pure, as have β-ethoxyethyldiethylamine and γ-ethoxypropyldiethylamine. 2-Diethylamino-2-methyl-1-propanol has been prepared by a method similar to the previously unsuccessful diethylation of 2-amino-2-methyl-1-propanol[1] and the successful ethylation of 2-ethylamino-2-methyl-1-propanol.[2]

### Experimental[3]

**Diethyl-*n*-propylamine.**—A mixture of 70 g. of *n*-propyl bromide, 32 g. of ethylene glycol and 61 g. of diethylamine was refluxed for forty hours. The amine was liberated with alkali and extracted with ether. After the ether solution was dried over potassium hydroxide the ether was removed, and 19 g. (27%) of diethyl-*n*-propylamine was distilled at 111.5–112.5° (750 mm.); $n^{20}{}_{D}$ 1.4064; $d^{20}{}_{4}$ 0.742.

*Anal.* Calcd. for $C_7H_{17}N$: C, 72.97; H, 14.88; N, 12.16; $MR_D$, 38.35. Found: C, 73.10; H, 15.01; N, 12.14; $MR_D$, 38.18.

The **ethiodide** melted at 262–263° (cor.) with decomposition (von Auwers and Mauss reported 255–256°[4]).

The **picrate** was prepared in and recrystallized from ether as long yellow needles, m. p. 82–84° (cor.).

*Anal.* Calcd. for $C_{13}H_{20}N_4O_7$: C, 45.34; H, 5.86; N, 16.27. Found: C, 45.41; H, 5.91; N, 16.14.

The **picrolonate** was prepared in ether and recrystallized from ethanol–ether as orange-yellow elongated prisms, m. p. 140–141° (cor.).

*Anal.* Calcd. for $C_{17}H_{25}N_5O_5$: C, 53.81; H, 6.64; N, 18.46. Found: C, 53.92; H, 6.69; N, 18.41.

**Diethylisopropylamine Picrolonate.**—Prepared from diethylisopropylamine[5] in ether, the picrolonate was recrystallized from absolute ethanol in leafy clusters of yellow prisms, m. p. 164–165.5° (cor.).

**Diethylisopropylamine Ethiodide.**—Formed by refluxing diethylisopropylamine in benzene with excess ethyl iodide, the microcrystalline ethiodide melted at 264–266° (cor.) with decomposition.

**β-Ethoxyethyldiethylamine.**—A mixture of a six to one molar proportion of diethylamine (50 g.) and β-ethoxyethyl bromide (16.7 g.) was heated under reflux for twenty-four hours. The product was isolated as in the method for diethyl-*n*-propylamine; b. p. 63–64° (25 mm.); $n^{20}{}_{D}$ 1.4179.

*Anal.* Calcd. for $C_8H_{19}NO$: C, 66.15; H, 13.18; N, 9.64. Found: C, 65.81; H, 12.96; N, 9.64.

No picrate, picrylsulfonate, picrolonate, methiodide or mineral acid salt could be formed.

**γ-Ethoxypropyldiethylamine.**—Fifty grams of diethylamine and 19 g. of γ-ethoxypropyl bromide were heated under reflux and the product was isolated in the usual manner; b. p. 78–81° (25 mm.); $n^{20}{}_{D}$ 1.4223.

*Anal.* Calcd. for $C_9H_{21}NO$: C, 67.87; H, 13.29; N, 8.80. Found: C, 68.01; H, 13.01; N, 8.84.

Prepared in and recrystallized from ethanol, the **picrolonate** melted with decomposition at 213–215° (uncor.).

*Anal.* Calcd. for $C_{19}H_{29}N_5O_6$: C, 53.89; H, 6.93. Found: C, 53.75; H, 6.92.

**2-Diethylamino-2-methyl-1-propanol.**—2-Diethylamino-2-methyl-1-propanol was prepared by a method similar to that of Olson and Whitacre and Bachman and Mayhew[2]; b. p. 82–83° (22 mm.); $n^{20}{}_{D}$ 1.4421.

*Anal.* Calcd. for $C_8H_{19}NO$: N, 9.64. Found: N, 9.61.

The **picrolonate** was recrystallized from benzene containing a small amount of ethanol as elongated yellow prisms; m. p. 185.5–187° (uncor.) with decomposition.

*Anal.* Calcd. for $C_{18}H_{27}N_5O_6$: C, 52.80; H, 6.65. Found: C, 52.73; H, 6.67.

The **picrate** was recrystallized from ethanol–petroleum ether solution as yellow prisms; m. p. 156° (uncor.).

*Anal.* Calcd. for $C_{14}H_{22}N_4O_8$: C, 44.92; H, 5.92. Found: C, 45.00; H, 5.89.

**Diethylaminoacetone Picrolonate.**—Formed from diethylaminoacetone[6] in ether and recrystallized from ethanol, the picrolonate formed clusters of yellow prisms, m. p. 143–144° (cor.).

*Anal.* Calcd. for $C_{17}H_{23}N_5O_6$: C, 51.90; H, 5.89; N, 17.80. Found: C, 51.74; H, 6.11; N, 17.81.

**5-Diethylamino-2-pentanone Picrolonate.**—Prepared from Noval ketone in ether and recrystallized from ethanol–ether, the picrolonate formed stout yellow prisms, m. p. 105–107° (cor.).

*Anal.* Calcd. for $C_{19}H_{27}N_5O_6$: C, 54.14; H, 6.46; N, 16.62. Found: C, 54.32; H, 6.67; N, 16.67.

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[1] Olson and Whitacre, THIS JOURNAL, **65**, 1019 (1943).

[2] Bachman and Mayhew, *J. Org. Chem.*, **10**, 243 (1945).

[3] The microanalyses were performed by Miss Theta Spoor. Boiling points are uncorrected for emergent stem error.

[4] von Auwers and Mauss, *Ber.*, **61**, 2411 (1928).

[5] Caspe, THIS JOURNAL, **54**, 4457 (1933).

[6] Stoermer and Dzimiski, *Ber.*, **28B**, 2220 (1895).

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## Conversion of Benzylamine to N-Substituted Thiobenzamides

BY FREEMAN H. MCMILLAN[1]

In a previous publication[2] the modified Willgerodt reaction[3] was applied to styrene in the presence of a series of amines and the yield of phenylacetic acid obtained by hydrolyzing the crude reaction mixture was measured. In some instances there was isolated from the crude reaction mixture a little of the pure thioamide for characterization and analysis. It has been found that the compound isolated and called N-benzylphenylthioacetamide was in reality N-benzylthiobenzamide. Since there was no doubt that it was phenylacetic acid which was obtained from the hydrolysis of the crude reaction mixture, the hydrolysis of pure N-benzylthiobenzamide was investigated. It was found that this thioamide was very slowly attacked by refluxing 50% (by weight) sulfuric acid (the conditions used for hydrolyzing the crude thioamides), thus explaining the absence of benzoic acid in the hydrolysate from the crude reaction mixture of styrene, sulfur and benzylamine. The identity of N-benzylthiobenzamide was established by hydrolysis with refluxing 65% (by weight) sulfuric acid followed by isolation of benzoic acid and benzylamine in the form of its picrate.

Since none of the other amines used to prepare thioamides reported in ref. 2 had the possibility of undergoing a reaction analogous to that which benzylamine underwent, there is no reasonable doubt as to their identity.

Although it is possible that the N-benzylthiobenzamide could have arisen through cleavage[4]

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[2] King and McMillan, THIS JOURNAL, **68**, 2335 (1946).

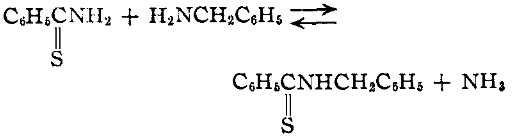
[3] Schwenk and Bloch, *ibid.*, **64**, 3051 (1942).

[4] For discussion of cleavage in Willgerodt reaction *cf.* McMillan and King, *ibid.*, **69**, 1207 (1947).

of styrene, such cleavage has not been observed with other amines, *e. g.*, morpholine, where the yield of phenylthioacetmorpholide is very good, and consequently this mode of formation is not considered probable. An alternative mode of formation is by oxidation (replacement of two hydrogens by sulfur) of part of the benzylamine used.[5]

It was found that by heating equimolecular portions of benzylamine and sulfur a 91% yield of N-benzylthiobenzamide was obtained. Wallach[6] reported that the reaction of benzylamine with sulfur in a sealed tube at 180° gave thiobenzamide. The discrepancy between our results and those of Wallach may be explained by the fact that ammonia was given off copiously from our reaction. Any reaction in which ammonia is one of the products would be favored in an open reaction vessel where the ammonia could escape and would be suppressed in a sealed tube where it would remain at the site of the reaction. Two such possible reactions which would lead to our product would be

$$C_6H_5CH_2NH_2 + H_2NCH_2C_6H_5 \rightleftarrows C_6H_5CH_2NHCH_2C_6H_5 + NH_3 \quad (1)$$



$$C_6H_5C(=S)NH_2 + H_2NCH_2C_6H_5 \rightleftarrows C_6H_5C(=S)NHCH_2C_6H_5 + NH_3 \quad (2)$$

It was also found that heating an equimolecular mixture of benzylamine and morpholine with sulfur gives thiobenzmorpholide, presumably by the same route as the benzylamine–sulfur reaction.

**Acknowledgment.**—The author wishes to acknowledge the helpful criticisms of Dr. John A. King in the preparation of this manuscript.

### Experimental[7,8]

**Reaction of Benzylamine with Sulfur.**—A mixture of benzylamine (21.4 g., 0.20 mole) and sulfur (8.0 g., 0.25 mole) was heated at reflux for forty-five minutes. Evolution of ammonia was noticed almost immediately after heating was begun. The cooled reaction mixture was treated with Skellysolve "C" (100 ml.) and then filtered. The solid material weighed 19.5 g. (91%) and melted at 81–83°. After crystallization from Skellysolve "C" (250 ml.) it melted at 84–85°.

*Anal.* Calcd. for $C_{14}H_{13}NS$: N, 6.16; S, 14.10. Found: N, 5.85; S, 14.10.

There was no depression in melting point when this compound was mixed with the material reported to be N-benzylphenylthioacetamide[2] but now known to be N-benzylthiobenzamide.

**Hydrolysis of above Reaction Product.**—The compound melting at 84–85° (2.0 g.) was refluxed for one hour with 65% (by weight) sulfuric acid (30 ml.). The hydrolysis mixture was cooled and extracted with two 30-ml. portions of ether. The combined ether extracts were extracted with 25 ml. of 10% sodium hydroxide solution and the caustic extract was acidified with dilute hydrochloric acid. The acidified solution was extracted with two 30-ml. portions of ether; the ether solution was dried over anhydrous sodium sulfate and the ether was removed under vacuum. The residue was crystallized from water giving white crystals (0.4 g.) melting at 120–121°, undepressed when mixed with an authentic sample of benzoic acid.

The hydrolysis mixture was made alkaline with 10% sodium hydroxide solution and then extracted with three 100-ml. portions of ether. The ether was dried over anhydrous potassium carbonate and the ether was removed under vacuum. The residue was treated with saturated alcoholic picric acid solution and gave a picrate which after crystallization from alcohol melted at 193–195°, undepressed when mixed with an authentic sample of benzylamine picrate.[9]

**Reaction of Benzylamine, Morpholine and Sulfur.**—A mixture of benzylamine (10.7 g., 0.10 mole), morpholine (8.7 g., 0.10 mole) and sulfur (6.4 g., 0.20 mole) was heated at 160° for one hour. The cooled reaction mixture was taken up in 150 ml. of boiling alcohol and then chilled. The solid that formed weighed 8.4 g. (40.6%) and melted at 137–138°, undepressed when mixed with an authentic sample of thiobenzmorpholide.[5]

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[5] For discussion of this type of oxidation see McMillan and King, submitted for publication in THIS JOURNAL.

[6] Wallach, *Ann.*, **259**, 300 (1890).

[7] Melting points uncorrected.

[8] Analyses performed under the direction of Mr. M. E. Auerbach.

[9] Moureu and Lazennec, *Bull. soc. chim.*, [3] **35**, 1183 (1906).

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## Diffusion Coefficient of Nitroglycerin in Rocket Powder and in Cellulose Acetate[1]

BY S. S. PENNER[2] AND S. SHERMAN[3]

Double base rocket powders, consisting of approximately 60% nitrocellulose, 40% nitroglycerin and some minor components, constitute one type of widely used rocket propellant. These powders burn easily over their entire exposed surface. In order to restrict burning to a preferred direction and thereby lengthen the total burning time it is necessary to cover a portion of the powder surface with a strongly bonded inert material such as cellulose acetate. These wrappings of cellulose acetate, though initially almost noncombustible, lose their protective action in the course of time because of the diffusion of nitroglycerin into the cellulose acetate. By determining the nitroglycerin concentration as a function of the distance from the cellulose acetate–powder interface at a given time, it is possible to ascertain the average diffusion coefficient of nitroglycerin in cellulose acetate and in powder. Knowledge of the maximum allowable nitroglycerin concentration in the cellulose acetate permits calculation of maximum safe storage times at all temperatures for which diffusion coefficients are available.

A complete experimental study was not carried through. In view of the limited experimental

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[1] This paper is based on OSRD report No. 4963 (PB report No. 50864) on the "Diffusion of Nitroglycerin in Wrapped Powder Grains." The diffusion study was carried out at the Allegany Ballistics Laboratory, Cumberland, Maryland, operated by the George Washington University under OSRD contract OEMsr-273. Analytical work was performed by J. J. Donovan and N. Marans.

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