Photochemical Addition of Esters to 9,10-Phenanthrenequinone. Preferential Formation of Ether Radicals

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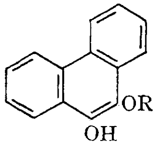
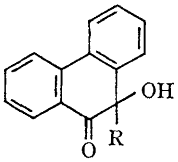
EXTENSIVE investigation of the photochemistry of 9,10-phenanthrenequinone (PQ) has established that this quinone undergoes cycloadditions with sulphur dioxide[1] and with olefins[2] as well as additions with aldehydes,[3] ethers,[4] and substituted toluenes[5a,b] to give adducts of type I (1,4-addition) and type II (1,2-addition). We now report the addition of esters to PQ.

Irradiation through Pyrex of a solution of PQ in ethyl acetate under helium with light from a high-pressure mercury-vapour lamp resulted in formation of a crystalline 1 : 1 adduct (Ia), m.p. 125°, which could be isolated by direct crystallization from di-isopropyl ether or chromatography on silica gel. Compound (Ia) exhibited ultraviolet (255, sh. 270, 297, 307, 344, 360 mμ) and infrared (2·75, 2·95, 5·75, 6·15, 6·25 μ) absorption characteristic of 1,4-adducts (type I). *A priori*, two possible 1,4-adducts, (Ia) or (Ib), resulting from reaction α to the ether or carbonyl functions might be considered likely. In the n.m.r. spectrum of the adduct the characteristic ethyl absorption of ethyl acetate had disappeared and was replaced by a quartet at τ 3·69 (1H) and a doublet at 8·35 (3H). The protons of the methyl group adjacent to the carbonyl remained as a singlet at τ 7·92 (3H). These results clearly require that the adduct have the structure (Ia). Further proof was provided by the observation that reaction of the adduct with potassium carbonate in ethyl acetate followed by acidification afforded acetaldehyde and the known[6] monoacetate (Id) of 9,10-dihydroxyphenanthrene. Analogous results were obtained when PQ was irradiated in ethyl propionate solution.



(I) a; $R{=}MeCO_2\overset{\vert}{C}HMe$
b; $R{=}CH_2{\cdot}CO_2Et$
c; $R{=}EtCO_2\overset{\vert}{C}HMe$
d; $R{=}CO{\cdot}Me$
e; $R{=}Me\overset{\vert}{C}H{\cdot}CO_2Et$



(II)

$RCH_2{\cdot}CO_2{\cdot}\dot{C}HMe$

(III)

$R\dot{C}H{\cdot}CO_2Et$

(IV)

The quantum yield for the disappearance of PQ at 4358 Å in degassed ethyl acetate solution was unity, as observed[7] in other PQ photoadditions. When PQ was irradiated on a preparative scale at this wavelength[8] in degassed solutions of ethyl acetate or ethyl propionate and the solvent removed by evaporative distillation at low pressure without heat, crystalline (Ia) or (Ic) was obtained directly. The infrared spectra of these crude reaction products were identical with those of the analytical samples and the n.m.r. spectra exhibited none of the absorptions which would be expected for (Ib) or (Ie). Thus, *reaction occurred exclusively at the carbon atom adjacent to the ether oxygen in these cases.*

It has previously been shown[7] that photoadditions to PQ involve abstraction of a hydrogen atom by photoexcited PQ to form a pair of radicals which then combine to form products. In the case of the esters investigated in this work, the observed results require that the ether radical (III) be formed at a much more rapid rate than the enol radical (IV). In other words, *photo-excited PQ abstracts hydrogen from an ester to form an ether radical much more rapidly than it abstracts hydrogen to generate an enol radical.* Further, it has been observed that the rate of disappearance of PQ when irradiated in ethyl methyl ketone solution is at least ten times slower than in dioxan solution.

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[8] (Ia) and (Ic) were unchanged after prolonged exposure at 4358 Å.
[9] The possibility that enol radicals (IV) are formed but react at a very slow rate seems unlikely. No products derived from dimerization or other reactions of such radicals were observed.