[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Phenylallyl Ether Rearrangement. The Allyl and Crotyl Ethers of 2,4-Dimethyl-6-propenylphenol

BY WALTER M. LAUER AND DONALD W. WUJCIAK[1,2a,2b]

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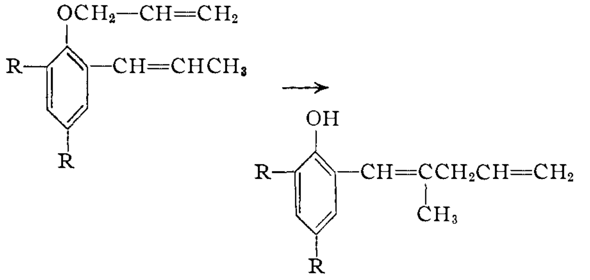
Rearrangement of the allyl ether of 2,4-dimethyl-6-propenylphenol was reported by Claisen and Tietze to yield 2,4-dimethyl-6-(2-methyl-1,4-pentadienyl)-phenol. Accordingly, the allyl residue becomes attached not to the benzene ring, but to the β-carbon of an *o*-propenyl side chain. The present investigation supplies evidence for the structure of this rearrangement product and describes the preparation and rearrangement of the corresponding crotyl ether. In this case thermal rearrangement leads to a product formed by attachment of the non-inverted crotyl group to the β-carbon of the *o*-propenyl side chain. Pyrolyses of this kind lead to more complex mixtures than those obtained in the usual Claisen rearrangement.

In 1926, Claisen and Tietze[3] reported a second type of rearrangement of substituted phenylallyl ethers. Unlike the then known rearrangements of phenylallyl ethers in which the migrating allyl group eventually becomes attached directly to the aromatic nucleus, this rearrangement proceeds in such a manner that the allyl residue becomes attached, not to the benzene ring, but to the β-carbon of an *o*-propenyl side chain. Thus the allyl ethers of 2,4-dimethyl-6-propenylphenol, 2-methoxy-4-propyl-6-propenylphenol and 2,4-dichloro-6-propenylphenol were rearranged to phenolic products to which the following structures were assigned: 2,4-dimethyl-6-(2-methyl-1,4-pentadienyl)-phenol, 2-methoxy-4-propyl-6-(2-methyl-1,4-pentadienyl)-phenol and 2,4-dichloro-6-(2-methyl-1,4-pentadienyl)-phenol, respectively.



It has been demonstrated[4,5] that the *para*-Claisen rearrangement yields products which are consistent with the proposal of Hurd and Pollack involving a double inversion and results suggest that this rearrangement proceeds through a dienone intermediate. An interesting similarity of the rearrangement of an allyl residue to an *o*-propenyl side chain to the *para*-Claisen rearrangement becomes apparent on comparison of the routes traversed by the migrating allyl group in the two cases.

The object of the present investigation was (a) to supply definitive evidence concerning the structures of the rearrangement products, which Claisen and Tietze[3] had obtained and (b) to determine whether rearrangements of this type proceed with or without inversion of the migrating allyl group. The allyl and crotyl ethers of 2,4-dimethyl-6-propenylphenol were chosen for study, since rearrangement in the second case would lead to different products depending upon whether or not inversion takes place.

The allyl ether of 2,4-dimethyl-6-propenylphenol was prepared and rearranged by heating under reduced pressure in an atmosphere of nitrogen. The liquid product, 2,4-dimethyl-6-(2-methyl-1,4-pentadienyl)-phenol (I), was obtained in 26% yield along with 2,4-dimethyl-6-propenylphenol and a high-boiling non-acidic residue. In order to convert the phenolic rearrangement product into a more easily synthesized compound, the terminal double bond was isomerized into conjugation with the other double bond and the phenolic hydroxyl group was methylated. These steps were accomplished by treatment with methanolic potassium hydroxide, followed by direct treatment of the reaction mixture with dimethyl sulfate. The resulting methyl ether of 2,4-dimethyl-6-(2-methyl-1,3-pentadienyl)-phenol (II) was synthesized in the following way. The methyl ether of 2,4-dimethyl-6-propenylphenol (III) was converted to the glycol IV by means of hydrogen peroxide and formic acid and this glycol was in turn cleaved with lead tetraacetate to produce the methyl ether of 3,5-dimethylsalicylaldehyde (V). This aldehyde was also prepared in another manner. Bromination of 2,4-dimethylphenol, followed by methylation gave the methyl ether of 2,4-dimethyl-6-bromophenol (VI). Compound VI was converted to the corresponding Grignard reagent, which was treated with ethyl orthoformate. Hydrolysis of the resulting acetal yielded V. The methyl ether of 3,5-dimethylsalicylaldehyde has not been reported previously, although 3,5-dimethylsalicylaldehyde has been reported in several instances.

Treatment of the methyl ether of 3,5-dimethylsalicylaldehyde (V) with the Grignard reagent prepared from 4-bromo-2-pentene, followed by dehydration with potassium bisulfate yielded the methyl ether of 2,4-dimethyl-6-(2-methyl-1,3-penta-

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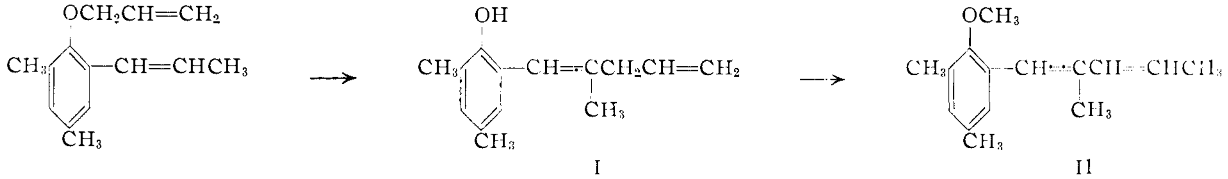
(1) Allied Chemical and Dye Corp. Fellow 1953–1954.

(2) (a) Ph.D. Thesis submitted August, 1954. (b) An independent study of the rearrangement of the allyl ether of 2,4-dimethyl-6-propenylphenol using C14-labeling was carried out by K. Schmid, P. Fahrni and H. Schmid of the Chem. Institut der Universitat, Zurich. Professor Hans Schmid has very kindly advised us of the results of their study, an account of which will appear shortly in the *Helv. Chim. Acta*. Our conclusions are in agreement with those of the Swiss group.

(3) L. Claisen and E. Tietze, *Ann.*, **449**, 81 (1926).

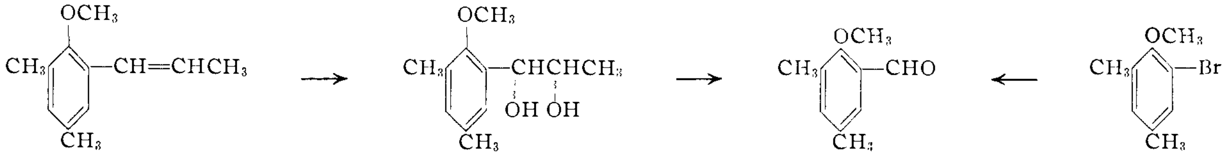
(4) *Inter alia* C. D. Hurd and M. A. Pollack, *J. Org. Chem.*, **3**, 550 (1939); O. Mumm, H. Hornhardt and J. Diederichsen, *Ber.*, **72**, 100, 1523 (1939).

(5) E. R. Alexander and R. W. Kluiber, THIS JOURNAL, **73**, 4304 (1951); J. P. Ryan and P. R. O'Connor, *ibid.*, **74**, 5866 (1952); S. J. Rhoads, R. Raulins and R. D. Reynolds, *ibid.*, **75**, 2531 (1953); **76**, 3456 (1954); E. N. Marvell, A. V. Logan, L. Friedman and R. W. Ledeen, *ibid.*, **76**, 1922 (1954); H. Conroy and R. A. Firestone, *ibid.*, **75**, 2530 (1953); D. Y. Curtin and H. W. Johnson, Jr., *ibid.*, **76**, 2276 (1954); K. Schmid, W. Haegele and H. Schmid, *Helv. Chim. Acta*, **37**, 1080 (1954).



I

II



III

IV

V

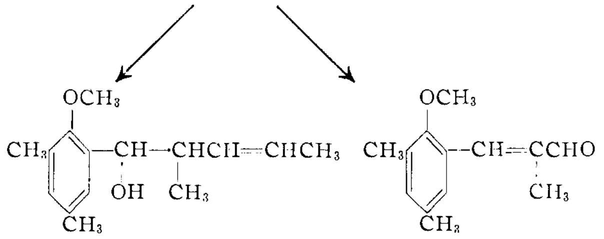
VI

dienyl)-phenol (II). A comparison of the infrared spectrum of this synthetic material with that of the material obtained by isomerization and methylation of the thermal rearrangement product proved their identity. Thus, the structure assigned by Claisen and Tietze to this rearrangement product is confirmed.

A second proof of structure was accomplished by means of oxidative degradation with ozone. Ozonolysis of the methyl ether of 2,4-dimethyl-6-(2-methyl-1,3-pentadienyl)-phenol (II) yielded a 2,4-dinitrophenylhydrazone which melted at 219–220°. This derivative proved to be the 2,4-dinitrophenylhydrazone of 2-methoxy-α-3,5-trimethylcinnamaldehyde (VIII). The condensation of the methyl ether of 3,5-dimethylsalicylaldehyde (V) with propionaldehyde yielded 2-methoxy-α,3,5-trimethylcinnamaldehyde (VIII) which formed a 2,4-dinitrophenylhydrazone identical with that obtained from the ozonolysis of the methyl ether of 2,4-dimethyl-6-(2-methyl-1,3-pentadienyl)-phenol (II).

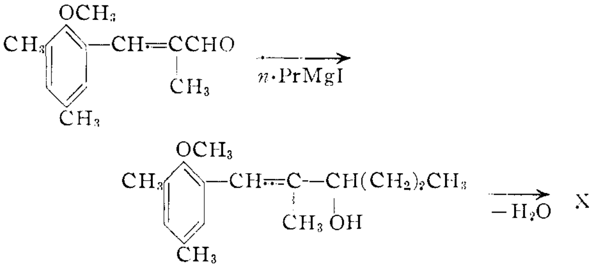
The Rearrangement of the Crotyl Ether of 2,4-Dimethyl-6-propenylphenol.—The crotyl ether was prepared by the action of crotyl bromide on 2,4-dimethyl-6-propenylphenol in the presence of potassium carbonate and acetone. In order to establish its structure, the crotyl ether was catalytically hydrogenated and the saturated product obtained in 90% yield was compared with the *n*-butyl and *sec*-butyl ethers of 2,4-dimethyl-6-propylphenol. The infrared spectrum of the reduction product of the crotyl ether of 2,4-dimethyl-6-propenylphenol was identical with that of the *n*-butyl ether of 2,4-dimethyl-6-propylphenol and differed from that of the *sec*-butyl ether.

Rearrangement of the crotyl ether produced 2,4-dimethyl-6-(2-methyl-1,4-hexadienyl)-phenol (22.6%) (IX), 2,4-dimethyl-6-propenylphenol (25.4%) and a high boiling residue. Our experience, like that of Claisen and Tietze, indicates that this type of rearrangement is accompanied by other changes and leads to more complex results than the usual Claisen rearrangement. In order to convert the 2,4-dimethyl-6-(2-methyl-1,4-hexadienyl)-phenol into a more easily synthesized compound, it was isomerized and methylated. The resulting methyl ether of 2,4-dimethyl-6-(2-methyl-1,3-hexadienyl)-phenol (X) was then subjected to ozonolysis. A 2,4-dinitrophenylhydrazone, m.p. 219–220°, which showed no depression in mixed melting point with the 2,4-dinitrophenylhydrazone of 2-methoxy-α,3,5-trimethylcinnamaldehyde (VIII) was obtained. The fact that ozonolysis yielded an α-methylcinnamaldehyde derivative, instead of a derivative of the methyl ketone XI with one more carbon, indicates that the point of attachment of the propenyl group was through a primary carbon of the migrating four-carbon fragment. It was therefore concluded that the structure of the compound obtained from the thermal rearrangement product by base-catalyzed isomerization of the double bond and methylation is the methyl ether of 2,4-dimethyl-6-(2-methyl-1,3-hexadienyl)-phenol (X).

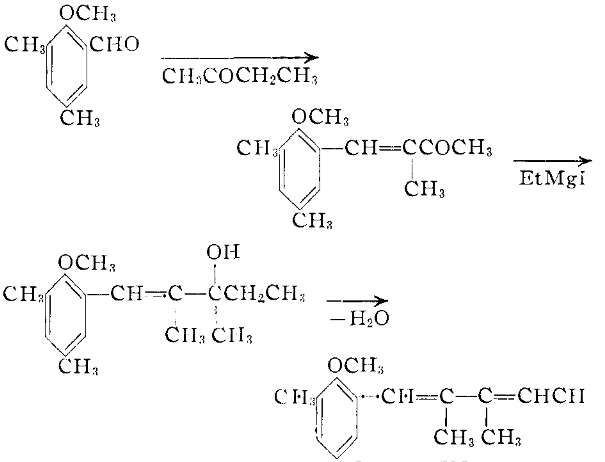


VII → II

VIII



X

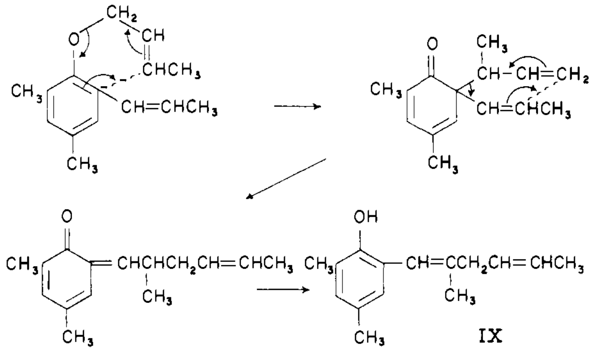


XI

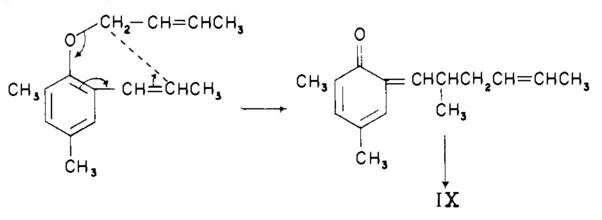
A second proof of structure was provided by synthesis of the previously unknown isomeric methyl ethers of 2,4-dimethyl-6-(2-methyl-1,3-hexadienyl)-phenol (X) and 2,4-dimethyl-6-(2,3-dimethyl-1,3-pentadienyl)-phenol (XI) and comparison of their infrared spectra with that of the material obtained by way of the rearrangement product. The preceding chart outlines the way in which these syntheses were accomplished.

The infrared spectrum of the material obtained from the rearrangement product resembled that of the methyl ether of 2,4-dimethyl-6-(2-methyl-1,3-hexadienyl)-phenol (X) although some significant deviations were apparent. Most of these differences were eliminated when the synthetic ether, which had been prepared under acidic conditions, was subjected to the same alkaline conditions which were used to shift the double bond into conjugation in the case of the rearrangement product.

In view of the above findings it is concluded that the crotyl ether of 2,4-dimethyl-6-propenylphenol upon thermal rearrangement gives 2,4-dimethyl-6-(2-methyl-1,4-hexadienyl)-phenol (IX) along with other products. The formation of product IX establishes the fact that if an intramolecular rearrangement is involved in its formation, the crotyl group migrates without inversion or that a migration involving an even number of steps occurs. By analogy with the *para*-Claisen rearrangement this process can be formulated as a double inversion as



An alternate single step migration involving a six-membered ring transition state is an attractive possibility.



The present work does not eliminate mechanisms involving dissociation followed by recombination of ions or radicals.

Experimental

All melting points and boiling points are uncorrected. Infrared spectra are available in the Ph.D. thesis, which is on file in the library of the University of Minnesota.

I. The Preparation and Rearrangement of the Allyl Ether of 2,4-Dimethyl-6-propenylphenol. 1. **2,4-Dimethyl-6-propenylphenol.**—The preparation of this compound was patterned after the method of Claisen and Tietze with the following modifications: the inorganic products of the initial reaction were removed by filtration and the final product was purified by steam distillation. The 2,4-dimethyl-6-propenylphenol (m.p. 73.5–74.0°) was obtained in 71% yield. A phenylurethan (m.p. 137–139°) was prepared from this phenol.

2. **Allyl Ether of 2,4-Dimethyl-6-propenylphenol.**—A mixture of 2,4-dimethyl-6-propenylphenol (40.5 g., 0.250 mole), potassium carbonate (37.0 g., 0.263 mole) and dry acetone (100 ml.) was stirred at its reflux temperature for two hours and then a solution of allyl bromide (40.4 g., 0.334 mole) in acetone (100 ml.) was added. The heating and stirring were continued for 24 hr. The mixture was cooled and water (200 ml.) was added to dissolve the inorganic solids. The two layers were separated and the acetone was removed from the organic layer by distillation and replaced by petroleum ether (50 ml., b.p. 60–68°). The aqueous layer was extracted twice with petroleum ether (b.p. 60–68°) and these extracts were added to the organic layer. This organic layer was then extracted with a 5% aqueous sodium hydroxide solution to remove 2,4-dimethyl-6-propenylphenol. The organic layer was then washed with water and dried over anhydrous potassium carbonate and magnesium sulfate. The solvent was removed *in vacuo*, and the residue was distilled under reduced pressure. The product, the allyl ether of 2,4-dimethyl-6-propenylphenol (44.06 g., 87%), was collected at 96–97° (0.9 mm.) or 88–89° (0.5 mm.).

Anal. Calcd. for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.01; H, 9.07.

3. **2,4-Dimethyl-6-(2-methyl-1,4-pentadienyl)-phenol: The Thermal Rearrangement of the Allyl Ether of 2,4-Dimethyl-6-propenylphenol.**—The allyl ether (20.2 g., 0.100 mole), in an atmosphere of nitrogen, was heated under reduced pressure at its reflux temperature for 13 hours until the temperature of the liquid reached 184° (34 mm.). The reaction product was dissolved in petroleum ether (80 ml., b.p. 60–68°). The petroleum ether solution was extracted as follows: nine times with a 5% aqueous sodium hydroxide solution, twice with a 10% sodium hydroxide solution, once with a 20% sodium hydroxide solution and seven times with Claisen alkali. After the organic layer was washed with water and dried over magnesium sulfate, it yielded an undistillable residue. Acidification of the aqueous base extracts yielded 2,4-dimethyl-6-propenylphenol (1.6 g., 10%, m.p. 72–74°).

The Claisen alkali extracts were neutralized by pouring each portion into a beaker filled with ice and concd. hydrochloric acid (26 ml.). The material which separated was extracted with petroleum ether (125 ml., b.p. 60–68°). After these petroleum ether extracts were combined and dried over magnesium sulfate, the solvent was removed *in vacuo*. Distillation of the residue yielded the thermal rearrangement product, 2,4-dimethyl-6-(2-methyl-1,4-pentadienyl)-phenol (5.28 g., 26.1%, b.p. 95–97° (0.55 mm.), n^{25}_{D} 1.5427).

Anal. Calcd. for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.44; H, 9.33.

A phenylurethan derivative, m.p. 115–116°, was prepared.

4. **The Methyl Ether of 2,4-Dimethyl-6-(2-methyl-1,3-pentadienyl)-phenol: Isomerization and Methylation of the Thermal Rearrangement Product.**—In a 25-ml. pear-shaped flask were placed 2,4-dimethyl-6-(2-methyl-1,4-pentadienyl)-phenol (3.88 g., 0.0192 mole) and a saturated solution (12 ml.) of potassium hydroxide in methanol. A thermometer was immersed in the solution and the methanol was distilled until the temperature reached 110°. The solution was heated under reflux at 110° for six hours. The solution was then cooled and water (5 ml.) and methanol (5 ml.) were added to dissolve the contents of the flask. The flask was immersed in an ice-bath and dimethyl sulfate (2.53 g., 0.021 mole) was then added. The cooled mixture was stirred for 30 min. and then heated to 50° for 15 min. The resulting mixture was neutralized by adding the contents of the flask to a mixture of ice and concd. hydrochloric acid. The organic material was extracted with ethyl ether. The ether extracts were combined, extracted with Claisen alkali, washed with water, and dried ($MgSO_4$). Distillation yielded the methyl ether of 2,4-dimethyl-6-(2-methyl-1,3-

pentadienyl)-phenol (1.20 g., 30%, b.p. 80–82° at 0.04 mm., $n^{25}\text{D}$ 1.5650).

Anal. Calcd. for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.10; H, 9.33.

II. **Proof of Structure of the Methyl Ether of 2,4-Dimethyl-6-(2-methyl-1,3-pentadienyl)-phenol.** 1. **Ozonolysis.**—The methyl ether of 2,4-dimethyl-6-(2-methyl-1,3-pentadienyl)-phenol was dissolved in ethanol and added to an aqueous alcoholic solution of 2,4-dinitrophenylhydrazine sulfate. Ozone was then bubbled through this alcoholic solution for two hours. The precipitated 2,4-dinitrophenylhydrazone was separated and purified by chromatography on alumina using a mixture of chloroform and petroleum ether (b.p. 60–68°) to develop and elute the column. After several recrystallizations from a solution of chloroform and methanol, the red platelets of the 2,4-dinitrophenylhydrazone melted at 219–220°.

2. **1-(2-Methoxy-3,5-dimethylphenyl)-1,2-propanediol.**—In a 50-ml. flask equipped with a stirrer were placed the methyl ether of 2,4-dimethyl-6-propenylphenol (3.4 g., 0.020 mole, $n^{25}\text{D}$ 1.5311), 30% hydrogen peroxide (3.3 g., 0.029 mole) and 88% formic acid (15 ml.). The stirrer was started and after an induction period of several minutes, an ice-bath was applied to keep the temperature of the reaction mixture below 40°. When the reaction subsided, the ice-bath was replaced by an oil-bath heated to 40°. After 24 hours, the solution was cooled and the major portion of the solvent was removed *in vacuo*. To the residue was added 25 ml. of a 20% sodium hydroxide solution and the mixture was heated at its reflux temperature for one hour. The alkaline mixture was extracted several times with ethyl acetate. The ethyl acetate extracts were washed with water. The ethyl acetate was then removed *in vacuo* and replaced by petroleum ether (b.p. 60–68°). Crystallization gave colorless needles of 1-(2-methoxy-3,5-dimethylphenyl)-1,2-propanediol (3.0 g., 72%, m.p. 86.5–87°).

Anal. Calcd. for $C_{12}H_{18}O_3$: C, 68.54; H, 8.63. Found: C, 68.77; H, 8.57.

3. **The Methyl Ether of 3,5-Dimethylsalicylaldehyde.** A.—To the above glycol (7.0 g., 0.033 mole) and glacial acetic acid (100 ml.), acid–wet lead tetraacetate was added portionwise with stirring until the solution gave a blue-black positive test for tetravalent lead with wet starch–iodide paper. Addition of solution of sodium hydroxide (60 g.) in water (100 ml.) neutralized approximately three-fourths of the acetic acid. The cloudy mixture was then steam distilled to obtain about 500 ml. of distillate. Any acetic acid in the distillate was neutralized with a saturated solution of sodium carbonate. The distillate was extracted with petroleum ether (b.p. 30–60°); the extract was then washed with water, dried and concentrated. Distillation yielded the methyl ether of 3,5-dimethylsalicylaldehyde (3.50 g., 65%, b.p. 69–72° (0.2 mm.), $n^{25}\text{D}$ 1.5337).

Anal. Calcd. for $C_{10}H_{12}O_2$: C, 73.14; H, 7.37. Found: C, 73.02; H, 7.51.

A **2,4-dinitrophenylhydrazone**, m.p. 238–239°, was prepared.

Anal. Calcd. for $C_{16}H_{16}N_4O_5$: C, 55.81; H, 4.68; N, 16.27. Found: C, 55.61; H, 4.88; N, 16.19.

B.—The methyl ether of 3,5-dimethylsalicylaldehyde was synthesized from 2,4-dimethyl-6-bromophenol. The methyl ether of 2,4-dimethyl-6-bromophenol (21.5 g., 0.100 mole) was converted to the corresponding Grignard reagent. This Grignard reagent formed very slowly and precipitated from the ether solution. Refluxing and stirring facilitated its formation. A solution of ethyl orthoformate (14.8 g., 0.100 mole) in ether (40 ml.) was added to the Grignard reagent and the reaction mixture was heated at its reflux temperature for five hours and then the solvent was removed by distillation. When the last traces of solvent were removed, the residue (originally a white semi-solid) became a tan liquid. This residue was heated by a hot water-bath for one hour and the ether was replaced after cooling. The reaction mixture except for the acetal, was hydrolyzed by the addition of a saturated solution (15 ml.) of ammonium chloride. The ether solution, together with the ether extracts were treated with 6 *N* hydrochloric acid (15 ml.). After removal of the ether, the material remaining was subjected to steam distillation. The distillate, about one liter, was then extracted with petroleum ether (b.p. 60–68°). This petroleum ether extract yielded upon distillation the methyl ether of 3,5-dimethylsalicylaldehyde (9.18 g., 56%). The 2,4-dinitrophenylhydrazone, m.p. 237.5–239° (mixed m.p. with corresponding product described in A 237.5–239°) was prepared.

C.—The methyl ether of 3,5-dimethylsalicylic acid, m.p. 97–98°, was obtained by oxidation (hydrogen peroxide) of the methyl ether of 3,5-dimethylsalicylaldehyde. Demethylation of the methyl ether of 3,5-dimethylsalicylic acid gave 3,5-dimethylsalicylic acid, m.p. 180–180.5°, which was identical with a sample prepared from 2,4-dimethylphenol by means of the Kolbe reaction.

4. **1-(2-Methoxy-3,5-dimethylphenyl)-2-methyl-3-penten-1-ol.**—In a 250-ml. flask were placed magnesium (3.66 g., 0.151 mole) and 10 ml. of a solution of 4-bromo-2-pentene[6] (22.4 g., 0.150 mole, b.p. 61–64° at 95–107 mm., $n^{25}\text{D}$ 1.4712) in dry ether (100 ml.). When the reaction started, a solution of the methyl ether of 3,5-dimethylsalicylaldehyde (4.92 g., 0.030 mole) in ethyl ether (50 ml.) was mixed with the remaining solution of 4-bromo-2-pentene. This mixed solution was then added to the reaction mixture over a period of one hour. The resulting mixture was heated at its reflux temperature for one hour, then cooled and treated with a saturated solution of ammonium chloride. The supernatant ether solution together with the ether extracts were washed with water, dried over anhydrous magnesium sulfate and distilled; b.p. 89–90° (1.2 mm.), $n^{25}\text{D}$ 1.5165, 6.10 g., 87% (1-(2-methoxy-3,5-dimethylphenyl)-2-methyl-3-penten-1-ol).

Anal. Calcd. for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46. Found: C, 76.64; H, 9.59.

5. **The Methyl Ether of 2,4-Dimethyl-6-(2-methyl-1,3-pentadienyl)-phenol.**—A mixture of 1-(2-methoxy-3,5-dimethylphenyl)-2-methyl-3-penten-1-ol (1.17 g., 0.0050 mole) and freshly fused potassium bisulfate (2.0 g., 0.015 mole) was heated to 190° for one hour. After cooling, the reaction mixture was extracted with small portions of petroleum ether (b.p. 60–68°). The combined extracts were chromatographed over alumina using petroleum ether to elute the column. The eluate (*ca.* 100 ml.) was concentrated and the residue distilled under reduced pressure. The methyl ether of 2,4-dimethyl-6-(2-methyl-1,3-pentadienyl)-phenol (0.47 g., 45%) was collected at 95–96° (2 mm.).

Anal. Calcd. for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.30; H, 9.50.

Ozonolysis yielded a dark red 2,4-dinitrophenylhydrazone, m.p. 219–220°. A mixed melting point of this material and the 2,4-dinitrophenylhydrazone described in section II, part 1, showed no change.

6. **2-Methoxy-α,3,5-trimethylcinnamaldehyde.**—The methyl ether of 3,5-dimethylsalicylaldehyde (0.50 g., 0.0030 mole), propionaldehyde (0.20 g., 0.0034 mole) and potassium hydroxide (0.018 g., 0.0003 mole) were dissolved in absolute ethanol (1.0 ml.) containing one drop of water. This solution was allowed to stand overnight at room temperature and then poured onto a mixture of ice and dilute hydrochloric acid. The organic material which separated was extracted with petroleum ether (b.p. 30–60°). After washing and drying, these extracts were subjected to distillation. The product, 2-methoxy-α,3,5-trimethylcinnamaldehyde (0.28 g., 46%), was collected at 82–83° (0.04 mm.).

Anal. Calcd. for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.66; H, 7.43.

A **2,4-dinitrophenylhydrazone**, m.p. 219–220°, was prepared.

Anal. Calcd. for $C_{19}H_{20}N_4O_5$: C, 59.37; H, 5.24; N, 14.58. Found: C, 59.44; H, 5.61; N, 14.30.

Mixed melting points of the 2,4-dinitrophenylhydrazone of 2-methoxy-α,3,5-trimethylcinnamaldehyde with the 2,4-dinitrophenylhydrazone described above (section II, parts 1 and 5) showed no depression.

III. **The Preparation, Proof of Structure and Rearrangement of the Crotyl Ether of 2,4-Dimethyl-6-propenylphenol.** 1. **The Crotyl Ether of 2,4-Dimethyl-6-propenylphenol.**—A mixture of 2,4-dimethyl-6-propenylphenol (16.2 g., 0.100 mole), dry potassium carbonate (15.1 g., 0.110 mole) and

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(6) This compound was prepared by Clifford Benton by the addition of methylmagnesium bromide to crotonaldehyde and then by the conversion of the alcohol to the bromide by means of hydrobromic acid.

dry acetone (100 ml.) was stirred at room temperature for two hours and then a solution of crotyl bromide (16.9 g., 0.125 mole, obtained by the action of gaseous hydrobromic acid on crotyl alcohol, followed by a fractional distillation) in acetone (35 ml.) was added. The reaction mixture was stirred and heated at its reflux temperature for 24 hours. After filtration, the reaction mixture was concentrated and the acetone replaced by petroleum ether (b.p. 60–68°). The solution was then extracted with 5% aqueous sodium hydroxide, washed with water and dried over anhydrous magnesium sulfate. Distillation yielded, after a small forerun, the crotyl ether of 2,4-dimethyl-6-propenylphenol (17.43 g., 80.7%, b.p. 77–84° (0.04–0.08 mm.), n^{25}D 1.5317; no absorption in the region around 3500 cm.$^{-1}$).

Anal. Calcd. for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.13; H, 9.54.

2. **The Catalytic Hydrogenation of the Crotyl Ether of 2,4-Dimethyl-6-propenylphenol.**—Catalytic hydrogenation in 95% ethanol in the presence of Raney nickel gave the *n*-butyl ether of 2,4-dimethyl-6-propylphenol (b.p. 63–64° at 0.02 mm., n^{25}D 1.4875, 90.5% yield).

Anal. Calcd. for $C_{15}H_{24}O$: C, 81.76; H, 10.98. Found: C, 81.71; H, 11.06.

The *n*-butyl ether of 2,4-dimethyl-6-propylphenol was also prepared from 2,4-dimethyl-6-propylphenol. The *sec*-butyl ether of 2,4-dimethyl-6-propylphenol (n^{25}D 1.4918) was prepared for purposes of comparison by the catalytic hydrogenation of the *sec*-butyl ether of 2,4-dimethyl-6-propenylphenol.

3. **The Thermal Rearrangement of the Crotyl Ether of 2,4-Dimethyl-6-propenylphenol.**—The crotyl ether of 2,4-dimethyl-6-propenylphenol (21.6 g., 0.100 mole) was heated under reduced pressure at its reflux temperature for five hours until the temperature of the liquid reached 174° (44 mm.). The reaction product was dissolved in petroleum ether (100 ml., b.p. 60–68°). The petroleum ether solution was extracted: nine times with a 5% aqueous sodium hydroxide solution and seven times with Claisen alkali. After the organic layer was washed with water and dried over anhydrous magnesium sulfate, the organic layer yielded an undistillable residue. Acidification of the aqueous base extracts gave 2,4-dimethyl-6-propenylphenol (4.13 g., 25.4%, m.p. 72–73.5°).

The Claisen alkali extracts were neutralized by pouring into a beaker half-filled with ice and concentrated hydrochloric acid (26 ml.). The material which separated was taken up in petroleum ether (100 ml., b.p. 60–68°). After the petroleum ether extracts were combined and dried over anhydrous magnesium sulfate, the solvent was removed *in vacuo*. Distillation of the residue yielded the thermal rearrangement product, 2,4-dimethyl-6-(2-methyl-1,4-hexadienyl)-phenol (4.88 g., 22.6%, b.p. 76–80° at 0.05 mm., n^{25}D 1.5369).

Anal. Calcd. for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.01; H, 9.42.

A phenylurethan derivative, m.p. 117–118°, was prepared.

Anal. Calcd. for $C_{22}H_{25}NO_2$: C, 78.77; H, 7.51; N, 4.18. Found: C, 78.57; H, 7.62; N, 4.15.

4. **The Methyl Ether of 2,4-Dimethyl-6-(2-methyl-1,3-hexadienyl)-phenol: Isomerization and Methylation of the Rearrangement Product.**—In a 25-ml. flask were placed 2,4-dimethyl-6-(2-methyl-1,4-hexadienyl)-phenol (2.16 g., 0.010 mole) and a saturated solution (12 ml.) of potassium hydroxide in methanol. The methanol was removed by distillation until the temperature of the solution reached 110°. The condenser was then replaced by a reflux condenser and the solution was heated at 110–120° for six hours. Water (5 ml.) and methanol (5 ml.) were added to dissolve the contents of the flask. The reaction mixture was then treated with dimethyl sulfate (2.52 g., 0.020 mole) at the temperature of an ice-bath. After 30 minutes, the ice-bath was removed and the reaction mixture was heated to 55° for 15 minutes. Extraction with petroleum ether (b.p. 60–68°) followed. The combined extracts were then extracted with Claisen alkali and washed with water. The organic layer was chromatographed over alumina using petroleum ether to develop and elute the column. The eluate yielded on distillation the methyl ether of 2,4-dimethyl-6-(2-methyl-1,3-hexadienyl)-phenol (0.63 g., 27%, b.p. 97–99° at 0.2 mm., n^{25}D 1.5469).

Anal. Calcd. for $C_{16}H_{22}O$: C, 83.43; H, 9.63. Found: C, 83.24; H, 9.65.

IV. **The Proof of Structure of the Methyl Ether of 2,4-Dimethyl-6-(2-methyl-1,3-hexadienyl)-phenol.** 1. **Ozonolysis.**—The methyl ether was dissolved in ethanol and added to an aqueous ethanolic solution of 2,4-dinitrophenylhydrazine sulfate. Ozone was bubbled through this solution for five hours. The solution was decanted from the dark red tarry precipitate. This precipitate was dissolved in chloroform and chromatographed over alumina using a solution of chloroform and petroleum ether (b.p. 60–68°) to develop and elute the column. The eluate was concentrated and the precipitated material was recrystallized (three times) from a mixture of chloroform and acetone until the melting point remained constant at 218–220°. A mixed melting point of this material and the 2,4-dinitrophenylhydrazone of 2-methoxy-α,3,5-trimethylcinnamaldehyde was 218–220°.

2. **1-(2-Methoxy-3,5-dimethylphenyl)-2-methyl-1-hexen-3-ol.**—The Grignard reagent prepared from magnesium (0.49 g., 0.02 mole), *n*-propyl iodide (3.4 g., 0.02 mole) and dry ethyl ether (10 ml.) was treated with a solution of 2-methoxy-α,3,5-trimethylcinnamaldehyde (1.5 g., 0.0073 mole) in ethyl ether (15 ml.). The reaction mixture was heated to its reflux temperature for two hours, then cooled and hydrolyzed with a saturated solution (5 ml.) of ammonium chloride in water. The ether solution was decanted from the precipitated solid and this solid was washed twice with ethyl ether. The ether solutions were combined, washed with water and dried over anhydrous magnesium sulfate. The solvent was removed by distillation and the product, 1-(2-methoxy-3,5-dimethylphenyl)-1-hexen-3-ol (1.21 g., 49%), was collected at 104–110° (0.18 mm.), n^{26}D 1.5361.

Anal. Calcd. for $C_{16}H_{24}O_2$: C, 77.37; H, 9.74. Found: C, 78.08; H, 9.93.

3. **The Methyl Ether of 2,4-Dimethyl-6-(2-methyl-1,3-hexadienyl)-phenol.**—A mixture of 1-(2-methoxy-3,5-dimethylphenyl)-2-methyl-1-hexen-3-ol (1.10 g., 0.0044 mole) and freshly fused potassium bisulfate (1.0 g., 0.0073 mole) was placed in a 10-ml. distilling flask. The flask was partially immersed in a bath heated to 190° for 30 minutes. The reaction mixture was then cooled and extracted several times with petroleum ether (b.p. 60–68°). The extracts were chromatographed over alumina using petroleum ether to develop and elute the column. The eluate was distilled. The methyl ether of 2,4-dimethyl-6-(2-methyl-1,3-hexadienyl)-phenol (0.67 g., 66%) was collected at 98–102° (0.2 mm.), n^{25}D 1.5538.

Anal. Calcd. for $C_{16}H_{22}O$: C, 83.43; H, 9.63. Found: C, 83.28; H, 9.85.

The methyl ether and a saturated solution (10 ml.) of potassium hydroxide in methanol were placed in a 25-ml. flask and the methanol was removed by distillation until the temperature of the contents of the flask reached 110°. The reaction mixture was refluxed for six hours and then extracted with petroleum ether (b.p. 60–68°). The extracts were washed with water and chromatographed over alumina using petroleum ether to develop and elute the column. The eluate was concentrated and distillation yielded the methyl ether of 2,4-dimethyl-6-(2-methyl-1,3-hexadienyl)-phenol, n^{25}D 1.5458.

4. **Ozonolysis of the Synthetic Methyl Ether of 2,4-Dimethyl-6-(2-methyl-1,3-hexadienyl)-phenol.**—A solution of the methyl ether of 2,4-dimethyl-6-(2-methyl-1,3-hexadienyl)-phenol (0.23 g., 0.0010 mole) in ethanol (10 ml.) was added to an aqueous alcoholic solution of 2,4-dinitrophenylhydrazine sulfate. A mixture of ozone and oxygen was bubbled through this solution for 4.25 hours. The precipitated red solid (0.164 g., 42.5%, m.p. 180–196°) was separated and crystallized from a mixture of chloroform and methanol; m.p. 219–220°. A mixed melting point of this material with the 2,4-dinitrophenylhydrazone of 2-methoxy-α,3,5-trimethylcinnamaldehyde (section II, part 6) was 219–220°.

5. **1-(2-Methoxy-3,5-dimethylphenyl)-2-methyl-1-buten-3-one.**—A solution of the methyl ether of 3,5-dimethylsalicylaldehyde (8.2 g., 0.050 mole) in butanone (7.2 g., 0.10 mole) was treated with dry hydrogen chloride. The reaction mixture was then allowed to stand in the refrigerator for 48 hours. The mixture was then poured onto ice and 5% aqueous sodium hydroxide solution (10 ml.). The or-

ganic material was taken up in petroleum ether and this solution was washed with water. Distillation yielded 1-(2-methoxy-3,5-dimethylphenyl)-2-methyl-1-buten-3-one (7.19 g., 66%, b.p. 92–94° (1.0 mm.), $n^{25}\mathrm{D}$ 1.5510).

Anal. Calcd. for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 76.61; H, 8.67.

A **2,4-dinitrophenylhydrazone** derivative, m.p. 196.5–197°, was prepared.

Anal. Calcd. for $C_{20}H_{22}N_4O_5$: C, 60.29; H, 5.51; N, 14.06. Found: C, 60.20; H, 5.60; N, 13.79.

6. 1-(2-Methoxy-3,5-dimethylphenyl)-2,3-dimethyl-1-penten-3-ol.—The Grignard reagent prepared from magnesium (0.49 g., 0.020 mole), ethyl iodide (3.12 g., 0.020 mole) and dry ethyl ether (20 ml.) was treated with a solution of 1-(2-methoxy-3,5-dimethylphenyl)-2-methyl-1-buten-3-one (2.18 g., 0.010 mole) in ether (25 ml.). The reaction mixture was heated under reflux for one hour and hydrolyzed with a saturated solution (5 ml.) of ammonium chloride in water. Ether extraction, followed by distillation under reduced pressure yielded an impure sample of 1-(2-methoxy-3,5-dimethylphenyl)-2,3-dimethyl-1-penten-3-ol (1.84 g., 74%, b.p. 105–110° at 0.12 mm., $n^{25}\mathrm{D}$ 1.5350).

7. The Methyl Ether of 2,4-Dimethyl-6-(2,3-dimethyl-1,3-pentadienyl)-phenol.—A mixture of 1-(2-methoxy-3,5-dimethylphenyl)-2,3-dimethyl-1-penten-3-ol (1.2 g., 0.0050 mole) and freshly fused potassium bisulfate (1.5 g., 0.011 mole) was heated to 185° for 30 minutes. The reaction mixture was then extracted with petroleum ether (b.p. 60–68°). The extracts were chromatographed over alumina using petroleum ether to develop and elute the column. The eluate upon distillation gave the methyl ether of 2,4-dimethyl-6-(2,3-dimethyl-1,3-pentadienyl)-phenol (0.73 g., 64%, b.p. 94–96° at 0.20 mm., $n^{25}\mathrm{D}$ 1.5487).

Anal. Calcd. for $C_{16}H_{22}O$: C, 83.43; H, 9.63. Found: C, 83.13; H, 9.67.

Ozonolysis of this ether (0.24 g.) dissolved in an aqueous ethanolic solution of 2,4-dinitrophenylhydrazine sulfate gave an orange precipitate (0.150 g., 36%, m.p. 160–178°). Crystallization from a mixture of chloroform and methanol gave a product, m.p. 194–195.5°. A mixed melting point with the 2,4-dinitrophenylhydrazone described in section IV, part 5, was 194.5–195.5°.

MINNEAPOLIS 14, MINNESOTA

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Telomers from Carbon Monoxide and Olefins

BY R. E. FOSTER, A. W. LARCHAR, R. D. LIPSCOMB AND B. C. MCKUSICK

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It is known that free-radical initiators can cause ethylene and carbon monoxide to copolymerize to polyketones of high molecular weight. When the copolymerization of olefins and carbon monoxide is carried out in the presence of active telogens (AB), telomers of two general types are formed: $ACO(CH_2CHR)_nB$ and $A(CH_2CHR)_nCOB$. Telogens which have been studied include mercaptans, alcohols, ketones, aldehyde derivatives, carbon tetrachloride and chlorine. The products of these reactions are aldehydes, ketones or derivatives of acids.

Free radical initiators can cause ethylene and carbon monoxide to copolymerize to polyketones of high molecular weight.[1] This paper reports an extension of this work. When the copolymerization is done in the presence of active chain-transfer agents, telomers[2] are formed. The propagation steps of the chain reactions whereby the chain transfer agent or telogen, AB, reacts with $CH_2{=}CHR$ and carbon monoxide to give products of two distinct types, $ACO(CH_2CHR)_nB$ and $A(CH_2CHR)_nCOB$, may be written

$$A\cdot + n(CH_2{=}CHR) \longrightarrow A(CH_2CHR)_n\cdot \qquad (1)$$

$$A(CH_2CHR)\cdot_n + CO \longrightarrow A(CH_2CHR)_n\dot{C}{=}O \qquad (2)$$

$$A(CH_2CHR)_n\dot{C}{=}O + AB \longrightarrow A(CH_2CHR)_nCOB + A\cdot \qquad (3)$$

and

$$A\cdot + CO \longrightarrow A\dot{C}{=}O \qquad (4)$$

$$A\dot{C}{=}O + n(CH_2{=}CHR) \longrightarrow ACO(CH_2CHR)_n\cdot \qquad (5)$$

$$ACO(CH_2CHR)_n\cdot + AB \longrightarrow ACO(CH_2CHR)_nB \qquad (6)$$

As described in the following sections, the nature of AB governs which of these two modes of telomerization occurs, and the type of products formed: aldehydes, ketones or derivatives of acids. In addition, in most of the solvents investigated, ethylene telomers were formed as by-products without the participation of carbon monoxide. Table I shows the products of various telomerizations with olefins and carbon monoxide.[3]

Mercaptans as Telogens.—When ethyl mercaptan was treated with propylene and carbon monoxide in the presence of di-(*t*-butyl) peroxide at 130° and a pressure of 3000 atm., 3-ethylmercapto-2-methylpropanal and ethyl *n*-propyl sulfide were obtained in 16 and 50% yields, respectively. The structure of the aldehyde was proved by comparison of its 2,4-dinitrophenylhydrazone with an authentic sample. The probable chain-propagation steps are

$$EtS\cdot + CH_2{=}CHMe \rightleftarrows EtSCH_2\dot{C}HMe \qquad (7)$$

$$EtSCH_2\dot{C}HMe + CO \rightleftarrows EtSCH_2CHMe\dot{C}{=}O \qquad (8)$$

$$EtSCH_2CHMe\dot{C}{=}O + EtSH \rightleftarrows EtSCH_2CHMeCHO + EtS\cdot \qquad (9)$$

That all three steps are reversible was shown by heating the aldehyde with di-(*t*-butyl) peroxide, which caused decomposition to propylene, carbon monoxide and ethyl mercaptan. Since peroxides normally decompose RCHO to CO and RH,[4,5] ethyl *n*-propyl sulfide was the expected product, but none was detected. The reversibility of equation 8 suggests that a high pressure of carbon monoxide is desirable for telomerizations with carbon

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