Acetylation of 2,3-Diphenyl-6-hydrazinopyrazine. (a) Formation of 1,2,2-Triacetyl-1-(2,3-diphenyl-6-pyrazinyl)-hydrazine.—The hydrazinopyrazine (1.0 g., 0.004 mole), acetic anhydride (2 ml.), and acetic acid (2 ml.) were heated under reflux for 2.5 hr. The acetylation mixture was evaporated and the residue recrystallized from methanol (charcoal) from which it separated as colorless rhombs, m.p. 178–179°. Ultraviolet spectrum in ethanol: λ_{max} 228, 283, 324 mμ; ε 24,000, 12,000, 12,000.

Anal. Calcd. for $C_{22}H_{20}N_4O_3$: C, 68.0; H, 5.2; N, 14.4. Found: C, 68.2; H, 5.3; N, 14.6. Mol. wt.: calcd., 388; found, 400.

(b) Formation of 1,2-Diacetyl-1-(2,3-diphenyl-6-pyrazinyl)-hydrazine.—The hydrazinopyrazine (1.0 g., 0.004 mole), dissolved in dry pyridine (6 ml.), was treated with acetyl chloride (0.4 ml.; 0.004 mole) added dropwise. After 1 hr. at room temp. the reaction mixture was poured into ice water and the resulting solid collected. The crude diacetyl compound (0.85 g.) crystallized from benzene–petrol as small, white needles, m.p. 167–168° and repeated recrystallization was necessary to effect complete removal of the unchanged hydrazine present.

Anal. Calcd. for $C_{20}H_{18}N_4O_2$: C, 69.4; H, 5.2; N, 16.2. Found: C, 69.1; H, 5.2; N, 16.2.

This same product was obtained from the above triacetyl compound by dissolving it in methanol and evaporating the solution to dryness on the water bath. More methanol was added and the diacetyl derivative was first crystallized from methanol and then benzene–petrol. The triacetyl compound also tended to decompose slightly on prolonged boiling in toluene.

Attempted Synthesis of 3-Mercapto-5,6-diphenyl-*s*-triazolo[4,3-*a*]-pyrazine. (a) Using Carbon Disulfide.—2,3-Diphenyl-6-hydrazinopyrazine (1.0 g., 0.004 mole), carbon disulfide (2 ml., 0.025 mole), and pyridine (10 ml.) were heated under reflux until hydrogen sulfide ceased to be evolved (7 hr.). The solvent was evaporated and the residue recrystallized from a tetrahydrofuran–ethanol mixture. 1,3-Di(5,6-diphenyl-2-pyrazinylamino)thiourea separated in poor yield as a pale yellow, microcrystalline solid, m.p. 239–240°.

Anal. Calcd. for $C_{38}H_{26}N_8S\cdot0.5H_2O$: C, 68.8; H, 4.7; N, 19.6; S, 5.6. Found: C, 68.4; H, 4.5; N, 19.3; S, 5.9.

(b) Using Phenyl Isothiocyanate.—The above hydrazine (1.0 g., 0.004 mole), phenyl isothiocyanate (0.7 g., 0.005 mole), and trichlorobenzene (5 ml.) were heated under reflux for 5 hr. The solvent was removed (at 0.05 mm.) and, after attempts at purification by crystallization failed, the residue was sublimed at 150°/0.001 mm. The sublimate crystallized from benzene–petrol as white needles, m.p. 187–188° and was identified as 5,6-diphenyl-*s*-triazolo[4,3-*a*] pyrazine by mixed m.p. determination and comparison of its infrared spectrum with that of an authentic specimen.

Acknowledgment—P. N. is grateful for the award of a University Research Grant from the University of Adelaide Research Fund and grateful acknowledgment is also made for partial support of this work by PHS research grant CY-5973 from the National Cancer Institute, Public Health Service.

5-Trifluoromethyltetrazole and Its Derivatives

WILLIAM P. NORRIS

Organic Chemistry Branch, Chemistry Division, U.S. Naval Ordnance Test Station, China Lake, California

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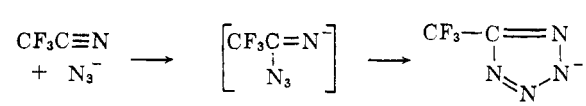
Sodium 5-trifluoromethyltetrazole was readily prepared from trifluoroacetonitrile and sodium azide. The salt was converted to the free tetrazole, which is a strong, stable, organic nitrogen acid, methylated to give 1- and 2-methyl-5-trifluoromethyltetrazole and chlorinated to give N-chloro-5-trifluoromethyltetrazole.

Trifluoroacetonitrile at atmospheric pressure and room temperature reacts exothermally with sodium azide in acetonitrile to give sodium 5-trifluoromethyltetrazole (I). These are the mildest conditions yet reported for the formation of a tetrazole from a nitrile and an inorganic azide.[1,2] The high reactivity of trifluoroacetonitrile is in agreement with the observation[1] that electronegative groups on the nitrile facilitate tetrazole formation; for example, *p*-nitrobenzonitrile, terephthalonitrile, and perfluorocaprylonitrile reacted readily with sodium azide at 100° in dimethylformamide to form 5-substituted tetrazoles. Benzonitriles with more electropositive substituents and aliphatic nitriles required higher temperatures and acid catalysis to give good yields of tetrazole.

These data and the results reported in this paper indicate that more than one mechanism is operating in tetrazole formation from nitriles and inorganic azides. Hence the general mechanism[3] as stated by Henry, Finnegan, and Lofquist[1] may be separated into two mechanisms: (1) In the case of electronegatively substituted nitriles no acid catalyst is needed and the reaction probably proceeds by attack of azide ion on the carbon of the nitrile



group followed by ring closure to give the salt of the tetrazole. The electronegative substituent on the nitrile facilitates initial attack by azide ion and stabilizes the negative charge of the intermediate by its inductive effect. The positively charged

(1) A variety of aromatic and aliphatic nitriles reacted with ammonium azide in dimethylformamide at 95–125° to give 5-substituted tetrazoles. [W. G. Finnegan, R. A. Henry, and R. Lofquist, *J. Am. Chem. Soc.*, **80**, 3908 (1958).]

(2) 5-Substituted tetrazoles were prepared from substituted acetonitriles and aluminum azide in refluxing tetrahydrofuran [H. Behringer and K. Kohl, *Ber.*, **89**, 2648 (1956).]

(3) "The general mechanism for the reaction appears to be a nucleophilic attack of azide ion on the carbon of the nitrile group, followed by ring closure of the imino azide to form the tetrazole ring."[1]

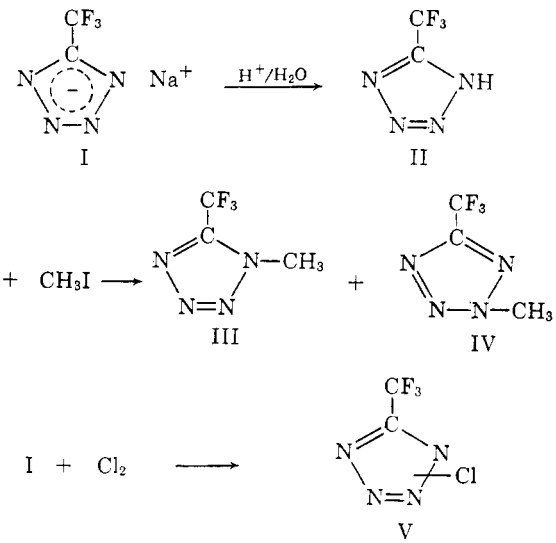
sodium ion is undoubtedly associated with the negatively charged intermediate, further stabilizing it.

(2) In the case of electropositively substituted nitriles acid catalysis is required. For example, with acetonitrile and sodium azide no sodium 5-methyltetrazole is formed even at 200° after eighteen hours. However, by the addition of one mole of ammonium chloride per mole of sodium azide acetonitrile reacted readily at 150° to give 5-methyltetrazole. The acid-catalyzed reaction may proceed by the path outlined.[1]

Under certain circumstances tetrazole formation may proceed by more than one route in the same reaction mixture, *e.g.*, benzonitrile which can react directly with sodium azide but reacts more rapidly in the presence of an acid catalyst.[1]

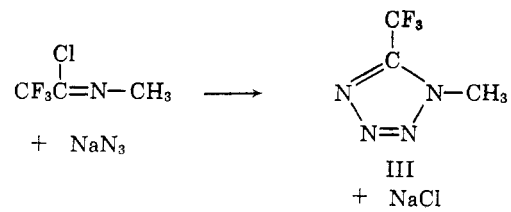
In addition to the above reaction paths, a third might be operating in acidic systems, that is, condensation of molecular hydrazoic acid and the nitrile analogous to tetrazole formation from alkyl azides and nitriles.[4]

Sodium 5-trifluoromethyltetrazole (I)[5] is a white crystalline compound, insoluble in diethyl ether but quite soluble in tetrahydrofuran, acetonitrile, dimethylformamide, and water. (These were the only solvents tested.) Treatment of I with hydrochloric acid gives 5-trifluoromethyltetrazole (II), a colorless, slightly viscous liquid, distilling at 81–82° at 5 mm. 5-Perfluoroheptyltetrazole[1] is a liquid but all other 5-substituted tetrazoles investigated are solids at room temperature.[6] 5-Trifluoromethyltetrazole (II) is a very strong organic acid, pK_a 1.14, weaker than trifluoroacetic acid[7] by less than a pK_a unit. It can be isolated in pure form and is stable. These properties make II rather unique among the "nitrogen acids" since many of the stronger acids of this class exist only in solution or are unstable materials if isolated.[8,9] 5-Methylnitraminotetrazole,[10] pK_a 2.88, is quite a strong acid of this class but not as strong as II. 5-Azidotetrazole[11] is reported to be a strong acid but no dissociation constant is given. The substitution of fluorines for hydrogens on the methyl group of 5-methyltetrazole greatly increases its acidity. In fact, the difference in pK_a units between 5-methyltetrazole[12] and II is 4.42 and between acetic acid[13] and trifluoroacetic acid[7] is 4.49 indicating that the effect of the trifluoromethyl group is transmitted as effectively through the tetrazole group as through the carboxyl group. This property of the tetrazole ring has been noted previously.[10] The proton nuclear magnetic resonance spectrum of II (neat) gave a single sharp line, −312 c.p.s./60 Mc. with respect to the proton on an external trifluoroacetic acid standard.[14] The absorption band is very narrow and shows no fine structure. This may be due to a rapid proton exchange reaction or to some special structural feature which prevents coupling of the proton with nitrogen or the fluorine of the trifluoromethyl group.



Methyl iodide reacts with I to give 1-methyl-5-trifluoromethyltetrazole (III) and 2-methyl-5-trifluoromethyltetrazole (IV), both colorless liquids, in a ratio of about 1 to 6.[15] These compounds have rather low boiling points for tetrazoles, 189° (712 mm.) for III and 144°(712 mm.) for IV. The melting point of the 2-isomer is higher, −1–0°, than the melting point of the 1-isomer, −30–−29°. This is the reverse of the usual order although Henry and Finnegan[15] found that 2-methyl-5-nitrotetrazole melted higher than the 1-isomer.

The structure of III was established by an unambiguous synthetic route. N-Methyltrifluoro-



(4) W. Carpenter, *J. Org. Chem.*, **27**, 2085 (1962).

(5) The coördinating tendency of this compound is being investigated under the direction of Prof. H. B. Jonassen at Tulane University who has found that fairly stable complexes are formed with nickel (II) and copper (II). The coördinating tendency of this compound will be compared with its hydrogen analog, sodium 5-methyltetrazole.

(6) F. R. Benson, *Chem. Rev.*, **41**, 1 (1947).

(7) A. L. Henne and C. J. Fox, *J. Am. Chem. Soc.*, **73**, 2323 (1951).

(8) L. Birckenbach and K. Huttner, *Z. anorg. allgem. Chem.*, **190**, 1 (1930).

(9) W. J. Middleton, E. L. Little, D. D. Coffman, and V. A. Engelhardt, *J. Am. Chem. Soc.*, **80**, 2795 (1958).

(10) J. A. Garrison and R. M. Herbst, *J. Org. Chem.*, **22**, 278 (1957).

(11) E. Lieber, S. H. Patinkin, and H. H. Tao, *J. Am. Chem. Soc.*, **73**, 1792 (1951).

(12) J. S. Mihina and R. M. Herbst, *J. Org. Chem.*, **15**, 1082 (1950).

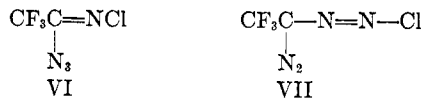
(13) J. F. J. Dippy, *J. Chem. Soc.*, 1222 (1938).

(14) The nuclear magnetic resonance spectrum was obtained by Donald W. Moore of this laboratory.

(15) Alkylations of salts of tetrazoles with electronegative substituents in the 5-position give predominantly 2-isomers while those with electropositive groups in the 5-position give predominantly 1-isomers [R. A. Henry and W. G. Finnegan, *J. Am. Chem. Soc.*, **76**, 923 (1954)].

acetimidoyl chloride[16] reacted with sodium azide to give III. The structure of IV then must be that of the 2-isomer.

Sodium 5-trifluoromethyltetrazole, in aqueous solution, reacts with chlorine to give a water-insoluble, dense, strongly oxidizing, highly explosive liquid (V). The infrared spectrum of V resembles that of IV, more than that of III. The most significant similarities between IV and V occur in the 6.6, 9–10, and 13 μ regions (see Experimental). There is no absorption in the 4.5–4.8-μ region eliminating structures such as VI or VII. On the



VI VII

basis of the method of preparation, the active chlorine analysis, and its infrared spectrum, there seems little doubt but that V is an N-chloro-5-trifluoromethyltetrazole and it would appear from the spectrum that the chlorine is on the 2-position. Since methylation predominantly gives the 2-isomer, chlorination may well do likewise. This is the first reported example of a 1- or 2-substituted chlorotetrazole.[17]

Experimental

Sodium 5-Trifluoromethyltetrazole (I).—A suspension of 130 g. (2.0 moles) of powdered sodium azide in 1500 ml. dry acetonitrile was stirred vigorously while 225 g. (2.4 moles) of trifluoroacetonitrile[18] gas was added through a diffuser tube below the liquid surface. (Dimethylformamide may be used as a solvent but it is difficult to remove from the product.) The system was fitted with a Dry Ice–acetone condenser to return unchanged trifluoroacetonitrile to the reaction vessel. The temperature of the reaction mixture rose spontaneously to 60° and was maintained at this temperature by regulating the rate of addition of trifluoroacetonitrile until near the end of the reaction when it became necessary to apply external heat to maintain a temperature of 60°. When all the sodium azide had reacted, as evidenced by the disappearance of solids, the hot solution was filtered and concentrated, by boiling, to about 800 ml. Upon cooling, 200 g. of fine white needles crystallized from solution. Concentration of the filtrate, until crystals began to appear, followed by cooling, gave an additional 87 g. for a total of 287 g. (75% yield based on trifluoroacetonitrile) of sodium 5-trifluoromethyltetrazole. A sample of the salt was recrystallized from tetrahydrofuran and heated to 100° at 0.01 mm. pressure for 8 hr. This sample was submitted for elemental analysis.

Anal. Calcd. for $C_2F_3N_4Na$: C, 15.01; F, 35.62; N, 35.01; Na, 14.36. Found: C, 14.80; F, 35.43; N 34.52; Na, 14.48.

The infrared spectrum in a potassium bromide disk gave absorption bands at the following wave lengths in microns: 6.08, 6.62, 7.05, 8.11, 8.45, 8.58, 8.84, 9.64, 12.88, 13.81.[19]

5-Trifluoromethyltetrazole (II).—Sodium 5-trifluoromethyltetrazole (46 g.) was dissolved in 50 ml. of water and treated with 30 ml. of 37% hydrochloric acid. Two liquid phases developed. The more dense phase was separated and the top layer was extracted with two 100-ml. portions of methylene chloride.[20] The methylene chloride portions were combined with the initially separated dense phase again resulting in a two-phase liquid system. The addition of anhydrous calcium chloride soon caused the appearance of a single liquid phase. After 24 hr. the methylene chloride solution was decanted onto Drierite and allowed to stand another 24 hr. The methylene chloride was then evaporated and the residue distilled to give 33.4 g. (83% yield) of 5-trifluoromethyltetrazole, b.p. 81–82° (5 mm.), $n^{25}D$ 1.3787, d^{25} 1.578.

Anal. Calcd. for $C_2HF_3N_4$: C, 17.40; H, 0.73; F, 41.29; N, 40.58, neut. equiv. 138.1. Found: C, 17.69, 17.51; H, 0.97, 0.84; F, 41.16, 41.25; N, 40.61, 40.38; neut. equiv. 137.9, 138.0, pK_a 1.14 (water at 25°).[21]

The infrared spectrum gave absorption bands at the following wave lengths in microns: 3.19, 3.39, 3.51, 6.54, 6.70, 7.14, 8.10, 8.5, 9.50, 9.82, 12.81, 13.27.

Methylation of Sodium 5-Trifluoromethyltetrazole.—Methyl iodide (71 g., 0.50 mole) was added to 80 g. (0.50 mole) of sodium 5-trifluoromethyltetrazole dissolved in 200 ml. of tetrahydrofuran. The solution was heated at reflux temperature for 4 hr. The solvent was evaporated and the sodium iodide separated from the liquid residue which was then fractionated to give as the first fraction, 42 g. (55% yield) of 2-methyl-5-trifluoromethyltetrazole (IV), b.p. 67–68° (46 mm.) [143–144° (712 mm.)], m.p. −1–0°, $n^{25}D$ 1.3654, d^{25} 1.386, with infrared absorption bands, in microns at 3.3, 3.4 (both very feeble), 6.58, 6.85, 7.12, 7.35, 7.80, 8.25, 8.6 (broad), 9.44, 9.70, 12.40, 13.05, 14.21.

Anal. Calcd. for $C_3H_3F_3N_4$: C, 23.69; H, 1.99; F, 37.48; N, 36.84. Found: C, 23.84; H, 2.12; F, 38.73; N, 35.40.

An intermediate fraction of 3 g. was collected while the distillation temperature rose from 68–101°. This fraction was presumably a mixture of 1- and 2-methyl-5-trifluoromethyltetrazole.

The next fraction gave 7.5 g. 1-methyl-5-trifluoromethyltetrazole (III), b.p. 101–102° (46 mm.) [189° 712 mm.], m.p. −30 to −29°, $n^{25}D$ 1.3810, d^{25} 1.445, with infrared absorption bands, in microns, at 3.3, 3.4 (both very weak), 6.52, 6.79, 6.90, 7.10, 7.68, 7.90, 8.24, 8.3–8.8 (total absorption), 8.88, 9.32, 9.80 (weak), 10.16, 13.10, 13.25, 14.30.

Anal. Calcd. for $C_3H_3F_3N_4$: C, 23.69; H, 1.99; F, 37.48; N, 36.84. Found: C, 23.67; H, 2.37; F, 37.99; N, 36.09.

1-Methyl-5-trifluoromethyltetrazole (III).—N-Methyltrifluoroacetimidoyl chloride[14] (49 g., 0.34 mole) was added to 32 g. (0.5 mole) of powdered sodium azide in 200 ml. of dry acetonitrile. The reaction mixture was heated at reflux with stirring for 12 hr. The reaction mixture was filtered and the solvent evaporated. The residue was distilled at 20 mm. pressure to give 39.1 g. (76% yield), b.p. 82–83°. This material was then fractionated on a preci-

(16) W. P. Norris and H. B. Jonassen, *J. Org. Chem.*, **27**, 1449 (1962).

(17) A white, water-insoluble, N-chloro-5-phenyltetrazole, m.p. 87–87.5°, has also been prepared by Dr. Ronald A. Henry of this laboratory. The unpurified product contained 18.1% active chlorine; the theoretical value for N-chloro-5-phenyltetrazole is 19.6% chlorine. Attempts to recrystallize the compound from methylene chloride gave only 5-phenyltetrazole. When the compound was dissolved in diethyl ether to form a saturated solution at room temperature and the solution cooled to 5°, 5-phenyltetrazole crystallized. From this latter attempt a yellow, hexane-soluble oil was recovered which was not identified but was shown not to be β,β'-dichlorodiethyl ether.

(18) H. Gilman and R. G. Jones, *J. Am. Chem. Soc.*, **65**, 1458 (1943).

(19) A Perkin-Elmer Infracord spectrophotometer was used to obtain the spectra reported in this paper. Some of the very small peaks and shoulders on larger peaks are not reported.

(20) Ether, which is a much better solvent for the tetrazole, may be used instead of methylene chloride. However, a detectable amount of ether remains in the tetrazole even after distillation.

(21) A. Weissberger, "Physical Methods of Organic Chemistry," Vol. I, Part II, 2nd ed., Interscience Publishers, Inc., New York, 1946, pp. 1747–1748.

sion distillation apparatus to give 35 g. of 1-methyl-5-trifluoromethyltetrazole, b.p. 101–102° (46 mm.). The infrared spectrum was identical with that of the higher boiling fraction (III) obtained from the methylation of sodium 5-trifluoromethyltetrazole.

Anal. Calcd. for $C_3H_3F_3N_4$: C, 23.69; H, 1.99; F, 37.48; N, 36.84. Found: C, 23.69; H, 2.52; F, 38.09; N, 36.05.

N-Chloro-5-trifluoromethyltetrazole (V).—Chlorine gas was passed into an aqueous solution of 5 g. of sodium 5-trifluoromethyltetrazole until approximately 1 ml. of a dense, slightly yellow, liquid separated from the water. The dense liquid, N-chloro-5-trifluoromethyltetrazole, was dried over anhydrous calcium chloride. A weighed sample of the dried liquid was treated with aqueous potassium iodide and the liberated iodine was titrated with standard thiosulfate solution.

Anal. Calcd. for $C_2ClF_3N_4$: Cl, 20.6. Found: Cl, 21.2.

The infrared spectrum shows absorption bands, in microns, at: 6.59, 7.00 (weak), 7.20, 7.40, and 7.60 (weak), 7.92, 8.1–8.7 (broad), 9.09 (weak), 9.70, 10.04, 12.93, 13.16. The spectrum resembles that of 2-methyl-5-trifluoromethyltetrazole in the 6.6, 9–10, and 13-μ regions quite closely.

Caution: N-Chloro-5-trifluoromethyltetrazole is extremely sensitive to shock and heat.

Attempted Reaction of Sodium Azide with Acetonitrile.—Sodium azide (71 g., 1.1 moles) and 150 ml. of acetonitrile were sealed in a pressure vessel. The reaction mixture was heated to 125°, with agitation, for 66 hr. The solid was filtered off, dried, and weighed to give 70 g. of solid. Titration of a weighed sample of the dried solid with standard sodium triiodide (catalyzed with sodium thiosulfate) showed the solid to be sodium azide.

Powdered sodium azide (35 g., 0.55 mole) and 150 ml. of acetonitrile were heated in a pressure vessel to 200°, with agitation, for 18 hr. The sodium azide crystallized from the hot solvent upon cooling depositing a layer of crystals on the inside of the reaction vessel. The solid was filtered from the reaction mixture and dried to give 34.5 g. of material. It required 263 ml. of 1.00 *N* sodium triiodide to react with all the solid. This is equivalent to 0.53 mole, 96%, of the initial amount of sodium azide. Allowing for mechanical losses and the slight solubility in cold acetonitrile this is essentially a quantitative recovery of sodium azide. Sodium 5-methyltetrazole does not react with sodium triiodide in the presence of sodium thiosulfate catalyst.

5-Methyltetrazole.—Sodium azide (33 g., 0.50 mole), 27 g. (0.50 mole) of ammonium chloride, and 150 ml. of acetonitrile were placed in a pressure vessel and heated at 150°, with agitation, for 25 hr. The solids were filtered off, dried, dissolved in 200 ml. of water and 50 ml. of concentrated hydrochloric acid. The water was evaporated and the residue dried at 100°/0.1 mm. pressure. The residue was then extracted with three 100-ml. portions of boiling ethyl acetate. The ethyl acetate was evaporated and the solid sublimed to give 36 g. (100% yield) of 5-methyltetrazole, m.p. 144–146° (lit., m.p.[12] 148–148.5°).

Acknowledgment.—Many helpful discussions with Dr. R. A. Henry are gratefully acknowledged.

cis- and *trans*-3-Methyl-2-phenylmorpholine

FRANK H. CLARKE[1a]

Medicinal Chemical Research Department, The Schering Corporation, Bloomfield, New Jersey

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The synthesis of racemic *cis*- and *trans*-5-methyl-6-phenyl-3-morpholinone and 3-methyl-2-phenylmorpholine is described.

The first synthesis of an optically active morpholine derivative was achieved by Otto[1b] in 1956 by the acid-catalyzed cyclization of *l*-N-(2-hydroxyethyl)ephedrine to *d*-3,4-dimethyl-2-phenylmorpholine. Subsequently Foltz and Witkop,[2] in commenting on this synthesis, pointed out that whether the ring closure proceeds by a concerted process or *via* a benzyl carbonium ion, the product must have the more stable *trans* configuration. This is apparently the only instance in which the configuration has been assigned to a 2,3-disubstituted morpholine.

We have repeated the acid-catalyzed cyclization reaction using the *N*-(2-hydroxyethyl) derivatives (III and VIII) of racemic norephedrine[3] (I) and nor-ψ-ephedrine[3] (VI), respectively, and in each case racemic *trans*-3-methyl-2-phenylmorpholine (X) hydrochloride[4] was isolated in good yield. A concerted mechanism would have given at least some of the *cis* isomer in the latter case, but there was no evidence of this in the infrared spectrum[5] of the crude product. It is clear from these experiments that the preparation of the *cis* isomer requires a different method, one which does not involve the formation of an intermediate benzyl carbonium ion.

A successful synthesis of *cis*-5-methyl-6-phenyl-3-morpholinone (IV) was achieved when the sodio derivative of norephedrine (I) was treated in benzene solution with ethyl chloroacetate. Subsequent reduction with lithium aluminum hydride resulted in a stereospecific synthesis of *cis*-3-methyl-2-phenylmorpholine (V). Treatment of the sodio derivative of nor-ψ-ephedrine (VI) in a

(1a) Present address: Geigy Research Laboratories, Ardsley, N. Y.

(1b) W. G. Otto, *Angew. Chem.*, **68**, 181 (1956).

(2) C. M. Foltz and B. Witkop, *J. Am. Chem. Soc.*, **79**, 201 (1957).

(3) The configurations of norephedrine and nor-ψ-ephedrine have been firmly established and the compounds have been related to the corresponding ephedrines. See H. E. Zimmerman and J. English, Jr., *ibid.*, **76**, 2291 (1954).

(4) Ravensberg G.m.b.H., Belgian Patent 580,045 (1959).

(5) The infrared spectra of the hydrochlorides of the isomers (Nujol mulls) are readily distinguished in the region above 9 μ. In this region intense bands of the *cis* isomer occur at 9.02, 9.24, 13.39, and 14.30 μ while those of the *trans* isomer are found at 9.13, 9.74, 13.27, and 14.44 μ.