when 2.35 g. (0.0100 mole) of di-*n*-butyltin dihydride was mixed with 0.60 g. (0.1000 mole) of acetic acid the rate of gas evolution followed and infrared spectra were taken at 31%, 67%, 78%, and 100% of gas evolved. (The graph of gas evolution *vs.* time for this run is shown in Fig. 3.) The yield of gas obtained in these runs ranged from 95% to 98%.

*Reaction of di-n-butyltin dihydride with acetic acid in 1:1 mole ratio in n-hexane.* To 1.18 g. (0.0050 mole) of di-*n*-butyltin dihydride was added 5.0 ml. of *n*-hexane followed by 0.30 g. (0.0050 mole) of glacial acetic acid. A graph of gas evolution *vs.* time is shown in Fig. 5. Twelve infrared spectra taken throughout the course of the reaction revealed no trace of the Sn—H band for di-*n*-butylacetoxytin hydride at 1880 cm.$^{-1}$ Further study of the carbonyl absorption region of these spectra showed that di-*n*-butyltin diacetate appeared very early in the reaction, reached a maximum, and was not present at the end. 1,1,2,2-Tetra-*n*-butyl-1,2-diacetoxyditin on the other hand appeared at about 67% gas evolution and was the only species present at the end. Subsequently, 0.0050 mole of di-*n*-butylacetoxytin hydride was prepared from di-*n*-butyltin dihydride and di-*n*-butyltin diacetate and quickly diluted with 5.00 ml. of *n*-hexane. An infrared spectrum, taken immediately thereafter, showed no trace of the Sn—H band at 1880 cm.$^{-1}$ but did show a strong band for di-*n*-butyltin dihydride at 1832 cm.$^{-1}$. The large carbonyl absorption band originally present at 1560 cm.$^{-1}$ had been replaced by a band at 1607 cm.$^{-1}$ which is characteristic of di-*n*-butyltin diacetate. When di-*n*-butylacetoxytin hydride was prepared as above and diluted with an equal volume of ethyl acetate, only a faint suggestion of the band at 1880 cm.$^{-1}$ remained along with a strong band at 1832 cm.$^{-1}$

*Determination of the initial slopes of the reactions.* To solutions containing 0.0050 mole of hydride species in *n*-hexane (0.152 molal) was added the appropriate amount of acetic acid and 0.1 g. of Norit (which has been found to eliminate the initial lag in gas evolution which has often been observed in these reactions).[5] The mixture was placed in a constant temperature bath at 25° and gas evolution was measured at intervals. These data, for reactions of di-*n*-butyltin dihydride with acetic acid in both 2:1 and 1:1 mole acid-hydride ratios and for the di-*n*-butylacetoxytin hydride equilibrium with acetic acid in a 1:1 mole acid-hydride ratio with acetic acid, are shown in Fig. 7.

DURHAM, N. H.

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(5) M. S. Newman and E. G. Caflisch, Jr., *J. Am. Chem. Soc.*, **80**, 862 (1958).

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[CONTRIBUTION NO. 1636 FROM STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

# Electron Exchange Polymers. XVIII. Selective Reactivity of *n*-Butyllithium on 1,4-Dimethoxy-2,3,5-trimethylbenzene[1,2]

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*Received October 20, 1961*

When 1,4-dimethoxy-2,3,5-trimethylbenzene (I) is reacted with *n*-butyllithium, and then treated with acetaldehyde, the major product is 1,4-dimethoxy-2,5-dimethyl-3β-hydroxy-propylbenzene, the lithium having attacked the benzylic hydrogen of methyl group 3, rather than the aromatic hydrogen in position 6. On dehydration of this secondary alcohol there is produced 2,3-dihydro-5-methoxy-2,4,7-trimethylbenzofuran. In the reaction of I with *n*-butyllithium there is also produced a small amount of the pseudocumohydroquinone monomethyl ether: 1-methoxy-4-hydroxy-2,3,5-trimethylbenzene. These substances are characterized, and directions for their preparation are given along with properties and preparations for the compounds 1,4-dimethoxy-2,5-dimethyl-3-chloro-methylbenzene and 1,4-dimethoxy-2,5-dimethyl-3-deuteromethylbenzene.

During our study of methylated vinylhydroquinones,[4] as monomers for preparing electron exchange polymers (redox polymers), an interesting reaction was observed between 1,4-dimethoxy-2,3,5-trimethylbenzene (I) and *n*-butyllithium. When treated at 0° in ether, then with acetaldehyde, there were obtained two products: a viscous oil boiling between 119 and 125° at 0.5 mm. (II), and a crystalline material melting at 101–102° (III). The homogeneity of the oil was indicated by a single zone in a vapor phase chromatogram (detergent column) and sharp peaks in its NMR spectrogram. Its formula corresponded to $C_{13}H_{20}O_3$ and showed a strong hydroxyl group in the infrared absorption region. Attempts to dehydrate this alcohol under mild conditions such as distilling from fused potassium acid sulfate,[5] refluxing in dried toluene containing catalytic quantities of sulfuric acid or *p*-toluenesulfonic acid, refluxing in glacial acetic acid with dry hydrogen chloride[6] were unsuccessful. Heating the alcohol at 100° with several drops of concentrated sulfuric acid gave a product melting at 49–50° on purification. This substance (IV) contains by microanalysis one methoxyl group, by infrared an aromatic system with no hydroxyl group. Its formula was $C_{12}H_{16}O_2$, having lost water and a methylene group.

Comparison of the NMR spectra of 1,4-dimethoxy-2,3,5-trimethylbenzene (I) (spectrum

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(1) This paper is taken from the dissertation submitted by Kenneth A. Kun to the Graduate School of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

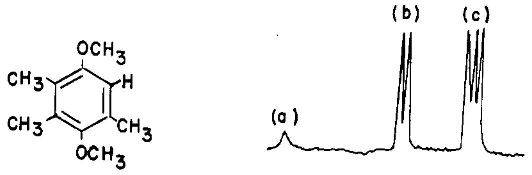
(2) For previous papers in this series see K. A. Kun and H. G. Cassidy, *J. Org. Chem.*, 26, 3223 (1961).

(3) Present address: Rohm & Haas Co., Research Laboratories, Bristol, Pa.

(4) K. A. Kun and H. G. Cassidy, *J. Polymer Sci.*, *in press.*

(5) C. G. Overberger and J. H. Saunders, *Org. Synthesis*, Coll. Vol. III, 204 (1955).

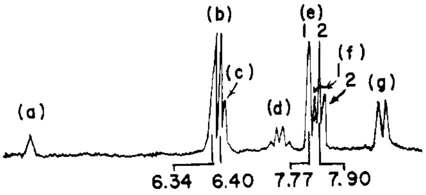
(6) K. A. Kun and P. E. Spoerri, *J. Am. Chem. Soc.*, **77**, 4676 (1955).



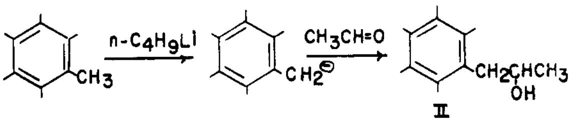
I

Spectrum 1. 1,4-Dimethoxy-2,3,5-trimethylbenzene

1), the alcohol (II) (spectrum 2), and the dehydration product (IV) (spectrum 3) shows the starting material, 1,4-dimethoxy-2,3,5-trimethylbenzene with an aromatic hydrogen (a), two methoxyl groups (b), and three methyl groups (c). Alcohol II, spectrum 2, has an aromatic proton (a), two methoxyl groups (b), a proton from a hydroxyl group (c), and a set of peaks which may be explained as follows. Spectrum 2 indicates that acetaldehyde did not replace the aromatic or methoxyl hydrogens. Therefore, *n*-butyllithium abstracted a proton from one of the methyl groups on the aromatic ring. These benzylic hydrogens are acidic, and one may be removed with a strong base to give a carbanion which yields a substituted isopropyl alcohol when treated with acetaldehyde.



Spectrum 2. Alcohol II

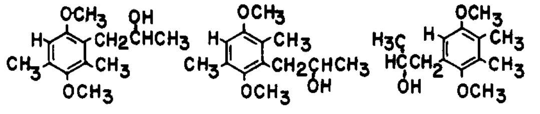


II

Figure 3

This is consistent with spectrum 2: Two peaks marked (e) are two methyl groups and are two of the three original methyl groups attached to the ring. Peaks (d), (f), and (g) account for the grouping $—CH_2—\underset{\underset{OH}{|}}{CH}—CH_3$ while peaks (d) and (g) are typical for a single hydrogen on a tertiary carbon alpha to a methyl group, *e.g.*, —CH—CH₃. Methyl hydrogens (g) are split into a doublet by the methine proton whose peak (d) is split into a symmetrical quadruplet by the three methyl protons. The methine hydrogen also splits the methylene protons alpha to it. The split methylene group (f) is found overlapping methyl group (e-2); the two peaks are designated (f-1) and (f-2). It was expected to find the methylene protons splitting the quadruplet of the methine hydrogen but presumably the instrument could not resolve these small intensity peaks.

Compound II may have three possible structures depending upon which benzyl hydrogen was removed by *n*-butyllithium.



IIa IIb IIc

Figure 4

To determine the correct structure of the substituted isopropyl alcohol, its NMR spectrum was compared to previously reported model compounds.[2] Chemical shifts of methyl groups for both 1,4-dimethoxy-2,5-dimethylbenzene and 1,4-dimethoxy-2,3,5,6-tetramethylbenzene show single peaks at 7.88 and 7.89 $\tau$, respectively. 1,4-Dimethoxy - 2,3,5 - trimethylbenzene shows three methyl peaks at 7.81, 7.88, and 7.95 $\tau$. Thus, the addition of one methyl group to the aromatic ring of 1,4-dimethoxy-2,5-dimethylbenzene causes a difference in chemical shift between the methyl groups. The addition of another methyl group to the aromatic ring, to give 1,4-dimethoxy-2,3,5,6-tetramethylbenzene, causes the differentiation to be lost. It has also been shown that the chemical shift of the methyl groups of 1,4-dimethoxy-2,5-dimethylbenzene is 7.88 $\tau$. Addition of a vinyl group, as with the addition of a methyl group, caused a differentiation between the two methyl groups. 2,5-Dimethoxy-3,6-dimethylstyrene has chemical shifts of its methyl groups at 7.81 and 7.88 $\tau$. But, addition of a third methyl group to this styrene, shows this methyl group to be similar to one of the other two. 2,5-Dimethoxy-3,4,6-trimethylstyrene has chemical shifts at 7.84 and 7.90 $\tau$ with the area under the latter peak twice as large as under the former. This suggests that the vinyl group influences the chemical shift of one methyl group. Vinyl groups may cause either up- or down-field shifts of the peaks of its neighboring groups. If the vinyl group of a styrene may change its orientation relative to the adjacent groups and the aromatic ring, the shift which occurs cannot be accurately described. This is not true of the above styrenes. These styrenes are di-*ortho* substituted, and therefore the vinyl group is fixed perpendicular to the ring. Since the vinyl group cannot change its orientation relative to the ring, its effect on the aromatic methyl groups may be suggested. Addition of a vinyl group to 2,5-dimethoxy-3,6-dimethylbenzene caused one methyl group to shift to 7.81 $\tau$. This suggests that one methyl group, probably the one *ortho* to the vinyl group, has shifted down-field. A similar down-field shift may be observed for one methyl group in 2,5-dimethoxy-3,4,6-trimethylstyrene.[2] Here also there are two methyl groups with equivalent environments located at 7.90 $\tau$

while the third methyl group is shifted down-field to 7.84 $\tau$.

In the above examples two of the three methyl groups of 1,4-dimethoxy-2,3,5-trimethylbenzene become equivalent when the aromatic proton is replaced with alpha-carbon containing groups. Whether the 2- and 3- or 3- and 5-methyl groups are equivalent cannot be determined conclusively from the available data. It is suggested that the three methyl peaks of 1,4-dimethoxy-2,3,5-trimethylbenzene may be partially identified as follows: 7.81 $\tau$, the 2- or 5-methyl; 7.88 $\tau$, the 3-methyl; and 7.95 $\tau$, the 2- or 5-methyl.

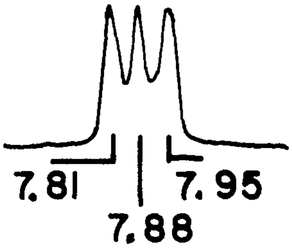
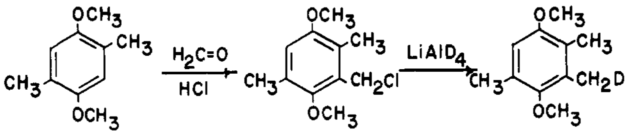


Figure 5

The assumption for the 3-methyl group may be tested by labeling this methyl group with deuterium; deuterium, being transparent in the NMR spectrum, would be detected by a decrease in the area under the peak of the labelled group. By the following set of reactions, the 3-methyl group was tagged:



V VI VII

Figure 6

1,4-Dimethoxy-2,5-dimethylbenzene (V) was chloromethylated by the procedures of Nauta[7] and Smith,[8] using 40% formalin and hydrochloric acid to give a mixture of the mono- and dichloromethylated products. Separation of these two compounds was accomplished by fractional crystallization from methanol and *n*-hexane. The desired monochloromethylated product (VI) was isolated from methanol while the dichloromethylated material was crystallized from *n*-hexane. Treatment of VI with lithium aluminum deuteride gave 1,4-dimethoxy-2,3,5-trimethylbenzene with deuterium on the 3-methyl group (VII). An NMR spectrum of the tagged compound showed the following set of peaks in the methyl region. The middle peak has decreased in size, and therefore it is suggested that the identification of the middle peak is correct.

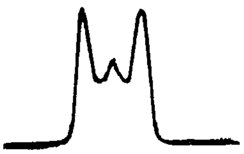
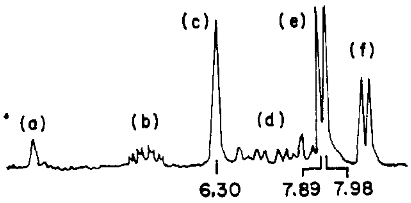


Figure 7

Treating the starting material, 1,4-dimethoxy-2,3,5-trimethylbenzene, with *n*-butyllithium and decomposing the complex with deuterium oxide places deuterium on the methyl group of the stable carbanion. An NMR spectrum of the methyl region of this reaction product shows a decrease in the size of the methyl peak associated with the 3-methyl group, thus strongly suggesting IIb as the reaction product.

The dehydration product of the above alcohol (IV) has a spectrum 3, which shows a major change in structure. The aromatic hydrogen (a) is still present as are the two ring methyl groups (e) and the methyl group similar to the one at the end of the substituted isopropyl alcohol grouping (f) which is split by a methine hydrogen. But the hydrogens of the methylene group and of one methoxyl group in addition to the hydroxyl proton are missing. During the dehydration with sulfuric acid at 100° at 0.2 mm., it is quite possible that an ether bond was broken. Cleavages of phenolic ethers by sulfuric acid at 100° are described by Burwell.[9]



Spectrum 3. Dehydration product

The splitting of a methyl aryl ether in the presence of water, from the dehydration, would yield a phenol of the type:

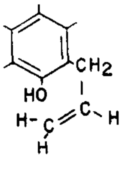


Figure 9

Systems of this type will cyclize to dihydrobenzofurans (coumarans) at a high temperature under acid conditions.[10]

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[7] W. R. Nauta and J. W. Dienske, *Rec. trav. chim.*, **50**, 1000 (1936).

[8] L. I. Smith and F. L. Austin, *J. Am. Chem. Soc.*, **64**, 528 (1942).

[9] R. L. Burwell, Jr., *Chem. Revs.*, **54**, 615 (1954).

[10] Reactions of this kind have been summarized by R. C. Elderfield and V. B. Meyer, *Heterocyclic Compounds*, Vol. 2, John Wiley & Sons, Inc., New York, 1951, Chap. 1.

It is not necessary for the dehydration to take place independently of the cleavage of the ether. Actually, the initiation of the dehydration may aid the cleavage in the following manner:

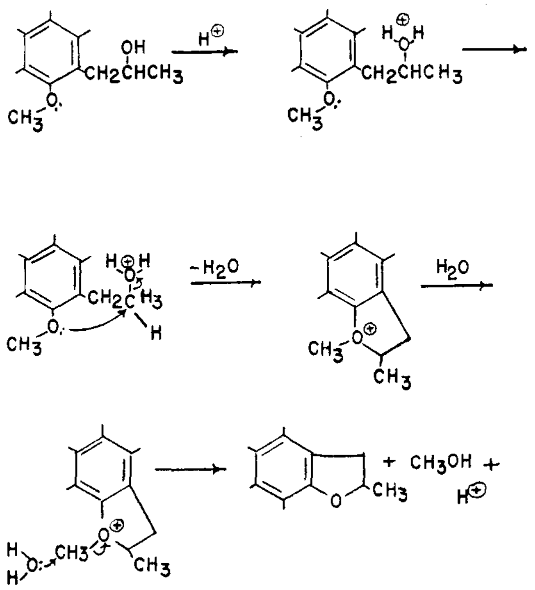

Figure 10

Furans are easily decomposed under acidic conditions to resinous materials.[10] This would account for the poor yields obtained in the dehydration. A dihydrobenzofuran derivative would fit spectrum 3.

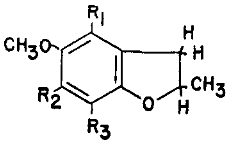

Figure 11

Groups $R_1$, $R_2$, and $R_3$ represent the aromatic hydrogen and the two ring methyl groups, peaks (a) and (e). The methoxyl group(c) is obvious as is the methyl group (f) split by the methine proton while the complex splitting pattern of peaks (b) and (d) are due to the proton alpha to the ring-oxygen and the two protons in the beta position.

Cagniant and Cagniant[11] have shown that the dihydrobenzofuran ring system is characterized by three strong bands in the infrared region. These are between 7.93 and 8.33 μ, 10.0 and 10.2 μ, and at 10.6 μ. The latter two peaks appear to be influenced by substitution. The isolated dihydrobenzofuran has the first two peaks in the appropriate positions while the peak at 10.6 μ has been shifted to 10.98 μ. This shift may be due to the influence of the substituents in the dihydrobenzofuran system. An attempt was made to synthesize 2,3-dihydro-5-methoxy-2,4,7-trimethylbenzofuran (Ring Index numbering) using the procedure of Smith and co-workers,[12] for the preparation of 2,3-dihydro-5-hydroxy-2,4,6,7-tetramethylbenzofuran. The product would be expected readily to convert to the methoxy derivative.[13] Attempts to prepare the 2,3-dihydro-5-hydroxy-2,4,7-trimethylbenzofurans from 2,5-dimethylhydroquinone with allyl bromide or allyl alcohol both with and without catalysts yielded mixtures which did not contain the desired product. The reaction proceeded as described using 2,3,5-trimethylhydroquinone. Dihydrobenzofurans are easily isolated, if formed, from side products by steam distillation. Similar results were found by Smith in his attempts to prepare 2,3 - dihydro - 5 - hydroxy - 2,4,6 - trimethylbenzofuran.[14] The failure of this reaction to give the desired product is probably due to further reactions at the sites of the aromatic hydrogens.

The second product of the reaction with *n*-butyllithium, III, was isolated as long, white needle-like crystals, m.p. 101–102°. Microanalysis showed III to have the empirical formula $C_{10}H_{14}O_2$ and to contain only one methoxyl group. Infrared showed a hydroxyl peak at 2.95 μ, aromatic system peaks at 6.17 and 6.28 μ, aryl methyl ether peaks at 8.15 and 9.25 μ, and carbon-oxygen stretching peaks characteristic of a phenolic group at 7.58 and 8.41 μ. The NMR spectrum of this material showed one aromatic hydrogen, one methoxyl group, one hydroxyl group and three methyl groups. The above data indicate that III is the monomethyl ether of pseudocumohydroquinone. Treatment of this material with dimethyl sulfate and alcoholic potassium hydroxide yields the starting material 1,4-dimethoxy-2,3,5-trimethylbenzene. In this case an ether linkage was broken by *n*-butyllithium. Burwell[9] describes lithium alkyls which attack simpler alkyl ethers to give phenoxides. Though the mechanism of anisole cleavage is not known, one possibility may be a direct displacement giving the more stable phenoxide anion:

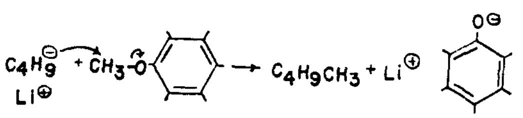

Figure 12

Thus, the monomethyl ether of 2,3,5-trimethylhydroquinone, III, may have one of two possible structures:

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(11) Mme. P. Cagniant and P. Cagniant, *Bull. soc. chim. France*, 838 (1957).

(12) L. I. Smith and H. E. Ungnade, *J. Org. Chem.*, **4**, 298 (1939); L. I. Smith, H. E. Ungnade, H. H. Hoehn, and S. Wawzonek, *J. Org. Chem.*, **4**, 305 (1939); L. I. Smith, H. H. Hoehn, and A. G. Whitney, *J. Am. Chem. Soc.*, **62**, 1863 (1940).

(13) L. I. Smith and C. W. MacMullen, *J. Am. Chem. Soc.*, **58**, 629 (1936).

(14) L. I. Smith, H. E. Ungnade, J. R. Stevens, and C. C. Christman, *J. Am. Chem. Soc.*, **61**, 2615 (1939).

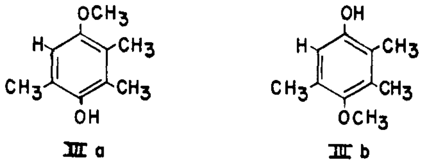
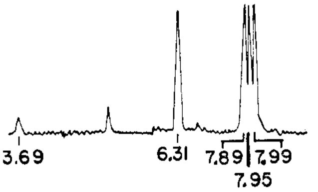


Figure 13

It is reported in a preceding paper[2] that a methoxyl group *ortho* to a ring-proton and a methyl group has a chemical shift at approximately 6.33 $\tau$ and a methoxyl group with two *ortho* methyl groups has a chemical shift at approximately 6.48 $\tau$. From this information and NMR spectrum 4, the correct isomer of the monomethyl ether of pseudocumohydroquinone may be suggested. This spectrum is very similar to the starting material with resolution of the three methyl groups and the equal spacing between the three peaks. The methoxyl peak at 6.31 $\tau$ would be indicative of a methoxyl group with a methyl and an aromatic hydrogen in *ortho* positions. Therefore, the suggested structure for III is 4-methoxy-2,3,6-trimethylphenol (IIIa). This cleavage of the methoxy group *ortho* to two methyl groups is analogous to the hydrolysis to pyrogallol trimethyl ether in which the middle methoxy group is cleaved.[15] In general, the methyl ethers of dihydric phenols appear more reactive than anisole.[16] Though less reactive, even methyl substituted anisole shows an increased rate of cleavage with increasing *ortho* substitution of a methyl group to the methoxy group, *i.e.*, the methoxy group of *o*-methyl anisole cleaves faster than that of anisole.[9]



Spectrum 4

It is strongly suggested that the following set of reactions has taken place where a proton was abstracted from a specific methyl group by *n*-butyllithium and where one methoxyl group is more susceptible to attack than the other.

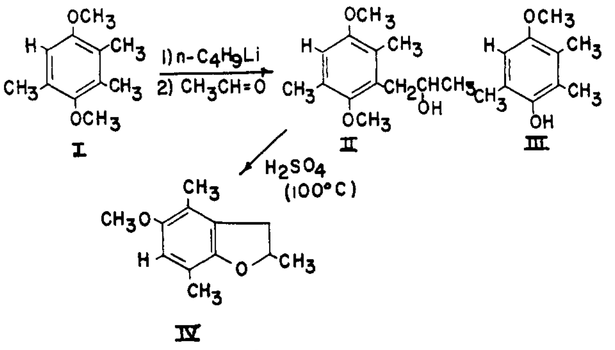


Figure 15

EXPERIMENTAL[17]

*Reaction product of 1,4-dimethoxy-2,3,5-trimethylbenzene with n-butyllithium and acetaldehyde (1,4-dimethoxy-2,5-dimethyl-3β-hydroxypropylbenzene).* Into a 3-l. three neck round bottom flask fitted with a stirrer, low temperature thermometer, reflux condenser, dropping funnel, and a nitrogen inlet tube, 20.8 g. of lithium wire (cut to 7-mm. lengths) was added to 700 ml. of anhydrous ether. Several drops of *n*-butyl bromide solution (206.0 g. in 200 ml. of ether) was added to start the reaction. The remaining portion of etheral *n*-butyl bromide was added dropwise over a period of 1.5 hr.; during this addition the reaction temperature was kept at −30°. When the addition was completed, the reaction was warmed to 0° and stirred for 2 hr. at 0°, until all the lithium had reacted with the halide. Maintaining the temperature at 0°, 64.0 g. of 1,4-dimethoxy-2,3,5-trimethylbenzene in 200 ml. of ether was added rapidly over a period of 15 min. The reaction was warmed to room temperature (27°) and stirring was continued overnight (*ca.* 20 hr.).

The solution was cooled to 0° and 110.0 g. of acetaldehyde was added dropwise over a period of 1.5 hr., keeping the reaction temperature below 10°. When the addition was completed, the reaction was warmed to room temperature and stirred for another 3.5 hr. The organic fraction was separated, and the aqueous fraction was extracted five times with ether. The products were separated by steam distillation. In the distillate were found starting material as well as the monomethyl ether (see below). The nonsteam volatile fraction consisted entirely of the alcohol. Distillation yielded 63.0 g. of the alcoholic product boiling at 119–125° at 0.5 mm.

*Anal.* Calcd. for $C_{13}H_{20}O_3$: C, 69.60; H, 9.00. Found: C, 69.75; H, 8.93.

*Dehydration of the reaction product of 1,4-dimethoxy-2,3,5-trimethylbenzene with n-butyllithium and acetaldehye (2,3-dihydro-5-methoxy-2,4,7-trimethylbenzofuran).* Thirty-seven grams of the above alcohol was placed in a small distillation apparatus containing concd. sulfuric acid so the acid may be added to the alcohol while heating the alcohol *in vacuo.* The alcohol was heated to 90° at 0.5 mm., two drops of sulfuric were added and a fraction boiling between 80–90° at 0.5 mm. was collected. When the distillate temperature reached 90° several drops of sulfuric acid were added, and the distillate again came over between 80 and 90°. Twenty-seven grams of crude material was collected. Approximately 10 g. of a resinous material remained in the distillation flask. The crude distillate was redistilled to yield 9.0 g. of product boiling at 88–90° at 0.5 mm. and 17.0 g. of starting material boiling at 125–129° at 0.5 mm. Crystallization of the reaction product from methanol yielded a white solid melting at 49–50°. Several recrystallizations from methanol gave a material having at constant melting point at 50°.

*Anal.* Calcd. for $C_{12}H_{16}O_2$: C, 74.91; H, 8.39. Found: C, 74.85, 74.93; H, 8.23, 8.31.

*Isolation of pseudocumohydroquinone monomethyl ether.* The crude alcohol obtained by the treatment of pseudocumohydroquinone dimethyl ether with *n*-butyllithium and acetaldehyde was purified by steam distillation, which removed the steam-volatile starting material, as well as the monomethyl ether, leaving behind the alcohol. The steam distillate was extracted with ether, the ethereal solution

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(15) Basler Chemische Fabrik, German Patent 162,658; *Chem. Zentr.*, 11, 1961 (1905).

(16) E. Merck, German Patent 78,910; *Chem. Zentr.*, 1, 719 (1895).

(17) Melting points and boiling points are uncorrected.

dried over anhydrous potassium carbonate, filtered, and the product isolated by distilling the solvent *in vacuo.* This residue was dissolved in hot *n*-hexane and, on cooling to room temperature, white needle-like crystals were formed. The crystals melted at 96–97°. A sample was recrystallized several times from *n*-hexane, until a constant melting point at 101–102° was obtained. This material sublimed quite easily.

*Anal.* Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 71.92; H, 8.34.

*Preparation of pseudocumohydroquinone dimethyl ether from the monomethyl ether.* Two grams of pseudocumohydroquinone monomethyl ether was dissolved in a solution of 25 ml. of absolute methanol and 3 g. of freshly distilled dimethyl sulfate. This solution was heated to reflux, and the heat source was then removed. A saturated solution of methanolic potassium hydroxide was added dropwise, at a rate to maintain a moderate reflux, until the reaction mixture was alkaline to litmus paper. Steam distillation yielded a distillate containing an aqueous methanolic solution of the product. After diluting with water, the distillate was extracted with ether, ether fractions were combined, dried over anhydrous potassium carbonate, filtered, and the solvent distilled *in vacuo* to yield a light yellow liquid residue which was crystallized from methanol. Recrystallization of this solid from methanol yielded a material melting at 35–36°. A mixed melting point with 1,4-dimethoxy-2,3,5-trimethylbenzene showed no depression, and infrared spectra, in chloroform, of both samples were identical.

*Preparation of 1,4-dimethoxy-2,5-dimethyl-3-chloromethylbenzene (2,5-dimethoxy-3,6-dimethylbenzylchloride).* Twenty-five grams of 1,4-dimethoxy-2,5-dimethylbenzene was combined with 12.3 g. of 40% formalin and 150 ml. of concd. hydrochloric acid. The mixture was stirred at 70°C. for 6 hr. with hydrogen chloride bubbling through the reaction mixture at a moderate rate. On cooling, the aqueous solution was extracted with ether, the ether extracts were combined and washed three times with 200 ml. of water, washed twice with 200 ml. of saturated sodium bicarbonate solution, and finally washed with another 200 ml. of water. The ether solution was dried over anhydrous calcium chloride, filtered, and the solvent was removed from the filtrate *in vacuo* to give 27 g. of crude product. The crude product was recrystallized from *n*-hexane to yield a white solid melting at 166° which gave a positive Beilstein test. This material was 1,4-dimethoxy-2,5-dimethyl-3,6-dichloromethylbenzene, a side product of the desired reaction. Smith[18] describes this compound and reports its melting point at 165–166°. Solvent was distilled from the above crystallization filtrate leaving a white solid which was recrystallized from methanol. The product was recrystallized to give a white solid melting at 68–69°, which gave a positive Beilstein test.

*Anal.* Calcd. for $C_{11}H_{15}O_2Cl$: C, 61.07; H, 7.04; Cl, 16.51. Found: C, 61.27; H, 7.06; Cl, 16.31.

*Preparation of 1,4-dimethoxy-2,5-dimethyl-3-deuteromethylbenzene.* To a solution of 0.3 g. of 2,5-dimethoxy-3,6-dimethyl benzyl chloride in 10 ml. of ether a slight excess of lithium aluminum deuteride was added portionwise. The resulting mixture was heated at reflux for 5 hr. After refluxing for 0.5 hr., a white solid began to form. This indicated the formation of lithium and aluminum chlorides. Excess lithium aluminum deuteride was decomposed with ethyl acetate and 3 ml. of water was then added to decompose the organometallic complexes. The ether solution was decanted from the hydrated inorganic salts. Distilling the solvent from the dry organic solution yielded a light yellow liquid. This liquid was crystallized from methanol and recrystallized once to give a white solid melting at 36°.

*Acknowledgment.* The authors wish to thank Dr. Harold Conroy and Dr. Gary Griffin for their helpful discussions during this investigation. We also acknowledge with pleasure the support given this work by Research Corporation and through a research grant A3304 from the Division of Research Grants, the National Institutes of Health, Public Health Service.

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[CONTRIBUTION FROM THE ORGANIC CHEMISTRY DEPARTMENT, NATIONAL RESEARCH CENTER]

# Carbonyl and Thiocarbonyl Compounds. VI.[1] (a) Synthesis of Newer Fluorenylidene Cyclic Ethers from Tetrahalo-*o*-benzoquinones. (b) The Reductive Cleavage of Methylenedioxy Compounds by Lithium Aluminum Hydride

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*Received January 6, 1961*

The halogenated cyclic ethers IIc–IIf are obtained by the action of 2-bromo- and 2,7-dibromo-9-diazofluorene on tetrachloro- and tetrabromo-*o*-benzoquinone, respectively. The diazofluorenes are prepared in excellent yields by oxidizing the corresponding ketohydrazones with yellow mercuric oxide in the presence of alkali. IIc–IIf are also produced by the action of the appropriate tetrahalo-*o*-benzoquinone on the corresponding ketohydrazone or on the bromofluorenes themselves.

In contrast to other methylenedioxy compounds previously investigated xanthylene cyclic ethers of the general formula IV are quantitatively cleaved by lithium aluminum hydride. Similar compounds derived from fluorene are also attacked, but not so readily, by this reagent under similar conditions. A reaction mechanism, based on the formation of resonance stabilized carbonium ions, is suggested.

The preparation of cyclic ethers of the general formula I by the action of diazo compounds on *o*-quinones has been investigated by various authors.[2,3] Schönberg and Latif[4] synthesized various

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