Photorearrangements of Oxo-oxetans. A Low-energy Triplet Sensitization

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RECENTLY we reported the formation of dioxole derivatives on irradiation of phenanthrenequinone in the presence of some olefins, *e.g.*, *cis*-di-t-butylethylene.[1] Preliminary investigations indicated that in this reaction an initially formed oxo-oxetan (Ia) was the precursor of the dioxole (IIa). We have studied the photolysis of oxo-oxetans of general formula (I) and find that three photorearrangements (B—D) of (I) may compete with the photodecomposition to quinone and olefin (path A).

N.m.r. and u.v. study of the photolysis of (Ia) indicated partial decomposition and the formation of two new compounds, (IIIa) and (IVa). The latter compound (Bu^t signals at τ 8·69 and 9·25, in C_6D_6) which was not isolated, readily yielded (IIa) with traces of HCl, on heating the solution, or during chromatographic work-up. This acid-catalysed reaction and the u.v. data (vibrational structure, 0–0 transition at $\sim$27,700 cm.$^{-1}$) support the structure (IVa). Further evidence was obtained by irradiation of (Ia) in dry benzene and subsequent treatment of the solution with acidified D_2O, yielding monodeuterio-(IIa).

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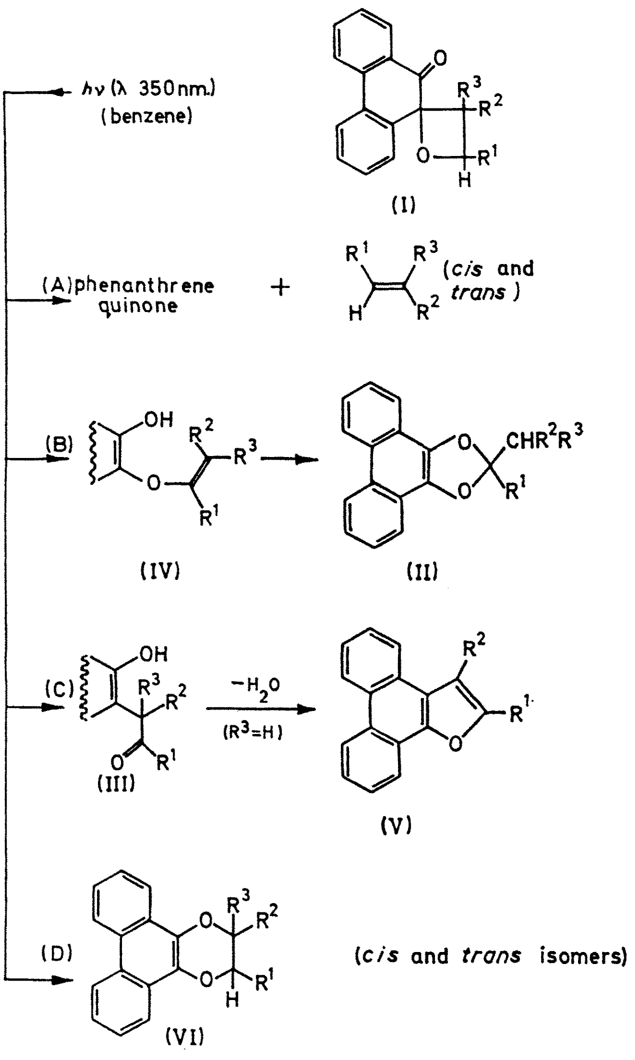
Photolysis of (Ib), a stereoisomer of (Ia) formed by photoaddition of phenanthrenequinone to *trans*-di-t-butylethylene, afforded neither (IIIa) nor (IVa). In this case, valence isomerization (path D) to the dihydrodioxin (VIa) competes with decomposition (path A). Photolysis of (Ic—g) gave different ratios of products according to paths (A—D) (Scheme 1). Following the photolysis of *cis*- and *trans*-(Ic), traces of HCl gas yielded (IIc) by cyclization of (IVc), whereas with an excess of HCl, dimethylphenanthrofuran (Vc) is formed by elimination of H_2O from (IIIc).

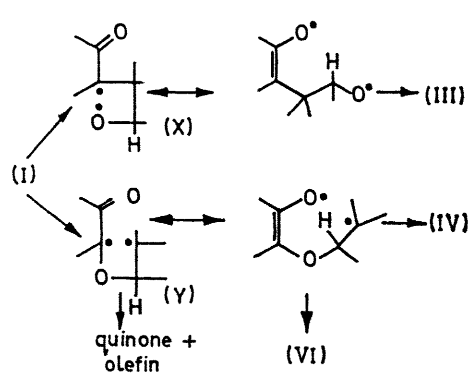


SCHEME 1

Obvious mechanisms for these photorearrangements involve the formation of the "biradical intermediates" X and Y (Scheme 2) by C–O or C–C bond cleavage followed by intramolecular hydrogen abstraction to give (III) and (IV), respectively, 1,6-radical termination to give (VI), or a second bond fission resulting in decomposition to quinone and olefin.

The rearrangement of (If) to (IIf) and (VIf) could also be achieved in low yield on heating at 170° in decalin.

Insight into the stereochemistry of the photorearrangement (I) → (VI) was obtained from the product distribution of the photolysis of the *cis* and *trans*-isomers of (Id). To avoid re-addition of the components after decomposition by path A, an excess of ethyl vinyl ether was added. This olefin reacts efficiently with phenanthrenequinone yielding a photostable dihydrodioxin. As indicated by n.m.r., no isomerization *cis*-(Id) ⇌ *trans*-(Id) is effected by light. On the other hand, both *cis*- and *trans*-(VId) were formed on irradiating either *cis*- or *trans*-(Id). The degree of stereospecificity of this reaction can be expressed in terms of the ratio *r* (as defined in Table 2) which would vary between 1 for completely stereoequilibrated mixtures and ∞ in case of pure stereospecific reactions.



SCHEME 2

TABLE 1

(I)[a]		R¹	R²	R³	A :	B :	C :	D
a		Bu^t	Bu^t	H	24	37	39	—
b		Bu^t	Bu^t	H	87	—	—	13
c	*cis*	Me	Me	H	42	10	48	—
	trans				29	14	57	—
d	*cis*	OPh	Ph	H	53	—	—	47
	trans				54	—	—	46
e		H	Me	Me	85	—	—	15
f		Me	Me	Me	59	6	—	35
g		Cl	Cl	Cl	52	—	—	48

[a] In the photolysis of the corresponding coumarone and indene adducts recleavage (path A) is the only observable reaction.[2]

The stereochemistry of (Ia, b) has not yet been established. (Ia) m.p. 146—148°, (Ib) m.p. 165—170°.

TABLE 2

Product distribution and stereospecificity of the photorearrangement (Id) → (VId)

Solvent	Benzene[a]		t-Butyl alcohol[a]
Temperature	−2°	+30°	+30°
$p = \left[\frac{cis\text{-(VI)}}{trans\text{-(VI)}}\right]$ *cis*-(I)	4·23	3·45	4·33
$q = \left[\frac{cis\text{-(VI)}}{trans\text{-(VI)}}\right]$ *trans*-(I)	2·01	2·40	3·00
$r = p/q$	2·1	1·44	1·44

[a] 20% Ethyl vinyl ether was added to each solution.

The results given in Table 2 are in accordance with a "biradical intermediate" (Scheme 2) in which rotation about the C–C bond competes with the cyclization to (VI) ("memory effect"). The stereospecificity decreases with increasing temperature, indicating a higher activation energy for the rotation than for the cyclization. In t-butyl alcohol the formation of *cis*-(VId) is more favoured over *trans*-(VId) than in benzene. The stereospecificity, however, is the same in both solvents at the same temperature.

Selectively excited phenanthrenequinone (E_T 50 ± 0·5 kcal./mole,‡ lit.[3] 48·9) or benzil (E_T 53·7 kcal./mole[4]) were found to sensitize the rearrangements of (Ia, b, f, g) (E_T 59—60 kcal./mole‡) to the same products (paths B—D) as in the corresponding unsensitized photolysis. Although both sensitizers undergo efficient intersystem crossing,[5] a classical triplet–triplet energy transfer appears for energetic reasons to be improbable. Hammond *et al.* reported two examples of similar low-energy triplet-sensitized isomerizations involving saturated centres. They suggested different mechanisms for the energy-transfer step.[6] A common feature of all these reactions is that the energy transfer formally results in a fission of a weak single bond in a strained ring.

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‡ From the O–O transition of the phosphorescence spectrum in IPMC as well as in ethanol at 77° K.

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