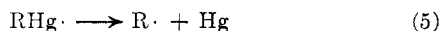
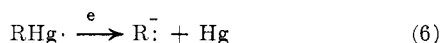


electron transfer from electrode to cation (eq 2).^{4b} In any case, several possible fates await the organomercury radical produced at a platinum electrode.

As the second bond dissociation energy of diorganomercury compounds is thought to be very low (the bond dissociation energy of the methylmercury radical is approximately 7 kcal/mole⁷ and that of phenyl- or benzylmercury radical will be lower⁸), dissociation 5



would be favored. Moreover, in the polarographic study of organomercuric salts^{4b} it is observed that the organomercury radical is reduced further to form carbanion and mercury (eq 6). However, the previous



observations^{5a,d} and an experiment of ours⁹ have shown that during the electrolysis of organomercuric salts the disproportionation reaction of organomercury radicals occurs predominantly to form diorganomercury compounds and mercury, and that reactions 5 and 6 can participate to a small extent only.

On the other hand, the present studies have shown that, when the reaction is carried out in the presence of carbon tetrachloride, the organomercury radical, especially phenyl- and cyclohexylmercury radical, abstracts predominantly the chlorine atom to form organomercuric chloride (eq 4), and the disproportionation reaction (eq 3) is suppressed. Although the benzylmercury radical can also abstract the chlorine atom to some extent, the disproportionation reaction is predominant. The fate of trichloromethyl radical is not established.

Finally, it is not clear why the reduction of phenylmercuric cation by means of ferrocene^{6b} furnishes the phenyl radical (eq 5) and the reduction by chromous ion¹⁰ or electrolytic method does not. At present it is not certain as well why the benzylmercury radical does not abstract the chlorine atom strongly.

Experimental Section

Materials.—Methanol was refluxed in the presence of calcium oxide and was purified by fractional distillation. Carbon tetrachloride and phenylmercuric acetate (mp 149°) were commercial products. Phenylmercuric chloride (mp 251°),¹¹ diphenylmercury (mp 125°),¹² benzylmercuric acetate (mp 126°),¹³ benzylmercuric chloride (mp 103°),¹³ dibenzylmercury (mp

(7) (a) C. M. Laurie and L. H. Long, *Trans. Faraday Soc.*, **53**, 1431 (1957); (b) S. J. U. Price and A. F. Trotman-Dickenson, *ibid.*, **53**, 939 (1957); (c) B. G. Gowenlock, J. C. Polanyi, and E. Warhurst, *Proc. Roy. Soc. (London)*, **A218**, 264 (1953).

(8) The average bond dissociation energy of dialkylmercury compounds decreases with increasing stability of the alkyl radical: B. G. Gowenlock, R. M. Haynes, and J. R. Majer, *Trans. Faraday Soc.*, **58**, 1905 (1962).

(9) The electrolysis of phenylmercuric acetate in methanol leads to a quantitative production of diphenylmercury and mercury; it does not produce benzene or biphenyl as would be expected if reactions 5 or 6 occur (a small amount of benzene was detected by ultraviolet spectroscopy).

(10) R. J. Ouellette and B. G. van Leuwen, *J. Org. Chem.*, **30**, 3967 (1965).

(11) A. N. Nesmeyanov, *Ber.*, **62**, 1013 (1929).

112°),¹³ cyclohexylmercuric acetate (mp 92°),¹⁴ cyclohexylmercuric chloride (mp 163°),¹⁵ and dicyclohexylmercury (mp 78°)¹⁵ were prepared according to known procedures.

Electrolysis of Phenylmercuric Acetate.—The electrolysis was carried out by using two platinum plate electrodes (15 × 20 mm²), of which a space was 4 mm. At the beginning of the electrolysis a potential of 150 v produced a current of 0.01 amp. This of course fell off as the concentration of the phenylmercuric salt in the solution decreased. In order to maintain the current (0.01 amp), voltage was gradually shifted from 150 to 1000 v. A solution of phenylmercuric acetate (3.37 g, 0.01 mole) and carbon tetrachloride (30 ml) in methanol (60 ml) was electrolyzed in a nitrogen atmosphere for 13 hr. During this time, the internal temperature remained between 10 and 15°, and a white crystal was formed. Filtration of the reaction mixture afforded 0.75 g of solid (mp 253–255°). This material was identified as phenylmercuric chloride by mixture melting point measurement.

The clear filtrate was distilled at atmospheric pressure. After removal of methanol and carbon tetrachloride, the distillation residue was separated by fractional crystallization. It consisted of 0.85 g of phenylmercuric acetate, 0.46 g of diphenylmercury, and 0.46 g of phenylmercuric chloride. Phenylmercuric acetate was isolated owing to its solubility in hot water. The latter two compounds were separated by fractional crystallization from ethanol. Phenylmercuric acetate and diphenylmercury were identified by mixture melting point measurements.

The mercury deposited to cathode was dissolved in nitric acid and titrated (0.41 g).¹⁶

Electrolysis of Benzylmercuric Acetate.—A solution of benzylmercuric acetate (3.51 g, 0.01 mole) and carbon tetrachloride (30 ml) in methanol (60 ml) was electrolyzed at 7–12° for 13 hr (0.01 amp, 100–200 v). The resulting solution was worked up as above to give mercury (0.50 g), benzylmercuric acetate (1.02 g), benzylmercuric chloride (0.05 g), and dibenzylmercury (0.87 g). The latter two compounds were separated by fractional crystallization from carbon tetrachloride. These products were identified by mixture melting point measurements.

Electrolysis of Cyclohexylmercuric Acetate.—A solution of cyclohexylmercuric acetate (3.43 g, 0.01 mole) and carbon tetrachloride (30 ml) in methanol (60 ml) was electrolyzed at 7–10° for 13 hr (0.01 amp, 100–250 v). The resulting solution was distilled at atmospheric pressure. After removal of methanol and carbon tetrachloride, the distillation residue was separated by a combination of column and thin layer chromatography (benzene on silica gel). Dicyclohexylmercury (0.11 g), cyclohexylmercuric chloride (1.05 g), and cyclohexylmercuric acetate (0.49 g) were isolated. These products were identified by mixture melting point measurements. The amount of mercury was 0.40 g.

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(13) P. Wolff, *Ber.*, **46**, 64 (1913).

(14) M. C. Sneed and J. L. Maynard, *J. Am. Chem. Soc.*, **44**, 2946 (1922).

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Halomethyl-Metal Compounds. XI. The Reaction of Phenyl(trihalomethyl)mercury Compounds with Tertiary Amines¹

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The recent communication by Parham and Potoski⁴ concerning the reaction of phenyl(trichloromethyl)-

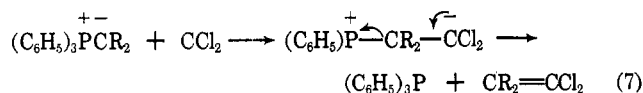
(1) Part X: D. Seyferth, J. M. Burlitch, H. Dertouzos, and H. D. Simons, Jr., *J. Organometal. Chem.*, in press.

(2) Alfred P. Sloan Foundation Fellow, 1962–1966.

(3) (a) National Institutes of Health Predoctoral Fellow, 1963–1966; (b) National Institutes of Health Predoctoral Fellow, 1964–1966.

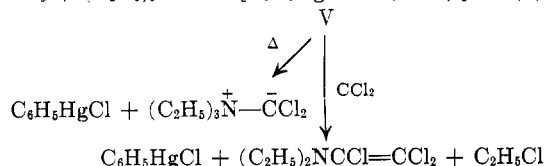
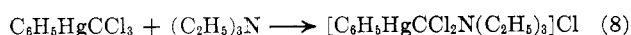
(4) W. E. Parham and J. R. Potoski, *Tetrahedron Letters*, 2311 (1966).

BuOK reactions, and the reactions of phosphorus ylides with dihalocarbenes are believed to proceed *via* betaine intermediates similar to IV (eq 7).¹¹ We



are not aware of any precedent for the reaction indicated by eq 6, but suggest that such stabilization of the betaine IV is a possibly favorable alternative to β elimination of triethylamine. The intermediacy of CCl_2 (or of a "dichlorocarbenoid" reagent) in the $\text{C}_6\text{H}_5\text{HgCCl}_3 + (\text{C}_2\text{H}_5)_3\text{N}$ system was confirmed by allowing the mercurial and amine to react in benzene at reflux in the presence of cyclohexene. The products formed were 7,7-dichloronorcarane (13%) and $(\text{C}_2\text{H}_5)_2\text{NCCl}=\text{CCl}_2$ (13%).

The formation of an intermediate ammonium salt V, *i.e.*, attack by the amine at carbon or chlorine of the CCl_3 group, also was considered (eq 8). Attempts to



prepare V or $[\text{C}_6\text{H}_5\text{HgCCl}_2\text{N}(\text{C}_2\text{H}_5)_3]\text{Br}$ (*via* $\text{C}_6\text{H}_5\text{HgCCl}_2\text{Br}$) were not successful and led only to formation of unstable oils. However, $[\text{C}_6\text{H}_5\text{HgCHClN}(\text{C}_2\text{H}_5)_3]\text{Br}$ was obtained from the reaction of phenyl(bromochloromethyl)mercury with triethylamine at room temperature as a stable, crystalline salt, mp 164° dec. This ammonium salt was thermally stable in refluxing benzene, and attempts to cause its reaction with CCl_2 (*via* $\text{C}_6\text{H}_5\text{HgCCl}_2\text{Br}$) gave inconclusive results.

The question of the mechanism of the reaction between $\text{C}_6\text{H}_5\text{HgCCl}_3$ and triethylamine which leads to formation of N,N-diethyltrichlorovinylamine can by no means be considered resolved. In terms of available evidence, the sequence of eq 2-6 seems plausible, but the low yields of the trichlorovinylamine and the formation of tars in large quantity suggest that other competing reactions of unknown nature are occurring.

Since the $\text{C}_6\text{H}_5\text{HgCCl}_3 + (\text{C}_2\text{H}_5)_3\text{N}$ reaction has no preparative utility, the product, $(\text{C}_2\text{H}_5)_2\text{NCCl}=\text{CCl}_2$, being more easily prepared by the procedure of Speziale and Freeman,¹² and because of the poor yields and the intractable nature of the reaction mixtures, a more detailed study of the interaction of tertiary amines with phenyl(trihalomethyl)mercury compounds was not undertaken. The reaction of phenyl(trichloromethyl)mercury with tri-*n*-butylamine was studied briefly to the extent that it was determined that $(n\text{-C}_4\text{H}_9)_2\text{NCCl}=\text{CCl}_2$ had been formed in low yield.

Experimental Section

General Comments.—All reactions were carried out under an atmosphere of prepurified nitrogen. Phenyl(trichloromethyl)mercury was prepared by the method of Schweizer and O'Neill,¹³

but high-speed stirring was used. The preparation of phenyl(bromodichloromethyl)mercury has been described in part I.¹⁴

Reaction of Phenyl(trichloromethyl)mercury with Triethylamine.—In a typical experiment, a dry, 50-ml, three-necked flask equipped with a reflux condenser, internal thermometer, and a magnetic stirring assembly was charged with 3.96 g (10 mmoles) of phenyl(trichloromethyl)mercury, evacuated for 2 hr, and refilled with prepurified nitrogen. Then 1.02 g (10 mmoles) of triethylamine (Eastman, dried over KOH pellets and distilled from barium oxide) and 10 ml of dry benzene were added using a syringe. No reaction appeared to occur when the mixture was stirred at room temperature for 1 hr. The reaction mixture then was heated to reflux. At 50° the solution began to turn faintly yellow and at 80° a definite, brown, viscous layer had separated to the bottom. After the mixture had been heated at reflux for 4 hr, thin layer chromatography¹⁴ showed that the starting mercurial had been consumed completely. At this time the solution was black. The reaction mixture was trap-trap distilled at 0.02 mm (pot temperature up to 80°) into a receiver at -78°. The black pot residue was triturated with 95% ethyl alcohol and filtered, giving a pale brown solid, mp 253-256°. This solid, crude phenylmercuric chloride, was recrystallized from dioxane to give 2.60 g (83%) of phenylmercuric chloride, mp 255-257°. Glpc analysis of the distillate (MIT isothermal gas chromatograph, 10-ft analytical column, G.E. SE-30 silicone rubber gum on Chromosorb P, jacket at 30°, 10 psi of helium, *o*-dichlorobenzene internal standard) showed the presence of ethyl chloride and chloroform, which were identified by comparison of their glpc retention times and their infrared spectra with those of authentic samples. Glpc analysis at 155° established the presence of a higher boiling compound (14% yield) which was characterized as N,N-diethyltrichlorovinylamine by its elemental analysis, infrared and nmr spectra, and refractive index. It had n_D^{25} 1.4856 *vs.* lit.¹² n_D^{25} 1.4850. Its infrared spectrum matched that reported by Speziale and Freeman¹² exactly. Its nmr spectrum (CCl_4) showed a three-proton triplet centered at 1.08 ppm and a two-proton quartet centered at 2.76 ppm downfield from internal tetramethylsilane.

Anal. Calcd for $\text{C}_8\text{H}_{10}\text{Cl}_3\text{N}$: C, 35.58; H, 4.98. Found: C, 35.99; H, 5.31.

The identical reaction performed in 1,2-dimethoxyethane (DME) instead of benzene afforded the same product in 16% yield. Similarly, 10 mmoles of $\text{C}_6\text{H}_5\text{HgCCl}_3$ reacted with 44 mmoles of triethylamine in refluxing benzene for 12 hr to give $(\text{C}_2\text{H}_5)_2\text{NCCl}=\text{CCl}_2$ in 18% yield. When 20 mmoles of the mercurial was heated at reflux in pure triethylamine for 12 hr, a 15% yield of the trichlorovinylamine was obtained.

In another experiment, a dry, 50-ml, three-necked flask equipped with a reflux condenser, magnetic stirring assembly, and a pressure-equalizing dropping funnel was charged with 10 mmoles of phenyl(trichloromethyl)mercury. Twenty milliliters of dry benzene was added and the solution was heated to reflux. A solution of 43 mmoles of triethylamine in 5 ml of benzene was added dropwise over a 30-min period. The reaction mixture was heated for 15 hr after the addition was complete. The usual work-up procedure showed that the trichlorovinylamine had been formed in 23% yield.

Reaction of Phenyl(trichloromethyl)mercury with Triethylamine in the Presence of Cyclohexene.—Using the procedure described initially in the section above, a solution of 10 mmoles of $\text{C}_6\text{H}_5\text{HgCCl}_3$, 11 mmoles of triethylamine, and 30 mmoles of cyclohexene in 20 ml of benzene was heated at reflux with stirring under nitrogen for 3 hr. After 15 min of reflux the mixture was brown, after 3 hr it was black. Work-up as before and glpc analysis at 145° showed the presence of 7,7-dichloronorcarane (13%) and N,N-diethyltrichlorovinylamine (13%). The products were identified by comparison of their glpc retention times and their infrared spectra with those of authentic samples.

Reaction of Phenyl(trichloromethyl)mercury with Tri-*n*-Butylamine.—A solution of 30 mmoles of $\text{C}_6\text{H}_5\text{HgCCl}_3$ and 34 mmoles of tri-*n*-butylamine (Eastman, dried over KOH) in 25 ml of dry benzene was heated at reflux with stirring under nitrogen for 5 hr. Within 15 min the solution had turned orange and a white, flakey precipitate had appeared. After 5 hr the reaction mixture was deep brown. Glpc analysis (4-ft analytical column, 150°) showed the presence of two compounds boiling higher than the solvent. Upon continued heating, the more volatile of these disappeared. The remaining compound was

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(13) E. E. Schweizer and G. J. O'Neill, *J. Org. Chem.*, **28**, 851 (1963).

(14) D. Seyferth and J. M. Burlitch, *J. Organometal. Chem.*, **4**, 127 (1965).

collected for characterization by preparative glpc. Its nmr spectrum (CCl_4) showed characteristic $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ absorption, *i.e.*, complex multiplets centered at 2.66, 1.32, and 0.91 ppm downfield from TMS. Its infrared spectrum (pure liquid) showed bands at 2965 (s), 2940 (s), 2870 (m), 1680 (m), 1610 (w), 1460 (m), 1377 (m), 1193 (s), 1104 (s), 948 (m), 913 (m), 874 (w), 831 (w), 806 (w), and 762 (s), cm^{-1} . The band at 1610 cm^{-1} can be identified as $\nu_{\text{C}=\text{C}}$,¹² and the band at 948 cm^{-1} as $\nu_{\text{C}-\text{N}}$.¹² The mass spectrum of the product showed molecular ion peaks at m/e 257, 259, 261, and 263 in a ratio of 27:25:9:1 (calcd: 257, 259, 261, 263 in a ratio of 27:27:9:1). The other major peaks occurred at m/e 222, 224, 226 (9:6:1 ratio), corresponding to $\text{M} - \text{Cl}$; 214, 216, 218, 220 (ratio 27:26:9:1), corresponding to $\text{M} - \text{C}_3\text{H}_7$; 180, 182, 184 (9:6:1 ratio), corresponding to $\text{M} - \text{C}_2\text{H}_5$ and Cl ; 172, 174, 176, 178 (27:27:9:1), corresponding to $\text{M} - \text{C}_3\text{H}_7$ and C_3H_5 . Although a satisfactory combustion analysis could not be obtained, the data above are consistent with the identification of the product as $(\text{C}_6\text{H}_5)_2\text{NCCl}=\text{CCl}_2$. This compound was formed in this reaction in 20% yield; phenylmercuric chloride was produced in 80% yield.

Reaction of Phenyl(bromochloromethyl)mercury with Triethylamine at Room Temperature.—A 25-ml flask was charged with 1.34 g (3.3 mmoles) of $\text{C}_6\text{H}_5\text{HgCHBrCl}$ ¹⁵ (mp 65–66°), 1.35 g (13.2 mmoles) of triethylamine, and 4 ml of dry benzene. After the mixture had been stirred for 10 min, a pale yellow oil separated to the bottom of the flask. After 1 hr, the oil apparently had solidified. The reaction mixture was evaporated under reduced pressure, leaving 1.60 g of pale yellow solid, mp 142–160° dec. Recrystallization from 1:1 ether–THF afforded 1.30 g (48%) of a white, powdery material, which melted at 162° with decomposition. This compound was characterized as $[\text{C}_6\text{H}_5\text{HgCHCl}(\text{C}_2\text{H}_5)_3]\text{Br}$ by its elemental analysis and its spectroscopic properties, and by synthesis of its tetraphenylborate derivative.

Anal. Calcd for $\text{C}_{13}\text{H}_{21}\text{BrClNHg}$: C, 30.78; H, 4.17; halogen, 30.75 mg of sample should give 20.07 mg of AgX ; Hg, 39.54; N, 2.76. Found: C, 30.61; H, 3.92; halogen, 30.75 mg of sample gave 20.75 mg of AgX ; Hg, 38.42; N, 2.65.

The infrared spectrum (KBr pellet) of the compound showed absorptions at 3060–3000 (w), 2980 (m), 2950 (w), 1578 (w), 1480–1450 (s), 1395 (m), 1300 (w), 1278 (w), 1189 (w), 1158 (s), 1105 (w), 1078 (w), 1054 (w), 1030 (m), 1004 (m), 902 (w), 795 (m), 738 (s), 708 (s), and 620 (m), cm^{-1} . Its nmr spectrum (CDCl_3) showed phenyl absorption from 7.82 to 6.85, a one-proton singlet at 5.50, a six-proton quartet at 3.52, and a nine-proton triplet at 1.38 ppm downfield from TMS.

The tetraphenylborate was prepared by treating 0.507 g (1 mmole) of this product with 0.350 g (1 mmole) of sodium tetraphenylborate in 5 ml of chloroform. After 15 min the reaction flask was filled with solid. Filtration afforded 0.83 g of white, flakey material, mp 170° dec. Recrystallization from methylene chloride and from 1:1 ether–THF gave 0.71 g of white flakes, mp 164° dec.

Anal. Calcd for $\text{C}_{37}\text{H}_{41}\text{ClNBHg}$: C, 59.52; H, 5.54; Cl, 4.75; N, 1.88. Found: C, 58.91; H, 5.59; Cl, 4.72; N, 2.12.

The infrared spectrum (KBr) of this derivative showed absorptions at 3070–2960 (w), 1580 (w), 1475 (s), 1430 (m), 1390 (w), 1270 (w), 1190 (m), 1158 (m), 1069 (w), 1032 (w), 1000 (w), 925–890 (w), 855 (w), 778 (w), 743 (s), 711 (s), and 605 (m) cm^{-1} .

Reaction of Phenyl(trichloromethyl)mercury with Triethylamine in Acetone Solution.—A dry, 50-ml, three-necked flask fitted with a reflux condenser and a magnetic stirring assembly was charged with 10 mmoles of $\text{C}_6\text{H}_5\text{HgCCl}_3$. Ten milliliters of anhydrous acetone and 12 mmoles of triethylamine were added and the reaction mixture was heated at reflux with stirring. Within 5 min a white precipitate formed, but this redissolved within 1 hr. The reaction mixture was heated for 22 hr; at that time the solution was yellow-orange in color and thin layer chromatography¹⁴ showed that the starting mercurial had been consumed completely. The reaction mixture was distilled at 0.02 mm (pot temperature up to 80°) into a receiver at –78°. The clear distillate was analyzed by glpc (chlorobenzene internal standard); triethylamine, acetone, and chloroform (80%) were found to be present. At best only a trace (<1%) of dimethyl-

(trichloromethyl)carbinol was present. The distillation residue, a brown oil, contained some white crystals which were identified as diphenylmercury by thin layer chromatography.

The $\text{C}_6\text{H}_5\text{HgCCl}_3 + (\text{C}_2\text{H}_5)_3\text{N} + \text{acetone}$ reaction is more complicated than is apparent at first sight. Firstly, dimethyl-(trichloromethyl)carbinol is formed in only trace yield, whereas in the displacement of CCl_3^- from $\text{C}_6\text{H}_5\text{HgCCl}_3$ by sodium iodide in acetone, this alcohol is formed in substantial yield.⁹ Furthermore, in another experiment which was interrupted at a stage just before precipitation of the white solid mentioned above by distillation of all volatiles under vacuum at room temperature, it was established that triethylamine consumption had been less than 20%, but that the chloroform yield already was 50%.

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A Novel Ketone Reduction by Diimide

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We wish to report an example of the reduction of ketones to alcohols by diimide ($\text{NH}=\text{NH}$). Even more surprising, one ketone (1) retained a carbon-carbon double bond which is generally reduced by diimide.^{1,2} Carbonyl-group reduction by this reagent has been reported to occur with benzaldehyde,³ but ketones were found to be unreactive.

While the reactions of benzophenone were being compared with those of 5H-dibenzo[*a,d*]cyclohepten-5-one (1) and 10,11-dihydro-5H-dibenzo[*a,d*]cyclohepten-5-one (2), it was noted that tosylhydrazone formation did not occur with these ketones under conditions which caused benzophenone to react. The preparation of these tosylhydrazones has recently been reported without experimental details.⁴ When the reaction was forced (refluxing ethanol for 15 hr), a nitrogen-free product was obtained in each case; no tosylhydrazone was isolated. The infrared spectrum of the product from ketone 1 showed sulfone bands (1310 and 1140 cm^{-1}) and the nmr spectrum (Experimental Section) suggested structure 3 for the sulfone. An independent synthesis of compound 3 from 5-chloro-5H-dibenzo[*a,d*]cycloheptene and sodium *p*-toluenesulfinate confirmed this assignment. Similarly, the product from ketone 2 was found to be the corresponding sulfone, 10,11-dihydro-5H-dibenzo[*a,d*]cyclohepten-5-yl *p*-tolyl sulfone (4).

The most reasonable mechanism for the formation of sulfone 3 is reduction of ketone 1 to alcohol 5, which then reacts with *p*-toluenesulfonic acid to form the product. The reducing agent, diimide, is provided by

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