

COMPETITIVE PHOTOADDITIONS OF ACETYLENES TO THE C=C AND C=O BONDS OF p-QUINONES

S. Farid, W. Kothe and G. Pfundt

Max-Planck-Institut für Kohlenforschung, Abt. Strahlenchemie, Mülheim-Ruhr

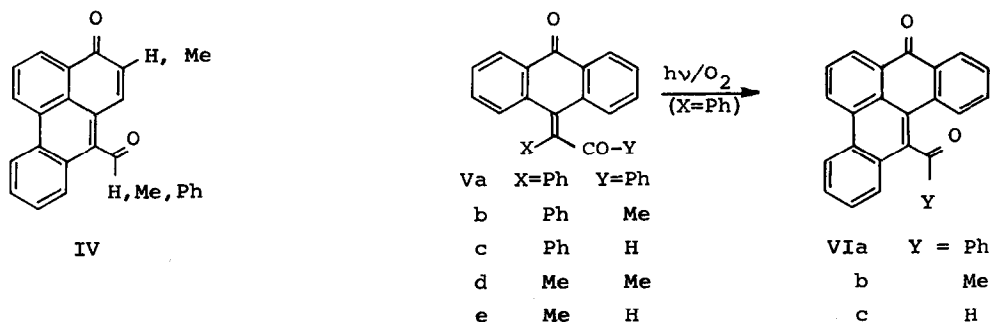
(Received in UK 16 May 1968; accepted for publication 26 May 1968)

As previously reported¹⁾ photochemical cycloaddition of olefins to the C=C bond of naphthoquinone (NQ) yielding cyclobutanes competes with addition to the carbonyl group to give oxetans. Photoaddition of diphenyl acetylene to the C=O group of p-quinone yielding a quinone methide by rearrangement of the primarily formed oxete²⁾ and the photoadditions of several acetylenes to methoxy-p-quinone giving cyclobutene derivatives³⁾ have also been reported.

We have found that in the photoreactions of NQ with acetylenes both types of additions are competing. In connection with a systematic study of the mechanisms of these competing reactions we investigated the influence of substituents by reacting NQ, 2-methyl naphthoquinone (MNQ) and 2,3-dimethyl-naphthoquinone (DMNQ) with mono- and di-substituted acetylenes. The product distribution has been estimated by NMR; analytical samples were obtained by column and layer chromatography and by fractional crystallisation.

The unsubstituted acetylene gives with NQ in poor yield the cyclobutene derivative, the corresponding methide could not be detected. Substituted acetylenes, however, were found to react much more readily. The adducts formed via the most stable biradical intermediates are favoured. Thus, with MNQ and asymmetrically substituted acetylenes the cyclobutenes I predominate over the isomers II; also C₃O-cycloaddition occurs at the carbonyl group at position 4, and in all cases III were the only methides we could detect and isolate.

Irradiation of the methides III ($X = \text{phenyl}$) leads to *cis-trans*-isomerisation and in high yield to dehydro-cyclisation yielding IV. This reaction represents a simple synthesis for such benzanthrones and related compounds.



The photoreactions of anthraquinone with the acetylenes listed in the table give in 40-90 % yield the corresponding methides Va-e*. The formation of Va from the photoreaction with diphenyl acetylene has been recently reported by BRYCE-SMITH et al.⁴⁾ The spectroscopic data given by these authors are identical with those we obtained with this compound.

On irradiating Va and Vb ($\lambda > 366 \text{ nm}$ in benzene/ O_2 or I_2) the cyclisation products VIa (m.p. 229-230°) and VIB (m.p. 173-174°) are obtained in almost quantitative yields. According to our UV-data the compound detected by HENSON et al.⁵⁾ in the photoreaction of anthraquinone with diphenyl acetylene in oxygen-saturated hexane solution should be VIa, formed by subsequent photodehydrocyclisation of Va. In the presence of O_2 we could obtain the cyclisation products directly without isolating the methides.

In contrast to III and V the cyclisation products IV and VI give rise to vibrational patterns in the UV. The NMR spectra of IV and VI (strongly deshielded protons (1.0 - 1.4 τ) in accordance with the planar fixation of the molecules) and the mass-spectroscopical determination of the molecular weights support the structure assignments.

* The reaction can be also induced by γ -irradiation in benzene solution as shown for the addition to phenyl propyne.

The physical and detailed spectroscopical data of the new compounds will be given in the main publication. For NMR data of the cyclobutenes see the following paper.

References:

- 1) C.H. Krauch and S. Farid, Tetrahedron Letters, 4783 (1966)
- 2) H.E. Zimmermann and L. Craft, ibid., 2131 (1964)
D. Bryce-Smith, G.I. Fray and A. Gilbert, ibid., 2137 (1964)
- 3) S.P. Pappas and B.C. Pappas, ibid., 1597 (1967)
- 4) D. Bryce-Smith, A. Gilbert and M.G. Johnson, ibid., 2863 (1968)
- 5) R.C. Henson, J.L.W. Jones and E.D. Owen, J.chem.Soc., A 116 (1967)