polymerize slowly to rubber-like products, but as substitutes for rubber these products are inferior to polychloroprene.

A method for the synthesis of oxyprenes from vinylacetylene has been described which involves as its final step the thermal decomposition of compounds of the formula $ROCH_2CH_2C(OR)_2CH_3$. A number of intermediates of types $ROCH_2CH_2COCH_3$, $ROCH_2CH_2C(OR)_2CH_3$, $ROCH_2CH{=}C(OR)CH_3$ and $CH_2{=}CHC(OR)_2CH_3$ have been prepared and characterized.

WILMINGTON, DELAWARE RECEIVED AUGUST 27, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF OHIO WESLEYAN UNIVERSITY]

Alkyl Ethers of 2,2-Bis-(4-hydroxyphenyl)-propane. I. Some Dialkyl Ethers[1]

BY G. R. YOHE AND J. F. VITCHA

The condensation of two molecules of phenol with one of acetone in the presence of hydrogen chloride or sulfuric acid yields 2,2-bis-(4-hydroxyphenyl)-propane, $HOC_6H_4C(CH_3)_2C_6H_4OH$. This compound, with some of its simple derivatives, has been described in the literature.[2] Of the ethers of this compound only the dimethyl ether has been described.[2a,2b,3]

Some time ago the writers began the preparation of a series of the monoalkyl ethers of this dihydric phenol. The preparation of these monoalkyl ethers resulted in the incidental formation of the corresponding dialkyl ethers as well; several of these are described herewith. The monoalkyl derivatives will be described in a subsequent communication.

The general method followed was to allow an excess of the phenol in aqueous sodium or potassium hydroxide solution to react with the suitable dialkyl sulfate. Commercial dimethyl and diethyl sulfates were used, *n*-propyl and *n*-butyl sulfates were prepared by the method of Barkenbus and Owen,[4] while *n*-amyl sulfate was prepared by the action of sulfuryl chloride on *n*-amyl alcohol[5] and used without being isolated for the alkylation reaction. The ethers described herein were isolated from the alkali-insoluble portions of the reaction mixtures and purified by distillation or by recrystallization from methanol or ethanol solution cooled with a solid carbon dioxide–ether mixture; in some cases both distillation and crystallization procedures were used. In general the yields were low and the compounds rather difficult to purify.

The di-*n*-propyl ether gave the most difficulty in purification. It was contaminated with a rather large amount of a substance of similar boiling point, but of higher refractive index. Isolation was finally accomplished by dissolving the crude compound in petroleum ether (b. p. 40–60°) and cooling the solution with solid carbon dioxide–ether mixture, whereupon the impurity separated out as a gum, leaving the desired dipropyl derivative in solution. The identity of the impurity has not been established.

The solid dialkyl ethers of 2,2-bis-(4-hydroxyphenyl)-propane are white needle crystals; in the molten state they may be easily supercooled to liquids of moderate viscosity. These compounds are soluble in the usual organic solvents; the higher members of the series are only sparingly soluble in methanol.

The properties of these *n*-alkyl ethers through amyl are listed in Table I.

The reactions described below are typical of the relative amounts and conditions used in all reactions. No doubt higher yields of the dialkyl derivatives could have been obtained by using the alkyl sulfates in excess. This, however, would have minimized the formation of the monoalkyl ethers.

Experimental Part

Dibutyl Ether of 2,2-Bis-(4-hydroxyphenyl)-propane. Use of the Dialkyl Sulfate.—A mixture of 114 g. (0.5 mole) of 2,2-bis-(4-hydroxyphenyl)-propane, 60 g. (1.5 moles) of sodium hydroxide and 300 cc. of water was heated to boiling, 42 g. (0.2 mole) of di-*n*-butyl sulfate added,

(1) A part of this work was reported at the 44th annual meeting of the Ohio Academy of Science at Columbus, Ohio, March 30, 1934.

(2) (a) Beilstein's "Handbuch," 4th ed., Vol. VI, pp. 1011, 1012, Supplement Vol. VI, p. 493; (b) A. Dianin, *J. Russ. Phys.-Chem. Soc.*, **23**, 492 (1891); (c) T. Zincke and M. Grueters, *Ann.*, **343**, 85 (1905); (d) T. Szeky, reprint from *Ber. d. med.-naturw.*, Section d. Siebenbürg. Museumvereines, 1–13 19/11 (1904); *Chem. Zentr.*, **75**, II, 1737 (1904); (e) J. Schmidlin and R. Lang, *Ber.*, **43**, 2814 (1910); (f) L. H. Baekeland and H. L. Bender, *Ind. Eng. Chem.*, **17**, 225–37 (1925); (g) J. v. Braun, *Ann.*, **472**, 65 (1929).

(3) Wulff, *J. Russ. Phys.-Chem. Soc.*, **23**, 498 (1891).

(4) C. Barkenbus and J. Owen, THIS JOURNAL, **56**, 1204 (1934).

(5) Unpublished work from the writer's laboratory.

TABLE I

DIALKYL ETHERS OF 2,2-BIS-(4-HYDROXYPHENYL)-PROPANE, $ROC_6H_4C(CH_3)_2C_6H_4OR$

R	CH_3	C_2H_5	C_3H_7	C_4H_9	C_5H_{11}
M. p., °C.	59–61.5	49–50	....	20	34.5–35.5
B. p., °C. (mm.)	190 (5)	....	200–202 (3)	212–213 (3)	225–230 (3)
$n^{20}D$	1.5696[a]	1.5556[a]	1.5448	1.5368	1.5306[a]
d^{20}_4	....	....	1.0156	0.9961	....
Calcd. % C	79.63	80.23	80.72	81.11	81.46
Found % C	....	79.81	80.65	80.79	81.34
Calcd. % H	7.88	8.52	9.03	9.49	9.86
Found % H	....	8.57	9.14	9.37	9.89

[a] Value determined using the supercooled liquid.

and the heating continued for three hours. The alkali-insoluble portion of the reaction product was isolated by ether extraction, and the dibutyl derivative obtained by distillation of this solution. The yield was 35 g., or 51% of the theoretical, assuming the utilization of only one of the alkyl groups of the sulfate. It was necessary to further purify this material.

Diamyl Ether of 2,2-Bis-(4-hydroxyphenyl)-propane. The Alcohol-Sulfuryl Chloride Method.—One mole (88 g.) of pentanol-1 was cooled with an ice-bath, and 0.5 mole of sulfuryl chloride added slowly so that the reaction mixture remained cold. This was allowed to stand protected from moisture for one week. It was then neutralized with sodium hydroxide solution (approximately 0.75 mole in the form of a 10 *N* solution was needed), and a solution of 0.5 mole of 2,2-bis-(4-hydroxyphenyl)-propane in 150 cc. of potassium hydroxide (500 g. per liter) added. This was then treated and worked up as described above. The yield was 24 g., or 26% of the theoretical, assuming the formation of 0.5 mole of diamyl sulfate and the utilization of one of the alkyl groups of this sulfate in the alkylation. The product was further purified by recrystallization from methanol.

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Summary

This paper describes the preparation and properties of the di-*n*-alkyl ethers of 2,2-bis-(4-hydroxyphenyl)-propane from methyl to amyl.

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[CONTRIBUTION FROM THE NATIONAL INSTITUTE OF HEALTH, U. S. PUBLIC HEALTH SERVICE]

The Chemistry of the Tetrose Sugars. I. A Crystalline Triacetate of *d*-Threose from the Degradation of Strontium Xylonate with Hydrogen Peroxide. Nomenclature in the Tetrose Group[1]

BY ROBERT C. HOCKETT

Within recent years so many sugars previously prepared by synthetic methods in the laboratory have been found playing an important role in natural processes that new attention is focused upon the necessity of filling those gaps which still remain in the sugar family. Particularly does this necessity apply to the sugars of low carbon atom content which are those most likely to be encountered as intermediates in the physiological degradation of glucose. The tetroses are still among the least known members of the sugar group despite the fact that the first efforts toward their preparation were made nearly fifty years ago.[2] The general methods of degrading sugars devised by Wohl and Ruff seemed at first to furnish a very promising means of attacking the problem, and centered an interest upon the tetroses particularly from 1899 to 1901,[3] but the results proved disappointing in that all the classic methods of preparing sugars are beset by special difficulties when applied to this group, so that very few crystalline compounds were prepared and few data recorded. Except for the later application of Weerman's[4] method of degradation

(1) Publication authorized by the Surgeon General, U. S. Public Health Service. An abstract of this paper was presented before the Organic Division of the American Chemical Society in Chicago, September, 1933.

(2) Fischer and Tafel, *Ber.*, **20**, 1090 (1887).

(3) Wohl, *Ber.*, **26**, 743 (1893); *ibid.*, **32**, 3666 (1899); Ruff and Meusser, *ibid.*, **32**, 3672 (1899); Ruff, Meusser and Kohn, *ibid.*, **34**, 1362 (1901); Maquenne, *Compt. rend.*, **130**, 1402 (1900); Bertrand, *ibid.*, **130**, 1330 (1900); Fenton and Jackson, *J. Chem. Soc.*, **75**, 1 (1899); Morrell, *ibid.*, **81**, 674 (1902); Jackson, *ibid.*, **77**, 130 (1900).

(4) Weerman, *Rec. trav. chim.*, **37**, 16 (1918).