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HOMOLYTIC AROMATIC ipso-SUBSTITUTION IN ARYL ETHERS BY BENZOXYL RADICALS

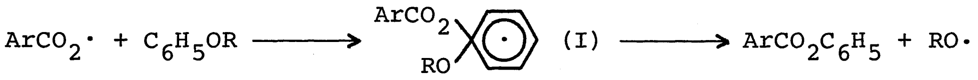
Keiko NOWADA, Hirochika SAKURAGI,* Katsumi TOKUMARU,
and Masayuki YOSHIDA*
Institute of Chemistry, The University of Tsukuba, Sakura-mura,
Niihari-gun, Ibaraki 300-31
* Department of Chemistry, Faculty of Science, The University of Tokyo,
Hongo, Bunkyo-ku, Tokyo 113

Thermal decomposition of dibenzoyl peroxide and bis(4-substituted benzoyl) peroxides in diphenyl ether or anisole affords phenyl benzoate and 4-substituted benzoates, respectively, arising from ipso-substitution in the aryl ethers by the corresponding benzoxyl radicals.

Phenyl radicals are known to replace a hydrogen atom on aromatic nuclei to give biaryls,1) while benzoxyl radicals cannot usually replace the aromatic hydrogen atom unless oxidants such as oxygen2) and copper(II) salts3) are present. Some aroyloxyl radicals have, however, been reported to undergo ipso-substitution4) in halobenzenes,5) and DeTar and Hlynsky6) reported that the decomposition of bis(2-phenoxybenzoyl) peroxide in benzene gives phenyl salicylate possibly through intramolecular rearrangement of intermediate 2-phenoxybenzoxyl radicals. During the course of investigation into the reactivity of acyloxyl radicals we have found that the decomposition of diisopropyl peroxydicarbonate in a mixture of diphenyl ether and carbon tetrachloride affords efficiently isopropyl phenyl carbonate via aromatic ipso-substitution.7) We now wish to demonstrate that aroyloxyl radicals generally undergo ipso-substitution in aromatic ethers.

Decomposition of dibenzoyl peroxide (BPO, 0.02 M) in diphenyl ether at 80°C under nitrogen atmosphere gave phenyl benzoate (0.46 mole per mole of the peroxide) and phenoxybiphenyls (0.85 mole, in a ratio of 58:28:14 for ortho:meta:para isomer) together with phenoxyphenyl benzoates (trace amounts of three isomers) as determined by GLPC. Among these products the efficient formation of phenyl benzoate is quite unusual and can be mostly attributed to the ipso-substitution in diphenyl ether in view of the fact that the thermolysis of BPO in most aromatic solvents usually gives phenyl benzoate as a geminate product in a yield of less than 0.03 mole.8) Likewise bis(4-chlorobenzoyl), bis(4-methoxybenzoyl), and bis(4-nitrobenzoyl) peroxide, on heating in diphenyl ether at 80°C, afforded phenyl 4-chlorobenzoate, 4-methoxybenzoate, and 4-nitrobenzoate in yields of 0.77, 0.46, and 0.61 mole, respectively. These substituted benzoates clearly arise from replacement of phenoxy group on diphenyl ether by the aroyloxyl radicals. A contribution of a free-radical pathway to the formation of the ipso-substitution products is confirmed by the finding that addition of styrene (5 vol %) in the thermolysis of BPO in diphenyl ether remarkably reduced the yield of phenyl benzoate (0.23 mole) as well as that of phenoxybiphenyls (0.19 mole).

Therefore, it is reasonable to consider that the *ipso*-substitution proceeds through the reaction of the aroyloxyl radicals with diphenyl ether to give cyclohexadienyl radicals (I) followed by elimination of phenoxy radicals.



Ar: C_6H_5, p-ClC_6H_4, p-$CH_3OC_6H_4$, p-$NO_2C_6H_4$; R: C_6H_5, CH_3

Anisole was also found to react with aroyloxyl radicals to give *ipso*-substitution products, which seem to have been overlooked in previous works.[9)] Thus, thermolysis of BPO in anisole at 80°C gave phenyl benzoate (0.20 mole) together with well-established products such as methoxybiphenyls (0.78 mole) and methoxyphenyl benzoates (trace). Similarly bis(4-chlorobenzoyl) peroxide, when heated in anisole, afforded phenyl 4-chlorobenzoate (0.42 mole).

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