Photoreactions of *o*-Quinones with Olefins: Competition between Cyclo- and R–H-addition

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THE reactions of photoexcited *o*-quinones with olefins yield 1,4- and/or 1,2-cycloadducts.[1]

1,2- and/or 1,4-R–H-Addition products were obtained[2,3] from the photoreactions of *o*-quinones with aldehydes, alkylbenzenes, ethers, and esters. This communication deals with the competition between the cyclo- and R–H-additions in the photoreaction of phenanthrenequinone with alkenes. G. Pfundt has previously investigated some of these reactions spectroscopically and concluded that in addition to the isolated photostable 1,4-cyclo-adducts, photo-unstable 1,2-addition products should be formed.[2]

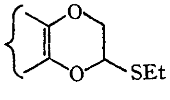
From the photoreactions of phenanthrenequinone with the olefins listed in the Table we have isolated compounds of the general formulae (I—IV).

The product distribution was studied by column chromatography and subsequent n.m.r. investigation of the eluates. Analytically pure samples were prepared by additional preparative layer chromatography or fractional crystallization.

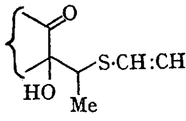
The increase of the quantum yield† and the reaction constants of R–H- and cyclo-additions parallels the number of methyl substituents on the double bond. According to the product distribution the R–H-addition is easier than cycloaddition with increasing degree of methyl substitution.

This increase of the R–H-addition reaction constants is analogous to that of hydrogen-abstraction from alkenes with peroxide radicals,[5] which would be expected for a two-step mechanism (*cf.* ref. 3). The allyl radical formed after the hydrogen abstraction by the excited quinone would add the semiquinone radical to yield (III) or (IV), respectively.

The reaction constants have been estimated from the slopes of the Stern–Volmer plot at two different concentrations of the olefins (in benzene) using anthracene as a triplet quencher [$E_{T\,(\text{phenanthrenequinone})} = 48{\cdot}8$,[6] $E_{T\,(\text{anthracene})} = 42$ kcal./mole[7]] and assuming the bimolecular quenching constant[8] at 25° to be 8×10^9 l. mole^{-1} sec.$^{-1}$. The fact that the product distribution in the reaction of phenanthrenequinone with dimethylbutene does not change in the presence of a molar quantity of anthracene sufficient to reduce Φ_q by one half and the linearity of the Stern–Volmer plots indicate



(V)



(VI)

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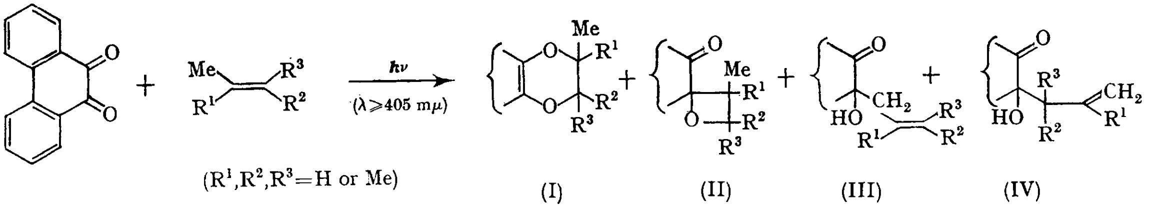
† According to Pfundt[2] Φ_q of the reaction with alkenes is higher than that with aromatic substituted olefins.

TABLE



Alkene	Φ_q[a]	k_{qa}[b] × 10^8	Yield (%)		Remarks
			(I) + (II)[c]	(III) + (IV)	
2-Methylpropene[d]	0·21	1	85	10	(III) and (IV) are identical
trans-But-2-ene	0·34	1	81	9	*cis*- and *trans*-Isomers of (I) (*cf.* ref. 4)
cis-But-2-ene	0·36	1·6	85	9	two of the four possible isomers of (II) and both diastereomers of (IV) were obtained in both cases. The geometry of the starting olefin is retained in (III).
2-Methylbut-2-ene[d]	0·45	4	78	14	The three possible isomers of (III) are formed, that with $R^1 = H$, $R^2 = R^3 = Me$ predominates. Whereas both diastereomers of (IV) ($R^1 = Me$; R^2, $R^3 = H$, Me) were isolated (IV) ($R^1 = H$; $R^2 = R^3 = Me$) could not be detected.
2,3-Dimethylbut-2-ene	0·79	13	65	29	(IV) could not be detected among the reaction products.

[a] Φ_q is the quantum yield of the quinone disappearance.

[b] k_{qa} is the sum of the reaction constants for the reactions of triplet quinone with the alkene (R–H- and cycloadditions as well as deactivation to the ground state) in l. mole^{-1} sec.$^{-1}$. The addition constants may vary between k_{qa} and $k_{qa} \times \Phi_q$.

[c] The yield of (II) ranges between 10% (from 2-methylpropene) and 2% (from 2,3-dimethylbut-2-ene).

[d] The oxetans (II) formed are those derived from the most stabilized biradical intermediate.

that both cyclo- and R–H-additions follow from the same excited state of the quinone, the triplet state.

In the photoreaction of phenanthrenequinone with ethyl vinyl sulphide R–H-addition also competes with the cycloaddition. We have previously shown[9] that this reaction yields the 1,4-cycloadduct (V) (69%) and other hydroxylic 1 : 1-adducts (21%), which have been now identified as a 2 : 3 mixture of the two diastereomers (VI).

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