Photoaddition of Phenanthraquinone to Alkyl-substituted Alkoxyacetylenes.[1] Formation of 1,3-Dioxoles

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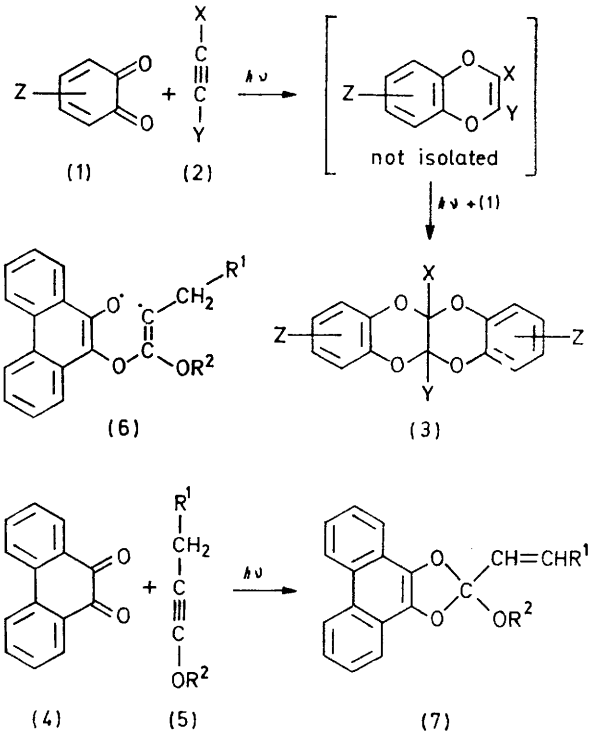
Summary Photochemical addition of phenanthraquinone (**4**) to alkyl-substituted alkoxyacetylenes gives rise to the 1,3-dioxoles (**7**) *via* a 1,2-hydrogen shift in the intermediate (**6**).

PHOTOADDITION of 9,10-phenanthraquinone to the alkoxyacetylenes (**2**; X = H, Y = OMe and OEt)[2] and of tetrachloro-*o*-benzoquinone to diphenylacetylene (**2**; X = Y = Ph)[3] gives rise to the 2:1 adducts (**3**).[4] Dihydro-1,4-dioxin derivatives are also formed from alkenes[5] and allenes.[6]

Photoreaction of 9,10-phenanthraquinone (**4**) (0·01 M) with 1-methoxyprop-1-yne (**5**; R^1 = H, R^2 = Me) (0·03 M) in benzene, however, affords the acid-sensitive 1:1 adduct (**7**; R^1 = H, R^2 = Me) in 50% yield (^{1}H n.m.r.). After dry-column chromatography[7] on neutral or basic alumina, crystals, m.p. 93—94°, were isolated in 30% yield. Elemental analyses and ^{1}H n.m.r., u.v., i.r., and m.s. data are in conformity with the structure assigned. Acid-catalysed methanolysis afforded methyl acrylate.

Photoaddition of (**4**) to the homologous alkoxyacetylenes (**5**; R^1 = H, R^2 = Et; R^1 = Me, R^2 = Me and Et) gave the corresponding adducts (**7**) in 35—50% yield. In the example with R^1 = Me a *cis* + *trans* mixture was obtained.

The formation of (**7**) probably proceeds *via* attack of excited (**4**) on C-1 of the acetylene (**5**), as with monoketones,[1] to afford (**6**). A 1,2-hydrogen shift[8] leads to an allylic biradical adduct, which can ring close to form (**7**).



(1) (2) (6) (3) (4) (5) (7)

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