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. RECEIVED APRIL 26, 1951

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 RECEIVED JUNE 4, 1951

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.

version of this halide to its dibromide and of this dibromide to the ester are described. Molar refraction was calculated using the constants given by Kabachnik.[2]

Experimental

p-Ethylbenzenedichlorophosphine[3,4,5] was prepared by the reaction of *p*-ethylbenzene with phosphorus trichloride using aluminum chloride as catalyst. Excess phosphorus trichloride was removed by vacuum distillation prior to addition of phosphorus oxychloride to decompose the product–aluminum chloride complex. The phosphorus oxychloride–aluminum chloride complex was precipitated by addition of petroleum ether and separated by filtration.[6] The crude product obtained on evaporation of the solvent was used in the following reaction without purification. A study of yields from varying proportions of aluminum chloride, ethylbenzene and phosphorus trichloride gave a maximum yield of 70% of crude product with a molar ratio of 0.5/1/3, respectively, for preparations starting with 0.5 mole of ethylbenzene.

_p_-Ethylbenzenedichlorophosphine dibromide was prepared by addition of bromine to a carbon tetrachloride solution of the crude dichloride with cooling to dissipate the heat of reaction. The orange precipitate was not isolated but used directly in the esterification.

Dimethyl _p_-ethylbenzenephosphonate was prepared by addition of absolute methanol to the carbon tetrachloride suspension of the tetrahalide. Excess bromine was removed by washing with 10% sodium sulfite solution. The ester, which separates from the solution, was collected and fractionated under vacuum. The yield of ester boiling at 131–137° at 2 mm. was 70 g. from 53 g. of ethylbenzene or 66% of the theoretical amount. The yield based on the amount of dichloride used is 94% of the theoretical. The ester was refractionated to give a fraction boiling 133–135° at 2 mm. for analysis; n^{25}_D 1.5003; sp. gr. 1.141; d^{25}_0 1.141.

Anal. Calcd. for $C_{10}H_{15}O_3P$: P, 14.48; sapn. equiv., 107; molar refraction, 55.66. Found: P, 14.79; sapn. equiv., 106.8; molar refraction, 55.26.

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(2) Kabachnik, *Izvesti. Akad. Nauk* (*U. S. S. R.*), 219 (1948).

(3) Jackson, Davies and Jones, *J. Chem. Soc.*, 2298 (1930).

(4) Jones, *et al.*, *ibid.*, 1446 (1947).

(5) Michaelis, *Ann.*, **293**, 193 (1896); **294**, 1 (1896).

(6) Dye, THIS JOURNAL, **70**, 2595 (1948).

DEPARTMENT OF CHEMISTRY
COLLEGE OF ARTS AND SCIENCES
UNIVERSITY OF LOUISVILLE
LOUISVILLE 8, KENTUCKY

RECEIVED MAY 24, 1951

A Partial Criterion for the Comparison of Different Softwood Lignins

BY CONRAD SCHUERCH, JR.

A clear body of evidence has been developing which indicates that wood material is an interpenetrating system of hydrophilic and hydrophobic polymeric materials insoluble in neutral solvents. Although it is known that holocellulose contains several different hydrolyzable polysaccharides, there appear to be few research tools presently available which could establish the existence or non-existence of comparable heterogeneity in the hydrophobic or ligneous portion of wood.

Even in the case of hardwoods where the presence of two types of monomeric unit is proven and from which fractions of differing methoxyl content have frequently been isolated,[1] the degree of order in the substrate is difficult to assess because of uncertainty regarding the reliability of fractionation techniques and molecular weight determinations used up to the present. A single macromolecule with a single recurring pattern of guaiacyl and syringyl units would be expected to yield on random cleavage low molecular weight fractions of substantially different analyses, and these could give a false idea of the complexity of the system.

With softwood lignins, where the criteria of heterogeneity are still less obvious, it is commonly assumed that only polymer systems based on propylguaiacyl units are present and in consequence analyses are usually reported in terms of a hypothetical monomeric skeleton of nine carbon atoms. Although this hypothesis has been fruitful, a primary aim of structural studies should be to establish whether lignin is in fact a single polymeric material or several. To do so will require criteria which can establish whether or not isolated lignins are artifacts, that is, whether during each degradation process no new bonds are formed either by intermolecular polymerization or by intramolecular reaction.[2] Careful studies of molecular weight changes of fractionated lignins during chemical reaction might aid in establishing the absence of repolymerization but such studies have rarely been attempted. Perhaps the only evidence bearing on the second possibility (intramolecular reaction) is that obtained from comparative permanganate oxidations and hydrogenations of wood and isolated lignins.[1b,3,4,5] Other methods of comparison between derived lignins are highly desirable.

One simple method of evaluating softwood lignin preparations can be based on the fact that polymeric materials containing only propylguaiacyl units have an invariant ratio of per cent. methoxyl to per cent. skeletal carbon (C_{10}) equal to 31/120 or 0.258. So long as neither carbon nor methoxyl is lost or gained, the ratio remains the same—no matter what reactions the material has undergone, what number of entire propylguaiacyl units have been lost by scission, what fine structures are present, or what their degree of oxygenation or polymerization. It is therefore possible to compare this ratio in pure lignin preparations of the most divergent history or of widely different molecular weight. Fluctuations can be ascribed to the loss or gain of skeletal carbon or methoxyl in isolation *or to heterogeneity in the original starting material* but cannot be due to repolymerization or condensation reactions. In view of the frequency with which the latter are called upon to explain anomalous results, this ratio represents a useful limitation of uncertainty.

In Table I, there are listed the values of the methoxyl:carbon ratio for many isolated softwood lignins. It is apparent that these products are significantly different even according to this simple test of identity, and that all have lower ratios than

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(1) C. Schuerch, THIS JOURNAL, **72**, 3838 (1950), (a) Table II and footnote 8; (b) footnote 19.

(2) The frequently applied criteria of color and solubility in a sulfite cook are tests of chemical change only and as such have utility in comparing "native" or supposedly unchanged lignins. They are clearly not applicable to derivatives of lignin which have been changed by the removal of reactive functional groups or by the introduction of elements of a hydrophobic solvent.

(3) D. Read and C. B. Purves, unpublished results indicate that cyclization occurs during some isolation methods.

(4) H. Richtzenhaim, *Ber.*, **83**, 488 (1950); *Acta Chem. Scand.*, **4**, 206 (1950).

(5) H. Adkins, R. L. Frank and E. S. Bloom, THIS JOURNAL, **63**, 549 (1941).