β-aminoethyl functions in a para relationship.
2. Pressor, bronchodilator and antihistamine activity tests have been made on the amines.
3. Several new compounds intermediate in the formation of the amines are reported.

RECEIVED AUGUST 30, 1948

[CONTRIBUTION FROM WESTERN REGIONAL RESEARCH LABORATORY[1]]

Ethers of *p*-Hydroxydiphenylamine as Alkyl Halide Identification Derivatives

BY DAVID F. HOUSTON

The preparation of several ethers of *p*-hydroxydiphenylamine as intermediates for other syntheses drew attention to their value as derivatives for the identification of alkyl halides. These ethers offer an alternative choice to previously reported[2,3,4,5] derivatives.

The hydroxydiphenylamine is commercially available and can be readily purified. The synthesis of the ethers was convenient, and the products were easily crystallized. Ether formation from primary halides was general. *s*-Butyl chloride gave unreacted amine together with oil and tarry matter. Tertiary halides were not investigated. Mixtures of two ethers with closely similar melting points showed melting-point depressions of several degrees.

Data on the ethers are collected in the accompanying table. The melting points follow the usual trend for a homologous series, and those for the even-carbon alkyl ethers above the hexyl compound follow a smooth curve.

TABLE I

p-HYDROXYDIPHENYLAMINE ETHERS, $ROC_6H_4NHC_6H_5$

Halide used	M. p., °C.	Empirical formula	Analytical data, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found
n-Propyl iodide	62.2–62.9	$C_{15}H_{17}NO$	79.26	79.4	7.54	7.55	6.16	6.06
Isopropyl[a]	86.3–87.1	$C_{15}H_{17}NO$	79.26	79.3	7.54	7.56	6.16	6.12
n-Butyl bromide	46.9–47.3	$C_{16}H_{19}NO$	79.63	79.6	7.94	7.90	5.80	5.80
n-Amyl iodide	40.9–41.3	$C_{17}H_{21}NO$	79.96	80.2	8.29	8.31	5.49	5.46
n-Hexyl bromide	41.0–41.5	$C_{18}H_{23}NO$	80.25	80.4	8.60	8.59	5.20	5.18
n-Heptyl bromide	44.9–45.3	$C_{19}H_{25}NO$	80.52	80.5	8.89	8.92	4.94	4.89
n-Octyl bromide	45.5–46.3	$C_{20}H_{27}NO$	80.76	80.9	9.15	9.03	4.71	4.69
n-Dodecyl bromide	61.3–61.9	$C_{24}H_{35}NO$	81.53	81.6	9.98	9.88	3.96	3.94
n-Hexadecyl bromide	74.5–75.3	$C_{28}H_{43}NO$	82.10	82.2	10.57	10.44	3.42	3.39
Benzyl chloride	95.2–95.8	$C_{19}H_{17}NO$	82.88	82.9	6.22	6.17	5.09	5.08

[a] Purified from commercial product; see text.

Experimental

Materials.—The *p*-hydroxydiphenylamine was a sample of commercial product with a stated 92% purity. It was further purified by distillation with superheated steam,[6] collecting the product distilling at 170–180°. The dark still residue contained some diphenyl-*p*-phenylenediamine. Final recrystallizations from benzene–hexane gave material melting at 69–70° in agreement with the reported[7] value of 70°. Less rigorous purification may be satisfactory, as indicated by the fact that the octyl ether prepared directly from the commercial *p*-hydroxydiphenylamine, though remaining somewhat dark colored, melted at 45.5–46.2° in complete agreement with the analytical sample from the purified amine.

n-Propyl and *n*-amyl iodides, heptyl bromide, and *s*-butyl and benzyl chlorides were obtained from Eastman Kodak Company. The hexyl, octyl, dodecyl and hexadecyl bromides were research-grade chemicals (boiling within a two degree range) obtained from a commercial supplier of halogen chemicals. *n*-Butyl bromide had been prepared and fractionally distilled in this Laboratory.

The isopropoxydiphenylamine was a commercial product. It was distilled at reduced pressure, and the portion distilling at 140–145° at 1.5 mm. was purified by decolorizing a methanol solution with charcoal and crystallizing the product from aqueous methanol (1:3).

Procedure.—Preparation of the ethers, essentially the same in all cases, is illustrated by synthesis of the *n*-propyl compound. Equivalent amounts (0.02 mole) of *p*-hydroxydiphenylamine (3.70 g.) and *n*-propyl iodide (2.46 g.) were added to 18 cc. of 10% alcoholic potassium hydroxide (0.03 equivalent). The solution was refluxed three hours with stirring by magnetic stirrer, cooled, diluted to 200 cc. with water, acidified slightly with hydrochloric acid, and chilled to 0°. The dark solids were filtered off, and decolorized with charcoal in 85 cc. of alcohol. The filtrate was diluted with water to clouding, cooled to 0°, and again filtered. The yield at this point was 2.78 g. (61%). Two recrystallizations from aqueous alcohol gave pearly flakes melting at 40.9–41.3° (cor.).

The halides used, and the melting points and analytical data for the ethers formed, are presented in the table.

Acknowledgment.—I wish to express my appreciation to E. B. Kester for his interest in this

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[1] Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyright.

[2] L. L. Merritt, Jr., S. Levey and H. B. Cutter, THIS JOURNAL, **61**, 15 (1939).

[3] R. D. Drew and J. M. Sturtevant, *ibid.*, **61**, 2666 (1939).

[4] W. M. Lauer, P. A. Sanders, R. M. Leekley and H. E. Ungnade, *ibid.*, **61**, 3050 (1939).

[5] H. B. Cutter and H. R. Golden, *ibid.*, **69**, 831 (1947).

[6] A. A. Morton, "Laboratory Technique in Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1938, pp. 144–145.

[7] A. Calm, *Ber.*, **16**, 2799 (1883).

investigation, and to L. M. White and Geraldine Secor for performing the microanalyses.

Summary

Alkyl ethers of *p*-hydroxydiphenylamine have been prepared from a variety of alkyl halides and have properties suitable for use in identification of alkyl halides. Ether formation from primary halides was general, but secondary alkyl halides did not always operate satisfactorily. Tertiary halides were not investigated.

RECEIVED JULY 20, 1948

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE SPRAGUE ELECTRIC COMPANY]

Pentachlorophenyl Derivatives. III. The Effect of Temperature on the Composition of the Product in the Chlorination of Ethylpentachlorobenzene

BY SIDNEY D. ROSS, MOUSHY MARKARIAN AND MATTHEW NAZZEWSKI

In previous reports from this Laboratory[1] it was shown that the major product isolated from the chlorination of ethylpentachlorobenzene was 1-pentachlorophenyl-2-chloroethane, I. Bromination, on the other hand, resulted in an almost quantitative yield of the α-substitution product, 1-pentachlorophenyl-1-bromoethane. This difference in the direction of substitution was attributed to a combination of two factors—the greater reactivity of the chlorine atom[2] and steric hindrance about the α-position. Evidence indicating the presence of steric hindrance in systems of this type has been presented in a previous report.[3] We have postulated that with ethylpentachlorobenzene the energy barrier for reaction is smaller for an attack at the α-position but that this position is so shielded sterically by the ortho chlorine substituents that many collisions occur at the β-position before a collision occurs at the α-position. The chlorine atom is so reactive that even a collision at the β-position is sufficiently effective to result in reaction, but with the less reactive bromine atom only a collision at the α-position is effective and no β-bromide is formed.

On the above basis it would be predicted that β-chlorination would be favored over α-chlorination at higher temperatures but that with decreasing temperature the ratio of β- to α-chlorination would decrease. In our previous work we studied the products of the chlorination at both 200 and 68–73°. At both temperatures the predominant product was I. At the higher temperature the only other products isolated were hexachlorobenzene and a highly chlorinated ethylpentachlorobenzene which was not fully characterized. At the lower temperature the other isolable products were hexachlorobenzene and pentachlorostyrene, II, and it was suggested that II arose from decomposition of 1-pentachlorophenyl-1-chloroethane, III, during the distillation process and constituted indirect evidence for the occurrence of some α-chlorination at the lower temperature. In both cases the yield of β-chloride, I, actually isolated was never more than 35% so that the possibility of some α-chlorination even at the higher temperature was not eliminated. It is our present purpose to show that some α-chlorination takes place at both 70–75° and 180° and that the relative amounts of β- and α-chlorination at the two temperatures support the postulated mechanism to account for the difference in the direction of substitution on bromination and chlorination.

If ethylpentachlorobenzene, is chlorinated and then reacts, without purification, with benzene in the presence of aluminum chloride the major product is a mixture of two solids, one melting from 110.5–112.5° and the other from 153–155°. Although the two compounds distil at similar temperatures and pressures they can be readily separated by crystallization and both analyze correctly for $C_{14}H_4Cl_5$. The lower melting one, IV, was synthesized from both 1-pentachlorophenyl-1-bromoethane and pentachlorostyrene by reaction with benzene in the presence of aluminum chloride and must, therefore, be 1-pentachlorophenyl-1-phenylethane. The higher melting product, V, is the isomeric 1-pentachlorophenyl-2-phenylethane and was synthesized by treating I with benzene and aluminum chloride. V can result only from the presence of I in the crude chlorination mixture. IV can result either from III or from pentachlorostyrene. However, since pentachlorostyrene itself probably results from III it is still valid to assume that the amounts of IV and V isolated from the coupling reaction are indicative of the amounts of α- and β-chlorination in the chlorination reaction and we have applied this criterion to the products obtained by chlorination at 180 and 70–75°.

Chlorination of 1000 g. of ethylpentachlorobenzene at 180° followed by coupling with benzene at 50° gave a crude product which yielded five fractions on distillation—a forerun weighing 229 g., the main fraction weighing 546 g., an intermediate fraction of 60 g., a high boiling fraction of 123 g., and a final fraction of 36 g. collected after decomposition of the pot residue had started.

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[1] Ross, Markarian and Nazzewski, THIS JOURNAL, **69**, 1914, 2468 (1947).

[2] Schumacher, *Angew. Chem.*, **53**, 501 (1940).

[3] Ross, THIS JOURNAL, **70**, 4039 (1948).