otherwise the yields were uniformly in the range 8 to 15%.

TABLE IV

FRACTIONATION OF AN ETHER-SOLUBLE MAPLE ETHANOL LIGNIN

Extraction number	Yield, %	$\eta_{sp}/c \times 10^5$	Methoxyl, %
1	6.5	545	..
2	15.0	540	..
3	14.5	540	25.2
4	9.8	540	24.8
5	8.0	550	..
6	5.6	545	..
7	12.1	540	23.1
8	13.0	545	..
Residue	15.5	550	26.3

Summary

1. A new method is described for the fractionation of lignins, which involves the distribution of the lignin between two immiscible layers of solvent in the system methanol–water–chloroform–carbon tetrachloride. By varying the concentration of chloroform, the percentage of lignin extracted into the non-aqueous layer may be controlled over a wide range of values.

2. This new method should, it is suggested, be applicable to a wide variety of high polymeric substances.

MONTREAL, CANADA

RECEIVED MAY 2, 1941

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Many-Membered Ring Compounds by Direct Synthesis from Two ω,ω'-Bifunctional Molecules

BY ROGER ADAMS AND L. N. WHITEHILL[1]

Only two methods have been employed successfully in the synthesis of many-membered ring compounds. The first consists of a ring closure within an ω,ω'-bifunctional molecule making use of the high dilution principle.[2] Here two active groups at the ends of long chains are allowed to react in a solution so dilute that the rate of linear polymerization is slowed down sufficiently to permit formation of monomeric large rings. The other and less general method[3] is a depolymerization process and involves a series of mutually dependent and quantitative reversible reactions where constant removal of the more volatile cyclic compound leads ultimately to complete conversion to this product.

By the high dilution technique, many-membered cyclic lactones from ω-hydroxy acids,[4] iminonitriles from ω,ω'-dinitriles,[5] and phenolic ethers from ω-bromoalkoxyphenols[6] have been synthesized.

The depolymerization process[3] has been used in the preparation of macrocyclic esters and anhydrides. The method used by Ruzicka[7] to prepare large ring ketones, the heating of the calcium, thorium, cerium and yttrium salts of ω,ω'-aliphatic dibasic acids, possibly follows this same course.[8]

The adaptability of the dilution process for synthesizing many-membered rings is limited by the difficulty of obtaining molecules of appropriate size with ω,ω'-functional groups capable of interaction. Theoretically, it should be possible to form macrocyclic rings by allowing two bifunctional molecules to react with each other at high dilution provided the proper physical conditions are established. To illustrate in a general way a synthesis of this nature, the reaction between an ω,ω'-glycol and ω,ω'-dibasic acid may be considered. The first reaction that must take place regardless of the dilution is between one molecule of glycol and one molecule of dibasic acid. The ω-hydroxy-ω'-carboxy dimer (I) will then react either with a molecule of glycol or of dibasic acid to form a trimer (II) or (III) which, in turn, may react further to give the tetramer (IV). The tetramer may also be produced from two mole-

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(1) An abstract of a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry.

(2) Ruggli, *Ann.*, **392**, 92 (1912).

(3) Carothers and Hill, THIS JOURNAL, **55**, 5023, 5031 (1933).

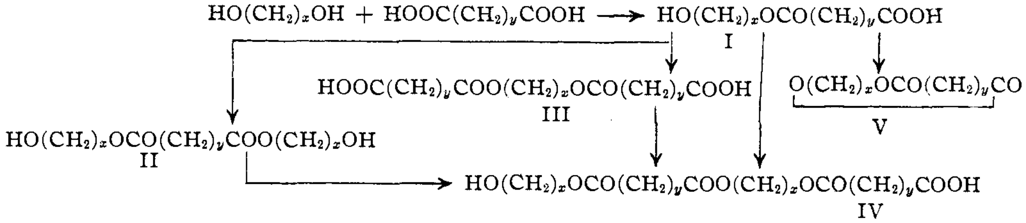
(4) Stoll and Rouve, *Helv. Chim. Acta*, **17**, 1283 (1934); Stoll, Rouve, and Stoll-Comte, *ibid.*, **17**, 1289 (1934).

(5) Ziegler and Aurnhammer, *Ann.*, **513**, 43 (1934); **528**, 114 (1937).

(6) Lüttringhaus and Ziegler, *ibid.*, **528**, 155 (1937); Ziegler, Lüttringhaus and Wohlzemuth, *ibid.*, **528**, 162 (1937); Lüttringhaus, *ibid.*, **528**, 181, 211, 223 (1937); *Ber.*, **72**, 887 (1939); Lüttringhaus and Kohlhaas, *ibid.*, **72**, 897, 907 (1939); Lüttringhaus and Bucholz, *ibid.*, **72**, 2057 (1939); Lüttringhaus and Gralheer, *Naturwissenschaften*, **28**, 255 (1940).

(7) Ruzicka, Brugger, Pfeiffer, Schintz and Stoll, *Helv. Chim. Acta*, **9**, 499 (1926); Ruzicka, Brugger, Seidel and Schinz, *ibid.*, **11**, 496 (1928); Ruzicka, Stoll and Schinz, *ibid.*, **11**, 670 (1928); Ruzicka, Schinz and Pfeiffer, *ibid.*, **11**, 686 (1928).

(8) Carothers and Hill, THIS JOURNAL, **55**, 5043 (1933).



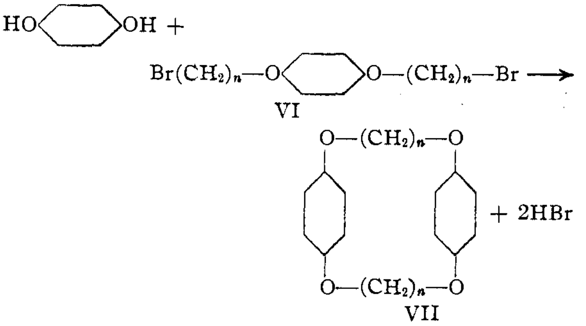
cules of dimer (I). The formation of linear polymers will proceed by proper condensations of the original reactants with II, III or IV or by interaction of molecules II, III or IV. On the other hand, the dimer may react intramolecularly to give a many-membered ring (V). The problem is whether, at the appropriate high dilution and under other fixed physical conditions, it is possible to diminish the rates of the several possible linear reactions below that of the cyclization reaction so that a satisfactory yield of the cyclic compound will result. The formation of rings from the tetramer or larger linear molecules would be of secondary importance.

Such an experiment involving a reaction between two molecules at high dilution would undoubtedly require a different concentration and time for complete reaction than one involving merely a ring closure. In the former case, time must be given not only for the molecules to come in contact with each other while possessing sufficient activation energy for reaction to occur, but also for the terminal groups of the intermediate (I) to react with each other intramolecularly before another molecule capable of reaction is encountered in the solution.

The value of such a direct procedure for preparing many-membered rings, if successful, would obviously be of practical importance since the pure dimers in the above described reactions of long-chained ω,ω'-bifunctional molecules of the type necessary for intramolecular ring closure are relatively difficult to make and purify.

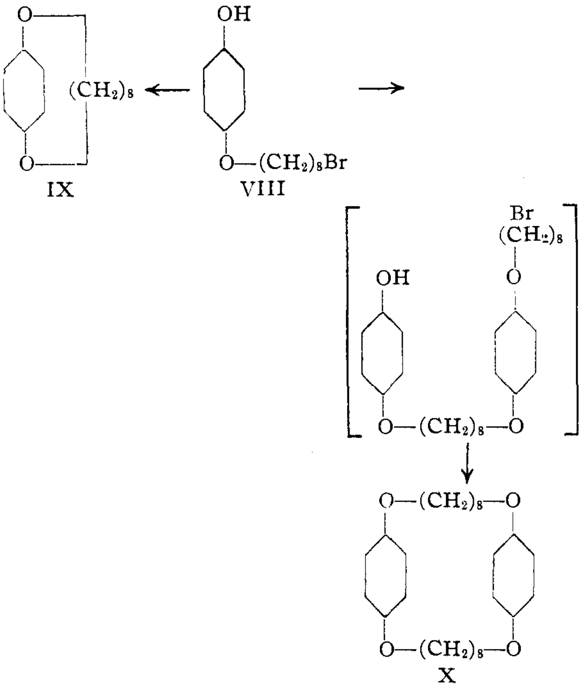
Ruggli's[2] initial synthesis in application of the high dilution technique involved a reaction between two bifunctional molecules but was one of a very special type. He allowed succinyl chloride to condense with *o,o'*-diaminotolane. This latter product, owing to its structure, probably retains constantly a strictly linear configuration with the consequence that the two amino groups are held in fixed positions relative to each other and are not far from each other. This situation is markedly different from that in a saturated aliphatic molecule where mobility results in a constant change in configuration with the ends of the molecule always at variable distances from each other.

For initiation of this research, the condensation of hydroquinone and a *bis*-(ω-bromoalkyl) ether of hydroquinone (VI) was studied in an attempt to prepare directly a many-membered ring (VII).

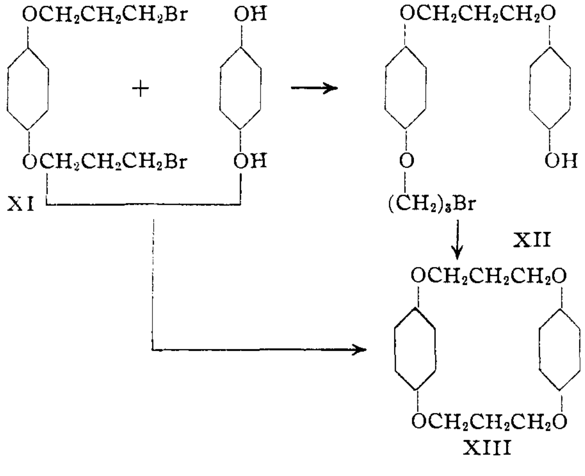


Such a reaction was selected for several reasons. Ziegler and Lüttringhaus have demonstrated that cyclic compounds of the phenol ether type are readily prepared by the usual cyclization procedure. It is a slow reaction. The reactants may be added together and will not interact until they are refluxed in the presence of potassium carbonate. The products are well-crystallized solids readily purified. The reacting substances may be selected so that there is small likelihood of stereochemical difficulties interfering with the formation of the product. Moreover, Lüttringhaus, who cyclized the mono-ω-bromoöctyl ether of hydroquinone (VIII) to the octamethylene ether of hydroquinone (IX), observed as a by-product the cyclic dimer 1,1',4,4'-*bis*-(octamethylenedioxy)-dibenzene (X). The presence of such a by-product can best be accounted for by the interaction of two molecules of compound VIII followed by cyclization.

Synthesis of 1,1',4,4'-*bis*-(trimethylenedioxy)-dibenzene (XIII) was first accomplished by the standard procedure. It was thus possible to learn the physical properties of the product and at the same time to study in this dilution step the most desirable concentrations.



The *bis*-(γ-bromopropyl) ether of hydroquinone (XI) first was allowed to react with hydroquinone in a ratio of two moles of ether (XI) to one of hydroquinone. With this ratio the starting material XI was present in greater amounts than the desired product XII at all times during the course of the reaction. This favored the formation of XII and minimized the amount of by-product formed by further condensation of XII with hydroquinone. Even then XII was isolated in low yield (24%) as is generally the case in reactions in which bifunctional molecules react with each other. Linear polymerization is prone to occur regardless of various precautions and, as here, the desired product is not often easily separated.



The cyclization of XII to the 1,1',4,4'-*bis*-(trimethylenedioxy)-dibenzene (XIII) was carried out in the dilution equipment previously described by Adams and Kornblum[9] and resulted in a 59% yield. The product is a well-crystallized solid, m. p. 195–195.5°. It was proved to be a many-membered ring compound and not an open chain isomer by determination of its molecular weight, its failure to reduce permanganate and by the absence of halogen or active hydrogen.

The direct formation of the cyclic compound XIII was then attempted by allowing equivalent molar quantities of hydroquinone and the *bis*-(γ-bromopropyl) ether of hydroquinone to react in high dilution under variable conditions not materially different from those in the cyclization of compound XII to compound XIII. The results are recorded in Table I.

The maximum yield of product was 18%, obtained when the reactants in concentration of about 1.6×10^{-5} mole per liter of isoamyl alcohol were introduced at the rate of 0.8 cc. per minute into the reaction flask containing 2 liters of isoamyl alcohol and anhydrous potassium carbonate. This yield is about 3% better than the over-all yield obtained when the cyclic ether was obtained in the two-step process through the monoether (XII). This reaction is thus an entirely feasible one for synthesis of compound XIII and eliminates the less satisfactory reaction in the two-step procedure.

There are several difficulties which exclude in this reaction a quantitative study of the best conditions for production of the cyclic ether. The hydroquinone becomes dark in alkaline solution and unless nitrogen is passed through the circulatory system, decomposition occurs. At the temperature of the bath (about 200°), the *bis*-(γ-bromopropyl) ether of hydroquinone has some tendency to lose hydrogen bromide and the resulting unsaturated compound formed in the decomposition makes the isolation of the desired product troublesome. High dilution causes both of these factors to be more pronounced since the time necessary for reaction increases with increase in dilution. In fact as shown in the first set of data in the table, no cyclic product was obtained when the reaction was carried out in very dilute solution over a long period of time. No starting material was recovered and ionizable halogen was present in the salt. It seems prob-

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(9) Adams and Kornblum, THIS JOURNAL, **63**, 188 (1941).

TABLE I

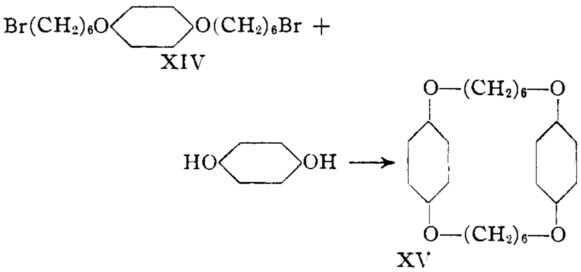
Solvent in reacn. flask in cc.	Moles of reactants used	Period of introduction (hr.)	Yield g.	Yield %	Moles of reactants entering per minute	Concn. of reactants as they enter, moles/l.	Initial concn. in reaction flask
1,1′,4,4′-*bis*-(Trimethylenedioxy)-dibenzene							
2750	0.0025	73	0	0	5.7×10^{-7}	5.7×10^{-6}	2.1×10^{-9}
2000	.005	54	0.278	18.6	1.6×10^{-6}	1.6×10^{-5}	8×10^{-9}
2000	.005	35	.223	14.9	2.4×10^{-6}	2.4×10^{-5}	1.2×10^{-8}
1500	.005	44	.226	15.1	1.9×10^{-6}	1.9×10^{-5}	1.3×10^{-8}
2000	.01	48	.368	12.3	3.5×10^{-6}	3.5×10^{-5}	1.8×10^{-8}
2000	.01	41	.247	8.3	4.1×10^{-6}	4.1×10^{-5}	2.2×10^{-8}
1500	.01	28	.108	3.6	6.0×10^{-6}	6.0×10^{-5}	4.0×10^{-8}
1,1′,4,4′-*bis*-(Hexamethylenedioxy)-dibenzene							
1400	.005	40	.287	15.0	2.1×10^{-6}	2.1×10^{-5}	1.5×10^{-8}
1,1′,4,4′-*bis*-(Ethylenedioxy)-dibenzene							
1200	.005	38	0	0	2.2×10^{-6}	2.2×10^{-5}	1.8×10^{-8}

able that at this concentration the reaction becomes so slow that decomposition of the dibromide occurs before condensation takes place. In general, however, up to a certain maximum a definite increase in yield appears to accompany increase in dilution.

Unfortunately, the linear polymeric material was dark and amorphous, nondistillable in a molecular still so that a quantitative determination was impossible.

Another necessity to an accurate study of such reactions is a test which will indicate whether the reactants are converted immediately to the cyclic product or whether a higher concentration of reactants than at the beginning is gradually built up in the reaction flask.

In a similar manner, hydroquinone and the *bis*-(ω-bromo-*n*-hexyl) ether of hydroquinone (XIV) were condensed to 1,1′,4,4′-*bis*-(hexamethylenedioxy)-dibenzene (XV) in 15% yield. The same conditions were observed as in the reaction with the corresponding trimethylene ether and the results were about identical (see table).



XIV

XV

An attempt to condense the *bis*-(β-bromoethyl) ether of hydroquinone and hydroquinone failed. This may have been due to the lack of flexibility in the molecule as deduced from the study of Stuart models or more likely it was due to the anomalous activity encountered in β-halogenethyl ethers of phenols. Difficulties were also experienced in the condensation of the *bis*-(ω-bromo-*n*-octyl) and *bis*-(ω-bromo-*n*-decyl) ethers of hydroquinone with hydroquinone. In these cases, the *bis*-alkyl ethers were so insoluble in cold amyl alcohol that even very dilute solutions had to be kept warm in order that the solute would not crystallize from solution. As a consequence, the apparatus and the procedure used in the other experiments were not satisfactory. Even though the entering solution was kept warm, the *bis*-ether crystallized in the inlet tubes which could not be heated conveniently. Normal results were thus not obtained. There is little doubt that with an appropriate change in the process these ethers would condense satisfactorily.

Experimental

Hydroquinone-*bis*-(γ-bromopropyl) Ether (XI).—A mixture of 110 g. (1 mole) of hydroquinone, 808 g. (4 moles) of trimethylene dibromide, 500 cc. of acetone, 125 cc. of water and 500 g. of potassium carbonate was refluxed with stirring on a steam-bath for five hours, after which an additional 175 g. of potassium carbonate was added and stirring and refluxing continued for three hours longer. The acetone was then distilled off with stirring to prevent bumping.

The reaction mixture was then washed three times with 500 cc. of water and subjected to steam distillation. Thus, 402 g. of unchanged trimethylene dibromide was recovered. When no turbidity could be detected in the distillate, the distillation was stopped, and the contents of the distilling flask was allowed to cool. A tan, flocculent solid separated out. It was recrystallized from 600 cc. of absolute ethanol. Considerable insoluble polymeric material was present, which was discarded.

The product was then distilled under diminished pressure in a 100-cc. modified Claisen flask, since distillation in larger amounts resulted in some decomposition; white crystals, b. p. 174–177° (4 mm.); m. p. 78–79° (cor.); yield, 101.7 g. (28.9%).

Anal. Calcd. for $C_{12}H_{16}O_2Br_2$: C, 40.90; H, 4.59. Found: C, 41.07; H, 4.77.

The product is very soluble in chloroform, somewhat soluble in hot methanol or ethanol but only slightly soluble in these solvents when cold.

α-*p*-Hydroxyphenoxy-γ-(*p*-γ-bromopropoxy-phenoxy)-propane.—A solution of 0.19 g. (0.003 mole) of potassium hydroxide in 20 cc. of absolute ethanol was added over a period of four hours to a boiling well-stirred solution of 7.14 g. (0.02 mole) of hydroquinone-*bis*-(γ-bromopropyl) ether and 1.1 g. (0.01 mole) of hydroquinone in 60 cc. of absolute ethanol. Stirring and refluxing were continued for two hours longer, at which time the mixture was neutral to litmus. The ethanol was then distilled from the reaction mixture with stirring. About 50 cc. of water was added to the contents of the flask, and the solid separating out was filtered off, ground in a mortar, and washed with 300 cc. of water at 40° to remove all unchanged hydroquinone. The solid residue was filtered off, dried overnight and then ground in a mortar, and treated with 200 cc. of Claisen's potash. The solution was filtered, and the filtrate rendered acid to litmus with 10% hydrochloric acid. The phenol thus precipitated was filtered off by suction, dried, and recrystallized from petroleum ether (b. p. 60–110°); white plates, m. p. 100–101° (cor.); yield, 2.14 g. (23.7%).

Anal. Calcd. for $C_{18}H_{21}O_4Br$: C, 56.70; H, 5.51. Found: C, 56.39; H, 5.65.

The product is soluble in methanol and acetic acid. It is insoluble in saturated aqueous potassium hydroxide and in 10% sodium hydroxide, but dissolves quite readily in Claisen's potash.

1,1',4,4'-*bis*-(Trimethylenedioxy)-dibenzene by Intramolecular Ring Closure.—The cyclization was performed in the apparatus previously described by Adams and Kornblum.[9] Into a 2-liter three-necked reaction flask were placed 550 cc. of dry isoamyl alcohol and 3 g. of finely powdered, anhydrous potassium carbonate which had been heated in an open dish over a free flame for thirty minutes. A solution of 2.79 g. (0.008 mole) of α-*p*-hydroxyphenoxy-γ-(*p*-γ-bromopropoxy-phenoxy)-propane in 850 cc. of dry isoamyl alcohol was added to the boiling alcohol–potassium carbonate mixture over a period of eighteen (not consecutive) hours. After stirring and heating an additional hour, the mixture was allowed to cool, filtered, and the solution concentrated to about 400 cc. It was then placed in the icebox and allowed to stand overnight. Crystals (1.2 g.) were deposited. On further evaporation of the filtrate to 50 cc., 0.3 g. more of impure crystals was obtained. The combined material was recrystallized twice from petroleum ether (b. p. 60–110°); white crystals, m. p. 195–195.5° (cor.); yield, 1.31 g. (59.2%).

Anal. Calcd. for $C_{18}H_{20}O_4$: C, 71.95; H, 6.72; mol. wt., 300. Found: C, 71.96; H, 7.02; mol. wt. (b.$CHCl_3$), 278.

The compound is soluble in chloroform and in hot petroleum ether (b. p. 60–110°) and in hot methanol and ethanol. It is only slightly soluble in cold methanol and cold petroleum ether. It is insoluble in Claisen's potash and in 10% aqueous sodium hydroxide.

It does not decolorize a 2% solution of potassium permanganate, and a Zerewitinoff determination shows no active hydrogen atoms.

1,1',4,4'-*bis*-(Trimethylenedioxy)-dibenzene by Intermolecular Ring Closure.—This reaction was carried out a number of times using different dilutions and different rates of introduction of the starting materials into the reaction flask. The length of time required, dilution, amounts of reactants used, and other significant data are recorded in the table. The general procedure used in all cases was the same. A solution of equimolecular amounts of hydroquinone-*bis*-(γ-bromopropyl) ether and hydroquinone in 850 cc. of dry isoamyl alcohol was introduced into the reaction mixture over a period of time specified in the table. A current of nitrogen was run through the circulatory system in order to minimize any oxidation of the hydroquinone which might take place. The solvent was always refluxed for half an hour after all the reactants had been introduced to ensure complete reaction. The solution acquired a yellow to red color during the course of the reaction.

The reaction mixture was cooled, filtered to remove the inorganic salts present and evaporated under diminished pressure on a water pump until only traces of isoamyl alcohol remained. The dark, viscous material remaining was dissolved in chloroform and then the chloroform was evaporated under an air blast. The residue was then placed in a Soxhlet extractor, and extracted with 300 cc. of petroleum ether (b. p. 60–110°) for three to four hours. The solution was then concentrated to about 15 cc. and placed in an icebox overnight. The cyclic ether deposited in flake-like crystals, and upon two recrystallizations from petroleum ether (b. p. 60–110°) and one from methanol, was obtained pure.

The constants were identical with those for this substance when prepared by the indirect route.

Hydroquinone-*bis*-(ω-bromo-*n*-hexyl) Ether.—A mixture of 244 g. (1 mole) of hexamethylene dibromide, 22 g. (0.2 mole) of hydroquinone, 150 cc. of acetone, 40 cc. of water and 100 g. of anhydrous potassium carbonate (freshly heated) was stirred and refluxed for a period of eighteen hours. The stirring and heating were then interrupted and when the reaction mixture had cooled to room temperature, 30 g. more of potassium carbonate was added. Heating and refluxing were continued for four additional hours. The acetone was then distilled off with stirring to prevent bumping. The material in the flask was transferred, after cooling, to a separatory funnel and the top aqueous layer was decanted off and discarded. The lower hexamethylene layer was shaken twice with 300 cc. of water. The unchanged hexamethylene dibromide (120 g., b. p. 84–86° [2 mm.]) was distilled off under reduced pressure. The residue (59 g.) was poured into an evaporating dish and upon cooling solidified to a microcrystalline mass. The crude material was recrystallized twice from absolute ethanol and then sublimed in the molecular still apparatus at 125–140° (10^{-3} mm.). This product was then recrystallized from ethanol; white flaky crystals, m. p. 96–97° (cor.); yield, 55 g. (63.2%).

Anal. Calcd. for $C_{18}H_{28}O_2Br_2$: C, 49.54; H, 6.42; Br, 36.65. Found: C, 49.51; H, 6.34; Br, 36.61.

1,1',4,4'-*bis*-(Hexamethylenedioxy)-dibenzene.—The same cyclization apparatus was used as in previous cyclization experiments. In the reaction flask was placed 1400 cc. of dry isoamyl alcohol and 5 g. of powdered potassium carbonate which had been heated to a red heat for twenty-five minutes. A solution of 0.55 g. (0.005 mole) of hydroquinone and 2.18 g. (0.005 mole) of hydroquinone-*bis*-(ω-bromo-*n*-hexyl) ether in 850 cc. of dry isoamyl alcohol was introduced into the reaction flask over a period of forty hours.

The solution was cooled, filtered with suction to remove all the insoluble material present, and the solvent was distilled off under diminished pressure until only traces of isoamyl alcohol remained. The dark red mass was dissolved in chloroform and the chloroform evaporated under the air blast. The residue was extracted for five hours in a Soxhlet extractor with 500 cc. of petroleum ether (b. p. 60–110°). Upon concentrating the solution to 15 cc. and allowing to stand in the icebox overnight, light brown crystals were obtained. After recrystallization once from petroleum ether (b. p. 30–60°) and once from methanol, the product was pure; white flakes, m. p. 141° (cor.); yield, 0.287 g. (15%).

Anal. Calcd. for $C_{24}H_{32}O_4$: C, 74.95; H, 8.39; mol. wt., 394. Found: C, 75.15; H, 8.41; mol. wt. (b.$CHCl_3$), 405.

The cyclic ether is very soluble in chloroform and benzene, but only moderately soluble in methanol and ethanol. It does not decolorize 2% potassium permanganate and a Zerewitinoff determination shows no active hydrogen atoms.

Hydroquinone-mono-(ω-bromo-*n*-octyl) Ether.—This substance was obtained during an attempt to prepare the di-ether by the procedure described for synthesis of hydroquinone-di-(γ-bromopropyl) ether. Its properties agreed with those for the same compound as described by Lüttringhaus[10]; waxy crystals from 75% ethanol, m. p. 76–77° (cor.).

Anal. Calcd. for $C_{16}H_{25}O_2Br$: C, 58.36; H, 7.66. Found: C, 58.67; H, 7.72.

Hydroquinone-*bis*-(ω-bromo-*n*-decyl) Ether.—A solution of 48 g. (0.16 mole) of decamethylene dibromide, 4.4 g. (0.04 mole) of hydroquinone, 50 cc. of acetone, 12 cc. of water, and 20 g. of potassium carbonate was refluxed and stirred on a steam cone for thirty-six hours.

At the end of this time the acetone was distilled off and the reaction mixture was shaken three times with 100 cc. of water. The product was dissolved in 500 cc. of boiling absolute ethanol and the insoluble polymeric material filtered. On cooling the filtrate, a light brown precipitate was formed. This was removed and sublimed in a molecular still at 10^{-4} mm. with bath temperature of 160–180°. It was finally recrystallized from ethanol; white crystals, m. p. 88.5–89.5° (cor.); yield, 9.7 g. (47%). For analysis, this product was melted and heated to 100° *in vacuo.*

About 21 g. of decamethylene dibromide was recovered.

Anal. Calcd. for $C_{26}H_{44}O_2Br_2$: C, 56.92; H, 8.08. Found: C, 57.29; H, 7.98.

The same product could be obtained by refluxing for seven hours a mixture of two moles of decamethylene dibromide and one mole of hydroquinone-mono-(ω-bromodecyl) ether under the usual conditions. A yield of 73% was obtained.

Hydroquinone-*bis*-(ω-bromo-*n*-octyl) Ether.—This compound was prepared in exactly the same manner as the *bis*-(ω-bromo-*n*-decyl) ether. A yield of 42.8% was obtained.

The product formed white crystals, m. p. 78.5–79.5° (cor.).

Anal. Calcd. for $C_{22}H_{38}O_2Br_2$: C, 53.68; H, 7.38. Found: C, 53.88; H, 7.28.

Hydroquinone-*bis*-(β-bromoethyl) Ether.—This was prepared[11] in the same way as the corresponding γ-bromopropyl ether. From 282 g. (1.5 moles) of ethylene dibromide, 27.5 g. (0.25 mole) of hydroquinone, 125 cc. of acetone, 30 cc. of water and 125 g. of potassium carbonate, 11.2 g. (29.6%) of product was obtained; white crystals, b. p. 145–147° (2 mm.), m. p. 114° (cor.).

Summary

1. A discussion is given of the effect of dilution upon the reaction of two ω,ω'-bifunctional molecules.

2. By the direct condensation of *bis*-(γ-bromopropyl) ether or *bis*-(ω-bromo-*n*-hexyl) ether of hydroquinone with hydroquinone in amyl alcohol with dry potassium carbonate, using high dilution technique, 1,1′,4,4′-*bis*-(trimethylenedioxy)-dibenzene and 1,1′,4,4′-*bis*-(hexamethylenedioxy)-dibenzene were synthesized. The yields were somewhat better than those usually obtained in a two-step process for preparing the same products.

URBANA, ILLINOIS

RECEIVED MAY 21, 1941

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(10) Lüttringhaus, *Ann.*, **528**, 199 (1937).

(11) Renshaw and Hopkins, THIS JOURNAL, **55**, 1525 (1933).