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

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As previously reported<sup>1)</sup> 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 oxete<sup>2)</sup> and the photoadditions of several acetylenes to methoxy-p-quinone giving cyclobutene derivatives<sup>3)</sup> 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 C<sub>3</sub>O-cycloaddition occurs at the carbonyl group at position 4, and in all cases III were the only methides we could detect and isolate.

Product Distribution of the Reactions a)

(cis and trans)

100

of Naphthoquinones	with	Acetylenes:
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A	В	X = Me	Ph	Me	Ph	Ph	
		Y = H	н	Ме	Me	Ph	
н	н	28	24	9	12	14	
Me	н	> 95 <sup>b)</sup>	92 <sup>c )</sup>	75	61 <sup>d)</sup>	68	
Me	Me e)	<b>4</b>		~ 100 -			

- a) Irradiation in benzene; quinone: 0,05 M; acetylene: 0,2 M (20°C)
- b) II could not be detected among the reaction products
- c) I : II ≈ 85 : 15
- d) I : II ≈ 90 : 10
- e) The reaction of DMNQ with phenyl acetylene, butyne or phenyl propyne produces in addition small amounts of unidentified compounds.

As indicated by the table, addition to the C=O bond is enhanced by methyl and phenyl substitution of the acetylene. Addition to the C=C bond is favoured by methyl substitution of the quinone double bond. These findings will be discussed in a separate paper dealing with the kinetic and mechanistic aspects. Preliminary results also show a temperature dependence (10-70°C) of the competing reactions with cyclobutene formation favoured at lower temperature in the reactions of MNQ with butyne and diphenyl acetylene.

<sup>\*</sup> We have observed an analogous effect in the reactions of NQ with cyclic olefins 1).

Irradiation of the methides III (X = 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.

O 
$$H$$
, Me

 $X = CO - Y$ 
 $Y = Ph$ 
 $Y = Ph$ 

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.<sup>4)</sup>. The spectroscopic data given by these authors are identical with those we obtained with this compound.

On irradiating Va and Vb ( $\lambda > 366$  nm in benzene/O<sub>2</sub> or I<sub>2</sub>) 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.<sup>5</sup>) 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<sub>2</sub> 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  $\tau$ ) 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  $\gamma$ -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:

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