Photoreactions of o-Quinones with Olefins: a New Type of Reaction leading to Dioxole Derivatives

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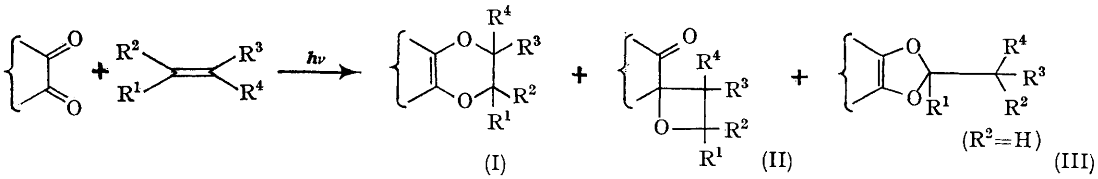
IN the photoreaction of *o*-quinones with olefins the 1,2-cyclo-addition yielding α-keto-oxetans (II) competes with the 1,4-addition which gives 2,3-dihydro-1,4-dioxins (I).[1-3] Moreover, competition between cyclo- and R-H-additions may take place if the olefin molecule can be dehydrogenated by the excited quinone.[4,5]

We report the formation of dioxole derivatives (III) by irradiating phenanthrenequinone in the presence of olefins.

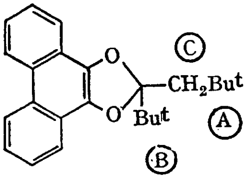


The compounds of type (I) and (III) derived from phenanthrenequinone include a phenanthrene system and therefore show a vibrational structure in their u.v. spectra ($\Delta\nu$ = 1400 cm.$^{-1}$).[4] The first maxima ($0 \rightarrow 0'$ transition) of the phenanthro-2,3-dihydro-1,4-dioxins (I; R^1—R^4 = H, alkyl- or aryl-substituents) are observed[4] between 26,500 and 27,300 cm.$^{-1}$. With increasing number of heterosubstituents (-SR, -NCOR, -OR, or -Cl) this maximum is shifted to higher frequencies.[1,3,6] For example (I; R^1—R^4 = Cl)[7] shows the first maximum at 28,500 cm.$^{-1}$.

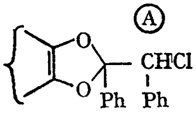
However, phenyl- and diphenyl-phenanthrodioxoles[4] show similar spectra with the first maximum at 25,750 cm.$^{-1}$, but in some photoreactions of phenanthrenequinone with olefins we observed u.v. absorptions which might indicate the presence of phenanthrodioxoles in the reaction mixtures.[7] We have now isolated and ascertained the structure of such compounds (IIIa—c) as by-products (about 10% yield) from the photoreactions of phenanthrenequinone with 1,2-di-t-butylethylene, chlorostilbene, and *NN*-diphenylimidazolinone respectively. Their spectral data are given in the Table.

All phenanthro-2,3-dihydro-1,4-dioxins (I) have

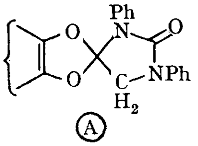
TABLE



(IIIa)



(IIIb)



(IIIc)

	m.p. (°C)	First u.v. max.† (cm.$^{-1}$)	$\nu_{C=O}$ (cm.$^{-1}$) (KBr)	τ (CDCl$_3$)
(IIIa)	172—173	24,870	1677	A, 9·05 B, 8·91 C, 7·89
(IIIb)	153—155	25,700	1670	A, 4·47
(IIIc)	198—200	26,150	1670	A, 5·23

† In the corresponding adducts of structure (I) the first absorption bands are shifted 1500 cm.$^{-1}$ to higher wave numbers.

a strong C=C stretching vibration[1] at 1635—1650 cm.$^{-1}$. In phenyl, diphenyl, and related phenanthrodioxoles the corresponding band is shifted to higher wave numbers (1664—1670 cm.$^{-1}$).[8] The i.r. frequencies of (IIIa—c) given in the Table are clearly in accordance with the five-membered ring structure.

The chemical shifts of the protons C in (IIIa) and A in (IIIc) are in the range expected for such methylene groups. Further confirmations for the suggested structures are the non-equivalence of the two t-butyl groups in (IIIa) and of the two phenyl groups in (IIIc)† and the symmetry of the phenanthrene system, as indicated from the equivalence of the corresponding protons on both rings [analysed in case of (IIIa) as an ABCD spectrum according to Batterham *et al.*[9]]. The mass spectra are also in accordance with structure (III); *e.g.* (IIIa) gives an $M - 57$ (–CMe$_3$) ion which further eliminates the mass 56. Such splittings are not detected in the spectrum of the corresponding adduct (I). As expected (IIIb) efficiently loses the unit –C(Ph)HCl.

Experiments to elucidate the mechanism of the dioxole formation in these reactions are under investigation. Preliminary results indicate that in the reaction with di-t-butyl ethylene a 2,3-dihydro-1,4-dioxin (I) and an oxetan (II) are formed initially. The latter reacts further with selectively excited quinone to yield (IIIa) and other products.

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† As indicated from the spectrum at 220 Mc./sec. (G. Steffan and J. Leitich, to be published).

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