[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE WASHINGTON SQUARE COLLEGE OF NEW YORK UNIVERSITY]

The Rearrangement of Alkenyl Phenyl and Cresyl Ethers and the Syntheses of Isopropenyl Phenols and their Reduction Products[1]

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Theoretical Part

In previous publications report was given on the successful rearrangement of saturated alkyl phenyl ethers[2] brought about chiefly by the action of an acetic–sulfuric acid mixture. That the chemical nature of the catalyzer does not play any integral part in these molecular migrations had been shown[3] and has been further verified recently by Sowa, Hinton and Nieuwland,[4] who checked the experimental findings of this Laboratory in the synthesis of thymol and its isomers from the corresponding isopropyl phenyl ethers. The purpose of the research presented in this communication was to extend these studies in molecular rearrangements to short-chain, alkenyl phenyl ethers (isopropenyl phenyl and cresyl ethers) in order to establish the limitations, general applicability, rules of migration, and, in general, to obtain a better theoretical understanding of this phenomenon. The latter object gains in interest, especially in view of the present-day conceptions of the reaction mechanism involved in such molecular transitions. As will be shown later, the accomplished rearrangement of the various isopropenyl phenyl ethers, as set forth herein, makes a rigid application of some of the present-day theories quite difficult. Therefore, in the following, attempts have been made to harmonize and to bridge various gaps between such accepted theories and the new experimental findings by broadening the scope of the former and incorporating certain physico-chemical energy principles.

Any such attempts, however, required first of all the determination of the structure and especially the position taken up by the migrating group in the benzene nucleus.

The isopropenyl phenyl and cresyl ethers mentioned above were prepared by treating isopropenyl bromide with the appropriate potassium phenolate. The rearrangement of the ethers was carried out by refluxing with a 10% solution by volume of sulfuric in glacial acetic acid.

Ortho Rearrangement.—The first point of attack was isopropenyl

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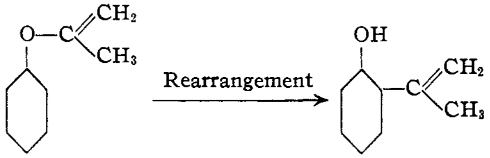
[1] From Part I of the thesis presented by Edward A. Storch to the Faculty of the Graduate School of New York University in candidacy for the degree of Doctor of Philosophy.

[2] Niederl and Natelson, THIS JOURNAL, **53**, 272, 1928 (1931); **54**, 1063 (1932).

[3] Rheinische Kampfer-Fabrik, Swiss Patent 144,207 (1931); Schoeller, U. S. Patent 1,835,344 (1931).

[4] Sowa, Hinton and Nieuwland, THIS JOURNAL, **54**, 2019 (1932).

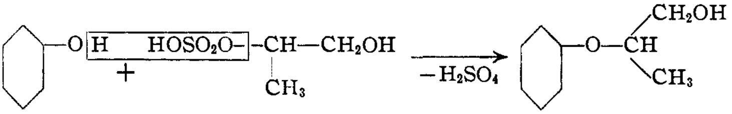
phenyl ether. Its rearrangement gave rise to a product, the main portion of which was identified as *o*-isopropenylphenol.[5] It yielded upon catalytic reduction *o*-isopropylphenol,[6] which was identified as *o*-isopropylphenoxyacetic acid.[7] The original isopropenylphenol yielded a crystalline hexabromo derivative which was different from the corresponding bromine derivative of *p*-isopropenylphenol, reported in the literature.[8] The above evidence suggests that ortho migration was favored and that the final product was *o*-isopropenylphenol.



This same product was resynthesized from allyl alcohol and phenol in the presence of concentrated sulfuric acid in the cold. A polymer was obtained which on distillation gave *o*-isopropenylphenol, and the following mechanism explaining its formation has been shown to be a general one for addition of phenols to an ethylenic linkage, with sulfuric acid as the condensing agent.[9] The first step involved the addition of sulfuric acid to allyl alcohol with the formation of α-allylol sulfate

$$CH_2{=}CHCH_2OH + H_2SO_4 \longrightarrow CH_3CH(CH_2OH)OSO_2OH$$

In the next step ether formation can be assumed to take place[10] with the formation of β-phenoxypropylene glycol



From here on, as shown below, the reaction may have proceeded in two ways: first, elimination of water in the presence of concentrated sulfuric acid at this stage, followed by rearrangement; or, second, spontaneous rearrangement with subsequent elimination of water under the given anhydrous condition. In any case, the polymer of *o*-isopropenylphenol was isolated. This polymer, on subsequent pyrolysis, finally yielded the *o*-isopropenylphenol, the physical and chemical properties of which checked with the material obtained upon the rearrangement of the isomeric ether and with the constants given in the literature.

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[5] (a) Béhal and Tiffeneau, *Bull. soc. chim.*, [4] **3**, 315 (1908); (b) Hoering and Baum, German Patent 208,886 (1909); (c) Fries and Volk, *Ann.*, **379**, 95 (1911).

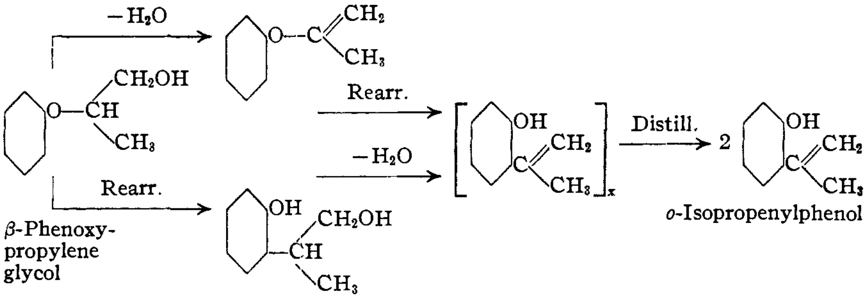
[6] (a) Spica, *Gazz. chim. ital.*, **9**, 42 (1879); *Jahresb.*, 663 (1880); (b) Niederl and Natelson, THIS JOURNAL, **53**, 1933 (1931).

[7] Fileti, *Gazz. chim. ital.*, **16**, 129 (1886).

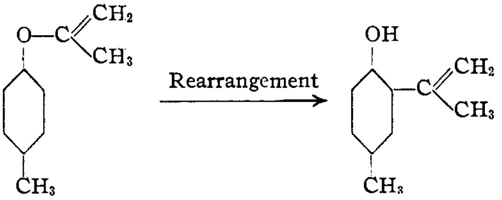
[8] Zincke and Greuters, *Ann.*, **343**, 94 (1905).

[9] Smith and Niederl, THIS JOURNAL. **53**, 806 (1931); Niederl, Smith and McGreal, *ibid.*, **53**, 3390 (1931).

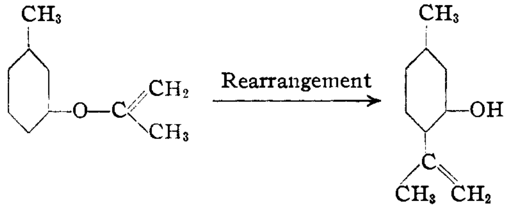
[10] Niederl and Natelson, *ibid.*, **53**, 273 (1931).



In the rearrangement of isopropenyl *p*-cresyl ether, the isopropenyl group could migrate to the ortho position only, the para position being occupied and meta rearrangement being unusual. The properties of the resulting product, 1-hydroxy-4-methyl-2-isopropenylbenzene, were in agreement with the literature.[11] As before, the same product was prepared from allyl alcohol and *p*-cresol in the presence of sulfuric acid. The compound obtained was identical with the one mentioned above and its formation by rearrangement may be represented as follows



The rearrangement of the isopropenyl *m*-cresyl ether resulted in a phenol which corresponded with the 3-hydroxy-1-methyl-4-isopropenylbenzene known in the literature.[11] The product obtained by the condensation of allyl alcohol and *m*-cresol was identical with the above. The phenol yielded a bromine derivative corresponding with the pentabromodehydrothymol ($2,5,6,4^2,4^2$-pentabromo-3-hydroxy-1-methyl-4-isopropenylbenzene) reported in the literature.[12] This evidence would tend to indicate that the isopropenyl group migrated to the ortho position.



This product was reduced catalytically first to thymol and further to a menthol.

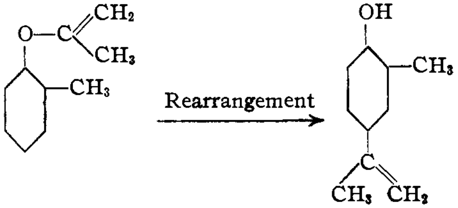
[11] (a) Fries and Fickewirth, *Ann.*, **362,** 46 (1908); (b) Guillaumin, *Bull. soc. chim.*, [4] 7, 381 (1910).

[12] Baeyer and Seuffert, *Ber.*, **34,** 47 (1901).

It may be mentioned that in the case of the condensation of *o*-cresol and allyl alcohol an alkali-insoluble higher boiling liquid was obtained in small amounts as a by-product. The formation of such a compound is open to several interpretations, included among which are a dehydration reaction or possibly migration into the side chain ortho to the hydroxyl group[13] followed by ring closure.

Para Rearrangement.—The rearrangement of the isopropenyl *o*-cresyl ether yielded chiefly a product which proved to be the 1-hydroxy-2-methyl-4-isopropenylbenzene. A product obtained on condensing allyl alcohol with *o*-cresol was identical with it. As mentioned above, along with this main product in each case was isolated a small quantity of higher boiling, alkali-insoluble liquid.

Inasmuch as all the foregoing reactions showed the isopropenyl residue migrating in an ortho position to the hydroxyl group, the above case seems to show a peculiarity in that para rearrangement is favored.



Furthermore, this case is worthy of careful study since Hurd[14] states, "If either one of the ortho atoms of the aromatic nucleus is unsubstituted, the allyl group almost invariably migrates into the ortho position; if both, however, are substituted, para rearrangement occurs."

There have been cases recorded where although one or even both ortho positions were vacant, para rearrangement ensued.[3,4,15]

In attempting to establish the structure, the product obtained by the rearrangement of isopropenyl *o*-cresyl ether was reduced catalytically and the crude material on distillation at ordinary pressure yielded a colorless liquid the characteristics of which were in close agreement with 1-hydroxy-2-methyl-4-isopropylbenzene.[16]

On bromination of this reduced product and recrystallization of the reaction material from alcohol, there was isolated a crop of very characteristic lustrous, golden-yellow plates which resembled in physical appearance those described in the literature.[17] However, on continued purification

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[13] Van Alphen, *Rec. trav. chim.*, **46**, 287 (1927).

[14] Hurd, p. 214, "The Pyrolysis of Carbon Compounds," Chemical Catalog Co., Inc., New York, 1929.

[15] (a) Van Alphen, *Rec. trav. chim.*, **46**, 288, 799 (1927); (b) Niederl and Natelson, THIS JOURNAL, **53**, 1931 (1931).

[16] (a) Kelbe, *Ann.*, **210**, 40 (1881); (b) Spica, *Gazz. chim. ital.*, **12**, 552 (1882).

[17] Jesurun, *Ber.*, **19**, 1414 (1886).

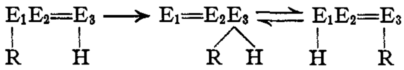
this product not only showed a higher melting point, but also analysis proved it to be a tetrabromo derivative.

The 1-hydroxy-2-methyl-4-isopropenylbenzene was itself further characterized by an acetic acid and a pentabromo derivative.

In conclusion, on the basis of the work done so far with the isopropyl, vinyl, and isopropenyl phenyl and cresyl ethers and the corresponding phenols, it appears that migration of the alkyl or alkenyl side chain ortho to the hydroxyl group is favored, except where one or both of the ortho positions are already occupied or are influenced by steric hindrance, then para rearrangement predominates.

As was previously stated, in view of these advances in the rearrangement of alkyl and alkenyl ethers a satisfactory reaction mechanism that would be in harmony with these experimental findings should be sought. Evidently, Claisen's mechanism[18] for the rearrangement of unsaturated alkyl phenyl ethers, in which the migration is claimed to take place through the gamma carbon atom, cannot be applied to the cases cited here due to the absence of the required atomic grouping. Hurd and Cohen's[19] suggestion of free radical formation would require the production of certain by-products, that so far could not be found, while Kursanov's[20] hypothesis of scission of the ether into an alkali halide and recombination with a nuclear carbon atom in the manner of the Friedel–Crafts reaction[21] is *a priori* out of the question for the cases cited. In consideration of the rearrangement mechanism offered by Van Alphen,[13] involving oxonium compound formation and the one advanced by Lapworth[22] for various other types of molecular rearrangements and already applied in the synthesis of thymol, its derivatives and homologs,[22a] the following reaction mechanism is herewith offered.

As the following arrangement of atomic groupings appears to be fundamental for the migration of the alkyl radical to the nuclear carbon atom ortho to the ether oxygen



$$\underset{\mathrm{R}}{\mathrm{E_1}}\mathrm{E_2}{=}\underset{\mathrm{H}}{\mathrm{E_3}} \longrightarrow \mathrm{E_1}{=}\underset{\mathrm{R\ \ H}}{\mathrm{E_2E_3}} \rightleftharpoons \underset{\mathrm{H}}{\mathrm{E_1}}\mathrm{E_2}{=}\underset{\mathrm{R}}{\mathrm{E_3}}$$

it must be applicable to the cases presented herein. Where ortho rearrangement takes place, namely, isopropenyl phenyl, *m*-cresyl and *p*-cresyl ethers, the following reaction mechanism could be given. It should be noted that these ethers possess two of the active atomic groupings.

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[18] Claisen, *Ber.*, **45**, 3157 (1912); *Ann.*, **237**, 261 (1887); **401**, 21 (1914); **418**, 69 (1919); *Z. angew. Chem.*, **36**, 478 (1923); Claisen and Tietze, *Ber.*, **58**, 275 (1925); **59**, 2344 (1926).

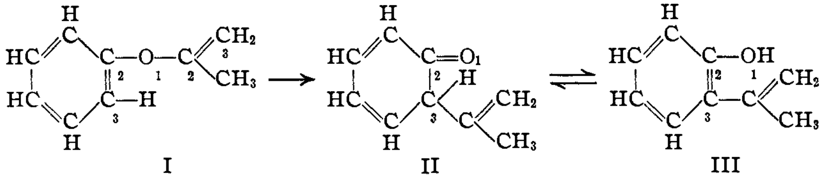
[19] Hurd and Cohen, THIS JOURNAL, **53**, 1917 (1931).

[20] Kursanov, *J. Russ. Phys.-Chem. Soc.*, **48**, 1172 (1914).

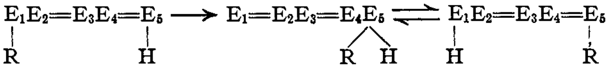
[21] Friedel and Crafts, *Ann. chim. phys.*, [6] **1**, 502 (1884).

[22] Lapworth, *J. Chem. Soc.*, **73**, 445 (1898).

[22a] Niederl and Natelson, THIS JOURNAL, **54**, 1063 (1932).

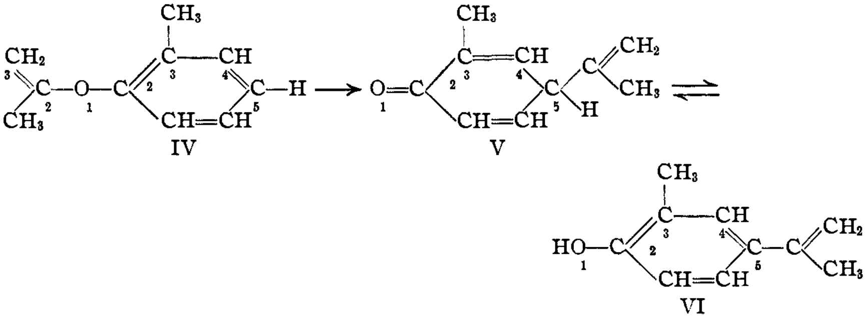


The original Lapworth theory must be extended to explain the formation of a para isomer.



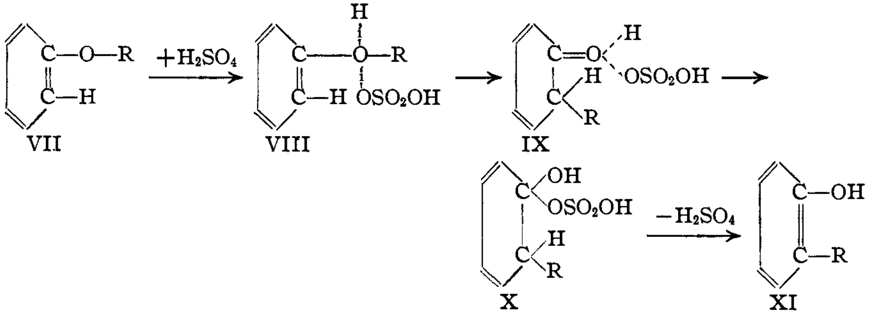
$$\underset{\substack{|\\ R}}{E_1}E_2=E_3E_4=\underset{\substack{|\\ H}}{E_5} \longrightarrow E_1=E_2E_3=E_4\underset{R\quad H}{E_5} \rightleftharpoons \underset{\substack{|\\ H}}{E_1}E_2=E_3E_4=\underset{\substack{|\\ R}}{E_5}$$

Applied to the case of the observed formation of the para isomer of isopropenyl *o*-cresol, the intramolecular rearrangement can then be illustrated in the following manner.



Quite obviously, the ether does not pass to the quinoid form (II) without some impulse; nor is it expected that the ether changes directly to the phenol, in spite of the fact that the phenol has a lower energy potential than the ether. It is assumed therefore that the ether first passes to the intermediate structure II, at a higher energy level, from which it now readily goes to the phenol III, at the lowest energy level.

The impulse for the change from the ether to the intermediate compound is postulated as arising directly from an addition of sulfuric acid to the ether oxygen, forming a transitory phenyl isopropenyl oxonium sulfate (VIII) with a higher energy potential.



Related oxonium sulfates of ethers are known in the literature.[23]

The oxonium compound then passes to the more stable quinoid configuration (IX—similar to II). These quinoid addition compounds have been reported by Richter.[24]

The next step in the mechanism involves a change from the quinoid carbonyl addition compound to a still more stable one of a hemi-acetal structure (X). Hydrolysis with the elimination of sulfuric acid is brought about resulting in the final phenolic product (XI).

An effective rationalization of the suggested mechanism may be attained from a consideration of the repulsion energies of the atomic kernels in the bonds involved. The following scheme represents the changes in the bonds during the rearrangement.

$$\underset{\text{VII. Ether}}{(\mathrm{O{-}C}) + (\mathrm{C{-}H})} \longrightarrow \underset{\text{VIII. Ether oxonium compound}}{(\mathrm{O{-}C}) + (\mathrm{O{-}H}) + (\mathrm{O{-}O}) + (\mathrm{C{-}H})} \longrightarrow$$

$$\underset{\text{IX. Quinoid carbonyl addition compound}}{(\mathrm{O{-}H}) + (\mathrm{O{-}O}) + (\mathrm{C{-}H}) + (\mathrm{C{-}C})} \longrightarrow \underset{\text{X. Quinoid hemi-acetal}}{(\mathrm{O{-}H}) + (\mathrm{O{-}C}) + (\mathrm{C{-}H}) + (\mathrm{C{-}C})} \longrightarrow$$

$$\longrightarrow \underset{\text{XI. Phenol}}{(\mathrm{O{-}H}) + (\mathrm{C{-}C})}$$

According to Latimer[25] the values of the repulsion energies expressed in kilocalories, in the above linkages are

(C—H)	550 kilocal.	(O—C)	2800 kilocal.
(O—H)	940 kilocal.	(O—O)	4550 kilocal.
(C—C)	1700 kilocal.		

Substituting these values in the above equation

$$\underset{\text{VII}}{3350} \xrightarrow[+5490]{} \underset{\text{VIII}}{8840} \xrightarrow[-1150]{} \underset{\text{IX}}{7690} \xrightarrow[-1700]{} \underset{\text{X}}{5590} \xrightarrow[-3350]{} \underset{\text{XI}}{2640}$$

It can now be seen that to pass from the ether (VII) to the oxonium compound (VIII) involves a gain of repulsion energy amounting to 5490 kilocalories, which appears to furnish the necessary impulse for the following changes. All the succeeding intramolecular rearrangements are accompanied by losses of repulsion energy amounting to 1150, 1760 and 3350 kilocalories, respectively, until the more stable phenol with the least intramolecular energy content is obtained.

This mechanism is not specific for a rearranging mixture of sulfuric and glacial acetic acids. Where boron trifluoride[4] or other substances have been used, the reaction mechanism may be postulated as being quite similar except that an addition of boron trifluoride takes place instead of sulfuric acid to form the transitory oxonium compound.

Furthermore, in isolated cases (allyl, cinnamyl and diisobutyl phenyl

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[23] Erlenmeyer and Kirchbaumer, *Ber.*, **7**, 699 (1874); Tschelinzew and Koslow, *J. Russ. Phys.-Chem. Soc.*, **46**, 711 (1915).

[24] Richter, *Ber.*, **43**, 3600 (1910).

[25] Latimer, THIS JOURNAL. **51**, 4168 (1929).

ethers) where heat alone has been employed to effect rearrangement, the above mechanism offers a satisfactory explanation. Assuming the formation of oxonium compounds between identical molecules, then the succeeding transitory bimolecular addition compounds of the quinhydrone type may be formed and finally the substituted phenol is obtained.

In regard to the velocity of reaction in the rearrangement of alkyl and alkenyl phenyl ethers, work in this Laboratory with vinyl, isopropyl, isopropenyl, secondary-butyl and -amyl and diisobutyl phenyl ethers tends to indicate that the longer the wandering side chain (greater the molecule), the more rapid is the migration. On the basis of physical principles such a tendency may be explained as being due to the greater possibility of collision with larger molecules proceeding through the changes indicated by the above mechanism ("Zweistoss" system).

In the accomplished rearrangement of isopropenyl phenyl ethers, the postulated mechanism, based upon the changes in the inner energy potentials of the compounds suggested, is further enhanced by the fact that these migrations involve the passing from an isolated system of double bonds to a conjugated system. Examination of the structures I and IV indicates that the unsaturation of the alkenyl group of the ethers is not in conjugation with the double bonds in the cyclic nucleus, forming an isolated system. On the other hand, the phenol structures III and VI have the double bonds arranged in the form of conjugated systems. Henrich[26] states that substances which possess conjugated double linkages "are more highly saturated" than substances which possess two separate pairs of double bonds. This would account for the greater stability of the conjugated system and elucidates once more the tendency of the isopropenyl phenyl ethers to pass to the corresponding phenols under the proper conditions.

Experimental Part

Preparation of Isopropenyl Phenyl and Cresyl Ethers.—The isopropenyl phenyl and cresyl ethers were obtained by the action of isopropenyl bromide upon potassium phenolate (cresolate). 2,2-Dibromopropane was first prepared by the method of Friedel,[27] which consists in treating acetone with phosphorus dibromotrichloride. The dibromopropane was converted to isopropenyl bromide by the method of Réboul[28] whereby hydrogen bromide is eliminated by the use of sodium ethylate. The potassium phenolate was then prepared by adding a mole of potassium hydroxide to a mole of the phenol with mild heating. When a homogeneous system was obtained a mole of the isopropenyl bromide was slowly added and the whole refluxed for two hours. Water was then added to dissolve the potassium bromide, and the ether separated as a colorless liquid. On distillation at ordinary pressure the pure product was obtained.

Rearrangement of Isopropenyl Phenyl and Cresyl Ethers.—The ethers prepared

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[26] Henrich, "Theories of Organic Chemistry," Johnson and Hahn, John Wiley and Sons, Inc., New York, 1922, p. 38.

[27] Friedel, *Ann. chim. phys.*, [4] **16**, 356 (1869).

[28] Réboul, *ibid.*, [5] **14**, 475 (1878).

in the above manner were rearranged according to the method found most satisfactory in this Laboratory for phenyl ethers.[29,15b] The ether was refluxed for five hours with a 10% solution of sulfuric acid in glacial acetic acid, where the quantity of sulfuric acid was equimolar to the ether. The reaction mixture was allowed to stand overnight. After transferring to a separatory funnel, a volume of salt solution somewhat greater than that of the reaction mixture was added and the liquid layer which separated was drawn off. This consisted of unrearranged ether and the substituted ether; this latter was extracted with a 10% caustic potash solution and reprecipitated with concentrated hydrochloric acid. An ether extract was made; this was dried with calcium chloride and the substituted phenol was obtained pure by distillation.

Preparation of Isopropenylphenols and Cresols by the Condensation Method.—The method employed in these condensations is a modification of that reported in earlier articles.[30] To a solution of molar quantity of allyl alcohol and of the phenol, a fifth mole of sulfuric acid was added drop by drop. The mixture was cooled in an ice-bath and well shaken throughout the addition of the acid. The reaction flask was then stoppered with a stopper containing a calcium chloride drying tube and slowly allowed to come to room temperature. After standing for one week, the reaction mixture, a hard reddish mass, was pulverized and then washed with cold water to remove unreacted allyl alcohol, sulfonic acids and sulfuric acid. The washed product, an orange-red solid was a polymer of the isopropenylphenol. On distillation at ordinary pressure (slight decomposition took place), depolymerization was effected and a monomer was obtained as a colorless liquid which darkened on standing.

Catalytic Reduction of Isopropenylphenols and Cresols to the Corresponding Isopropyl Compounds.—With the use of a catalytic reduction apparatus a calculated quantity of hydrogen was allowed to react with a weighed sample of the unsaturated alkyl phenol in an absolute alcohol solution. A platinic oxide catalyst was employed. After the required amount of hydrogen had reacted the solution was decanted from the catalyzer, and the alcohol allowed to evaporate spontaneously, while the solution was kept free from dust. The resulting product was then fractionally distilled to yield the pure isopropylphenol.[31]

Preparation of Phenoxy and Cresoxy Acetic Acids.—Two grams of the substituted phenol was added to one gram of solid potassium hydroxide dissolved in 15 cc. of water. This mixture was warmed on a water-bath until complete solution took place. Two grams of bromoacetic acid was dissolved in 10 cc. of water and 3 drops of phenolphthalein added; 10% potassium hydroxide was then added until a permanent pink color was obtained. The two solutions were then mixed and gently boiled for ten minutes. When cool, the mixture was placed in an ice-bath and neutralized with concentrated hydrochloric acid. Precipitation in the cold avoids the formation of undesirable oils. If an oil was formed, it solidified on standing. The product was then recrystallized from water.

Preparation of Bromine Derivatives.—These were prepared by treating the pure phenol with an excess of bromine in the cold, without the use of a solvent. The whole was then allowed to stand until all the hydrogen bromide and excess bromine had evaporated. The dark mass was then transferred to a porous tile and washed suc-

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[29] Niederl, Natelson and Smith, Indianapolis Meeting of the American Chemical Society, 1931; Niederl and Natelson, THIS JOURNAL, **54**, 1068 (1932).

[30] Niederl, *ibid.*, **50**, 2230 (1928); **51**, 2426 (1929); *Z. angew. Chem.*, **44**, 467 (1931); *Monatsh.*, **60**, 150 (1932); Niederl and Casty, *ibid.*, **51**, 1028 (1929); Niederl and Natelson, THIS JOURNAL, **53**, 272 (1931); Smith and Niederl, *ibid.*, **53**, 806 (1931); Niederl, Smith and McGreal, *ibid.*, **53**, 3390 (1931).

[31] R. A. Smith, private communication, New York University.

TABLE I

PHYSICAL CONSTANTS AND ANALYSES OF THE COMPOUNDS PREPARED

Compound	Formula	M. p., °C.	B. p., °C.	Sp. gr.	n_D	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
Products with Phenol									
Isopropenylphenyl ether[32]	$CH_2{=}C(CH_3)OC_6H_5$		169	0.998^{23}	1.5172^{23}	80.55	80.18	7.52	7.64
o-Isopropenylphenol (by rearrangement of above)[5]	$CH_2{=}C(CH_3)C_6H_4OH$		203–208	1.024^{28}	1.5452^{28}	80.55	80.23	7.52	7.25
o-Isopropenylphenol (by condensation)	$CH_2{=}C(CH_3)C_6H_4OH$		204–207	1.026^{28}	1.5448^{28}	80.55	80.18	7.52	8.36
Hexabromo-*o*-isopropenylphenol	$C_9H_4OBr_6$	84				17.73	17.40	0.82	0.97
o-Isopropylphenol (by reduction of *o*-isopropenylphenol)[6]	$CH(CH_3)_2C_6H_4OH$		212–214	1.016^{22}	1.5351^{22}				
o-Isopropylphenoxyacetic acid (from *o*-isopropylphenol)[6,7]	$CH(CH_3)_2C_6H_4OCH_2COOH$	130							
Products with *p*-Cresol									
Isopropenyl *p*-cresyl ether	$CH_2{=}C(CH_3)OC_6H_4CH_3$		189–190	0.977^{27}	1.5118^{27}	81.03	81.38	8.17	8.39
2-Isopropenyl-4-methylphenol (by rearrangement of above)[11]	$CH_2{=}C(CH_3)C_6H_3(CH_3)OH$		222–224	1.012^{24}	1.5362^{24}	81.03	80.73	8.17	8.00
2-Isopropenyl-4-methylphenol (by condensation)	$CH_2{=}C(CH_3)C_6H_3(CH_3)OH$		223–226	1.009^{25}	1.5399^{25}	81.03	81.31	8.17	8.46
Products with *m*-Cresol									
Isopropenyl *m*-cresyl ether	$CH_2{=}C(CH_3)OC_6H_4CH_3$		188–189	0.978^{21}	1.5117^{21}	81.03	80.66	8.17	7.91
5-Methyl-2-isopropenylphenol (by rearrangement of above)[6a,11]	$CH_2{=}C(CH_3)C_6H_3(CH_3)OH$		225	1.026^{25}	1.5402^{25}	81.03	81.40	8.17	8.38
5-Methyl-2-isopropenylphenol (by condensation)	$CH_2{=}C(CH_3)C_6H_3(CH_3)OH$		222–225	1.020^{26}	1.5360^{25}	81.03	81.21	8.17	8.53
2,5,6,4^2,4^2-Pentabromo-3-hydroxy-1-methyl-4-isopropenylbenzene[12]	$CBr_2{=}C(CH_3)C_6Br_3(CH_3)OH$	103–104				22.32	22.09	1.62	1.29
x-Menthol (by reduction of 5-methyl-2-isopropenylphenol)	$C_{10}H_{20}O$		195–200			76.92	77.48	12.82	11.69
Products with *o*-Cresol									
Isopropenyl *o*-cresyl ether	$CH_2{=}C(CH_3)OC_6H_4CH_3$		184–185	0.983^{27}	1.5122^{27}	81.03	81.35	8.17	7.82
2-Methyl-4-isopropenylphenol (by rearrangement of above)	$CH_2{=}C(CH_3)C_6H_3(CH_3)OH$		225–228	1.026^{28}	1.5395^{28}	81.03	80.68	8.17	8.35
2-Methyl-4-isopropenylphenyl (by condensation)	$CH_2{=}C(CH_3)C_6H_3(CH_3)OH$		224–228	1.029^{27}	1.5359^{27}	81.03	80.74	8.17	8.38
Pentabromo-2-methyl-4-isopropenylphenol	$C_{10}H_7OBr_5$	202				22.32	22.63	1.62	1.40
2-Methyl-4-isopropenylphenoxyacetic acid	$CH_2{=}C(CH_3)C_6H_3(CH_3)OCH_2COOH$	110–111				69.90	69.51	6.79	7.18
2-Methyl-4-isopropylphenol (by reduction of 2-methyl-4-isopropenylphenol)[6b,16]	$CH(CH_3)_2C_6H_3(CH_3)OH$		230–234	0.987^{20}	1.5138^{20}				
2-Methyl-4-isopropylphenoxyacetic acid	$CH(CH_3)_2C_6H_3(CH_3)OCH_2COOH$	140–141				69.23	68.95	7.69	7.98
Tetrabromo-2-methyl-4-isopropylphenol (from 2-methyl-4-isopropylphenol[a]	$C_{10}H_{10}OBr_4$	236–237				25.75	25.42	2.14	1.93

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[32] Ruhemann and Wragg, *J. Chem. Soc.*, **79**, 1190 (1901).

[a] The lustrous, golden-yellow plates obtained were shown to be identical with the 2,4,5-tribromo-6-hydroxy-1-methyl-3-isopropylbenzene, melting point 223°, reported previously by Niederl and Natelson. THIS JOURNAL, **53**, 1931 (1931). It is postulated that it is also identical with the 2,4,5-tribromo-6-hydroxy-1-methyl-3-isopropylbenzene, melting point 221°, reported by Jesurun, *Ber.*, **19**, 1414 (1886), who offered no analysis for the compound.

cessively with small quantities of benzene to remove the tarry material and last traces of bromine. Recrystallizations were then effected from alcohol or benzene.

The quantitative determinations were performed microanalytically according to Pregl.[33]

Summary

1. Short-chain alkenyl phenyl ethers (isopropenyl phenyl and cresyl ethers) were rearranged to the corresponding isomeric substituted phenols by means of a mixture of concentrated sulfuric and glacial acetic acids. Proofs for the structure of the products were advanced and a general rule as to the position of migration of the alkenyl side chain was postulated.

2. The rearranged products were resynthesized by the addition of the corresponding phenols to allyl alcohol. These extensions of this addition reaction show that addition of phenols to allyl alcohol is a general process.

3. A reaction mechanism was advanced for the rearrangement as well as for the addition reaction, involving the postulations of Van Alphen, Lapworth, Latimer and others.

4. The generally acknowledged rearrangement mechanism of Claisen for unsaturated alkyl phenyl ethers was found inapplicable to isopropenyl phenyl ethers. Preliminary work in the field of related compounds such as cinnamyl alcohol, cinnamyl chloride, the various cinnamyl phenyl ethers and esters, further indicate the insufficiency of the Claisen mechanism.

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[33] Pregl, "Quantitative Organic Microanalysis," P. Blakiston's Sons and Co., Philadelphia, Pa.