The following method proved more successful. A mixture of the ketone (V) (4 g.) and ***phosphorus pentoxide*** (6.3 g.) was heated at 135–140° for one-half hour under nitrogen at 20 mm. and then distilled at 0.5 mm. pressure. The yellow oil (b.p. 195–200°) began to crystallize immediately. The product was recrystallized from benzene–methanol, m.p. 172–174° (0.3 g., 8.1%). Further recrystallization from acetic acid raised the melting point to 174–175°, which was not depressed by admixture of 1,2,5,6-dibenzfluorene. The red residual oil was dissolved in benzene, washed with sodium bicarbonate solution and water and recovered (2 g.) by evaporation of the solvent. It was dehydrogenated with 0.48 g. of sulfur at 220–260° (20 minutes). After evaporative distillation at 0.1 mm. pressure (170–240°), the dark oil was treated with 3.4 g. of picric acid in glacial acetic acid. The dark-red crystals, after trituration with ethanol containing some picric acid, melted at 184–186° (0.6 g.). The picrate was chromatographed on alumina and eluted with benzene. Recrystallization from glacial acetic acid gave 0.17 g. (4.6%, calcd. on (V)) of slightly pinkish crystals, m.p. and mixed m.p. 174–175°.

TEL-AVIV, ISRAEL

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, SMITH COLLEGE]

The Formation of Azides in the Reaction of Hydrogen Azide with Diarylethylenes[1]

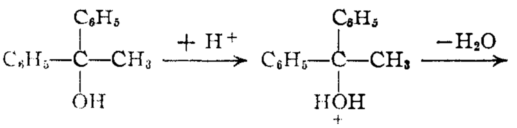
BY SEYHAN N. EGE AND KENNETH W. SHERK

RECEIVED AUGUST 11, 1952

The Schmidt reaction with 1,1-diarylethylenes in benzene solution using trichloroacetic acid as a catalyst leads to the formation of azides. These azides on treatment with stronger acids, such as sulfuric acid, decompose and undergo the typical Schmidt rearrangement. The migration aptitudes of several para substituted phenyl groups have been measured and correlated with their sigma values.

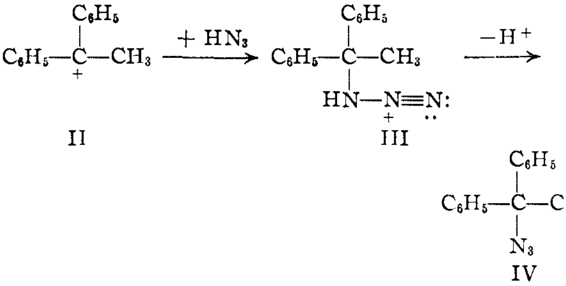
The investigation of the Schmidt reaction with different classes of compounds[2–6] under varying conditions has led to a better understanding of the factors involved in the rearrangement. Since the Schmidt reaction with olefins carried out by McEwen and co-workers[4] and Kuhn and Di Domenico[7] leads to relatively large amounts of by-product through the polymerization of 1,1-diphenylethylene to 3-methyl-1,1,3-triphenylindane,[4a] it was decided to study the reaction of hydrogen azide with olefins using a milder acid catalyst. The experimental conditions used in the present work involve the passage of dry gaseous hydrogen azide through a benzene solution of the reactant and catalyst. Trichloroacetic acid was chosen as the catalyst because it afforded a homogeneous reaction medium.

From the reaction of hydrogen azide with diphenylmethylcarbinol in the presence of trichloroacetic acid, a neutral product containing nitrogen was obtained instead of the expected aniline and acetophenone. This product, a colorless, high boiling oil, was shown to be 1,1-diphenylethyl azide. The same product was obtained when 1,1-diphenylethylene was allowed to react with hydrogen azide under similar conditions. The steps of the reaction may be outlined as



$$C_6H_5-\overset{C_6H_5}{\underset{OH}{C}}-CH_3 \xrightarrow{+\ H^+} C_6H_5-\overset{C_6H_5}{\underset{\underset{+}{HOH}}{C}}-CH_3 \xrightarrow{-H_2O}$$

I



$$C_6H_5-\overset{C_6H_5}{\underset{+}{C}}-CH_3 \xrightarrow{+\ HN_3} C_6H_5-\overset{C_6H_5}{\underset{H\underset{+}{N}-N\equiv \underset{\cdot\cdot}{N}:}{C}}-CH_3 \xrightarrow{-H^+} C_6H_5-\overset{C_6H_5}{\underset{N_3}{C}}-CH_3$$

II III IV

The azide was found to be very stable, showing no explosive tendencies even when rapidly heated or dropped on a piece of red-hot iron.

One factor that influences the formation of the azide seems to be the acid strength of the reaction medium. It was found experimentally that the concentration and the inherent strength of acids played a large part in effecting the decomposition of 1,1-diphenylethyl azide. While pure trichloroacetic acid caused decomposition only when warmed, slow evolution of nitrogen took place at room temperature with trifluoroacetic acid and with anhydrous stannic chloride. The use of ethanesulfonic acid or sulfuric acid greatly increased the rate of evolution of nitrogen. The role of an acid in the decomposition of azides has been pointed out in earlier publications.[8,9] It is reasonable to assume that the intermediate III and the azide IV are in a state of equilibrium. In this case, the strength of the acid catalyst would influence the degree of ionization of the conjugate acid III of the azide. The stronger acids would depress this ionization and lead to decomposition of the azide, probably through the inhibition of the resonance in the azide group.

This seems to indicate that the decomposition of the azide belongs in the class of specific acid-catalyzed reactions where the rate-determining step is preceded by an equilibrium between the sub-

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[1] From the M.A. Thesis of Miss Ege at Smith College, 1952.

[2] P. A. S. Smith, THIS JOURNAL, **70**, 320 (1948).

[3] L. H. Briggs and J. W. Lyttleton, *J. Chem. Soc.*, 421 (1943).

[4] (a) W. E. McEwen, M. Gilliland and B. I. Sparr, THIS JOURNAL, **72**, 3212 (1950); (b) W. E. McEwen and N. B. Mehta, *ibid.*, **74**, 526 (1952).

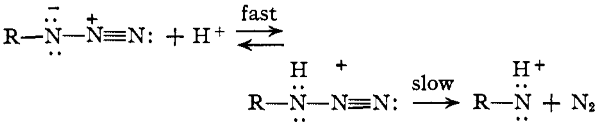
[5] H. Wolff, The Schmidt Reaction, "Organic Reactions," Vol. 3, John Wiley and Sons, Inc., New York, N. Y., 1946, pp. 307–336.

[6] W. E. McEwen, W. E. Conrad and C. A. VanderWerf, THIS JOURNAL, **74**, 1168 (1952).

[7] L. P. Kuhn and J. Di Domenico, *ibid.*, **72**, 5777 (1950).

[8] K. W. Sherk, A. G. Houpt and A. W. Browne, *ibid.*, **62**, 329 (1940).

[9] P. A. S. Smith and B. B. Brown, *ibid.*, **73**, 2438 (1951).



$$R{-}\underset{\cdot\cdot}{\overset{\cdot\cdot\,-}{N}}{-}\overset{+}{N}{\equiv}N: + H^+ \overset{\text{fast}}{\rightleftarrows}$$

$$R{-}\underset{\cdot\cdot}{\overset{H}{\ddot{N}}}{-}\overset{+}{N}{\equiv}N: \xrightarrow{\text{slow}} R{-}\underset{\cdot\cdot}{\overset{H^+}{\ddot{N}}} + N_2$$

strate and its protonated form.[10] If the decomposition of the azide were of the general acid catalysis type where the slow step is the addition of a proton followed by a fast decomposition of the adduct,[10] the azide would not have been recovered.

It is interesting to note that while the addition of hydrogen azide as the whole molecule to carbonium ions has been assumed in mechanisms for the Schmidt reaction[2-6] the isolation of an azide[11] from the reaction is definite evidence in favor of this point. It also indicates that the role of the catalyst is dual. The first part the catalyst plays involves the production of a carbonium ion sufficiently polar to attract the hydrogen azide molecule and form a bond with it. The second part the catalyst plays involves the decomposition of the adduct formed. This point has not been brought out before, perhaps because the reaction has never been carried out under conditions where the intermediate has more than a transient existence. It was only when a mild catalyst and a compound capable of leading to a stable azide were used, that the importance of the catalyst in the decomposition of the intermediate became apparent. The effect of the acid strength of the catalyst on the rate of decomposition of acid azides has been pointed out by Newman and Gildenhorn.[12]

In a strong acid medium, such as sulfuric acid, the azide loses nitrogen and rearrangement takes place. This decomposition probably follows the path proposed by McEwen, Gilliland and Sparr[4] for the decomposition of the intermediate in the Schmidt reaction with olefins. If different groups are present, the question of competitive migration arises. The preparation and rearrangement of a series of unsymmetrically substituted diarylethyl azides was, therefore, undertaken. The ratios of the groups migrating were measured by the determination of the neutralization equivalents of the mixed amine hydrochlorides isolated from the rearrangement. This analytical method has been used earlier by Bailar[13] and by Hatt and coworkers[14] for the determination of mixed benzoic acids from the alkaline cleavage of pinacolones.

The results obtained in this investigation, as well as those of McEwen and co-workers[4] and that of Kuhn and Di Domenico,[7] are given in Table I together with the migration aptitudes shown by the same groups in the rearrangement of symmetrical diaryl pinacols.[15]

TABLE I

MIGRATION APTITUDES OF VARIOUS GROUPS

Group	Schmidt reacn. with olefins[4]	Rearrange. of azides	Rearrange. pinacols[15]
p-BrC_6H_4	0.54	0.33	0.7
p-ClC_6H_4	0.62	0.30	0.7
C_6H_5	1.00	1.00	1.0
p-$CH_3C_6H_4$	5.00	4.00	15.7
p-$OCH_3C_6H_4$	6.12	>99	500
p-$OCH_3C_6H_4$	*ca.* 3[7]		

A comparison of these results shows qualitative if not quantitative agreement. If the logarithms of the values obtained in this investigation are plotted (Fig. 1) against the σ-values given by Hammett[16] for these substituents, a curve is obtained which rather closely resembles the curve drawn by McEwen[4] through the points for the pinacol rearrangement. It is comforting to note that the arbitary value of 1.00 for the phenyl group falls on the curve.

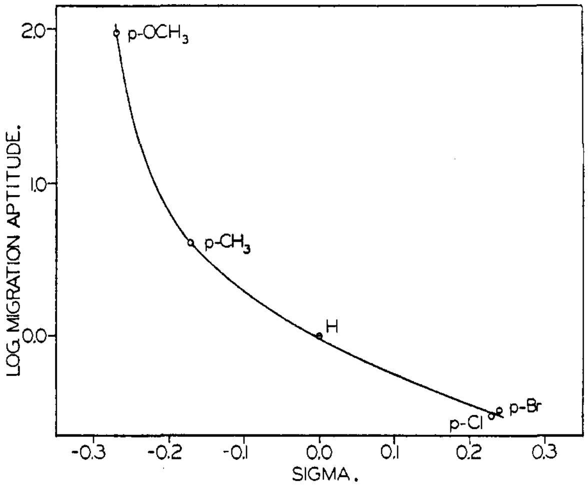


Fig. 1.—Log migration aptitude *vs.* σ-value for several para substituted phenyl groups in the rearrangement of diarylethyl azides.

Since the σ-values for these substituents are calculated from the effect they have on some constant such as the acidity constant of benzoic acid, it would seem that they represent the combined inductive and mesomeric effects of the group on the permanent state of the molecule. When these effects are the only ones operating in a reaction, a linear relation exists between the logarithm of the factor measured, such as a rate constant or an acidity constant, and the σ-values for the substituents. In a rearrangement such as that of the azides, however, where the slow step seems to be the loss of nitrogen, the electron-donating qualities due to the polarizability of the substituent play a more important part and the rearrangement is more discriminating. A tendency for the more polarizable group to exert some push on the departing nitrogen while the group moves over to fill the open sextet being left behind is shown. In the case of the pinacol rearrangement where the departing

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[10] (a) J. D. Roberts and W. Watanabe, THIS JOURNAL, **72**, 4872 (1950); (b) J. D. Roberts, C. M. Regan and I. Allen, *ibid.*, **74**, 3679 (1952).

[11] Triphenylmethyl azide has been obtained from the Schmidt reaction with triphenylcarbinol, C. L. Arcus and R. J. Mesley, *Chemistry & Industry*, 701 (1951).

[12] M. S. Newman and H. L. Gildenhorn, THIS JOURNAL, **70**, 317 (1948).

[13] J. C. Bailar, *ibid.*, **52**, 3596 (1930).

[14] H. H. Hatt, A. Pilgrim and E. F. M. Stephenson, *J. Chem. Soc.*, 478 (1941).

[15] (a) W. E. Bachmann and J. W. Ferguson, THIS JOURNAL, **56**, 2081 (1934); (b) W. E. Bachmann and F. H. Mosher, *ibid.*, **54**, 1124 (1932).

[16] L. P. Hammett, "Physical Organic Chemistry," 1st ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 184–199.

fragment is water instead of nitrogen which has a higher heat of formation, the curve is still more pronounced, probably indicating an even greater degree of discrimination.

The curves obtained by plotting the logarithms of the migration aptitudes for various groups in the rearrangements of azides and pinacols against their σ-values indicates the nature of the mechanisms for these decompositions and rearrangements. Linearity for such a plot is not to be expected in the case of the azide reaction which has been called "a specific oxonium catalysis with a non-protolytic rate-determining step involving participation of the π-electrons of the aryl rings."[17,17a]

Experimental

The Starting Materials.—The following compounds were prepared by methods described in the literature: diphenylmethylcarbinol,[18] 1,1-diphenylethylene,[18] 1-*p*-tolyl-1-phenylethylene,[19] 1-*p*-anisyl-1-phenylethylene[20] and benzohydrol.[21]

1-*p*-Bromophenyl-1-phenylethylene.—The Grignard reagent was prepared from 7.3 g. (0.30 mole) of magnesium and 47 g. (0.29 mole) of bromobenzene. To it was added an ether solution of *p*-bromoacetophenone (40 g., 0.21 mole). After refluxing one hour, the mixture was poured into cold dilute sulfuric acid and the organic layer worked up for the neutral fraction. Drying with anhydrous magnesium sulfate, removal of the solvent and subsequent distillation yielded the olefin, b.p. 192–194° at 16 mm. (lit.[22] 195–201° at 19 mm), 38.7 g. or 75.5% yield.

1-*p*-Chlorophenyl-1-phenylethylene.—An ether solution of 36.8 g. (0.24 mole) of *p*-chloroacetophenone was added to the Grignard reagent prepared from 6.5 g. (0.27 mole) of magnesium and 41 g. (0.26 mole) of bromobenzene. The carbinol obtained by hydrolysis of the mixture with saturated ammonium chloride solution was dehydrated by refluxing with 60 ml. of 20% sulfuric acid for an hour. After the usual recovery and solvent removal, the ethylene was distilled under reduced pressure, b.p. 134–136° at 1.5 mm., (lit.[23] 164° at 16 mm.), 31.0 g. or 60.3% yield.

The Reaction of Hydrogen Azide with Diarylethylenes.—The apparatus used for this reaction was similar to that described by Specht, Browne and Sherk.[24] The generator was kept at 65–70° and the reaction flask at room temperature. The hydrogen azide was generated by the action of sulfuric acid, diluted 2:3, on a solution (approximately 0.8 *N*) of sodium azide. The mixture of hydrogen azide and air was dried and drawn through the well stirred solution of the reactant and trichloroacetic acid in dry benzene for 2–3 hours. The product was worked up by pouring the mixture into water, separating the layers and washing the benzene layer with water until the washings were no longer acidic. The benzene layer was dried over anhydrous magnesium sulfate and the solvent removed under reduced pressure. The products were oils ranging from pale yellow to light brown in color.

Preparation and Isolation of 1,1-Diphenylethyl Azide.—From the reaction of 8 g. (0.04 mole) of diphenylmethylcarbinol dissolved in 100 ml. of benzene, and hydrogen azide (generated from 6 g. (0.09 mole) of sodium azide) in the presence of 16 g. (0.096 mole) of trichloroacetic acid, 7.5 g. of a light brown oil was isolated. It was found to contain nitrogen but no halogen. No common functional group except unsaturation (attributed to the ethylene formed by dehydration of the carbinol) could be detected in the mixture.

Reduction of an alcoholic solution of the mixture (3.6 g.) with zinc (7 g.) and concentrated hydrochloric acid (33 ml.) yielded 1,1-diphenylethylamine, isolated and identified as its hydrochloride, m.p. 229–231°.[25]

Anal. Calcd. for $C_{14}H_{16}NCl$: Cl, 15.17. Found: Cl, 14.93.

The benzoyl derivative, m.p. 147.5° (lit.[26] 150°), and the urethan, m.p. 66° (lit.[26] 66.5°), were also used for identification. The point of attachment of the nitrogen to the carbon skeleton was thus shown. That the three nitrogens were present as an azide group was shown by refluxing the mixture (1 g.) with a solution of 1 g. of potassium hydroxide in 100 ml. of 50% ethanol for 10 hours. On cooling, acidification and distillation, the distillate produced a red color with ferric chloride and a white precipitate (soluble in dilute nitric acid) with silver nitrate solution. The azide group was also indicated by the liberation of bubbles of nitrogen when the mixture was treated with concentrated sulfuric acid.

The refractive index, $n^{25}\text{D}$, of the 1,1-diphenylethylene was 1.6056 and that of the mixture was 1.5873. The small spread of refractive indices of the fractions obtained by distillation indicated that the boiling points of the components were fairly close. The separation was achieved by passing a petroleum ether (20–40°) solution of the mixture through an alumina column (1 cm. diameter and 10 cm. long) to remove the color, followed by fractional crystallization from the same petroleum ether at Dry Ice temperatures until the melted crystals (after removal of solvent) had a constant refractive index, $n^{25}\text{D}$ 1.5820. This material of uniform refractive index was then fractionally distilled. After a small fore-run ($n^{25}\text{D}$ 1.5820), the bulk of the product distilled as a water white oily liquid at 118° at 1.5 mm., $n^{25}\text{D}$ 1.5812–1.5815.

Anal. Calcd. for $C_{14}H_{13}N_3$: C, 75.31; H, 5.87; N, 18.82. Found: C, 75.48; H, 6.08; N, 18.54.

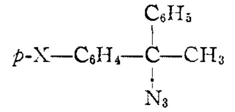
A consideration of refractive indices indicated the presence of 70–75% azide in the reaction product. However, the amount of pure azide (2 g. from 11.5 g. of mixture) that could be isolated was small.

Formation of Unsymmetrical Diarylethyl Azides and Measurement of Migration Aptitudes.—A series of unsymmetrical diarylethyl azides were prepared by the methods described above. No attempt was made to purify these azides; instead, the oil isolated from the reaction was dissolved in dry benzene and stirred with concentrated sulfuric acid until the evolution of nitrogen ceased. The contents of the reaction flask were poured into water and shaken thoroughly, the layers separated and the organic layer set aside. The water layer was washed several times with ether, made basic with sodium hydroxide solution and extracted five times with ether. These ether extracts were dried over anhydrous magnesium sulfate, filtered and treated with dry hydrogen chloride gas. The amine hydrochlorides that precipitated were washed several times with anhydrous ether and dried overnight in a vacuum oven at approximately 77°. Weighed samples of the hydrochlorides were then titrated with standard base to determine their neutralization equivalent. Several titrations on duplicate runs were performed.

Table II shows the azides formed and the results obtained

TABLE II

REARRANGEMENT OF SEVERAL DIARYLETHYL AZIDES



$$p\text{-X—}C_6H_4\text{—}\underset{N_3}{\overset{C_6H_5}{C}}\text{—}CH_3$$

X	Yield, %	Neut. equiv., amine·HCl	% Migration, subst. group
Br	48	149.5 ± 0.9	25.2
Cl	25	137.6	23.3
CH_3	43	140.8 ± 0.4	80.1
OCH_3	37	159.9 ± 0.1	100

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[17] J. D. Roberts, private communication.

[17a] *Cf.* John G. Burr, Jr., and Leon S. Ciereszko, THIS JOURNAL, **74**, 5426 (1952); Leon S. Ciereszko and John G. Burr, Jr., *ibid.*, **74**, 5431 (1952).

[18] H. Masson, *Compt. rend.*, **135**, 533 (1902).

[19] M. Tiffeneau, *Ann. chim. phys.*, [8] **10**, 322 (1907) [*C.A.*, **2**, 266 (1908)].

[20] C. D. Hurd and C. N. Webb, THIS JOURNAL, **49**, 546 (1927).

[21] W. Tzchelinzeff, *Ber.*, **37**, 4539 (1904).

[22] R. Stoermer and M. Simon, *ibid.*, **37**, 4168 (1904).

[23] E. Bergmann and H. Bondi, *ibid.*, **64**, 1455 (1931).

[24] H. E. M. Specht, A. W. Browne and K. W. Sherk, THIS JOURNAL, **61**, 1083 (1939).

[25] All melting points are uncorrected.

[26] M. Brander, *Rec. trav. chim.*, **37**, 67 (1917) [*C. A.*, **12**, 1467 (1918)].

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.

NORTHAMPTON, MASSACHUSETTS

[CONTRIBUTION NO. 115 FROM JACKSON LABORATORY, E. I. DU PONT DE NEMOURS AND COMPANY]

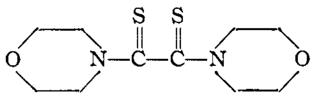
Synthesis of Acetomorpholide and Thioacetomorpholide from Morpholine and Sulfur

BY NEAL O. BRACE

RECEIVED NOVEMBER 15, 1951

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.

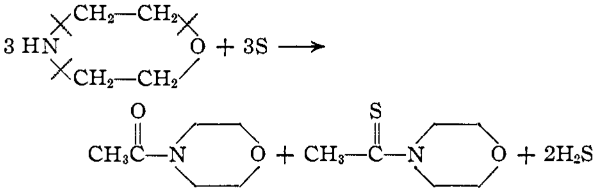
McMillan and King[1] isolated dithioöxalomorpholide (I) from the reaction of morpholine and sulfur with certain olefins under reflux conditions, and Horton and Van Den Berghe[2] showed that this compound was formed by refluxing morpholine and sulfur alone.[3] The compound was obtained in low yields. It was suggested by McMillan and King[1] that the formation of this product arose through $[\cdot CH_2S\cdot]$ radicals and may have been analogous to the Creigee cleavage of glycols.



(I)

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 dithioöxalomorpholide, 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 dithioöxalomorpholide.

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 $[\cdot CH_2\overset{O}{\overset{\|}{C}}\cdot]$ and $[\cdot CH_2\overset{S}{\overset{\|}{C}}\cdot]$ which probably react with morpholine as the ketene forms, $CH_2{=}C{=}O$ and $CH_2{=}C{=}S$, to give acetomorpholide and thioacetomorpholide, respectively, as indicated by the partial equation



Further reaction of thioacetomorpholide with morpholine and sulfur with evolution of hydrogen sulfide has been shown to give dithioöxalomorpholide.[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.	Analysis S, %	N, %
I	45–84	Atm.	....	..	..	..
II	56–95	42–24 mm.	1.4600	1.1	..	..
III	110–142	23–24	1.4912	16.0	4.7	12.1
IV	143–154	24	1.5108	8.0	10.0	10.0
V	130–160	2.6	Solid	4.6	..	..
VI	Residue	...	....	*ca.* 10.0	..	..

Fraction III, when redistilled, had b.p. 125–132° (24 mm.), $n^{25}D$ 1.4853. *Anal.* Calcd. for $C_6H_{11}O_2N$: 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 $C_6H_{12}O_2NBr$: 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]

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[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.

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

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