

PHOTOADDITION OF ALKYNES TO METHOXY-p-BENZOQUINONE

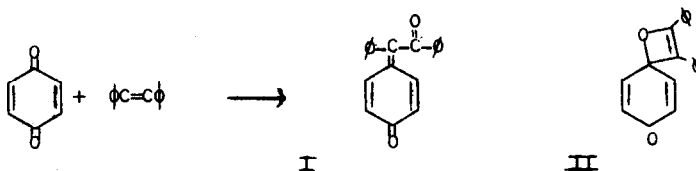
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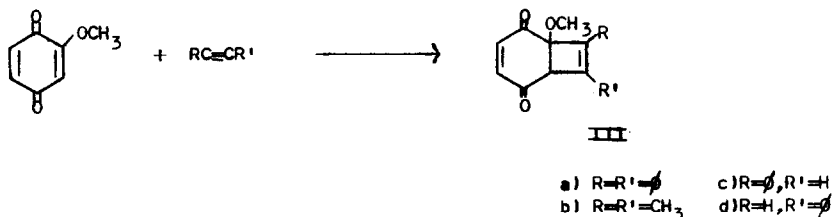
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The photoaddition of olefins and 1,3-dienes to p-benzoquinone has received considerable attention.<sup>1</sup> The light-induced addition of diphenylacetylene (tolan) to p-benzoquinone is known<sup>2</sup> to afford the adduct I in high yield, presumably via the intermediate oxetene II.<sup>2a</sup> Herein we report that alkynes undergo photoaddition to methoxy-p-benzoquinone efficiently

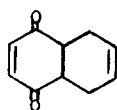


and stereoselectively to afford the novel bicyclo [4.2.0] octa-3,7-diene-2,5-dione ring system.

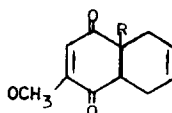
Irradiation<sup>3</sup> of an acetonitrile solution (40 ml) containing methoxy-p-benzoquinone (435 mg, 0.079 M) and diphenylacetylene (4.15 g, 0.58 M) for two hours, followed by careful silica gel chromatography, resulted in the isolation of a single adduct and unreacted starting materials. After recrystallization from ether-hexane, the adduct, m.p. 130-131°C, was isolated in about 50% yield (based on recovered starting material) and was assigned the structure IIIa on the basis of infrared, ultraviolet, nmr, and mass spectra.



The elemental analysis (Calc. for  $C_{21}H_{16}O_3$ : C, 79.7; H, 5.1. Found: C, 79.8; H, 5.2.) and molecular weight (316 by mass spectrometry)<sup>4</sup> are consistent with this formulation. The ultraviolet spectrum exhibits  $\lambda_{\max}^{\text{ethanol}}$  382 m $\mu$  (774) (shoulder), 292 ( $1.08 \times 10^4$ ), and 223 ( $3.07 \times 10^4$ ), indicating the presence of both the cis-stilbene ( $\lambda_{\max}^{\text{cyclohexane}}$  275 ( $1.07 \times 10^4$ ) and 224 ( $2.26 \times 10^4$ ))<sup>5</sup> and 1,3-dione-2-ene chromophores (for IV,<sup>6</sup>  $\lambda_{\max}^{\text{ethanol}}$  360 (60) and 223 ( $1.19 \times 10^4$ )). The spectrum is incompatible with a 1,3-dione-2-methoxy-2-ene part structure (for V (R=CH<sub>3</sub>),<sup>7</sup>  $\lambda_{\max}^{\text{ethanol}}$  345 (160) (shoulder) and 269 ( $8.4 \times 10^3$ )). The infrared spectrum of the adduct shows a single carbonyl band at 5.93  $\mu$  in contrast to that of V(R=H),<sup>8</sup> which exhibits carbonyl bands at 5.88 and 6.04  $\mu$  lending further support to our formulation.



IV



V

Four regions of resonances in the area ratios of 10:2:1:3 for aromatic, vinyl, methine, and methoxyl hydrogens, respectively, are displayed in the nmr spectrum<sup>9</sup> of IIIa. The aromatic hydrogens appear as a complex multiplet at lowest field; the vinyl hydrogens, as an AB quartet centered at 395 cps ( $J=10$  cps) with A calculated at 401 cps, B, at 389, and B further split into a doublet ( $J \approx 1.5$  cps). The methine and methoxyl hydrogens appear at 255 cps (broad) and 203 cps, respectively. Viewed in total the physical and spectral properties of the adduct provide compelling evidence for the assignment IIIa.

An interesting feature of the mass spectrum of IIIa is noteworthy. While the most intense line corresponds to the molecular ion at  $m/e$  316 (arbitrarily taken as 100%), the most abundant ion fragment is at  $m/e$  191 (57%) as compared to  $m/e$  178 (19%), which probably represents the diphenylacetylene ion radical. This suggests that the ionization process resulting in the 191 fragment is more important than retro-addition. A likely candidate for this fragment is the diphenylcyclopropenium ion.

Photoaddition to methoxy-*p*-benzoquinone is not restricted to aromatic alkynes. Thus, 2-butyne reacts<sup>3</sup> to afford the adduct IIIb together with considerable amounts of ether-insoluble polymeric material. After purification by silica gel chromatography and recrystallization from ether-hexane, the pure adduct, *m.p.* 50–51°C, was isolated in 30% yield.

It provides the correct elemental analysis (Calc. for  $C_{11}H_{12}O_3$ : C, 68.7; H, 6.3. Found: C, 68.8; H, 6.4) and molecular weight (192 by mass spectrometry). The ultraviolet spectrum exhibits  $\lambda_{\text{max}}^{\text{ethanol}}$  387m  $\mu$  ( $\epsilon$  155), 283 (299) (shoulder), and 223 ( $1.30 \times 10^4$ ); the carbonyl band in the infrared spectrum appears at 5.94  $\mu$ .

Four regions of resonances are displayed in the nmr spectrum of IIIb with area ratios of 2:1:3:6 for vinyl, methine, methoxyl and C-methyl hydrogens, respectively. The vinyl hydrogens appear as an AB quartet centered at 394 cps ( $J=10$  cps) with A calculated at 397, B, at 391, and finer splittings superimposed on all the lines. The methine and methoxyl hydrogens appear at 215 cps (broad) and 199 cps, respectively; the C-methyl hydrogens, as a complex multiplet centered at 102 cps.

Phenyl acetylene undergoes photoaddition<sup>3</sup> to methoxy-*p*-benzoquinone efficiently and stereoselectively to afford a single adduct, m.p. 124-125°C, isolated in 80% yield after purification (Calc. for  $C_{15}H_{12}O_3$ : C, 75.0; H, 5.0. Found: C, 74.9; H, 5.1.). The spectral properties of the adduct clearly indicate that addition occurs, as with diphenylacetylene and 2-butyne, to the methoxyl-side of the quinone;<sup>10</sup> however, this evidence may be accommodated, as well, by structure IIIc or IIId. Pertinent to this problem is the nmr spectrum of the adduct, which displays four regions of resonances in the area ratios of 5:3:1:3 for aromatic, vinyl, methine and methyl hydrogens, respectively. The three vinyl hydrogens appear as four peaks at 403, 401, 397, and 395 cps, the area ratio of the former two peaks to the latter two being 1/2. Possibly, the cyclobutene hydrogen resonance is under the X half of an AX pattern; however, definitive assignments are not possible. The methoxyl hydrogens appear at 203 cps, as compared with 203 for IIIa and 199 for IIIb, indicating that the phenyl rings in IIIa and the phenylacetylene adduct do not influence these resonances appreciably. On the other hand, the methine hydrogens are considerably deshielded by the phenyl rings. For the phenylacetylene adduct this resonance appears as a broad singlet with fine splittings at 234 cps, as compared with 255 for IIIa and 215 for IIIb, indicating that deshielding by each of the two phenyl rings in IIIa is equally efficient and additive. While these deshielding effects are of interest, they, unfortunately, do not allow structure elucidation by nmr spectroscopy.

Replacement of a hydrogen atom on *p*-benzoquinone by a methoxy group results in a striking change on the course of photoaddition to alkynes vide supra. This finding is not surprising,

however, in view of the profound influence that this replacement has on the nature of the chromophoric groups. While the present data clearly do not allow definitive mechanistic conclusions, the products from *p*-benzoquinone and methoxy-*p*-benzoquinone suggest that  $n, \pi^*$  and  $\pi, \pi^*$  reactive states, respectively, may be involved.

Structure elucidation of the phenylacetylene adduct by chemical methods, mechanistic aspects of photoaddition, and chemical transformations of the photoproducts are currently under active investigation.

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#### REFERENCES

1. For example, see D. Bryce-Smith and A. Gilbert, Proc. Chem. Soc., 87 (1964); J. A. Barltrop and B. Hesp, J. Chem. Soc., 5182 (1965).
2. (a) H. E. Zimmerman and L. Craft, Tetrahedron Letters, 2131 (1964); (b) D. Bryce-Smith, G. I. Fray and A. Gilbert, ibid. 2137 (1964).
3. A "Black Light" source (G.E. H100PSP38-4) was utilized and placed about 10 cm from the reaction vessel (a Pyrex jacketed-beaker), which was fitted with a rubber stopper with two serum-capped openings for  $N_2$  entry and exhaust, and aliquot removal.  $N_2$  was passed through the solutions for twenty minutes prior to irradiation, which was conducted at  $0^\circ$  (except in experiments with diphenylacetylene which were conducted at  $15^\circ$  C due to its insolubility).
4. We are indebted to Dr. Luther H. Smithson, Jr. of Varian Associates for providing the mass spectra.
5. T. Katsumota, Bull. Chem. Soc. Japan, 33, 242 (1960)
6. This spectrum was determined in our laboratories.
7. H. Bastron, R. E. Davis, and L. W. Butz, J. Org. Chem., 8, 515 (1943)
8. G. I. Birnbaum, ibid., 25, 1660 (1960).
9. The nmr spectra were obtained in deuteriochloroform solution on a Varian A-60 spectrometer. All resonances are reported in cps from TMS as an internal reference.
10. This is in contrast to thermally-induced Diels-Alder addition which occurs at the unsubstituted side of this quinone. For example, see ref. 8.