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HALOMETHYL-METAL COMPOUNDS
XVIII[a]. INSERTION OF HALOCARBENES INTO THE MERCURY-HALOGEN BOND[b]

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SUMMARY

A study of the $PhHgCCl_2Br/PhHgCl$, $PhHgCCl_2Br/p\text{-}CH_3C_6H_4HgCl$, $PhHgCCl_2Br/HgCl_2$ and the $PhHgCHClBr/PhHgCl$ systems (in benzene at reflux) has established that dichloro- and monochlorocarbene insert into the Hg–Cl bond under these conditions to give $Hg\text{–}CCl_3$ and $Hg\text{–}CHCl_2$ compounds, respectively. The reaction with *p*-tolylmercuric chloride, which gave only *p*-tolyl(trichloromethyl)-mercuric chloride, showed that CCl_2 transfer into the Hg–Cl linkage is involved. Indirect evidence was also obtained for the insertion of CBrCl and CBr_2 into the mercury–chlorine bond.

When Reutov and Lovtsova[3] reported the preparation of aryl(trihalomethyl)-mercury compounds by the reaction of arylmercuric halides, haloform and potassium tert-butoxide, they suggested that this reaction proceeded via dihalocarbene insertion into the mercury–halogen bond. We have shown that this is not the case and that nucleophilic attack by CX_3^- at mercury is involved instead[4]. A similar reaction, the preparation of (trichloromethyl)mercurials by the decarboxylation of sodium trichloroacetate in the presence of organomercuric halides, also was shown not to involve CCl_2 insertion into the mercury–halogen linkage[5]. Finally, in 1965, Razuvaev and Vasileiskaya reported the formation of (trichloromethyl)mercuric chloride by the photolysis of chloroform in the presence of mercuric chloride and pyridine, and they suggested that this reaction proceeded by way of dichlorocarbene insertion into the Hg–Cl bond[6]. Alternative polar or radical mechanisms, however, were not excluded and the process by which CCl_3HgCl is formed in this reaction is by no means proven.

We report here concerning a preparation of (trichloromethyl)- and (dichloromethyl)mercury compounds which very likely proceeds by way of dichlorocarbene or chlorocarbene insertion into the mercury–chlorine bond.

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In 1962 we discovered that phenyl(trihalomethyl)mercury compounds were excellent dihalocarbene transfer agents which could be used to good advantage in the preparation of *gem*-dihalocyclopropanes from olefins[7-9]. In kinetic studies of the $PhHgCCl_2Br$/cyclooctene reaction it was found that the initial rate of the reaction tended to decrease with the extent of the reaction. Also, the rate of thermal decomposition of phenyl(bromodichloromethyl)mercury, on the basis of qualitative observations, seemed to depend on the nature of the substrate employed to trap the CCl_2, being rapid when olefins such as cyclohexene were used and slower in the presence of substrates such as ethylbenzene or cyclohexane. A possible explanation for these observations involved a two step mechanism for such mercurial-derived CX_2 transfer reactions, in which the first step, the extrusion of CX_2 from the organomercury reagent was reversible (eqn. 1 and 2). The steady state approximation gives rate eqn. (3), and the fact that there is a rate dependence on the nature of the substrate thus would have found an explanation. A more detailed kinetic study[10] in which the effect of added phenylmercuric bromide on the rate of the $PhHgCCl_2Br$/olefin reaction was determined did indeed provide confirmation of these ideas.

$$PhHgCX_2Br \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} PhHgBr + CX_2 \qquad (1)$$

$$CX_2 + \text{Substrate} \xrightarrow{k_p} \text{Product} \qquad (2)$$

$$-\frac{dx}{dt} = \frac{k_1(PhHgCX_2Br)}{1 + \frac{k_{-1}(PhHgBr)}{k_p(\text{Substrate})}} \qquad (3)$$

The suggestion that phenyl(bromodichloromethyl)mercury decomposition is a reversible process, *i.e.*, that CCl_2 can insert into the Hg–Br bond under these neutral reaction conditions, led to the prediction that the decomposition of phenyl(bromodichloromethyl)mercury in the presence of an organomercuric chloride (or mercuric chloride itself) should result in formation of a (trichloromethyl)mercury derivative. The greater thermal stability of phenyl(trichloromethyl)mercury as compared with phenyl(bromodichloromethyl)mercury has been stressed before[9,11]. Thus in the $PhHgCCl_2Br$/ArHgCl systems the following reactions would occur if CCl_2 insertion into the Hg–Cl bond was indeed taking place:

$$PhHgCCl_2Br \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} PhHgBr + CCl_2 \qquad (1)$$

$$CCl_2 + ArHgCl \underset{k_2}{\overset{k_{-2}}{\rightleftharpoons}} ArHgCCl_3 \qquad (4)$$

It is expected that the insertion of CCl_2 into the Hg–Cl and the Hg–Br bonds will be fast, but that the CCl_2 extrusion reactions will be much slower, so that the product-determining rate constants will be k_1 and k_2. Since, as indicated, $k_1 \gg k_2$, we should expect the net process in this system to be that shown in eqn. (5). Experimental verification of this prediction was obtained in several systems.

$$PhHgCCl_2Br + ArHgCl \rightarrow PhHgBr + ArHgCCl_3 \qquad (5)$$

RESULTS AND DISCUSSION

In the initial experiment, a mixture of 10 mmoles each of phenyl(bromodichloromethyl)mercury and phenylmercuric chloride in 25 ml of benzene was heated at reflux for two hours. The reaction mixture contained a flaky, white solid which was filtered and subsequently identified by its thin layer chromatographic (TLC) and melting behavior as phenylmercuric bromide containing admixed smaller amounts of phenylmercuric chloride. The filtrate was distilled at reduced pressure. Gas–liquid partition chromatography (GLPC) showed it to contain tetrachloroethylene (4%, based on available CCl_2 groups). The solid distillation residue (m.p. 105–109°) was recrystallized from chloroform/hexane to give 2.46 g (62%) of phenyl(trichloromethyl)mercury, m.p. 115.5–116.5°, whose identity was confirmed by its mixture melting point and infrared spectrum. In an identical experiment, the presence of Cl_3C–Hg groups was proven by their brominolysis; the reaction mixture was filtered, the filtrate evaporated and the crude residue treated with bromine in carbon tetrachloride. GLPC analysis of the volatile cleavage products showed the presence of bromotrichloromethane (70%), dibromodichloromethane (3%) and bromobenzene (72%). This reaction, in which the aryl groups of the two organomercury reactants are identical did not serve to prove that the reaction corresponding to eqn. (5) had taken place, since, in terms of the products alone, an exchange process involving chlorine on mercury and bromine on carbon was not excluded. For this reason, the reaction of *p*-tolylmercuric chloride with phenyl(bromodichloromethyl)mercury was investigated. In this case the product was *p*-tolyl(trichloromethyl)mercury (57%), *not* phenyl(trichloromethyl)mercury. Thus the $ArHgCCl_3$ forming reaction proceeds by way of CCl_2 transfer from $PhHgCCl_2Br$ to the ArHg–Cl bond, not by the exchange process mentioned above.

In a similar reaction, heating of a 2.5 fold excess of phenyl(bromodichloromethyl)mercury with mercuric chloride in benzene at 80° for 3 h produced bis(trichloromethyl)mercury in 47% yield and (trichloromethyl)mercuric chloride in 18% yield. The latter could not be separated from admixed phenylmercuric bromide; its yield is based on brominolysis of the crude RHgX mixture. The formation of (trichloromethyl)mercuric chloride in this reaction may be the result of the reaction of only one Hg–Cl bond of a part of the mercuric chloride, but another route may also have contributed to formation of this product: insertion of CCl_2 into the Hg–C bond of bis(trichloromethyl)mercury, followed by β-elimination (eqn. 6). Support for such a

$$Cl_3C\text{–}Hg\text{–}CCl_3 + CCl_2 \rightarrow Cl_3C\text{–}Hg\text{–}CCl_2CCl_3 \rightarrow Cl_3CHgCl + Cl_2C{=}CCl_2 \quad (6)$$

possibility was provided by an experiment in which bis(trichloromethyl)mercury and phenyl(bromodichloromethyl)mercury were heated together in benzene solution for 3 h (conditions under which the former mercurial alone decomposes only to a minor extent); a mixture of phenylmercuric bromide and (trichloromethyl)mercuric chloride resulted. It may be noted that the insertion of dichlorocarbene into the mercury–carbon bond of dialkylmercurials has been observed previously[12].

(Dichloromethyl)mercury compounds can be prepared by a similar procedure. The reaction of phenyl(bromochloromethyl)mercury with phenylmercuric chloride in chlorobenzene solution at 130° for 34 h resulted in formation of phenyl(dichloromethyl)mercury in 79% yield, as determined by bromination of the crude reaction product and subsequent GLPC analysis of the resulting bromodichloromethane

$$PhHgCHClBr + PhHgCl \rightarrow PhHgBr + PhHgCHCl_2 \xrightarrow{Br_2} HCCl_2Br \qquad (7)$$

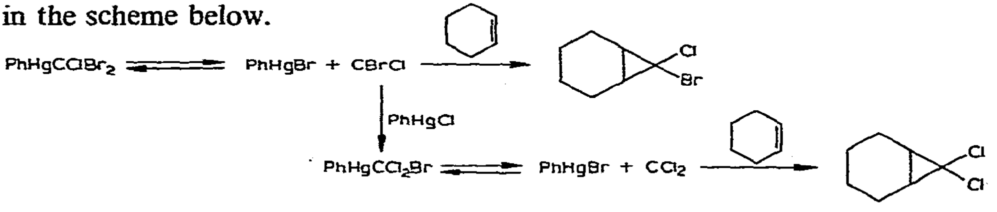
(eqn. 7). It was possible to monitor the formation of phenyl(dichloromethyl)mercury in this reaction by infrared spectroscopy, since the methine carbon–hydrogen deformations occur at 1205 cm^{-1} in $PhHgCHCl_2$ and 1180 cm^{-1} in PhHgCHClBr[13].

In order to obtain some idea of the reactivity of the Hg–Cl bond toward dichlorocarbene, as compared to an olefin, for instance, a competition experiment was carried out in which 30 mmoles each of *p*-tolylmercuric chloride and cyclohexene were allowed to compete for 10 mmoles of phenyl(bromodichloromethyl)mercury-derived dichlorocarbene. The observed product yields, 59.2% 7,7-dichloronorcarane and 16.6% *p*-tolyl(trichloromethyl)mercury, allowed the calculation of a $k_{rel} = k(\text{Hg–Cl})/k(\text{Cyclohexene}) = 0.31$. This competition was carried out in 1,2-dimethoxyethane solution and the reaction mixture was homogeneous. However, the results of this experiment are only semi-quantitative. The yield of the 7,7-dichloronorcarane could be determined precisely by means of GLPC, but the yield of *p*-tolyl(trichloromethyl)mercury depended upon the amount of pure product which could be isolated by recrystallization. Furthermore, *p*-tolyl(trichloromethyl)mercury, while much more stable than phenyl(bromodichloromethyl)mercury, will have decomposed to a small extent, and, to this extent, will have contributed to formation of 7,7-dichloronorcarane. We feel that the first factor has been the more important one and thus the relative reactivity determined, in our opinion, represents the lower limit. It may be noted that in our kinetic study $k(\text{Hg–Br})/k(\text{Cyclooctene})$ was determined[10] to be *ca.* 1.1. The fact thus demonstrated, that the Hg Cl linkage can compete with the olefinic double bond for a carbene, was used to show indirectly that bromochloro- and dibromocarbene are capable of inserting into the mercury–chlorine bond. Thus, for instance, it would not be possible to demonstrate the reactions shown in eqns. (8) and (9) because the products decompose at rates comparable to the decomposition

$$PhHgCClBr_2 + PhHgCl \rightarrow PhHgBr + PhHgCCl_2Br \qquad (8)$$

$$PhHgCBr_3 + PhHgCl \rightarrow PhHgBr + PhHgCClBr_2 \qquad (9)$$

rates of the starting phenyl(trihalomethyl)mercurials. That such reactions occur was shown in the following way. Phenyl(dibromochloromethyl)mercury was allowed to decompose at 80° in benzene solution in the presence of 1.5 molar equivalents each of phenylmercuric chloride and cyclohexene (a heterogeneous reaction mixture). Work-up of the reaction mixture demonstrated the formation of 7-bromo-7-chloronorcarane in 67% yield and 7,7-dichloronorcarane in 5% yield. Since the phenyl(dibromochloromethyl)mercury was not contaminated with phenyl(bromodichloromethyl)mercury, the formation of 7,7-dichloronorcarane finds explanation as shown in the scheme below.



A similar reaction carried out with phenyl(tribromomethyl)mercury and the phenylmercuric chloride/cyclohexene substrate mixture gave 7,7-dibromonorcarane in 59% yield and 7-bromo-7-chloronorcarane in 5% yield. Thus good proof has been obtained for the insertion of CBrCl and CBr_2 into the mercury–chlorine linkage.

It was such dibromocarbene insertion into the Hg–Cl bond which caused the complications observed in the reaction of phenyl(tribromomethyl)mercury with hydrogen chloride in benzene at 85°. In addition to the expected product of CBr_2 insertion into H–Cl, $HCBr_2Cl$, bromodichloromethane and chloroform were obtained[14]. The formation of these minor haloform products was quite puzzling to us until the studies above showed that insertion of CX_2 into the Hg–Cl bond was possible. The insertion of CBr_2 into the Hg–Cl linkage of $ClHgCBr_3$, formed by HCl cleavage of the phenyl group of phenyl(tribromomethyl)mercury, followed by further dihalocarbene extrusion and insertion reactions then provided ready explanation of the results observed.

The results of our kinetic study[10], as mentioned, were best interpreted in terms of a mechanism in which the insertion of dichlorocarbene into the Hg–Br bond was involved (eqn. 1), and thus we consider the reactions discussed in the present report also to be bona fide dihalocarbene transfer reactions. As noted, these reactions occur rapidly only at temperatures at which the decomposition of the phenyl(trihalomethyl)mercurials is rapid, and thus we tend to discount a bimolecular reaction between the phenyl(trihalomethyl)mercury compound and the arylmercuric chloride. However, more detailed studies are required before more definite statements concerning the mechanism of these reactions can be made.

The insertion of dihalocarbenes into metal–halogen bonds appears not to be restricted to halides of mercury. We have found such insertion to occur also into the tin–halogen bond[15], but not into the silicon–chlorine bond of trimethyl- and triethylchlorosilane and dimethyldichlorosilane[16]. Further studies in this general area are in progress.

EXPERIMENTAL

General comments

All reactions were carried out under an atmosphere of prepurified nitrogen. Analyses were performed by Dr. S. M. Nagy (MIT) and the Galbraith Laboratories (Knoxville, Tenn.). Thin-layer chromatography utilizing 50 × 150 mm glass plates coated with Silica Gel G (Brinkman Instruments) served in the qualitative determination of phenylmercuric chloride and bromide. The plates were spotted, eluted with 20% benzene in cyclohexane, developed for 15 min in an iodine chamber and developed subsequently with a sodium sulfide spray (10% sodium sulfide in 50% aqueous ethanol). The mercurials appeared as black spots. Phenylmercuric chloride had an R_f time about twice as great as that of phenylmercuric bromide.

Since bromine cleavage of organic groups from the mercurials studied was used extensively, the cleavage of the starting material, phenyl(bromodichloromethyl)mercury by bromine is described in detail to illustrate the method used. To a 50 ml three-necked flask equipped with a magnetic stirring assembly and a 60 ml pressure-equalizing dropping funnel topped by a nitrogen inlet tube was added 2.20 g (5 mmoles) of $PhHgCCl_2Br$ and 10 ml of dry benzene. Over a 10 min period, 11.5 ml

(11.5 mmoles) of 1 *M* bromine in carbon tetrachloride was added dropwise. The mixture was stirred for 3.5 h; then 1.5 g of anhydrous magnesium sulfate and 3.5 g of finely powdered $Na_2S_2O_3 \cdot 5H_2O$ were added. Stirring was continued until the bromine color was discharged. The reaction mixture was trap-to-trap distilled (0.1 mm, pot temperature to 40°). The dried distillate was analyzed by GLPC (MIT isothermal unit, 7 ft. × 8 mm glass column packed with 20% General Electric Co. SE-30 silicone rubber gum on 80–100 mesh Johns Manville Chromosorb W at 98°, 12 psi helium, external standard method) and found to contain dibromodichloromethane (97% yield) and bromotrichloromethane (1.2%). The latter resulted from the presence of a minor chloroform impurity in the bromodichloromethane used to prepare phenyl(bromodichloromethyl)mercury.

Reaction of phenyl(bromodichloromethyl)mercury with phenylmercuric chloride

A dry, 50 ml three-necked flask equipped with a reflux condenser topped with a nitrogen inlet tube and a magnetic stirring unit was charged with 4.41 g (0.01 mole) of phenyl(bromodichloromethyl)mercury[4] and 3.13 g (0.01 mole) of phenylmercuric chloride (m.p. 254–257°, prepared by mercuric chloride cleavage of tetraphenyltin[4] and purified by Soxhlet extraction of the crude product with benzene). The system was evacuated for 3 h and then filled with nitrogen. Dry benzene (25 ml) was added and the reaction mixture was heated with stirring at vigorous reflux for 2.25 h. The resulting flaky, white solid in a pale yellow solution was filtered, giving 4.27 g of material, melting range 277–284°. Thin-layer chromatography showed it to be a mixture of phenylmercuric bromide and chloride. The pale yellow filtrate was distilled (trap-to-trap) at 0.05 mm (pot temperature to 25°) to give 28.71 g of distillate which GLPC showed to contain tetrachloroethylene in 4% yield. The solid distillation residue was pale yellow and weighed 3.30 g, m.p. 105–109°. Recrystallization from 4/1 hexane/chloroform gave phenyl(trichloromethyl)mercury in 62.3% yield (in two crops, m.p. 115.5–116.5 and 108–114°. Lit.[4] m.p. 116.5–118°. This product was identified by means of its undepressed mixture m.p. with authentic material[17] and its infrared spectrum. An identical experiment gave 3.34 g of crude solid (84%), m.p. 97–102°, recrystallization of which yielded 2.35 g (60%) of $PhHgCCl_3$. A reaction in which 15 mmoles of phenyl(bromodichloromethyl)mercury and 10 mmoles of phenylmercuric chloride were allowed to react under these conditions gave phenyl(trichloromethyl)mercury in 62% yield.

These reactions were run again and this time the crude solid obtained upon removal of volatiles from the original filtrate was treated with an excess of bromine in carbon tetrachloride. A work-up and analysis as described under *General comments* gave the following results: 10 mmole $PhHgCCl_2Br$/10 mmole PhHgCl reaction: bromotrichloromethane, 70%; dibromodichloromethane, 3%; bromobenzene, 72%; 7.5 mmoles $PhHgCCl_2Br$/5 mmoles PhHgCl: bromotrichloromethane, 68%; dibromodichloromethane, 4%.

Reaction of phenyl(bromodichloromethyl)mercury with p-tolylmercuric chloride

Using the procedure described above, 6.54 g (0.02 mole) of *p*-tolylmercuric chloride (m.p. 238–239°, prepared by the reaction of mercuric chloride with di-*p*-tolylmercury in benzene) and 8.82 g (0.02 mole) of phenyl(bromodichloromethyl)mercury in benzene were heated for three hours at vigorous reflux. The crude, benzene soluble solid, m.p. 92–97° with residue, weighed 8.04 g. Recrystallization from hexane gave 4.66 g (57%) of white flakes, m.p. 120–122°. At approximately 150° the molten solid decomposed and resolidified (p-$CH_3C_6H_4HgCCl_3 \rightarrow p$-$CH_3C_6H_4HgCl$). p-Tolyl(trichloromethyl)mercury was identified by its analysis and spectroscopic properties. (Found: C, 23.18; H, 1.77; Cl, 25.29. $C_8H_7Cl_3Hg$ calcd.: C, 23.43; H, 1.72; Cl, 25.94%.) The NMR spectrum (in $CDCl_3$) showed the phenyl protons at 7.14 ppm and the methyl protons as a singlet at 2.34 ppm downfield from internal tetramethylsilane (Varian A60). The infrared spectrum (KBr pellet) showed the following absorptions: 3070 m, 3050–3025 s, 2975 m, 2930 s, 2870 m, 1910 m, 1805 w, 1648 w, 1600 m, 1500 s, 1451 m, 1399 m, 1218 s, 1198 m, 1120 w, 1079 m, 1024 s, 798 s, 730 m, 720–650 s, 579 w, 482 s, cm^{-1}.

Reaction of phenyl(bromodichloromethyl)mercury with mercuric chloride

A mixture of 11.02 g (25 mmoles) of $PhHgCCl_2Br$ and 2.71 g (10 mmoles) of mercuric chloride (Mallinckrodt analytical reagent) in 40 ml of dry benzene was heated at reflux for 3 h. Filtration gave 8.19 g of white solid, m.p. 276–279° (mostly PhHgBr, m.p. 283–286°). The filtrate was evaporated to dryness to leave *ca.* 5 g of white solid, melting range 110–125°. Fractional crystallization of the latter from chloroform/hexane gave (*1*) 0.94 g, white powder, m.p. 150–155° (dec. to black liquid) and (2) 2.38 g, white crystalline solid, m.p. 138–143° (crude yield, 54%). Recrystallization of fraction (2) from chloroform/hexane gave pure bis(trichloromethyl)mercury (1.91 g, 44%), m.p. 140.5–143°; lit.[5] m.p. 140–142°. (Found: C, 5.29; Cl, 48.60; Hg, 45.88. C_2Cl_6Hg calcd.: C, 5.49; Cl, 48.64; Hg, 45.87%.) The IR spectrum (KBr) showed bands at 779 m, 720 vs, 689 (sh) and 648 m, cm^{-1}.

Thin-layer chromatographic analysis of fraction (*1*) demonstrated the presence of phenylmercuric bromide and another mercury-containing compound. Its IR spectrum showed bands at 1475 w, 1430 w, 1018 w, 994 w, 755 m, 721 (sh), 712 s, 690 (sh) and 653 m, cm^{-1}. Attempts to separate the latter from phenylmercuric bromide by fractional crystallization failed, and, therefore, the mixture was analyzed by brominolysis. This analysis indicated the presence of bromotrichloromethane as well as of bromobenzene, and from the quantity of the former a yield of CCl_3–Hg groups, presumably present as CCl_3HgCl, of 18% was calculated.

Reaction of phenyl(bromodichloromethyl)mercury with bis(trichloromethyl)mercury

A mixture of 1.59 g (3.61 mmoles) of phenyl(bromodichloromethyl)mercury and 1.56 g (3.58 mmoles) of bis(trichloromethyl)mercury in 15 ml of benzene was heated at reflux for 3 h. Filtration gave phenylmercuric bromide (1.1 g, 85%, m.p. 277–280°). The filtrate was evaporated to dryness, leaving 2.02 g of white solid whose recrystallization from chloroform/hexane gave (*1*) 0.5 g, m.p. 140° partial, remainder at 170–175°; (*2*) 0.7 g, m.p. 137–142°; (*3*) gummy residue. Fraction (*2*) was unconverted bis(trichloromethyl)mercury (by IR, TLC and m.p.). TLC analysis and the infrared spectrum showed fraction (*1*) to be a mixture of PhHgBr and CCl_3HgCl similar to that obtained in the previous experiment.

Reaction of phenyl(bromochloromethyl)mercury with phenylmercuric chloride

A mixture of 4.06 g (10 mmoles) of phenyl(bromochloromethyl)mercury[13] and 1.56 g (5 mmoles) of phenylmercuric chloride in 17 ml of dry chlorobenzene was stirred and heated at reflux under nitrogen for 34 h. (The b.p. of chlorobenzene is 131°). As mentioned in the discussion, it was possible to follow the progress of the reaction by infrared spectroscopy. Phenylmercuric halide, m.p. 281–284° (*i.e.*, mostly the bromide), 2.37 g, was filtered. The filtrate was analyzed for $CHCl_2$ groups by brominolysis and subsequent GLPC analysis (at 76°) of the bromodichloromethane formed. A $PhHgCHCl_2$ yield of 79% was indicated.

Competition of phenyl(bromodichloromethyl)mercury for an excess of cyclohexene and p-tolylmercuric chloride

A mixture of 4.41 g (0.01 mole) of phenyl(bromodichloromethyl)mercury, 9.82 g (0.03 mole) of *p*-tolylmercuric chloride and 2.70 g (0.033 mole) of cyclohexene in 150 ml of 1,2-dimethoxyethane (freshly distilled under nitrogen from potassium) was stirred and heated at reflux under nitrogen for 2 h. During this time the homogeneous reaction mixture turned pale yellow; no solid precipitated throughout the course of the reaction. The reaction mixture was allowed to cool to room temperature. The internal standard (0.7712 g of 1,2,4-trichlorobenzene) was added directly, and the crude mixture was analyzed by GLPC. 7,7-Dichloronorcarane (59.2%) was identified by its GLPC retention time and by the infrared spectrum of a collected sample.

The reaction mixture then was evaporated to dryness at reduced pressure, leaving 12.94 g of pale yellow residue which softened at 80° in the m.p. tube. To the residue was added 300 ml of chloroform; the slurry was cooled to −70° and filtered, giving 11.25 g of white, flaky solid, m.p. 217° (with residue) and a pale yellow filtrate. After evaporation of this filtrate to dryness under reduced pressure, 1.28 g of crude *p*-tolyl(trichloromethyl)mercury, m.p. 113° with residue, remained. The crude product was recrystallized from hexane, affording 0.68 g (first and second crops), m.p. 120–122°, and a third crop, 0.21 g, with m.p. 85° (softens, leaving residue). The yield of *p*-tolyl(trichloromethyl)mercury thus isolated is 16.6%.

Thermolysis of phenyl(dibromochloromethyl)mercury in the presence of phenylmercuric chloride and cyclohexene

Into a 50 ml three-necked flask equipped with a magnetic stirring unit and a reflux condenser topped with a nitrogen inlet tube was charged 2.42 g (5 mmoles) of phenyl(dibromochloromethyl)mercury[4], 2.35 g (7.5 mmoles of phenylmercuric chloride, 0.62 g (7.5 mmoles) of cyclohexene and 15 ml of benzene. The reaction mixture was stirred and heated at reflux for 3 h. Phenylmercuric halide (4.11 g, m.p. 265–269°) was removed by filtration. The filtrate was distilled at 0.1 mm (pot temperature to 80°) into a receiver at −78°. GLPC analysis at 155° showed the presence of 7-bromo-7-chloronorcarane (67%) and 7,7-dichloronorcarane (5%). Both products were identified by comparison of their GLPC retention times and their infrared spectra with those of authentic samples[9].

Thermolysis of phenyl(tribromomethyl)mercury in the presence of phenylmercuric chloride and cyclohexene

A similar experiment was carried out with 5 mmoles of $PhHgCBr_3$[4], 7.5 mmoles each of phenylmercuric chloride and cyclohexene, and 15 ml of benzene. GLPC analysis of the filtrate at 154° showed the presence of 7,7-dibromonorcarane (59%) and 7-bromo-7-chloronorcarane (5%). Both products were identified by comparison of their GLPC retention times and infrared spectra with those of authentic samples[9].

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