# A New Route to Free Radical Aromatic Substitution

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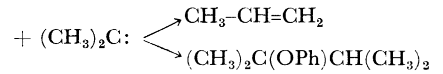
The mechanism of free radical aromatic substitution has been studied extensively[1-5] and shown to follow the scheme

$$\mathrm{ArH} + \mathrm{R}\cdot \longrightarrow \underset{\mathbf{1}}{\mathrm{RArH}\cdot} \xrightarrow{\mathrm{R}'\cdot} \mathrm{ArR} + \mathrm{R}'\mathrm{H}$$

where $\mathrm{R}'\cdot$ may be **1** or other radicals. The reactions of this type involve intermolecular hydrogen-transfer. We could expect a reaction involving intramolecular hydrogen-transfer if the composite radical **1** has an appropriate leaving group.

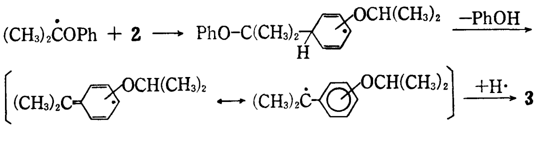
In this communication we wish to report a new example for free radical aromatic alkylation. A mixture of phenyl isopropyl ether (**2**) and di-*t*-butylperoxide (DTBP) (2 : 1 in mole ratio) was irradiated in a pyrex flask for 20 hr at 25°C with a high-pressure mercury lamp (Riko-kagakusangyo 400 W, principal wavelength 3150 and 3660 Å). Product analyses[6] showed the presence of a mixture of *o*- (predominant), *m*- and *p*-isomers of isopropoxycumene (**3**) (51.5%)[7] and phenol (**4**) (42.5%)[7] along with other minor products. Photolysis of a solution of azobis(2-phenoxy)-2-propane in **2** (0.25M) also resulted in the formation of **3** (21.3%) and **4** (15.3%).

The fact that neither dimer nor trimer of phenols could be detected from the reaction mixture, together with the absence of Pummerer's ketone in the products of photolysis of azobis(2-*p*-methylphenoxy)-2-propane, reveals that phenol is not produced from free phenoxy radical.[8,9] Furthermore, it is difficult to attribute the formation of **3** to carbene reaction because no information is obtained for the presence of propylene and 2-phenoxy-2,3-dimethylbutane that are expected from the reaction:[10]



$$(\mathrm{CH_3})_2\dot{\mathrm{C}}\mathrm{OPh} \longrightarrow \mathrm{PhO}\cdot + (\mathrm{CH_3})_2\mathrm{C}\colon \begin{cases} \nearrow \mathrm{CH_3\text{-}CH{=}CH_2} \\ \searrow (\mathrm{CH_3})_2\mathrm{C(OPh)CH(CH_3)_2} \end{cases}$$

Thus, the most probable mechanism for the formation of **3** is



where the driving force of the reaction may be the stability of phenol and aromatization of the composite radical.

Henbest and co-workers[11] obtained methylanisoles, phenoxymethylanisoles and phenol as products of the reaction of anisole with DTBP at 140°C. This clearly supports the first step of the above mechanism. Although they interpret the formation of methylanisoles as aromatic substitution with methyl radical, a part of it could be another example of intramolecular hydrogen abstraction.

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[1] a) D. H. Hey, M. J. Perkins and G. H. Williams, *Tetrahedron Lett.*, **1963**, 445; b) D. H. Hey, M. J. Perkins and G. H. Williams, *J. Chem. Soc.*, **1965**, 110.

[2] D. F. DeTar and R. A. J. Long, *J. Amer. Chem. Soc.*, **80**, 4742 (1958).

[3] a) E. L. Eliel, M. Eberhardt, O. Simamura and S. Meyerson, *Tetrahedron Lett.*, **1962**, 749; b) T. Inukai, K. Kimura, O. Simamura and T. Suehiro, This Bulletin, **35**, 129 (1960).

[4] J. F. Garst and R. S. Cole, *Tetrahedron Lett.*, **1963**, 679.

[5] T. Suehiro, A. Kanoya, T. Yamauchi, T. Komori and S. Igeta, *Tetrahedron*, **24**, 1551 (1968).

[6] Identities with authentic samples were confirmed by VPC, NMR, IR, and mass spectra together with other evidence.

[7] Based on consumed **2**.

[8] See, for example, A. I. Scott, *Quart. Rev.* (London), **1965**, 1.

[9] T. Matsuura and K. Omura, *Chem. Commun.*, **1966**, 127.

[10] The sulfur analog of the radical undergoes this type of reaction.

[11] H. B. Henbest, J. A. W. Reid and C. J. M. Stirling, *J. Chem. Soc.*, **1961**, 5239.