

ciable 1,3-reaction has occurred, each Q group which originally contained n substituents will contain $n - 1$ unreacted substituents. After the possibilities for 1,3-reaction have been exhausted, there will remain as isolated substituents a fraction given by

$$\frac{1}{2} \sum_2^{\infty} S_{n-1} Q_n = \sum_1^{\infty} S_n \left(\frac{1}{2}\right)^{n+2}$$

Upon substituting (6) for S_n this summation reduces readily to $1/2e$, the same result obtained above.

A somewhat similar analysis has been applied to the third case. The result is again $1/2e$. Since these three extreme cases all give the same result, it is probable that for all intermediate relative rates of reaction of 1,2- and 1,3-pairs the same result would be obtained. Thus, the fraction of isolated substituents remaining after intramolecular reaction of pairs of substituents of a random polymer will be $1/2e = 0.1840$ provided only that 1,4-pairs do not react. From precise quan-

titative determination of extent of reaction it should be possible to differentiate between a uniform 1,3-structure and a random structure by comparison with the above calculated result and with the result obtained for 1,3-polymers, 0.1353.

Summary

The condensation of pairs of consecutive substituents X of a high molecular weight polymer composed of $-\text{CH}_2-\text{CHX}-$ structural units has been analyzed statistically. When the units are regularly oriented so that the X's occur on alternate atoms along the chain, 13.53% of them are prevented from reacting due to isolation between reacted pairs. Analogous condensations in polymers which have their substituents oriented at random have been discussed. If reaction between 1,4-pairs of substituents does not occur, 18.40% of the substituents of a random polymer remain isolated after the possibilities for 1,2- and 1,3-reactions have been exhausted.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE PENNSYLVANIA STATE COLLEGE]

Hydrogen Fluoride as a Condensing Agent. VI.¹ The Alkylation of Benzene with Compounds Containing an "Allylic" Group

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In the course of our investigations concerning the utility of hydrogen fluoride as a condensing agent, we have studied the reactions of compounds containing an "allylic" grouping in the molecule. Cinnamic acid, benzyl chloride, allyl alcohol, and allylbenzene were caused to react with benzene in the presence of hydrogen fluoride. In the case of the alcohol, reaction took place at both the double bond and the hydroxyl group. The other compounds studied contained only one reactive group.

Benzyl chloride reacted with benzene to produce diphenylmethane. As it is difficult to account for this reaction on any hypothesis that requires an olefinic compound as an essential intermediate, its occurrence presents strong evidence against the postulation of any such mechanism.²

(1) For the previous paper of this series see Simons, Archer and Passino, *THIS JOURNAL*, **60**, 2956 (1938).

(2) For postulated mechanisms of this type see McKenna and Sowa, *ibid.*, **59**, 470 (1937).

When the proportion of cinnamic acid to benzene was small enough to prevent polysubstitution from taking place to any considerable extent, β,β -phenylpropionic acid was the only isolable product. That the α,β -acid was not formed is reasonable, as the carboxyl group is attached to the alpha carbon atom.

Two main products were formed in the reaction of allyl alcohol with benzene in the presence of hydrogen fluoride. Allylbenzene was identified as one of them by comparing the melting points and mixed melting point of a crystalline tribromide of the product with that of a tribromide of allylbenzene made through the Grignard reaction. The higher boiling product did not yield well-defined or reproducible derivatives, when treated with the usual reagents for such purposes. As it must be one of two possible isomers, 1,2- or 1,3-diphenylpropane, whose physical properties differ widely, a choice was made on the basis of the boiling point, density, and refrac-

tive index. Konowalow and Dobrowolski³ report these properties of the former as b. p. 280–281° at 758 mm., $d^{23.5}$ 0.9809 and $n^{23.5}$ 1.5591, and of the latter as 298–299°, d^{20} 1.0071 and n^{20} 1.5760. Our product had b. p. 277° at 730 mm., d^{20} 0.9817 and n^{20} 1.5574 and was therefore the 1,2-isomer.

When sulfuric acid was used to condense allyl alcohol and benzene, no product corresponding to allylbenzene was found. 1,2-Diphenylpropane and a large amount of a tarry residue were obtained.

Allylbenzene reacted with benzene at 0° to produce 1,2-diphenylpropane in a 62.5% yield. Some material was also formed which was probably polyalkylated benzenes.

Experimental

Reaction between Cinnamic Acid and Benzene.—The technique described in the previous papers of this series was employed. The hydrogen fluoride was removed by heating, and, after the benzene was removed by distillation, crude diphenylpropionic acid was obtained from the residue by crystallization from ethanol. Residual cinnamic acid was removed by treatment with three portions of hot water. Recrystallization from dilute alcohol gave a product that melted at 153.5–155°.⁴ The yield was about 53%. Its methyl ester melted at 45–46°⁵ and anilide melted at 175–176°.⁴

Reaction between Benzyl Chloride and Benzene.—This mixture with hydrogen fluoride was heated in a copper bomb at 100° for fifteen hours. The diphenylmethane obtained in a yield of 56% was nitrated to the 4,4'-dinitro-diphenylmethane, which melted at 180–182° after recrystallization from alcohol.⁶ No depression was observed in a mixed melting point with a known sample of the nitro compound.

Reaction of Allyl Alcohol with Benzene Using Hydrogen Fluoride.—The usual technique was employed, and two

(3) Konowalow and Dobrowolski, *Chem. Centr.*, **76**, 11, 826 (1905).

(4) Eijkman, *ibid.*, **79**, 11, 1100 (1908), reports the melting points of the acid and anilide as 154–155° and 177–178°, respectively.

(5) Kohler and Heritage, *Am. Chem. J.*, **33**, 26 (1905), report the melting point of the methyl ester as 47°.

(6) Staedel, *Ann.*, **283**, 181 (1894), reports 183° as the melting point.

main fractions were obtained from the distillation. The one was allylbenzene which boiled at 154.5–156° at 737 mm., n^{20} 1.5092–9. It was converted into the tribromide and the mixed melting point with a known sample determined. The other fraction boiled at 142.5° at 12 mm. and 277° at 730 mm., n^{20} 1.5574–5, d^{20} 0.9817. It has been shown to be 1,2-diphenylpropane. The proportions of the two products varied in different experiments. In two cases these were 13 g. of one to 23.8 g. of the other and 26.1 g. to 16.1 g., which corresponded to yields of 11, 12, 20, and 7.5%.

Reaction of Allyl Alcohol with Benzene Using Sulfuric Acid.—The reaction was allowed to proceed for about thirty-five hours. After separation and distillation 1,2-diphenylpropane boiling at 111° at 4 mm. and 274° at 730 mm., n^{20} 1.5580–90, was obtained in a yield of about 32%. The only other product was a tarry residue.

Reaction of Allylbenzene with Benzene.—This reaction was allowed to proceed at 0° for about six hours: 1,2-diphenylpropane, b. p. 105.5–108° at 3 mm. and 277° at 730 mm., n^{20} 1.5570–80, was obtained in a yield of 62.5%, and also a small amount of higher boiling material.

Alternate Synthesis of Allylbenzene.—Allyl bromide was added to a phenyl Grignard in ether. The product, allylbenzene, b. p. 155–155.5° at 737 mm., n^{20} 1.5100–6 was obtained in 55 to 60% yield.

Bromination of Allylbenzene.—One cubic centimeter of the hydrocarbon was added to a solution of bromine in 10 cc. of carbon tetrachloride. The addition was accompanied by the evolution of heat and hydrogen bromide. The mixture was then heated for one-half hour on the steam-bath. Chilling in ice caused a white crystalline compound to separate. Two crystallizations from methanol gave a tribromide of m. p. 124.5–125°. *Anal.* Calcd. for $C_9H_9Br_3$: Br, 67.2. Found: Br, 67.3.

Summary

Hydrogen fluoride has been used to obtain reaction between a number of "allylic" compounds and benzene. β,β -Diphenylpropionic acid was obtained from cinnamic acid; diphenylmethane from benzyl chloride; both allylbenzene and 1,2-diphenylpropane from allyl alcohol; and 1,2-diphenylpropane from allylbenzene. A crystalline tribromide derivative of allylbenzene has been prepared.

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