

Formation of Diphenylmethane Derivatives during the Jacobsen Reaction

By H. SUZUKI* and Y. TAMURA

(Department of Chemistry, Faculty of Science, Kyoto University, Sakyo-ku, Kyoto, Japan)

A LITTLE KNOWN feature of the Jacobsen reaction¹ is a disproportionation of pentamethylbenzene and monochlorotetramethylbenzenes. We report the preparation of several diphenylmethanes by this reaction. Our result is of interest in connection with the recent suggestion of diphenylalkane intermediates for the disproportionation of primary alkylaromatics in the Friedel-Crafts reaction.²

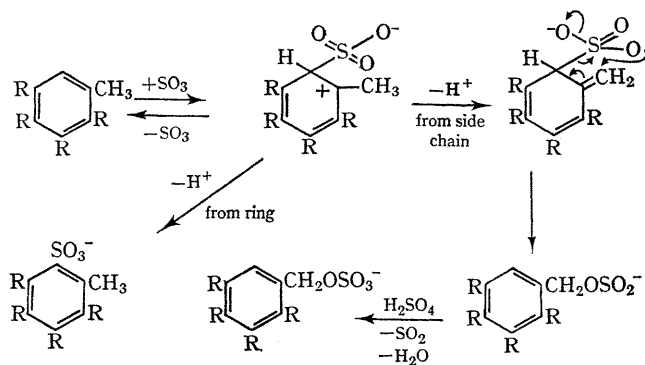
Treatment of 1-chloro-2,3,5,6-tetramethylbenzene with sulphuric acid at room temperature gave chloropentamethylbenzene and a crystalline by-product (m.p. 205—207°), the structure of which was established as 3',4-dichloro-2,2',3,4',5,5',6-heptamethyldiphenylmethane (m.p. 213—215°) by condensing 4-chloro-2,3,5,6-tetramethylbenzyl chloride with 1-chloro-2,3,5-trimethylbenzene in trifluoroacetic acid. Both 1-chloro-2,3,4,6-tetramethylbenzene and 1-chloro-2,3,4,5-tetramethylbenzene gave a

mixture of two dichloroheptamethyldiphenylmethanes, in which the major component was identified, respectively, as 2',5-dichloro-2,3,3',4,4',5',6-heptamethyldiphenylmethane (m.p. 219—220°) and 2',6-dichloro-2,3,3',4,4',5,5',6-heptamethyldiphenylmethane (m.p. 226—227°) by unequivocal synthesis. The partial skeletal rearrangement observed in the latter is probably to be attributed to the isomerization of the initially formed 5',6-dichloro-2,2',3,3',4,4',5-heptamethyldiphenylmethane. Sulphur dioxide and hydrogen chloride were liberated during the reaction.

Preferential condensation with the methyl group *ortho* to the hydrogen may be explained by the nuclear-to-lateral migration of the sulphonic acid group to yield the benzyl sulphite or sulphate, which would then act as a benzylating agent to give a diphenylmethane.³ The process is analogous to those suggested to explain the chlorination of hexamethylbenzene to form 2,3,4,5,6-pentamethylbenzyl chloride,⁴ and the nitration of penta-alkylbenzenes to give 2,3,4,5-tetra-alkylbenzyl nitrates.⁵

Electrophilic attack on certain polyalkylbenzenes leads to the formation of similar diphenylmethane derivatives; the nitration of 1,2,3,5-tetramethylbenzene is said to yield a polymethyldiphenylmethane,⁶ and the positive hydroxylation of 1-chloro-2,4,6-trimethylbenzene and 1,2,3,4-tetramethylbenzene is reported to give 2',3-dichloro-4'-hydroxy-2,3',4,5',6-pentamethyldiphenylmethane,⁷ and 2,2',3,3',4,4',5,5'-octamethyldiphenylmethane,⁸ respectively.

(Received, October 14th, 1968; Com. 1408.)



¹ H. J. Shine, "Aromatic Rearrangements", Elsevier, London, 1967, p. 23.

² A. Streitwieser, jun., and L. Reif, *J. Amer. Chem. Soc.*, 1964, **86**, 1988; R. M. Roberts, A. A. Khalaf, and R. N. Green, *ibid.*, p. 2864.

³ Z. Földi, *Ber.*, 1928, **61**, 1609.

⁴ E. Baciocchi, A. Ciana, G. Illuminati, and C. Pasini, *J. Amer. Chem. Soc.*, 1965, **87**, 3953.

⁵ H. Suzuki, K. Nakamura, and K. Maruyama, *Bull. Chem. Soc. Japan*, 1968, **41**, 1487.

⁶ H. Zollinger, unpublished observations. We confirmed the formation of 2,2',3,3',4,4',5,5',6-nonamethyldiphenylmethane in the nitration of pentamethylbenzene.

⁷ C. A. Buehler and H. Hart, *J. Amer. Chem. Soc.*, 1963, **85**, 2177.

⁸ H. Hart and C. A. Buehler, *J. Org. Chem.*, 1964, **29**, 2393.