393. *Preparation of Some Chromans from* 1,3-*Diaryloxypropanes.*

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The preparation of chromans has been reviewed by Maitte [1] who regarded the action of stannic chloride on 3-aryloxypropyl halides as superior to other methods available to him. He reported the preparation of chroman in 85% yield, methylchroman (85% yield), and 6-chlorochroman (20% yield). In our hands, the method gave variable yields of product which required gas chromatography for purification.

We have found, however, that the readily prepared 1,3-diphenoxypropane reacts smoothly with aluminium chloride (1·3 mol.) in boiling benzene to give chroman and phenol. Chroman of high purity is isolated without difficulty and in high yield (72%). Similar treatment of 1,3-di-*p*-tolyloxy- and 1,3-di-*p*-chlorophenoxy-propane gives 6-methyl- (92%) and 6-chloro-chroman (65%), respectively. In each case the accompanying phenol

[1] Maitte, *Ann. Chim.* (*France*), 1954, **9**, 431.

is also recovered in high yield. Increasing the amount of aluminium chloride to 1·7 mol. has little effect on the production of chroman; 1·05 mol. appears to be insufficient for complete breakdown. Sulphuric acid does not promote formation of the chroman and hydrobromic acid is brought into reaction only at 250° (sealed tube) and then gives only poor yields.

Experimental.—Diaryloxypropanes. In a typical preparation, 1,3-dibromopropane (70 g.) was added dropwise to a stirred solution of phenol (150 g.) and sodium hydroxide (47 g.) in water (200 ml.). The mixture was refluxed for 3 hr. and then cooled whilst being stirred. The product was filtered off and washed with 3% aqueous alkali and with water. Recrystallisation from ethanol gave 1,3-diphenoxypropane (60 g., 76%), m. p. 60°. Similarly were obtained 1,3-di-*p*-tolyloxy- (77% after recrystallisation from ethanol), m. p. 91°, and 1,3-di-*p*-chlorophenoxy-propane (82% after recrystallisation from acetic acid), m. p. 120—121°. In each case, ~90% of the excess of phenol was recovered from the alkaline wash-liquors.

Decomposition of diaryloxypropanes. In a typical experiment, anhydrous aluminium chloride (26·5 g.) was added to a stirred slurry of 1,3-diphenoxypropane (35 g.) in anhydrous benzene (300 ml.). The mixture was refluxed for 4 hr., cooled, and poured on ice (250 g.). Concentrated hydrochloric acid was added and the benzene layer was separated. The aqueous layer was extracted with ether (3 × 100 ml.). The combined organic liquids were washed thoroughly with 3% aqueous alkali and with water and were dried ($MgSO_4$). The solvents were removed by distillation. Fractionation of the residue gave chroman (14·8 g., 72%), b. p. 96—100°/16 mm., n_D^{17} 1·5505, (lit.,[1] n_D^{16} 1·5505) (Found: C, 80·0; H, 7·4; O, 11·85. Calc. for $C_9H_{10}O$: C, 80·6; H, 7·45; O, 11·95%). The infrared spectrum was identical with that of authentic chroman prepared by Maitte's method [1] and purified by gas chromatography. Our product was also converted [2] into 6-nitrochroman, m. p. 102° undepressed on addition of an authentic sample. The alkaline wash-liquor from the chroman preparation was treated by standard methods to yield phenol (13 g.).

Decomposition of 1,3-di-*p*-tolyloxypropane (40 g.) gave 6-methylchroman (21·2 g., 92%), b. p. 103—105°/14 mm., n_D^{15} 1·5442 (lit.,[1] n_D^{16} 1·5441) (Found: C, 81·25; H, 8·15; O, 11·1. Calc. for $C_{10}H_{12}O$: C, 81·1; H, 8·1; O, 10·8%), and *p*-cresol (13·9 g.).

From 1,3-di-*p*-chlorophenoxypropane (65 g.) were obtained 6-chlorochroman (24·0 g., 65%), b. p. 86—89°/1 mm., n_D^{15} 1·5653 (lit.,[1] $n_D^{14.5}$ 1·5648) (Found: C, 64·2; H, 5·35; O, 9·5. Calc. for C_9H_9ClO: C, 64·15; H, 5·35; O, 9·5%), and *p*-chlorophenol (24·5 g.).

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[2] Hach, *Coll. Czech. Chem. Comm.*, 1959, **24**, 3136.