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

The Addition of Phenols to the Ethylenic Linkage. The Action of Phenols on Alkylene Halides[1]

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It has been demonstrated in previous communications that phenolic bodies will add to unsaturated linkages, principally of the ethenoid type, in the presence of sulfuric acid or other cationoid condensing agents. The products generally are substituted phenols or phenyl ethers.[2]

In this report it will be shown that this type of condensation can be extended to unsaturated halides. The three cresols and phenol were condensed with allyl chloride in the presence of sulfuric acid. The products were identified as isopropenylphenols. These products have been resynthesized in several ways: (a) by the condensation of phenols with allyl alcohol,[3] (b) allyl esters,[4] (c) allyl ethers, and[5] (d) by direct rearrangement of the isomeric isopropenyl phenyl ethers.[2]

Two types of condensation are described. The first consists simply in allowing the phenol, the unsaturated halide and sulfuric acid to stand for an appropriate time at room temperature. The reaction rate is very slow. The second type is more rapid; heat is employed and glacial acetic acid is used in the capacity of a diluent to minimize sulfonation.

The experimental results are consistent with the reaction mechanism which has been advanced previously.

Experimental Part

Slow Condensation.—Phenol and the three cresols were condensed by this method. The procedure involved in all four condensations was similar. A mixture of one mole of the phenol, one mole of allyl chloride, and one mole of sulfuric acid was allowed to stand in a flask, protected from moisture by a calcium chloride drying tube, for a period of six months. The condensation products of phenol, *o*- and *p*-cresol were subjected to the same treatment for the isolation of the reaction product. A volume of water twice that of the reactants was added and the whole then neutralized with sodium carbonate. The organic layer which separated was then removed, water washed and dried with anhydrous sodium sulfate. Distillation at atmospheric pressure was used to obtain the final product. The refractive index and density were taken immediately after distillation to avoid possible errors due to polymerization. In the case of *m*-cresol, the condensation product separated as a crystalline solid, and this was merely filtered off and recrystallized. All of the products have been obtained by resynthesis, as has been stated, and the agreement in properties is satisfactory.

At periods during the condensations, the gases evolved were collected in silver nitrate solutions; it was found in each case that a precipitate of silver chloride was formed.

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(1) Presented at the Washington Meeting of the American Chemical Society, 1933.

(2) Niederl and Storch, THIS JOURNAL, **55**, 284 (1933), and references therein cited.

(3) Niederl, Smith and McGreal, *ibid.*, **53**, 3390 (1931).

(4) Adams, M.Sc. Thesis, New York University, 1930.

(5) Storch, M.Sc. Thesis, New York University, 1930.

PHYSICAL CONSTANTS AND ANALYSES OF THE COMPOUNDS PREPARED

Compound and formula	Prepared from	B. p., °C.	Sp. gr.	n_D	Carbon, %		Hydrogen, %	
					Calcd.	Found	Calcd.	Found
2-Hydroxy-1-isopropenylbenzene,[a] $CH_2{=}C(CH_3)C_6H_4OH$	Isopropenyl phenyl ether	203–208	1.024_{28}	1.5452_{28}	80.55	80.23	7.52	7.25
	Allyl chloride and phenol	200	1.020_{26}	1.5320_{26}		80.18		8.36
4-Hydroxy-1-methyl-3-isopropenylbenzene,[b] $CH_2{=}C(CH_3)C_6H_3(CH_3)OH$	Isopropenyl *p*-cresyl ether	222–224	1.012_{24}	1.5362_{24}	81.07	80.73	8.17	8.00
	Allyl chloride and *p*-cresol	225	1.015_{26}	1.5286_{26}		81.31		8.46
2-Hydroxy-1-methyl-5-isopropenylbenzene,[c] $CH_2{=}C(CH_3)C_6H_3(CH_3)OH$	Isopropenyl *o*-cresyl ether	225–228	1.020_{28}	1.5395_{28}		80.68		8.35
	Allyl chloride and *o*-cresol	225	1.017_{29}	1.5386_{31}		80.74		8.38
3-Hydroxy-1-methyl-4-isopropenylbenzene,[d] $CH_2{=}C(CH_3)C_6H_3(CH_3)OH$	Isopropenyl *m*-cresyl ether	225	1.026_{25}	1.5402_{25}		81.40		8.38
	Allyl chloride and *m*-cresol	220–225	1.025_{26}	1.5358_{26}		81.43		8.52
1-Hydroxy-2-*m*-cresoxypropane (impure), $CH_2(OH)CH(CH_3)O_6C_6H_4(CH_3)$	Allyl chloride and *m*-cresol	218–220			72.28	73.72	8.43	8.55
2-*m*-Cresoxypropene-1 (impure), $CH_2{=}C(CH_3)OC_6H_4(CH_3)$	Allyl chloride and *m*-cresol	about 200			81.07	79.35	8.17	8.12
Dimer of 3-hydroxy-1-methyl-4-isopropenyl,[d] benzene,[b] ($C_{10}H_{12}O_2$)	Allyl chloride and *m*-cresol	74 (m. p.)						
Hexabromothymol,[e] $(CH_3)(CHBr_2)CBr(C_6Br_3)OH$	3-Hydroxy-1-methyl-4-isopropenylbenzene	149 (m. p.)						
Pentabromodehydrothymol,[e] $CBr_2{=}C(CH_3)C_6Br_3(CH_3)OH$	Hexabromothymol	102 (m. p.)						

[a] Béhal and Tiffeneau, *Bull. soc. chim.*, [4] **3**, 315 (1908); Hoering and Baum, Ger. Pat. 208,886 (1909); Fries and Volk, *Ann.*, **379**, 95 (1911); Fries, Gorss, Selbeck and Wicke, *ibid.*, **402**, 306 (1914).

[b] Guillaumin, *Bull. soc. chim.*, [4] **7**, 381 (1910); V. Auwers, *Ann.*, **413**, 304 (1917); Fries, *ibid.*, **372**, 229 (1910).

[c] Zincke, *Ann.*, **400**, 45 (1913).

[d] Fries and Fickewirth, *ibid.*, **362**, (1908); *Ber.*, **41**, 371 (1908); Guillaumin, *Bull. soc. chim.*, [4] **7**, 381 (1910); Hoering and Baum, German Patent 208,886 (1909).

[e] Baeyer and Seuffert, *Ber.*, **34**, 41 (1901); Fries and Fickewirth, *ibid.*, **41**, 371 (1908).

A blank run containing allyl chloride and sulfuric acid under the same experimental conditions did not yield a precipitate of silver chloride.

More Rapid Condensation.—It is possible to carry out the condensation at more elevated temperatures and so greatly decrease the reaction time. The method allows the isolation of the intermediate phenoxy compound in good yields where this is desired. If the reaction mixture be heated for a short time, the primary reaction product will be the ether; further heating increases the amount of the substituted phenol and decreases the relative amount of ether. The substituted phenol alone may be obtained as the final product. The condensation agent is again sulfuric acid; however, where heat is employed it is necessary to use a diluent to prevent sulfonation. Glacial acetic acid is used in this capacity. Equimolar quantities of allyl chloride, *m*-cresol and sulfuric acid (present as 33% of a glacial acetic acid solution) when refluxed for eight hours yielded approximately equal parts of the ether and the substituted phenol with about 30% of the *m*-cresol having reacted. It is advisable to use an excess of allyl chloride as there is some loss due to volatilization. After refluxing, the reactants were thrown upon water; the organic layer which separated was water washed and extracted with ten per cent. caustic potash. The alkali-insoluble portion was dried with anhydrous sodium sulfate and distilled. Analysis indicated the loss of water on distillation.

The alkaline extract was neutralized with 15% hydrochloric acid, the resulting organic liquid layer water washed and dried with anhydrous sodium sulfate. Distillation yielded isopropenyl-*m*-cresol. The hexa- and pentabromo derivatives were made from samples of this compound prepared by both the slow and rapid condensation. The procedure has been given in a former publication.[3]

Summary

The condensation of phenolic type compounds with the ethylenic linkage has been extended to unsaturated halides and the resulting condensation products were identified.

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The Common Basis of Intramolecular Rearrangements. II.[1] The Dehydration of Di-*tert*-butylcarbinol and the Conversion of the Resulting Nonenes to Trimethylethylene and Isobutylene

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The older conception of molecular rearrangements as involving primarily the migration of groups (positive, negative or neutral free radicals) has been superseded in this Laboratory by the hypothesis that the metathetical and elimination reactions[1] of organic chemistry which give rise to most rearrangements, involve the following steps: (1) removal of a group with a complete octet of electrons, leaving an atom with six electrons. The ensuing changes may include the following: (2a) union with

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[1] Whitmore, THIS JOURNAL, **54**, 3274 (1932).

[2] Presented in partial fulfilment of the requirements for the Ph.D. degree.