Halomethyl-Metal Compounds. XXIV. Rearrangements of Mercurial-Derived (Dialkoxymethyl)chlorocarbenes[1]

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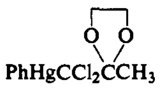
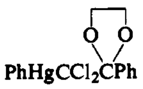
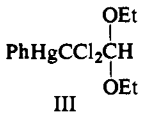
Abstract: The organomercurials, $PhHgCCl_2R$ [R = $-C(R')-O-CH_2-CH_2-O$ (R′ = Me (I), Ph (II), H (IV)) and $-CH(OET)_2$ (III)] have been prepared by the low-temperature organolithium route using the respective RLi reagents. Thermolysis of these mercurials has been studied. In all cases the expected carbene was generated *via* α elimination of phenylmercuric chloride, but the carbenes rearranged to olefinic products. With I alkoxy migration gave 2-chloro-3-methyl-1,4-dioxene. With II phenyl migration giving phenylchloroketene ethylene acetal occurred. III decomposed to give products derivable from $(EtO)_2C{=}CHCl$ (H migration), as well as *cis*- and *trans*-1-chloro-1,2-diethoxyethylenes (OEt migration). IV gave only products derivable from chloroketene ethylene acetal (H migration). Also investigated was the HCl cleavage of these mercurials.

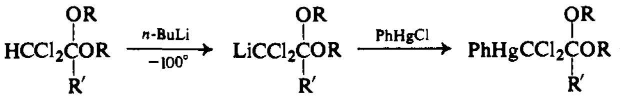
During the course of our investigations of halomethylmercury compounds and their application as divalent carbon transfer agents, we have developed organomercury systems which transfer CCl_2,[4] CClF,[5] CBr_2,[4] CClBr,[4] CHCl,[6] CHBr,[6] CH_2,[7] and Me_3SiCCl[8] to various organic and inorganic substrates. Kinetic studies established that dichlorocarbene was an intermediate in the reaction of phenyl(bromodichloromethyl)mercury with olefins in benzene solution.[9] We are now engaged in a broad program devoted to the synthesis and evaluation of organomercury systems which are precursors for functional carbenes and report here concerning the preparation and thermolysis of some phenyl(1,1-dichloro-2,2-dialkoxyalkyl)mercury compounds.


I


II

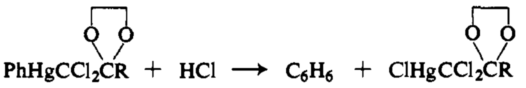

$$PhHgCCl_2\overset{OEt}{\underset{OEt}{C}}H$$
III


IV


$$HCCl_2\overset{OR}{\underset{R'}{C}}OR \xrightarrow[-100°]{n\text{-BuLi}} LiCCl_2\overset{OR}{\underset{R'}{C}}OR \xrightarrow{PhHgCl} PhHgCCl_2\overset{OR}{\underset{R'}{C}}OR \quad (1)$$

The organomercury compounds I–IV have been prepared by the organolithium route (eq 1). For each preparation the appropriate 1,1-dichloro-2,2-dialkoxyalkyllithium intermediate was prepared at −100° in tetrahydrofuran-diethyl ether by the reaction of *n*-butyllithium with the respective dichloroacetal or dichloroketal. Although the organolithium reagents used in this study are new, they were prepared in a straightforward manner using procedures reported previously by Hoeg[10] and Köbrich[11] for the preparation of polychloromethyllithium species such as CCl_3Li, $CHCl_2Li$, and $PhCCl_2Li$. These 1,1-dichloro-2,2-dialkoxyalkyllithium compounds reacted with phenylmercuric chloride to give the respective mercurials in moderate yield. Since both the organolithium reagents used and phenylmercuric chloride were in large part insoluble in the solvent system used at −100°, the use of a high-speed stirring apparatus was found to be essential to the success of these syntheses. The phenyl(1,1-dichloro-2,2-dialkoxyalkyl)mercury compounds I–IV are white, crystalline solids which are stable indefinitely when stored at 5°. However, they do decompose to some extent on standing at room temperature. Analytical and spectral data which support their structures are given in the Experimental Section.

All four organomercury compounds reacted with anhydrous hydrogen chloride in *p*-xylene. Mercurials I and II were cleaved cleanly to give benzene and the alkylmercuric chloride (eq 2). However, compounds III and IV reacted with hydrogen chloride under the same conditions to give both phenyl–mercury and alkyl–mercury cleavage. Thus, in the case of III the cleavage reaction gave phenylmercuric chloride (54%), benzene (20%), and dichloroacetaldehyde diethyl acetal (7%). An additional volatile product (*ca.* 16% yield) was formed, but its apparent thermal instability precluded its identification. The pure alkylmercuric chloride could not be isolated from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(1) Part XXIII: D. Seyferth, F. M. Armbrecht, Jr., and B. Schneider, *J. Am. Chem. Soc.*, in press.

(2) National Science Foundation Trainee, 1966–1967; National Science Foundation Graduate Fellow, 1967–1969.

(3) Fellow of the John Simon Guggenheim Memorial Foundation, 1968.

(4) D. Seyferth, J. M. Burlitch, R. J. Minasz, J. Y.-P. Mui, H. D. Simmons, Jr., A. J.-H. Treiber, and S. R. Dowd, *J. Am. Chem. Soc.*, **87**, 4259 (1965).

(5) D. Seyferth and K. V. Darragh, *J. Organometal. Chem.* (Amsterdam), **11**, P9 (1968).

(6) D. Seyferth, H. D. Simmons, Jr., and G. Singh, *ibid.*, **3**, 337 (1965).

(7) D. Seyferth, M. A. Eisert, and L. J. Todd, *J. Am. Chem. Soc.*, **86**, 121 (1964).

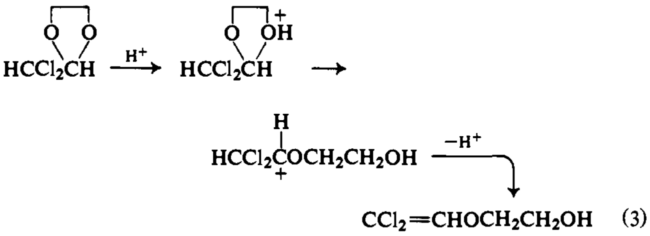
(8) D. Seyferth and E. M. Hanson, *ibid.*, **90**, 2438 (1968).

(9) D. Seyferth, J. Y.-P. Miu, and J. M. Burlitch, *ibid.*, **89**, 4953 (1967).

(10) D. F. Hoeg, D. I. Lusk, and A. L. Crumbliss, *ibid.*, **87**, 4147 (1965).

(11) G. Köbrich, *Angew. Chem.*, **79**, 15 (1967) (review).

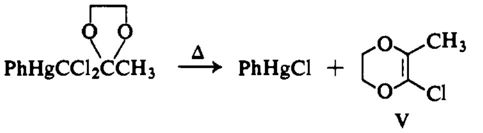
the reaction solids. Hydrogen chloride cleavage of IV gave phenylmercuric chloride (56%), dichloroacetaldehyde ethylene acetal, and 2,2-dichlorovinyl 2′-hydroxyethyl ether. The latter very likely was formed by acid-catalyzed isomerization of the acetal (eq 3).[12] Again,


(3)

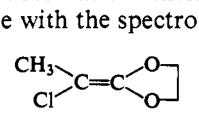
pure alkylmercuric chloride could not be isolated. A discussion of these results is not warranted in view of the lack of information concerning all of the products formed in the case of HCl cleavage of III and IV.

At the outset of the present study it was hoped that one or more of the mercurials prepared might serve to transfer the respective (dialkoxymethyl)chlorocarbene to organic and inorganic substrates. In the case of reactions with olefins, one might hope to obtain aldehyde or ketone-substituted cyclopropanes upon hydrolysis of the initial adducts. Such, however, was not the case: the carbenes derived from mercurials I and III rearranged faster than they added to olefinic double bonds or inserted into silicon–hydrogen bonds; the same should be true for II and IV.

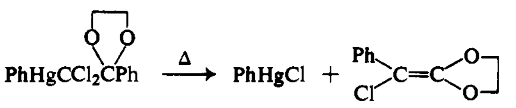
Mercurial I, phenyl(1,1-dichloro-2,2-ethylenedioxypropyl)mercury, was decomposed thermally at 130–145° in the presence of various carbene-reactive substrates such as cyclohexene, tetramethylethylene, and triethylsilane and also in the absence of substrate, in benzene or *p*-xylene solution. In each case the same two products were formed: phenylmercuric chloride and 2-chloro-3-methyl-1,4-dioxene (V), both in high yield. The latter was


V (4)

identified on the basis of its analysis and mass spectrum, which established the molecular formula $C_5H_7ClO_2$, its nmr spectrum (in benzene) which showed resonances at δ 1.82 (s, 3 H, CH_3) and 4.02 ppm (m, 4 H, $-OCH_2CH_2O-$), its infrared spectrum which showed a strong C=C stretching frequency at 1690 cm^{-1} and its hydrogenation over a palladium catalyst which gave methyl-1,4-dioxane. This last observation excluded structure VI which was compatible with the spectroscopic data.

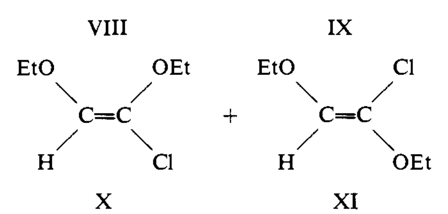

VI

Phenyl(1,1-dichloro-2,2-ethylenedioxy-2-phenylethyl)mercury (II) decomposed in refluxing xylene. The single organic product which resulted was identified as phenylchloroketene ethylene acetal, VII. Its nmr spectrum consisted of multiplets at δ 4.18 (4 H, $-OCH_2CH_2O-$) and 7.28 ppm (5 H, phenyl protons) and its infrared spectrum showed $\nu_{C=C}$ at 1670 cm^{-1}. Reaction of VII (without


VII (5)

prior isolation) from another such reaction with anhydrous hydrogen chloride[13] gave β-chloroethyl phenylchloroacetate, $PhCHClCO_2CH_2CH_2Cl$, in 83% over-all yield.

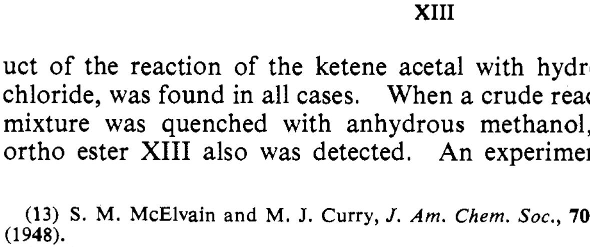
Thermolysis of mercurials III and IV in which the "R′" group is hydrogen gave evidence of similar rearrangement products although the reactions did not proceed as cleanly. Four volatile products could be isolated from the thermal decomposition of phenyl(1,1-dichloro-2,2-diethoxyethyl)mercury (III): ethyl chloroacetate, ethyl ethoxyacetate, and the *cis* and *trans* isomers of 1-chloro-1,2-diethoxyethylene. The total product yield was only 49%, but a



(6)

substantial amount of oily, black tar, probably deriving from the thermal decomposition and polymerization of the primary products X–XI,[13,14] was formed as well. Ethyl chloroacetate most likely resulted from reaction of chloroketene diethyl acetal with hydrogen chloride or ethanol, both of which are potential by-products of the decomposition or polymerization of X and XI.[13,15] Similarly, the production of ethanol would allow formation of IX from X or XI.

Thermal decomposition of IV gave only products derivable from chloroketene ethylene acetal. This compound has been noted as being unstable[13] and its failure to survive our reaction conditions in significant amounts is not surprising. β-Chloroethyl chloroacetate, the product of the reaction of the ketene acetal with hydrogen chloride, was found in all cases. When a crude reaction mixture was quenched with anhydrous methanol, the ortho ester XIII also was detected. An experiment in



(7)

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[12] J. F. Arens, J. Vegter, and T. De Boer, *Rec. Trav. Chim.*, **77**, 753 (1958).

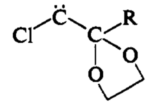
[13] S. M. McElvain and M. J. Curry, *J. Am. Chem. Soc.*, **70**, 3781 (1948).

[14] (a) S. M. McElvain and C. H. Stammer, *ibid.*, **75**, 2154 (1953); (b) A. Magnani and S. M. McElvain, *ibid.*, **60**, 2210 (1938).

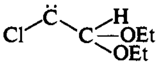
[15] H. Baganz, L. Domaschke, and G. Schneider, *Chem. Ber.*, **91**, 1751 (1958).

which hydrogen chloride was bubbled into the reaction mixture after an initial trap-to-trap distillation in order to convert the ketene acetal to the ester served to demonstrate the instability of the ketene acetal. The yield of phenylmercuric chloride in this experiment was 87%, but the yield of the ester was only 15%. A large amount of tarry residue remained after the trap-to-trap distillation. No evidence was found for the formation of 2-chloro-1,4-dioxene.[16]

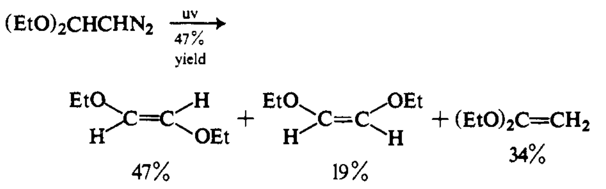
An explanation of the above results obtained in the thermolyses of mercurials I–IV in terms of intermediate carbenes XIV–XVII is quite reasonable. The previous work of Kirmse and Buschoff[17a] and Shechter and Robson[17b] is very pertinent in this connection. The results of the former authors are shown in eq 8 and 9. Carbenes are undoubtedly involved as intermediates in these photolyses. In both cases (eq 8 and 9) the 1,1-dialkoxyethylenes were not isolated as such, rather their solvolysis and photolysis products were characterized. Thus the carbenes XVI and XVII are very similar to their nonchlorine-containing analogs in their rearrangement reactions.



XIV, R = CH_3
XV, R = Ph
XVII, R = H



XVI



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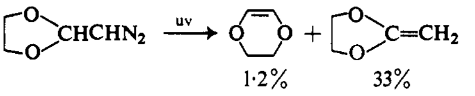
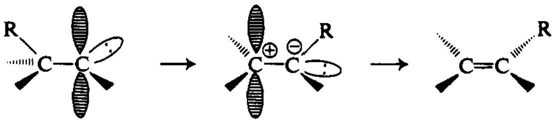


(9)

In the case of carbene XIV exclusive alkoxy migration to form the dioxene V occurred. This is as expected, since methyl migrations in alkylcarbenes are in general quite slow relative to migration of other moieties.[18] Phenyl migration is more rapid and was the exclusive process which occurred when carbene XV was generated. The difference between carbenes XVI and XVII with respect to hydrogen *vs.* alkoxy migration is probably due to conformational factors in the migration process. In the case of carbene XVI both the *cis* and *trans* isomers of 1-chloro-1,2-diethoxyethylene were formed. The isomeric ratio was close to 1, but in view of the apparent instability of these olefins and the possibility that one isomer could have decomposed to a greater extent than the other, no significance can be attached to this observation.

The formation of an olefin *via* rearrangement of a carbene can be pictured[17] (in terms of extremes) as shown in eq 10. As has been pointed out,[17] an alkoxy group on the carbon atom α to the carbene carbon should stabilize the (partial) positive charge and thus should facilitate such rearrangement. The examples given in the present study and by Kirmse and Buschhoff[17] are in full accord with this view.



(10)

Experimental Section

General Comments. All reactions were carried out under a prepurified nitrogen atmosphere using flame-dried glassware. Syringes were used for all liquid transfers. Melting points are corrected. Elemental analyses were performed by Dr. S. M. Nagy (MIT), the Galbraith Laboratories, and the Schwarzkopf Microanalytical Laboratory. Infrared spectra were recorded using a Perkin-Elmer Infracord 337 spectrophotometer, nmr spectra using a Varian Associates A-60 or T-60 spectrometer. Chemical shifts are given in parts per million (ppm) downfield from internal TMS.

Gas–liquid partition chromatography (glpc) 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 or 5754 gas chromatograph. Several different columns were used: (A) 6 ft × 0.25 in. 10% DC-200 silicone oil; (B) 4 ft × 0.25 in. 10% UC-W98 silicone rubber; (C) 6 ft × 0.25 in. 10% Carbowax 20M; (D) 6 ft × 0.25 in. 20% DC-200 silicone oil; (E) 6 ft × 0.25 in. 20% UC-W98 silicone rubber; (F) 6 ft × 0.25 in. 20% nitrile silicone gum XE-60. All columns were packed on Chromosorb W; a helium carrier gas flow rate of *ca.* 40 cc/min commonly was employed.

The solvents used were rigorously dried and distilled before use. *n*-Butyllithium in hexane was purchased from Foote Mineral Co.

Preparation of 1,1-Dichloro-2-propanone Ethylene Ketal. A solution of 30.0 g of 1,1-dichloro-2-propanone,[19] 25 ml of ethylene glycol, and 1.25 g of *p*-toluenesulfonic acid in 200 ml of benzene was heated at reflux overnight while the water formed was removed using a Dean-Stark trap. The reaction mixture then was neutralized with aqueous sodium bicarbonate, dried, concentrated, and distilled using a 30-cm Vigreux column to give 28.7 g (71%) of the desired product (purity better than 95% by glpc), bp 93–94° (27 mm); $n^{25}D$ 1.4671. The nmr spectrum (in CCl_4) showed singlets at 1.53 (3 H, CH_3) and 5.59 (1 H, $HCCl_2$-) and a multiplet (4 H, -OCH_2CH_2O-) centered at 4.07 ppm.

Anal. Calcd for $C_5H_8Cl_2O_2$ (glpc sample): C, 35.11; H, 4.71. Found: C, 35.20; H, 4.91.

Preparation of 2,2-Dichloroacetophenone Ethylene Ketal. A solution of 36.4 g (0.193 mol) of 2,2-dichloroacetophenone,[20] 42 ml of ethylene glycol, and five drops of concentrated sulfuric acid was heated with stirring in a distillation apparatus consisting of a 30-cm Vigreux column and a variable reflux head. An azeotropic mixture of ethylene glycol–water (bp 97°) was distilled from the reaction mixture at a steady rate for about 2.5 hr, at which point the vapor temperature rose above 100°. The mixture was left to cool, and the large, brown, prismatic crystals which formed were filtered and dissolved in diethyl ether. The ether solution was washed with aqueous sodium bicarbonate, dried, concentrated at reduced pressure, and finally distilled to give 22.2 g (49%) of the product, a clear liquid, bp 110–120° (0.05 mm), which solified slowly at room temperature. An analytical sample was obtained by recrystallization from hexane at 5°, mp 59–61°. The nmr spectrum (in CCl_4) showed a singlet at 5.73 (1 H, $HCCl_2$-) and multiplets at 3.75–4.45 (4 H, -OCH_2CH_2O-) and 7.13–7.77 ppm (5 H, Ph).

Anal. Calcd for $C_{10}H_{10}Cl_2O_2$: C, 51.53; H, 4.32; Cl, 30.42.

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[16] R. K. Summerbell and H. E. Lunk, *J. Am. Chem. Soc.*, **79**, 4802 (1957); H. E. Lunk, Ph.D. Thesis, Northwestern University, 1958.

[17] (a) W. Kirmse and M. Buschhoff, *Chem. Ber.*, **100**, 1491 (1967); (b) J. H. Robson and H. Shechter, *J. Am. Chem. Soc.*, **89**, 7112 (1967).

[18] Note, for instance, that photolysis of isopropyldiazomethane gave $Me_2C{=}CH_2$ (H migration) (52% of total product), methylcyclopropane (C–H insertion) (39% of total product), and *cis*- and *trans*-2-butenes (Me migration) (only 9% of total product).[17a]

[19] D. P. Wyman, *J. Org. Chem.*, **29**, 1956 (1964).

[20] Prepared in a manner analogous to 1,1-dichloro-2-propanone;[19] properties in agreement with those reported in the literature.[21]

[21] (a) J. G. Aston, J. D. Newkirk, D. M. Jenkins, and J. Dorsky, "Organic Syntheses," Coll. Vol. III, John Wiley & Sons, Inc., New York, N. Y., 1955, p 538; (b) Sadtler Standard Spectrum No. 27877, Sadtler Research Laboratories, Philadelphia, Pa.

Found: C, 51.58; H, 4.38; Cl, 30.79.

Preparation of the Mercury Compounds. The reactions were carried out under dry nitrogen in a 500-ml or 1000-ml Morton (creased) flask equipped with a high speed stirrer ("Stir-O-Vac," Labline Catalog No. 1280), a pressure-equalizing dropping funnel and a Claisen head topped with a rubber septum and a gas inlet tube. The apparatus was flame-dried, charged with the reactants and a pentane thermometer was substituted for the septum.

a. **Phenyl(1,1-dichloro-2,2-ethylenedioxypropyl)mercury (I).** A solution of 27.48 g (0.161 mol) of 1,1-dichloro-2-propanone ethylene ketal, 250 ml of dry tetrahydrofuran, 50 ml of diethyl ether, and 50 ml of pentane was prepared in the reaction flask and cooled to −100° using liquid nitrogen. This temperature was maintained throughout the reaction period. *n*-Butyllithium in hexane (0.161 mol of 1.50 *N* solution) then was added dropwise over a 30-min period and the resulting yellow slurry was stirred for an additional 50 min to ensure complete formation of the organolithium intermediate. Phenylmercuric chloride (51.5 g, 0.161 mol) was subsequently added as a solid and the resulting mixture was stirred for 2 hr. The reaction mixture then was warmed slowly to room temperature; color changes from light, cloudy gray, to dark, cloudy gray to dark, clear green-brown were noted. Dioxane (50 ml) was added to precipitate the lithium chloride formed as the dioxanate. After filtration under nitrogen the filtrate was evaporated at reduced pressure to leave a yellow, semisolid residue. The latter was dissolved in 300 ml of benzene, filtered from a small amount of residual phenylmercuric chloride, and the benzene solution was evaporated. The yellow solid which remained was crystallized from hexane in several crops to give 30.3 g (42%) of product, mp 113–117°. A further recrystallization gave pure material, mp 114–116°. The nmr spectrum (in $CDCl_3$) showed a singlet at 1.67 (3 H, CH_3) and multiplets centered at 4.12 (4 H, $-OCH_2CH_2O-$) and 7.22 ppm (5 H, Ph).

Anal. Calcd for $C_{11}H_{12}Cl_2O_2Hg$: C, 29.50; H, 2.70; Cl, 15.84; Hg, 44.81. Found: C, 29.52; H, 2.74; Cl, 15.36; Hg, 45.25.

b. **Phenyl(1,1-dichloro-2,2-ethylenedioxy-2-phenylethyl)mercury (II).** Using the procedure described in a, 27.87 g (0.120 mol) of 2,2-dichloroacetophenone ethylene ketal in 200 ml of THF and 60 ml of diethyl ether was treated with 0.121 mol of *n*-butyllithium in hexane at −100°. Solid phenylmercuric chloride (37.6 g, 0.120 mol) was added and the reaction mixture was stirred at −100° for 1.5 hr. Subsequently, the mixture was allowed to warm to 0°, and the solvents were removed at reduced pressure to leave a white, solid residue. Addition of 800 ml of benzene and 50 ml of water to this solid followed. The benzene layer was filtered and evaporated. Crystallization of the residual solid in two crops from benzene–hexane gave 39.5 g (64%) of the mercurial, a white, amorphous solid, mp 170–173°. An analytical sample (from hexane), white needles, mp 175–176°, had an nmr spectrum (in $CDCl_3$) which showed multiplets at 3.70–4.47 (4 H, $-OCH_2CH_2O-$) and 7.03–7.93 ppm (10 H, Ph).

Anal. Calcd for $C_{16}H_{14}O_2Cl_2Hg$: C, 37.70; H, 2.77; Cl, 13.91. Found: C, 37.75; H, 2.77; Cl, 13.66.

c. **Phenyl(1,1-dichloro-2,2-diethoxyethyl)mercury(III).** The required organolithium reagent was prepared at −100° from 21.58 g (0.115 mol) of dichloroacetaldehyde diethyl acetal (Aldrich Chemical Co.) in 200 ml of THF and 60 ml of diethyl ether by adding 0.115 mol of *n*-butyllithium in hexane *dropwise* over a 35-min period. The resulting solution was stirred at −100° for 30 min, and then 36.10 g of phenylmercuric chloride was added. After the reaction mixture had been stirred for 2 hr it was allowed to warm slowly to room temperature and evaporated at reduced pressure. The oily residue was taken up in 700 ml of pentane; filtration was followed by concentration of the filtrate to 200 ml. Rapid cooling yielded a white solid which was quickly filtered. A further crop of solid was obtained from the mother liquor. The combined solids were recrystallized from cold pentane to give 27.90 g (52.3%) of the mercury compound, a white, amorphous solid, mp 40–41°. An analytical sample (from methanol at −70°) had mp 41–43° and its nmr spectrum (in $CDCl_3$) showed a triplet at 1.27 (J = 7.0 cps) (6 H, CH_3CH_2O-), a quartet at 3.83 (J = 7.0 cps) (4 H, CH_3CH_2O-), a singlet at 5.01 (1 H, $(EtO)_2CH-$), and a multiplet at 7.33 ppm (5 H, Ph).

Anal. Calcd for $C_{12}H_{16}O_2Cl_2Hg$: C, 31.08; H, 3.48; Cl, 15.29. Found: C, 31.06; H, 3.40; Cl, 15.17.

d. **Phenyl(1,1-dichloro-2,2-ethylenedioxyethyl)mercury (IV).** The same general procedure was used to prepare this mercurial by reaction of the organolithium reagent prepared at −100° from 18.72 g (0.119 mol) of dichloroacetaldehyde ethylene acetal[13] and 0.119 mol of *n*-butyllithium (250 ml of THF, 70 ml of diethyl ether) with 37.3 g (0.119 mol) of phenylmercuric chloride. Extraction of the residue obtained upon evaporation of solvents with benzene (600 ml) followed by removal of the benzene left a dark oil which could be crystallized from methanol at 5° (150 ml) to give 12.66 g (mp 92–96°). A second crop, mp 88–92°, was obtained by cooling the concentrated mother liquor to −5° (5.63 g). The total amount of product represented a yield of 30%. An analytical sample (from 4:1 hexane–benzene) melted at 97–99°; its nmr spectrum in $CDCl_3$ showed a multiplet at 4.15 (4 H, $-OCH_2CH_2O-$), a singlet at 5.62 (1 H, $-OCHO-$), and a multiplet at 7.35 ppm (5 H. Ph).

Anal. Calcd for $C_{10}H_{10}O_2Cl_2Hg$: C, 27.69; H. 2.32; Cl, 16.35. Found: C, 27.83; H, 2.30; Cl, 16.21.

Hydrogen Chloride Cleavage Reactions. a. **Cleavage of Mercurial II.** A mixture of 5.16 g (10.1 mmol) of II and 50 ml of dry xylene was charged into a 100-ml, three-necked flask equipped with a gas inlet tube, a magnetic stirring assembly and a nitrogen bubbler. Anhydrous hydrogen chloride (Matheson Co.) then was bubbled into the vigorously stirred mixture for 1 hr. At the end of the reaction period solid sodium bicarbonate was added to neutralize the excess hydrogen chloride. The filtered reaction solids were extracted in a Soxhlet extractor with 300 ml of benzene for 20 hr. From the cooled benzene extract there was obtained 2.85 g of white, crystalline 1,1-dichloro-2,2-ethylenedioxy-2-phenylethylmercuric chloride, mp 193–195°. Additional product (0.88 g, mp 194–197°) was obtained by evaporating the filtrate and recrystallizing the residue from hexane–benzene.

Anal. Calcd for $C_{10}H_9Cl_3O_2Hg$: C, 25.65; H, 1.94. Found: C, 25.94; H, 1.88.

The filtered reaction solution was trap-to-trap distilled under vacuum into a trap at −78° to give a clear liquid and 0.83 g of solid residue. The latter was shown by means of its infrared spectrum to contain additional alkylmercuric chloride. Glpc analysis of the distillate (column A, 70°, toluene standard) showed the presence of benzene in 80% yield.

b. **Cleavage of Mercurial I.** The HCl cleavage of 2.12 g (4.74 mmol) of I gave 1.84 g (96%) of 1,1-dichloro-2,2-ethylenedioxypropylmercuric chloride, mp 177–188° dec. Recrystallization (from hexane–benzene) afforded white plates, mp 180–186° slow dec.

Anal. Calcd for $C_5H_7Cl_3O_2Hg$: C, 14.79; H, 1.74. Found: C, 15.16; H, 1.76.

Glpc analysis of the filtrate indicated the formation of benzene in 84% yield.

c. **Cleavage of Mercurial III.** Soxhlet extraction of the solids obtained in the HCl cleavage of 13.93 g (30.0 mmol) of III gave 5.03 g (54%) of phenylmercuric chloride, mp 255–256°. Additional solid (3.99 g total, mp 193–201°) was isolated from the extraction filtrate and from the residue after trap-to-trap distillation of the reaction solution. Infrared analysis showed that additional phenylmercuric chloride was present, but attempts to further purify this solid were not successful. The reaction solution distillate was found to contain benzene (20%), dichloroacetaldehyde diethyl acetal (7%), and an additional product (*ca.* 16%) which was slightly more volatile than the acetal and which could not be identified because of its thermal lability.

d. **Cleavage of Mercurial IV.** Cleavage of 2.17 g (5.00 mmol) of IV in xylene with HCl was carried out as described above. Trap-to-trap distillation of the reaction mixture at reduced pressure was followed by glpc analysis of the distillate. Benzene (56%), dichloroacetaldehyde ethylene acetal (*ca.* 2%), and a third product (*ca.* 14%) slightly less volatile than the acetal were present. A sample of the latter could be isolated by glpc (column E, 160°) after the filtrate had been concentrated. It was identified as 2,2-dichlorovinyl 2′-hydroxyethyl ether on the basis of its spectra and analysis: nmr spectrum (in CCl_4): singlets at 2.10 (1 H, $-OH$) and 6.57 (1 H, $C{=}C{-}H$ and a multiplet at 3.87 ppm (4 H, $-OCH_2CH_2O-$). Infrared spectrum (liquid film): 3355 (-OH), 1642 (C=C), 1241, 1181, and 1073 (C—O) cm^{-1}; $n^{25}D$ 1.4928 (lit.[22] $n^{22}D$ 1.4935).

Anal. Calcd for $C_4H_6Cl_2O_2$: C, 30.60; H, 3.85. Found: C, 30.44; H, 3.80.

The solid distillation residue was washed with 25 ml of 4:1 benzene–hexane and filtered to give 1.32 g of white solid, mp 193–197°. Recrystallization from 35 ml of benzene gave 0.50 g of white flakes, mp 199–203°. The infrared spectra of the purified and

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(22) H. Normant and J. Villieras, *Compt. Rend.*, **260**, 4535 (1965).

unpurified materials were essentially the same, indicating the presence of a large proportion of phenylmercuric chloride. Evaporation of the hexane-benzene wash solution left a small amount of brown oil whose infrared spectrum indicated the presence of an aliphatic residue (strong bands in the 3000–2800-cm^{-1} region).

Thermolysis of the Mercurials. a. Thermal Decomposition of I. A solution of 13.21 g (29.5 mmol) of I in 20 ml of benzene was prepared in a dry, 30-ml combustion tube. The tube was sealed under nitrogen and heated at 143° for 96 hr. At the end of the reaction period 7.78 g (84%) of phenylmercuric chloride, mp 249–253°, was filtered from the light-brown reaction solution. The filtrate was trap-to-trap distilled (0.3 mm) (pot temperature to 60° maximum) into a trap at −78°, leaving a small amount of brown, solid residue. A portion of the distillate was set aside for yield analysis and the remainder concentrated. A single product was isolated from the concentrate by preparative glpc (column D, 110°) and was identified as 2-chloro-3-methyl-1,4-dioxene (V), $n^{25}\text{D}$ 1.4710; mass spectrum (68 eV) *m/e* 134, 136 (3:1 ratio) (M$^+$). Nmr and infrared spectral data are given in the Discussion section.

Anal. Calcd for $C_5H_8ClO_2$: C, 44.62; H, 5.25; Cl, 26.35. Found: C, 44.40; H, 5.16; Cl, 25.90.

Glpc analysis (column A, 110°, *n*-dodecane standard) showed that this product had been formed in 89% yield.

As further proof of structure of V, 11.0 mmol of this product in *ca.* 38 g of *p*-xylene was shaken under 3 atm of hydrogen in the presence of 0.21 g of 10% Pd–C catalyst and 1.4 g of sodium bicarbonate until gas uptake had ceased. Methyl-1,4-dioxane was isolated by preparative glpc of the filtered and trap-to-trap distilled reaction mixture (column D, 80°). It had $n^{25}\text{D}$ 1.4176 (lit.[23] $n^{25}\text{D}$ 1.4187). The nmr spectrum (in CCl_4) showed a doublet at 1.00 (J = 5.8 cps) (3 H, CH_3) and a multiplet at 3.20–3.70 ppm (7 H, dioxane ring). Glpc analysis (column A, 80°, tetrachloroethylene standard) indicated a 55% conversion.

Mercurial I also was decomposed in the presence of cyclohexene, tetramethylethylene, and triethylsilane in benzene solution and cyclohexene in 1,2-dimethoxyethane solution. In each case V and phenylmercuric chloride were the only products isolated. The yields were on the order of 80% based on the reacted mercurial.

Thermal Decomposition of II. The mercurial (15.30 g, 30.0 mmol) and 75 ml of xylene were charged into a 100-ml, three-necked flask equipped with a magnetic stirring assembly and a condenser topped with a gas inlet tube. The mixture was heated under nitrogen at reflux for 8 days, then was cooled and filtered *under nitrogen* to remove 9.05 g (96%) of phenylmercuric chloride, mp 253–257°. Solvent was removed from the filtrate at reduced pressure; subsequent short-path distillation of the residue afforded a light brown liquid believed to be phenylchloroketene ethylene acetal (VII) (61%), bp 104–130° (0.1–0.07 mm). Its nmr spectrum (in $CDCl_3$) showed multiplets at 4.18 (4 H, $-OCH_2CH_2O-$) and 7.28 ppm (5 H, Ph). In its infrared spectrum (liquid film) the C═C stretching frequency was observed at 1670 cm^{-1}.

Qualitative hydrolysis of VII in aqueous acetone–acetic acid gave β-hydroxyethyl phenylchloroacetate, examined only as the crude oil. Its nmr spectrum (in $CDCl_3$) showed a singlet at 2.04 ppm (1 H, $-OH$), a multiplet at 3.44–4.38 (4 H, $-OCH_2CH_2OH$), a singlet at 5.55 (1 H, PhC*H*Cl–), and a multiplet at 7.05 ppm (5 H, Ph). In its infrared spectrum (liquid film) bands at 3440 cm^{-1} (O—H) and 1750 cm^{-1} (C═O) were observed. Its basic hydrolysis afforded *dl*-mandelic acid upon acid work-up, mp 119–120° (lit.[24] mp 120.5°); infrared spectrum in agreement with that of an authentic sample.[25]

In a separate experiment, 5.09 g (10.0 mmol) of II in 25 ml of xylene was heated at reflux under nitrogen for 6 days. The reaction mixture was cooled and anhydrous hydrogen chloride was bubbled through it for 1 hr, followed by bubbling of nitrogen to purge unconverted HCl. Phenylmercuric chloride (3.10 g, 99%), mp 251–256°, was filtered from the light yellow solution. Solvent was removed from the filtrate by distillation at reduced pressure. Filtration of the residue was followed by short-path distillation of β-chloroethyl phenylchloroacetate, 1.94 g (83%), bp 94–99° (0.07 mm). An analytical sample was obtained by careful refractionation, bp 95–97° (0.07 mm).

Anal. Calcd for $C_{10}H_{10}Cl_2O_2$: C, 51.53; H, 4.32. Found: C, 51.84; H, 4.67.

Its nmr spectrum (in $CDCl_3$) showed triplets at 3.50 (J = 5.5 cps; 2 H, $-OCH_2CH_2Cl$) and 4.30 (J = 5.5 cps; 2 H, $-OCH_2CH_2Cl$), a singlet at 5.37 (1 H, PhC*H*Cl–), and a multiplet at 7.35 ppm (5 H, Ph). The C═O stretching frequency was observed at 1758 cm^{-1} (liquid film).

c. Thermal Decomposition of III. The mercurial (6.92 g, 14.9 mmol) and 15 ml of benzene were sealed under partial vacuum in a 40-ml combustion tube and heated at 135° for 4 days. Upon completion of the reaction the tube was opened and the contents (dark solution, white solid) were trap-to-trap distilled (0.3 mm) into a receiver at −78° to give a clear distillate and a dark solid residue. The latter was rinsed with 30 ml of benzene in two portions and filtered to give 4.28 g (92%) of phenylmercuric chloride, mp 254–257°. The filtrate was evaporated, leaving 0.69 g of dark tar. Glpc analysis (column A, 90°) of the distillate showed the presence of four components other than solvent, eluting at 3.8, 6.2, 8.6, and 10.1 min in the ratio of 1.6:1.0:1.3:1.6 (*ca.* 49% over-all yield, *n*-decane standard). The filtrate was concentrated and analytical samples of these components were isolated by preparative glpc (columns E and F). The products eluting first and second were identified as ethyl chloroacetate and ethyl ethoxyacetate by comparison of their infrared spectra with those of authentic samples. The products eluting third and fourth were quite similar in their spectral properties and were assigned the structures of *cis*- and *trans*-1-chloro-1,2-diethoxyethylenes, X and XI. The first had $n^{25}\text{D}$ 1.4370; nmr (in CCl_4): triplets at 1.27 (J = 7 cps, 3 H, CH_3-CH_2O-) and 1.30 (J = 7 cps, 3 H, CH_3CH_2O-), quartets at 3.77 (J = 7 cps, 2 H, CH_3CH_2O-) and 3.92 (J = 7 cps, 2 H, CH_3-CH_2O-), and a singlet at 5.67 ppm (1 H, C═C*H*); infrared spectrum: $\nu_{C=C}$ at 1678 (m) cm^{-1} (liquid film). The second had $n^{25}\text{D}$ 1.4383; nmr (in CCl_4): triplets at 1.16 (J = 7 cps, 3 H, CH_3CH_2O-) and 1.20 (J = 7 cps, 3 H, CH_3CH_2O-), quartets at 3.72 (J = 7 cps, 2 H, CH_3CH_2O-) and 3.75 (J = 7 cps, 2 H, CH_3CH_2O-), and a singlet at 6.13 ppm (1 H, C═CH); infrared spectrum: $\nu_{C=C}$ at 1682 (w) cm^{-1}. Baganz and Krüger[26] report $n^{25}\text{D}$ 1.4340 for 1-chloro-1,2-diethoxyethylene (*cis*/*trans* ratio not specified). A loosely stoppered sample of a mixture of X and XI decomposed to ethyl ethoxyacetate on standing for 2 weeks.

d. Thermal Decomposition of IV. The mercurial (4.66 g, 10.8 mmol) in 20 ml of *p*-xylene was heated (under nitrogen, at reflux) for 6 days. Trap-to-trap distillation (0.2 mm) (pot temperature to 70°) followed. The distillate was treated with anhydrous hydrogen chloride for 30 min and again trap-to-trap distilled. Glpc analysis of the distillate (column C, 170°, iodobenzene standard) showed the presence of a single product in low yield (15%) as well as of a small (1%) amount of dichloroacetaldehyde ethylene acetal (probably from reaction of HCl with undecomposed IV). The product was isolated by preparative glpc (column F, 160°) after concentration of the distillate and identified as β-chloroethyl chloroacetate (XII), $n^{25}\text{D}$ 1.4605 (lit.[13] 1.4619). Its nmr spectrum showed triplets at 3.72 (J = 5.5 cps, 2 H, $ClCH_2CH_2O-$) and 4.45 (J = 5.5 cps, 2 H, $ClCH_2CH_2O-$) and a singlet at 4.15 ppm (2 H, $ClCH_2COO-$). In the infrared spectrum (liquid film) $\nu_{C=O}$ appeared at 1758 cm^{-1}.

Anal. Calcd for $C_4H_6Cl_2O_2$: C, 30.60; H, 3.85. Found: C, 30.88; H, 4.05.

The crude distillation residue was rinsed with benzene and filtered to leave 2.93 g (87%) of phenylmercuric chloride, mp 254–257°.

In a separate experiment, 6.50 g (15.0 mmol) of IV in 15 ml of dry benzene was heated in a sealed combustion tube for 4 days at 145°. The tube was opened under nitrogen and 2 ml of anhydrous methanol was added to the contents. Phenylmercuric chloride (3.61 g, 77%) was filtered and the filtrate trap-to-trap distilled. Glpc analysis of the distillate (column D, 110°) indicated the presence of two products in approximately equal amounts. These were isolated by means of preparative glpc and identified as XII and the orthoester XIII. The latter had $n^{25}\text{D}$ 1.4462 (lit.[13] 1.4449). The nmr spectrum (neat liquid, external standard) showed a singlet at 3.23 (3 H, CH_3O-), a singlet at 3.60 (2 H, $ClCH_2-$), and a multiplet at 4.10 ppm (4 H, $-OCH_2CH_2O-$).

Acknowledgments. The authors are grateful to the Air Force Office of Scientific Research (SRC)-OAR for generous support of this work through USAF Grant No. AFOSR-68-1350 and to M & T Chemicals, Inc. for gifts of chemicals.

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