Oxidation of Secondary Aromatic Alcohols with N-Bromo-amides

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N-Bromo-amides and -imides have been widely used for the oxidation of secondary aliphatic and alicyclic alcohols.¹ It has been concluded² that N-bromoacetamide, one of the most common reagents, fails towards aromatic alcohols other than those of benzylic type. On the contrary, our results indicate that N-bromoacetamide, as well as 1,3-dibromo-5,5-dimethylhydantoin, can be successfully used for the oxidation of secondary aromatic alcohols, independently of the relative positions of the hydroxyl group and the aromatic ring (see Table).

The oxidant (0.003 mole of N-bromacetamide or 0.0015 mole of the dibromodimethylhydantoin), pyridine (0.003 mole), and the alcohol (0.0025 mole) in a mixture of acetone (25 ml.) and water (8 ml.) were kept in the dark at 25° until reaction was complete (iodometry). The upper layer formed on addition of water and ether was repeatedly washed with water and dried. The solvent was

distilled off and the residue heated at 65° with passage of nitrogen to remove traces of acetone.

The ketones were isolated as semicarbazones (benzyl n-propyl ketone as 2,4-dinitrophenyl-hydrazone) and identified by m.p. and mixed m.p.

		% Yield of ketone	
Alcohol		A	B
Ph·CHMe·OH	 	61	
Ph·CH ₂ ·CHMe·OH	 	51	44
Ph·CH2·CHPr·OH	 	43	
Ph·CH ₂ ·CHPr ¹ ·OH	 	53	58*
Ph·[CH ₂] ₂ ·CHMe·OH	 	74	72†
$Ph \cdot [CH_2]_3 \cdot CHMe \cdot OH$	 	64	59

- A, by use of 1,3-dibromo-5,5-dimethylhydantoin. B, by use of N-bromoacetamide.
- * Run as described in ref. 2; isolated as semicarbazone.
- \uparrow With the conditions of ref. 2, the yield of semicarbazone was 78%.

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For recent surveys see (a) R. Filler, Chem. Rev., 1963, 63, 21, (b) R. A. Reed, Chem. Products, 1960, 299.
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