

butyllithium (76 ml of a 1.65 M solution, 0.125 mole) in hexane. The reaction mixture was maintained at -100° while $4a^4$ (3.5 g, 0.025 mole) was added. The temperature of the mixture was allowed to warm slowly to -65° at which time the reaction mixture darkened and the temperature of the mixture rose approximately 25° . The mixture was allowed to warm to 30° and the tetrahydrofuran was removed. The reaction product was diluted with pentane (~ 50 ml) and filtered. Evaporation of the pentane (rotary evaporator) gave 4.5 g of oil. The infrared spectrum of the crude product showed it to contain no N,N-diethyl-1,2,2-trichlorovinylamine.⁴ Distillation of the crude reaction product gave, in addition to undistilled tar, 0.63 g (11% yield) of **5a** [bp $49-50^\circ$ at (0.15 mm), n_D^{25} 1.4704]. The picrate of the product melted at $134-136^\circ$ and did not depress the melting point of an authentic sample of the picrate of **5a**.

2. **N-Methyl-N-(3-methyl-2-butenyl)aniline (4b)**.—The crude product obtained from **4b** (2.62 g, 0.025 mole) as described in 1, above, was chromatographed on 120 g of alumina. Elution of the column with petroleum ether (bp $60-68^\circ$) gave 1.6 g of a liquid mixture. The spectra (infrared and nmr) indicated the possible presence of small amounts of N-methyl-N-phenyl-1,2,2-trichlorovinylamine.⁴ The composition of this fraction was not determined and positive identification of the vinylamine was not accomplished in repeated experiments.

Further elution of the column with 25% benzene-petroleum ether (bp $60-68^\circ$) gave 2.6 g of a liquid. The nmr spectrum showed it to be a mixture of **4b** (20% recovery) and **5b** (1.7 g, 26% yield). Treatment of the mixture with picric acid reagent

gave a picrate (mp $134-139^\circ$ and $143-145^\circ$ from ethanol) which did not depress the melting point when admixed with an authentic picrate of **5b**.

3. **N,N-Diphenyl-3-methyl-2-butenylamine (4c)**.—The crude product from **4c** (2.37 g, 0.01 mole) was chromatographed on alumina (110 g). Elution of the column with petroleum ether (bp $60-68^\circ$) afforded N-(2,2-dichloro-3,3-dimethylcyclopropylmethyl)-N,N-diphenylamine (**5c**, 2.35 g, 73% yield, mp $45-63^\circ$). The cyclopropane **5c** melted at $70-71^\circ$ (55% yield) after recrystallization from ethanol.

Reaction of N-Methyl-N-(3-methyl-2-butenyl)aniline (4b) with Ethyl Trichloroacetate and Sodium Methoxide.—Ethyl trichloroacetate (26.2 g, 0.137 mole) was added over a 10-min period to an ice-cooled, stirred mixture of **4b** (12.0 g, 0.068 mole), sodium methoxide (8.10 g, 0.150 mole) and pentane (100 ml, olefin free) under a dry nitrogen atmosphere. The mixture was allowed to warm to 30° and stir overnight, and was then washed with water (50 ml). The water extract was washed with ether (50 ml) and the combined organic layers were dried ($MgSO_4$). Evaporation of the solvent gave 18 g of dark oil. The oil was distilled and 6.40 g (53% recovery) of **4b** was collected [bp $68-95^\circ$ (0.03 mm), n_D^{25} 1.5442-1.5482]. The distillation pot residue was chromatographed on alumina (100 g) and the column was eluted with petroleum ether (bp $60-68^\circ$, 600 ml). There was obtained 3.23 g (18.4% yield) of N-(2,2-dichloro-3,3-dimethylcyclopropylmethyl)-N-methylaniline (**5b**). Distillation of this material through a short-path apparatus gave 2.15 g (12.2% yield) of **5b** [bp $93-95^\circ$ (0.01 mm), n_D^{25} 1.5560].

The Reaction of Allylamines with Phenyl(trichloromethyl)mercury¹

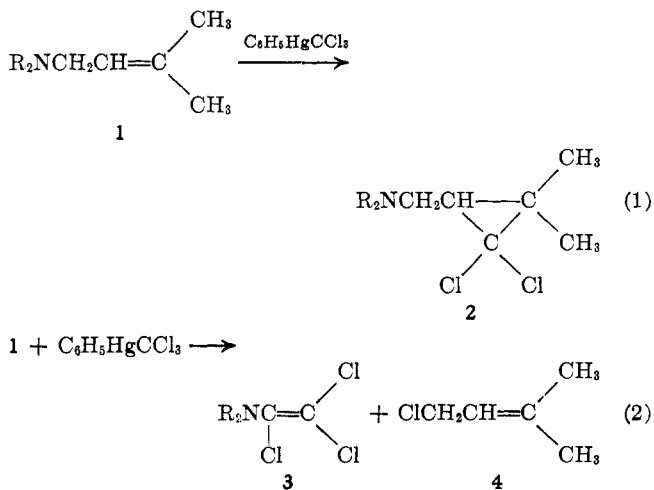
WILLIAM E. PARHAM AND JOHN R. POTOSKI²

School of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

Received August 9, 1966

The reaction of allylamines, in which the allyl chain contains at least four carbon atoms, with phenyl(trichloromethyl)mercury results in (a) cyclopropane formation and (b) a cleavage reaction leading to trichlorovinylamines. The yields of cyclopropanes increase as the basicity of the nitrogen atom is decreased, and the yields of vinylamines vary inversely with cyclopropane formation.

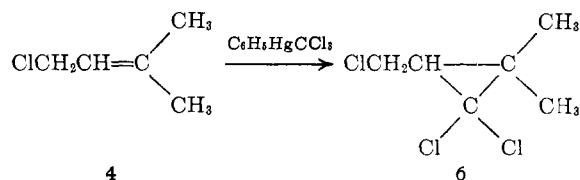
A study of the reaction of a series of acyclic butenylamines with phenyl(trichloromethyl)mercury (the Seyferth³ procedure for generating dichlorocarbene) establishes two principal reaction paths as shown in eq 1 and 2. Isoprene, the cyclopropanes derived by addition of dichlorocarbene to isoprene and to **4**, phenylmercuric chloride (90-100% yield), and chloroform are also reaction products.



The results of reaction of the amines (**1a-d**, 1 equiv) with phenyl(trichloromethyl)mercury (2 equiv) in boiling benzene (25-36 hr) are summarized in Table I.

It can be seen from Table I that the yield of cyclopropane **2** increases as the nucleophilic character or basicity of the nitrogen decreases and that the yield of vinylamine **3** varies inversely with cyclopropane formation. This observation is consistent with the conclusion that the nitrogen atom and the olefinic π bond compete for the electrophilic dichlorocarbene (or mercury reagent).

A study of the stoichiometry of the reaction was made by varying the molar ratio of phenyl(trichloromethyl)mercury to **1b** from 1:1 to 3:1. The results, which are summarized in Table II, show that there is an apparent leveling of yield of vinylamine at the mole ratio of 2:1 under the conditions employed. The yield of isoprene, although never large, decreased significantly in the 3:1 reaction. However, in the latter case, a 21% yield of 1-chloromethyl-2,2-dichloro-3,3-dimethylcyclopropane (**6**) was isolated. This product was identified by its composition and spectra



(1) Supported by the National Science Foundation Grant GP-3357.

(2) From the Ph.D. Thesis of J. R. Potoski, the University of Minnesota, 1966.

(3) D. Seyferth, J. M. Burlitch, and J. K. Heeren, *J. Org. Chem.*, **27**, 1491 (1962).

TABLE I

| Starting amine | Formula | Cyclopropane 2 % | Vinylamine 3 , % | HCCL ₃ (1 mole), % | Isoprene, ^a % | Other products (%) |
|----------------|--|----------------------------|----------------------------|----------------------------------|-----------------------------|-----------------------------------|
| 1a | $(C_2H_5)_2NCH_2CH=C \begin{matrix} /CH_3 \\ \backslashCH_3 \end{matrix}$ | 0 | 44 | 77 | 8 | |
| 1b | $C_6H_5NCH_2CH=C \begin{matrix} /CH_3 \\ \backslashCH_3 \\ \backslashCH_3 \end{matrix}$ | 1.3 | 36 | 35 | 11 | 1b (12) 5b (0.4) |
| 1c | $(C_2H_5)_2NCH_2CH=C \begin{matrix} /CH_3 \\ \backslashCH_3 \\ \backslashCH_3 \end{matrix}$ | 56 | <1 | 33 | 0 | |
| 1d | $CH_3C(=O)N(CH_3)CH_2CH=C \begin{matrix} /CH_3 \\ \backslashCH_3 \\ \backslashCH_3 \end{matrix}$ | 60 | 0 | .. | 0 | |

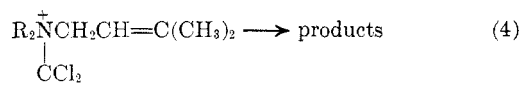
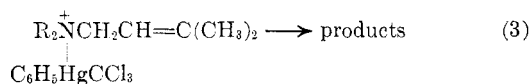
^a The yield of isoprene (detected by gc) is not in itself significant since it was subsequently shown that a primary product is 1-chloro-3-methyl-2-butene (**4**) which decomposes to isoprene during gas chromatography. ^b Compound **5** was shown to have the same retention time in gc as 1,1-dichloro-3-methyl-2-vinylcyclopropane prepared from isoprene, chloroform, and potassium *t*-butoxide.

TABLE II

| Molar ratio of C ₆ H ₅ HgCCl ₃ : amine 1b | Yield, % | | |
|--|----------------------|-------------------|----------|
| | Vinylamine 3b | HCCL ₃ | Isoprene |
| 1:1 | 21 | 23 | 3.2 |
| 2:1 | 36 | 35 | 11.0 |
| 3:1 | 34 | 28 | 1.4 |

(infrared and nmr) and had properties (boiling point, refractive index, gc retention time, infrared and nmr) essentially identical with those of authentic **6** prepared (22% yield) by reaction of phenyl(trichloromethyl)mercury with 1-chloro-3-methyl-2-butene. These results suggest that the allyl fragment is leaving the nitrogen as 1-chloro-3-methyl-2-butene.

The question as to whether mercury participation is necessary for the cleavage reaction (eq 3), or whether the reaction is a consequence of ylid formation (eq 4)

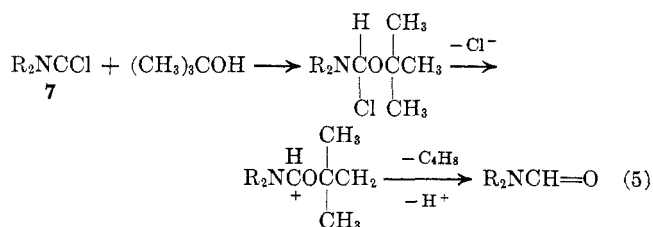


with dichlorocarbene was considered by examining the reactions of other carbenoid reagents (chloroform-butoxide, butyllithium-carbon tetrachloride, ethyl trichloroacetate-methoxide) with butenylamines. No conclusive evidence for vinylamine formation was obtained⁴ when these reagents were employed, which suggests that participation of the mercury reagent is involved in the cleavage step.

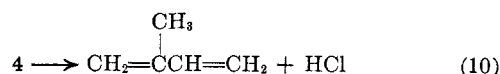
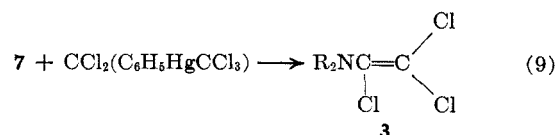
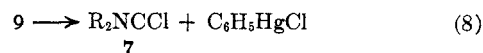
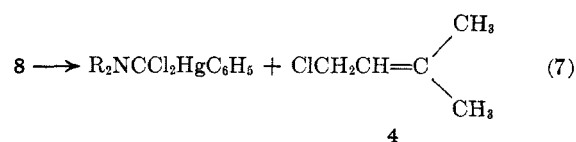
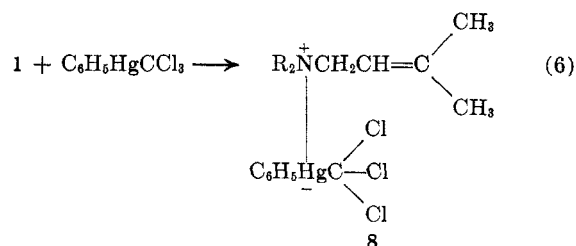
An attempt was made to intercept intermediates in the cleavage reaction by carrying out the reaction of **1b** (1 equiv) in boiling benzene with phenyl(trichloromethyl)mercury (2 equiv) in the presence of *t*-butyl alcohol (1 equiv). In addition to trichlorovinylamine (**3b**, 9.3% yield) and recovered amine (**1b**, 11% recovery), there was obtained a 24% yield of *N*-methylformanilide. It appears that the *t*-butyl alcohol is intercepting an intermediate in vinylamine formation

(4) W. E. Parham and J. R. Potoski, *J. Org. Chem.*, **32**, 275 (1967). Failure to detect vinylamines from these reactions is not conclusive, for they may have been destroyed under reaction conditions.

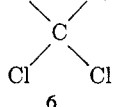
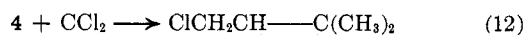
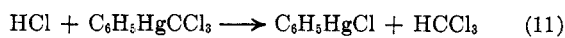
after the allyl group has left and before the new nitrogen intermediate forms the two-carbon side chain. Such an observation is consistent with intermediates such as **7**⁵ (eq 5) or *N*-dichloromethyl-*N*-methylaniline.⁵



While the facts obtained from the reaction of allylamines with phenyl(trichloromethyl)mercury do not permit definition of the mechanism, the reaction sequence shown in eq 6-12 seem to be consistent with the

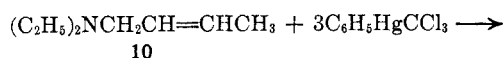


(5) W. E. Parham and J. R. Potoski, *Tetrahedron Letters*, No. 21, 2311 (1966).

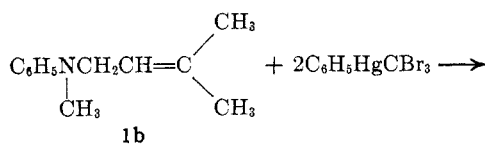
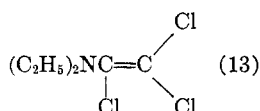


data. Proposed intermediate **9** resembles phenyl-(trichloromethyl)mercury, and its decomposition to phenylmercuric chloride and carbene **7** seems reasonable. Equation 9 has been discussed⁵ in connection with the formation of trichlorovinylamines by reaction of phenyl(trichloromethyl)mercury with secondary amines.

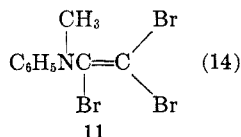
The cleavage of allylamines to trichlorovinylamines appears to be general provided that the allyl group contains at least four carbon atoms. Thus, reaction of *N,N*-diethyl-2-butenylamine (**10**) with phenyl(trichloromethyl)mercury and reaction of *N*-methyl-*N*-(3-methyl-2-butenyl)aniline (**1b**) with phenyl(trichloromethyl)mercury gave analogous products as shown in eq 13 and 14.



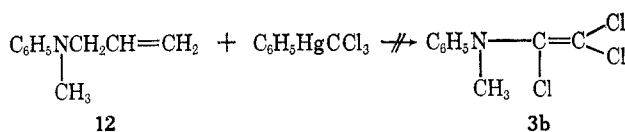
10



1b

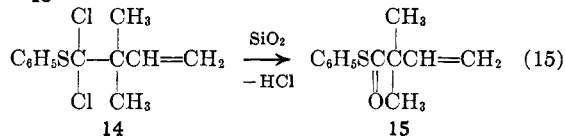
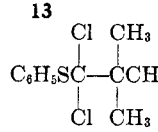
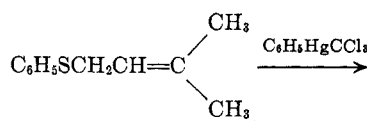


Trichlorovinylamine formation does not occur in the one case studied, in which the allyl group contains a simple three-carbon chain. When *N*-methyl-*N*-allyl-aniline (**12**) was treated with phenyl(trichloromethyl)mercury no *N*-methyl-*N*-phenyl-1,2,2-trichlorovinylamine (**3b**) was formed, although phenylmercuric chloride was obtained in high yield. The reaction obviously



followed an entirely different course from those described for **1a-d**. Much tar was formed together with a small amount of unidentified material which contains two different allyl groups (by nmr). This observation is not necessarily inconsistent with the scheme proposed in eq 6-12. The expected allyl chloride (formed by reaction of type shown in eq 7) cannot lose hydrogen chloride; consequently, it would be expected to react rapidly with starting amine to form quaternary salts.

The reaction of phenyl(trichloromethyl)mercury (1 equiv) with γ,γ -dimethylallyl phenyl sulfide (**13**, 1 equiv) was carried out at 80° in benzene for 41 hr.



Phenylmercuric chloride (94% yield) was isolated but no isoprene was detected. Chromatography of the crude reaction mixture on silica gel gave a 27% crude yield of **15**. It appears that the reaction of γ,γ -dimethylallyl phenyl sulfide with phenyl(trichloromethyl)mercury is proceeding by essentially the same mechanism as that observed when ethyl trichloroacetate and sodium methoxide is used as the source of dichlorocarbene.⁶ No evidence was observed for a cleavage reaction similar to that observed with the allylic amines.

Experimental Section^{7,8}

Reaction of *N,N*-Diethyl-3-methyl-2-butenylamine (1a) with Phenyl(trichloromethyl)mercury.—A solution of **1a** (7.05 g, 0.05 mole, bp 154–156°, n_D^{25} 1.4398, picrate mp 101–102°; lit.⁹ bp 158–160°, n_D^{20} 1.4390, picrate mp 101–102°) and phenyl(trichloromethyl)mercury (39.6 g, 0.10 mole) in dry benzene (225 ml) was heated at the reflux temperature under a dry nitrogen atmosphere for 25 hr. Benzene (210 ml) was then distilled from the reaction mixture at atmospheric pressure. The benzene was analyzed by gas chromatography. Isoprene (0.27 g, 8% yield) and chloroform (3.1 g, 77% yield) were detected.

The reaction mixture, after removal of all benzene, was diluted with petroleum ether (bp 60–68°) and crude phenylmercuric chloride (35.5 g) was precipitated. The phenylmercuric chloride weighed 27.5 g (88% yield) after washing with 5% hydrochloric acid and with acetone. The petroleum ether extract was concentrated and the brown oil (5.5 g) was distilled through a short-path apparatus to give *N,N*-diethyl-1,2,2-trichlorovinylamine (**3a**): bp 55–58° (4.5 mm), n_D^{25} 1.4852, 4.45 g, 44% yield [lit.⁵ bp 67–71° (6.2 mm), n_D^{25} 1.4850]. The infrared and nmr spectra of this product were essentially identical with those of authentic **3a**.

The distillation pot residue was treated with aqueous 5% hydrochloric acid. No organic bases were recovered from the acid extracts.

Reaction of *N,N*-Diethyl-2-butenylamine (10) with Phenyl(trichloromethyl)mercury.—The reaction of **10a** (6.35 g, 0.05 mole, bp 136–137°, n_D^{25} 1.4294; lit.¹⁰ bp 137.5–139°, n_D^{25} 1.4301) with phenyl(trichloromethyl)mercury (59.5 g, 0.150 mole) was carried out as described for **1a**. The products detected were chloroform (76%) and *N,N*-diethyl-1,2,2-trichlorovinylamine (**3a**): bp 63–65° (6.0 mm), n_D^{25} 1.4852, 4.04 g, 40% yield.

Reaction of *N*-Methyl-*N*-(3-methyl-2-butenyl)aniline (1b) with Phenyl(trichloromethyl)mercury. A.—The reaction of **1b**¹¹ [8.75 g, 0.05 mole, bp 115–118° (6.0 mm), n_D^{25} 1.5475; lit.¹² bp 102–107° (7 mm), n_D^{25} 1.5510] with phenyl(trichloromethyl)mercury (39.6 g, 0.10 mole) in dry benzene (250 ml) was carried out for 33 hr as described for **1a**. A trap containing heptane and immersed in a Dry Ice–acetone bath was placed after the water condenser to collect any volatile products not retained by the con-

(6) W. E. Parham and S. H. Goren, *J. Org. Chem.*, **31**, 1694 (1966).

(7) All nmr spectra, unless otherwise stated, were run as 20–25% solutions in carbon tetrachloride with tetramethylsilane as internal standard on a Varian A-60. Weights were obtained by integration.

(8) All gc analyses were conducted on silicon oil DC-710 and silicone oil DC-30 on 20–100 Chromosorb W at 50, 70, and 120° with helium eluent gas at 17 cc/min. The columns were stainless steel, 1/8 in. × 6 ft.

(9) N. Nazarov, V. N. Racheeva, and L. I. Shomonina, *Zh. Obshch. Khim.*, **22**, 611 (1952).

(10) W. G. Young, I. D. Webb, and H. L. Goering, *J. Am. Chem. Soc.*, **73**, 1076 (1951).

(11) V. L. Tweedie and J. C. Allabashi, *J. Org. Chem.*, **26**, 3676 (1961).

(12) A. T. Babayan, G. T. Marterossjan, N. G. Wartanjian, and M. G. Indshikjan, *Zh. Obshch. Khim.*, **30**, 2263 (1960).

denser. At the end of the reflux period 150 ml of benzene was distilled at atmospheric pressure and the remaining benzene was removed at 60° (20 mm). The benzene distillates and the heptane solution were analyzed by gas chromatography.⁸ Isoprene (0.38 g, 11% yield), chloroform (2.08 g, 35% yield), and 1,1-dichloro-2-methyl-2-vinylcyclopropane¹³ (0.03 g, 0.4% yield) were detected.

Phenylmercuric chloride (30.1 g, 96% yield) was precipitated from the residue by adding petroleum ether (bp 60–68°) and the organic layer was extracted with 5% hydrochloric acid. Concentration of the petroleum ether extract gave an oil (8.8 g) which was distilled through a short-path apparatus to give N-methyl-N-phenyl-1,2,2-trichlorovinylamine (**3b**): bp 67–73° (0.01 mm), n_D^{25} 1.5855, 4.30 g, 36.4% yield. The sample of **3b** was identical (infrared and nmr) with authentic material prepared by two independent methods.^{5,14}

The acid extract of the petroleum ether solution was neutralized with potassium carbonate and extracted with ether. The dried (MgSO₄) ether solution was concentrated and the residue (1.25 g) was shown by its nmr spectrum to contain starting amine **1b** (1.08 g, 12% recovery) and N-(2,2-dichloro-3,3-dimethylcyclopropylmethyl)-N-methylaniline⁴ (**2b**, 0.17 g, 1.3% yield).

B.—The reaction was repeated but 3 equiv of phenyl(trichloromethyl)mercury was used. These were obtained isoprene (1.4% yield), chloroform (28% yield), phenylmercuric chloride (94% yield), 1-chloromethyl-2,2-dichloro-3,3-dimethylcyclopropane [**6**, 2.02 g, 21.6% yield, n_D^{25} 1.4872, bp 30–45° (0.07 mm)], and N-methyl-N-phenyl-1,2,2-trichlorovinylamine [**3b**, bp 77–79° (0.07 mm), n_D^{25} 1.5855, 4.04 g, 35% yield]. The vinylamine and cyclopropane **6** were characterized by comparison with authentic samples.

C.—The reaction of **1b** with phenyl(trichloromethyl)mercury (1 equiv) gave isoprene (3.2% yield), chloroform (23% yield), phenylmercuric chloride (98% yield), N-methyl-N-phenyl-1,2,2-trichlorovinylamine [**3b**, bp 62–65° (0.05 mm), n_D^{25} 1.5840, 2.48 g, 21% yield] and recovered **1b** (48% recovery).

D.—The reaction of **1b** (1 equiv) and phenyl(trichloromethyl)mercury (2 equiv) in benzene (125 ml) containing *t*-butyl alcohol (1 equiv) was carried out for 39 hr. The volatile products were not analyzed. The crude organic product, obtained subsequent to removal of phenylmercuric chloride (90% yield), was shown to contain N-methyl-N-phenyl-1,2,2-trichlorovinylamine (**3b**, 9.3% yield), N-methyl-N-(3-methyl-2-butenyl)aniline (**1b**, 11% recovery), and N-methylformanilide (24% yield). The nmr spectrum (CHO at τ 1.58, wt 1) and infrared spectrum of N-methylformanilide (bp 107–110°) were identical with those of authentic material.¹⁵

1-Chloromethyl-2,2-dichloro-3,3-dimethylcyclopropane (6).—A solution of 1-chloro-3-methyl-2-butene [15.7 g, 0.15 mole, bp 54–55° (110 mm), n_D^{25} 1.4465; lit.¹⁶ bp 111–113°, n_D^{20} 1.4480] and phenyl(trichloromethyl)mercury (39.6 g, 0.10 mole) in dry benzene (200 ml) was heated at the reflux temperature under an atmosphere of dry nitrogen for 43 hr. Benzene (180 ml) was then distilled from the reaction mixture and petroleum ether (bp 60–68°, 100 ml) was added to the cooled (30°) concentrate. Phenylmercuric chloride (29.8 g, 95% yield) was removed and the filtrate was concentrated and distilled through a 10-cm Vigreux column. There was obtained 4.07 g (22% yield) of 1-chloromethyl-2,2-dichloro-3,3-dimethylcyclopropane (**6**): bp 63–68° (10 mm), n_D^{25} 1.4820–1.4836.

Anal. Calcd for C₆H₈Cl₂: C, 38.4; H, 4.8; Cl, 56.7. Found: C, 39.1; H, 5.1; Cl, 56.1.

The infrared and nmr spectra of this product were essentially identical with the product obtained from **1b**. The nmr spectra showed CH₂ (septet, τ 6.06–6.75, $J_{ab} = 11$ cps, $J_{ax} = 7$ cps, $J_{bx} = 8$ cps, wt 2), cyclopropyl hydrogen (triplet, τ 8.27–8.52, $J_{ax} = 7$ cps, $J_{bx} = 8$ cps), and CH₃ (singlets at τ 8.57 and 8.70, wt 7.4, including the cyclopropyl hydrogen).

N,N-Diphenyl-3-methyl-2-butenylamine (1c).—Potassium metal (9.4 g, 0.24 g-atom) was dissolved in a solution of diphenylamine (40.5 g, 0.24 mole) and boiling benzene (500 ml) under an atmosphere of dry nitrogen. The mixture (containing a yellow

solid) was cooled (30°) and 1-chloro-3-methyl-2-butene (25.2 g, 0.24 mole) was added dropwise. The mixture was then heated at the reflux temperature for 0.5 hr and was then cooled, washed with water, and dried (MgSO₄). Evaporation of benzene gave an oily residue which was treated with acetyl chloride (16.5 g, 0.21 mole) and potassium acetate (20.6 g, 0.21 mole). After the exothermic reaction had subsided, the mixture was heated at 100° for 0.5 hr, cooled, washed with water, and extracted with ether. The ether layer was washed with saturated sodium bicarbonate and was dried (MgSO₄) and concentrated. The ether-free residue was diluted with petroleum ether (~50 ml) and the mixture was cooled and filtered. N,N-Diphenylacetamide (16 g, 21% yield, mp 94–97°; lit.¹⁷ mp 100°) was collected and the filtrate was concentrated to a yellow oil. The oil was chromatographed on alumina (400 g) using petroleum ether as eluent. There was obtained 27.1 g of slightly impure (infrared showed small NH absorption) **1c**. The crude product was distilled to give 22.9 g of **1c**: bp 122–126° (0.20 mm), n_D^{25} 1.5960–1.5964, 40% yield.

Anal. Calcd for C₁₇H₁₉N: C, 86.03; H, 8.07; N, 5.90. Found: C, 85.96; H, 8.27; N, 5.83.

The nmr spectrum of **1c** showed aromatic hydrogen (complex, τ 2.70–3.39, wt 10.1), CH= (complex triplet centered at τ 4.68, wt 1), CH₂ (complex doublet centered at τ 5.76, wt 1.9), and CH₃ (two singlets centered at τ 8.37, wt 6).

Reaction of N,N-diphenyl-3-methyl-2-butenylamine (1c, 1 equiv) with phenyl(trichloromethyl)mercury (2 equiv) was carried out (36 hr) as described for **1b** (procedure A). Chloroform (33% yield), but not isoprene, was detected.

The concentrated organic mixture (12 g, from 7.12 g, 0.03 mole of **1c**), obtained subsequent to removal of phenylmercuric chloride (99% yield), was chromatographed on silica gel (290 g) using (1) petroleum ether (250 ml, bp 60–68°), (2) benzene (20%)–petroleum ether (450 ml), and (3) benzene (20%)–petroleum ether (1.5 l.). Fraction 2 (0.11 g) was shown by thin layer chromatography (silica gel eluted with 20% benzene–petroleum ether using ceric sulfate–phosphoric acid developer) to contain N,N-diphenyl-1,2,2-trichlorovinylamine⁸ (**3c**, ~0.11 g, 1.2% yield). Fraction 3 gave 5.43 g (56% yield) of N-(2,2-dichloro-3,3-dimethylcyclopropylmethyl)-N,N-diphenylamine (**2c**, mp 58–65°). This product melted at 66–68° after recrystallization from ethanol and caused no depression in melting point when admixed with authentic⁴ **2c**.

N-Methyl-N-(3-methyl-2-butenyl)acetamide (1d).—Potassium metal (12.5 g, 0.32 g-atom) was dissolved in a solution of N-methylacetamide¹⁸ (24.1 g, 0.33 mole) and dry benzene (250 ml) heated at the reflux temperature under an atmosphere of dry nitrogen. To the resulting cooled (30°) mixture of yellow solid and liquid was added, dropwise, a solution of 1-chloro-3-methyl-2-butene (35.7 g, 0.34 mole) in benzene (50 ml). The mixture was heated at the reflux temperature for 20 min, cooled (30°), washed with water, and dried (MgSO₄). The solution was concentrated and distilled twice through a spiral-wire column to give **1d**: bp 98–103° (9.5 mm), n_D^{25} 1.4663–1.4683, 13.2 g, 29% yield. The analytical sample had bp 99–100° (9.5 mm), n_D^{25} 1.4682.

Anal. Calcd for C₈H₁₅NO: C, 68.04; H, 10.71; N, 9.92. Found: C, 67.91; H, 10.48; N, 9.72.

The nmr spectrum of **1d** showed CH= (triplet centered at τ 4.90, $J = 7$ cps, wt 1), CH₂ (doublet centered at τ 6.13, $J = 7$ cps, wt 2), NCH₃ (doublet at τ 7.17 which merges to a singlet on warming, wt 2.9), CH₃CO (singlet at τ 8.05, wt 3.1), and CH₃ (singlet, τ 8.29, wt 5.9).

Reaction of N-methyl-N-(3-methyl-2-butenyl)acetamide (1d, 0.032 mole) with phenyl(trichloromethyl)mercury (0.062 mole) in benzene (150 ml) was carried out (40 hr) as described for **1b** (procedure A). The crude oil (7.6 g), obtained subsequent to removal of phenylmercuric chloride (96% yield) was distilled through a spiral-wire column to give **1d** [bp 46–50° (0.10 mm), n_D^{25} 1.4680, 0.39 g, 8.7% recovery] and N-(2,2-dichloro-3,3-dimethylcyclopropylmethyl)-N-methylacetamide [bp 87–90° (0.10 mm), n_D^{25} 1.4941, 4.33 g, 60.4% yield]. This material solidified when seeded and the product (mp 64–66°) was identical with authentic⁴ **2d** (melting point, mixture melting point, and infrared spectra).

Reaction of N-allyl-N-methylaniline¹¹ (12, 0.085 mole) with phenyl(trichloromethyl)mercury (0.17 mole) in benzene (400 ml) was carried out (36 hr) as described for **1b** (procedure A).

(17) L. Forrest, D. Liddel, and S. H. Tucker, *ibid.*, 454 (1946).

(18) A. Galat and G. Elion, *J. Am. Chem. Soc.*, **65**, 1566 (1943).

(13) 1,1-Dichloro-2-methyl-2-vinylcyclopropane (**5**) was prepared (66% yield, bp 142–144°, n_D^{25} 1.4763) as described by A. Ledwith and R. M. Bell [*Chem. Ind. (London)*, 459 (1959)] and by M. Orthen and E. C. Herrick [*J. Org. Chem.*, **24**, 139 (1959)].

(14) A. J. Speziale and L. R. Smith, *J. Am. Chem. Soc.*, **84**, 1868 (1962).

(15) L. F. Fieser and J. E. Jones, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 590.

(16) A. J. Ultee, *J. Chem. Soc.*, 530 (1948).

The crude oil (21 g), obtained subsequent to removal of phenylmercuric chloride (99% yield), was shown to contain no N-methyl-N-phenyl-1,2,2-trichlorovinylamine⁵ by analysis using thin layer chromatography (silica gel, 20% benzene-petroleum ether, bp 60–68°, ceric sulfate-phosphoric acid developer).

The crude mixture was not resolved. Attempts to distill the product at a bath temperature of 130° resulted in extensive decomposition. A small amount of oil [\sim 1 g, bp 45–70° (0.01 mm)] was obtained which was purified by chromatography on alumina using petroleum ether as eluent. This product was not identified; the nmr spectrum shows two different allyl groups.

Reaction of N-Methyl-N-(3-methyl-2-butenyl)aniline with Phenyl(tribromomethyl)mercury.—A solution of **1b** (5.25 g, 0.03 mole) and phenyl(tribromomethyl)mercury¹⁹ (31.8 g, 0.06 mole) in benzene (100 ml) was heated at reflux temperature for 1.75 hr. Analysis of 90 ml of benzene which was then distilled showed 2.3% yield of isoprene. The oil (8.5 g) obtained subsequent to removal (see procedure for **1b**) of phenylmercuric bromide (91% yield) had an infrared spectrum very similar to the crude product obtained when phenyl(trichloromethyl)mercury was used (*i.e.*, to crude **3b**). Tribromovinylamine **11** was thermally unstable and was not obtained pure. Hydrolysis occurred when crude **11** was chromatographed on alumina (200 g). Elution of the column with petroleum ether and benzene gave 2.1 g of glassy material which was not characterized, and elution

with ethyl acetate gave 3.10 g (34% yield) of crude 2,2-dibromo-N-methylacetanilide (mp 94–103°), the expected hydrolysis product⁵ of **11**. The amide was purified to mp 109–110° by recrystallization from petroleum ether.

Anal. Calcd for $C_9H_9Br_2NO$: C, 35.21; H, 2.95; N, 4.56. Found: C, 35.41; H, 2.76; N, 4.52.

The nmr spectrum of 2,2-dibromo-N-methylacetanilide showed aromatic *H* (complex, τ 2.4–2.8, wt 5), $CHBr_2$ (singlet, τ 4.22, wt 1), and CH_3N (singlet, τ 6.67, wt 3).

Reaction of γ,γ -Dimethylallyl Phenyl Sulfide (13**) with Phenyl(trichloromethyl)mercury.**—A solution of **13**⁶ (8.9 g, 0.05 mole) and phenyl(trichloromethyl)mercury (19.8 g, 0.05 g-atom) in benzene (125 ml) was heated for 41 hr. The conditions and processing were similar to those described for **1b** (procedure A). No isoprene was detected in the benzene distillate. The crude black oil (10.1 g), obtained subsequent to removal of phenylmercuric chloride, had infrared and nmr spectra similar to, but not identical with, those of the product⁶ when ethyl trichloroacetate and sodium methoxide were used as the carbene source. The oil was placed on silica gel (250 g) and evolution of hydrogen chloride was noted.⁶ Elution with 33% benzene-petroleum ether (bp 60–68°) gave 3.6 g of uncharacterized oil which decomposed upon standing. Further elution of the column with benzene gave 2.8 g (27% yield) of thiophenyl ester of 2,2-dimethyl-3-butenic acid, the infrared spectrum of which was essentially identical with that reported.⁶ The ester was further purified by distillation [bp 75–79° (0.07 mm), n_D^{20} 1.5552] [*lit.*⁶ bp 56–57° (0.01 mm), $n_D^{22.5}$ 1.5550] and the product was identical (infrared and nmr) with authentic ester.

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

Nucleophilic Displacement Reactions of β -Amino Mercaptans

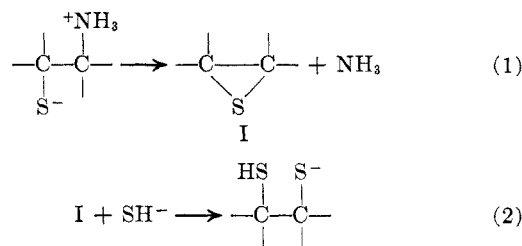
J. S. DIX AND C. R. BRESSON

Phillips Petroleum Company, Research Division, Bartlesville, Oklahoma

Received August 29, 1966

β -Amino mercaptans have been found to undergo intramolecular nucleophilic displacement of the amino group by the neighboring mercaptide group. Reaction of episulfides formed *in situ* with bisulfide or mercaptides offers a novel route to polythiols and mercapto thio ethers.

In the course of another study, a quantity of 1-amino-2,3-propanedithiol was required.¹ An attempt to prepare this compound by Stocken's procedure² (heating a methanolic solution of 2,3-dibromopropylamine hydrobromide and excess ammonium bisulfide for 16 hr at 90°, then isolating product by adding ammonium hydroxide and extracting with benzene) gave 1,2,3-propanetrithiol instead of the aminodithiol. By modifying the work-up procedure, both 1-amino-2,3-propanedithiol and 1,2,3-propanetrithiol were isolated from the reaction mixture (Table I). We assumed that the propanetrithiol was derived through reaction of initially formed 1-amino-2,3-propanedithiol with ammonium bisulfide. Further investigation has established that this synthesis is an example of a general reaction involving episulfide formation through the nucleophilic displacement of a β -amino group by a mercaptide group. Snyder and Stewart³ speculated that an episulfide might be formed in the thermal decomposition of N-substituted β -amino mercaptans upon attempted distillation; however, to our knowledge, our synthesis is the first established example of displacement of the amino group with episulfide formation. We believe that the amino mercaptan exists as a zwitterion, and that elimination of ammonia occurs as shown in eq 1.



That this displacement reaction is applicable to simple β -aminomercaptans was demonstrated by the preparation of 1,2-propanedithiol in 58% yield by treating 1-amino-2-propanethiol with excess ammonium bisulfide at 90°. To facilitate isolation, water was used as solvent in this and other examples involving β -amino mercaptans.

The β -amino mercaptans can also be formed *in situ* and treated further with ammonium bisulfide (Table II). Reaction of propylenimine with excess ammonium bisulfide in water at 125° led to formation of 1,2-propanedithiol in 42% yield. Since the intermediate 2-amino-1-propanethiol possesses the amino group on a secondary carbon, a higher temperature was required to displace the amino group than in the case of the isomeric 1-amino-2-propanethiol. At 90°, less than 2% propanedithiol was obtained. Similarly, reaction of ethylenimine and ammonium bisulfide at 125° produced 1,2-ethanedithiol in 38% yield.

The modest yields presumably are the result of by-product formation from the reaction of the intermediate

(1) This work was done in part under Contract DA-49-193-MD-2069 with U. S. Army Medical Research and Development Command.

(2) L. A. Stocken, *J. Chem. Soc.*, 592 (1947).

(3) H. R. Snyder, J. M. Stewart, and J. B. Ziegler, *J. Am. Chem. Soc.*, **69**, 2672 (1947).