preparations. The alcohol filtrate was evaporated and the residue was freed of solid by triturating with alcohol or water, filtering and evaporating to dryness. This was repeated several times and the residual sirup treated with concentrated ammonium hydroxide. The solid obtained on evaporation was then recrystallized from an alcohol–ethyl acetate mixture and identified as the ammonium salt[12] of ethylsulfonic acid.

The sulfone (2 g.), 2-ethylsulfonyl-4-ethoxy-5-methylpyrimidine (II, $X = OC_2H_5$, $R = CH_3$), on refluxing for several hours with 2.5% sodium hydroxide in 90% alcohol gave 2,4-diethoxy-5-methylpyrimidine.[14] The diethoxypyrimidine (0.9 g.) was extracted with petroleum ether after removal of the alcohol under diminished pressure.

Summary

The action of chlorine gas on ethylmercaptopyrimidines has led to the preparation of nine ethylsulfones in the pyrimidine series.

It has been shown that this method is applicable to ethoxy-, chloro-, amino- and carbethoxyethylmercaptopyrimidines.

On acid hydrolysis the pyrimidine sulfones yield the corresponding oxypyrimidines.

NEW HAVEN, CONN. RECEIVED SEPTEMBER 5, 1935

---

[14] Johnson and Schmidt-Nickels, THIS JOURNAL, **52**, 4514 (1930).

[CONTRIBUTION NO. 161 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS & COMPANY, INC.]

Acetylene Polymers and their Derivatives. XXIII. The Preparation and Polymerization of Oxyprenes

BY HARRY B. DYKSTRA

Recent studies[1] have revealed that of the various derivatives of butadiene-1,3 which are known, those having a single substituent in the 2-position have outstanding properties from the standpoint of rubber synthesis. The term orthoprene has been suggested for compounds of this type.[2] Only a few orthoprenes are known. Prior to the discovery of the haloprenes, chloro-2-butadiene-1,3[3] and bromo-2-butadiene-1,3,[4] isoprene and ethylbutadiene were the only members of this class which had been described. To this list have recently been added the butyl, *t*-butyl, hexyl, phenyl and benzyl butadienes,[5] and the formoxy, acetoxy, chloroacetoxy and butyroxy butadienes.[6]

The interesting properties of the orthoprenes, particularly those containing a negative substituent, have prompted the preparation and examination of other members of this class. The present paper is concerned with orthoprenes in which the substituent is an ether group. The designation "oxyprene" is suggested for these compounds. They are obtained by the series of reactions illustrated below for ethoxyprene (V).

$$\underset{\text{I}}{CH_2{=}CHC{\equiv}CH} + H_2O \longrightarrow \underset{\text{II}}{CH_2{=}CHCOCH_3}$$

$$\text{II} + C_2H_5OH \longrightarrow \underset{\text{III}}{C_2H_5OCH_2CH_2COCH_3}$$

$$\text{III} + HC(OC_2H_5)_3 \longrightarrow \underset{\text{IV}}{C_2H_5OCH_2CH_2C(OC_2H_5)_2CH_3} + HCOOC_2H_5$$

$$\text{IV} \longrightarrow \underset{\text{V}}{CH_2{=}CHC(OC_2H_5){=}CH_2} + 2C_2H_5OH$$

The hydration of vinylacetylene to methyl vinyl ketone[7] and the addition of alcohols to methyl vinyl ketone[8] are recorded elsewhere and will not be described in detail. The conversion of the ether ketones (III) into the ether ketals (IV) by means of orthoformic esters takes place almost quantitatively at room temperature in the presence of alcohol and hydrogen chloride. Physical and analytical data for the ether ketals are given in Table IA.

At sufficiently high temperatures, generally above 130°, the decomposition of the ketal (IV) to the oxyprene (V) is fairly complete, but at lower temperatures intermediate compounds involving the elimination of only one molecule of alcohol are formed. These are the unsaturated ketals (VI) formed when acidic catalysts are used, and the unsaturated ethers (VII) formed with basic catalysts. By further heating, these compounds, particularly VI, are in turn converted to the oxyprenes. Physical and analytical data for the intermediates VI and VII are given in

---

[1] Whitby and Gallay, *Can. J. Research*, **6**, 280 (1932); Carothers, *Ind. Eng. Chem.*, **26**, 30 (1934).

[2] Carothers and Berchet, THIS JOURNAL, **55**, 2813 (1933).

[3] Carothers, Williams, Collins and Kirby, *ibid.*, **53**, 4203 (1931).

[4] Carothers, Collins and Kirby, *ibid.*, **55**, 786 (1933).

[5] Carothers and Berchet, *ibid.*, **55**, 2813 (1933); Backer and Strating, *Rec. trav. chim.*, **53**, 524 (1934).

[6] Werntz, THIS JOURNAL, **57**, 204 (1935).

[7] Nieuwland, Calcott, Downing and Carter, *ibid.*, **53**, 4197 (1931); Carter, U. S. Patent 1,896,161 (1933); Conaway, U. S. Patent 1,967,225 (1934).

[8] Rothrock, U. S. Patent 2,010,828 (1935).

Table IB and IC. Similar data for the oxyprenes are recorded in Table ID.

Below the dissociation temperatures any of the compounds V, VI and VII will reunite with alcohols yielding the ketals (IV). The reaction therefore is reversible as illustrated in the equations

$$\underset{\mathrm{V}}{\mathrm{CH_2{=}CHC(OR){=}CH_2}} \xrightleftharpoons[-\mathrm{ROH}]{+\mathrm{ROH}}$$

$$\left\{\begin{matrix} \underset{\mathrm{VI}}{\mathrm{CH_2{=}CHC(OR)_2CH_3}} \\ \underset{\mathrm{VII}}{\mathrm{ROCH_2CH{=}C(OR)CH_3}} \end{matrix}\right\} \xrightleftharpoons[-\mathrm{ROH}]{+\mathrm{ROH}} \underset{\mathrm{IV}}{\mathrm{ROCH_2CH_2C(OR)_2CH_3}}$$

The unsaturated compounds also unite with phenols and mercaptans.

The ease with which compounds, such as V, VI and VII, add alcohols or phenols makes it possible to prepare mixed ethers and ketals of types IV, VI and VII. This also provides a method for converting one oxyprene into another as illustrated in the following scheme.

$$\mathrm{CH_2{=}CHC(OC_2H_5){=}CH_2} \xrightarrow{\mathrm{C_4H_9OH}}$$

$$\mathrm{CH_2{=}CHC(OC_2H_5)(OC_4H_9)CH_3} \xrightarrow{-\mathrm{C_2H_5OH}} \mathrm{CH_2{=}CHC(OC_4H_9){=}CH_2}$$

The oxyprenes which have been prepared are clear, mobile liquids having ethereal odors. The structures assigned to these products are based on the following reactions observed for the ethoxy derivative. On treatment with dilute mineral acids the ethoxy derivative is converted into methyl vinyl ketone which has been identified by its odor and its reaction product with phenylhydrazine, namely, methyl-3-phenyl-1-pyrazoline.[9] The structure of the ethoxy derivative has been further confirmed by its reaction with naphthoquinone (Diels–Alder diene reaction) to yield, after oxidation, ethoxy-2-anthraquinone.[10] In carbon tetrachloride solution the ethoxy derivative absorbs four atoms of bromine, the end-point being fairly sharp. On hydrogenation at room temperature with a platinum black catalyst it absorbs but two atoms of hydrogen, forming what appears to be ethoxy-2-butene-2. Its behavior toward alcohols and phenols has already been indicated.

Under ordinary conditions the oxyprenes show much less tendency to polymerize than chloroprene. Samples can be stored in the laboratory for several months without the formation of more than a few per cent. of polymer. Polymerization is greatly accelerated by light, heat and various catalysts, such as peroxides, sodium, metallic halides, iodine and certain acids, including acetic and hydrocyanic. The polymers may be liquids, resins or rubber-like products, depending upon experimental conditions. Use of low temperatures and the absence of diluents and catalysts favor the formation of rubber-like polymers. Thus, a 20% yield of rubber-like polymer comparatively free from liquid and resinous polymers is obtained by exposing ethoxyprene to ultraviolet light at room temperature for one week. Elevated temperatures promote the formation of liquid polymers. At 100° a 15% yield of polymer is obtained in six days, the product consisting of about 25% of liquid polymer (largely dimer) and 75% of rubber-like resin. At 130° substantially complete polymerization occurs in two weeks, the amounts of liquid and rubber-like polymer being approximately equal. A comparison of these data with those reported for isoprene[11] and for chloroprene[1] would indicate that ethoxyprene polymerizes about one-third as fast as isoprene and $^1/_{2000}$ as fast as chloroprene. Certain catalysts, notably iodine and hydrogen cyanide, bring about rapid polymerization of ethoxyprene to liquid polymers of low molecular weight. On the other hand, metal halides and acetic acid cause polymerization to resinous polymers. The polymerization of oxyprenes, like that of vinyl ethers,[12] takes place almost explosively in the presence of metal halides, such as stannic chloride.

The rubber-like polymer derived from ethoxyprene (and other oxyprenes) is plastic and readily soluble in ethyl acetate and in benzene. It is elastic and resilient but lacks the snap and high tensile strength of natural rubber or polymerized chloroprene. On heating with dilute hydrochloric acid the polymer is hydrolyzed to a polymeric ketone, identical in composition with methyl vinyl ketone.

As already indicated two types of intermediates, VI and VII, are formed in the preparation of the oxyprenes. Compounds VI are assigned the unsaturated ketal formula, $\mathrm{CH_2{=}CHC(OR)_2CH_3}$, on the basis of the following reactions of the diethoxy derivative. On treatment with dilute acids, the diethoxy derivative is readily hydrolyzed to methyl vinyl ketone.

---

(9) Maire, *Bull. soc. chim.*, (4) **3**, 272 (1908).

(10) Liebermann and Hagen, *Ber.*, **15**, 1798 (1882).

(11) Whitby and Crozier, *Can. J. Research*, **6**, 203 (1932).

(12) Chalmers, *ibid.*, **7**, 472 (1932).

TABLE I

R	B. p., °C./mm.	d^{20}_4	n^{20}_D	MR		Analyses, %			
						Calcd.		Found	
				Calcd.	Found	C	H	C	H
A. PHYSICAL AND ANALYTICAL DATA FOR ETHER-KETALS, $ROCH_2CH_2C(OR)_2CH_3$									
CH_3	61–63/20	0.9398	1.4112	39.45	39.15	56.71	10.84	56.82	10.72
C_2H_5	75/9	.8940	1.4148	53.31	53.25	63.10	11.66	64.14	11.83
C_4H_9	120/3	.8745	1.4310	81.02	81.19	70.36	12.50	69.42	12.04
B. PHYSICAL AND ANALYTICAL DATA FOR UNSATURATED KETALS, $CH_2{=}CHC(OR)_2CH_3$									
CH_3	98–100/760	0.8756	1.4038	32.73	32.41	62.01	10.42	62.51	10.47
C_2H_5	69/100	.8470	1.4062	41.96	41.82	66.61	11.19	66.82	11.04
C_4H_9	79–80/8	.8497	1.4238	60.44	60.09	71.93	12.09	70.69	12.10
C_2H_5	81/2	1.0345	1.5128	56.83	55.79	74.96	8.38	75.31	8.37
C. PHYSICAL AND ANALYTICAL DATA FOR UNSATURATED ETHERS, $ROCH_2CH{=}C(OR)CH_3$									
C_2H_5	101/100	0.8711	1.4242	41.96	42.24	66.61	11.19	66.01	10.98
C_4H_9	91–93/4	.8633	1.4342	60.44	60.42	71.93	12.09	71.09	11.92
D. PHYSICAL AND ANALYTICAL DATA FOR OXYPRENES, $CH_2{=}CHC(OR){=}CH_2$									
CH_3	75/760	0.8281	1.4442	26.00	26.98	71.37	9.58	70.73	9.31
C_2H_5	96.5/760	.8153	1.4401	30.62	31.71	73.41	10.28	73.81	10.55
C_4H_9	65/54	.8223	1.4445	39.85	40.78	76.12	11.19	76.13	11.02

Unlike vinyl ethers, it is not polymerized appreciably by iodine. It reacts with hydrogen in the presence of platinum black to form the diethyl ketal of ethyl methyl ketone.

The structure of compounds VII has not been established with absolute certainty. Structure $ROCH_2CH{=}C(OR)CH_3$ appears most probable on the basis of the following data. The diethoxy derivative yields beta-ethoxyethyl methyl ketone (III) on hydrolysis with dilute acid. It is readily polymerized by iodine. On oxidation with potassium permanganate it yields ethyl acetate and acetic acid.

Experimental Part

Triethoxy-1,3,3-butane.—A mixture of 232 g. of beta-ethoxyethyl methyl ketone, 315 g. of ethyl orthoformate, 282 g. of absolute alcohol and 0.136 g. of hydrogen chloride was placed in a stoppered flask. After four days the mixture was made alkaline with ammonium hydroxide, dried over magnesium sulfate and distilled. The yield of the triethoxy compound, boiling at 72–75° at 9 mm., was 351 g. or 92% of the theoretical. This compound can also be prepared directly from methyl vinyl ketone and ethyl orthoformate.

The corresponding trimethoxy and tributoxy compounds were prepared in a similar manner.

Ethoxy-2-butadiene-1,3.—During the course of about four hours triethoxy-1,3,3-butane was dropped slowly into a heated distilling flask containing 0.01 g. of potassium bisulfate. The triethoxy compound was added at such a rate that approximately 20 g. was present in the flask at all times. The temperature of the flask was maintained at 120–140° to cause steady distillation of the decomposition products, *i. e.*, ethyl alcohol and ethoxy-2-butadiene-1,3. Some of the intermediate, diethoxy-3,3-butene-1, also distilled off. The decomposition products were collected in dilute potassium carbonate solution and were worked up by further washing with potassium carbonate solution followed by drying and distilling. From 126 g. of the triethoxy compound there was obtained in this manner 39 g. of ethoxybutadiene (59% conversion) and 12 g. of diethoxybutene (13% conversion). The latter can be returned to the process to yield more ethoxybutadiene.

Methoxybutadiene and butoxybutadiene were similarly prepared. Other catalysts which have been used in the preparation of the oxyprenes are magnesium sulfate, *p*-toluenesulfonic acid and *d*-camphorsulfonic acid. When aluminum oxide is used as catalyst, the chief product is dialkoxy-1,3-butene-2.

Butoxy-2-butadiene-1,3.—A mixture of 15 g. of ethoxy-2-butadiene-1,3 and 11 g. of butyl alcohol was heated in a distilling flask until the temperature of the distilling vapors reached 95° and then distillation was continued under reduced pressure. The distillate consisted of 2 g. of ethyl alcohol, 6 g. of butyl alcohol and 6 g. of dibutoxy-3,3-butene-1. The residue in the flask was a viscous brown oil. On heating the dibutoxybutene with potassium bisulfate it decomposed into butyl alcohol and butoxy-2-butadiene-1,3.

Ethoxybutadiene plus Alcohols.—Seven grams of ethyl alcohol and 3.5 g. of ethoxy-2-butadiene-1,3 were heated together in a sealed glass tube at 100° for twenty-four hours and then distilled under 10 mm. pressure. The products consisted chiefly of ethyl alcohol (4.5 g.), triethoxy-1,3,3-butane (4 g.) and polymerized ethoxybutadiene (1 g.). When the reaction was carried out at 130°, only a small amount of the triethoxy compound was obtained, the chief product being diethoxy-3,3-butene-1. The latter compound adds alcohol at 100° to form the triethoxy compound.

A mixture of 14.7 g. of ethoxy-2-butadiene-1,3 and 12.4 g. of ethylene glycol was heated in a sealed tube for twenty-four hours at 110°. Distillation of the homogeneous reaction mixture thus obtained gave 9 g. of ethyl alcohol, 12 g. of a compound boiling at 56° at 100 mm. and 5 g. of resinous product. The compound boiling at 56° at 100 mm. gave methyl vinyl ketone on hydrolysis with dilute acid, indicating that it was either $CH_2{=}CHC(OCH_2CH_2OH){=}CH_2$ (VIII) or $CH_2{=}CH{-}\overline{C(CH_3)OCH_2CH_2{-}O}$, (IX). The product showed no tendency to polymerize. These data, together with the following, favor structure IX: $d^{20}{}_4$ 0.9547; $n^{20}{}_D$ 1.4213; MR calcd. for VIII, 33.24; MR calcd. for IX, 31.63; MR found, 30.32.

Anal. Calcd. for $C_6H_{10}O_2$: C, 63.11; H, 8.83. Found: C, 63.39; H. 8.58.

Phenol and thiophenol add readily to ethoxy-2-butadiene-1,3 at ordinary temperatures.

Reaction of Ethoxybutadiene with Naphthoquinone.—A mixture of 12 g. of ethoxy-2-butadiene-1,3, 10 g. of 1,4-naphthoquinone and 15 g. of benzene was refluxed for six hours and then allowed to stand overnight. The yellow crystalline mass which separated was dried in air. This caused the mass to become gray. The product was next suspended in a water-alcohol mixture containing sodium hydroxide, and air was passed through the dark colored mixture until it took on a yellowish-orange appearance. The solid was separated and recrystallized twice from acetic acid. The product, ethoxy-2-anthraquinone, melted at 136° as compared with 135° reported by Liebermann and Hagen.[10]

Anal. Calcd. for $C_{16}H_{12}O_3$: C, 76.16; H, 4.80. Found: C, 76.01; H, 4.68.

The identity of the ethoxy-2-anthraquinone was further established by heating it with concentrated sulfuric acid as described by Liebermann and Hagen. The product, hydroxy-2-anthraquinone, melted at 302° as reported by these authors and gave a red coloration with alkali.

Hydrolysis of Ethoxybutadiene.—A small amount of ethoxy-2-butadiene-1,3 was added to dilute hydrochloric acid. Solution took place readily and the sharp odor of methyl vinyl ketone developed. On reaction of this mixture with phenylhydrazine, methyl-3-phenyl-1-pyrazoline was obtained, melting at 75–76° as compared with a value of 76–77° reported by Maire.[9]

Hydrogenation of Ethoxybutadiene.—A solution of 14.4 g. (0.147 mole) of ethoxy-2-butadiene-1,3 in 30 cc. of absolute alcohol was hydrogenated in a Burgess–Parr apparatus using 0.2 g. of platinum oxide as the catalyst. Reaction ceased within one and one-half hours after 0.17 mole of hydrogen had been absorbed. Addition of fresh catalyst failed to bring about further absorption. The hydrogenated product boiled almost completely from 88 to 93° and had a refractive index of $n^{20}{}_D$ 1.4006. These properties suggest that the product is ethoxy-2-butene-2, ethoxy-2-butene-1 or a mixture of these compounds.[13] In a similar experiment using acetone as solvent, 0.117 mole of ethoxybutadiene absorbed 0.129 mole of hydrogen.

Polymerization of Ethoxybutadiene.—Forty grams of ethoxy-2-butadiene-1,3 was heated in a sealed glass tube at 130° for thirteen days. The product consisted of 20 g. of liquid polymer (mainly dimer, b. p. 105–125° at 5 mm.) and 17 g. of solid polymer. The latter was a light-colored, soft, rubber-like resin soluble in acetone, ethyl acetate and benzene, but insoluble in water and in alcohol.

A few drops of a 25% solution of stannic chloride in benzene was added to 5 g. of ethoxybutadiene. A vigorous reaction occurred which converted the ethoxybutadiene into a dark viscous mass within a few minutes. Acetic acid also converted ethoxybutadiene into resinous products, but the reaction was less violent and gave a lighter-colored product. When iodine was used as catalyst, 65% of the polymer consisted of liquid dimer and trimer and the remainder of soft resin.

Polymerization of Butoxybutadiene.—Exposure of butoxy-2-butadiene-1,3 in a quartz tube to ultraviolet light from a mercury arc for one week resulted in a 13% yield of polymer. The polymer was a white, opaque, fibrous solid which was somewhat sticky and elastic. It was insoluble in alcohol, acetone and ethyl acetate; in chloroform and benzene it lost its opacity but did not dissolve.

Diethoxy-3,3-butene-1.—This product, obtained in yields of 10–30% when triethoxy-1,3,3-butane was heated in the presence of acidic catalysts, was readily hydrolyzed by shaking with dilute hydrochloric acid. The product of the hydrolysis, methyl vinyl ketone, was characterized by its odor and reaction product with phenylhydrazine.

An ethanol solution of the diethoxy compound was treated with hydrogen in the presence of platinum oxide in a Burgess–Parr apparatus. Approximately 0.7 equivalent of hydrogen was absorbed. Distillation of the hydrogenated products showed that side reactions had occurred; only a 40% yield of the expected $CH_3CH_2C(OC_2H_5)_2CH_3$ was obtained. Properties observed for this product are: b. p. 68–69° at 100 mm.; $d^{20}{}_4$ 0.8423; $n^{20}{}_D$ 1.4012; MR calcd., 42.43; MR found, 42.18. A boiling point of 68° at 100 mm. is reported for this compound.[14]

Diethoxy-1,3-butene-2.—A mixture of 57 g. of $C_2H_5OCH_2CH_2C(OC_2H_5)_2CH_3$ and 0.1 g. of aluminum oxide was heated in a distilling flask. Decomposition started at about 110° and proceeded smoothly at 110–165° with the removal of alcohol. On distilling the residue in the flask under diminished pressure, 41 g. (95% yield) of product believed to be diethoxy-1,3-butene-2 was obtained.

Ten grams of this diethoxy compound was treated with 20 cc. of 1% hydrochloric acid and shaken for a few minutes. The product (6 g.) of the hydrolysis, separated by extraction with ether, proved to be beta-ethoxyethyl methyl ketone, identical with that obtained by addition of ethyl alcohol to methyl vinyl ketone. Some of its properties are: b. p. 57° at 24 mm.; $d^{20}{}_4$ 0.9024; $n^{20}{}_D$ 1.4089.

A mixture of 58 g. of the diethoxy compound and 600 g. of water was treated with potassium permanganate (350 g.) until no further reaction occurred. From the oxidation products, there was separated in the usual way 40 g. of an acetic acid–ethyl acetate mixture. The acetic acid was identified by its *p*-toluidide (m. p. 145–147°) and the ethyl acetate by its physical properties (odor, b. p. 78°; $n^{20}{}_D$ 1.3780).

The author wishes to express his thanks to Dr. Wallace H. Carothers for his interest in this work and for his helpful suggestions.

Summary

The methyl, ethyl and butyl ethers of hydroxy-2-butadiene-1,3 have been prepared and characterized. The designation oxyprene is suggested for products of this structure. The oxyprenes

---

[13] Lauer and Spielman, This Journal, 53, 1533 (1933).

[14] Reitter and Hess, *Ber.*, 40, 3020 (1907).

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.