

Reactions of 2,2'-(Azo-2-phenoxypropane) with Bromine: a Novel Route to *o*- and *p*-Bromophenol

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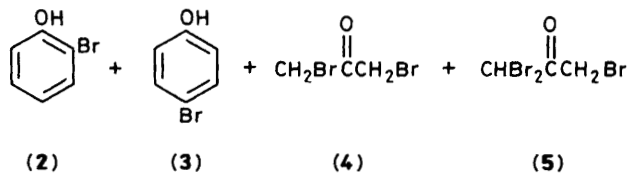
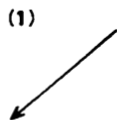
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o- and *p*-Bromophenol have been synthesized from the reactions of 2,2'-(azo-2-phenoxypropane) with different concentrations of bromine in 68 and 88% yields, respectively.

In connection with a mechanistic study on the reaction of 2,2'-(azo-2-phenoxypropane) (1) with cation radicals,¹ we studied the reaction of (1) with bromine and found a useful route for obtaining *o*- (2) and *p*-bromophenol (3) by controlling the concentration of bromine. Although there have been extensive studies on the bromination of phenol under various conditions,² little is known about efficient methods to prepare (2).³ Pearson *et al.*⁴ reported a complicated method for nearly specific halogenation *ortho* to the hydroxy group, which involved the use of bromine, *t*-butylamine, and toluene at

−70 °C, giving a 60% yield of (2). Another method requires careful control of conditions and gives only a 40% yield.³ We report here our results on the bromination of (1) (Scheme 1). Compound (1) is readily prepared from acetone by the route in Scheme 2.

With a molar ratio of (1) to Br₂ of ~1 : 2, the yields of (2) and (3) were 68 and 2%, respectively, based on (1). However, by increasing the proportion of bromine to about 1 : 7, only (3) was isolated, in 88% yield. To our knowledge, this is the first example in which both (2) and (3) may be synthesised in good

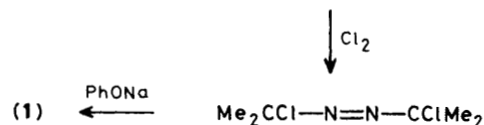
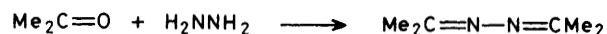


Scheme 1. Amounts (mmol) of bromine and products:^a

Br_2	(2)	(3)	(4)	(5)
19.41	13.70	0.44	1.34	Trace
67.94	0	17.81	1.64	1.61

^a To a stirred solution of (1) (10.07 mmol) in MeCN (60 ml) was added Br_2 in CCl_4 (30 ml) at room temperature. The reaction was completed in a few minutes. The products were identified by comparison of spectroscopic and physical data with those of authentic samples. Yields are for isolated products after column chromatography on silica gel: (5) and (4), hexane as eluant; (3), benzene; and (2), CH_2Cl_2 .

yields from the same reaction by controlling the bromine concentration. 1,3-Dibromopropanone (4) and 1,1,3-tribromopropanone (5)⁵ could readily be separated, and their yields also depended on the concentration of bromine. The



Scheme 2

mechanism of the formation of (2) and (3) is uncertain. However, (1) appears to be readily hydrolysed to give acetone^{1,6} which then undergoes bromination to yield (4) and (5).

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