

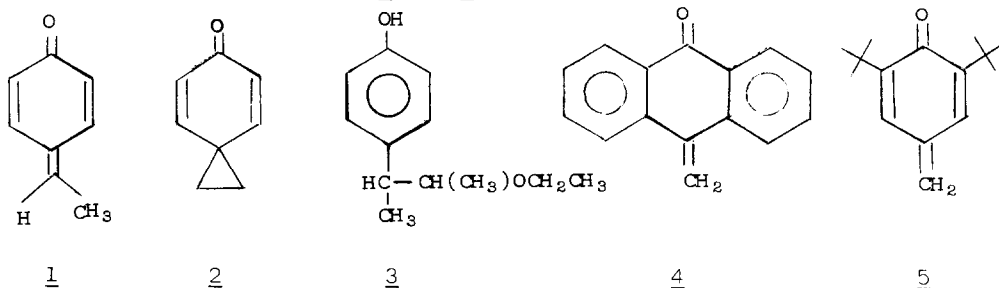
THE PHOTOCHEMISTRY OF SOME QUINONE METHIDES<sup>(1)</sup>

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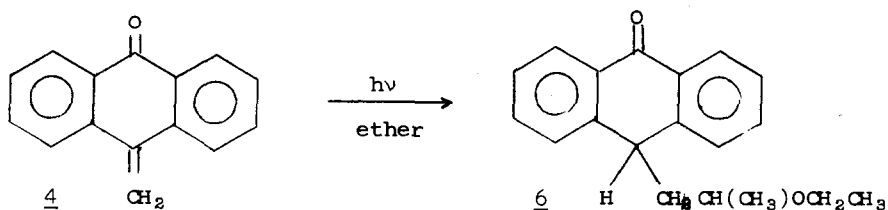
The intermediacy of the quinone methide 1 in the photochemical transformations of spirodienone 2 was deduced on the basis of formation of the ether-incorporated product 3.<sup>(2,3)</sup> This postulate was strengthened as a result of experiments with spirodienone 1 labeled with deuterium on the cyclopropane ring.<sup>(4)</sup> To confirm the proposed mechanism for formation of 3, and other features of these reactions, we have studied the photochemistry of the simple quinone methides 4 and 5.



Photolysis of 4<sup>(5)</sup> in ethyl ether under nitrogen, using a 450-watt high pressure Hanovia mercury arc and Pyrex filters, could be followed by disappearance of the UV maximum at 273 nm and concomitant appearance of a new maximum at 261 nm. The quantum yield for disappearance of 4 in ether was found to be 0.80 at 366 nm, using a Bausch and Lomb high intensity grating

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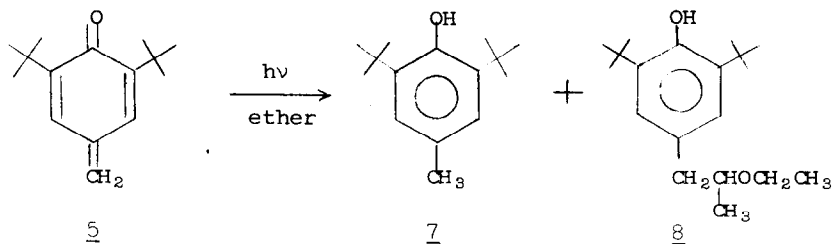
monochromator. The main product (20% yield) was isolated, and structure 6 was assigned on the basis of spectral data. The infrared band at  $1665\text{ cm}^{-1}$  is typical of substituted anthrones. The mass spectrum showed principal peaks at  $m/e$  280, 265, 237, 235, 208 (base), 193, 180, 152, 126, 73 and 45, exactly as expected for 6 by analogy with spectra for other ether incorporated products.<sup>(2-4)</sup> The NMR spectrum showed resonances at 7.0-8.3 (aromatic H), 3.0-3.8 (H on ether carbon), 2.0-2.5 ( $\alpha$  methylene group) and 0.8-1.8 p.p.m. (methyls). Other products besides 6 were formed but were not identified.



A more extensive investigation of the photochemistry of the simple monocyclic quinone methide 5<sup>(6)</sup> was undertaken. Photolysis of 5 in ethyl ether under the conditions described above was much slower than for 4. The quantum yield for disappearance of 5 at 366 nm was 0.065. Gas chromatographic analysis<sup>#</sup> of the products showed the presence of a main product (65-70%) and three minor products. One of the minor products was identified as 4-methyl-2,6-di-~~t~~-butylphenol 7 from spectral data and comparison with authentic material<sup>(7)</sup> synthesized by  $\text{LiAlH}_4$  reduction of 5.<sup>(8)</sup> The main product 8 was isolated by preparative glpc. The IR spectrum of 8 indicated hydroxyl and aromatic moieties. The mass spectrum again was virtually a proof of structure, with principal peaks at  $m/e$  292, 277, 247, 231, 220, 219 (base), 205, 189, 105, 91, 73, 57 and 45. The NMR spectrum completely supports the structure: 6.9 (s, 2H, aromatic), 4.95 (s, 1H, hydroxyl), 3.3-3.7 (multiplet, 3H, H on ether carbon), 2.4-2.8 (multiplet, 2H, benzylic  $\text{CH}_2$ ) and 1.1-1.7 ppm (24H, methyls).

<sup>#</sup> 6' x 1/8" column of Carbowax 20M, 15% on Chromosorb W, A/W, treated with DMCS, column temperature 200°

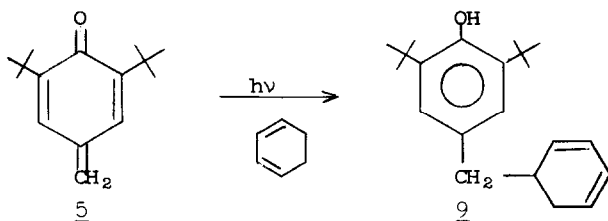
The remaining minor products, about 10% of the reaction mixture, were not cleanly separated by glpc and were not further investigated.



Photolysis of 5 at shorter wavelengths, principally 254 nm, gave substantially reduced yields of the above products. The main product was insoluble in ether and has not as yet been identified.

Experiments were carried out to determine the multiplicity of the excited state(s) leading to the products in the case of quinone methide 5. Sensitization was seen (merry-go-round experiments)<sup>(9)</sup> with the following sensitizers, given with their triplet energies:<sup>(10)</sup> acetophenone (73 kcal/mole), benzophenone (68.5), thioxanthone (65.5) and anthraquinone (62.4). The reaction could be quenched by naphthalene (60.9), but the quenching behavior was for unknown reasons not quantitatively reproducible, so that a reliable Stern-Volmer plot could not be obtained. The use of other potential triplet quenchers (cis and trans-piperylene, 1,3-cyclohexadiene, trans-stilbene) accelerated rather than quenched the disappearance of 5 in ethyl ether. Analysis by glpc indicated the formation of new products, suggesting that these olefins were reacting with 5. In the case of 1,3-cyclohexadiene, a new compound was isolated by column chromatography of the photolysate, and spectral data indicated it was indeed an adduct. IR spectra showed hydroxyl and aromatic bands, while the mass spectrum showed m/e 293, 283, 242, 229, 220, 219(base), 205, 203, 161, 145, 128, 115, 105, 91, 80, 79, 77, 67, 57, and 41. The base peak (219) shows loss of a cyclohexadienyl group (79), virtually requiring that the cyclohexadiene ring is attached to the benzylic carbon atom, as indicated in structure 9. At high concentrations of cyclohexadiene,

glpc analysis of the photolysate indicated the presence of cyclohexadiene dimers<sup>(11)</sup> identified by comparison with dimers formed by photosensitized dimerization of cyclohexadiene.<sup>(11)</sup> Thus, triplet energy transfer to cyclohexadiene is competitive with hydrogen abstraction.



The formation of adducts of quinone methide 5 with ethyl ether and 1,3-cyclohexadiene may well be examples of a general and useful photochemical reaction of quinone methides with compounds containing readily abstractable hydrogens. Although not isolated and characterized, adducts with piperylene are probably formed with similar structures.

These experiments provide strong evidence that the photochemistry of quinone methide 5 proceeds through a triplet state whose energy is approximately 60-62 kcal/mole above the ground state. No phosphorescence from 5 could be observed in a glass at 77° in MCIP or ethanol. Phosphorescence from 4 under these conditions was readily observable, and strongly resembled the emission of anthraquinone. Together with the large difference in the quantum yields, these data suggest that, although the photochemical behavior of 4 and 5 are similar, the details of the excited state processes (e.g., lifetimes and efficiencies of intersystem crossing and non-radiative decay) are probably quite different.

In general, the photochemical behavior of 5 strongly supports the postulated role of the simple quinone methide 1 in the photochemistry of spirodienone 2,<sup>(2-4)</sup> details of which will be published in due course. Further support for these mechanistic postulates is found in the elegant work of Pirkle and Koser<sup>(12)</sup> on substituted spirodienones and related quinone methides described in the accompanying communication.

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## REFERENCES

1. Part XI of a series on the photochemistry of unsaturated ketones in solution. Part X: D. J. Patel and D. I. Schuster, J. Am. Chem. Soc., 89, 184 (1967).
2. D. I. Schuster and C. J. Polowczyk, J. Am. Chem. Soc., 86, 4502 (1964).
3. D. I. Schuster and C. J. Polowczyk, Ibid., 88, 1722 (1966).
4. D. I. Schuster and I. S. Krull, Ibid., 88, 3456 (1966).
5. E. Barnett and M. Matthews, Chem. Ber., 59B, 767 (1926); K. H. Meyer and A. Sander, Ann., 420, 113 (1920); R. Baird, private communication.
6. N. P. Neureiter, J. Org. Chem., 28, 3486 (1963); L. J. Filar and S. Winstein, Tetrahedron Letters No. 25, 9 (1960).
7. G. H. Stillson, D. W. Sawyer and C. K. Hunt, J. Am. Chem. Soc., 67, 303 (1945).
8. C. D. Cook and B. E. Norcross, Ibid., 78, 3797 (1956).
9. A. A. Lamola and G. S. Hammond, J. Chem. Phys., 43, 2129 (1965).
10. W. G. Herkstroeter, A. A. Lamola and G. S. Hammond, J. Am. Chem. Soc., 86, 4537 (1964).
11. D. Valentine, N. J. Turro and G. S. Hammond, Ibid., 86, 5202 (1964).
12. W. H. Pirkle and G. F. Koser, accompanying communication.