$$RHgOAc + e \Longrightarrow RHg \cdot + \neg OAc$$
 (1)

$$RHgOAc \Longrightarrow RHg^{+} + {}^{-}OAc$$
 (2)

$$\begin{array}{c} & \overset{e}{\longrightarrow} \operatorname{RHg} \cdot \\ & \overset{\operatorname{RHg}}{\longrightarrow} \operatorname{R}_{2}\operatorname{Hg} + \operatorname{Hg} \end{array} \tag{3} \\ \operatorname{RHg} \cdot - & \overset{\operatorname{CCl}_{4}}{\longrightarrow} \operatorname{RHgCl} + \cdot \operatorname{CCl}_{3} \end{aligned} \tag{4}$$

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 phenylor benzylmercury radical will be lower⁸), dissociation 5

$$RHg \cdot \longrightarrow R \cdot + Hg \tag{5}$$

would be favored. Moreover, in the polarographic study of organomercuric salts46 it is observed that the organomercury radical is reduced further to form carbanion and mercury (eq 6). However, the previous

$$RHg \cdot \xrightarrow{e} R = Hg \qquad (6)$$

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 Phenylmercuric chloride (mp 251°), ii diphenylproducts. mercury (mp 125°), 12 benzylmercuric acetate (mp 126°), 13 benzylmercuric chloride (mp 103°), 18 dibenzylmercury (mp $112^\circ),^{13}$ 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 imes 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 \mathbf{g}), benzylmercuric chloride (0.05 \mathbf{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

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)-

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 - (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.
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mercury with secondary amines prompts us to report the results of a brief exploratory study of the reaction of phenyl(trihalomethyl)mercury compounds with triethyl- and tri-n-butylamine.

Previous studies of reactions of tertiary amines with dichlorocarbene (generated via CHCl₃ + t-BuOK) have been reported by Saunders and Murray.⁵ The formation of the products they obtained, diethylformamide (15%) and N,N-diethyl- α -chloropropionamide (12%), was rationalized by Scheme I in which the first intermediate was the nitrogen ylide I.

SCHEME I

$$(C_{2}H_{5})_{3}N + CHCl_{3} + t\text{-BuOK} \longrightarrow (C_{2}H_{5})_{3}NCCl_{2}$$

$$I$$

$$I$$

$$CH_{2} = CH_{2} + (C_{2}H_{5})_{2}NCHCl_{2}$$

$$\downarrow H_{2}O$$

$$(C_{2}H_{5})_{2}NCHO$$

$$rearrangement + (C_{2}H_{5})_{2}NCCl_{2}CH_{2}CH_{3}$$

$$II$$

$$\Pi \xrightarrow{\text{Cl}^+(via \text{ CHCl}_3 + t \cdot \text{BuOK})} (C_2H_5)_2\text{NCCl}_2\text{CHClCH}_3 \xrightarrow{\text{H}_2\text{O}} (C_2H_5)_2\text{NCOCHClCH}_3$$

Since phenyl(trihalomethyl)mercury compounds have been shown to be very effective CX_2 transfer agents at 80° , a study of their reactions with tertiary amines seemed of interest. In our initial experiments we found that equimolar amounts of triethylamine and phenyl(trichloromethyl)mercury reacted in refluxing benzene solution during 4 hr to give phenylmercuric chloride, ethyl chloride, and N,N-diethyltrichlorovinylamine (eq 1). Several experiments were carried

$$2C_6H_5H_gCCl_3 + (C_2H_5)_3N \longrightarrow (C_2H_5)_2NCCl = CCl_2 + C_2H_5Cl + 2C_6H_5H_gCl \quad (1)$$

out in which temperature, solvent, and reagent ratio were varied. Table I shows the results of these studies. The yields of N,N-diethyltrichlorovinylamine

Table I

EFFECT OF REACTANT CONCENTRATION,
SOLVENT, TIME, AND TEMPERATURE ON THE
YIELD OF N,N-DIETHYLTRICHLOROVINYLAMINE

Yield.

Mmoles of C ₆ H ₆ - HgCCl ₃	$Mmoles^a$ of $(C_2H_b)_3N$	Solvent	$_{ m remp}$, $_{ m cC}$	Time,	$\%$, of $(C_2H_5)_2$ - NCCl= CCl ₂
10	3.2	C_6H_6	80	3	10
10	10	C_6H_6	80	3	14
20	90	$\mathrm{C_6H_6}$	80	1	12
20	90	$\mathrm{C_6H_6}$	80	4	20
20	90	$\mathrm{C_6H_6}$	80	17	20
10	11	$_{\mathrm{DME}}$	85	4	16
20	\mathbf{Neat}	$({ m C_2H_5})_{ m 3}{ m N}$	80	4	15
10	45^b	$\mathrm{C_6H_6}$	80	4	23
10	10	$\mathrm{C_6H_6}$	25	4	0

^a Unless otherwise specified, the reactions were carried out by mixing the reactants directly and heating the solution to reflux. ^b This reaction was performed by adding a benzene solution of the amine dropwise to the refluxing solution of C₆H₅HgCCl₃.

were calculated on the assumption that 2 moles of the mercurial would be required to form 1 mole of the trichlorovinylamine. The highest yield of $(C_2H_5)_2$ -NCCl=CCl₂ obtained was 23%. In all of these reactions a thick, viscous, oily layer separated to the bottom of the flask and began to decompose, undergoing color changes from orange to brown within the first 30 min, and other reaction products were black tars, some metallic mercury, and some chloroform.

The reaction of phenyl(bromodichloromethyl)mercury with triethylamine in benzene at 80° also produced N,N-diethyltrichlorovinylamine, but its yield was only 5%. Ethyl bromide, as well as ethyl chloride, was detected. In the case of this mercurial, a heavier, oily layer separated within 5 min and appeared to decompose immediately.

Several mechanisms may be considered for the $C_6H_5HgCCl_3 + (C_2H_5)_3N$ reaction. Of these we favor the formal mechanistic sequence outlined by eq 2-6.

$$C_6H_5H_gCCl_3 + (C_2H_5)_3N \longrightarrow [C_6H_5H_gN(C_2H_5)_3]^+[CCl_3]^- \quad (2)$$

$$III \longrightarrow CCl_2 + C_6H_5HgCl + (C_2H_5)_3N$$
 (3)

$$(C_2H_5)_3N + CCl_2 \longrightarrow (C_2H_5)_3NCCl_2$$
 (4)

$$(C_2H_5)_3NCCl_2 + CCl_2 \longrightarrow (C_2H_5)_3NCCl_2CCl_2$$
 (5)

$$(C_{2}H_{5})_{2}N \xrightarrow{C} CCl_{2} \longrightarrow (C_{2}H_{5})_{2}NCCl = CCl_{2} + C_{2}H_{5}Cl (6)$$

$$H_{5}C_{2} Cl$$

Although phenyl(trichloromethyl)mercury is a CCl₂ source at 80°, such CCl₂ extrusion is quite slow.⁶ Thus it seems unlikely that a mechanism in which CCl2 released by the mercurial reacts with the amine is operative. On the other hand, the reactions of C₆H₅Hg-CX₂Br compounds with some substrates containing lone electron pair atoms (phosphorus, as in triphenylphosphine,⁷ and nitrogen, as in carbodiimides⁸) are so much more rapid than those which these mercurials undergo with olefins, that it is believed that a carbene mechanism is not involved in these cases. Instead, some sort of bimolecular reaction between the organomercury reagent and the phosphine or carbodiimide (the exact nature of which is unknown) was postulated. We have demonstrated the facile displacement of CX₃ from C₆H₅HgCX₃ compounds by nucleophiles such as iodide and thiocyanate ion.9 Thus the nucleophilic displacement of CCl₃⁻ by triethylamine as shown in eq 2 is quite possible. Evidence in favor of this process was obtained when the C₆H₅HgCCl₃ + (C₂H₅)₃N reaction was carried out in acetone solution; chloroform was obtained in 80% yield.10

Precedent exists for the reactions shown in eq 4 and 5. The ylide I, as mentioned above, has been postulated as an intermediate in the $R_3N + CHCl_3 + t$ -

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⁽¹⁰⁾ The $C_6H_6HgCCl_3 + (C_2H_6)_2NH$ reaction, when carried out in acetone, gave chloroform in 86% yield. Thus a reaction analogous to eq 2 can be considered for the initial step of the diethylamine reaction.

Notes

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

$$(C_{6}H_{5})_{3}\overset{+-}{P}CR_{2} + CCl_{2} \longrightarrow (C_{6}H_{5})\overset{+-}{P}CR_{2}\overset{\checkmark}{C}Cl_{2} \longrightarrow (C_{6}H_{5})_{3}P + CR_{2}\overset{\checkmark}{=}CCl_{2}$$
 (7)

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 CCl₂ (or of a "dichlorocarbenoid" reagent) in the $C_6H_5HgCCl_3 + (C_2H_5)_3N$ 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 $(C_2H_5)_2NCCl=CCl_2(13\%).$

The formation of an intermediate ammonium salt V, i.e., attack by the amine at carbon or chlorine of the CCl₃ group, also was considered (eq 8). Attempts to

 $C_6H_5HgCCl_3 + (C_2H_5)_3N \longrightarrow [C_6H_5HgCCl_2N(C_2H_5)_3]Cl \quad (8)$

$$CCl_3 + (C_2H_5)_3N \longrightarrow [C_6H_5H_gCCl_2N(C_2H_5)_3]Cl \quad (8)$$

$$V$$

$$Ccl_2$$

$$C_6H_5HgCl + (C_2H_5)_3N - CCl_2$$

$$C_6H_5HgCl + (C_2H_5)_2NCCl - CCl_2 + C_2H_6Cl$$

prepare V or [C₆H₅HgCCl₂N(C₂H₅)₃]Br (via C₆H₅Hg-CCl₂Br) were not successful and led only to formation of unstable oils. However, $[C_6H_5HgCHClN(C_2H_5)_3]Br$ 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 CCl₂ (via C₆H₅HgCCl₂Br) gave inconclusive results.

The question of the mechanism of the reaction between $C_6H_5HgCCl_3$ 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 C₆H₅HgCCl₃ + (C₂H₅)₃N reaction has no preparative utility, the product, $(C_2H_5)_2NCCl=CCl_2$, 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-C₄H₉)₂NCCl=CCl₂ 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-totrap 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^{25} D 1.4856 vs. lit. n^{25} D 1.4850. Its infrared spectrum matched that reported by Speziale and Freeman¹² exactly. Its nmr spectrum (CCl₄) showed a threeproton triplet centered at 1.08 ppm and a two-proton quartet centered at 2.76 ppm downfield from internal tetramethylsilane. Anal. Caled for C₆H₁₀Cl₈N: 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 C₆H₅HgCCl₃ reacted with 44 mmoles of triethylamine in refluxing benzene for 12 hr to give (C₂H₅)₂NCCl=CCl₂ 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 C₆H₅HgCCl₃, 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 C₆H₅HgCCl₃ 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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collected for characterization by preparative glpc. Its nmr spectrum (CCl₄) showed characteristic NCH₂CH₂CH₂CH₃ 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 PC-C, 12 and the band at 948 cm⁻¹ as ν_{C-N} . 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 M — Cl; 214, 216, 218, 220 (ratio 27:26:9:1), corresponding to M — C_3H_7 ; 180, 182, 184 (9:6:1 ratio), corresponding to M — C_3H_6 and Cl; 172, 174, 176, 178 (27:27:9:1), corresponding to M — C_3H_7 and C_3H_6 . Although a satisfactor of the statement of the st factory combustion analysis could not be obtained, the data above are consistent with the identification of the product as (C₄H₉)₂NCCl=CCl₂. 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 C₆H₅HgCHBrCl¹⁵ (mp 65-66°), 1.35 g (13.2 mmoles) of triethylamine, and 4 ml of dry benzene. 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 $[C_6H_5HgCHClN(C_2H_5)_3]Br$ by its elemental analysis and its spectroscopic properties, and by synthesis of its tetraphenylborate derivative.

Anal. Calcd for C13H21BrClNHg: 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 (CDCl₃) showed phenyl absorption from 7.82 to 6.85, a oneproton singlet at 5.50, a six-proton quartet at 3.52, and a nineproton 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, flakev 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. Caled for C₈₇H₄₁ClNBHg: 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)

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 C₆H₅HgCCl₃. 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 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 $C_6H_6HgCCl_3 + (C_2H_6)_3N + acetone reaction is more complicated than is apparent at first sight. Firstly, dimethyl-$ (trichloromethyl)carbinol is formed in only trace yield, whereas in the displacement of CCl₃-from C₆H₅HgCCl₃ 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 (NH=NH). Even more surprising, one ketone (1) retained a carboncarbon 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 ptoluenesulfinate 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-toluenesulfinic acid to form the product. The reducing agent, diimide, is provided by

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