

Short Communications

Synthesis of 1,2,4,5,7,8-Hexachloroxanthene

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Hexachlorophene [bis-(2-hydroxy-3,4,6-trichlorophenyl)methane] has been used extensively for the past 20 years as an antibacterial agent in soaps, cosmetics and antiseptic solutions. Toxic reactions due to absorption of the agent through the skin have recently been reviewed.^{1,2} In connection with studies concerning the occurrence and structure of neutral, polycyclic compounds as contaminants in commercial samples of hexachlorophene,³ attempts were made to prepare the corresponding xanthene derivative. Treatment of hexachlorophene with polyphosphoric acid at 220° gave a complex reaction mixture, containing only small amounts of neutral products. Prolonged treatment of the phenol (1 mol) in hot diglyme with *p*-toluenesulphonyl chloride (2 mol) and an excess of sodium hydroxide, however, gave a 77 % yield of 1,2,4,5,7,8-hexachloroxanthene.

This type of reaction does not appear to have been used as a route to xanthenes containing halogen or other electron-withdrawing substituents. A somewhat analogous reaction with the formation of xanthenes from 2-hydroxy-2'-methoxybenzophenones under mild basic conditions has, however, been reported.^{4,5}

Experimental. Hexachlorophene (Koch-Light, pure, free from neutral contaminants) (2.04 g, 5 mmol) and sodium hydroxide (1.0 g, 25 mmol) in dry diglyme (40 ml) were heated with magnetic stirring under argon to 135–

140° (bath temperature) during one hour. *p*-Toluenesulphonyl chloride (1.90 g, 10 mmol) was added and heating was continued as above for 27 h. Water (10 ml) was added to the cool reaction mixture. The crystalline material was collected after one night in the refrigerator. It was washed with 0.5 M sodium hydroxide solution and water and dried; yield, 1.5 g. The product was chromatographically pure (TLC, Kieselgel HF (Merck); methanol-carbon tetrachloride 1 : 5). Crystallisation from toluene-acetone gave needles, which were sublimed at 140°/0.05 mmHg. M.p. 261–262° (closed capillary). (Found C 39.7; H 1.2; Cl 54.35. C₁₃H₄Cl₆O (388.9) requires C 40.1; H 1.0; Cl 54.75.) UV-spectrum: λ_{\max} (EtOH) 207 nm (ϵ 35 000), 226(29 000), 262 (shoulder, 13 000), 267(14 000), 292 (4300) and 302 nm (ϵ 4500). The NMR-spectrum (Varian A60-A, 0.005 M in carbon tetrachloride) showed two signals of equal intensity, δ = 4.13 ppm and δ = 7.48 ppm (tetramethyl silane as internal standard). The mass spectrum (LKB-9000) showed molecular ions at m/e = 386, 388, 390, 392, 394, and 396 m.u. with relative intensities *ca.* 1.0 : 1.9 : 1.5 : 0.65 : 0.15 : 0.04, respectively, accompanied by the corresponding ions M⁺ - 1.

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