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PHOTOREARRANGEMENTS OF
1-METHOXY-8-PHENYLBICYCLO[4.2.0]OCTA-3,7-DIENE-2,5-DIONE *

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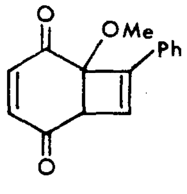
Recently Pappas and Pappas (1) have shown that acetylenes add photochemically to methoxy-p-benzoquinone to give derivatives of bicyclo[4.2.0]octa-3,7-diene-2,5-dione. The exact structure (Ia or Ib) of the phenylacetylene-methoxybenzoquinone adduct I was not determined. We have now found that this adduct can be rearranged (2) photochemically (450-watt Hanovia medium-pressure mercury lamp with Pyrex filter) in benzene solution to two structural isomers, II and III. Thus the original adduct must have structure Ia.

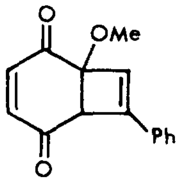
Compounds II and III were separated by silica-gel chromatography, with benzene as eluant. They gave correct elementary analyses and their structures follow from the evidence given below. Isomer II was obtained in 55% yield as orange plates, mp 128-129°, has λ_{max} (95% EtOH), 2520Å (ϵ 13,400), 2140(15,200) 2330(11,000), 2600(8,800); ν_{max} 1670 cm^{-1}, m/e 240. The nmr spectrum (Fig. I) shows the disappearance of the cyclobutene resonance present in IA (Fig. I) and the appearance of a high field AB quartet τ 5.83, 6.18, J = 4.0 Hz, assigned to the vicinal methine protons (3,4).

Isomer III obtained in 20% yield as colorless prisms, mp 168-169° dec. has λ_{max} (95% EtOH), 2260(ϵ 10,130), 2915(1740), ν_{max} 3450, 1675 cm^{-1}, m/e 240. The nmr spectrum (Fig. I) shows a collapsed AB quartet τ = 5.23, 5.32, J = 7.0 Hz, for the methylene protons on the oxetane ring (5,6) and a low field AB quartet τ 3.24, 3.98, J = 10.5 Hz for the enone olefinic protons.

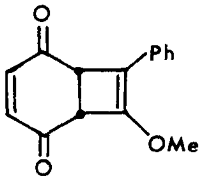
TABLE I



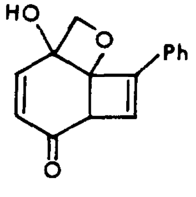
IA



IB



II



III

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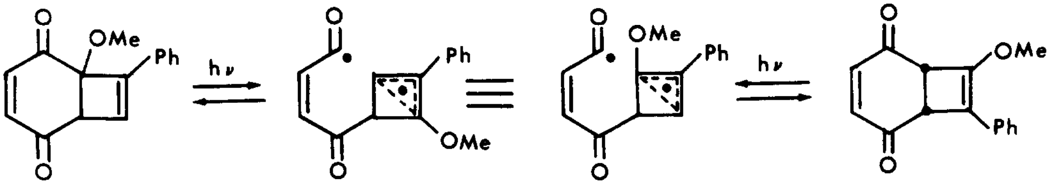
The formation of II is analogous to photorearrangements of eucarvone (7) and has been observed in several systems of this type (8). Norrish type I cleavage of IA yields an allylic diradical which can collapse to give II. This evidence shows that IA is indeed the correct structure of the adduct I.

TABLE II



The photoequilibrium (Ia $\rightleftharpoons$ II) must lie far on the side of isomer II since irradiation of II leads to none of the adduct IA nor to any buildup of the 3-oxetanol (III). Irradiation of the deuterated phenylacetylene (PhC ≡ CD) adduct of methoxy-p-benzoquinone gives a deuterated isomer of II whose nmr spectrum has a methine singlet (τ 5.82). Thus more deep-seated photorearrangements (9) are not taking place in the rearrangement of IA to II.

The colors of IA and II are markedly different. IA is light yellow [$\lambda_{max}(CHCl_3)$ 3820 Å (ϵ 3.1), $\lambda(CHCl_3)$ 4500(0.35), 4700(0.00)]; II is orange [$\lambda_{max}(CHCl_3)$ 3820 Å (ϵ 3.8), $\lambda(CHCl_3)$ 4500 (2.0), 5000 (0.64) 5500 (0.00)]. We attribute this difference to the improved donor properties of the vinyl ether moiety to the enedione acceptor in isomer II, thus giving rise to a longer wave-length charge-transfer band.

The formation of isomer III is analogous to cyclobutanol formation (10, 11) and has been observed by Yates and Szabo (5) on irradiation of simple α-alkoxy ketones. Abstraction of a methyl hydrogen γ to the carbonyl, followed by closure of the diradical can lead to an oxetanol.

TABLE III

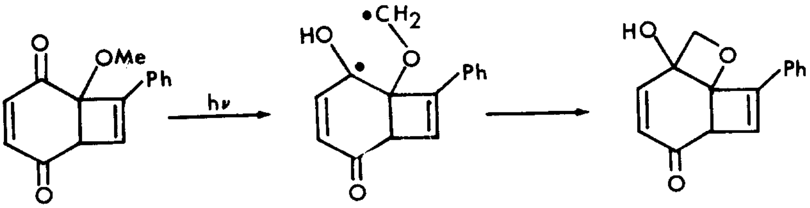
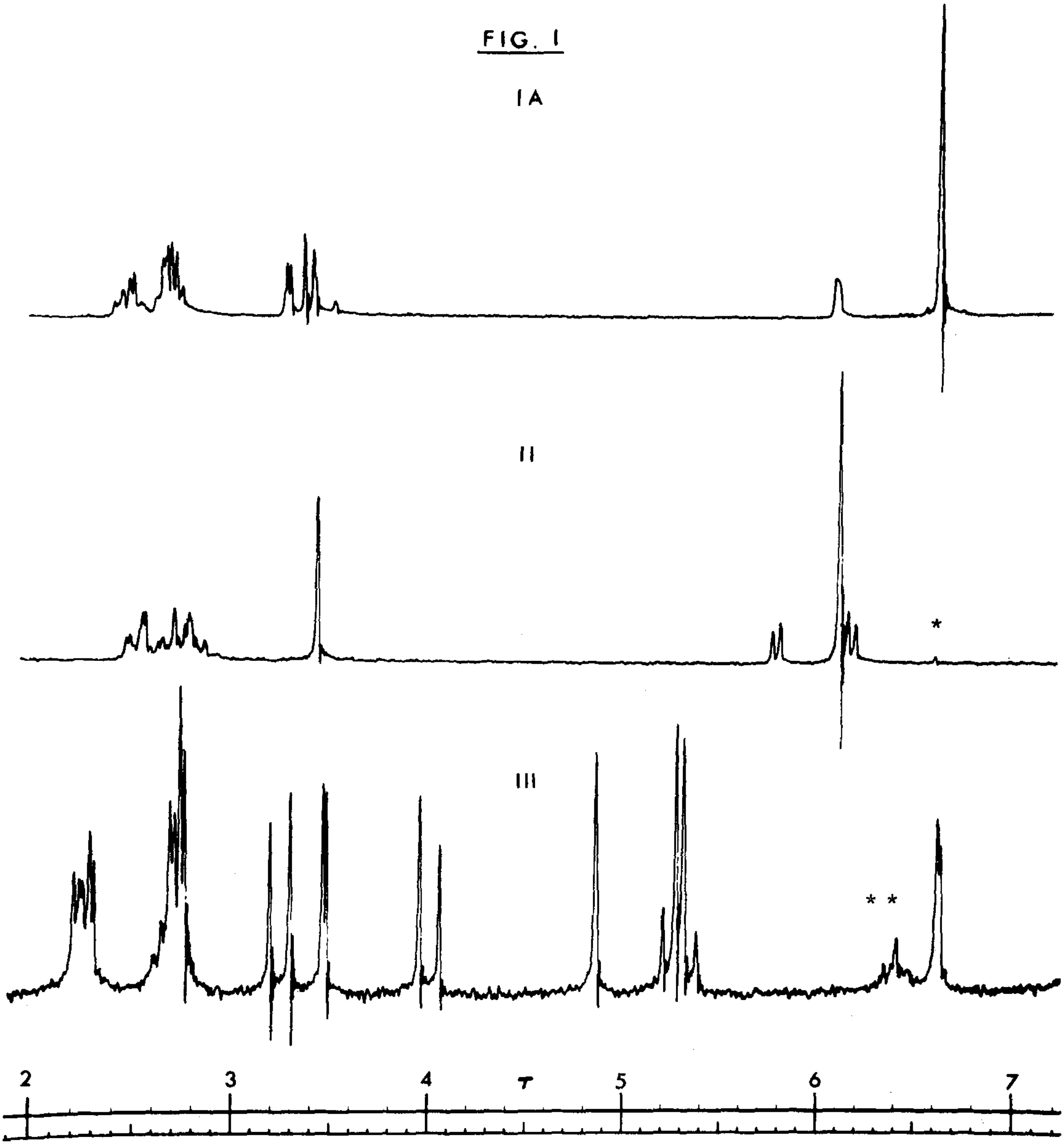


FIG. I

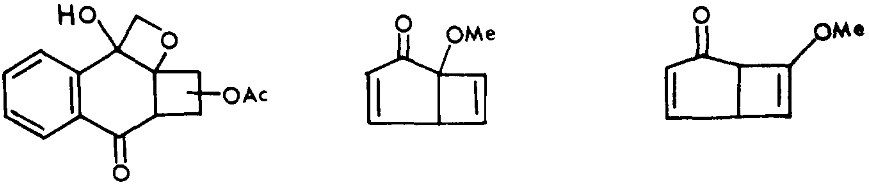


100 MHz spectra of compounds IA and II in deuterochloroform and compound III in acetone-d_6.

The small peak denoted by a single asterisk (*) is the methoxyl resonance of a trace of IA in the sample of II. The peak denoted by two asterisks (**) is due to an impurity in the acetone-d_6.

Irradiation of a mixture of methoxy-p-napthoquinone and vinyl acetate in benzene solution gave a single adduct whose nmr, mass spectrum and analysis are in agreement with IV.

TABLE IV



IV V VI

The position and configuration of the acetoxy group have not been determined.

The formation of oxetanols in the [4.2.0] ring system occur in high yields even though these products must be very strained. Not surprisingly photolysis of the photoisomer V of α-tropolone methyl ether is reported to give VI and not a 3-oxetanol (9).

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