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

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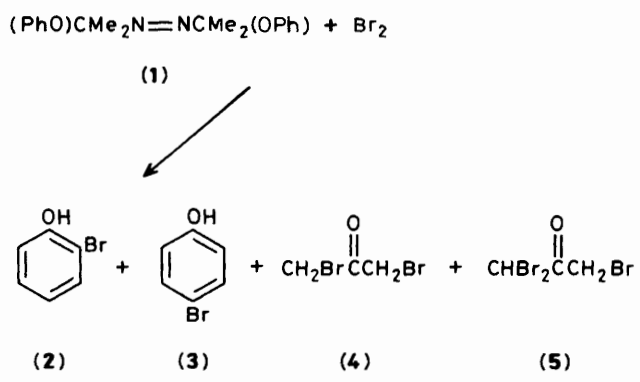
o- and *p*-Bromophenol have been synthesized from the reactions of 2,2′-(azo-2-phenoxypropane) with different concentrations of bromine in 68 and 88% yields, respectively.

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 Br_2 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

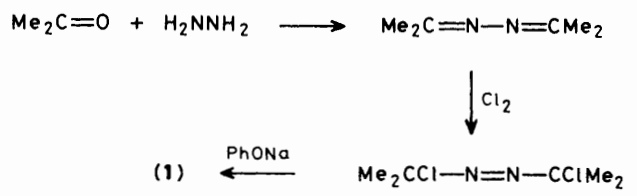


Scheme 1. Amounts (mmol) of bromine and products:[a]

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 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**).



Scheme 2

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