[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

Mechanisms of Elimination Reactions. XII. The Reaction of *cis*- and *trans*-*p*-Nitro-β-bromostyrene with Ethanolic Alkali[1,2]

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cis and *trans*-*p*-nitro-β-bromostyrene isomers, upon reaction with ethanolic sodium hydroxide, are converted to *p*-nitrophenylacetylene and 1,1-diethoxy-2-*p*-nitrophenylethane, respectively. The formation of the acetylene from the *cis* haloölefin (*trans* elimination) is 2300 times as rapid as the formation of the acetal from the *trans* haloölefin. Various reaction paths by which the acetal may be formed are considered.

In the course of our work on elimination from *cis* and *trans* haloölefins, we undertook a study of alkaline dehydrobromination from the isomers of *p*-nitro-β-bromostyrene. Our first experiments were conducted using ethanolic sodium hydroxide as the basic reagent. Dann, Howard and Davies[4] found that *cis*-*p*-nitro-β-bromostyrene produced bromide ion with ethanolic sodium hydroxide at a faster rate than does the *trans* isomer, but the extent of the superiority was not measured quantitatively, nor were the products of the reaction characterized. We have now studied both the kinetics and the products of these reactions.

When *cis*-*p*-nitro-β-bromostyrene was treated with a 10-fold excess of 2 M sodium hydroxide in 95% ethanol for 25 minutes at room temperature (this is about 90 half-lives of the reaction), it was converted quantitatively to the elimination product, *p*-nitrophenylacetylene. The *trans* isomer is much less reactive (see below), and under the conditions described above, less than 4% of the *trans* isomer would react. Accordingly the *trans* isomer was treated with a 10-fold excess of 0.23 M sodium hydroxide in 95% ethanol at 43° for 20 days.[5] The product which was obtained in 88% yield was 1,1-diethoxy-2-*p*-nitrophenylethane. The structure of this acetal was deduced from its analysis, the fact that it gave no tests for unsaturation, and the fact that it was readily converted to derivatives of *p*-nitrophenylacetaldehyde with carbonyl reagents in acid solution.

These are several possible paths by which this acetal might originate. One possibility involves base-promoted elimination of hydrogen bromide to give *p*-nitrophenylacetylene, followed by base-catalyzed addition of ethanol as in equations 1 to 3. This path appears reasonable in view of the fact that treatment of the *trans* haloölefin with sodium hydroxide in isopropyl alcohol or with sodium *t*-butoxide in *t*-butyl alcohol does lead to formation of the acetylene.[2] A further test of this path was made by subjecting *p*-nitrophenylacetylene to the action of 0.5 M sodium hydroxide in ethanol at 43° for 21 hours (less than 4 half-lives of the bromide-producing reaction of *trans*-*p*-nitro-β-bromostyrene). Under these conditions *p*-nitrophenylacetylene was largely converted to the acetal, presumably *via* equations 2 and 3, demonstrating that the rates of these steps are comparable in magnitude to or greater than that of the over-all reaction, a necessary (but not sufficient) condition for the proposed path.

$$p\text{-}O_2NC_6H_4CH{=}CHBr + OH^- \longrightarrow p\text{-}O_2NC_6H_4C{\equiv}CH + H_2O + Br^- \quad (1)$$

$$p\text{-}O_2NC_6H_4C{\equiv}CH + C_2H_5OH \xrightarrow{OH^-} p\text{-}O_2NC_6H_4CH{=}CHOC_2H_5 \quad (2)$$

$$p\text{-}O_2NC_6H_4CH{=}CHOC_2H_5 + C_2H_5OH \xrightarrow{OH^-} p\text{-}O_2NC_6H_4CH_2CH(OC_2H_5)_2 \quad (3)$$

Alternatively, the acetal could arise from a substitution of bromide by ethoxide to give ethyl *p*-nitrophenylvinyl ether, as in equation 4, followed

$$ArCH{=}CHBr + {}^-OC_2H_5 \longrightarrow ArCH{=}CHOC_2H_5 + Br^- \quad (4)$$

by the step represented by equation 3. This possibility finds analogy in the accepted mechanisms for base-catalyzed solvolysis of esters and acid halides,[6] nucleophilic substitution in aromatic systems,[7] and in mechanisms suggested for the displacement of fluorine by alkoxide in hexafluorocyclobutene[8] and of chlorine or bromine from β-halopentachlorostyrene by ethoxide,[9] although other mechanisms are possible for the latter two reactions.

A third possibility involves base-catalyzed addition of ethanol to the *p*-nitrostyrene system, *viz.*

$$ArCH{=}CHBr + C_2H_5OH \xrightarrow{OH^-} ArCH_2CHBrOC_2H_5 \quad (5)$$

followed by transformation of this α-bromo ether to the product acetal by displacement of bromide by ethoxide or by dehydrobromination to the styryl ether followed by equation 3. Analogies to this mechanism may be found in the rapid addition of alcohols to conjugated nitroölefins under basic catalysis,[10] although such additions to *p*-nitro-

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(1) This paper was presented in part before the Division of Organic Chemistry at the Fall 1949 meeting of the American Chemical Society in Atlantic City, New Jersey.

(2) Previous paper in series: S. J. Cristol and W. P. Norris, THIS JOURNAL, **76**, 3005 (1954).

(3) Deceased December 15, 1951.

(4) A. T. Dann, A. Howard and W. Davies, *J. Chem. Soc.*, 605 (1928).

(5) This is about 34 half-lives of the bromide-ion producing reaction.

(6) (a) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, chapter XI; (b) M. L. Bender, THIS JOURNAL, **73**, 1626 (1951).

(7) J. F. Bunnett and R. E. Zahler, *Chem. Revs.*, **49**, 273 (1951).

(8) J. D. Park, M. L. Sharrah and J. R. Lacher, THIS JOURNAL, **71**, 2337 (1949).

(9) S. D. Ross, W. A. Leach and I. Kuntz, *ibid.*, **74**, 2908 (1952).

(10) P. Friedländer and M. Lazarus, *Ann.*, **229**, 234 (1885); J. Thiele and S. Haeckel, *ibid.*, **325**, 1 (1902); J. Meisenheimer and F. Heim, *Ber.*, **38**, 467 (1905); K. W. Rosenmund, *ibid.*, **46**, 1034 (1913); J. Loevenich, J. Koch and U. Pucknat, *ibid.*, **63**, 636 (1930); A. Lambert, C. W. Scaife and A. E. Wilder-Smith, *J. Chem. Soc.*, 1474 (1947).

styrene have apparently not been studied. The addition of ethanol to *p*-nitrophenylacetylene must of course involve addition to a *p*-nitrostyrene system (equation 3).

Several experiments were carried out in the hope that reactions 1 to 3 could be demonstrated by trapping the presumable intermediate, *p*-nitrophenylacetylene. *trans*-*p*-Nitro-β-bromostyrene was treated with a 10-fold excess of 0.15 *M* sodium hydroxide in ethanol containing a suspension of mercuric oxide. The reaction mixture was stirred and heated for six days at 43° (8 half-lives of the reaction of the haloölefin with alkali). There was isolated only 17% of bis-(*p*-nitrophenylethynyl)-mercury along with about 50% of the acetal. *p*-Nitrophenylacetylene gave a 75% yield of the dialkylmercury in a few minutes at room temperature, although the yield was lowered to 44% by a six-hour reflux period in ethanol. The lower yield obtained with the haloölefin led us to abandon this test; isolation of the dialkynylmercury does not establish the necessary proof for the existence of the acetylene intermediate, even for a portion of the reaction, as it is still necessary to show whether or not the rate of the bromide-producing reaction was influenced by the mercuric oxide (the *trans* halide was observed to be relatively inert toward mercuric oxide in refluxing ethanol).

It was observed that thiophenoxide ion would compete successfully with ethoxide for *p*-nitrophenylacetylene to give one of the geometric isomers of phenyl *p*-nitrophenylvinyl thioether, but experiments revealed also that the rate of producing bromide ion from the *trans* haloölefin in alkaline solution was enhanced markedly by the presence of thiophenoxide ion. No evidence is available, therefore, to show that the acetal arises, in the *trans* system, *via* an elimination process, and the other reaction paths must be considered.

Determination of Reaction Rates.—The rates were determined in ordinary commercial ethanol (92.6 wt. %), and the extent of reaction was estimated by Volhard titration, substantially as described previously.[2,11] The data obtained are given in Table I. The rate runs were generally run to 70% completion, although good straight lines were obtained to 80–90% completion. Activation energies and entropies were calculated in the usual fashion[11] from the data in Table I, and these and rate constants read off the activation energy curves at 30° are given in Table II. Also included in Table II are similar data for the known dehydrobromination[2] of the isomeric *p*-nitro-β-bromostyrenes with sodium hydroxide in isopropyl alcohol. The rate constants for the isopropyl alcohol solvent were extrapolated by an Arrhenius plot from the data reported previously.[2]

TABLE I

DATA AND SECOND-ORDER RATE CONSTANTS FOR THE REACTION OF THE ISOMERS OF *p*-NITRO-β-BROMOSTYRENE WITH 92.6 WT. % AQUEOUS ETHANOLIC SODIUM HYDROXIDE

Isomer	Temp., °C.	Halide, *M*	NaOH, *M*	10^4k, l./sec./mole
cis (H and Br *trans*)	11.01	0.00826	0.0479	26.7
		.00830	.0479	25.7
			Ave.	26.2
	19.95	.00957	.0431	95.3
		.00974	.0431	99.8
		.00874	.0431	98.1
			Ave.	97.7
	25.17	.00745	.0180	195
		.01054	.0360	181
		.01019	.0596	189
			Ave.	188
	29.96	.00380	.0215	373
		.00441	.0215	365
			Ave.	369
trans (H and Br *cis*)	30.42	.00728	.0859	0.168
		.00800	.0859	.171
			Ave.	.170
	35.21	.00707	.0859	.311
		.00684	.0859	.307
			Ave.	.309
	40.17	.00705	.0859	.581
		.00704	.0859	.573
			Ave.	.577

TABLE II

SECOND-ORDER RATE CONSTANTS AND QUANTITIES OF ACTIVATION FOR THE REACTIONS OF THE ISOMERS OF *p*-NITRO-β-BROMOSTYRENE WITH SODIUM HYDROXIDE IN 92.6 WT. % ETHYL AND ISOPROPYL ALCOHOL AT 30°

Isomer	Alcohol	10^4k, l./sec./mole	$E_{act.}$, kcal./mole	$\Delta S^{\ddagger}$, cal./deg./mole
cis	Ethyl	370	23.9	+12
	Isopropyl	11400[a]	17.1[b]	− 4[b]
trans	Ethyl	0.158	23.8	− 4
	Isopropyl	.553[a]	21.3[b]	−10[b]

[a] Extrapolated from the data given in ref. 2. [b] Reference 2.

The data in Table II are of interest. *trans* Elimination of the elements of hydrogen bromide by alkali in ethanol from the *cis* haloölefin is 2300 times more rapid than whatever process is occurring in the *trans* haloölefin and is therefore much more rapid than *cis* elimination. Thus the discussion given previously for the system in isopropyl alcohol[2] is strengthened by these results. A comparison of the rates in isopropyl alcohol and in 92.6 wt. % ethanol indicates that in the *trans* elimination case (*cis* isomer), a change from ethanol to isopropyl alcohol increases the rate constant by about 30-fold, the increase in rate being due to a large decrease in energy of activation which is partly compensated by a decrease in entropy of activation. For the *trans* isomer, the increase in rate is only 3.5-fold, although again the decrease in activation energy is partly compensated by an entropy decrease. The smaller increase in rate for the *trans* isomer may be due to different effects of solvent upon the different mechanisms involved in *cis* and *trans* elimination,[2,12] but is equally well explained by the assumption that the reactions outlined in equations 4 or 5 are involved in the reaction of the *trans* isomer in ethanol, going at a rate about ten

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[11] S. J. Cristol, THIS JOURNAL, **69**, 338 (1947); S. J. Cristol, N. L. Hause and J. S. Meek, *ibid.*, **73**, 674 (1951).

[12] S. J. Cristol and W. Barasch, *ibid.*, **74**, 1658 (1952).

times that of the elimination process summarized in equation 1.

The fact that the rates of reaction in isopropyl alcohol are greater than those in 92.6 wt. per cent. ethanol is consistent with the Hughes–Ingold theory of kinetic solvent effects.[13] These authors have complained[14] of the criticism of their theory by Cristol and Barasch,[12] who pointed out the fact that certain experimental data on ion-neutral molecule reactions (including examples of substitution, elimination and ester hydrolysis) are inconsistent with their theory, particularly when small changes in solvent character are involved. Cristol and Barasch advised against a literal interpretation of the theory in terms of either rate constant or activation energy, although it is quite clear that the theory often leads to correct rate predictions, particularly where large effects are predictable on the basis of large changes in medium.[15] The latest paper[14] does not appear to present evidence or justification for a change in advice.

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Experimental

cis-p-**Nitro-β-bromostyrene**, m.p. 48–49°, and the *trans* **isomer**, m.p. 156–157°, were prepared as described earlier.[2]

Dehydrobromination of *cis-p*-Nitro-β-bromostyrene with Ethanolic Sodium Hydroxide.—To a solution of 20 g. (0.50 mole) of sodium hydroxide in 250 ml. of 95% ethanol, 11.5 g. (0.0505 mole) of *cis-p*-nitro-β-bromostyrene was added, and the reaction mixture was allowed to sit at room temperature for 25 minutes. Twenty-six ml. of glacial acetic acid was then added to neutralize the excess base. Alcohol was removed under reduced pressure until a slush remained. Cold water was added to dissolve the salts, and the organic material was filtered off, washed with 100 ml. of cold water and dried. There was obtained 7.45 g. (100%) of *p*-nitrophenylacetylene, m.p. 148–149°. C. L. Müller[16] and H. Wieland[17] report m.p. 149°.

Reaction of *trans-p*-Nitro-β-bromostyrene with Ethanolic Sodium Hydroxide.—To a solution of 4.16 g. (0.104 mole) of sodium hydroxide in 450 ml. of 95% ethanol was added 2.38 g. (0.0104 mole) of *trans-p*-nitro-β-bromostyrene. The reaction mixture was maintained at 43° for 20 days. The alcohol was removed under reduced pressure, 50 ml. of water was added to the residue and the mixture was extracted with two 50-ml. portions of ether. The ether extracts were combined and washed with 75 ml. of water. The ether was evaporated and the residue taken up in 25 ml. of carbon tetrachloride and poured onto an alumina column containing 50 g. of activated alumina (80–200 mesh). One hundred and fifty ml. of carbon tetrachloride was required to elute the material from the column. The carbon tetrachloride was removed under reduced pressure and 2.19 g. (88%) of a yellow oil, m.p. 14–15.5°, was obtained. After recrystallization from ether the melting point was 15–16°. This compound did not add bromine nor was it attacked by cold dilute potassium permanganate solution. Hence it was not unsaturated. The analytical data and the *derivatives prepared from this compound indicate that the* material is the ethyl acetal of *p*-nitrophenylacetaldehyde, **1,1-diethoxy-2-*p*-nitrophenylethane**.

Anal. Calcd. for $C_{12}H_{17}O_4N$: C, 60.24; H, 7.16. Found: C, 60.66; H, 6.94.

Preparation of *p*-Nitrophenylacetaldoxime.—Four drops of *p*-nitrophenylacetal were added to 1 ml. of 50% aqueous ethanol, containing 0.25 g. of hydroxylamine hydrochloride. The mixture was heated to 60–70° whereupon the organic layer turned orange and disappeared upon shaking. When cooled white flaky crystals appeared. The crystals were washed with water and when dried had a melting point of 154–155°. Weerman[18] gives m.p. 155°.

Preparation of the 2,4-Dinitrophenylhydrazone of *p*-Nitrophenylacetaldehyde from *p*-Nitrophenylacetal.—Four drops of *p*-nitrophenylacetal were added to 15 ml. of a solution of 2,4-dinitrophenylhydrazine in ethanol containing sulfuric acid. A yellow precipitate formed immediately which when recrystallized from ethyl acetate gave shiny gold needles, m.p. 190–193°.

Anal. Calcd. for $C_{14}H_{11}N_5O_6$: N, 20.28. Found: N, 20.11.

Reaction of *p*-Nitrophenylacetylene with Ethanolic Sodium Hydroxide.—A solution of 740 mg. (5 mmoles) of *p*-nitrophenylacetylene and 2.9 g. (0.050 mole) of sodium hydroxide in 100 ml. of 95% ethanol was kept at 43° for 21 hours. The ethanol was removed under reduced pressure and 150 ml. of water was added to the residue and then extracted with two 25-ml. portions of ether. The ether was evaporated, the residue was taken up in carbon tetrachloride and passed through a short alumina column; 950 mg. (79%) of crude 1,1-diethoxy-2-*p*-nitrophenylethane, m.p. 9–13°, was obtained. After treatment with silver nitrate solution, to remove a little unreacted acetylene, and recrystallization from ether, the melting point was 14–15°. A mixed melting point with the ethyl acetal of *p*-nitrophenylacetaldehyde prepared from *trans-p*-nitro-β-bromostyrene showed no depression; hence the above product was also the ethyl acetal of *p*-nitrophenylacetaldehyde.

Reaction of *p*-Nitrophenylacetylene and Mercuric Oxide in Basic Ethanol Solution.—To 100 ml. of 95% ethanol was added 1.18 g. (8 mmoles) of *p*-nitrophenylacetylene, 0.32 g. (8 mmoles) of sodium hydroxide and 1.74 g. (8 mmoles) of mercuric oxide. The mixture was placed on a mechanical shaker for 10 minutes. The precipitate was filtered off and extracted with boiling acetone to give 1.5 g. of yellow solid, m.p. 272–274°. This represented a yield of 75% of **bis-(*p*-nitrophenylethynyl)-mercury**.

Anal. Calcd. for $C_{16}H_8HgN_2O_4$: N, 5.65. Found: N, 5.29.

p-Nitrophenylacetylene (632 mg., 4.3 mmoles) was added to a solution of 1.8 g. of sodium hydroxide in 300 ml. of 95% ethanol containing 5 g. of suspended mercuric oxide. The mixture was shaken for 10 minutes, then heated at reflux for 6 hours. The solution was concentrated to 100 ml. and filtered. The solids were extracted with two 50-ml. portions of hot acetone and the acetone was evaporated giving 1.04 g. of sticky solid. The solid was extracted with 20 ml. of hot 75% ethanol, then with 10 ml. of 95% ethanol. The resulting *bis-(p-nitrophenylethynyl)-mercury* weighed 463 mg. (43%).

Reaction of *trans-p*-Nitro-β-bromostyrene with Alcoholic Sodium Hydroxide in the Presence of Mercuric Oxide.—To 300 ml. of 95% ethanol containing 1.8 g. (0.045 mole) of sodium hydroxide and 5 g. (0.024 mole) of mercuric oxide was added 970 mg. (4.3 mmoles) of *trans-p*-nitro-β-bromostyrene. The reaction mixture was stirred continuously for 6 days while being maintained at 43°. The solid was then filtered off and washed with alcohol. The residue was extracted with 200 ml. of acetone and 174 mg. (17%) of bis-(*p*-nitrophenylethynyl)-mercury, m.p. 274–275°, was recovered. There was also recovered from the reaction mixture 500 mg. of a yellow oil which gave a positive test with 2,4-dinitrophenylhydrazine reagent and was apparently *p*-nitrophenylacetal.

When sodium hydroxide was absent, no bromide ion was formed.

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[13] E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 244 (1935); *Trans. Faraday Soc.*, **37**, 657 (1941); K. A. Cooper, M. L. Dhar, E. D. Hughes, C. K. Ingold, B. J. MacNulty and L. I. Woolf, *J. Chem. Soc.*, 2043 (1948); K. A. Cooper, E. D. Hughes, C. K. Ingold, G. A. Maw and B. J. MacNulty, *ibid.*, 2049 (1948); C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 345–350.

[14] E. D. Hughes, C. K. Ingold and R. Pasternak, *J. Chem. Soc.*, 3832 (1953).

[15] See, for example, E. A. Moelwyn-Hughes, *Trans. Faraday Soc.*, **45**, 167 (1949).

[16] C. L. Müller, *Ann.*, **212**, 122 (1882).

[17] H. Wieland, *ibid.*, **328**, 233 (1903).

[18] R. A. Weerman, *ibid.*, **401**, 1 (1913).

Reaction of *p*-Nitrophenylacetylene with Thiophenol and Ethanolic Sodium Hydroxide.—A solution of 750 mg. (5 mmoles) of *p*-nitrophenylacetylene, 2.2 g. (20 mmoles) of thiophenol and 2.8 g. (70 mmoles) of sodium hydroxide in 150 ml. of 95% ethanol was heated at 43° for 3 days. After the ethanol had been removed under reduced pressure, water was added and the mixture was extracted with ether. The ether was removed by evaporation and the product was recrystallized from 95% ethanol to give 530 mg. (41%) of almost pure product, m.p. 70–71°. After several recrystallizations from 95% ethanol or petroleum ether the product, phenyl *p*-nitrophenylvinyl thioether, melted at 73–73.5°. The *cis* or *trans* nature of this product was not investigated.

Anal. Calcd. for $C_{14}H_{11}NO_2S$: N, 5.45. Found: N, 5.57.

Enhanced Reactivity of *trans*-*p*-Nitro-*β*-bromostyrene with Ethanolic Alkali in the Presence of Sodium Thiophenoxide.—A solution of 203 mg. (0.892 mmole) of *trans*-*p*-nitro-*β*-bromostyrene, 8.48 mmoles of sodium hydroxide and 220 mg. (2.0 mmoles) of thiophenol in 100 ml. of 95% ethanol was heated for 10 hours at 43°. A 10-ml. aliquot was removed and added to 15 ml. of 0.4 *M* nitric acid and extracted with 75 ml. of ether. The ether solution was washed with water. (This procedure had been shown to remove thiophenol from standard specimens of sodium chloride solution, which then gave satisfactory Volhard titrations.) Volhard titration of the remaining solution indicated that all of the haloölefin had been converted to bromide ion in the 10-hour period. The half-life for the reaction of the haloölefin with the alkali present is estimated from the rate constant given above as about 40 hours.

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[CONTRIBUTION FROM AVERY LABORATORY, UNIVERSITY OF NEBRASKA]

Reactions of Amines. I. A Novel Rearrangement of N,N-Dichloro-*sec*-alkylamines

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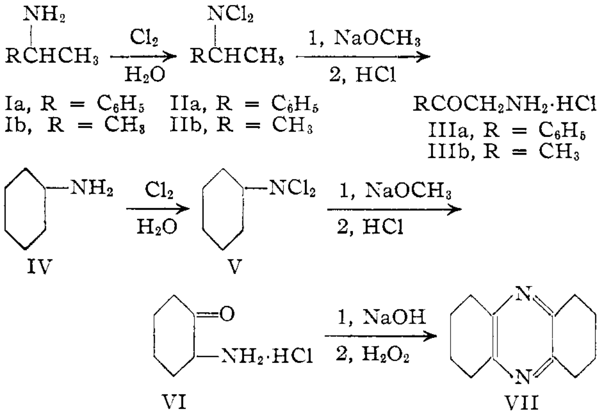
The reaction of N,N-dichloro-*α*-phenylethylamine, N,N-dichloroisopropylamine and N,N-dichlorocyclohexylamine with sodium methoxide followed by treatment with aqueous hydrochloric acid yielded phenacylamine hydrochloride, aminoacetone hydrochloride and *α*-aminocyclohexanone hydrochloride, respectively. The similar treatment of N,N-dichlorocyclohexylamine followed by oxidative cyclization yielded 1,2,3,4,6,7,8,9-octahydrophenazine. A mechanism for these reactions is suggested.

As part of an extensive study of the synthesis and reactions of dichloroamines Berg[2] reported that N,N-dichloroethylamine formed potassium acetate and acetonitrile (in unspecified yields) when treated with potassium hydroxide. Although variations on this general technique have constituted a general synthesis of nitriles from N,N-dihalo-*prim.*-alkylamines,[3] the reactions of N,N-dichloro-*sec*-alkylamines with alkaline reagents appear not to have been studied. The present communication records our observations on the reactions of N,N-dichloro-*α*-phenylethylamine (IIa), N,N-dichloroisopropylamine (IIb) and N,N-dichlorocyclohexylamine (V) with sodium methoxide.



Ia, R = C_6H_5 IIa, R = C_6H_5

Ib, R = CH_3 IIb, R = CH_3

$RCOCH_2NH_2 \cdot HCl$

IIIa, R = C_6H_5

IIIb, R = CH_3

IV V VI VII

The dichloroamines were prepared in 82–93% yields from the amines by acidifying a suspension of the amine in potassium hypochlorite solution with acetic acid, a procedure that was rapid, gave uniformly high yields and was much simpler than the earlier procedures of Berg[2] and of Jackson, Smart and Wright.[4] As pointed out by Berg[2] it is difficult to prepare dichloroamines from amines of the type $ArCHNH_2R$ by direct chlorination. Thus, although we were able to prepare crude IIa in good yield, the product was generally contaminated with other reaction products. Indeed, if the temperature of the chlorination was not kept below 30°, the principal product (in relatively poor yield) was acetophenone (formed probably by dehydrohalogenation and hydrolysis of the intermediate monochloroamine). Although this observation suggests that *sec*-alkylamines might be converted into the corresponding ketones by monochlorination and hydrolysis, in our hands only Ia gave any significant amount of the ketone. A modification of this technique will be reported later.

Based on a possible mechanistic similarity to the Neber rearrangement[5,6] it was predicted that the reaction of an N,N-dichloro-*sec*-alkylamine (II) with sodium methoxide would take the course. The first step, dehydrochlorination of II to the N-chloroketimine (VIII), probably would proceed by a concerted mechanism similar to that postulated for the base-catalyzed dehydrochlorination of alkyl halides, abstraction of the proton by methoxide ion with simultaneous shift of an electron pair and ejection of chloride ion.[7] The ease of

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[1] Standard Oil Company (of Indiana) Fellow, 1951–1953.

[2] A. Berg, *Ann. chim.*, [7] **3**, 289 (1894).

[3] V. Migrdichian, "The Chemistry of Organic Cyanogen Compounds," Reinhold Publ. Corp., New York, N. Y., 1947, p. 3.

[4] L. K. Jackson, G. N. R. Smart and G. F. Wright, THIS JOURNAL, **69**, 1539 (1947).

[5] (a) P. W. Neber and A. Friedolsheim, *Ann.*, **449**, 109 (1926); (b) P. W. Neber and A. Uber, *ibid.*, **467**, 52 (1928); (c) P. W. Neber and A. Burgard, *ibid.*, **493**, 281 (1932); (d) P. W. Neber and G. Huh, *ibid.*, **515**, 283 (1935); (e) P. W. Neber, A. Burgard and W. Thier, *ibid.*, **526**, 277 (1936).

[6] (a) D. J. Cram and M. J. Hatch, THIS JOURNAL, **75**, 33 (1953); (b) M. J. Hatch and D. J. Cram, *ibid.*, **75**, 38 (1953).

[7] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 420.