Tetrahedron Letters No.24, pp. 2863-2866, 1968. Pergamon Press. Printed in Great Britain.

PHOTOADDITIONS OF DIPHENYLACETYLENE, CYCLO-OCTA-1,3-DIENE, AND CYCLO-OCTENE TO ANTHRAQUINONE

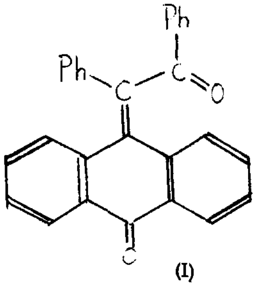
D. Bryce-Smith, A. Gilbert and M. G. Johnson

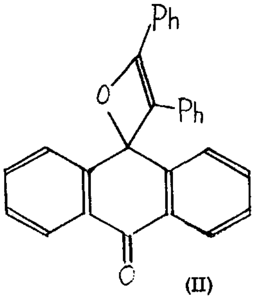
Department of Chemistry, The University, Reading.

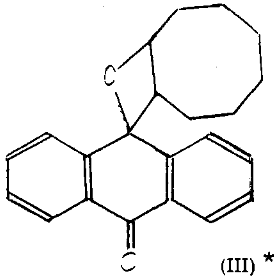
(Received in UK 1 March 1968; accepted for publication 19 March 1968)

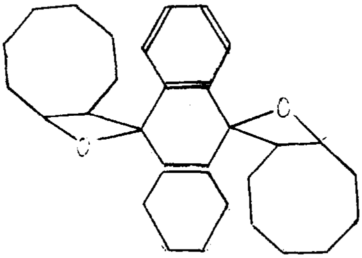
The known photochemistry of anthraquinone is largely restricted to hydrogen-abstraction reactions(1). In view of the frequent use of this compound as a photosensitiser, we wish to report that it undergoes certain photoaddition reactions.

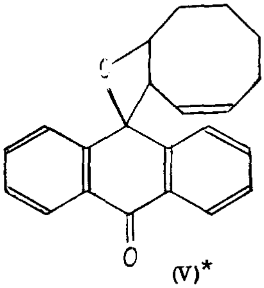
A stirred solution/suspension of anthraquinone (1.0 g.) in a solution of diphenylacetylene (2 g.) in benzene (250 ml.) was irradiated at 20-25° for 20 hr in a water-cooled borosilicate apparatus with four 150-w. tungsten lamps. The bright-yellow adduct (I), m.p. 197-198°, was isolated by fractional crystallisation in 40% yield: much of the starting material remained and the true yield was almost quantitative. [Found: C, 87.00; H, 4.60. Calc. for $C_{28}H_{18}O_2$: C, 87.00; H, 4.70%.] The ultraviolet spectrum in ethanol had $\lambda_{max.}$ (ϵ) 233 mμ (38,800), 253 mμ (29,800), 275 mμ (21,500), and 357 mμ (9,380): the infrared spectrum showed principal absorptions at 1655(s), 1600(m), 1310(m), 1250(m), 1212(w), 1168(w), 940(m), 845(w), 782(m), 761(m), 725(w), and 698(m) cm.$^{-1}$. The n.m.r. spectrum showed only aromatic protons as three complex multiplets between 1.6 and 3.0 τ, thereby excluding structures which would have resulted from additions to a benzenoid ring: the ultraviolet absorption excludes the oxeten structure (II). The assigned quinomethane structure (I) is wholly consistent with the spectroscopic data, and has precedents in the known modes of addition of diphenylacetylene to ketones(2) and p-benzoquinone(3). The above u.v. data differ completely from results recently given by Hensen et al. for a supposed adduct of structure (I) (not isolated) thought to be formed by irradiation of oxygenated solutions of anthraquinone and diphenylacetylene in hexane(4).


(I)


(II)


(III) *


(IV) *


(V)*

Irradiation as above of a stirred solution/suspension of anthraquinone (0.5 g.) in *cis*-cyclo-octene (250 ml.) led to the formation of two major products, (III) and (IV). These structural assignments are deduced from the following results. Compound (IV), a 2 : 1 adduct, was shown to be formed by photo-addition of cyclo-octene to the 1 : 1 adduct (III). The relative yields of adducts (III) and (IV) were time-dependent. Thus after 12 hr. irradiation, 50% conversion of anthraquinone had occurred to give 40% of (III) and 10% of (IV), whereas after 60 hr. (IV) was obtained in 90% yield, and (III) was not detected.

Adduct (III) was a white crystalline solid, m.p. 147 - 148°. The ultraviolet spectrum in ethanol had $\lambda_{max.}$ (ϵ), 278 mμ (13,780), 309 mμ (4,152), 355 mμ (194) and 367 mμ (124), and the infrared spectrum had significant absorptions at 1670(s), 1604(s), 1323(s), 1300(s), 1180(m), 1028(m), 986(s)†, 942(m), 824(w) and 768(s) cm^{-1}. The n.m.r. spectrum ($CDCl_3$) had complex absorptions centred at τ 2.15, 4.90 and 6.90 → 9.60 with relative areas 8 : 1 : 13 (compare ref. 5).

The 2 : 1 adduct of cyclo-octene and anthraquinone (IV) was a white crystalline solid m.p. 215 - 217°. Found: *M* (mass spectrograph) 428. Calc. for $C_{30}H_{36}O_2$: M, 428. The ultraviolet spectrum

---

[*] The stereochemistry has not yet been ascertained.

[†] Oxetan ring.

in dioxan had $\lambda_{\max.}$ (ϵ) 259 mμ (460), 266 mμ (575), and 275 mμ (418) showing an absence of conjugation between the aromatic rings: the absence of carbonyl and hydroxyl groups was shown by the infrared spectrum which had $\nu_{\max.}$ (Nujol) at 1300(m), 1280(m), 1220(m), 1135(w), 1090(w), 1060(w), 1025(m), 970(s)*, 880(w), and 760(s) cm^{-1}. The n.m.r. spectrum ($CDCl_3$) had complex absorptions centred at τ 1.90, 2.50, 4.90 and 6.80 → 9.50 with relative areas 2 : 2 : 1 : 13.

The formation of adduct (IV) represents the first photoaddition to both carbonyl groups of a quinone: neither p-benzoquinone nor 1,4-naphtnoquinone appears able to photoadd more than one molecule of an olefin even when the latter is used in great excess.

In contrast, photoaddition of cyclo-octa-1,3-diene to anthraquinone led to a single adduct (V) in almost quantitative yield. The spectral and analytical data of this adduct were consistent with its assigned structure. Catalytic hydrogenation of adduct (V) with 10% Pd/C in AcOH gave compound (III) (infrared spectrum, m.p., and mixed m.p.). No 2 : 1 adduct was detected.

In contrast with cyclo-octa-1,3-diene, buta-1,3-diene and 2,3-dimethylbutadiene showed no tendency to form photoadducts with anthraquinone, although they readily add to p-benzoquinone and other 1,4-quinones, usually to form dihydropyrans(6). Consideration of the following triplet energy levels permits an understanding of these facts: p-benzoquinone, 50; anthraquinone, 62.5; buta-1,3-diene, ~ 60; cyclo-octa-1,3-diene, 70 - 72 kcal.mole^{-1}. (The usually high triplet energy level of cyclo-octa-1,3-diene undoubtedly reflects the sterically enforced skew conformation of its diene system.) It can be seen that triplet p-benzoquinone cannot be quenched by buta-1,3-diene or cyclo-octa-1,3-diene, and is therefore open to addition reactions with such dienes(6), and also with mono-olefins (triplet energies ca. 80 kcal. mole^{-1})(5). On the other hand, triplet anthraquinone will be quenched by buta-1,3-diene and other 1,3-dienes capable of adopting a planar conformation, but not by cyclo-octa-1,3-diene: hence the planar 1,3-dienes should not, and do not, photoadd to anthraquinone. Anthraquinone is indeed known to photosensitise the dimerisation of buta-1,3-diene(7); but the cited

---

* Oxetan ring

triplet energy levels show that anthraquinone should not photosensitise the dimerisation of cyclo-octa-1,3-diene. In fact, small amounts of a mixture of dimers of cyclo-octa-1,3-diene were formed(8). This can reasonably be attributed to photosensitisation by the 1:1 photoadduct (V), which by analogy with benzophenones might well have a triplet energy around 70 kcal. mole^{-1}. Such quenching of triplet (V) by the diene accounts nicely (a) for the inability of cyclo-octa-1,3-diene to form a 2:1 adduct analogous to that [compound (IV)] formed by cyclo-octene, and (b) for the observed formation of photodimers from cyclo-octa-1,3-diene but not cyclo-octene.(9)

Engelhard Hanovia Limited and Gillette Industries Limited are thanked for financial support.

REFERENCES

1. For a general review see J. M. Bruce, Quart. Rev., 21, 405 (1967).
2. G. Büchi, J. T. Kofron, E. Koller and D. Rosenthal, J. Am. Chem. Soc., 78, 876 (1956).
3. H. E. Zimmermann and L. Craft, Tetrahedron Letters, 2131 (1964);
   D. Bryce-Smith, G. I. Fray and A. Gilbert, ibid, 2137.
4. R. C. Henson, J. L. W. Jones and E. D. Owen, J. Chem. Soc. A, 116 (1967).
5. D. Bryce-Smith and A. Gilbert, Proc. Chem. Soc., 87 (1964);
   D. Bryce-Smith, A. Gilbert and M. G. Johnson, J. Chem. Soc. C, 383 (1967).
6. J. A. Barltrop and B. Hesp, Proc. Chem. Soc., 195 (1964) and J. Chem. Soc. 5182 (1965).
7. N. J. Turro, Ph.D. Thesis (Pasadena: California Institute of Technology) 1963.
8. A mixture of isomeric cyclobutanes.
9. The triplet level of cyclo-octa-1,3-diene has been given by R.S.H.Liu, J.Amer.Chem.Soc.,98,112, (1967).