

A CONVENIENT ROUTE TO 4,4'-DIALKOXYAZOXYBENZENES*

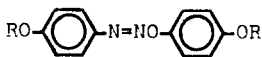
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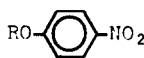
p-Azoxyanisole, and other 4,4'-dialkoxyazoxybenzenes, are among the most familiar materials that form liquid crystals, and such compounds have been used in a wide variety of studies of the liquid crystalline state (1). Recently there has been a marked revival of interest in this field, in particular in the use of liquid crystals as solvents for n.m.r. spectroscopy (2), and as stationary phases in gas chromatography (3); consequently there is now a considerable demand for materials that form liquid crystals, in particular for derivatives (I) of azoxybenzene.

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I



II

Compounds of this type have previously been prepared by reduction of the corresponding nitrophenyl ethers (II), either with sodium methoxide (4), or electrolytically (5). Neither of these procedures is altogether satisfactory; reduction with sodium methoxide leads to partial exchange of alkoxy by methoxy, while cathodic reduction requires special equipment and cannot easily be carried out on a large scale. Since we have had numerous enquiries concerning the preparation of pure I, we feel that the following simple procedure should be placed on record.

Various authors have reported the reduction of nitrobenzene and its derivatives to the corresponding azo compounds by lithium aluminum hydride (6), or lithium trimethoxyaluminum hydride (7). We have found that *p*-nitrophenyl ethers (II) are reduced to the corresponding 4,4'-dialkoxyazobenzenes in good yield by lithium aluminum hydride in ether at room temperature, and that the resulting azo compounds can be oxidized almost quantitatively to I by hydrogen peroxide in acetic acid to the corresponding (8) azoxy compounds (I). This route to I was further improved by carrying out the reductions at low temperatures, when the main product was the azoxy compound (I), contaminated with some of the corresponding azo derivatives. Oxidation of the crude reaction mixture with hydrogen peroxide in acetic acid gave pure I in excellent overall yield (67-76% from II). These reactions require no special equipment and can be carried out equally conveniently on a large scale.

Experimental

4,4'-Dihexyloxyazoxybenzene (I; R=n-C₆H₁₃). A solution of p-hexyloxy nitrobenzene (II; R=n-C₆H₁₃) (10.2 g.; 0.0457 mole) in dry ether (150 ml.) was added slowly to one of lithium aluminum hydride (2.5 g., 0.066 mole) in dry ether (300 ml.) at -70° and the resulting solution then allowed to warm up slowly to room temperature. Excess lithium aluminum hydride was then decomposed by adding water, the ether distilled, the residue dissolved in acetic acid (500 ml.), hydrogen peroxide (5.2 g. of 30%) added, and the solution held at 65° for 36 hours and then poured into water. The precipitate of 4,4'-dihexyloxyazoxybenzene crystallized from 95% ethanol in pale yellow needles (6.8 g., 75%), m.p. 81° (lit. (5) 81°), nematic+liquid transition 128° (lit. (5) 127°). Occasionally the product may still contain small amounts of unoxidized azo compounds at this stage; if so, the peroxide treatment can be repeated without significant loss.

Anal. Calcd. for C₂₄H₃₄N₂O₃: C, 72.30; H, 8.54; N, 7.03.
Found: C, 72.74; H, 8.61; N, 6.83.

Chromatography of the crude reduction product on alumina separated it into I, and the corresponding azo compound, in 2.3:1 ratio.

p-Azoxyanisole (I; R=Me). Prepared likewise from p-nitroanisole in 76% overall yield, the product had m.p. 119° (lit. (9) 118.5°), nematic+liquid transition, 135° (lit. (9) 135°) undepressed by authentic material.

p-Azoxyphenetole (I; R=Et). Prepared likewise from p-nitrophenetole in 67% overall yield, the product had m.p. 137° (lit. (10) 137°), nematic+liquid transition 167° (lit. (10) 167°). Anal. Calcd. for $C_{16}H_{18}N_2O_3$: C, 67.13; H, 6.29. Found: C, 66.78; H, 6.55.

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