ADDITION OF PHENOLS TO THE ETHYLENIC LINKAGE. II. THE ACTION OF PHENOLS OF ALLYL ALCOHOL, ALLYL ACETATE, VINYL ACETATE AND ALLYL ETHERS

BY JOSEPH B. NIEDERL, RICHARD A. SMITH AND MARTIN E. McGREAL[1]

A survey of the chemical literature prior to 1925 reveals a few isolated cases of reactions involving the addition of phenolic bodies to the ethylenic linkage, the majority of the cases concerned being of unsaturated hydrocarbons, to yield, in most cases, substituted phenols.[2] Niederl,[3] in that year, demonstrated that such reactions definitely involved the addition of the phenolic body to the ethylenic linkage; this fact led to a systematic study of the addition of phenols to different types of compounds containing the ethylenic linkage, and since that time cases have been reported concerning the reactions of phenols with unsaturated compounds of the following types: ketones,[4] alcohols,[5] ethers,[6] esters,[7] aldehydes[8] and hydrocarbons.[9]

Also, the mechanism of reaction has since then been considerably clarified. It is probable that the first step in the reaction is the addition of hydrogen sulfate to the ethylenic linkage; this addition compound then reacts with the phenol to regenerate hydrogen sulfate and form a phenyl ether. In the case of hydrocarbons these ethers have been isolated.[9]

However, the phenyl ether usually rearranges in the presence of concentrated sulfuric acid with the formation of a substituted phenol, and many examples of such rearrangements have been reported.[10]

[1] University of Pittsburgh.

[2] Claissen, German Patent, 374,142 (1923); Liebermann and Hartmann, *Ber.*, **24**, 2582 (1891); **25**, 957 (1892); Schrauth and Quasebarth, *ibid.*, **57**, 854 (1924); Koenig, *ibid.*, **24**, 3889 (1891); Wenzke and Nieuwald, THIS JOURNAL, **46**, 177 (1924).

[3] Niederl, "Inaugural Dissertation," University of Graz, Austria, 1925.

[4] Niederl, THIS JOURNAL, **50**, 2230 (1928); **51**, 2426 (1929); Niederl and Casty, *Monatsh.*, **51**, 1038 (1929); Knowles, Sc.M. Thesis, New York University, 1929; Sen and Quadrat I-Khuda, *J. Indian Chem. Soc.*, **7**, 167 (1930).

[5] Niederl and McGreal, Columbus Meeting of the American Chemical Society, 1929.

[6] Storch, Sc.M. Thesis, New York University, 1930.

[7] Adams, Sc.M. Thesis, New York University, 1930.

[8] Niederl, Smith and Wilson. Atlanta Meeting of the American Chemical Society, 1930.

[9] Niederl and Natelson, THIS JOURNAL, **53**, 272 (1931).

[10] Claisen, *Ann.*, **237**, 261 (1887); **401**, 21, 119 (1924); *Ber.*, **45**, 3157 (1912); **58**, 275 (1925); *Z. angew. Chem.*, **36**, 478 (1923); Van Alphen, *Rec. trav. chim.*, **46**, 799 (1927); Heller, *Ber.*, **45**, 418 (1912); Bucherer and Grolée, *ibid.*, **39**, 986 (1906); Kursanov, *J. Russ. Phys.-Chem. Soc.*, **48**, 1172 (1914); Eijkman, *Chem. Zentr.*, I, 1597 (1904); I, 814 (1905); Smith and Niederl, THIS JOURNAL, **53**, 806 (1931); Niederl, Natelson and Smith, Indianapolis Meeting of the American Chemical Society, 1931.

The purpose of the present communication is to show that phenolic compounds condense with unsaturated alcohols, esters and ethers and in so doing follow the mechanism just indicated.

As a search of the chemical literature revealed no data concerning reactions involving the ethylenic bond of an unsaturated alcohol and a phenol, it was somewhat surprising to find that addition of phenols to unsaturated alcohols was practically quantitative. Preliminary reports have been made regarding this reaction,[11] and in the present communication data supporting the proposed reaction mechanism and proofs of structure of the products will be given. The compound formed by the action of equimolar quantities of m-cresol and allyl alcohol in the presence of concentrated sulfuric acid, as being the best studied in the series, will be discussed here. The final reaction product appears to be o-isopropenyl-m-cresol (3-methyl-6-isopropenylphenol) and the following explanation for its formation is suggested: first, the addition of hydrogen sulfate to allyl alcohol with the formation of α-allylol sulfate

$$CH_2{=}CHCH_2OH + H_2SO_4 \longrightarrow CH_3CH(CH_2OH)OSO_2OH$$
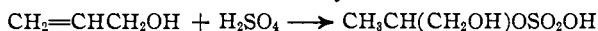
The second step is the elimination of hydrogen sulfate from the above addition compound and m-cresol, in a manner similar to that observed in the condensation reactions of unsaturated hydrocarbons

$$CH_3CH(CH_2OH)SO_2OH + HOC_6H_4(CH_3) \longrightarrow H_2SO_4 + CH_3CH(CH_2OH)OC_6H_4(CH_3)$$
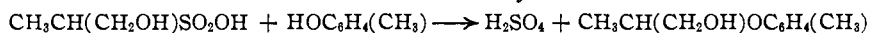
As concentrated sulfuric acid is also a strong dehydrating agent, it is quite possible that water could be eliminated from the above ether to form m-cresyl isopropenyl ether, and as analysis of the final product indicates that water is lost, it is very likely that such a loss occurs at this stage to constitute the third stage in the reaction as follows

$$CH_3C_6H_4OCH(CH_3)CH_2OH \xrightarrow{H_2SO_4} CH_3C_6H_4OC(CH_3){=}CH_2$$
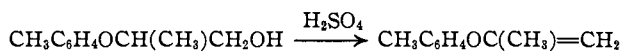
The final step proposed is the rearrangement of the above unsaturated ether to a substituted cresol, as follows

$$CH_3C_6H_4OC(CH_3){=}CH_2 \xrightarrow{H_2SO_4} CH_3C_6H_3(OH)C(CH_3){=}CH_2$$
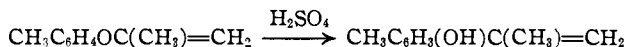
That this last step is not alone feasible but is most likely the one which occurs in the actual condensation is illustrated by the fact that the ether, m-cresyl isopropenyl ether, was synthesized from isopropenyl bromide and potassium cresylate, and then treated with sulfuric acid, when it rearranged to a product which yielded the same bromine derivative as the product obtained by direct condensation of m-cresol with allyl alcohol in the presence of sulfuric acid. The formation of o-isopropenyl-m-cresol as the end-product of this reaction appears justified from the standpoint of mechanism of reaction; further substantiation is indicated by
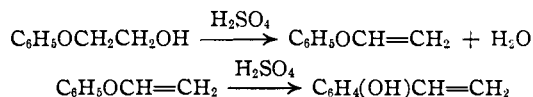
[11] Niederl and McGreal, Columbus Meeting of the American Chemical Society, 1929; Atlanta Meeting of the American Chemical Society, 1930.

comparison of its properties and those of its derivatives with those appearing in the literature.

The only report concerning the reactions of unsaturated esters with phenols is a British Patent[12] wherein phenyl acetate is formed from phenol and vinyl acetate at 100° in the presence of a catalyst. It was logical, after demonstrating that unsaturated alcohols would react additively with phenols, to carry out a study with the object of determining whether unsaturated esters would also undergo similar reactions. In this communication it will be shown that vinyl and allyl acetates condense quantitatively with phenols in the cold and in the presence of concentrated sulfuric acid to yield substituted phenols. In the case of vinyl acetate and phenol, the product expected by the proposed mechanism would be o-vinylphenol, and this was substantiated by the properties of the reaction product and its derivatives. The first steps, in accordance with statements already made, involve addition of hydrogen sulfate to the ethylenic linkage with subsequent elimination of hydrogen sulfate from phenol and the addition compound with the formation of phenoxyglycol acetate. This ester would hydrolyze

$$C_6H_5OCH_2CH_2OOCCH_3 + H_2O = C_6H_5OCH_2CH_2OH + CH_3COOH$$
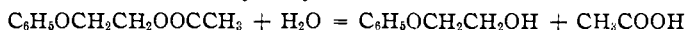
It was illustrated in the case of allyl alcohol and m-cresol that a phenyl ether with an alcohol group in the side chain can lose water to form an ethylenic type of compound, and, as this idea is applicable here, one should expect the concentrated sulfuric acid to cause dehydration with the formation of phenyl vinyl ether. This latter would rearrange to o-vinylphenol

$$C_6H_5OCH_2CH_2OH \xrightarrow{H_2SO_4} C_6H_5OCH=CH_2 + H_2O$$

$$C_6H_5OCH=CH_2 \xrightarrow{H_2SO_4} C_6H_4(OH)CH=CH_2$$

These last two steps very likely take place here, as it has been shown in another connection that phenyl β-hydroxyethyl ether is dehydrated and rearranged to form o-vinylphenol in the presence of concentrated sulfuric acid, in the cold.[13]

The mechanism suggested is not intended to be a rigid one, the order of the reactions may vary, and the dehydration may not precede the rearrangement. However, these variations are not fundamental to the proposed mechanism.

Allyl acetate was also condensed with phenols, as was vinyl acetate, and in this case the products were found to be identical with those obtained from allyl alcohol and phenols. The mechanism obviously would be a combination of those proposed for the m-cresol–allyl alcohol and the phenol–vinyl acetate systems, and need not be given here.

[12] British Patent 314,646 (1928).

[13] Smith and Niederl, THIS JOURNAL, **53**, 806 (1931).

Allyl ethyl ether and diallyl ether were also condensed with phenols. Inasmuch as allyl ethyl ether is easily hydrolyzed even by dilute sulfuric acid,[14] to allyl alcohol and ethyl alcohol, it would naturally be expected that a reaction mixture composed of allyl ethyl ether, phenol and sulfuric acid would yield the same final product as one composed of allyl alcohol, phenol and sulfuric acid. This was borne out by experimental evidence. Diallyl ether was also worked with; it hydrolyzes and yields the same final condensation products with phenols as does allyl alcohol.

Experimental Part

2-Isopropenyl-5-methylphenol, $CH_2=C(CH_3)C_6H_3(CH_3)OH$.—To a solution of molar quantities of m-cresol and allyl alcohol, a tenth mole of concentrated sulfuric acid was slowly added with cooling in an ice-bath. The reaction flask was then stoppered with a stopper containing a calcium chloride drying tube and allowed to stand for a few days. The reaction mixture, a gum-like mass, was then successively washed with cold and hot water to remove unreacted allyl alcohol, sulfonic acids and sulfuric acid. The washed product, an amorphous, yellow solid, was then dissolved in a slight excess of 10% potassium hydroxide solution (practically all went into solution), filtered, and reprecipitated with carbon dioxide or mineral acid in the cold. The solid so obtained was a polymer of o-isopropenyl-m-cresol; after drying over calcium chloride in a vacuum desiccator, this amorphous solid was converted to a crystalline product by careful distillation in a 4-mm. vacuum. The crystals so obtained could not be kept in the atmosphere at room temperature as they withered away to a liquid which, however, yielded crystals on treatment with ether. Long standing in the presence of concentrated sulfuric acid also gave rise to a crystalline product. These products could be recrystallized from dry ether, with some difficulty, in which case the dimer melting at 72–74° was obtained; these crystals contained one molecule of ether of crystallization; upon standing this ether was lost and the crystals turned to an amorphous, white powder which also melted at 72–74°. The liquid obtained by melting the above solids did not solidify on standing, but could again be converted to a crystalline product of the same melting point on treatment with ether. This curious behavior has been noticed in part by previous workers. Distillation at ordinary pressure yielded the monomer (there was a great deal of decomposition) which boiled at 220°. The boiling points to be found in the literature for this compound are 217°[15] and 222°.[16]

Anal. Calcd. for $C_{10}H_{12}O$: C, 81.07; H, 8.16. Found: C, 81.43; H, 8.52.

All the modifications of the isopropenyl-m-cresol described here were soluble in aqueous potassium hydroxide and organic solvents. The crystalline products colored aqueous ferric chloride dark green.

Allyl acetate and m-cresol with the same procedure as for allyl alcohol yielded the same product. The odor of acetic acid was quite discernible in the reaction chamber; in all other respects conditions in both cases were entirely analogous.

Allyl ethyl ether and diallyl ether under similar treatment also yielded o-isopropenyl-m-cresol as the final product. Here, however, a marked and interesting deviation in reaction velocity was encountered. Allyl ethyl ether reacted rather slowly, requiring a full mole of sulfuric acid, as compared to a fifth mole for allyl alcohol, and the condensation appeared to require a full week for completion; diallyl ether, on the other

[14] Eltekow, *Ber.*, 10, 1903 (1877).

[15] Fries and Fickewirth, *Ann.*, 362, 42 (1908).

[16] Hoering and Baum, German Patent 208,886 (1909).

hand, required but a small quantity of sulfuric acid to initiate reaction, and then the reaction was of explosive violence.

The two other cresols were also condensed under conditions as already outlined for *m*-cresol, and in all cases good yields were obtained of amorphous materials, indicating that the reactions had proceeded as in the cases of the *m*-cresol. The products are under further investigation as to structural configuration and are merely cited here to indicate that the condensations are general for phenols.[17]

2,5,6,4^1,4^2,4^2-Hexabromo-3-hydroxy-1-methyl-4-isopropylbenzene, $(CH_3)(CHBr_2)$-$CBrC_4Br_3(CH_3)OH$.—This bromine derivative was obtained by treating the monomer of isopropenyl-*m*-cresol in glacial acetic acid with an excess of bromine. The excess bromine, hydrogen bromide and solvent were allowed to evaporate spontaneously, and the resultant crystalline product purified by recrystallizations from chloroform. The compound was soluble in ethyl alcohol, ether, chloroform and acetone; it was insoluble in benzene and ligroin; it was not soluble in alkali without decomposition. The melting point was found to be 149°, which was in agreement with the literature.[18]

2,5,6,4^2,4^2-Pentabromo-3-hydroxy-1-methyl-4-isopropenylbenzene, $CBr_2 = C$ $(CH_3)C_6Br_3(CH_3)OH$.—The preparation of the hexabromo derivative of isopropenyl-*m*-cresol was not considered rigid proof that the derivative was the proper one, as it has been found that structurally related phenols often yield bromine derivatives with closely allied melting points, and as it was found that the condensation product also yielded other crystalline bromine derivatives. For these reasons the hexabromo derivative was proved to be the desired one by utilization of the fact that it gives up hydrogen bromide very readily to form a pentabromo derivative with a characteristic melting point of its own.

An ether solution of the hexabromo derivative was shaken with a dilute sodium bicarbonate solution for ten minutes; the ether layer was then drawn off and the ether allowed to evaporate spontaneously. The resultant crystals were purified by recrystallizations from chloroform. The product was soluble in alcohol, chloroform, ether and benzene. The melting point of 102–103° was in agreement with that in the literature.[18]

The same product was also synthesized by bromination of isopropenyl-*m*-cresol without the use of solvent. This method is recommended as being the best for identification purposes. The liquid monomer was treated with a large excess of bromine in the cold; the whole was then allowed to stand until all the hydrogen bromide and excess bromine had evaporated. Recrystallizations were then effected from alcohol; yellow crystals melting at 103–104° were obtained.

m-Cresyl Isopropenyl Ether, $CH_3C_6H_4OC(CH_3) = CH_2$.[19]—*m*-Cresyl isopropenyl ether was obtained by the action of isopropenyl bromide upon potassium cresylate. 2,2-Dibromopropane was first prepared by the method of Friedel,[20] which consists in treating acetone with phosphorus dibromotrichloride. The dibromopropane was converted to isopropenyl bromide by the method of Reboul[21] whereby hydrogen bromide is eliminated by the use of sodium ethylate. Potassium cresylate was then prepared by adding one mole of potassium hydroxide to a mole of *m*-cresol 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 and the ether separated

[17] Storch, research work in progress at New York University.

[18] Baeyer and Seufort, *Ber.*, **34**, 41 (1901).

[19] This ether was synthesized and rearranged by Mr. E. A. Storch in conjunction with research work for the doctorate at New York University.

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

[21] Reboul, *ibid.*, [5] 14, 475 (1878).

as a colored liquid layer. The ether even on repeated distillation still contained halogen and as yet has not been further purified; b. p. 188–189° (uncorr.); sp. gr. 0.9779 (21°); n_D^{21} 1.5117.

Anal. Calcd. for $C_{10}H_{12}O$: C, 81.07; H, 8.16. Found: C, 80.73; H, 8.00.

The above *m*-cresyl isopropyl ether was then rearranged according to the method found most satisfactory in this Laboratory for phenyl ethers.[22] 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. After cooling, a volume of salt solution somewhat greater than the volume of the reaction mixture was added and the liquid layer which separated was drawn off. This consisted of unrearranged ether and the substituted phenol; this latter was extracted with 10% caustic potash solution and reprecipitated with hydrochloric acid. An ether extract was then made; this was dried with calcium chloride and the *o*-isopropenyl-*m*-cresol was obtained pure by distillation; b. p. 225° (uncorr.); sp. gr. 1.069; n_D^{21} 1.5512. *Anal.* Calcd. for $C_{10}H_{12}O$: C, 81.07; H, 8.16. Found: C, 81.38; H, 8.39. This product upon bromination yielded the same pentabromo derivative that was obtained from the condensation product.

3-Methoxy-1-methyl-4-isopropenylbenzene, $CH_2{=}C(CH_3)C_6H_3(CH_3)OCH_3$.—This derivative of *o*-isopropenyl-*m*-cresol was prepared from the condensation product itself by the use of dimethyl sulfate. To a mole of the condensation product dissolved in a slight excess of potassium hydroxide solution commercial dimethyl sulfate was added cautiously; during this addition the whole was continually shaken. The flask was then closed with a stopper containing a thermometer and a glass tube bent in a spiral to prevent the liquid from spurting. The temperature was kept constant between 40 and 50°. When no more heat was evolved, the excess of dimethyl sulfate was destroyed by boiling under a reflux condenser with frequent shaking. After cooling, caustic soda was added until an alkaline reaction was obtained; the whole was then extracted with ether, the extract dried with anhydrous potassium carbonate and filtered. The ether was removed on a steam-bath. The solid residue was a polymer melting at 54–56° and boiling at 220° to a colorless liquid. These figures were in agreement with the literature.[23]

2-Hydroxyl-1-isopropenylbenzene, $CH_2{=}C(CH_3)C_6H_4OH$.—On substituting phenol for *m*-cresol in the condensations previously referred to, an amorphous solid of uncertain melting point was obtained: if the reactions were analogous to those with *m*-cresol, it would be expected that this amorphous product was a polymer of isopropenyl phenol; the experimental evidence is in agreement with this. Depolymerization was effected by distillation under ordinary pressure; a colorless, phenolic odored liquid somewhat soluble in water was obtained. The liquid boiled at 203–206° and polymerized readily on standing. The properties cited are in agreement with the literature, where this compound was prepared by other methods.[24]

o-Vinylphenol, $HOC_6H_4CH{=}CH_2$.—This product was obtained by condensing phenol with vinyl acetate in the presence of sulfuric acid in a manner similar to that given in detail for *m*-cresol and allyl alcohol. The reaction product was an amorphous solid, a polymer of *o*-vinylphenol. This upon distillation yielded a monomer, b. p. 56° at 4 mm., m. p. 29–29.5° (corr.). These figures are in agreement with results found before.[25]

---

[22] Niederl, Natelson and Smith, Indianapolis Meeting of the American Chemical Society, 1931.

[23] Béhal and Tiffeneau, *Bull. soc. chim.*, [4] 3, 732 (1908).

[24] Béhal and Tiffeneau, *ibid.*, [4] 3, 315 (1908); Boering and Baum, German Patent 208,886 (1909).

[25] Smith and Niederl, THIS JOURNAL, 53, 806 (1931); Fries and Fickewirth, *Ber.*, 41, 370 (1908).

$3,5,1^1,1^2$-Tetrabromo-2-hydroxy-7-ethylbenzene, $HOC_6H_2BR_2CHBrCH_2Br$.—*o*-Vinylphenol as prepared above in a chloroform solution was treated with an excess of bromine with cooling. After the reaction had subsided, the hydrogen bromide, excess bromine and chloroform were driven off by mild heating and the remaining solid was purified by recrystallization from benzene. The final product melted at 105°, which is in agreement with the literature.[25]

The cresols were also condensed as was phenol; positive condensations were obtained in each case; further studies are under way to determine the structural configurations of these products.

o-Vinylphenoxyacetic Acid, $HOOCCH_2OC_6H_4CH=CH_2$.—Molar quantities of *o*-vinylphenol as prepared above and bromoacetic acid were allowed to stand at room temperature in an alkaline solution for a few hours. The solution was then acidified and the resulting product purified by crystallization from benzene. Prisms melting at 137° were obtained. This also was in agreement with the literature.[25]

Summary

1. The studies in the addition reaction of phenols to the ethylenic linkage have been extended to unsaturated alcohols, esters and ethers; the results have been positive in all these cases.

2. Substituted phenols with an unsaturated side chain were obtained in the cases studied; *m*-cresol with allyl alcohol, allyl acetate, allyl ethyl ether and diallyl ether yielded *o*-isopropenyl-*m*-cresol; phenol with the above three unsaturated compounds yielded the corresponding isopropenyl phenol; phenol and vinyl acetate yielded *o*-vinylphenol.

3. A reaction mechanism was advanced and the one given in earlier cases was strengthened; the rearrangement assumed could be verified by resynthesis.

4. The physiological and bactericidal properties of these phenols with an unsaturated side chain are being investigated.

5. Further work on the addition reaction of phenols to unsaturated compounds, which at this time appears to be a general reaction, is being carried out.

New York, N. Y.