

N-4-Butenylmorpholine.—From the reaction of 20.9 g (0.1 mole) of phenylthiomethylmorpholine and the Grignard reagent formed from 24 g (0.2 mole) of allyl bromide, there was obtained 10.6 g of this compound (75% of the theory) that distills at 180–181°. In addition to the C–O–C and C–N bands of morpholine, its infrared spectrum showed absorption bands at 2.32, 6.68, and 11.0 μ , characteristic of monosubstituted vinyl compounds. (See Table II.) The picrate (from alcohol) had mp 115.5–116.5°.

Anal. Calcd for $C_{14}H_{18}N_4O_7$: C, 45.40; H, 4.90; N, 15.13. Found: C, 45.67, 4.72; N, 15.55.

In another run a solution of 15.7 g (0.13 mole) of allyl bromide and 20 g (0.1 mole) of N-phenylthiomethylmorpholine in 50 ml of ether was added to a suspension of 2.4 g (0.1 g-atom) of magnesium turnings in 100 ml of ether, without performing the Grignard reagent. The amine was obtained in only a 35% yield and from the neutral fraction was isolated in 28% yield allyl phenyl sulfide based upon the use of 0.1 mole of the N-phenylthiomethylmorpholine. Its infrared spectrum was identical with that of a sample of allyl phenyl sulfide prepared by the action of allyl bromide on C_6H_5SMgBr (see below).

N-Isobutylmorpholine.—Reaction of the Grignard reagent prepared from 25 g (0.2 mole) of isopropyl bromide with 20 g (0.1 mole) of phenylthiomethylmorpholine produced 9.8 g (68% of theory) of a colorless oil that had bp 167°. (See Table II.) The picrate (from alcohol) had mp 129–131°.

Anal. Calcd for $C_{14}H_{20}N_4O_8$: C, 45.15; H, 5.41; N, 15.05. Found: C, 45.22; H, 5.49; N, 15.15.

N-Benzylmorpholine.—From the reaction of 20 g (0.1 mole) of phenylthiomethylmorpholine with the Grignard reagent obtained from 23.59 g (0.15 mole) of bromobenzene there was collected 14.8 g (85% of the theory) of a colorless oil boiling at 73° (2 mm) and 253° (760 mm). The infrared spectrum of this compound showed strong bands at 13.5 and 14.3 μ typical of monosubstituted benzene rings. (See Table II.)

Allyl Phenyl Sulfide.—A solution of phenylmagnesium bromide in 100 ml of ether was prepared from 32 g (0.2 mole) of bromobenzene and magnesium turnings. This was converted into C_6H_5SMgBr by adding 17.6 g (0.16 mole) of thiophenol and refluxing for a short time. To this reaction mixture was then added 18 g (0.15 mole) of allyl bromide followed by refluxing for 3 hr. After hydrolysis with dilute HCl, the organic phase was washed with 10% NaOH and dried with anhydrous $MgSO_4$, and the volatile solvent was removed. From the residue was obtained 16 g (or 71% of the theory based upon the use of 0.15 mole of allyl bromide) of the thio ether, bp 68–75° (5–6 mm) and 219° (760 mm).²⁴ Its infrared spectrum had the characteristic absorption bands of terminal vinyl groups which appear at 6.02 and at 10.8 μ .

(24) C. D. Hurd and H. Greengard *J. Am. Chem. Soc.*, **52**, 3356 (1930) report bp 104–106° (25 mm) and 215–218° (750 mm).

The Reactions of Allylamines with Dichlorocarbene¹

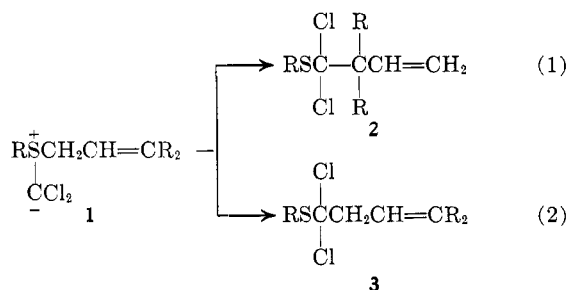
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The reaction of four allylamines, in which the basicity of the nitrogen is varied by appropriate substitution, with potassium *t*-butoxide–chloroform, *n*-butyllithium–carbon tetrachloride, and, in one case, ethyl trichloroacetate–sodium methoxide is reported. These amines, unlike the sulfur analogs, give cyclopropanes, and the yield of cyclopropane varies inversely with the basicity of the amine. In one case, an amide derived by a Stevens-type rearrangement was identified as a reaction product.

It has been shown that acyclic allyl sulfides react³ with ethyl trichloroacetate and sodium methoxide (dichlorocarbene) to give products derived by allylic



rearrangement of sulfur ylid 1 (eq 1), and, to a lesser extent, products derived by a Stevens-type rearrangement of 1 (eq 2). No cyclopropanes corresponding to addition of dichlorocarbene to the olefinic double bond have been observed in such reactions, an observation which suggests that the sulfur atom is more nucleophilic than the π -olefin bond to dichlorocarbene.

We wished to compare the course of reaction of acyclic allylamines with dichlorocarbene with the analogous reactions with allyl sulfides, and it was of particular interest to gain information relative to the effect of substitution on nitrogen on the reaction course.

(1) Supported by the U. S. Army Research Office (Durham) Contract No. DA-31-124-ARO-D-152.

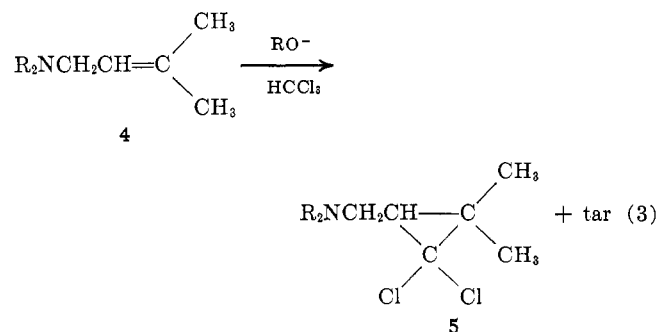
(2) From the Ph.D. Thesis of J. R. Potoski, the University of Minnesota, 1966.

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

Procedure

A. Reactions with Potassium *t*-Butoxide–Chloroform.—Each of these reactions was effected using amine (1 equiv), chloroform (2 equiv), and potassium *t*-butoxide (2 equiv) in benzene at 0°. The reaction mixtures were processed by chromatography and/or distillation, and in some cases also by extraction with dilute hydrochloric acid to separate neutral components. Products were examined by thin layer chromatography and particular attention was given to the possible presence of trichlorovinylamines. The trichlorovinylamines are normal reaction products of allyl amines with phenyl(trichloromethyl)mercury.⁴ In no case were such products detected.

The course of reaction of the amines studied is shown in eq 3, and the results are summarized in Table I.



(4) W. E. Parham and J. R. Potoski, *ibid.*, **32**, 278 (1967).

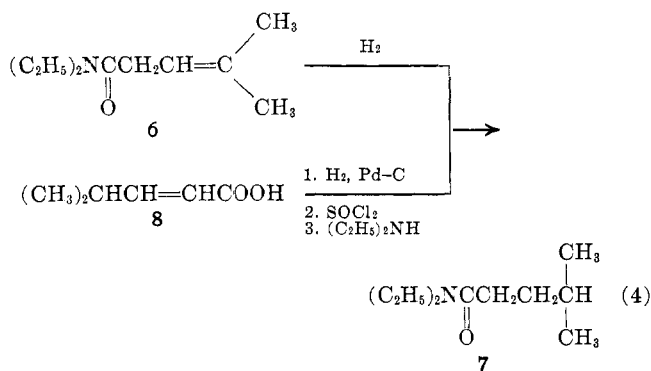
TABLE I

| Starting amine | Products (%) | | |
|---|--|--------------------|--|
| | From KOC ₄ H ₉ + CHCl ₃ | Other | From <i>n</i> -C ₄ H ₉ Li + CCl ₄ |
| $\begin{array}{c} \text{CH}_3 \\ \diagup \\ (\text{C}_2\text{H}_5)_2\text{NCH}_2\text{CH}=\text{C} \\ \diagdown \\ \text{CH}_3 \end{array}$ 4a | 5a (4.8) | 4a (10) 6 (6.5) | 5a (11) |
| $\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{C}_6\text{H}_5\text{NCH}_2\text{CH}=\text{C} \\ \diagdown \\ \text{CH}_3 \\ \\ \text{CH}_3 \end{array}$ 4b | 5b (28) | 4b (26) | 5b (26) 4b (20) |
| $\begin{array}{c} \text{CH}_3 \\ \diagup \\ (\text{C}_6\text{H}_5)_2\text{NCH}_2\text{CH}=\text{C} \\ \diagdown \\ \text{CH}_3 \end{array}$ 4c | 5c (45) | 4c (33) | 5c (73) |
| $\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{CH}_2\text{NCH}_2\text{CH}=\text{C} \\ \diagdown \\ \text{CH}_3 \\ \\ \text{O}=\text{CCH}_3 \end{array}$ 4d | 5d ^a (21.8) | 4d (44) | ... |

^a The lower yield observed with 4d may be associated with an expected attack by the nucleophile (RO⁻ or ⁻CCl₃) upon the carbonyl group of the amide function.

The yields of cyclopropanes shown in Table I are not optimum. The effect of changing the molar ratio of butoxide–chloroform to amine was studied using *N*-methyl-*N*-(3-methyl-2-butenyl)aniline (4b). When the ratio of carbene source to amine was varied from 1:1 to 2:1 to 3:1, the yields of 5b were 21, 28, and 54%, respectively.

The only neutral product identified from the reaction of amines 4a–d with chloroform–potassium *t*-butoxide was *N,N*-diethyl-4-methyl-3-pentanamide (6), obtained in 6.5% yield from 4a. This amide was identified by its infrared and nmr spectra (see the Experimental Section), and its structure was confirmed by an



independent synthesis of the derived *N,N*-diethyl-4-methylpentanamide (7) (see eq 4).

B. Reactions with *n*-Butyllithium–Carbon Tetrachloride.—The reaction of the amines 4a–c (1 equiv) with carbon tetrachloride (5 equiv) and *n*-butyllithium (5 equiv) was carried out at -65° in tetrahydrofuran.⁵ The solvent was evaporated and the residue was diluted with pentane and filtered. The organic product was processed by chromatography and/or distillation. The results are summarized in Table I.

(5) D. F. Hoeg, D. I. Lusk, and A. L. Crumbliss, *J. Am. Chem. Soc.*, **87**, 4147 (1965).

Chromatography of the product obtained from *N*-methyl-*N*-(3-methyl-2-butenyl)aniline (4b) gave, in addition to the products shown in Table I, a small quantity of impure material. The spectra (infrared and nmr) of this product suggested the possible presence of *N*-methyl-*N*-phenyl-1,2,2-trichlorovinylamine.⁴ The reaction was repeated, but no conclusive evidence for the presence of the vinylamine was obtained.

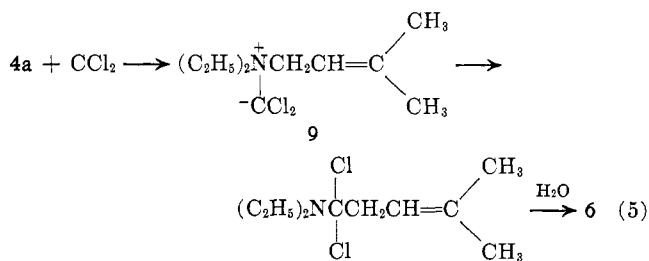
C. Reaction with Ethyl Trichloroacetate and Sodium Methoxide.—The reaction of 4b (1 equiv) with ethyl trichloroacetate–sodium methoxide (2 equiv) was carried out at 0° in pentane. There was obtained an 18% yield of *N*-(2,2-dichloro-3,3-dimethylcyclopropylmethyl)-*N*-methylaniline (5b) together with 53% recovery of 4b.

Discussion

The reaction of allylamines with dichlorocarbene (or its precursor) was found to be in sharp contrast to analogous reactions with the corresponding allyl sulfides. With the amines, reaction at the olefinic π bond occurs leading to cyclopropane formation. As can be seen from Table I, the yield of cyclopropane increases as the basicity of the nitrogen atom is decreased; however, large changes in basicity correspond to relatively small changes in yield.

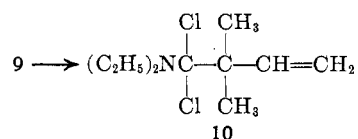
The difference observed between allylic amines and allylic sulfides may be in part a consequence of the relative stabilities of the nitrogen and sulfur ylids. The sulfur ylid is stabilized through resonance involving participation of sulfur *d* orbitals ($\text{R}_2\text{S}^+-\text{C}^- \leftrightarrow \text{R}_2\text{S}=\text{C}^-$). As a consequence, reactions proceeding through a nitrogen ylid may be less likely to occur than reactions proceeding through a sulfur ylid.

The fact that lower yields of cyclopropanes result with the more basic or nucleophilic nitrogen compounds (Table I) suggests that there is an expected competition between nitrogen and the olefinic π bond for the electrophilic dichlorocarbene. The formation of *N,N*-diethyl-4-methyl-3-pentanamide can be formulated as shown in eq 5. This reaction, formerly



analogous to the Stevens rearrangement, has been observed³ with the analogous allyl sulfides.

No products derived by allylic rearrangement of the proposed ylid 9, the predominant³ reaction with the cor-



responding allyl sulfides, was detected. Added steric requirements in the allylamines may have precluded formation of intermediates of type 10. However, it

seems more likely that such products were formed, but were precursors to the tars that accompanied the reactions.

Experimental Section^{6,7}

Reaction of *N,N*-Diethyl-3-methyl-2-butenylamine (4a) with Chloroform and Potassium *t*-Butoxide.—Freshly prepared potassium *t*-butoxide (from 6.2 g, 0.156 g-atom, of potassium) under an atmosphere of dry nitrogen was covered with a solution of 4a⁴ (10.6 g, 0.075 mole) in dry benzene (150 ml). The mixture was cooled to 0° and a solution of chloroform (18 g, 0.15 mole) in benzene (40 ml) was added dropwise. The mixture was stirred at 0° for 1 hr and at 30° for 1 hr. The resulting mixture was washed with 50 ml of water and with two 50-ml portions of 5% hydrochloric acid. The combined aqueous portions were extracted with three 50-ml portions of ether which was added to the organic layer.

Evaporation of the dry (MgSO₄) ether-benzene layer afforded 5 g of dark oil which gave on distillation (a) 0.37 g, bp 30–55 (0.1 mm), *n*_D²⁵ 1.4903–1.4783; and (b) 0.82 g (6.5% yield) of 6, bp 55–60° (0.1 mm), *n*_D²⁵ 1.4751. The amide 6 was refracted and collected at 57–58° (0.15 mm), *n*_D²⁵ 1.4680.

The nmr spectrum of 6 showed *CH*= (complex triplet, τ 4.56–4.87, wt 1), *CH*₂*CH*₂*N* (quartet, τ , 6.51–6.90, wt 4), *O=CCH*₂ (doublet, τ 6.90–7.17, wt 2), *CH*₃ (τ 8.20, 8.40, wt 5.9), *CH*₂*CH*₂ (triplet, τ 8.71–9.10, wt 6). The infrared spectrum of 6 showed C=O at 1640 cm⁻¹.

The acid extract was neutralized with sodium carbonate and extracted with ether. The dried (MgSO₄) extract was concentrated, and the oil (4.5 g) was distilled through a short-path distilling column. There was obtained 1.45 g (10% recovery) of 4a [bp 43–48° (5 mm), *n*_D²⁵ 1.4380] and 0.81 g (4.8% yield) of *N*-(2,2-dichloro-3,3-dimethylcyclopropylmethyl)-*N,N*-diethylamine [5a, bp 33–35° (0.025 mm), *n*_D²⁵ 1.4701].

The nmr spectrum of 5a showed *CH*₂ (complex quartet, τ 7.25–7.58, wt 5.8), *CH*₂ and *CH* (complex, six sharp peaks, τ 8.58–9.12, wt 13.2).

The cyclopropane 5a readily formed a picrate (mp 134–136° from ethanol).

Anal. Calcd for C₁₆H₂₂Cl₂N₄O: C, 42.40; H, 4.89; N, 12.36. Found: C, 42.67; H, 5.17; N, 12.13.

***N,N*-Diethyl-4-methylpentanamide (7).**—A solution of 4-methylpentanoic acid (11.4 g, 0.98 mole, prepared by catalytic reduction of 4-methyl-2-pentenoic acid⁸ and thionyl chloride (18 g, 0.15 mole) was heated at 140° for 45 min. Benzene (25 ml) was added and the mixture was distilled until the distilling temperature was 92°. The addition of benzene (25 ml) and distillation to 92° was repeated, and the solution was then cooled and added dropwise to a stirred solution of diethylamine (22 g, 0.30 mole) in benzene (25 ml). The mixture was stirred at 30° for 1 hr, washed with water and aqueous sodium bicarbonate, and dried (MgSO₄). *N,N*-Diethyl-4-methylpentanamide [7, 9.12 g, 55% yield, bp 67–69° (10.6 mm), *n*_D²⁵ 1.4423] showed the following absorption in the nmr spectrum: *CH*₂ (quartet, τ 6.5–6.89, wt 3.8), *CH*₂ (complex, τ 7.62–7.95, wt 2.1), *CH*₂ (complex, τ , 8.33–8.69, wt 2), and *CH* and *CH*₃ (complex, τ 8.72–9.20, wt 13.2).

Anal. Calcd for C₁₀H₂₁NO: C, 70.12; H, 12.36; N, 8.18. Found: C, 69.90; H, 12.00; N, 7.83.

N,N-Diethyl-4-methylpentanamide was also obtained by catalytic reduction of 6 with hydrogen and Pd-C in ethanol. The two samples of 7 had identical infrared and nmr spectra, and possessed identical retention times in gas chromatography.

Reaction of *N*-Methyl-*N*-(3-methyl-2-butenyl)aniline (4b) with Chloroform and Potassium *t*-Butoxide. A.—The reaction of 4b⁴ (8.75 g, 0.050 mole) with potassium *t*-butoxide (0.05 mole) and chloroform (0.05 mole) was carried out as described for 4a. The reaction mixture was washed with two 50-ml portions of water and the water extract was washed with 25 ml of benzene. The combined benzene layers were dried (MgSO₄) and concen-

trated. The brown oil (11.1 g which showed no C=O by infrared spectra) was placed on 240 g of alumina. Elution of the column with 10% benzene-petroleum ether (bp 60–68°, 1 l.) gave 8.5 g of yellow oil. The nmr spectrum of the product showed it to be a mixture of *N*-methyl-*N*-(3-methyl-2-butenyl)aniline (5.8 g, 66% recovery) and *N*-(2,2-dichloro-3,3-dimethylcyclopropylmethyl)-*N*-methylaniline (5b, 2.7 g, 21% yield). Distillation of the product gave 4b [bp 57–61° (0.015 mm), *n*_D²⁵ 1.5475, 4.92 g, 56% recovery] and 5b [bp 92–95° (0.015 mm), *n*_D²⁵ 1.5552, 2.14 g, 17% yield].

The nmr spectrum of 5b showed aromatic *H* (complex, τ 2.70–3.41, wt 5), *CH*₂ (doublet centered at τ 6.62, wt 2), *NCH*₃ (singlet, τ 7.10, wt 3), and *CH* and *CH*₃ (small peaks at τ , 8.62 and 8.73, large peaks at 8.69 and 8.80, wt 6.6). The cyclopropane 5b formed a picrate which melted at 143–145° (from ethanol).

Anal. Calcd for C₁₉H₂₀Cl₂N₄O: C, 46.83; H, 4.14; N, 11.50. Found: C, 47.10; H, 4.04; N, 11.37.

B.—The reaction was repeated using 4b (17.5 g, 0.10 mole) and 2 equiv of butoxide and chloroform. An aliquot of the benzene reaction mixture was filtered through a sintered-glass funnel and concentrated. Thin layer chromatography⁴ of the oil showed no vinylamine to be present. The infrared spectrum of the oil showed no carbonyl groups.

The benzene reaction product was washed with water, dried (MgSO₄), and concentrated, and the oil (21.5 g) was chromatographed on 400 g of alumina. The column was eluted with petroleum ether (bp 60–68°, 1.5 l.) and 11.55 g of greenish liquid was obtained. The nmr spectrum of this product showed it to contain 4.45 g (26% recovery) of 4b and 7.1 g (28% yield) of 5b. Distillation of this product through a short-path column gave 4b [4.05 g, 23%, bp 63–82° (0.01 mm), *n*_D²⁵ 1.5480–1.5500] and 5b [6.0 g, 23% yield, bp 92–95° (0.01 mm), *n*_D²⁵ 1.5550–1.5556].

C.—The reaction of 4b (0.05 mole, 1 equiv) with butoxide (3 equiv) and chloroform (3 equiv) was carried out as in B, above. The chromatographed product showed, by nmr analysis, 17% unchanged 4b and 54% yield of 5b. The product was distilled to give 4b (1.12 g, 12.8% recovery) and 5b [4.95 g, 39% yield, bp 93–96° (0.015 mm), *n*_D²⁵ 1.5558].

Reaction of *N,N*-Diphenyl-3-methyl-2-butenylamine with Potassium *t*-Butoxide and Chloroform.—The reaction of 4c⁴ (7.12 g, 0.03 mole), potassium *t*-butoxide (0.06 mole), and chloroform (7.2 g, 0.06 mole) was carried out as described for 4a and 4b. The benzene reaction product was washed with water, as described in procedure B, and the product was chromatographed on alumina (300 g). The nmr spectrum of the chromatographed product (mp 23–40°) showed it to contain 2.4 g (33% unchanged 4c), and 5.6 g (45% yield) of 5c. Recrystallization of the product gave 3.90 g (40% yield) of 5c (mp 70–71° from ethanol).

Anal. Calcd for C₁₈H₁₉Cl₂N: C, 67.51; H, 5.98; N, 4.37. Found: C, 67.59; H, 5.69; N, 4.33.

The nmr spectrum of 5c showed aromatic *H* (complex, τ 2.60–3.34, wt 10), *CH*₂ (octet, τ 5.90–6.72, wt 2), cyclopropyl *H* (quartet, τ 8.48–8.67, wt 1.1), and *CH*₃ (singlets at τ 8.81 and 9.11, wt 6).

Reaction of *N*-Methyl-*N*-(3-methyl-2-butenyl)acetamide (4d) with Chloroform and Potassium *t*-Butoxide.—The reaction of 4d⁴ (6.00 g, 0.0425 mole) with chloroform-butoxide (2 equiv) was carried out as in procedure B, above. The benzene solution was washed with water, dried, and distilled to give 4d [bp 48–53° (0.15 mm), *n*_D²⁵ 1.4718, 2.63 g, 44% recovery] and *N*-(2,2-dichloro-3,3-dimethylcyclopropylmethyl)-*N*-methylacetamide [5d, bp 91–94° (0.15 mm), mp 64–66°, 2.07 g, 21.8% yield]. The melting point of 5d was not changed by recrystallization of the product from petroleum ether.

Anal. Calcd for C₉H₁₅Cl₂NO: C, 48.23; H, 6.75; N, 6.25. Found: C, 48.48; H, 6.85; N, 6.02.

The nmr spectrum of 5d showed *CH*₂ and *NCH*₃ (complex τ 5.90–7.28, wt 4.8), *CH*₃C(=O)*H* (singlet, τ 7.98, wt 3.2), *CH*₃ and cyclopropyl proton (large peak at τ 8.60 with small peaks at 8.55 and 8.66, wt 3.8), and *CH*₃ (singlet, τ 8.78, wt 3.1).

Reactions with *n*-Butyllithium and Carbon Tetrachloride.—The reactions were carried out⁸ as described for 4a.

1. ***N,N*-Diethyl-3-methyl-2-butenylamine (4a).**—A solution of tetrahydrofuran (200 ml, dried over potassium hydroxide and distilled from lithium aluminum hydride) and carbon tetrachloride (19.3 g, 0.125 mole) was cooled to –105° (liquid N₂) under an atmosphere of dry nitrogen. To this stirred, cooled solution was added, dropwise, while the temperature of the mixture was maintained between –105 and –100°, a solution of *n*-

(6) All nmr spectra were run as 20–25% by weight solutions in carbon tetrachloride with tetramethylsilane as internal standard using a Varian A-60 spectrophotometer.

(7) All gas chromatography analyses were done on a Beckman G.C.-4 using hydrogen flame detectors. The columns were silicone oil DC 710 and DC 30 on 20/100 Chromosorb W heated at 50, 70, and 120° with helium at a flow of 17 cc/min.

(8) K. v. Auwers, *Ann.*, **432**, 46 (1923).

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

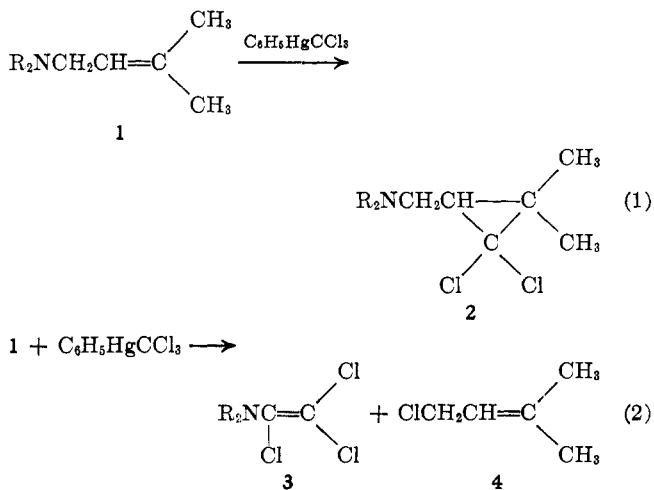
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The reaction of allylamines, in which the allyl chain contains at least four carbon atoms, with phenyl(trichloromethyl)mercury results in (a) cyclopropane formation and (b) a cleavage reaction leading to trichlorovinylamines. The yields of cyclopropanes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

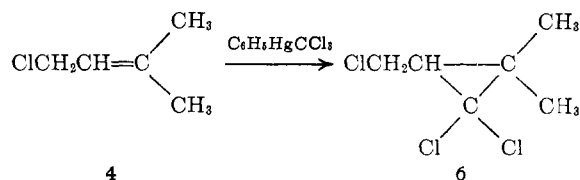
A study of the reaction of a series of acyclic butenylamines with phenyl(trichloromethyl)mercury (the Seyferth³ procedure for generating dichlorocarbene) establishes two principal reaction paths as shown in eq 1 and 2. Isoprene, the cyclopropanes derived by addition of dichlorocarbene to isoprene and 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).