Photochemical Cyclisation of Allylanisoles to Cyclopropylanisoles

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2- and 4-Allylanisoles are cyclised by u.v. light to the corresponding cyclopropylanisoles

In the light of many recent reports of biologically active compounds containing the cyclopropyl group, we describe a further method of introducing this substituent.

Although when directly attached to a benzene ring the cyclopropyl group is reasonably stable, it is often sensitive to both heat and acids. Thus, ring opening occurred when Friedel–Crafts alkylation of phenol with cyclopropyl bromide was attempted.[1] Cyclopropylanisoles have been prepared [2] by nitration of a phenylcyclopropane at $-50°$, separation of the isomeric mixture, reduction, diazotisation, and hydrolysis to the phenol, followed by methylation. The formation of the cyclopropane ring by u.v.-induced cyclisation of a propene grouping has been reported.[3-5] However u.v. light has also been reported to (1) open the cyclopropane ring,[6-8] (2) cause addition of solvent molecules to the olefin,[9] and (3) cause cyclisation of the olefin by interaction with other functional groups in the molecule [10,11] (*e.g.* the formation of cyclic ethers from 2-allylphenols).

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The feasibility of the photochemical synthesis of cyclopropylanisoles depends upon the incidence and extent of such reactions.

Initial irradiation experiments on 4-allylanisole in methanol showed that small changes occurred in the u.v. spectrum but these were not sufficiently marked for the course of the reaction to be followed. Direct injection of samples into a g.l.c. instrument showed the presence of a product with a longer retention time. The amount of this product increased with increasing reaction time until *ca.* 12% of the starting material remained, and then started to decrease. The irradiation time for optimum yield appeared to be 55 h. Preparative g.l.c. gave only very low yields of the product, and attempts at separation on silica gel or alumina columns were not successful, but the use of silica gel impregnated with silver nitrate resulted in a clear separation of pure 4-cyclopropylanisole.

Irradiation of 2-allylanisole in the same way produced 2-cyclopropylanisole.

EXPERIMENTAL

I.r., n.m.r. and mass spectra were recorded with Perkin-Elmer 257, Varian HA100 and LKB 9000 instruments respectively. ' Light petroleum ' refers to the fraction of b.p. 40—60°. Chromatography was carried out on silica gel (Merck type 60; 0·063—0·200 mm) or alumina (Camag, neutral; 100—250 mesh). G.l.c. was carried out on a Varian 1840 instrument (6 ft × 1/8 in stainless steel column packed with 1% OV 17 on GasChrom Q); compositions of mixtures were determined by using a disc integrator.

Irradiations were carried out with a Hanovia 100 W medium-pressure lamp in a quartz apparatus, the solution being stirred under nitrogen.

4-Cyclopropylanisole.—A solution of 4-allylanisole (1 g) in methanol or acetone (175 ml) was irradiated. Analytical g.l.c. at 90° showed a gradual loss of 4-allylanisole with the appearance of a product with longer retention time. The amount of product reached a maximum and then started to decrease. At the optimum time (55 h) 12% 4-allylanisole remained unchanged and the yield of 4-cyclopropylanisole was 40% (by g.l.c. based on 4-allylanisole consumed). Column chromatography on silica gel impregnated with silver nitrate (10% w/w) (eluant 1% ether–light petroleum) gave the product as a pure (g.l.c.) oil (250 mg, 25%), showing no i.r. bands (due to allyl groups) at 1640, 995, and 915 cm^{-1}; δ (CCl_4; 100 MHz) 0·92—0·55 (4H, m, $\overline{C\mathit{H}_2\cdot C\mathit{H}_2\cdot CH}$) and 1·9—1·65 (1H, m, $\overline{CH_2\cdot CH_2\cdot C\mathit{H}}$); mass spectrum as reported for 4-cyclopropylanisole.[12] Starting material was eluted with 25% ether–light petroleum.

2-Cyclopropylanisole.—2-Allylanisole (2 g) in acetone or methanol (175 ml) was irradiated for 55 h. Isolation as above gave 2-cyclopropylanisole (33% by g.l.c. based on 2-allylanisole consumed) as an oil (425 mg, 21%), showing no i.r. bands at 1640, 998, and 912 cm^{-1}; δ 0·92—0·55 (4H, m) and 2·2—1·95 (1H, m); mass spectrum as reported.[12]

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