Adamantyl-substituted Phenols

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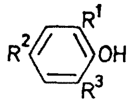
Summary A convenient one-step synthesis of adamantyl-substituted phenols from a mixture of a phenol and 1-bromoadamantane in *NN*-dimethylformamide is described.

It has been reported[1] that alkylation at the *ortho* and *para* positions in the aromatic ring increases the lability of the phenolic hydrogen and thus the antioxidant efficiency, which is further enhanced by the presence of very bulky *ortho*-substituents. Therefore it seemed to us that synthesis of adamantyl substituted phenols may be useful. We now report a convenient procedure for the mono-, di-, and tri-substitution of phenols at the *ortho* and *para* positions by 1-bromoadamantane.



(I) R^1 = Adamantyl, R^2 = Bu^t, R^3 = H
(II) R^1 = R^3 = Adamantyl, R^2 = Me_2CH–
(III) R^1 = R^2 = Adamantyl, R^3 = H
(IV) R^1 = R^2 = R^3 = Adamantyl

A mixture of 1-bromoadamantane, *p*-isopropylphenol, and sodium (molar ratio: 2 : 1 : 1) in *p*-xylene and *NN*-dimethylformamide after being heated under nitrogen at 83° for 25 h, gave 2,6-diadamantyl-4-isopropylphenol (II) (m.p. 202—204°, yield: 10%). The structure of the product was determined by elemental analysis and n.m.r. ($CDCl_3$): τ 8·8 (d, 6 isopropyl H; J = 6·6 Hz), signals centred at 8·21 and 7·87 (30 adamantyl H), at 7·48 (m, 1 isopropyl H), 4·85 (s, 1 phenolic H), and 3·05 (s, 2 Ar*H*). The chemical shift for the aromatic protons (τ 3·05) and the fact that they appear as a singlet, indicate that they are identical and, for steric reasons, *ortho* to R^2. The i.r. spectrum indicates the presence of phenolic OH (ν 3630 cm^{-1}); the i.r. band being sharp in contrast to the broad band present in the spectrum of the starting phenol. Treatment of (II) with lead dioxide gave a transient blue colour indicating the probable presence of phenoxy-radical.

It was found that this substitution reaction could be extended to other derivatives of phenol. Thus an approximately equimolar mixture of *p*-t-butylphenol and 1-bromoadamantane under the same conditions as for *p*-isopropylphenol yielded a mono-substitution product 2-adamantyl-4-t-butylphenol (I) m.p. 126·5—128° in 89% yield. Similarly a mixture of phenol and 1-bromoadamantane (molar ratio: approx. 1 : 2) under the same reaction conditions gave a mixture of products from which a di-substitution product, 2,4-diadamantylphenol (III) (m.p. 252—253°) and a tri-substitution product, 2,4,6-triadamantylphenol (IV) (m.p. >360°) were isolated. The structures of the products (I), (III), and (IV) were determined by elemental analyses, n.m.r. and i.r. spectra. For (I) n.m.r. ($CDCl_3$): τ 8·7 (s, 9 t-butyl H); 8·19, 7·85 (m, 15 adamantyl H); 6·20 (phenolic H); τ 4·54 (d), 4·10 quartet and 3·95 (d), (3 Ar*H*). For (III), n.m.r. ($CDCl_3$): τ 8·5, 8·21 (d, 30 H); 5·5H (s, 1 phenolic H); 4·28 (quartet), 4·05 (d) and 3·86 (s), (3 Ar*H*). For (IV) n.m.r. ($CDCl_3$): τ 8·37 (m, 45 adamantyl H); 5·68 (s, 1 phenolic H), 4·05 (s, 2 aromatic protons).

Thus this ready substitution reaction in an aprotic solvent provides a convenient means of synthesising a wide range of adamantyl substituted phenols.

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[1] "The Chemistry and Physics of Rubber-like Substances," ed. L. Bateman, McClaren & Sons, London, 1963, p. 647.