed. Internal standards were used in all yield analyses. Empirical response factors were determined separately using standard solutions.

Thin-layer chromatography (TLC) was carried out using Eastman silica gel TLC sheet, type K301-R. The sheet was developed using 20% benzene in cyclohexane. After it had been dried, the sheet was visualized in an iodine chamber followed by spraying with 10% sodium sulfide in 50% aq. ethanol.

Preparation of phenyl(1,1-dichloroethyl)mercury

In a 500-ml Morton flask equipped with a high-speed stirring device (Labline Catalog No. 1280), a pressure equalizing dropping funnel, and a Claisen adapter topped with a rubber septum and a nitrogen inlet tube was prepared a solution of 9.99 g (101 mmoles) of 1,1-dichloroethane (dried over $CaCl_2$ and distilled, b.p. 57–58°) and 35 ml of dimethyl ether in 100 ml of THF. To this solution, kept at $-105°$ to $-115°$ throughout, was added dropwise 63 ml of 1.60 *N* n-butyllithium in hexane (101 mmoles) over a 20 min period. After the mixture had been stirred for 2 h, 33.0 g (105 mmoles) of phenylmercuric chloride was added. Stirring was continued for 2 h at $-110°$. The reaction mixture was allowed to warm slowly to room temperature, at which point the volatiles were removed from the clear, dark solution under reduced pressure. The grey-white solid residue was extracted with two 400-ml portions of benzene. The combined benzene solutions were filtered and evaporated under reduced pressure, leaving a white powdery solid. Crystallization at 5° from 1500 ml of pentane afforded 15.6 g (41%) of the mercurial as short white needles, m.p. 88–90° (slow decompn. above 100°). A second crop was isolated from the concentrated mother liquor: 9.8 g (26%), m.p. 86–88°. A third crop was also obtained but was found to contain small amounts of impurity by infrared analysis: 6.2 g (16%), m.p. 73–76°. IR (KBr): 3057 m, 3040 m, 2967 w, 2950 w, 2907 w, 2838 w, 1941 w, 1882 sh, 1867 w, 1807 w, 1575 w, 1479 m, 1430 s, 1371 m, 1163 w, 1101 w, 1077 m, 1061 sh, 1051 vs, 1023 sh, 1012 vs, 996 m, 903 w, 730 vs, 722 vs, 693 vs, 618 vs, 450 sh, and 433 s cm^{-1}. NMR ($CDCl_3$): δ 2.38 [s, $J(^{199}Hg–H)$ 42.5 Hz, 3H, $HgCCl_2CH_3$] and 7.23 ppm (m, 5H, Ph).

A recrystallized sample, m.p. 76–79°, was obtained in a separate experiment. Although its crystalline form (amorphous) was decidedly different and its melting point was somewhat lower, an infrared spectrum showed it to be identical to the sample with m.p. 88–90° obtained above. (Found: C, 25.68; H, 2.21; Hg, 53.47. $C_8H_8Cl_2Hg$ calcd.: C, 25.58; H, 2.15; Hg, 53.40%.)

Reaction of phenyl(1,1-*dichloroethyl*)*mercury with anhydrous hydrogen chloride*

A solution of 5.65 g (15.0 mmoles) of the mercurial in 50 ml of chlorobenzene was placed in a 100-ml three-necked flask equipped with a magnetic stirring unit, a gas bubbler tube, and a gas exit tube. The flask was cooled in an ice bath and anhydrous hydrogen chloride (Matheson) was bubbled vigorously into the stirred mixture. A white precipitate formed very quickly and the ice bath was removed. After 30 min, the introduction of HCl was discontinued and the reaction mixture was stirred for 1 h at room temperature. Filtration afforded 3.63 g of white solid, m.p. 158° (dec.), which was recrystallized from 5/1 $CCl_4/CHCl_3$ in two portions to give 2.99 g of 1,1-dichloroethylmercuric chloride, long white needles, m.p. 162° (dec.). The filtrate was trap-to-trap distilled into a receiver at −78° (25°/0.10 mm), leaving 1.37 g of white solid residue. This residue, combined with the mother liquor from above, was used to crystallize an additional 0.96 g of product, m.p. 161° (dec.), for a total yield of 79%. A recrystallized sample, m.p. 163° (dec.), was characterized. NMR ($CDCl_3$): δ 2.52 ppm (s, CH_3CCl_2). IR (KBr): 2985 sh, 2970 w, 2922 w, 2855 w, 1432 m, 1368 m, 1261 w, 1094 s, 1057 s, 1029 s, 697 m-broad, 652 w, and 452 w cm^{-1}. (Found: C, 7.53; H, 0.91; Cl, 31.92. $C_2H_3Cl_3Hg$ calcd.: C, 7.19; H, 0.90; Cl, 31.85%.) 1,1-Dichloroethylmercuric chloride was found to give off fumes of HCl when melted in a small capillary.

Analysis of the trap-to-trap distillate from the cleavage reaction by GLC (Column C, 112°, toluene standard) indicated the formation of benzene in 88% yield.

Reaction of phenyl(1,1-*dichloroethyl*)*mercury with cyclooctene*

A solution of 7.513 g (20.0 mmoles) of the mercurial and 4.99 g (44.4 mmoles) of cyclooctene (distilled from sodium) in 20 ml of benzene was prepared in a 100-ml flask equipped with a magnetic stirring device and a condenser with a nitrogen inlet atop. The reaction mixture was stirred and heated in a 90–100° oil bath for 53 h. During this time the solution became dark and a grey-white solid precipitated. Examination of the reaction mixture by TLC showed only a faint trace of dialkylmercury compound(s) (possibly starting mercurial) and a very heavy concentration of products which spotted near the origin. Crude phenylmercuric chloride, m.p. 248–253° (1.46 g, 23%) was filtered. Trap-to-trap distillation of the filtrate into a receiver at −78° (30°/0.04 mm) left 4.77 g of dark solid residue. The distillate was examined by GLC (Column A, 80–180°) and was found to contain only trace amounts of products (<5%). The residue was sublimed in two stages: (*a*) 80° oil bath/0.04 mm, 1.24 g oily white solid; and (*b*) 85°/0.04 mm, 2.75 g white solid. Both portions had a strong noxious odor and were treated with due caution. The more volatile sublimate (*a*) was crystallized from chloroform/carbon tetrachloride to give white needles, m.p. 131–133°, which were identified as 1-chlorovinylmercuric chloride, $ClHgCCl=CH_2$. NMR ($CDCl_3$): δ 5.43 (d, *J* 2.1 Hz, 1H) and 6.02 ppm (d, *J* 2.1 Hz, 1H). An analytical sample was obtained by recrystallization from chloroform/carbon tetrachloride as platelets, m.p. 132–133°. IR ($CHCl_3$): 3010–2860 w (br), 1591 m (C=C), 1082 s, 1055 sh, and 903 vs ($=CH_2$) cm^{-1}. (Found: C, 8.14; H, 0.75. $C_2H_2Cl_2Hg$ calcd.: C, 8.07; H, 0.68. The less volatile sublimate (*b*) had m.p. 98–107° as obtained and was crystallized from 25 ml of chloroform to give 1.69 g of amorphous solid, m.p. 105–108°. The NMR spectrum of this material showed doublets attributable to 1-chlorovinylmercuric chloride and a sharp singlet at δ 2.55 ppm. Because TLC had shown that no dialkylmercury compounds were present in the sublimate, the δ 2.55 resonance was considered evidence for the presence of 1,1-dichloroethylmercuric chloride (see above). The ratio of the vinyl- to ethylmercuric chloride was greater than 3/1 (via NMR). The total weight of sublimates (3.99 g) represented a 64–67% yield of alkylmercuric halides based on the dichloroethyl groups in the starting mercurial.

Thermal decomposition of phenyl(1,1-*dichloroethyl*)*mercury without substrate*

A solution of 2.757 g (7.34 mmoles) of phenyl(1,1-dichloroethyl)mercury in 15 ml of chlorobenzene was prepared in a 50-ml flask equipped with a magnetic stirring apparatus and a condenser topped with a nitrogen inlet. The reaction mixture was stirred in an 87–95° oil bath for 48 h. At the end of this time the solution was allowed to cool and then was filtered from 0.380 g (17%) of crude phenylmercuric chloride (identified by IR). The reaction filtrate was trap-to-trap distilled (30°/0.04 mm) into a receiver at −78°, leaving 1.957 g of solid residue. GLC analysis of the distillate (Column C, 112°, toluene standard) showed that benzene, identified by means of its GLC retention time and NMR spectrum, had been formed in 67% yield. The distillation residue was crystallized from 250 ml of hexane in three crops: (*a*) 0.774 g, m.p. 89–94°; (*b*) 0.088 g, m.p. 92–93°, on cooling the mother liquor from (*a*) to −10°; and (*c*) 0.134 g, m.p. 108–110°, on concentrating and cooling the mother liquor from (*b*). NMR analyses (in $CDCl_3$) showed that each of the crops was a mixture of 1-chlorovinylmercuric chloride [δ 6.03 (d, 1 H, *J* 2 Hz) and 5.43 ppm (d, 1 H, *J* 2 Hz)] and 1,1-dichloroethylmercuric chloride [δ 2.50 ppm (s)]. The estimated yields (via NMR) were 30% and 16% respectively. Evaporation of the hexane mother liquor from (*c*) above left a light brown solid. An NMR spectrum of this material ($CDCl_3$) showed it to be a mixture of dialkylmercury compounds; doublets at δ 5.88, 5.83 (overlapping), and 5.33 ppm ($J \sim 1-2$ Hz, ratio ("5.83"+"5.88")/"5.33" = 1/1) and a singlet at δ 2.37 ppm were tentatively attributed to a mixture of bis(1-chlorovinyl)mercury and 1-chlorovinyl(1,1-dichloroethyl)mercury (vinyl/ethyl ratio 2.2/1). The mixture turned black on standing overnight.

Thermal decomposition of 1,1-*dichloroethylmercuric chloride*

(*a*). *In benzene.* A solution of 0.845 g (2.50 mmoles) of 1,1-dichloroethylmercuric chloride in 10 ml of benzene was prepared in a 50-ml flask equipped with a magnetic stirring unit and a condenser topped with a gas exit tube which led to a nitrogen bubbler.

The reaction mixture was heated for 3.0 days in an 85–95° oil bath. During this time moist neutral litmus was found to turn red (HCl fumes) when contacted with the vapors at the upper end of the condenser. However, on cooling, 0.707 g (84%) of the starting alkylmercuric halide, m.p. 163–164°, was recovered.

(*b*). *Without solvent.* A small sublimator containing 0.334 g (1.0 mmole) of 1,1-dichloroethylmercuric chloride was heated under nitrogen in a 130–140° oil bath for 2 h. On cooling, 0.93 g of white flakey solid was scraped from the probe and the sides of the apparatus leaving a dark tar at the bottom. NMR analysis showed the solid to be 75–80% pure 1-chlorovinylmercuric chloride contaminated with starting 1,1-dichloroethylmercuric chloride and a trace of an unidentified impurity characterized by a singlet at δ 1.53 ppm in its NMR spectrum.

Thermal decomposition of 1,1-*dichloroethylmercuric chloride with diphenylmercury*

A solution of 0.668 g (2.0 mmoles) of 1,1-dichloroethylmercuric chloride and 0.710 g (2.0 mmoles) of diphenylmercury in 10 ml of chlorobenzene was prepared in a 50-ml flask equipped with a magnetic stirring unit and a condenser topped with a nitrogen inlet tube. The solution was heated in an 85–95° oil bath for 48 h, allowed to cool, and then filtered from 0.835 g (2.66 mmoles) of phenylmercuric chloride, m.p. 254–257°. Trap-to-trap distillation of the filtrate into a receiver at −78° (25°/0.03 mm) gave a clear solution and 0.494 g of white solid residue. GLC analysis of the filtrate (Column C, 112°, toluene standard) showed the presence of benzene (0.97 mmoles) which was identified by its GLC retention time. An NMR spectrum of the distillation residue showed it to be a complex mixture of organomercury compounds. A singlet at δ 2.50 ppm was assigned to the starting ethylmercuric halide while doublets at δ 5.87, 5.82 and 5.35 ppm ($J \sim 1.5$ Hz, 2/13/15 ratio) and a singlet at δ 2.37 ppm were believed to be due to a trace of bis(1-chlorovinyl)mercury and a significant amount of 1-chlorovinyl(1,1-dichloroethyl)mercury. TLC confirmed the presence of both dialkylmercury compounds and alkylmercuric halides, but further attempts at separation proved unsuccessful.

Thermal decomposition of isopropyl(*α,α-dichloroisobutyl*)*mercury*

(*a*). *In benzene.* A solution of 1.68 g (4.55 mmoles) of isopropyl(α,α-dichloroisobutyl)mercury[10] in 10 ml of benzene was stirred for 50 h in a 75–85° oil bath under nitrogen. At the end of this time, TLC showed that the starting mercurial had decomposed completely. The cloudy reaction solution was trap-to-trap distilled into a receiver at −78° (25°/0.10 mm), leaving 1.27 g of white solid which was identified as crude isopropylmercuric chloride (99% yield), m.p. 87–89° on the basis of its NMR spectrum. A sample which was twice recrystallized from ethanol had m.p. 94–95° (lit.[9] 94–95°). NMR ($CDCl_3$): δ 1.50 (d, J 7 Hz, 6 H, CH_3) and 2.60 ppm (septet, J 7 Hz, 1 H, CH). The distillate was examined by GLC (Column C, 70°, toluene standard) and was found to contain a single major product which eluted before the solvent benzene. This product was identified as the expected[9] 1-chloro-2-methylpropene [see part (*b*)] and was found to be present in 86% yield.

(*b*). *With diphenylmercury in chlorobenzene.* Using the procedure outlined in part (*a*) above, 1.61 g (4.36 mmoles) of isopropyl-α,α-dichloroisobutylmercury and

1.55 g (4.36 mmoles) of diphenylmercury in 10 ml of chlorobenzene were stirred in an 80–85° oil bath for 40 h. At the end of this time the reaction mixture was allowed to cool and 0.166 g (0.53 mmoles, 12% based on starting diphenylmercury) of phenylmercuric chloride, m.p. 253–256° (residue), was filtered. The filtrate was again heated for 12 h; on cooling no additional precipitate was evident. Trap-to-trap distillation of the reaction solution (25°/0.04 mm) gave a clear mixture of volatiles which was examined by GLC (Column C, 70°, toluene standard). In addition to 1-chloro-2-methylpropene, found in 50% yield, the distillate also contained benzene in 21% yield. Product identification was based on GLC retention times and NMR spectra; authentic samples of both products were available. The distillation residue also was examined by NMR. In addition to the resonances observed for isopropylmercuric chloride in the preceding experiment, the spectrum (in $CDCl_3$) contained a multiplet in the δ 7.0–8.0 ppm region attributable to phenylmercury compounds, and a pair of overlapping singlets at δ 1.95 and 1.97 ppm. The latter were attributed to the nonequivalent methyl groups of 1-chloro-2-methylpropenylmercuric chloride or bis(1-chloro-2-methylpropenyl)mercury. An infrared spectrum (KBr) of the same mixture had a band of medium intensity at 1628 cm^{-1} (C=C), which supports this assignment.

Reaction of phenyl(1,1-*dichloroethyl*)*mercury with triethylsilane*

Into a 50-ml three-necked flask equipped in the usual way was placed 3.76 g (10.0 mmoles) of the mercurial and 7.3 g (63 mmoles) of triethylsilane (Peninsular ChemResearch, distilled from $LiAlH_4$) in 10 ml of benzene. The solution was heated at reflux (90°) for 69.5 h. At the end of this time a white solid and metallic mercury were filtered from the yellow solution. The solid was taken up in dimethylformamide (DMF), allowing the mechanical separation of 0.582 g (28%) of mercury. Evaporation of the DMF at reduced pressure left a white solid which was washed with 2/1 benzene/hexane to give 0.64 g (20%) of phenylmercuric chloride, m.p. 251–254°. The reaction filtrate was trap-to-trap distilled into a receiver at −78°, leaving 0.61 g of black tar. The major product was isolated by redistillation of the distillate (three components by GLC) using a short path apparatus. Material which was 70% pure, b.p. 77–78°/76 mm, was further purified by preparative GLC (Column D, 120°) and identified as triethylchlorosilane, n_D^{25} 1.4288 (lit.[19] n_D^{25} 1.4299), by comparison of its infrared spectrum and GLC retention time with those of an authentic sample. The less volatile products were isolated by preparative GLC (Column D, 185°). The first was identified as 1-chloroethyltriethylsilane, $n_D^{23.5}$ 1.4521 (lit.[20] n_D^{20} 1.4535). NMR (CCl_4): δ 0.37–1.28 (m, 15 H, Et_3Si), 1.52 (d, J 7.6 Hz, 3 H, $SiCClCH_3$), and 3.45 ppm (q, J 7.6 Hz, 1 H, SiCHCl). IR (film): 2950 vs, 2905 vs, 2870 vs, 2800 sh, 1455 s, 1438 sh, 1414 m, 1376 w, 1260 sh, 1236 m, 1169 w, 1070 sh, 1015 vs, 970 sh, 945 sh, 845 w, 833 w, 735 vs, and 773 s cm^{-1}. The last product was identified as hexaethyldisiloxane: $n_D^{23.5}$ 1.4331 (lit.[21] n_D^{25} 1.4323), infrared spectrum identical to that of an authentic sample. GLC analysis showed the following yields (Column A, 105–170°): 1-chloroethyltriethylsilane (dodecane standard), 18%; triethylchlorosilane (chlorobenzene standard), 4.39 mmoles; hexaethyldisiloxane (dodecane standard), 0.58 mmoles.

In a second experiment, 1.878 g (5.00 mmoles) of the mercurial and 10 ml of triethylsilane were heated in an 80–85° oil bath for 72 h. The reaction mixture was trap-to-trap distilled directly from the reaction vessel (100°/0.05 mm) and analyzed by GLC as before to obtain the following yields: 1-chloroethyltriethylsilane, 35%, and triethylchlorosilane, 1.39 mmoles. Benzene, identified by its GLC retention time, also was detected, being present in 34% yield based on starting mercurial (Column C, 70°, toluene standard). The solid which remained after the trap-to-trap distillation was extracted with benzene and washed onto a filter to obtain phenylmercuric chloride, m.p. 250–253°, with finely suspended particles of metallic mercury, 0.940 g total. The latter were separated (0.198 g, 20%) by dissolving the phenylmercuric chloride in dimethylformamide; thus the yield of phenylmercuric chloride was ca. 0.742 g (47%).

In a similar experiment, 3.76 g (10.0 mmoles) of phenyl(1,1-dichloroethyl)-mercury and 1.45 g (12.7 mmoles) of triethylsilane in 5.0 ml of benzene were heated 94.5 h in a 70–75° oil bath. Filtration of the cooled reaction mixture afforded 1.44 g (46%) of phenylmercuric chloride, m.p. 254–256°. Trap-to-trap distillation of the filtrate into a receiver at −78° (25°/0.04 mm) left a powdery solid residue. GLC analysis of the distillate showed the following yields: 1-chloroethyltriethylsilane, 12%, and triethylchlorosilane, 0.43 mmoles. Crystallization of the residue from carbon tetrachloride afforded 0.26 g of yellow solid, m.p. 134–136°. The NMR and IR spectra of this material showed it to be a mixture of phenylmercuric chloride and 1,1-dichloroethylmercuric chloride. The carbon tetrachloride mother liquor was evaporated, leaving a solid residue which was redissolved in hexane, filtered, and reevaporated to give 1.01 g of white solid, m.p. 68–72°. TLC showed that this material was primarily dialkylmercury compound(s) with only traces of alkylmercuric halide impurities. Its NMR spectrum consisted of vinylic doublets (J 1–2 Hz at 5.87 and 5.37 ppm and a methyl singlet at δ 2.35 ppm in a 1/1/3 ratio (impurities precluded a more accurate determination of the coupling constant); based on this spectrum the structure of the principal component most likely was 1-chlorovinyl(1,1-dichloroethyl)mercury. However, on standing in a sealed vial for a short time the solid darkened and further attempts at purification were unsuccessful.

Reaction of phenyl(1,1-dichloroethyl)mercury with allyltrimethylsilane

Into a 50 ml three-necked flask equipped in the usual way was placed 0.939 g (2.50 mmoles) of the mercurial and 1.56 g (13.7 mmoles) of allyltrimethylsilane in 10 ml of carbon tetrachloride. The resulting solution was heated at reflux for 69 h. Filtration of the cooled reaction solution afforded 0.338 g (43%) of phenylmercuric chloride, m.p. 256–258°. The filtrate was trap-to-trap distilled into a receiver at −78° (25°/0.04 mm), leaving a semiliquid residue. GLC analysis of the distillate on two columns (Column C, 70°; Column I, 110°; toluene standard) revealed the presence of five products: benzene, identified by retention time only, in 24% yield (Column C); a pair of trace products subsequently identified as trimethylchlorosilane and 1,1,1-trichloro-3-butene (*vide infra*); and the isomeric (*syn*- and *anti*-) 1-chloro-1-methyl-2-(trimethylsilylmethyl)cyclopropanes in ca. 31% yield (Column I). The cyclopropanes were isolated from the concentrated filtrate by preparative GLC (Column D, 120°) and were characterized: NMR [neat mixture (2/1 ratio), microcell, toluene standard]: δ 0.10 (s, 9 H, Me_3Si), 0.28–1.35 (m, $SiCH_2$, cyclopropyl H) and 1.55, 1.58 ppm [s (2), 3 H total, CH_3]. IR (film, mixed isomers): 3065 w, 2995 sh, 2950 s, 2923 sh, 2890 sh, 2797 sh, 1747 w, 1437 m, 1410 m, 1380 m, 1371 sh, 1296 sh, 1257 sh, 1247 vs, 1199 s, 1188 s, 1169 sh, 1157 sh, 1115 w, 1085 w, 1061 w, 1027 m, 1007 sh, 984 w, 950 w, 922 m, 888 sh, 860 vs (br), 796 w, 777 m, 758 m, and 695 s cm^{-1}. (Found: C, 54.55;

H, 9.76. $C_8H_{17}ClSi$ calcd.: C, 54.36; H, 9.69%.) The trap-to-trap distillation residue was heated at 100°/0.02 mm in a short path distillation apparatus to obtain ca. 0.3 to 0.5 g of additional liquid which was redistilled with b.p. 39–40°/0.03 mm. A GLC analysis (Column H, 100°) of the latter material gave indications that the compound was decomposing: two major peaks were evident in approximately equal proportion with the retention times of both being qualitatively short for the boiling point observed. A GLC-collected sample of the more volatile product was identified as trimethylchlorosilane on the basis of its NMR spectrum and its rapid reaction with moist air (evolution of HCl, litmus turns red). The less volatile product was also collected and was identified as 4,4,4-trichloro-1-butene, n_D^{22} 1.4658 (lit.[22] n_D^{20} 1.4664). NMR (microcell, neat, external standard): δ 3.72 (d, J 6.5 Hz, 2 H, CCl_3CH_2), and 5.42–6.68 ppm (m, 3 H, $CH{=}CH_2$). (Found: C, 30.15; H, 3.18. $C_4H_5Cl_3$ calcd.: C, 30.13; H, 3.16%.) The NMR spectrum of the 39–40°/0.03 mm distilled material was different from the NMR spectra of the GLC collected products, but was consistent with the structure expected for CCl_4 addition to allyltrimethylsilane: $Me_3SiCH^a_2$-$CH^bClCH^c_2CCl_3$. However, because of a large proportion of impurities (evidenced by GLC as well) it was not possible to assign specific resonances with any certainty. NMR (microcell, benzene standard): δ 0.02 (s, Me_3Si), 1.33 (d, J 7.5 Hz, (unsymmetric), H^a), 3.20, 3.12 [d (2), J 6.0 Hz, H^c] and 4.42 ppm (m, H^b).

In a separate experiment, 0.939 g (2.50 mmoles) of the mercurial and 1.39 g (12.2 mmoles) of allyltrimethylsilane in 10 ml of carbon tetrachloride were stirred at 80–90° for 108 h. After filtering 0.540 g (68% crude yield) of impure phenylmercuric chloride, m.p. 245–255° (residue), identified by IR, trap-to-trap distillation (30°/0.04 mm) gave a clear mixture of volatiles and a dry, grey solid residue. GLC analysis showed the presence of benzene in 40% yield, mixed cyclopropanes in 14% yield, and 0.57 mmole of 4,4,4-trichloro-1-butene. TLC indicated that the distillation residue contained mostly dialkylmercury compounds with only traces of alkylmercuric halides. An NMR spectrum ($CDCl_3$) of this residue showed doublets at δ 5.34 and 5.83 ppm (J 1–2 Hz) and a singlet at δ 2.35 ppm in an approximately 1/1/3 ratio. These signals were assigned tentatively to the vinyl and methyl protons of 1-chlorovinyl(1,1-dichloroethyl)mercury. Further attempts at purification proved to be unsuccessful.

Reaction of phenyl(1,1-dichloroethyl)mercury with triphenylphosphine

A solution of 1.88 g (5.00 mmoles) of phenyl(1,1-dichloroethyl)mercury and 1.31 g (5.00 mmoles) of triphenylphosphine (recrystallized from ethanol, m.p. 82–83°) in 20 ml of chlorobenzene was heated and shaken at 85° for 24 h in a 35 ml sealed tube. The cooled reaction mixture was filtered to give 0.975 g (49% based on triphenylphosphine) of bis(triphenylphosphine)mercuric chloride, m.p. 271–273° (lit.[16] 274–276°), identified by comparison of its infrared spectrum with that of an authentic sample. The filtrate was trap-to-trap distilled into a receiver at −78° (25°/0.04 mm), leaving a dark brown oily residue. GLC analysis of the distillate (Column C, 112°, toluene standards) showed the presence of 2.89 mmoles (58% based on starting mercurial) of benzene, identified by its GLC retention times on columns C and J. The distillation residue was heated with 30 ml of absolute ethanol and allowed to cool. Filtration afforded 0.852 g of white solid, m.p. 170–185°. This solid was recrystallized from chloroform to give 0.589 g of white crystals, m.p. 215–235°, which were identified as somewhat impure bis(triphenylphosphine)mercuric chloride by IR. TLC analysis of the ethanol extract showed that it contained mostly dialkylmercury compound(s) (R_f 0.5) with only a trace spot near the origin. The ethanol was evaporated at reduced pressure leaving 0.815 g of a brown oil. An NMR spectrum ($CDCl_3$) of this oil showed strong aromatic resonances, at δ 7.15–8.43 ppm (m), a pair of vinylic doublets at δ 5.93 and 5.47 ppm (J 5.5 Hz), and weak aliphatic multiplets at δ 3.47–4.00 and 0.92–2.17 ppm. Distillation of the oil was attempted using a short path apparatus at 0.03 mm. Heating slowly to 140° (oil bath temp) caused the sublimation of a white solid which condensed in the distillation head. After cooling, 0.212 g of white crystals were scraped from the apparatus. Recrystallization from pentane with a trace of chloroform gave fine white needles, m.p. 91–92°, which were identified as bis(1-chlorovinyl)mercury on the basis of the following analyses. NMR ($CDCl_3$): δ 5.87 and 5.30 ppm [d (2), J 1.2 Hz, 1/1 ratio, $C{=}CH_2$]. IR (KBr): 2985 w, 2922 w, 2852 w, 1580 s (C=C), 1358 w, 1262 w, 1059 m, 896 vs ($C{=}CH_2$ out-of-plane), 742 sh, 728 m, 714 m, and 479 m cm^{-1}. (Found: C, 14.33; H, 1.26. $C_4H_4Cl_2Hg$ calcd.: C, 14.85; H, 1.24%.) The purified material was found to be unstable over even short periods of time. A sample stored in a sealed vial at 5° turned yellow during a one week period. An NMR spectrum of the pot residue after the sublimation showed the absence of the vinylic doublets at δ 5.93 and 5.47 ppm.

ACKNOWLEDGEMENTS

The authors are grateful to the U.S. Air Force Office of Scientific Research (SRC)-OAR for generous support of this work (Grant AFOSR-71-1970).

REFERENCES

1 D. Seyferth, R. Damrauer, H. Shih, W. Tronich, W. E. Smith and J. Y.-P. Mui, in press.
2 D. Seyferth and D. C. Mueller, *J. Organometal. Chem.*, 25 (1970) 293.
3 D. Seyferth and D. C. Mueller, in press.
4 D. C. Mueller and D. Seyferth, *J. Amer. Chem. Soc.*, 91 (1969) 1754.
5 W. Kirmse, *Carbene Chemistry*, Academic Press, New York, 1964, Chapter 3.
6 W. Kirmse and B. von Bülow, *Chem. Ber.*, 96 (1963) 3316, 3323.
7 W. H. Graham, *J. Amer. Chem. Soc.*, 87 (1965) 4396.
8 M. R. Bridge, H. M. Frey and M. T. H. Liu, *J. Chem. Soc. A*, (1969) 91.
9 J. A. Landgrebe and R. D. Mathis, *J. Amer. Chem. Soc.*, 88 (1966) 3552.
10 J. A. Landgrebe and R. D. Mathis, *J. Amer. Chem. Soc.*, 88 (1966) 3545.
11 D. Seyferth and F. M. Armbrecht Jr., *J. Organometal. Chem.*, 16 (1969) 249.
12 F. R. Jensen and B. Rickborn, *Electrophilic Substitution of Organomercurials*, McGraw-Hill, New York, 1968, Chapters 3, 5–7.
13 D. Seyferth, J. Y.-P. Mui and J. M. Burlitch, *J. Amer. Chem. Soc.*, 89 (1967) 4953.
14 W. Kirmse and M. Buschhoff, *Chem. Ber.*, 100 (1967) 1491.
15 D. Seyferth, J. K. Heeren, G. Singh, S. O. Grim and W. B. Hughes, *J. Organometal. Chem.*, 5 (1966) 267.
16 D. Seyferth and R. H. Towe, *Inorg. Chem.*, 1 (1962) 185.
17 R. A. Moss and A. Mamantov, *J. Amer. Chem. Soc.*, 92 (1970) 6951.
18 W. I. Bevan, R. N. Haszeldine, J. Middleton and A. E. Tipping, *J. Organometal. Chem.*, 23 (1970) C17.
19 B. C. Curran, R. M. Witucki and P. M. McCusker, *J. Amer. Chem. Soc.*, 72 (1950) 4471.
20 V. A. Ponomarenko and V. F. Mironov, *Dokl. Akad. Nauk SSSR*, 94 (1954) 485.
21 C. Tamborski and H. W. Post, *J. Org. Chem.*, 17 (1952) 1400.
22 J. Villieras, *Bull. Soc. Chim. Fr.*, (1967) 1520.