Tetrahedron Letters No.39, pp. 4783-4788, 1966. Pergamon Press Ltd.
Printed in Great Britain.

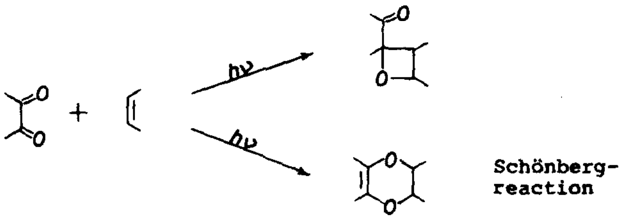
COMPETITION BETWEEN CYCLOBUTANE AND OXETANE FORMATION IN THE PHOTOADDITION OF 1.4-NAPHTHOQUINONE TO BENZOCYCLIC OLEFINS

C.H.Krauch and S.Farid[1)]

Max-Planck-Institut für Kohlenforschung, Abt. Strahlenchemie
(Direktor: Prof.Dr.G.O.Schenck)
Mülheim-Ruhr

(Received 25 July 1966)

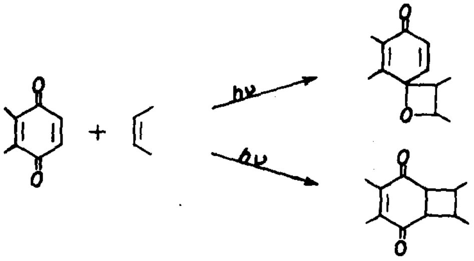
Recently we have shown[2)] that the photochemical 1.2-cycloaddition of benzocyclic olefins to only one carbonyl group of o-quinones, e.g. phenanthrene quinone, and 1.2-diketones, e.g. benzil, giving oxetane derivatives (Rc. 1), is in competition with the 1.4-cycloaddition leading to the formation of 1.4-dioxene derivatives (Rc. 2)[3)].



(1)

(2)

On investigating the photoreactions of benzocyclic olefins with p-quinones, we observed, in the case of 1.4-naphthoquinone, competition between the 1.2-cycloaddition to the carbonyl group forming oxetanes (Rc. 3)[4] and that to the C=C double bond forming cyclobutanes (Rc. 4)[5].



(3)

(4)

10 mMol quinone and 20 mMol olefin in 50 ccm benzene were irradiated[6] (3-5 h, at 15-20°) under argon through glass filter (GWV, Wertheim: complete absorption $\lambda < 370$ mμ) using a Philips HPK 125 W high pressure Hg lamp. For the work up, chromatography on florisil (Fluka) and/or fractional crystallisation were applied.

The results are summarised in table 1. It is of interest to note that the furocoumarin, xanthotoxin, and the furochromone, visnagin, yield predominantly the oxetane derivatives, but both types of adducts are obtained in comparable amounts from their parent compound, coumarone.

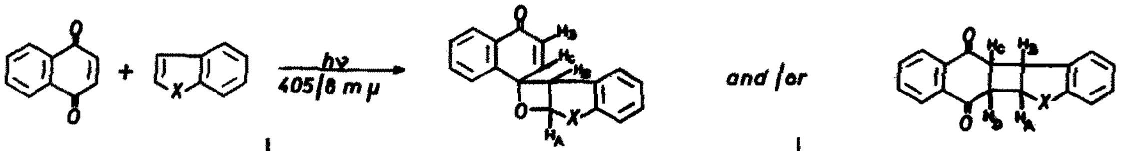
We have found that[2] coumarone and iso-coumarin, in contrast to their phenyl derivatives, react selectively with phenanthrene quinone to yield the α-ketooxetanes. With naphthoquinone the reverse is observed, i.e. the selectivity was only shown by the phenyl derivatives, giving the corresponding oxetanes.

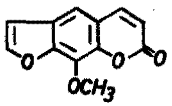
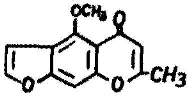
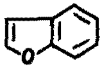
The structure of these derivatives was unambiguously determined from their NMR spectra. In the oxetane adducts from 1.4-naphthoquinone the two nonaromatic hydrogen atoms in the quinone part of the molecule show an AB-quadruplet in the range between 2.8 and 3.9 τ, $J = 10.5$ cps. The hydrogen atoms in the olefinic part also show an AB-spectrum, while in the case of phenyl substituted compounds the remaining proton (H_B) appears as a singlet.

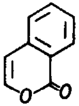
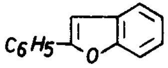
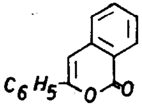
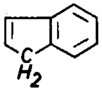
From the chemical shift of these protons the acetal structure of the adducts was assigned for the oxetane derivatives, relying on the considerations discussed previously2).

On the other hand, the four protons in the cyclobutane derivatives couple with each other giving more complicated spectra; each hydrogen atom showing eight signals. Moreover, there is additional splitting in the H_B-signals due to wide range couplings with aromatic protons, cf.2).

Satisfactory elementary analyses were obtained for the reaction products. 1.4-Naphthoquinone gives also oxetane and cyclobutane derivatives with olefinic hydrocarbons7).



Benzocyclic olefin	Oxetane derivative				Cyclobutane derivative		
	yield	m.p.	τ-values	J(cps)	yield	m.p.	τ-values
 Xanthotoxin	75%	158-161°	H_A 2.91 H_B 5.45 H_C 3.32 H_D 3.68	J_{AB} 4.4 J_{CD} 10.5	—		
 Visnagin	65%	159-162°	H_A 2.96 H_B 5.23 H_C 3.21 H_D 3.64	J_{AB} 4.5 J_{CD} 10.5	—		
 Coumarone	37%	131-133°	H_A 2.9 H_B 5.49 H_C 3.33 H_D 3.69	J_{AB} 4.3 J_{CD} 10.5	28%	195-200°	H_A 4.64 a) H_B 5.67 H_C 6.32 H_D 5.97

 Iso-coumarin	35%[b)]		H_A H_B H_C H_D	3.08 5.44 3.30 3.82	J_{AB} 6.3 J_{CD} 10.5	26%	186-189°	H_A 4.63±0.02 H_B 5.8 ±0.1 H_C 6.35±0.05 H_D 5.95±0.1
 2-Phenylcoumarone	60%	148-149°	H_B H_C H_D	5.22 3.16 3.68	J_{CD} 10.5	—		
 3-Phenyl-iso-coumarin	65%	147-151°	H_B H_C H_D	5.16 2.84 3.75	J_{CD} 10.5	—		
 Indene c)	—					20%	182-183°	the six nonaromatic hydrogens show complicated multiplet at 5.5 - 6.8 τ

The NMR spectra were taken in $CDCl_3$ at 60 M cps.

a) Approximate values for the coupling constants obtained from the splittings are in good accordance with expected values from measurements on related compounds.

b) This compound has not yet been obtained free from the cyclobutane derivative. The product distribution is determined from the NMR-spectrum of the crude reaction product.

c) The main product of the photoreaction of 1.4-naphthoquinone and styrene is a cyclobutane derivative (m.p. 121-123°, yield 42%).

References

1. Part of a lecture given at the Third International Congress of Radiation Research, Cortina d'Ampezzo, Italy, 26.6. - 2.7.1966 (Book of Abstracts, p. 8)
2. C.H.Krauch, S.Farid und G.O.Schenck,
   Chem. Ber. **98**, 3102 (1965)
3. A.Schönberg and A.Mustafa,
   Nature **153**, 195 (1944) ;
   J. chem. Soc. [London] **1944**, 387
4. D.Bryce-Smith and A.Gilbert,
   Proc. chem. Soc. [London] **1964**, 87 ;
   Tetrahedron Letters **1964**, 3471
5. G.O.Schenck,
   Z. Elektrochem., Ber. Bunsenges. physik. Chemie **64**, 997 (1960) ;
   G.Pfundt, Diplomarbeit, Univ. Göttingen 1958
6. G.O.Schenck, Dechema-Monographien **24**, 105 (1955)
7. D.Bryce-Smith, private communication