ABSTRACTS

and inactive p-nitrobenzoic acid. A similar oxidation and oxidative disruption prior to the nitration of desoxybenzoin-carbonyl-C¹ also take place and give benzil-carbonyl-C¹, benzoic acid-carboxyl-C¹ and inactive benzoic acid. The essential reaction routes are shown as follows.

Studies on Condensation Products of Chlorinated Phenols with Chlorkal. (I)

The Structure of Condensation Product of 2,4-Dichlorophenol or 2,4-Dichloroanisole with Chlorkal

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In recent paper, Riemschneider (J. Am. Chem. Soc., 76, 4853 (1952)) obtained a compound II, mp. 154°C, by methylating condensation product (I) of 2,4-dichlorophenol with chlorkal, and another compound V, mp. 160°C, by condensing 2,4-dichloroanisole with chlorkal. He proposed (1) these two compounds were stereoisomers of 1,1-bis-(2'-methoxy-3',5'-dichlorophenyl)-2,2,2-trichloroethane resulting from the restricted rotation of benzene rings, and (2) the dichloroethylene compounds III, mp. 166°C, and VI, mp. 157°C, obtained by dehydrochlorination of compounds II and V, respectively were also the same type stereoisomers.

This study was undertaken to ascertain the above results and obtained the following conclusion. To a mixture of above 1,1-bis-(x'-methoxy-y', z'-dichlorophenyl)-2,2,2-trichloroethane (compound II or V) and diethylene glycol was added a concentrated potassium hydroxide solution, and then the mixture was refluxed at 160-170°C for 5 hours. Bis-(x'-hydroxy-y', z'-dichlorophenyl)-methane (IV), mp. 167.5-168.5°C, was obtained from compound II through hydrolysis, decarboxylation and following demethylation. Compound IV was not identical with the corresponding compound VII, mp. 152.5-153.5°C, obtained from compound V. Compound IV was also prepared by condensing 3,4-dichlorophenol with paraformaldehyde. Compound IV was then dechlorinated to bis-(2-hydroxyphenyl)-methane, mp. 117-118°C, with sodium in liquid ammonia. From the above, it was confirmed that the structure of compound II is 1,1-bis-(2'-methoxy-3', 5'-dichlorophenyl)-2, 2, 2-trichloroethane which was identical with the structure proposed by Riemschneider.

On the other hand, a compound, mp. 96-97°C, which was obtained by the same procedure from compound VII, was identical with bis-(3-hydroxyphenyl)-methane.
derived from bis-(3-nitrophenyl)-methane. So the structure of compound V should be 1,1-bis-(2'-methoxy-4', 6'-dichlorophenyl)-2, 2, 2-trichloroethane, differing from the Riemenschneider's proposition.

From these facts, it was concluded that compounds II and V were not stereoisomers, but positional isomers of two benzene rings, and that the corresponding ethylene compounds (III and VI) were also not stereoisomers but positional isomers.