Boron Photochemistry: 1-Phenylcyclohexa-1,4-diene from Sodium Tetraphenylborate

By J. L. R. WILLIAMS, J. C. DOTY, P. J. GRISDALE, T. H. REGAN, and D. G. BORDEN
(*Research Laboratories, Eastman Kodak Company, Rochester, New York* 14650)

POTASSIUM TETRAPHENYLBORATE has been reported[1] to undergo photolysis in chloroform solution to produce benzene, biphenyl, phenol, and potassium chloride. We have investigated the ultraviolet irradiation of solutions of sodium tetraphenylborate in water and in isopropanol. When it was irradiated under nitrogen with light rich in wavelength 2537 Å, the products were biphenyl, 1-phenylcyclohexa-1,4-diene, and the sodium salt of diphenylboronic acid, Ph_2BONa. By careful exclusion of oxygen, mixtures of biphenyl and 1-phenylcyclohexa-1,4-diene containing as much as 97% of the latter were obtained. When air was present during the irradiation, a mixture of 77% of biphenyl and 23% of 1-phenylcylohexa-1,4-diene resulted. Phenol and phenylboronic acid which resulted from the nonphotochemical decomposition of Ph_2BONa were isolated also. Photolysis of $NaBPh_4$ in isopropanol solution under nitrogen yielded a mixture of 23% biphenyl, 70% 1-phenylcyclohexa-1,4-diene, and 6% of an additional diene which is an isomer of 1-phenylcyclohexa-1,4-diene. In addition, benzene and acetone were detected. When an analogous photolysis of a solution of $NaBPh_4$ in isopropanol was conducted under an atmosphere of air, the products were acetone, benzene, and mixtures ranging between 70—90% of biphenyl and 30—10% of *p*-terphenyl.

In a typical photolysis, $NaBPh_4$ (5 g.) in water (250 ml.), was irradiated for 5 hr. at 20° under nitrogen in a Rayonet photochemical reactor. From the reaction mixture 0·6 g. of a mixture consisting of 3% biphenyl and 97% 1-phenylcyclohexa-1,4-diene was isolated. Unreacted $NaBPh_4$ was recovered as the potassium salt (4 g.). By use of more powerful sources of ultraviolet light, together with longer reaction times, conversions of 76% have been attained, leading to yields of 90—95% of 1-phenylcyclohexa-1,4-diene. 1-Phenylcyclohexa-1,4-diene, which has not heretofore been reported, has the following physical properties: m.p. 89—90°; λ_{max} (cyclohexane): 249, ϵ 9300; n.m.r. (CCl_4): δ 2·90 (multiplet 4H), 5·72 (multiplet 2H), 5·98 (multiplet 1H), 7·2 (aromatic > 5H, biphenyl trace); infrared: 958 cm.$^{-1}$; mass spectrum parent ion *m/e* 156. The elemental analysis was consistent with the empirical formula.

Our current work is concerned with optimizing the reaction conditions–yield relationship, as well as the effect of other solvents and cations on the ratio of products.

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[1] G. A. Razuvaev and T. G. Brikina, *Zhur. obshchei Khim.*, 1954, **24**, 1415.