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PHOTOCHEMICAL CYCLOADDITION OF 9,10-PHENANTHROQUINONES TO ALLENES[1]

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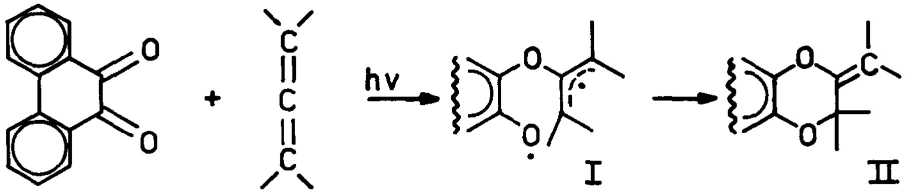
The reaction of triplet 9,10-phenanthroquinone (PQ) with allene and its derivatives yields mixtures of isomeric 2-alkylidene-2,3-dihydrophenanthro [9,10-_b_]-1,4-dioxins II[2].



I

II
(1-4 isomers)

These dioxins were obtained from the reaction of PQ with allene and with eight methyl, methoxy, and methylthio derivatives[2]. In the same way addition could also be performed with the allenes: C_6H_5-HC=C=CH_2, _t_-C_4H_9-HC=C=CH_2, C_6H_5O-HC=C=CH_2, _t_-C_4H_9O-HC=C=CH_2 and Br-HC=C=CH_2.

Rate constants k_2 were ascertained to get insight into the influence of substituents. Quantum yields were determined in benzene using light with $\lambda \geqslant 385$ nm. As actinometer the reaction of trans-stilbene with PQ ($\Phi = 0.066$) was used[3].

The quantum yield of quinone disappearance (Φ_{PQ}) varied from 0.09 for NC-HC=C=CH_2 to 0.98 for CH_3O-HC=C=CH_2. The quantum yield of adduct formation (Φ_{Add}) determined from NMR data, varied from 0.00 to 0.53 for these allenes respectively. For CH_3O-HC=C=CH_2 Φ_{PQ} and Φ_{Add} were independent of allene concentration. This indicates that neither appreciable decay to the ground state nor reversible addition takes place. Reversible addition was observed for reaction of PQ with C_2H_5O-HC=CH_2 ($\Phi_{PQ} = 0.40$); compare [3,4]. Probably with allenes the stable allylic adduct-biradical I is formed before ringclosure (cf. [5]).

The rate of adduct formation for CH_3O-HC=C=CH_2 was estimated from the slopes of a Stern-Volmer plot at two different allene concentrations, using anthracene as triplet quencher (compare [4]) and assuming the bimolecular quenching constant at 25° in benzene to be 8.8×10^9 ℓ.mole^{-1} s.$^{-1}$ [6] The rate constants k of other allenes were determined with aid of competition experiments (see table).

Rate constants of adduct formation k and Φ_{Add} concern all isomeric adducts II. The effect of methyl substituents on the rate constants for each double bond

Rate constants k of the reaction of PQ with allenes and substituent constants

Allene	$k_2 \times 10^7$	substituent	σ^8	$E_R{}^8$
$CH_3S-HC=C=CH_2$	86	CH_3S	0.00	0.44^b
$t-C_4H_9O-HC=C=CH_2$	77	$t-C_4H_9O$		
$C_6H_5O-HC=C=CH_2$	76	C_6H_5O	-0.32	0.13
$CH_3O-HC=C=CH_2$	69	CH_3O	-0.27	0.11
$C_6H_5-HC=C=CH_2$	28	C_6H_5	-0.01	0.52^c
$t-C_4H_9-HC=C=CH_2$	3.7	$t-C_4H_9$	-0.20	0.03
$Br-HC=C=CH_2$	$\approx 0.1^a$	Br	0.23	0.12
$(CH_3)_2C=C=C(CH_3)_2$	48			
$(CH_3)_2C=C=CH-CH_3$	28	CH_3	-0.17	0.03
$(CH_3)_2C=C=CH_2$	21	$2 \times CH_3$	-0.34	0.06
$CH_3-HC=C=CH-CH_3$	8			
$CH_3-HC=C=CH_2$	4.7			
$H_2C=C=CH_2$	0.5			

a) Estimated value for the bromo-substituted double bond.

b) Calculated from σ and σ^{+} [8] (compare [9])

c) Calculated from polymerisation data (Q -value[9])

in the allene system assuming central attack appears to be additive (see table).

The influence of substituents on free-radical reactions can be correlated with an extended Hammett relationship evaluated by Yamamoto and Otsu[6] $\log(k/k_0) = \rho\,\sigma + \gamma E_R$, where σ and E_R are polar and resonance substituent constants (table) and ρ and γ reaction constants. Applying this equation to our cycloaddition a linear correlation is obtained plotting $[\log(k/k_0)]/E_R$ versus σ/E_R with $\rho = -5.5$ and $\gamma = 5.9$ (correlation coefficient 0.98). The values for $t-C_4H_9$ and $2 \times CH_3$ are not correlated so good, which could be indicative for steric hindrance.

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