

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OREGON STATE COLLEGE]

The Claisen Rearrangement. I. Substituted Allyl Ethers in the *para* Rearrangement¹

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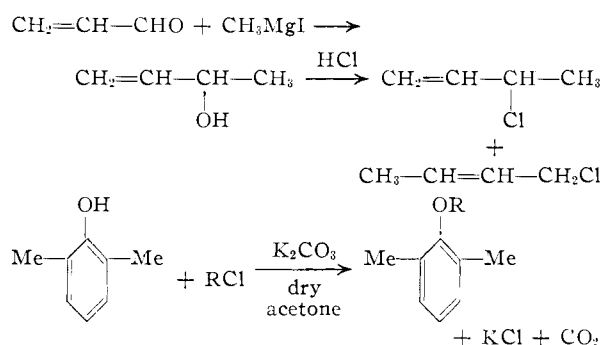
Previous work has established that γ -substituted allyl groups migrate to the *para* position without inversion. The rule of non-inversion in the *para* rearrangement has not been shown conclusively to apply generally to alpha substituted allyl groups. This paper reports the synthesis of the α -methylallyl and γ -methylallyl ethers of 2,6-dimethylphenol. Those ethers have been identified and submitted to rearrangement. The structures of the phenolic products have been established by analytical methods and by synthesis. This work has shown that the rule of non-inversion can now be extended to the α -substituted ethers.

In establishing a mechanism for the well-known *ortho* Claisen rearrangement² the inevitable inversion of the allyl group during migration played a particularly important role. Consequently it may be expected that inversion or lack of it will be a dominant factor in the development of understanding of the *para* rearrangement. A number of investigations have treated the case of γ -substituted allyl groups in the *para* rearrangement. These studies have shown that γ -methylallyl,³ γ -ethylallyl^{4,5} and γ -phenylallyl³ groups migrate to the *para* position without inversion. Thus the lack of inversion may be assumed to apply generally to γ -substituted allyl groups in the *para* rearrangement. The case for α -substituted allyl groups is not as simple.

The original, and until very recently the only, report^{3,5} on an α -substituted allyl group indicated surprisingly that inversion does occur. Unfortunately, however, sufficient proof of structure for the supposed α -ethylallyl group in the ether studied was not provided. A recent communication⁶ has shown in elegant fashion that the original workers were in error about the identity of their so-called α -ether. This later, more thorough study has shown that a mixture of α -ethylallyl and γ -ethylallyl ethers can be obtained essentially by the procedure of the earlier workers, and that the mixture can be treated so as to rearrange only the α -ether. The rearrangement of the α -ether very definitely appears to proceed without inversion.

The object of the research reported here is to provide a study of the migratory allyl group in which the structure of both the original ether and its rearrangement product are known definitely. The molecule chosen was α -methylallyl 2,6-dimethylphenyl ether, and for comparative purposes the γ -methylallyl 2,6-dimethylphenyl ether was prepared and studied concurrently. Neither of these ethers has been prepared previously. Preparation of both the desired ethers was accomplished

by the series of reactions shown below. The isomeric chlorides were employed instead of bromides because of their greater stability. They were purified by careful fractional distillation until their physical constants were in substantial agreement with those found by previous workers.⁷



The major problem here lies not in the preparation but in the proof of the structures of the ethers. It is, of course, the structure of the allyl portion of the ether which must be known. Cleavage of the allylic double bond was accomplished by ozonolysis, and the original products were reduced with zinc and acetic acid to a mixture of aldehydes. The problem of identification of formaldehyde in this mixture in at least a semi-quantitative manner proved formidable. In our hands the methone analysis did not give good results on mixtures obtained from model compounds such as allyl phenyl ether. That colorimetric procedure described in the experimental section was the best compromise. By that method the ether from α -methylallyl chloride gave $70 \pm 10\%$ formaldehyde while the ether from the isomeric chloride gave 1.5% formaldehyde.

The chemical analysis above was confirmed by the infrared spectra of the compounds (Fig. 1).⁸ Thus the strong band at 919 cm^{-1} in the α -ether can be attributed to the presence of a terminal methylene group.⁹ The band at 1263 cm^{-1} which appears in both ethers is undoubtedly due to the aryl ether grouping.⁸ It is most interesting to find a band in the $965\text{--}980 \text{ cm}^{-1}$ region in each ether since absorption here generally indicates an internal double bond of *trans* configuration.⁹ The strong absorption at 3420 cm^{-1} which appears in the re-

(7) J. D. Roberts, W. G. Young and S. Winstein, *ibid.*, **64**, 2157 (1942).

(8) For a complete review of the interpretation of infrared spectra see F. A. Miller in H. Gilman, "Organic Chemistry," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 122.

(9) W. B. Treumann and F. T. Wall, *Anal. Chem.*, **21**, 1161 (1949).

(1) Published with the approval of the Monograph Publications Committee, Oregon State College, as Research Paper No. 236, School of Science, Department of Chemistry. Presented in part before the Northwest Regional Meeting of the American Chemical Society at Corvallis, Oregon, June, 1952. This article is based on a thesis submitted by R. W. Ledeen in partial fulfillment of the requirements for the Ph.D. degree at Oregon State College.

(2) For a review of the Claisen rearrangement see S. Tarbell in R. Adams, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 1.

(3) O. Mumm and F. Moller, *Ber.*, **70**, 2214 (1937).

(4) O. Mumm, F. Hornhardt and J. Diederichsen, *ibid.*, **72**, 100 (1939).

(5) O. Mumm and J. Diederichsen, *ibid.*, **72**, 1523 (1939).

(6) S. J. Rhoads, R. Raulins and R. D. Reynolds, *THIS JOURNAL*,

75, 2531 (1953).

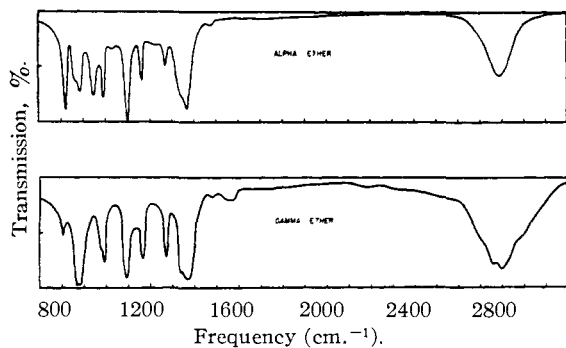


Fig. 1.—The infrared spectra of α -methylallyl 2,6-dimethylphenyl ether (top) and γ -methylallyl 2,6-dimethylphenyl ether (bottom).

arranged products (Fig. 2) but not the original ethers is apparently the result of associated phenolic hydroxyl groups.¹⁰ These data, therefore, give confirmation to the statement that the α -ether has the postulated structure but apparently is contaminated by a certain amount of γ -ether. Both ethers are substantially free from phenolic materials.

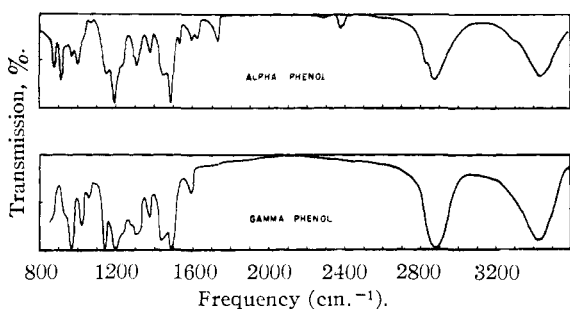


Fig. 2.—The infrared spectra of 2,6-dimethyl-4-(α -methylallyl)-phenol (top) and 2,6-dimethyl-4-(γ -methylallyl)-phenol (bottom).

Each of the ethers rearranged smoothly to give good yields of the *p*-allylated phenols. The oily phenols were isolated and purified as their phenylurethan derivatives. Although the melting point range of the urethan obtained from 2,6-dimethyl-4-crotylphenol seems unusually broad further recrystallization did not affect it. It may possibly be attributed to the presence of *cis-trans* isomers since the phenomenon disappears along with the double bond during hydrogenation. The position of the double bond in the allylic group was determined in each case by the ozonolysis method described above. The rearrangement product from the α -methylallyl ether again proved to have a terminal double bond (56% formaldehyde found), whereas the phenylurethan of the product from the isomeric ether did not (5% formaldehyde found). Infrared spectra confirmed these results since the α -product showed a strong band at 911 cm^{-1} where the isomer showed no absorption (Fig. 2). The presence of the band at 3420 cm^{-1} in both products is indicative of their phenolic nature.

(10) J. J. Fox and A. E. Martin, *Proc. Royal Soc. (London)*, **A162**, 419 (1937).

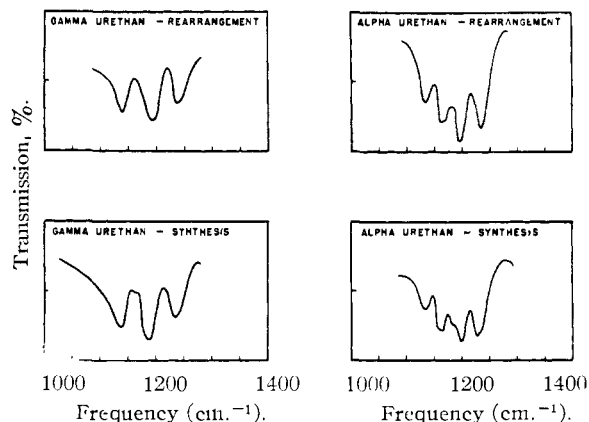
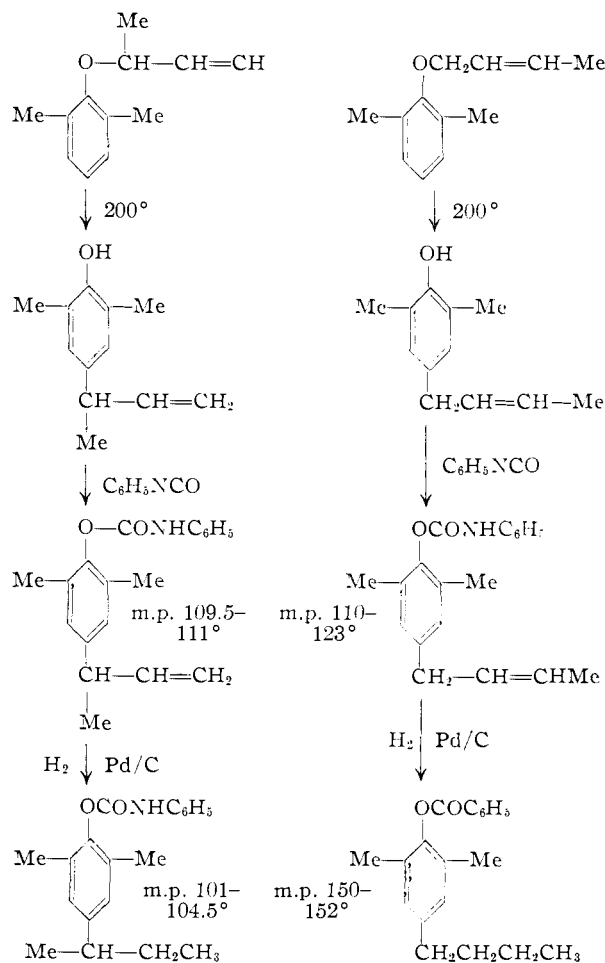


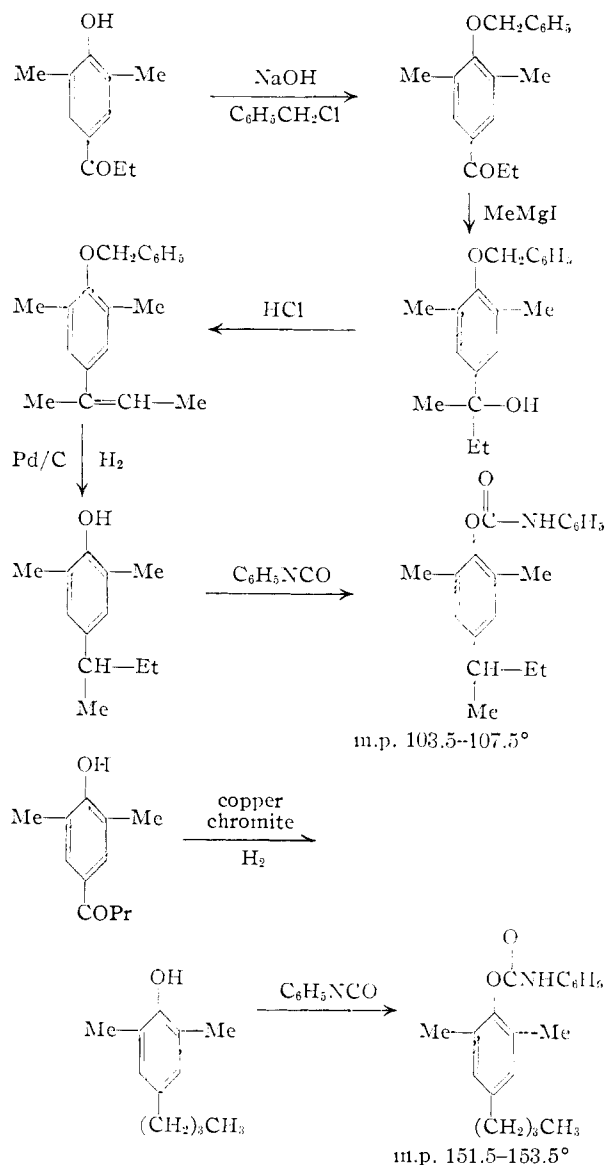
Fig. 3.—The infrared spectra of the urethans of 2,6-dimethyl-4-butylphenol (γ -urethan) and 2,6-dimethyl-4-(α -methylpropyl)-phenol (α -urethan).

Although the evidence presented above indicates strongly that rearrangement occurred in each case without inversion of the migratory methylallyl group, a more thorough proof of the structures of the products by synthetic means seemed desirable.



However, the presence of the double bond provides a special problem in the synthesis, and its position is of no importance to the question of inversion. Accordingly, therefore, both 1-(3,5-dimethyl-4-

hydroxyphenyl)-butane and 2-(3,5-dimethyl-4-hydroxyphenyl)-butane have been synthesized. Their preparation was simplified by the fact that both of the required *p*-acyl compounds had been prepared previously.¹¹ During the synthesis of 2-



(3,5-dimethyl-4-hydroxyphenyl)-butane dehydration of the tertiary alcohol proved to be unexpectedly difficult since the phenolic alcohol was sensitive to acids and the Hibbert method did not prove successful. The benzoyl ether of the ketone was a solid and provided sufficient protection to enable acid dehydration to be accomplished in good yield. Since the desired phenols are oils their phenylurethans were formed in order to provide solid materials for comparison studies. Melting points of mixtures of each synthetic urethan and its analog from the appropriate rearrangement product confirmed the earlier work. A comparison of the infrared spectra of the two synthetic urethans and the hydrogenated urethans from the rearrangement

(11) K. v. Auwers and E. Janssen, *Ann.*, **483**, 44 (1930).

again provided further evidence for the assignment of structures.

There can be no doubt now that the *para* rearrangement of an α -substituted allyl group, if that substituent is a simple alkyl radical, leads to a *para* allylic product of uninverted structure. Since γ -substitution whether alkyl or aryl, as well as unsubstituted allyl groups,¹² follow the rule of non-inversion, it is strongly to be suspected that all α -substituted allyl ethers also will follow that rule. The knowledge that a non-inversion rule can be applied generally to the *para* rearrangement seems to remove the last obstacle preventing acceptance of the Hurd-Pollack¹³ mechanism for the *para* Claisen rearrangement.

Acknowledgment.—The authors are most happy to acknowledge the aid given by Dr. J. C. Decius of Oregon State College in interpretation of infrared data used in this research. We also are indebted to the Shell Development Company for a gift of acrolein which speeded this work.

Experimental

1-Buten-3-ol.—This alcohol was prepared from acrolein by the procedure of Prevost.¹⁴ Purification was carried out by distillation; b.p. 94–99°, n_D^{20} 1.4126. The alcohol is reported¹⁵ to boil at 95.5–96.5° with n_D^{20} 1.412746. The crude alcohol can be used for subsequent preparations.

3-Chlorobutene-1 and 1-Chlorobutene-2.—Preparation of a mixture of these chlorides was accomplished by the method of Meisenheimer.¹⁶ Separation into the two isomeric chlorides was done in a 3' helices-packed column. The 3-chlorobutene-1 distilled in the low boiling fraction, b.p. 63.5–66° (lit.⁷ 63.5°), n_D^{20} 1.4148 (lit.⁷ 1.4150), d_{20}^{20} 0.8902 (lit.⁷ 0.8978). The higher-boiling fraction, 1-chlorobutene-2, distilled at 46–46.5° (191 mm.) (lit.⁷ 45.6–45.7° at a similar pressure), n_D^{20} 1.4348 (lit.⁷ 1.4351), d_{20}^{20} 0.9248 (lit.⁷ 0.9282).

γ -Methylallyl 2,6-Dimethylphenyl Ether.—Essentially the method of Claisen¹⁷ as recommended by Alexander¹⁸ was used for this preparation. A mixture of 48.0 g. (0.39 mole) of 2,6-dimethylphenol, 48.0 g. (0.53 mole) of 1-chlorobutene-2, 60 g. of anhydrous potassium carbonate and 120 ml. of dry acetone was boiled under reflux with constant stirring over a period of 12 hours. After standing at room temperature three to four hours longer the mixture was poured into 500 ml. of cold water. This material was extracted three times with 50-ml. portions of ether, the combined ether extracts washed with 10% sodium hydroxide until no further phenolic material was found in the wash liquor, then twice with distilled water and finally dried over anhydrous magnesium sulfate. After being separated from the desiccant and the ether the product was distilled under reduced pressure; b.p. 84–88° (1 mm.), n_D^{20} 1.5082, d_{20}^{20} 0.939, *M*_r calcd. 55.20, found 55.98. The yield was 20.5 g. or 30% of the theoretical.

Anal. Calcd. for $C_{12}H_{16}O$: C, 81.7; H, 9.15. Found: C, 81.6; H, 8.72.

α -Methylallyl 2,6-Dimethylphenyl Ether.—This ether was prepared by the process described above except that the temperature during the 12-hour period was maintained at 65–70°. The product was distilled under reduced pressure; b.p. 85–90° (approx. 5 mm.), n_D^{20} 1.5068, d_{20}^{20} 0.9399, yield 10.3%, *M*_r calcd. 55.20, found 55.77.

Anal. Calcd. for $C_{12}H_{16}O$: C, 81.7; H, 9.15. Found: C, 81.7; H, 8.86.

2,6-Dimethyl-4-(γ -methylallyl)-phenol.—Rearrangement of γ -methylallyl 2,6-dimethylphenyl ether was carried out

(12) J. P. Ryan and P. R. O'Connor, *This Journal*, **74**, 5866 (1952).

(13) C. D. Hurd and M. A. Pollack, *J. Org. Chem.*, **3**, 550 (1939).

(14) C. Prevost, *Ann. Chim.*, **10**, 112, 147 (1928).

(15) W. G. Young and J. P. Lane, *This Journal*, **69**, 2051 (1937).

(16) J. Meisenheimer and J. Link, *Ann.*, **479**, 254 (1930).

(17) L. Claisen and O. Eisleb, *ibid.*, **401**, 79 (1913).

(18) E. R. Alexander and R. W. Kluiber, *This Journal*, **73**, 4304 (1951).

by heating a small sample (4.9 g.) sealed in a Carius tube in an oven at 200° for six hours. The product was distilled *in vacuo*; b.p. 107–109.5° (1 mm.), n_{D}^{20} 1.5376, d_{4}^{20} 0.9537, yield 79%.

Anal. Calcd. for $C_{12}H_{16}O$: C, 81.7; H, 9.15. Found: C, 81.7; H, 8.55.

The phenylurethan of the above phenol was prepared by the procedure of Shriner and Fuson.¹⁹ However it was necessary to heat the reaction mixture for 45 minutes to ensure complete reaction. The urethan was recrystallized from ligroin; m.p. 110–123°. Further recrystallization from ligroin as well as a number of other solvents failed to shorten the melting range.

Anal. Calcd. for $C_{19}H_{21}O_2N$: C, 77.3; H, 7.16. Found: C, 77.3; H, 7.15.

Phenylurethan of 1-(3,5-Dimethyl-4-hydroxyphenyl)-butane.—The urethan of 2,6-dimethyl-4-(γ -methylallyl)-phenol was hydrogenated in dioxane at 29 p.s.i. with a palladium-on-charcoal catalyst. The resulting white solid, after two crystallizations from ligroin, melted at 150–152°.

Anal. Calcd. for $C_{19}H_{23}O_2N$: C, 76.7; H, 7.79. Found: C, 76.7; H, 7.76.

2,6-Dimethyl-4-(α -methylallyl)-phenol.—A sample of α -methylallyl 2,6-dimethylphenyl ether was rearranged by the method described for the γ -ether. The phenolic product boiled at 75–90° (1 mm.); n_{D}^{20} 1.5359, d_{20}^{20} 0.9574, yield 80%.

Anal. Calcd. for $C_{12}H_{16}O$: C, 81.7; H, 9.15. Found: C, 81.7; H, 8.89.

The phenylurethan of this product was prepared by the method described above. Repeated recrystallization from ligroin gave a crystalline material; m.p. 109.5–111°.

Anal. Calcd. for $C_{19}H_{21}O_2N$: C, 77.3; H, 7.16. Found: C, 77.3; H, 7.05.

Phenylurethan of 2-(3,5-Dimethyl-4-hydroxyphenyl)-butane.—The urethan of 2,6-dimethyl-4-(α -methylallyl)-phenol was hydrogenated in dry ether at 27 p.s.i. with a palladium-on-charcoal catalyst. The saturated urethan was recrystallized from ligroin; m.p. 101–104.5°.

Anal. Calcd. for $C_{19}H_{23}O_2N$: C, 76.7; H, 7.79. Found: C, 76.7; H, 7.68.

Terminal Methylene Group Analysis.—This process employs a standardized ozonolysis reaction followed by reduction of the ozonide to a mixture of aldehydes. Formaldehyde was determined by the colorimetric method of Deniges.²⁰ Careful standardization of every step is necessary since model compounds such as allyl phenyl ether give less than 100% formaldehyde.

A sample containing 0.006 mole of the unsaturated compound was dissolved in 30 ml. of dry carbon tetrachloride. The solution was cooled in an ice-bath while a stream of oxygen containing 2.3% ozone was passed in at a rate of 0.33 l./min. for 24 minutes. This solution was added to a cold (ice-bath) mixture of 35 ml. of glacial acetic acid, 35 ml. of distilled water and 6 g. of zinc dust. During the period of addition (20 minutes) the mixture was stirred and 14 mg. of zinc dust was added in small portions. After all of the zinc had dissolved the mixture was heated on a boiling water-bath for 45 minutes then cooled. Both zinc dust (if any) and the carbon tetrachloride layer were removed by filtration using a previously moistened filter paper. The carbon tetrachloride was extracted with three 10-ml. portions of distilled water and the extracts added to the original filtrate. The total solution was diluted then to a volume of 500 ml. with distilled water, and a 10-ml. aliquot analyzed for formaldehyde as described below.

A 10-ml. sample of formaldehyde solution was mixed with 5.0 ml. of sulfuric acid (150 ml. of concd. sulfuric acid and 300 ml. of distilled water) and 5.0 ml. of modified Schiff reagent²¹ (1.0 g. of rosaniline hydrochloride dissolved in 600 ml. of warm water, with 10.0 g. of anhydrous sodium bisulfate and 10 ml. of concd. hydrochloric acid added after cooling) were mixed in a 100-ml. volumetric flask and allowed to stand for three hours. The violet liquid was di-

luted to 100 ml. and a sample of that solution was diluted sixteen-fold and the absorption determined in Beckman model B spectrophotometer. The result was compared against a series of standards prepared from formaldehyde solutions of known concentration.

Duplicate runs on a sample of allyl 2,6-dimethylphenyl ether resulted in recovery of only 75% formaldehyde by this method. Thus a factor of 4/3 was applied to subsequent runs to allow for the low result.

The following results were obtained when the indicated compounds were treated by this method: α -methylallyl 2,6-dimethylphenyl ether (duplicate runs), 61%, 80% formaldehyde; γ -methylallyl 2,6-dimethylphenyl ether, 1.5% formaldehyde; 2,6-dimethyl-4-(α -methylallyl)-phenol, 56% formaldehyde; phenylurethan of 2,6-dimethyl-4-(γ -methylallyl)-phenol, 5% formaldehyde.

2,6-Dimethyl-4-butyrophenol.—Fifty grams of 2,6-dimethylphenol was esterified with 49.0 g. of butyryl chloride. The ester was purified by distillation; b.p. 87.5–95.5° (1 mm.), n_{D}^{20} 1.4920, yield 80%. This ester was rearranged by the Fries method according to the directions of Auwers.¹¹ After having stood at room temperature for 24 hours the reaction mixture was treated to separate the phenolic product from the nitrobenzene and aluminum chloride. The solid product crystallized nicely from hexane; m.p. 127–127.5° (lit.¹¹ 124–125°).

2,6-Dimethyl-4-propiofenol.—This product was prepared in a manner analogous to the above ketone by the Fries reaction.¹¹ The 2,6-dimethylphenyl propionate boiled at 122–124° (6 mm.), n_{D}^{20} 1.4941. The final product was a solid which melted, after recrystallization from hexane, at 106–108° (lit.¹² 106–106.5°).

Phenylurethan of 1-(3,5-Dimethyl-4-hydroxyphenyl)-butane.—A sample (2.80 g.) of 2,6-dimethyl-4-butyrophenol was hydrogenated in ethanol solution with copper chromite catalyst. An initial pressure of 145 atmospheres, and a temperature of 200° were employed. No attempt was made to isolate the 1-(3,5-dimethyl-4-hydroxyphenyl)-butane, but the oil was treated with phenyl isocyanate according to the directions of Shriner and Fuson.¹⁹ The solid urethan was recrystallized from ligroin; m.p. 148–151°. The melting point of a mixture of this urethan with the hydrogenated urethan from the γ -ether rearrangement product melted at 150–152.5°.

Benzyl 2,6-Dimethyl-4-propiofenyl Ether.—A mixture containing 5.5 g. (0.02 mole) of 2,6-dimethyl-4-propiofenol, 5.0 g. (0.04 mole) of benzyl chloride, 25 ml. of methanol, 5 ml. of water and 1.2 g. of potassium hydroxide was heated under reflux for five hours. The benzyl ether was taken up in ether and the solution washed with 15% potassium hydroxide and then with water. After the ether had been removed the white product was crystallized from petroleum ether; m.p. 70.5–72°.

Anal. Calcd. for $C_{18}H_{20}O_2$: C, 80.6; H, 7.51. Found: C, 80.6; H, 7.43.

Phenylurethan of 2-(3,5-Dimethyl-4-hydroxyphenyl)-butane.—A solution of methylmagnesium iodide prepared from 0.633 g. (0.026 mole) of magnesium and 2.4 ml. of methyl iodide was treated with 2.4 g. (0.009 mole) of the benzyl ether (above). The complex was destroyed with saturated ammonium chloride and the oily alcohol dehydrated directly by heating it under reflux for three hours with a mixture of 30 ml. of methanol and 0.2 ml. of concd. hydrochloric acid. The acid was neutralized and the methanol removed by distillation. Then the product was taken up in ether, the solution washed with water and dried over anhydrous magnesium sulfate. Evaporation of the ether produced an oil which gave a good test for unsaturation.

The unsaturated benzyl ether was hydrogenated in ether solution with palladium-on-charcoal catalyst using 2.5 atmospheres initial hydrogen pressure. The catalyst was removed by filtration, the ether by evaporation and the residual oil was shown to be a phenol since it was readily soluble in aqueous potassium hydroxide. The urethan was prepared in the manner described earlier and recrystallized from *n*-heptane; m.p. 103.5–107.5°. A mixture of this urethan and the hydrogenated urethan from the α -ether rearrangement product melted at 99–105.5°.

Measurement of Infrared Spectra.—The infrared spectra were measured with a Perkin-Elmer model 12C spectrometer remodeled to function as a double-beam continuous-recording instrument. In all cases sodium chloride cells

(19) R. L. Shriner and R. C. Fuson, "Systematic Identification of Organic Compounds," 3rd Edition, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 164.

(20) G. Deniges, *Compt. rend.*, **150**, 529 (1910).

(21) E. Elvove, *Ind. Eng. Chem.*, **9**, 295 (1917).

were employed. The spectra of the liquid ethers and phenols were determined from thin films of the pure liquids,

whereas the urethans were used as inulls in perfluorokerosene. CORVALLIS, OREGON

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN]

Unsaturated Sulfonic Acids. IV. Preparation and Properties of α -Bromoalkenesulfonyl Chlorides

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Unsaturated sulfonyl chlorides are readily prepared in good yields from β -chlorosulfonyl chlorides (from β -hydroxysulfonic acids) through the action of hindered bases at low temperatures. Unsaturated sulfonamides are available through reaction with amines, using low temperatures to suppress the competing addition to the double bond. Bromine adds to the chlorides in non-polar media to form dibromides which can be smoothly dehydrobrominated to α -bromo- α,β -unsaturated sulfonyl chlorides by hindered bases at low temperatures. α -Bromoethylenesulfonyl chloride reacts with triethylamine at -70° to form an unidentified compound, possibly acetylenesulfonyl chloride. α -Bromostyrenesulfonyl chloride reacts sluggishly with bases to eliminate (at least partially) the sulfo group; this effect is ascribed to its geometrical configuration.

Previous work with unsaturated sulfonic acids² indicated that its extension to acetylenic sulfonic acids would be of considerable interest. Accordingly, it was necessary to devise a synthetic procedure. There is only one report on an acetylenic sulfonic acid,³ and the evidence for its structure is only an analysis. It seems likely that the product obtained was derived by addition to the acetylenic triple bond rather than by hydrogen substitution. Accordingly, we sought other methods of synthesis.

An attempt to sulfonate phenylacetylene with dioxane-sulfotrioxide was unsuccessful. The bulk of the sulfur trioxide was converted to forms other than sulfate, but it was not possible to isolate a pure unsaturated sodium salt. The reaction of sodium phenylacetylide with dioxide-sulfotrioxide was likewise unsuccessful. A further study of these sulfonations is being made. Metal phenylacetylides did not appear to react with sulfur dioxide under standard sulfination conditions.

It then seemed reasonable to attempt the introduction of a triple bond by the dehydrobromination of either an α,β -dibromoalkanesulfonic acid or an α - or β -bromoalkenesulfonic acid. Accordingly, attention was turned to the synthesis and reactions of these compounds. It was previously known that α,β -unsaturated sulfonic acids were brominated rapidly in aqueous solution by substitution at the position *alpha* to the sulfo group.^{4,5} On the other hand, styrenesulfonyl chloride and styrenesulfonamide had been shown to brominate only slowly in carbon tetrachloride or acetic acid by (presumably) a free-radical mechanism. The products are dibromides which eliminate hydrogen bromide on treatment with base. It was known that dehydrobromination of α -bromoethylenesul-

fonic acid⁵ or α -bromostyrenesulfonic acid^{6,7} by the action of alkalis converted either compound largely into tarry materials and liberated sulfite ion. However, it seemed that dehydrobromination of a covalent derivative of the sulfonic acid might be successful.

Bromination and Dehydrobromination.—It was known that addition of bromine to styrenesulfonyl chloride in carbon tetrachloride solution is strongly light catalyzed and appears to be oxygen catalyzed.⁴ In the dark, no visible reaction occurred in fifteen days, and we found that addition was not accelerated by iodine. In ordinary room fluorescent illumination, the addition of one mole of bromine to the double bond was substantially complete in four to eight hours; under direct illumination by a 50-watt bulb, only an hour was needed. Oxygen is actually an anticatalyst for the bromination in carbon tetrachloride or acetic acid solution since, when the separate solutions of styrenesulfonyl chloride and bromine in carbon tetrachloride or acetic acid were first deaerated by bubbling nitrogen through them, the addition required only ten minutes.⁸ The oily dibromide could not be induced to crystallize, but it could be converted to α -bromostyrenesulfonyl chloride by 2,6-lutidine or triethylamine. The crystalline unsaturated bromosulfonyl chloride (82% yield) formed an amide identical with that prepared in low yield from sodium α -bromostyrenesulfonate by the action of phosphorus pentachloride and ammonia.⁶

Ethylenesulfonyl chloride added bromine more rapidly than its phenylated analog. In this case, the dibromide could be isolated by distillation (with partial dehydrobromination). The crude material was also converted directly into α -bromoethylenesulfonyl chloride, by the action of 2,6-lutidine in ether at -50° , in 68% yield based on ethylenesulfonyl chloride.

Further Dehydrobromination.— α -Bromoethylenesulfonyl chloride in absolute ether at -70° reacted vigorously with triethylamine to precipitate triethylamine hydrobromide. The filtrate upon

(1) The author is indebted to the Horace H. Rackham School of Graduate Studies for a Summer Faculty Research Fellowship which made possible this work. Presented before the Los Angeles meeting of the American Chemical Society, March, 1953.

(2) C. S. Rondestvedt, Jr., and J. C. Wygant, *THIS JOURNAL*, **76**, 509 (1954), and previous papers.

(3) F. Krafft and G. Heizmann, *Ber.*, **33**, 3586 (1900). Cf. C. M. Suter, "Organic Chemistry of Sulfur," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 175.

(4) F. G. Bordwell and C. S. Rondestvedt, Jr., *THIS JOURNAL*, **70**, 2429 (1948).

(5) R. P. Kohler, *Am. Chem. J.*, **24**, 340 (1899).

(6) W. E. Truce, Ph.D. thesis, Northwestern University, 1943.

(7) T. Y. Yi, unpublished experiments in this Laboratory.

(8) C. D. Ver Nooy and R. L. Grimsley, unpublished results in this Laboratory.