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.

BOULDER, COLORADO

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

BY HENRY E. BAUMGARTEN AND FRANK A. BOWER[1]

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
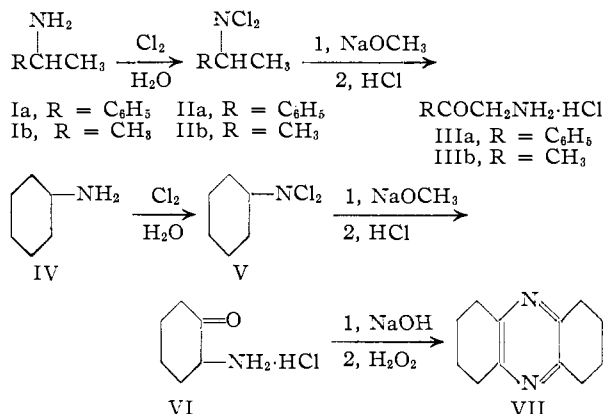
The dichloroamines were prepared in 82–93% yields from the amines by acidifying a suspension of the amine in potassium hypochlorite solution with acetic acid, a procedure that was rapid, gave

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

(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.
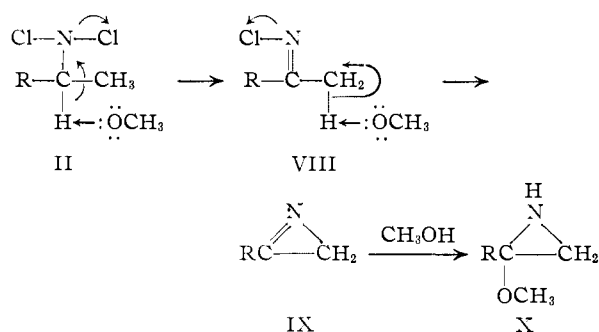
removal of hydrogen chloride should parallel the acidity of the hydrogen atom and thus should be somewhat greater for R = phenyl than for R = saturated alkyl (possibly explaining why IIa is less stable than IIb or V). Accordingly, the first amine studied was α-phenylethylamine (Ia). The reactions of N-halo mono- or dialkylketimines apparently have not been studied, but the behavior of N-haloarylaldimines with base[8] is analogous to that observed for aldoxime tosylates,[6b] nitriles being formed. Thus, within the limits of the analogy VIII could be expected to react further with alkoxide ion in a manner and by a mechanism similar to that recently described by Hatch and Cram[6b] for ketoxime tosylates (the Neber rearrangement), i.e., by base induced 1,3-elimination and cyclization. The end-product of this sequence would be the azirine (IX) or, more probably as demonstrated by Hatch and Cram,[6b] the methoxyethyleneimine (X). Treatment of the latter with aqueous hydrochloric acid would yield, as in the Neber rearrangement, the α-amino ketone hydrochloride.

As predicted, IIa reacted vigorously (qualitatively more vigorously than IIb or V) with methanolic sodium methoxide and following treatment with dilute hydrochloric acid gave 52% of phenacylamine hydrochloride (IIIa), identified by comparison with an authentic specimen prepared by another route. By a similar sequence IIb gave aminoacetone hydrochloride (IIIb) in 25% yield and V gave α-aminocyclohexanone hydrochloride (VI) in 46% yield. Both IIIa and IIIb have been prepared by the Neber rearrangement[5d,e]; VI has not been reported previously. However, Smith[9] has described the preparation of 1,2,3,4,6,7,-8,9-octahydrophenazine (VII) by a variation of the Neber rearrangement presumably involving the free base of VI as an unisolated intermediate. For the purpose of comparison with the latter synthesis, an aqueous extract containing VI (from the present rearrangement) was basified with sodium hydroxide and treated with hydrogen peroxide, giving 48% of VII.

Attempts to extend the Neber rearrangement to aldoxime tosylates have led, through an E₂ elimination of p-toluenesulfonic acid, to the formation of the corresponding nitrile,[6b] and the dehydrohalogenation of N,N-dihalo-prim.-alkylamines was stated above to be a general method of synthesis of nitriles.[3] Nevertheless, it was thought advisable

to subject an N,N-dihalo-prim.-alkylamine to the conditions of the present rearrangement. Thus, from the treatment of N,N-dichloro-β-phenylethylamine with sodium methoxide, phenylacetonitrile was obtained in 40% yield as the only isolable organic product.

Based on the logical starting materials, the amine in the present rearrangement and the ketone in the Neber rearrangement, the yields obtained from the former compare quite favorably with those from the latter (see Table I) except in the case of IIIb, which is obtained in considerably better yield in the Neber rearrangement. Furthermore, the present synthesis of VII appears to be more satisfactory than any previously reported.[9-12]

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TABLE I

COMPARISON OF NEBER AND DICHLOROAMINE REARRANGEMENTS

</div>

Starting material	Procedure[a]	Product	Over-all yield, %
Acetophenone[b]	A	IIIa	38
Ia	B	IIIa	45
Acetone[b,c]	A	IIIb	46
Ib	B	IIIb	22
Cyclohexanone[d]	A	VII	<5
IV	B	VII	45

[a] Procedure A = Neber rearrangement, procedure B = dichloroamine rearrangement. [b] Ref. 6d. [c] Calculation based on the upper limit of the yield of acetoxime (67–76%) as reported in "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 318. [d] Ref. 9.

The simplicity of the laboratory operations and the ease of isolation of products in the present rearrangement may recommend its use in syntheses where the amine is readily available. These and other applications and extensions of the method will be reported later.

Experimental[13]

N,N-Dichloro-α-phenylethylamine (IIa).—An approximately 1.5 M solution of potassium hypochlorite was prepared by dissolving 100 g. of commercial calcium hypochlorite ("HTH," Mathieson Chemical Corp., said to be at least 70% calcium hypochlorite) in 400 ml. of warm water, adding 70 g. of potassium carbonate in 200 ml. of water, shaking the resultant mixture until the curdy precipitate of calcium carbonate became finely granular, filtering the cooled mixture and washing the filter cake with 80 ml. of cold water. To the solution cooled to 5° in ice was added slowly with stirring 24.2 g. (0.20 mole) of α-phenylethylamine followed by the dropwise addition of 60 g. (1.0 mole) of glacial acetic acid, both additions being conducted at such a rate that the temperature was kept below 10°. The mixture was stirred an additional two hours at the low temperature. The yellow, oily lower layer was separated, washed with cold water, cold 50% sulfuric acid and twice again with cold water and dried over 2 g. of magnesium sulfate. Removal of the drying agent gave 32.5 g. (86%) of crude N,N-dichloro-α-phenylethylamine as a clear yellow oil. In other experiments the yield varied from 82–92%. In most experiments the chlorine content of the product (after an

(8) C. R. Hauser, A. G. Gillaspie and J. W. LeMaistre, THIS JOURNAL, **57**, 567 (1935), and earlier papers.

(9) P. A. S. Smith, *ibid.*, **70**, 323 (1948).

(10) M. Godchot and M. Mousseron, *Bull. soc. chim. France*, [4] **51**, 360 (1932).

(11) A. Treibs and D. Dinelli, *Ann.*, **517**, 152 (1935).

(12) It may be noted that the Neber rearrangement is doubly unsatisfactory in this instance because of the low yield and of the tendency of the ketoxime tosylate to deflagrate when exposed to air.[9]

(13) Reactions involving chloroamines should be carried out in a good hood. The vapors of these compounds, particularly the lower boiling members such as IIb, cause irritation of the eyes, nose and throat, and, if inhaled in more than minute amounts, cause headache and general discomfort.

additional washing with 5% sodium thiosulfate or sodium bisulfite) was found to be 34–36% (calcd. for C$_8$H$_{10}$NCl, 22.82; for C$_8$H$_9$NCl$_2$, 37.37).[14] It was advisable to use the crude product within a short time after preparation, for on standing extensive decomposition of the product took place.

Reaction of N,N-Dichloro-α-phenylethylamine with Sodium Methoxide.—To the hot solution resulting from the addition of 100 ml. of absolute methanol[15] to 9 g. (0.4 mole) of sodium, a solution of 32.5 g. (0.17 mole) of N,N-dichloro-α-phenylethylamine in an equal volume of absolute methanol was added dropwise with vigorous stirring at such a rate as to maintain a gentle reflux. Each drop reacted with a crisp, audible snap. After addition was complete, the mixture was stirred and warmed on the steam-bath for 15 minutes, cooled in ice and poured into 150 ml. of ether. The precipitated sodium chloride (dry weight, 85–95% of theory) was removed by filtration and washed with 50 ml. of ether. The ethereal solution was extracted cautiously (liberation of heat) with one 150-ml. and two 50-ml. portions of 2 N hydrochloric acid and the combined aqueous extracts were washed with 50 ml. of ether. The aqueous solution was pale yellow at this point.

The hydrochloric acid and water were distilled off under reduced pressure at a low temperature (< 40°) or allowed to evaporate at room temperature and pressure. The residue was dissolved in 100 ml. of hot absolute ethanol, 0.5 ml. of concentrated hydrochloric acid was added, and the solution was filtered from undissolved sodium chloride and chilled, giving 15.2 g. (52%) of phenacylamine hydrochloride, m.p. 185–186° dec., mixed m.p. with material prepared as described below 185–186°. Distillation of the ether extracts gave a variable small amount of acetophenone.

Phenacylamine Hydrochloride.—To a solution of 50 g. (1.2 moles) of sodium hydroxide in 1 l. of water, 192 g. (1.00 mole) of ethyl benzoylacetate was added and the mixture was stirred at room temperature for four hours and allowed to stand overnight. The solution was cooled to 2°, 69 g. (1.00 mole) of sodium nitrite was added and 350 ml. (1.25 moles) of 3.6 M sulfuric acid was added dropwise with stirring over a period of 45 minutes, the temperature being kept below 6° by periodic addition of crushed ice. After standing one hour at room temperature, the precipitated, crude isonitrosoacetophenone was collected and recrystallized from ethyl acetate–toluene, giving 93 g. (63%) of pure isonitrosoacetophenone, m.p. 128–129° (lit.[16] m.p. 126–128°). Reduction of the isonitrosoacetophenone with stannous chloride in concentrated hydrochloric acid[17] gave 70 g. (66%) of phenacylamine hydrochloride, m.p. 185–186° dec.

N,N-Dichloroisopropylamine (IIb) was prepared as described above for N,N-dichloro-α-phenylethylamine. From 11.8 g. (0.20 mole) of isopropylamine 22.5 g. (88%) of N,N-dichloroisopropylamine[4] was obtained.

Anal. Calcd. for C$_3$H$_7$NCl$_2$: Cl, 55.47. Found: Cl, 55.12.

Reaction of N,N-Dichloroisopropylamine with Sodium Methoxide.—N,N-Dichloroisopropylamine (22.5 g., 0.18 mole) was treated with the methanolic sodium methoxide from 9 g. of sodium and 100 ml. of methanol and worked up as described above for the reaction of N,N-dichloro-α-phenylethylamine. Evaporation of the nearly colorless acidic aqueous solution (preferably at room temperature) gave a tan residue which was dissolved in 50 ml. of absolute methanol, filtered from sodium chloride and treated with charcoal. Fractional precipitation by the addition of absolute ether (up to a total volume of 400 ml.) gave 4.7 g. (25%) of aminoacetone hydrochloride (after discarding the

first few fractions which were largely sodium chloride), m.p. 73–74° (lit.[18] m.p. 75°), as a very hygroscopic solid.

N,N-Dichlorocyclohexylamine (V) was prepared as described above for N,N-dichloro-α-phenylethylamine using double the quantities of all reagents. From 39.6 g. (0.4 mole) of cyclohexylamine 62.5 g. (93%) of N,N-dichloro-cyclohexylamine[4] was obtained.

Anal. Calcd. for C$_6$H$_{11}$NCl$_2$: Cl, 42.19. Found: Cl, 42.02.

Reaction of N,N-Dichlorocyclohexylamine with Sodium Methoxide.—N,N-Dichlorocyclohexylamine (62.5 g., 0.37 mole) was treated with the methanolic sodium methoxide from 18 g. (0.8 mole) of sodium and 200 ml. of methanol and worked up as described above for the reaction of N,N-dichloro-α-phenylethylamine. In all of the experiments with N,N-dichlorocyclohexylamine the methanolic reaction mixture became much darker (tan to dark brown) than with the other dichloroamines.[15] The aqueous acid extract was tan to red-brown, but most of the color could be removed by two or three treatments with charcoal. The resultant solution of α-aminocyclohexanone hydrochloride was used in the following experiments.

(a) One-half of the solution was allowed to evaporate to near dryness at room temperature. The resultant semi-crystalline mush was stirred with 50 ml. of absolute ethanol and allowed to evaporate to dryness The residue was a pale tan crystalline mixture of sodium chloride and α-aminocyclohexanone hydrochloride (22.2 g.). The solid was warmed with 120 ml. of absolute ethanol, 0.5 ml. of concentrated hydrochloric acid was added, and the undissolved sodium chloride was removed by filtration. On cooling more sodium chloride precipitated and was removed. Fractional precipitation by the addition of absolute ether (to give successive total volumes of solution of 250 ml., 500 ml. and 1 l.) followed by chilling in ice gave 12.8 g. (46%) of α-aminocyclohexanone hydrochloride as fine, nearly colorless crystals, m.p. 157–158° dec.

Anal.[19] Calcd. for C$_6$H$_{11}$NOCl: C, 48.17; H, 8.09; N, 9.36. Found: C, 47.71; H, 7.88; N, 9.65.

(b) One-sixth of the solution was evaporated and treated with ethanol and reëvaporated as described in (a). A solution of the crude solid in 50 ml. of water was stirred in ice and treated with 7 g. of benzoyl chloride followed by the slow addition of a solution of 10 g. of potassium hydroxide in 10 ml. of water. The mixture was shaken until the odor of benzoyl chloride disappeared. The filtered, sticky crude product was dissolved in hot ethanol (40 ml.) and treated twice with charcoal. On cooling colorless crystals (0.2 g.) deposited, which were recrystallized from dilute ethanol giving 0.18 g. of a product, m.p. 194–197°, whose analysis was consistent with that calculated for the monohydrate of 5,10-dibenzoyl-1,2,3,4,5,6,7,8,9,10-decahydrophenazine.[20]

Anal.[19] Calcd. for C$_{26}$H$_{28}$N$_2$O$_3$: C, 74.97; H, 6.78; N, 6.73. Found: C, 75.35; H, 6.64; N, 6.74.

Water (60 ml.) was added to the first ethanolic filtrate and the solution was warmed on the steam-bath and decanted from a small amount of oily material. The solution was treated with charcoal, cooled and filtered, giving 0.3 g. of N-benzoyl-α-aminocyclohexanone, m.p. 126.8–127.8°. Evaporation of the filtrate yielded an additional 1.1 g. of the N-benzoyl-α-aminocyclohexanone.

Anal.[19] Calcd. for C$_{13}$H$_{15}$NO$_2$: C, 71.85; H, 6.96; N, 6.45. Found: C, 72.09; H, 6.77; N, 6.76.

(c) To one-sixth of the aqueous extract, heated on the steam-bath for 15 minutes to expel dissolved solvents, was added 120 g. of 33% potassium hydroxide solution, followed by 10 ml. of 35% hydrogen peroxide. Heating was continued for 10 minutes and the mixture was cooled in ice. The crude product (2.95 g.) was collected, air-dried and recrystallized from petroleum ether (or acetone), giving 2.3 g. (40%) of 1,2,3,4,6,7,8,9-octahydrophenazine, m.p. 109.6–110.6° (lit.[9] m.p. 108–109°). The product gave a picrate melting at 164–166°; 1,2,3,4,6,7,8,9-octahydrophenazine is reported[9] to give a dipicrate, m.p. 162–163°.

(14) The analysis for chlorine was carried out in the following manner. A 100-mg. sample of the dichloroamine was weighed into a small vial and introduced into a flask containing a little more than the theoretical quantity of sodium methoxide in 10 ml. of absolute methanol. After standing overnight the mixture was heated to boiling on the steam-bath, diluted with 20 ml. of distilled water and acidified with nitric acid. The chloride was then determined gravimetrically as silver chloride.

(15) Drying the commercial absolute methanol as described by R. B. Loftfield and L. Schaad (THIS JOURNAL, **76**, 35 (1954)), seemed to have a small, favorable effect on the final yield and, in the case of N,N-dichlorocyclohexylamine, to lessen the darkening of the reaction mixture.

(16) L. Claisen and O. Manasse, *Ber.*, **20**, 2194 (1887).

(17) H. Rupe, *ibid.*, **28**, 251 (1895).

(18) S. Gabriel and G. Pinkus, *ibid.*, **35**, 3806 (1902).

(19) Analysis by Clark Microanalytical Laboratory, Urbana, Ill.

(20) Presumably this product arose from the condensation of two molecules of VI to give 1,2,3,4,4a,6,7,8,9,9a-decahydrophenazine which rearranged under the influence of base to 1,2,3,4,5,6,7,8,9,10-decahydrophenazine followed by benzoylation.

In eleven other experiments the yield of 1,2,3,4,6,7,8,9-octahydrophenazine varied from 39–53%, average yield, 48%. In small scale experiments the product was best isolated by extraction with ether. Evaporation of the ether caused the product to crystallize in large, colorless needles.

(d) One-sixth of the solution was treated as in (c) except that no hydrogen peroxide was added and the mixture was allowed to stand for one week. On first adding the potassium hydroxide a copious precipitate formed which slowly dissolved or reformed to a more compact precipitate, which was slowly oxidized by air to 1,2,3,4,6,7,8,9-octahydrophenazine, yield 2.2 g. (38%).

Reaction of N,N-Dichloro-β-phenylethylamine with Sodium Methoxide.—N,N-Dichloro-β-phenylethylamine was prepared in 95% crude yield by the procedure described above for N,N-dichloro-α-phenylethylamine. The crude product was treated with sodium methoxide and the product was worked up as described for N,N-dichloro-α-phenylethylamine. Evaporation of the acidic aqueous solution produced only sodium and ammonium chlorides. Distillation of the ethereal solution yielded (from 0.1 mole of the amine) 4.7 g. (40%) of phenylacetonitrile, b.p. 121–125° (15 mm.), identified by hydrolysis in aqueous acetic–hydrochloric acid solution (in poor yield) to phenylacetic acid.

LINCOLN 8, NEBRASKA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN]

The Demyanov Ring Expansion. II. Comparison of the Expansion of Five- and Six-Membered Rings[1]

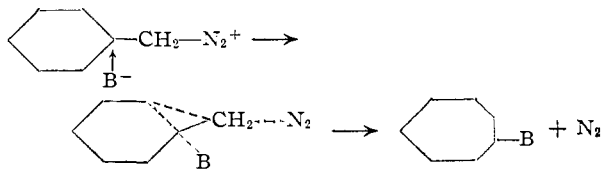BY PETER A. S. SMITH, DONALD R. BAER AND SEYHAN N. EGE

The Demyanov rearrangement has been attempted with cyclopentylcarbinylamine, 1-(1-phenylcyclopentyl)-ethylamine, cyclopentylphenylcarbinylamine, 1-cyclopentyl, 1-cyclohexyl- and 1-(4-methylcyclohexyl)-ethylamine. The composition of the alcohols produced was examined by infrared spectroscopy. Ring expansion was complete in only one case, and only occurred to a detectable extent when such expansion could be expressed as the conversion of a less stable to a more stable carbonium ion. Isomeric tertiary alcohols were formed in most cases in small to moderate amounts. n-Butylamine gave n-butyl chloride when treated with nitrosyl chloride. A number of alicyclic alcohols were characterized as their p-phenylazophenylurethans, but initial attempts to separate alcohol mixtures by chromatography of this derivative were unsatisfactory. A number of new alkylcyclopentylcarbinylamines has been prepared and characterized.

The Demyanov ring expansion is accomplished usually by treating an aminomethylcycloalkane with nitrous acid, and results in the formation of a cyclic alcohol containing one more carbon atom in the ring, usually accompanied by some olefin.[2] It has in practice been limited to compounds in which the amino group is separated from the alicyclic ring by an unsubstituted methylene group, although no extensive investigations of its limitations in this direction have been made. Occasional hypotheses regarding the mechanism of the reaction have been published[3]; it would seem to be best regarded as a special case of the type of rearrangement generally accompanying the treatment of primary aliphatic amines with nitrous acid. Perhaps the most widely accepted view of the nature of such rearrangements is that they involve the formation of a more stable carbonium ion from one of higher energy.[3a,c] The stability of carbonium ions is empirically correlatable with the number and nature of the substituents on the electron-deficient carbon, and such effects have been the subject of theoretical interpretation.[3a,4]

Three principal questions are apparent concerning the Demyanov ring-expansion. One is an explanation for the predominance of alkyl migration, leading to an apparent secondary carbonium ion by ring expansion, over hydrogen migration, leading to

a presumably more stable tertiary carbonium ion without ring expansion. The analogous open-chain situation, the formation from isobutylamine of sec-butyl alcohol by methyl migration vs. the formation of t-butyl alcohol by hydrogen migration, appears to result in complete predominance of hydrogen migration.[5] Another question is the extent to which the nature of the anion (chloride, hydroxide, acetate, etc.) to which the alkyl group is found attached in the final products has influenced the rearrangement. The third question is the relative importance of stereochemical and electrical effects in determining the direction of expansion of unsymmetrical rings.

In connection with these questions, our present work is influenced by the consideration that the loss of nitrogen from an aliphatic diazonium ion may not be a purely unimolecular process leading to the corresponding carbonium ion. It may well occur by two competitive processes: a displacement reaction by a nucleophilic agent, leading to an alkyl derivative of unrearranged structure; and an internal displacement by the migrating species (hydrogen or alkyl), leading to a carbonium ion of rearranged structure.[6] Furthermore, the latter process may be combined with the former in a con-

(1) Partly from the doctoral dissertation of D. R. Baer, 1952. Presented at the National Meeting, Am. Chem. Soc., Atlantic City, N. J., Sept., 1952.

(2) T. W. J. Taylor and W. Baker, "Sidgwick's Organic Chemistry of Nitrogen," Oxford University Press, London, 1952, p. 23, et seq.

(3) E.g., (a) E. R. Alexander, "Principles of Ionic Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1950, pp. 41, 49–50; (b) G. Darzens and M. Meyer, Compt. rend., 233, 749 (1951); (c) I. Elphimoff-Felkin and B. Tchoubar, ibid., 237, 726 (1953).

(4) I. Dostrovsky, E. D. Hughes and C. K. Ingold, J. Chem. Soc., 173 (1946).

(5) L. Henry and A. deWael, Compt. rend., 145, 899 (1907); E. Linnemann, Ann., 162, 24 (1872).

(6) Cf. J. D. Roberts and J. A. Yancey, THIS JOURNAL, 74, 5943 (1952); J. D. Roberts and C. M. Regan, ibid., 75, 2069 (1953); J. D. Roberts and M. Halmann, ibid., 75, 5759 (1953).