from their rearrangements. Yields of the azides are based on the amount of amine hydrochlorides recovered and represent the minimum percentage of azide in the reaction product.

Formation of Other Azides.—To test the generality of the method of forming azides from alcohols, the reaction was carried out in the same way with benzohydrol, benzyl alcohol and *t*-butyl alcohol. Of these, only benzohydrol gave evidence of azide formation which was detected by the evolution of nitrogen when concentrated sulfuric acid was added to the neutral fraction of the reaction product.

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Synthesis of Acetomorpholide and Thioacetomorpholide from Morpholine and Sulfur

By Neal O. Brace

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The reaction of sulfur and morpholine in a sealed tube at 200° gave thioacetomorpholide, acetomorpholide, hydrogen sulfide and an unidentified residue. Inclusion of an inert solvent or a reactive olefin did not affect the course of the reaction. The same products were also formed in small amount by refluxing sulfur and morpholine.

McMillan and King[1] isolated dithiooxalomorpholide (I) from the reaction of morpholine and
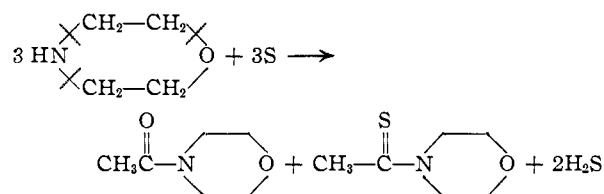

(I)
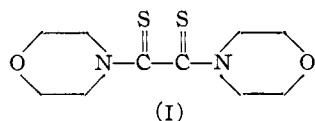
sulfur with certain olefins under reflux conditions, and Horton and Van Den Berghe[2] showed that this compound was formed by refluxing morpholine and sulfur alone.[3] The compound was obtained in low yields. It was suggested by McMillan and King[1] that the formation of this product arose through [·CH₂S·] radicals and may have been analogous to the Creigee cleavage of glycols.

On this basis, it was interesting to see if cyclohexene would yield dithioadipic morpholide, since olefins are known to undergo the Willgerodt–Kindler reaction. None of the expected product was isolated, however, and the products actually isolated from the reaction in a sealed tube at 200° were thioacetomorpholide, acetomorpholide and hydrogen sulfide. A similar result was obtained with diisobutylene or benzene (a non-reactive solvent) in place of cyclohexene or without any solvent at all. The same products, in addition to the dithiooxalomorpholide, were isolated in very low yield by repeating the reaction as done by Horton and Van Den Berghe and distilling the mixture under reduced pressure. An undistillable residue was obtained in each case which was not readily characterized, but may have contained some dithiooxalomorpholide.

These results substantiate the conclusion that cleavage of morpholine, itself, results in the formation of the aceto derivatives and hydrogen sulfide. The intermediate diradicals may actually be [·CH₂Ċ·] (with O) and [·CH₂Ċ·] (with S) which probably react with morpholine as the ketene forms, CH₂=C=O and CH₂=C=S, to give acetomorpholide and thioacetomorpholide, respectively, as indicated by the partial equation

(1) F. H. McMillan and J. A. King, This Journal, **69**, 1207 (1947).

(2) W. J. Horton and J. Van Den Berghe, *ibid.*, **70**, 2425 (1948).

(3) I am indebted to a referee for pointing out this reference to me.

Further reaction of thioacetomorpholide with morpholine and sulfur with evolution of hydrogen sulfide has been shown to give dithiooxalomorpholide.[4] This may account for the formation of this compound under reflux conditions in the reactions done by McMillan and King and Horton and Van Den Berghe.

Experimental

Reaction of Cyclohexene, Morpholine and Sulfur.—In an 18-inch Carius tube was placed 8.2 g. (0.1 mole) of cyclohexene, 35.0 g. (0.4 mole) of morpholine and 16.0 g. (0.5 atom) of sulfur. The tube was sealed, enclosed in a metal jacket and heated at 200° for five hours. The contents had turned brown and a solid had sublimed up into the exit end. The tube was chilled in a Dry Ice–acetone-bath and then in liquid nitrogen before opening. The hydrogen sulfide, evolved on warming, was collected in sodium hydroxide solution and amounted to 0.198 mole. The brown solution which remained was washed out with about 75 cc. 95% alcohol and distilled through an 8-inch Fenske column with a manual take-off head. The fractions taken are given in Table I.

TABLE I

	B.p., °C.	Pressure	N^{25}D	Wt., g.	S, %	N, %
1	45–84	Atm.	....	..	..	..
11	56–95	42–24 mm.	1.4600	1.1	..	..
111	110–142	23–24	1.4912	16.0	4.7	12.1
1V	143–154	24	1.5108	8.0	10.0	10.0
V	130–160	2.6	Solid	4.6	..	..
V1	Residue	...	....	ca. 10.0	..	..

Fraction III, when redistilled, had b.p. 125–132° (24 mm.), n^{25}D 1.4853. *Anal.* Calcd. for C₆H₁₁O₂N: C, 55.8; H, 8.58; N, 10.85. Found: C, 52.1; H, 8.47; N, 10.26; S, 2.45. Some thioacetomorpholide still contaminated the liquid. A crystalline hydrobromide salt was prepared in dry ether solution with anhydrous hydrogen bromide. From 1.0 g. of acetomorpholide of fraction III was obtained 1.42 g. of salt, m.p. 156–162°. *Anal.* Calcd. for C₆H₁₂O₂NBr: N, 6.64; Br, 37.9; neut. equiv., 210. Found: N, 6.9; Br, 39.9; neut. equiv., 237. An infrared spectrum of the acetomorpholide was compared with the authentic material, b.p. 240–242°, n^{25}D 1.4831 [reported, b.p. 242°].[5]

(4) C. L. Levesque, U. S. Patent 2,525,416 (October 10, 1950).

(5) L. Médard. *Bull. Soc. Chim.*, [5] **3**, 1343 (1936).

prepared from acetic anhydride and morpholine. The principal absorption bands were identical, but the unknown curve contained a few additional bands. The authentic acetomorpholide gave a hydrobromide, m.p. 172–175°, which gave a mixed melting point of (sinter 156) 169–171° with the hydrobromide above. These results show the liquid product to be principally acetomorpholide.

The solid, fraction V, was recrystallized from 95% alcohol. The melting point was 89–91.2° (reported[4] for thioacetomorpholide, m.p. 88–90.3°). *Anal.* Calcd. for $C_6H_{11}NOS$: N, 9.65; S, 22.05. Found: N, 9.43; S, 22.80. The amount of acetomorpholide formed as calculated from the analyses of fractions III–V was about 16 g. or 0.124 mole, and the yield of thioacetomorpholide was about 12.6 g. or 0.087 mole. The theoretical yield from 0.4 mole of morpholine is 0.125 mole for each compound. The residue was extracted with alcohol, treated with Nuchar, filtered and cooled, but no crystalline solid separated.

The same experiment with benzene in place of cyclohexene gave 0.148 mole of hydrogen sulfide. The liquid and solids were washed out of the Carius tube with anhydrous acetone to obviate any hydrolysis. Distillation gave I (after removal of solvent), 10.9 g. of liquid, b.p. 88–100° (3–2 mm.), $n^{25}D$ 1.4806; II, 9.3 g. liquid and 3.1 g. solid distilling at 113–135° (3–2 mm.). The residue weighed 12.0 g. and was a viscous black tar. The liquid fractions were redistilled to give 8.0 g. of acetomorpholide, b.p. 125–131.5° (24 mm.), $n^{25}D$ 1.4777. The solid was crystallized from alcohol to give thioacetomorpholide, m.p. 89.8–93.1°. Found: N, 9.73; S, 22.5.

An exactly similar reaction was done with 11.2 g. of diisobutylene (commercial product redistilled, b.p. 100.5–102.0°, $n^{25}D$ 1.4082), in place of cyclohexene. Distillation gave a small amount of unidentified C_8 mercaptans (1.1 g., b.p. 56–58° (25 mm.), $n^{25}D$ 1.4510); and (1.2 g. b.p. 72–80° (25 mm.), $n^{25}D$ 1.4565); 18 g. of acetomorpholide, mixed with thioacetomorpholide, b.p. 123–134° (26–28 mm.), $n^{25}D$ 1.4752 and 1.4896; and 7.3 g. of thioacetomorpholide, b.p. 96–135° (1.0–1.5 mm.) and m.p. 88–90°. No crystalline product could be isolated from the alcohol extract of the pot residue.

A fairly clean-cut separation of acetomorpholide from the liquid fractions was made by washing with 50 cc. of water and extracting the insoluble oil with ether. The ether dissolved most of the thioacetomorpholide and the aqueous solution when evaporated down was extracted with chloroform. Distillation of the chloroform solution gave acetomorpholide, b.p. 128–135° (25 mm.), $n^{25}D$ 1.4769. Found: C, 53.2; H, 8.3; S, 0.4; N, 10.8.

Morpholine and Sulfur Alone in Sealed Tube.—The reaction was done without any solvent present, but otherwise identical amounts and conditions as in previous experiments. There was obtained 0.16 mole of hydrogen sulfide, and working up as in the previous experiment gave I, 3.4 g. of liquid, b.p. 38–42° (120 mm.), nD^{25} 1.4009, II, 10.2 g. liquid, b.p. 112–119° (14 mm.), $n^{25}D$ 1.4800; III, 4.0 g. liquid, b.p. 92–100° (3–4 mm.), $n^{25}D$ 1.4858; and IV, 3.6 g., solidifying in side-arm, b.p. 102–117° (1.5 mm.). The residue was extracted with boiling alcohol and then acetone and the alcohol solution, when cool, deposited needles, m.p. 260–265°, 0.01 g., which may be dithioöxalomorpholide. Analysis of the distilled fractions showed II and III to be mostly acetomorpholide and IV to be mostly thioacetomorpholide.

Morpholine and Sulfur under Reflux Conditions.—The experiment reported by Horton and Van Den Berghe was repeated exactly as described using 35.0 g. (0.4 mole) of morpholine and 12.8 g. (0.4 atom) of sulfur, and the amount of dithioöxalomorpholide isolated was 2.44 g., m.p. range 205–210°. This is a yield of 14% based on a theoretical yield of 0.066 mole, assuming that only thioacetomorpholide is the intermediate. Distillation of the filtrate through a 5-inch Vigreux column gave I, 2.0 g., b.p. 38° (25 mm.), $n^{25}D$ 1.4520; II, b.p. 105° (2 mm.), 2.0 g. of liquid which was identified as principally acetomorpholide by its infrared spectrum; and finally III, b.p. 105–139° (2 mm.), 2.9 g. of liquid which solidified in the side-arm and when recrystallized melted at 89–92°. It was thioacetomorpholide. Found: N, 9.73; S, 22.10. The pot residue weighed 6.2 g. and was extracted with hot alcohol, treated with activated charcoal and filtered. The dark solution deposited 1.8 g. of solid of broad melting range which was not further examined.

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The Structure of the Products of Condensation between Primary β-Hydroxyamines and Aliphatic Carbonyl Compounds

BY ERNST D. BERGMANN, E. GIL-AV[1] AND S. PINCHAS

The dependence of the structure of the condensation products between primary β-hydroxyamines and aliphatic ketones (oxazolidines or Schiff bases), on the structure of the ketones has been investigated. Molecular refraction and infrared spectrum of the products have been used as criteria. Whilst, generally speaking, 3-methyl-2-amino-3-butanol, $(CH_3)_2$-(OH)-CH(CH_3)-NH_2, gives oxazolidines, ethanolamine yields with highly shielded ketones larger amounts of the Schiff base than with straight-chain ketones. Moreover, the structure of some of the condensation products is dependent on the concentration, the system oxazolidine ⇌ Schiff base being in a state of mobile equilibrium.

The reaction between primary β-hydroxyamines and carbonyl compounds, which can lead either to Schiff bases (A) or oxazolidines (B), tends to give the former (A) if their C=N double bond is stabilized by resonance, otherwise the cyclic compound (B).[2] However, exceptions from this rule have already been observed by Cope and Hancock[3] for products derived from methyl isobutyl ketone

and diisobutyl ketone, and by Bergmann, et al.,[4] for condensation products of aminoalcohols with pinacolone and 2-methyl-2-phenyl-4-pentanone and Daasch[5] has assigned a Schiff base structure to the condensation products of ethanolamine with methyl propyl and methyl amyl ketones, respectively, on the basis of a qualitative interpretation of their infrared spectra.

The structure of the condensation products of *aliphatic* ketones and primary β-hydroxyamines has, therefore, been reinvestigated to a better ap-

(1) Part of a Thesis presented by E. Gil-Av to the Hebrew University, Jerusalem, in partial fulfillment of the requirements for the degree of Ph.D.

(2) E. Bergmann, E. Zimkin and S. Pinchas, *Rec. trav. chim.*, **71**, 168 (1952).

(3) A. C. Cope and E. M. Hancock, THIS JOURNAL, **64**, 1503 (1942).

(4) E. Bergmann, E. Fischer, E. Zimkin and S. Pinchas, *Rec. trav. chim.*, **71**, 213 (1952).

(5) L. W. Daasch, THIS JOURNAL, **73**, 4523 (1951).