with sodium or sodium ethoxide at high temperatures. von Pechmann and Wolman[7] reported that their compound was transformed by potassium hydroxide fusion into an acid, m.p. 184° (dec.). Our product duplicated this behavior.

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[7] H. von Pechmann and L. Wolman, *Ber.*, **31**, 2014 (1898).

THE CHEMICAL LABORATORIES
THE JOHNS HOPKINS UNIVERSITY
BALTIMORE 18, MD.
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4,4'-Tetramethyldiaminodiphenyl Ether

BY GEORGE A. REYNOLDS

4,4'-Tetramethyldiaminodiphenyl ether has been prepared in the following manner: Commercially available 4,4'-dinitrodiphenyl ether was reduced, using Raney nickel catalyst, to give the corresponding diamine. Alkylation of the diamine with methyl iodide yielded tetramethyldiaminodiphenyl ether melting at 61–62°. The product formed a picrate which melted at 174–175°.

Holzmann[1] prepared this compound by heating an alcoholic solution of 4,4'-tetramethyldiaminodiphenyl sulfide with two equivalents of alcoholic ammoniacal silver nitrate. Holzmann reported that his product melted at 119° and its picrate at 150°. Since these melting points are almost identical with those of tetramethyldiaminodiphenyl sulfide and its picrate, mixed melting points with authentic samples of the sulfide and its picrate, and analyses were made. The results showed beyond doubt that the compound reported by Holzmann as the ether was actually the starting material.

Experimental

4,4'-Diaminodiphenyl Ether.—4,4'-Dinitrodiphenyl ether (25 g., 0.01 mole) was dissolved in 200 ml. of absolute ethanol. About 5 g. (wet weight) of Raney nickel was added and the mixture reduced in the Parr apparatus at 50 p.s.i. and 75°. The theoretical drop in pressure took place in approximately 30 minutes. The mixture was filtered hot and the filtrate allowed to cool. The product was collected on a Buchner funnel and air-dried (m.p. 186–187°; reported m.p. 186–187°[2]). The yield was 18 g. (90%).

4,4'-Tetramethyldiaminodiphenyl Ether.—A mixture of 11 g. (0.055 mole) of 4,4'-diaminodiphenyl ether, 31 g. (0.22 mole) of methyl iodide and 8.8 g. (0.22 mole) of sodium hydroxide in 9 ml. of water was placed in a pressure tube and the tube sealed. The sealed tube was heated at 100° for 12 hours. The reaction mixture was poured onto 100 ml. of water and the solid collected on a Buchner funnel. Recrystallization from dilute ethanol gave a compound which melted at 61–62° (7 g., 50%).

Anal. Calcd. for $C_{16}H_{20}N_2O$: C, 75.0; H, 7.9; N, 10.9. Found: C, 75.2; H, 8.0; N, 11.0.

The product formed a picrate which, after recrystallization from ethanol, melted at 174–175°.

Anal. Calcd. for $C_{28}H_{26}N_8O_{15}$: N, 15.2. Found: N, 15.0.

Compound Obtained by Holzmann's Method.—Tetramethyldiaminodiphenyl sulfide (20 g., 0.074 mole) reacted with ammoniacal silver nitrate as described by Holzmann.[1] The product obtained by this method melted at 118° after three recrystallizations from ethanol (reported m.p. 119°).[1] Admixture with a sample of tetramethyldiaminodiphenyl sulfide produced no depression in the melting point. Analysis of the compound showed that the starting material had been recovered.

Anal. Calcd. for $C_{16}H_{20}N_2S$: C, 70.4; H, 7.4; N, 10.3; S, 11.8. Found: C, 70.8; H, 7.4; N, 10.2; S, 12.0.

The compound formed a picrate melting at 147° (reported m.p. 150°).[1] Analysis showed this to be the picrate of the starting sulfide.

Anal. Calcd. for $C_{28}H_{26}N_8O_{14}S$: N, 15.4. Found: N, 15.5.

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[1] E. Holzmann, *Ber.*, **21**, 2056 (1888).

[2] C. Haeussermann and H. Teichmann, *ibid.*, **29**, 1449 (1896).

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A Synthesis of Unsymmetrical Dimethyl Hydrazine Using Lithium Aluminum Hydride

BY F. W. SCHUELER AND CALVIN HANNA

During the course of synthesizing a group of hydrazonium analogs related to acetylcholine[1] it was found that the laborious reduction of nitrosodimethylamine by zinc and acetic acid which involves subsequent steam distillation and evaporation[2] could be avoided through the use of lithium aluminum hydride in the reduction procedure.

Experimental

To 5.0 g. of lithium aluminum hydride in 150 ml. of dry ether was added slowly a solution of 5.0 g. of nitrosodimethylamine[2] in 100 ml. of absolute ether. After setting one hour wet ether was added to decompose the reaction mixture. To the resultant mixture was then added 75 ml. of 30% sodium hydroxide with stirring and the alkaline solution separated and washed three times with 50-ml. portions of ether. To the combined ether extracts, following filtration, was added 100 ml. of 20% hydrochloric acid solution with agitation and the whole was subsequently evaporated *in vacuo* to a thick sirup on the steam-bath. From this point on the procedure outlined by Hatt[2] was followed in the preparation of the anhydrous base.

Yield of the anhydrous base was 3.1 g. (78%) which formed a methiodide exhibiting no depression of the melting point when mixed with an authentic sample.[3,4]

An attempt was made to apply the above procedure toward the preparation of *unsym*-diphenylhydrazine through the reduction of nitrosodiphenylamine. To 5.0 g. of lithium aluminum hydride in 150 ml. of dry ether was added slowly a solution of 6.6 g. of nitrosodiphenylamine in 100 ml. of absolute ether. The attempted isolation of the hydrazine following the procedure outlined by Fischer[5] yielded only diphenylamine 4.1 g. (74%), m.p. 34.0°. A mixed melting point with an authentic sample of diphenylamine exhibited no lowering. The acetyl derivative melting at 101° likewise exhibited no depression when mixed with an authentic sample of the acetyl derivative of diphenylamine.

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[1] F. W. Schueler and Calvin Hanna, *Arch. Internat. Pharmacodyn. Therapie*, in press (1951).

[2] "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 250.

[3] C. Harris and T. Haga, *Ber.*, **31**, 57 (1898).

[4] E. Fischer, *Ann.*, **199**, 316 (1879).

[5] E. Fischer, *ibid.*, **190**, 175 (1878).

DEPARTMENT OF PHARMACOLOGY
COLLEGE OF MEDICINE
STATE UNIVERSITY OF IOWA
IOWA CITY, IOWA
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Dimethyl *p*-Ethylbenzenephosphate

BY RICHARD H. WILEY AND CHARLES HARRY JARBOE[1]

A search of the literature has failed to disclose any reference to the preparation or characterization of esters of *p*-ethylbenzenephosphonic acid. We have prepared and characterized the dimethyl ester. This Note presents the data observed. A study of the yields obtained in the preparation of *p*-ethylbenzenephosphine dichloride and some useful modifications in the experimental procedures for con-

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[1] This work was supported in part under Contract No. AT-(40-1)-229 between the Atomic Energy Commission and the University of Louisville. This note is taken from an Honors thesis submitted by Charles Harry Jarboe.