

## Radical Ions in Photochemistry. Anilinium Salts as Photochemical Arylation Reagents

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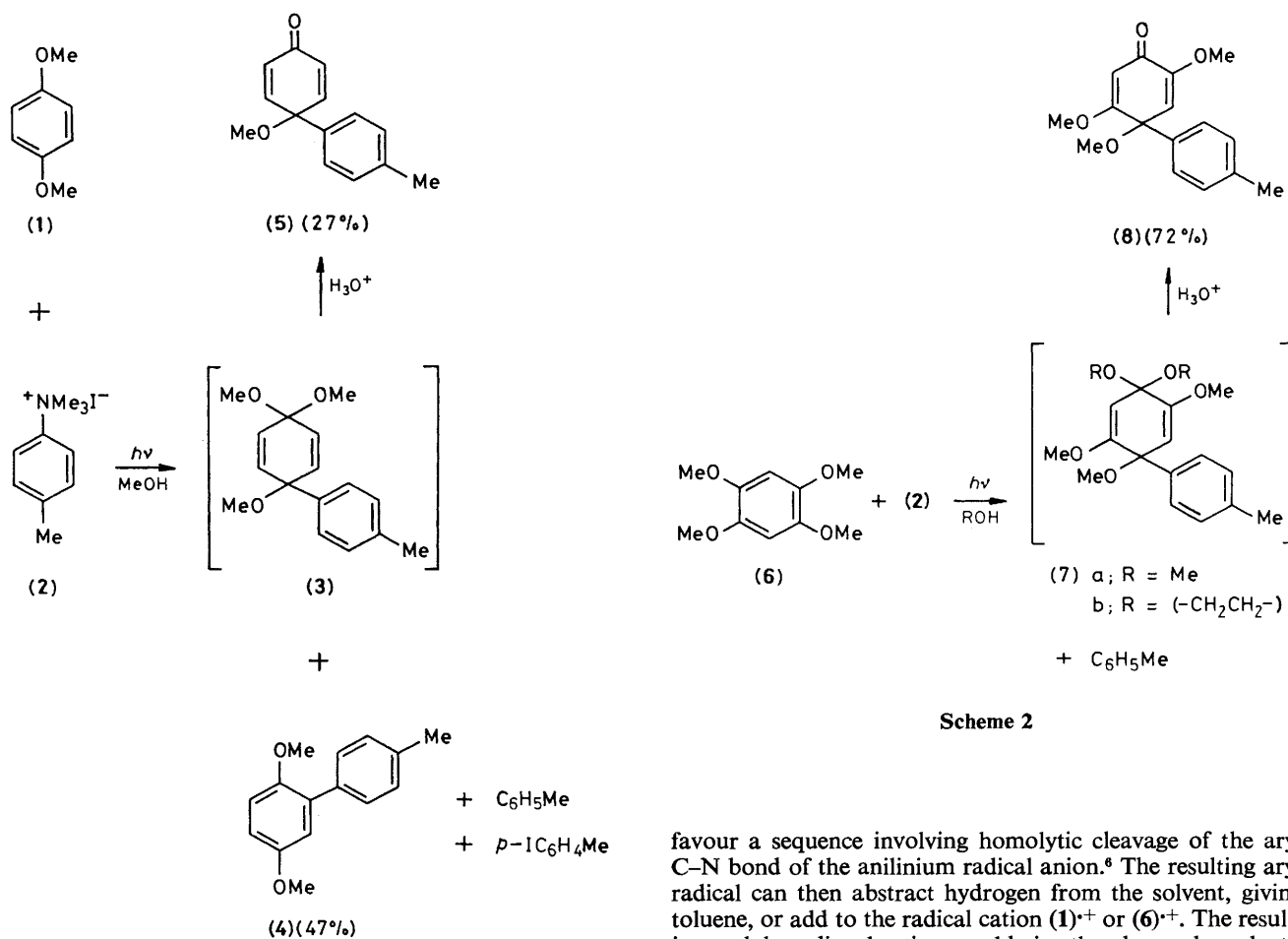
The u.v. irradiation of alcohol solutions of methoxy-substituted benzenes and anilinium salts yields products derived from cleavage of the aryl C-N bond and coupling of the radical pair.

It is now well established that radical ions can be generated upon irradiation of suitable reactant pairs in polar solvents.<sup>1,2</sup> The general synthetic utility of this process remains, however, essentially undefined. As this area develops, knowledge of the reactivity of the individual radical ions of the reactant pair generated electrochemically, can be used to design new reactions.

Anodic oxidation of methoxy-substituted benzenes, 1,4-dimethoxybenzene (**1**) for example, in methanol solution, leads to formation of 1,1,4,4-tetramethoxycyclohexadiene *via* an ECEC process.<sup>3</sup> Cathodic reduction of anilinium salts, trimethyl-4-tolylammonium (**2**) for example, gives toluene *via* the aryl radical formed upon loss of trimethylamine from the

radical anion.<sup>4</sup> This reactant pair, (**1**) and (**2**) is well suited for radical ion pair formation upon irradiation in methanol; if the individual radical ions show reactivity analogous to that observed upon electrolysis, coupling of the radical intermediates should result.

Irradiation of (**1**), 0.07 M, and (**2**), 0.35 M, in the form of the iodide, in methanol, using a medium-pressure mercury vapour lamp through Pyrex, gives (**4**), m.p. 66 °C, and (**5**), m.p. 87–88 °C, as major products. Toluene and 4-iodotoluene were also produced (Scheme 1). Only one coupling product (**8**), m.p. 147–148 °C, was isolated, along with toluene, when 1,2,4,5-tetramethoxybenzene (**6**) and (**2**), as the iodide, chloride, or acetate, was irradiated under these conditions (Scheme



Scheme 1

2). The intermediates (3) and (7a) are the primary photo-products in the reactions; hydrolysis during the workup yields (5) and (8). When the reaction in Scheme 2 was carried out in ethylene glycol, the more stable (7b), m.p. 124 °C, was readily isolated.†

Irradiation through Pyrex ( $\lambda > 280$  nm) assures preferential excitation of the methoxybenzenes (1) and (6). Fluorescence from (6) is rapidly quenched ( $k_q\tau = 15 \text{ dm}^3 \text{ mol}^{-1}$ ) by (2). Electron transfer quenching is predicted by the Weller equation<sup>5</sup> which indicates the process is favourable by ca. 64 kJ.‡ The coupling process can occur at several stages. We

† Structural assignments for the new compounds rests predominantly on an analysis of their n.m.r. spectra: <sup>1</sup>H n.m.r. (60 MHz) in CDCl<sub>3</sub> (excluding the signals for the 4-tolyl substituent): (3) (CCl<sub>4</sub>)  $\delta$  6.03 (2H, d, *J* 11 Hz), 5.70 (2H, d), and 3.25 (9H, br. s); (4)  $\delta$  6.95–6.75 (3H, m), 3.79 (3H, s), and 3.73 (3H, s); (5)  $\delta$  6.78 (2H, d, *J* 10.5 Hz), 6.35 (2H, d), and 3.41 (3H, s); (7b)  $\delta$  4.99 (1H, s), 4.60 (1H, s), 4.4–4.1 (4H, m), 3.60 (3H, s), 3.58 (3H, s), and 3.30 (3H, s); (8)  $\delta$  5.73 (1H, s), 5.30 (1H, s), 3.68 (3H, s), 3.64 (3H, s), and 3.30 (3H, s). <sup>13</sup>C N.m.r. (8)  $\delta$  182.3 (C-carbonyl) and 79.2 (C-4) p.p.m. U.v. (95% ethanol): (7b)  $\lambda_{\text{max}}$  (log  $\epsilon$ ) 272 (2.58), 266 (2.60), 263.5 (2.63), and 258 (2.49) nm; (8)  $\lambda_{\text{max}}$  (log  $\epsilon$ ): 302 (3.27), 249.5 (4.24), and 221.5 (4.15) nm.

‡ The potentials were taken from A. Zweig, W. G. Hodgson, and W. H. Jura, *J. Am. Chem. Soc.*, 1964, **86**, 4124 [+0.81 V for (6)]; and from C. K. White and R. D. Rieke, *J. Org. Chem.*, 1978, **43**, 4638, (–2.5 V for trimethylanilinium iodide) in acetonitrile vs. standard calomel electrode.  $\Delta E_{0-0}$  (6) = 378 kJ/mol (intercept of fluorescence and absorption at  $\lambda = 315$  nm).

Scheme 2

favour a sequence involving homolytic cleavage of the aryl C–N bond of the anilinium radical anion.<sup>6</sup> The resulting aryl radical can then abstract hydrogen from the solvent, giving toluene, or add to the radical cation (1)<sup>•+</sup> or (6)<sup>•+</sup>. The resulting cyclohexadienyl cation would give the observed products.

The yield of products (>70%) and the quantum efficiency [ $\Phi$  consumption of (6) with (2), 0.05 M =  $0.08 \pm 0.02$ ] are such that these examples illustrate a synthetically useful photochemical arylation reaction. Some limitations have been identified. The donor must absorb at longer wavelengths than the anilinium salt; thus, yields of arylation products were poor with the other dimethoxybenzenes which require irradiation through quartz. The anilium salt also absorbs under these conditions. Stable anilinium radical anions are ineffective; for example, no photoreaction occurred when 4-cyanophenyl-trimethylammonium iodide was used. The products, particularly the cyclohexadienones, are susceptible to further photolysis.

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