Upon cooling the mixture was poured into water and extracted with ethyl acetate. The residue was acetylated with acetic anhydride and pyridine in the usual manner to afford the diacetate (XIV). Recrystallization from methanol yielded the pure product, m.p. 149–150°. The product was identical by mixed melting point and infrared spectrum comparison with a sample prepared from the Δ^9-estrone.

Acknowledgment.—The authors are indebted to Misses H. Yamanouchi and K. Hayashi for the microanalyses and to Miss K. Arimoto for the infrared spectral data. One of the authors (S.N.) is grateful to the Japan Society for Promotion of Science for the award of research fellowship.

The Aluminum Phenoxide-catalyzed Reaction of Phenol with Dienes

K. C. DEWHIRST AND F. F. RUST

Shell Development Company, Emeryville, California

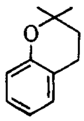
Received August 23, 1962

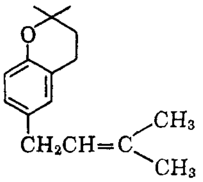
The reaction of phenol with dienes in the presence of aluminum phenoxide gives a mixture of alkenylphenols and chromans. With phenol and isoprene, a bisphenol possessing an unusual n.m.r. spectrum is also obtained. The mechanism of the reaction is discussed.

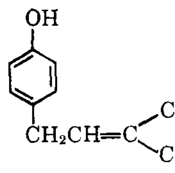
The use of aluminum phenoxide as a selective catalyst for the *ortho*-alkylation of phenol has been described.[1] In the cases of propylene and isobutylene good yields of 2,6-dialkylated phenols were obtained, whereas more complicated olefins gave somewhat poorer yields of mono- and dialkylated products. In the present paper we have examined the reaction of phenol with conjugated dienes.

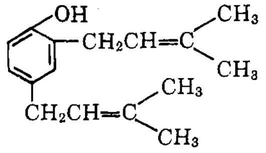
Results

When phenol is treated with isoprene in the presence of aluminum phenoxide at low temperatures and low phenol–isoprene ratios, compounds I–IV may be isolated from the reaction mixture. As may be seen from Table I, the product distribution varies considerably with reaction conditions, although the reaction could not be directed to a particular product. The products obtained under these conditions are identical with those obtained by Bader[2] using phosphoric acid as catalyst, except that under his conditions the double bonds were partially hydrated.


I


III


II


IV

When the aluminum phenoxide-catalyzed reaction was carried out at higher temperatures (>100°) in the presence of excess phenol, chroman I was obtained (36%), accompanied by a new compound, bisphenol V (see next section), in 38% yield.

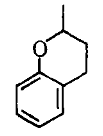
Under identical conditions, phenol reacted with 1,3-butadiene to give monoadducts VI, VIIa and VIIb in 5%, 8%, and 57% yields, respectively. Attempts to add a second mole of phenol to VIIb under more vigorous conditions failed. The relative sluggishness of the disubstituted olefin as compared with II (trisubstituted) is probably to be ascribed to weaker complex formation with aluminum phenoxide.

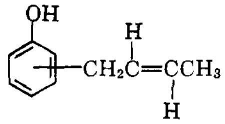
TABLE I

PRODUCT DISTRIBUTION IN THE ALUMINUM PHENOXIDE-CATALYZED REACTION OF PHENOL AND ISOPRENE

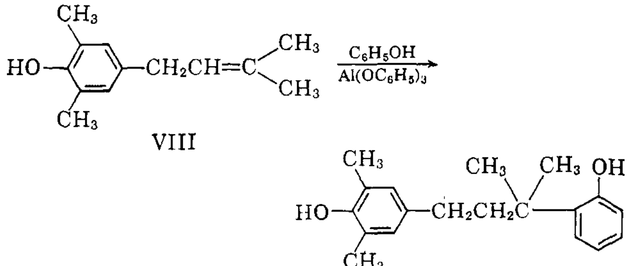
Reaction conditions			Product composition[a] (mole fraction)			
Phenol–isoprene	Temp. °C.	Solvent	I	II	III	IV
1.2:1	60	...	0.32	0.41	0.27	..
1.2:1	20	Benzene	0.35	0.52	0.14	..
1.2:2	80	...	0.38	0.25	0.24	0.13

[a] Combined yields average 70%.


VI


VIIa: *ortho*
VIIb: *para*

Similarly, 2,6-dimethylphenol reacted with isoprene in the presence of aluminum 2,6-dimethylphenoxide to give phenol VIII in 67% yield. Although VIII would not react further with 2,6-dimethylphenol, it did so with phenol to give an 89% yield of bisphenol IX. The structure of IX was not demonstrated, but inferred by analogy to bisphenol V (*vide infra*).



VIII
IX

The reaction also proceeded smoothly with β,β-dimethylstyrene to give phenol X in 75% yield. The structure of X was demonstrated by the occurrence in its n.m.r. spectrum of two sharp bands (area ratio 3:1) in the alkyl region, and by permanganate oxidation to acid XI.

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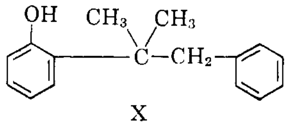
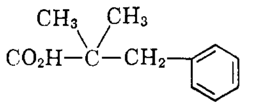
[1] A. J. Kolka, J. P. Napolitano, A. H. Filby, and G. G. Ecke, *J. Org. Chem.*, **22**, 642 (1957).

[2] A. R. Bader and W. C. Bean, *J. Am. Chem. Soc.*, **80**, 3073 (1958).



X

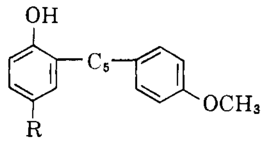


XI

Attempts to carry out alkylations with other conjugated olefins such as acrylonitrile and mesityl oxide failed.

The Structure of Bisphenol V.—The bisphenol isolated from the aluminum phenoxide-catalyzed reaction of phenol with isoprene possesses the expected molecular formula $C_{17}H_{20}O_2$. The infrared spectrum (potassium bromide pellet) of this material exhibited strong bands at 757 and 817 cm.$^{-1}$, indicative of *ortho-* and *para*-disubstituted benzene rings,[3] respectively, and a doublet centered near 1365 cm.$^{-1}$, indicative of a *gem*-dimethyl group.[4]

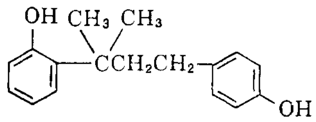
Chemical verification of both substitution patterns was obtained through the corresponding monomethyl ether, XIIa. Permanganate oxidation gave anisic acid, while nitration gave a nitrophenol, whose infrared spectrum indicated structure XIIb.



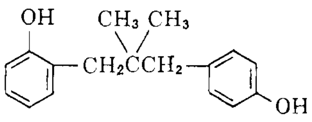
XIIa. R = H
XIIb. R = NO_2

The n.m.r. spectrum (tetramethylsilane, internal reference) of V showed the presence of six methyl protons (singlet, $\delta^5 = 1.38$,) and four other alkyl protons (singlet, $\delta^5 = 2.15$).

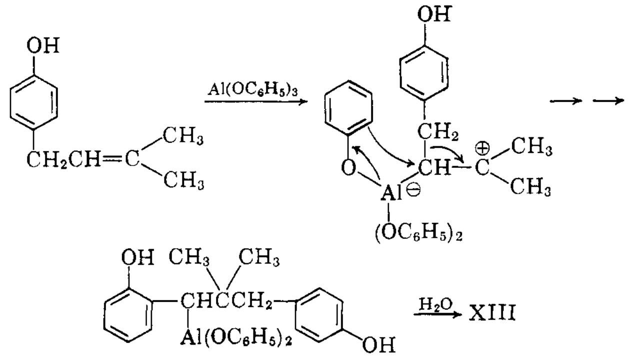
The only structures which are consistent with the data thus far are V and XIII. Of these two structures, XIII would certainly be favored on the basis of the singlet methylene resonance at $\delta = 2.15$, and indeed, a plausible mechanism for its formation may be postulated as follows:



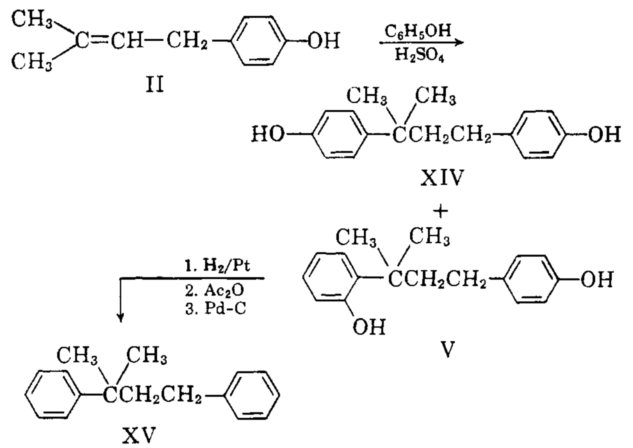
V



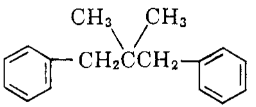
XIII



That the structure of this material is actually V, however, was demonstrated by the following chemical transformations:



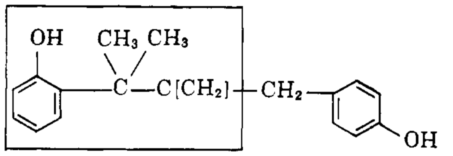
Alkylation of II with phenol in the presence of sulfuric acid gave a mixture of *ortho* and *para* isomers in 73% yield. The *para* isomer was shown to have the expected structure XIV by the presence in the alkyl region of its n.m.r. spectrum of a singlet methyl resonance and a *complex* methylene resonance, characteristic of an AA'BB' system of protons.[6] The *ortho* isomer, however, which should possess the same unrearranged structure showed only a singlet methyl resonance and *singlet* methylene resonance, and was identical with the bisphenol prepared *via* the aluminum phenoxide–catalyzed reaction of phenol and isoprene. Furthermore, dehydroxylation of V gave a hydrocarbon in 63% over-all yield which was not identical with XVI,[7] but which did now possess the typical AA'BB' pattern expected of XV.



XVI

Discussion

Steric Modification of Spectral Properties.—The n.m.r. spectrum of bisphenol V is quite unusual. Although in simple cases a methylene resonance[8] ($\delta \sim 1.2$) is quite removed from a benzyl resonance[8] ($\delta \sim 2.6$), the bracketed protons in this case are beta to two phenyl groups which moves their resonance position to lower field strength with a resulting AA'BB' pattern in the case of the *para* isomer XIV. The *ortho* isomer V further contains the boxed structural element studied by Reilly.[9] In phenols of this type, a substantial downfield shift of the methylene resonance was observed and attributed to oxygen–hydrogen interaction as in XVII.



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[3] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N.Y., 1958, p. 64.

[4] Ref. 3, p. 13.

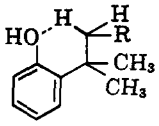
[5] δ = p.p.m. from tetramethylsilane.

[6] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N.Y., 1959, p. 95.

[7] E. R. Trotman, *J. Chem. Soc.*, **127**, 88 (1925).

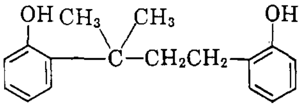
[8] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N.Y., 1959, pp. 52–58.

[9] C. A. Reilly and K. C. Dewhirst, unpublished work.



XVII

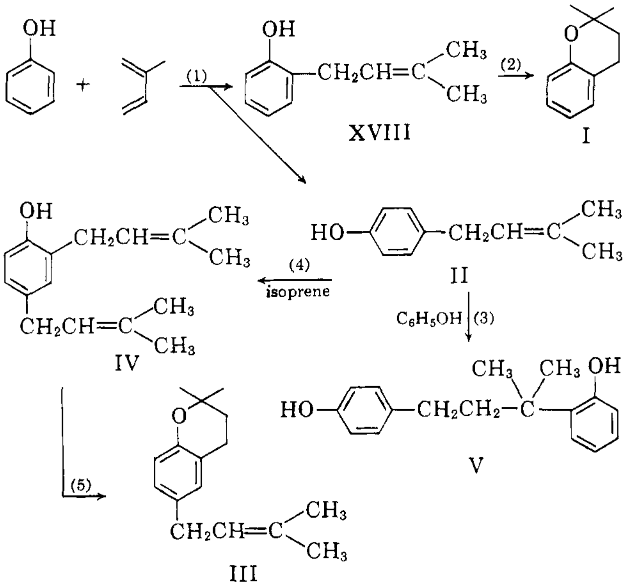
Thus, in bisphenol V, this additional downfield shift brings the two resonances into accidental coincidence, resulting in a single sharp line. Although the methylene resonance of bisphenol V could not be resolved under any conditions, the corresponding *ortho* isomer XXI



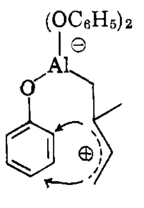
XXI

(*vide infra*) exhibited a complex methylene resonance when measured in pyridine[10] solution. In carbon tetrachloride solution, a single sharp line was observed.

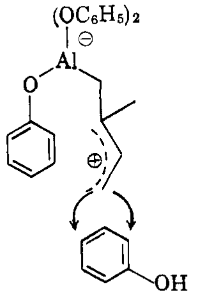
Mechanism of the Aluminum Phenoxide-catalyzed Alkylation of Phenol with Isoprene. All of the products isolated from the phenol–isoprene reaction may be accounted for by the following series of transformations:



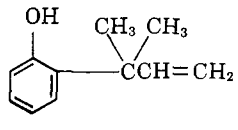
Step 1 most likely proceeds through a coordinated complex such as XIX which then alkylates intramolecularly as in XIXa or intermolecularly as in XIXb. Although both mechanisms would give the same *para* isomer II, the *ortho* isomer derived from XIXa would have structure XX, while that derived from XIXb would have structure XVIII. The presence of XVIII in the product indicates intermolecular mechanism XIXb to be the case. Step 2 was confirmed by the isolation of chroman I in 68% yield when XVIII was treated with excess phenol and aluminum phenoxide Only a small quantity of bisphenol XXI was isolated from the reaction mixture. Thus *ortho*-phenol XVIII prefers intramolecular addition as would be expected for entropy reasons.



XIXa



XIXb



XX

The *para*-phenol II may now partition itself between steps 3 and 4 depending on the relative ratio of phenol to isoprene. Thus II in the presence of excess phenol gave bisphenol V in 80% yield. Although step 4 was not demonstrated directly, it may be inferred from the data in Table I since in the presence of excess isoprene the mole fraction of II decreased while that of IV increased.

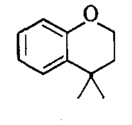
Experimental

All melting points are uncorrected; all boiling points are corrected. The n.m.r. data were determined with Varian Associates high resolution magnetic resonance spectrometer (V-4300) at 40 Mc./sec. using tetramethylsilane as internal reference.

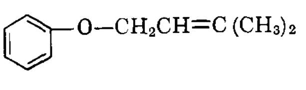
Unless otherwise specified, the aluminum phenoxide-catalyzed reactions followed the general procedure given below for the combination of phenol and isoprene.

Aluminum Phenoxide-catalyzed Reaction of Phenol with Isoprene.—Phenol, 4 moles, was placed in a three-necked flask in a nitrogen atmosphere and a small portion was distilled to remove traces of moisture. The temperature was lowered to 160° and maintained during the addition of 2.7 g. of polished aluminum. The mixture was then cooled to 110°, and 1 mole of isoprene was added under vigorous stirring during the course of 1 hr. Heating was continued an additional hour, and the reaction mixture was then cooled in ice, diluted with 1 l. of ether, and hydrolyzed with dilute hydrochloric acid. The ether layer was washed with sodium bicarbonate, water, and dried. Fractional distillation gave 58 g. (36%) of 2,2-dimethylchroman (I),[2] b.p. 109°, (20 mm.) and 2.0 g. (1.2%) of 4-(3-methyl-2-butenyl)phenol (II),[2] b.p. 120° (5 mm.).

2,2-Dimethylchroman (I) was further characterized by its infrared spectrum which showed the absence of C=C in the 1600-cm.$^{-1}$ region, but did show *ortho* substitution in the 700–750-cm.$^{-1}$ region, *gem*-dimethyl near 1380 cm.$^{-1}$, and cyclic ether by the profusion of bands near 1100 cm.$^{-1}$. The n.m.r. spectrum was in accord with the assigned structure, but neither for



nor



C_6H_5—O—$CH_2CH{=}C(CH_3)_2$

II was characterized by its infrared spectrum for OH (3200 cm.$^{-1}$), *p*-disubstituted benzene (820 cm.$^{-1}$), and trisubstituted double bond (860 cm.$^{-1}$). The conclusions were confirmed by n.m.r.

Compound III was characterized again by infrared and n.m.r. spectra. The expected features were those also found in compounds I or II.

The distillation residue was flashed through a Claisen flask, b.p. ~ 220°, and crystallized from benzene–hexane to give 79 g. (31%) of 2-(2-hydroxyphenyl)-4-(4-hydroxyphenyl)-2-methylbutane (V), m.p. ~ 120°.

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[10] G. Slomp and F. Mackellar, *J. Am. Chem. Soc.*, **82**, 999 (1960).

For analysis, a small sample was recrystallized from benzene–hexane, m.p. 128–129°.

Anal. Calcd. for $C_{17}H_{20}O_2$: C, 79.7; H, 7.9; Mol. Wt., 256. Found: C, 79.7; H, 7.9; mol. wt. (ebullioscopic in ethylene chloride), 245. The yield of bisphenol V could be increased to 38% by increasing the phenol–isoprene ratio to 8:1.

At lower phenol–isoprene ratios, bisphenol V was not found, and the major products were chroman I, monoalkenylphenol II, 2,2-dimethyl-6-(3-methyl-2-butenyl)chroman (III),[2] b.p. 171–175° (20 mm.), $n^{20}D$ 1.5278, and 2,4-bis(3-methyl-2-butenyl)-phenol (IV), b.p. ~135–145° (0.5 mm.). The structure of crude phenol IV was inferred from its boiling point and the presence in its infrared spectrum (neat) of bands at 1640 and 850 cm.$^{-1}$, characteristic of trisubstituted double bonds,[11] and at 820 cm.$^{-1}$, characteristic of *para*-disubstituted benzene rings.[4]

The relative distributions of these materials under various experimental conditions are listed in Table I.

2-(2-Hydroxyphenyl)-4-(4-hydroxyphenyl)-2-methylbutane Mono- and Dimethyl Ethers.—Bisphenol V, 25 g., 20 g. of potassium hydroxide, and 25 ml. of dimethyl sulfate in 125 ml. of water were allowed to stir at room temperature for 2 days, and then heated on a steam bath for 2 hr. The reaction mixture was cooled, diluted with 150 ml. of benzene, and acidified with dilute hydrochloric acid. The benzene layer was washed with water, dried, evaporated, diluted with hexane and cooled to give 6.7 g. (25%) of 2-(2-hydroxyphenyl)-4-(4-methoxyphenyl)-2-methylbutane (XIIa), m.p. 109–110°.

For analysis, a small sample was recrystallized from carbon tetrachloride–hexane, m.p. 110–111°.

Anal. Calcd. for $C_{18}H_{22}O_2$: C, 80.0; H, 8.2. Found: C, 80.0; H, 8.2.

The hexane filtrates were fractionally distilled to give 2-(2-methoxyphenyl)-4-(4-methoxyphenyl)-2-methylbutane, 16.2 g. (59%), b.p. 183–185° (2 mm.), m.p. 27–29°.

For analysis, a small sample was recrystallized from methanol, m.p. 27–28°.

Anal. Calcd. for $C_{19}H_{24}O_2$: C, 80.3; H, 8.5. Found: C, 80.4; H, 8.5.

The n.m.r. spectra of these two materials were identical to that of bisphenol V in the alkyl region.

Oxidation of monomethyl ether XIIa with aqueous potassium permanganate gave a small quantity of anisic acid, m.p. 180–181°, undepressed on admixture with an authentic sample.

2-(2-Hydroxy-5-nitrophenyl)-4-(4-methoxyphenyl)-2-methylbutane (XIIb).—Monomethyl ether XIIa, 5 g., was dissolved in a mixture of 15 ml. of benzene and 10 ml. of acetic acid at 0°. To this stirred solution was slowly added 4.7 ml. of 6 *N* nitric acid. The reaction mixture was kept at 0° 1 hr. and poured onto 100 ml. of ice–water. The benzene layer was washed with sodium bicarbonate and water, dried, and evaporated to give 1.8 g. (31%) of product, m.p. ~125°.

For analysis, a small sample was recrystallized from benzene, m.p. 130.5–131.5°.

Anal. Calcd. for $C_{18}H_{21}NO_4$: C, 68.5; H, 6.7. Found: C, 68.8; H, 6.8.

The infrared spectrum (bromoform) of this material showed a strong band at 825 cm.$^{-1}$ (*para*-disubstituted), but none near 750 cm.$^{-1}$ (*ortho*-disubstituted).

Dehydroxylation of 2-(2-Hydroxyphenyl)-4-(4-hydroxyphenyl)-2-methylbutane (V).—Bisphenol V, 67.8 g., was hydrogenated with 1.2 g. of platinum dioxide in 150 ml. of acetic acid to give 64.6 g. (91%) of the cyclohexanol derivative, b.p. ~180° (2 mm.).

This material was converted directly with acetic anhydride in pyridine to the corresponding diacetate in 91% yield.

The diacetate was placed in a small distilling column and heated with 10% by weight of 5% palladium on carbon at 285°. After the theoretical amount of acetic acid and hydrogen had been evolved, the reaction stopped. The cooled reaction mixture was dissolved in ether, filtered, washed with sodium bicarbonate and water, dried, and distilled to give 2,4-diphenyl-2-methylbutane, b.p.[10] 162–163°, $n^{25}D$ 1.5470, in 81% yield.

Anal. Calcd. for $C_{17}H_{20}$: C, 91.0; H, 9.0. Found: C, 90.6; H, 8.8.

The infrared spectrum (neat) of this material exhibited a strong doublet at 750 and 765 cm.$^{-1}$, and another at 700 and 710 cm.$^{-1}$, strongly indicative of two types of monosubstituted benzene rings.[4] The alkyl portion of the n.m.r. spectrum (neat) of this material showed a sharp methyl resonance at $\delta = 2.08$ and a complex methylene resonance (AA'BB' pattern) centered near $\delta = 1.33$.

Sulfuric Acid-catalyzed Reaction of 2-Methyl-4-(4-hydroxyphenyl)-2-butene (II) with Phenol.—Phenol II, 67 g., was treated with phenol (4 moles) at 110° using 0.5 mole % sulfuric acid as catalyst to give 80 g. (73%) of mixed alkylate, b.p. 200–220° (0.5 mm.).

The reaction mixture was fractionally distilled to give bisphenol V, b.p. 185° (0.4 mm.), m.p. 128–129°, undepressed on admixture with the bisphenol prepared *via* aluminum phenoxide-catalyzed alkalation of phenol with isoprene.

Fractional crystallization of the higher-boiling distillates gave 2,4-bis(4-hydroxyphenyl)-2-methylbutane (XIV), m.p. 112–113°.

For analysis, a small sample was recrystallized from benzene, m.p. 114–115°.

Anal. Calcd. for $C_{17}H_{20}O_2$: C, 79.7; H, 7.9. Found: C, 79.9; H, 7.9.

The n.m.r. spectrum (methanol) of this material exhibited a sharp methyl resonance and a complex methylene resonance in the alkyl region.

Aluminum Phenoxide-catalyzed Reaction of 2-Methyl-4-(4-hydroxyphenyl)-2-butene (II) with Phenol.—Phenol II, 75 g., was treated with phenol (4 moles) under the usual conditions to give 94 g. (80%) of bisphenol V, m.p. 127.5–128.0°, undepressed upon admixture with an authentic sample.

Aluminum Phenoxide-catalyzed Reaction of 2-Methyl-4-(2-hydroxyphenyl)-2-butene (XVIII) with Phenol.—Phenol XVIII, 50 g., reacted with 230 g. of phenol containing 1.0 g. of combined aluminum under conditions previously specified for treating phenol and isoprene. Chroman I (34 g., 68% yield) was obtained and identified by infrared spectral comparison with an authentic sample.

The distillation residue was diluted with benzene–hexane to give 4.5 g. (6%) of 2,4-bis(2-hydroxyphenyl)-2-methylbutane (XXI), m.p. 97–105°.

For analysis, a small sample was recrystallized from benzene–hexane, m.p. 110–111°.

Anal. Calcd. for $C_{17}H_{20}O_2$: C, 79.7; H, 7.9. Found: C, 79.8; H, 7.9.

The infrared spectrum (Nujol mull) exhibited a strong band at 760 cm.$^{-1}$, and none in the 810-cm.$^{-1}$ region. The n.m.r. spectrum showed two sharp resonances in the alkyl region.

Aluminum Phenoxide-catalyzed Reaction of Phenol with 1,3-Butadiene.—1,3-Butadiene was allowed to react with phenol in the usual manner to give 10 g. (5%) of crude 2-methylchroman[12] (VI), b.p. 96–102° (20 mm.), $n^{20}D$ 1.5285, 14 g. (8%) of crude *o*-crotylphenol[12] (VIIa), b.p. 120–130° (20 mm.), and 105 g. (57%) of *p*-crotylphenol[13] (VIIb), b.p. 143° (20 mm.), m.p. 36–37°.

Attempts to add a second mole of phenol under more vigorous conditions failed.

Aluminum Phenoxide-catalyzed Reaction of 2,6-Dimethylphenol with Isoprene.—Isoprene, 68 g., was treated with 2,6-dimethylphenol (4 moles) under the usual conditions to give 125 g. (67%) of 2,6-dimethyl-4-(3-methyl-2-butenyl)phenol (VIII), b.p. 107–109° (1 mm.).

For analysis, the material was redistilled.

Anal. Calcd. for $C_{13}H_{18}O$: C, 82.1; H, 9.5. Found: C, 82.0; H, 9.5.

The n.m.r. spectrum (carbon tetrachloride and a trace of formic acid) of this material showed resonances at $\delta = 1.68$ (singlet), 2.13 (singlet), 3.18 (doublet), 5.33 (triplet), and 6.73 (singlet), consistent with the proposed structure. A small quantity of the terminal double bond-isomer was also present as impurity.

Although phenol VIII would not react further with 2,6-dimethylphenol, it did so with phenol to give 2-(2-hydroxyphenyl)-4-(3,5-dimethyl-4-hydroxyphenyl)-2-methylbutane (IX), b.p. ~235° (0.7 mm.), in 89% yield.

Anal. Calcd. for $C_{19}H_{24}O_2$: C, 80.2; H, 8.5. Found: C, 80.2; H, 8.5.

The infrared spectrum (neat) of this material showed bands at 860 and 750 cm.$^{-1}$, characteristic of 1,2,3,5-tetrasubstituted and 1,2-disubstituted benzene rings,[4] respectively.

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2-Hydroxy-2-methyl-1-phenylpropane.—1-Phenyl-2-propanone, 268 g., was treated with methylmagnesium iodide to give 273 g. (82%) of product,[14] b.p. 98° (10 mm.), n^{20}_{D} 1.5133.

β,β-Dimethylstyrene.—2-Hydroxy-2-methyl-1-phenylpropane was dehydrated with a trace of 85% phosphoric acid in xylene solution to give a 76% yield of product,[14] b.p. 188–189°. Careful fractionation of the reaction mixture gave some 2-methyl-3-phenyl-1-propene, b.p. 177°.

2-(2-Hydroxyphenyl)-2-methyl-1-phenylpropane (X).—β,β-Dimethylstyrene, 132 g., was treated with phenol (4 moles) in the usual manner to give 162 g. (71%) of product, b.p. 147° (1 mm.).

Anal. Calcd. for $C_{16}H_{18}O$: C, 84.9; H, 8.0. Found: C, 85.0; H, 8.0.

The infrared spectrum (neat) of this compound exhibited a doublet at 1340 and 1380 cm.$^{-1}$, and none in the 810-cm.$^{-1}$ region.

Oxidation of 2-(2-Hydroxyphenyl)-2-methyl-1-phenylpropane (X) with Potassium Permanganate.—Phenol X, 42.2 g., was dissolved in 1.5 l. of water containing 40 g. of potassium hydroxide, and to the resulting stirred solution was slowly added 216 g. of potassium permanganate at 85°. The reaction mixture was filtered and the filtrate was acidified and extracted with ether. The ether layer was dried and evaporated, and the residue was dissolved in 150 ml. of dry methanol containing 7.5 g. concentrated sulfuric acid and refluxed for 2 hr. The cooled solution was diluted with water, extracted with ether, and the ether extract was washed with sodium bicarbonate and water. The dried ether solution was fractionally distilled to give 5.2 g. (20%) of methyl benzoate, b.p. 71° (10 mm.), 2.6 g. (7%) of methyl 2,2-dimethyl-3-phenylpropionate, b.p. 106°, (10 mm.), and 10.9 g. (27%) of methyl 3,3-dimethyl-2-keto-4-phenylbutanoate, b.p. 141° (10 mm.).

Methyl 2,2-dimethyl-3-phenylpropionate was identified by conversion in 76% yield to the corresponding anilide,[15] m.p. 108–108.5°.

The keto ester was redistilled for analysis.

Anal. Calcd. for $C_{13}H_{16}O_3$: C, 70.9; H, 7.3; sapon. equiv. 220. Found: C, 71.0; H, 7.3; sapon. equiv. 224.

The n.m.r. spectrum (neat) of this material exhibited sharp peaks at $\delta = 1.13$, 2.93, 3.63, and 7.13.

Reduction of this keto ester with lithium aluminum hydride gave, after chromatography on alumina, the corresponding glycol in 87% yield. The presence of a benzyl group was demonstrated by the presence in its nuclear magnetic resonance spectrum (neat) of a band at $\delta = 2.55$.[8]

Acknowledgment.—The authors are indebted to Dr. C. A. Reilly for the determination and interpretation of the n.m.r. spectra reported in this work. They also wish to acknowledge the initial isolation of bisphenol V by Dr. W. T. Tsatsos.

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Cyclic Dienes. XXVIII. 3,4-Dimethylenetetrahydrofuran[1,2]

WILLIAM J. BAILEY AND STANTON S. MILLER

Department of Chemistry, University of Maryland, College Park, Maryland

Received September 24, 1962

3,4-Dimethylenetetrahydrofuran, which is isomeric with 3,4-dimethylfuran, was prepared in a four-step synthesis from dimalonic ester. The key step involved the pyrolysis of a diacetate at 605° under reduced pressure to produce a 24% yield of the diene. The structure of the diene was indicated by analysis and ultraviolet, infrared, and nuclear magnetic resonance spectra, as well as by conversion to three solid Diels–Alder adducts.

In previous articles in this series the synthesis of isomers of aromatic compounds, such as 4,5-dimethylenecyclohexene[3] isomeric with *o*-xylene, 3,6-dimethylenecyclohexene[4] isomeric with *p*-xylene, and 5-methylene-1,3-cyclohexadiene[5] isomeric with toluene, have been reported. It was of interest to extend this series to include the preparation of some isomers of aromatic heterocycles. In view of Marvel's[6,7] failure to obtain 3,4-dimethylenethiophane by pyrolysis of the corresponding diacetate, the more stable furan system was studied. Thus the synthesis of 3,4-dimethylenetetrahydrofuran (I), which is isomeric with 3,4-dimethylfuran (I), was investigated. The diene I, also, can be regarded as an isostere of 4,5-dimethylenecyclohexene. This diene I was of additional interest for the preparation of a cyclic all-*cis* polymer[8] that could be opened under basic conditions to a noncyclic all-*cis* polymer. A method for the reductive cleavage of the tetrahydrofuran ring with lithium aluminum hydride and aluminum chloride was previously reported.[9]

Since the pyrolysis of esters had been successful for the preparation of other isomers of aromatic compounds,[3] this method was selected for the preparation of 3,4-dimethylenetetrahydrofuran (I). The required diacetate II was prepared in three steps from dimalonic ester III in an over-all yield of 17%. Thus ethyl 1,1,2,2-ethanetetracarboxylate (III) was dialkylated with α,α'-dichloromethyl ether with sodium hydride to give ethyl 3,3,4,4-tetrahydrofurantetracarboxylate (IV) in a 48% yield. (The formation of substantial quantities of a high boiling residue suggests the competing formation of a polymer or a larger ring.) Hydrolysis of IV, followed by decarboxylation, gave the solid 3,4-tetrahydrofurandicarboxylic acid (V); however, because of the high water solubility of V, it was usually not isolated but was directly esterified to give a 37% over-all yield of ethyl 3,4-tetrahydrofurandicarboxylate (VI). By the method of one-step reduction and acetylation with lithium aluminum hydride and acetic anhydride,[10] VI was converted to the diacetate II in a 60% yield. When these three steps were carried out without the isolation of any of the intermediates, a 17% yield of II from III was obtained.

When 3,4-di(acetoxymethyl)tetrahydrofuran (II) was added dropwise to a Vycor tube packed with glass helices at temperatures of 445 to 605°, the yield of 3,4-dimethylenetetrahydrofuran (I) was only 1 to 4%. Since pyrolysis under reduced pressure had been shown to increase dramatically the yields in the preparation of

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