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An Unusual Caged Oxetan Formed by Intramolecular Photocyclization onto the Carbonyl Group of a Polyalicyclic Enedione

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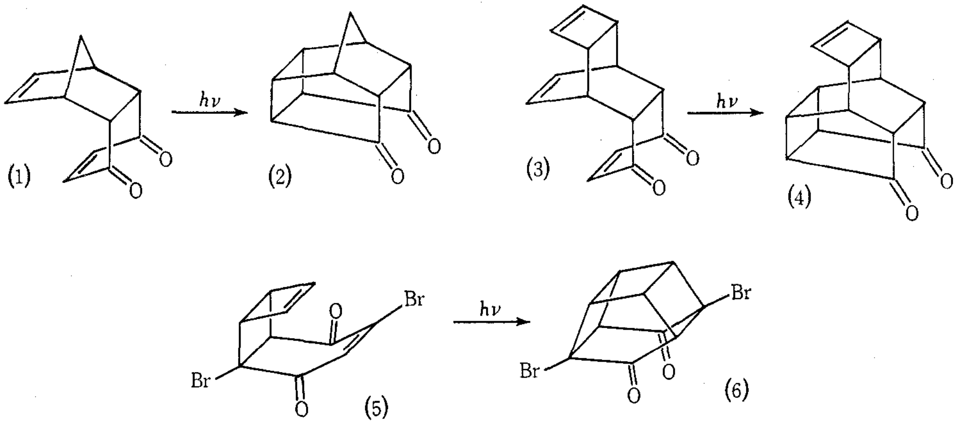
Abstract

p-Benzoquinone reacts with 1,4-dimethyl-2,3-diphenylcyclopentadiene and the similarly substituted cyclopentadienone to form exclusively the *endo* adducts (12) and (9) respectively. Photocyclization of these adducts in the *solid* state yields the respective cyclobutyl photocage compounds (10) and (13). Photolysis of the dienone adduct (9) in solution yields an unusual oxetan product (14) resulting from cyclization between a carbonyl group of the enedione and the proximate olefinic π-centre, as well as the normal cage product (10).

p-Benzoquinones are potent dienophiles in $[_{\pi}4_s + _{\pi}2_s]$ cycloaddition reactions.[1] The strong preference for *endo* addition, together with the long-wavelength absorption of the enedione chromophore, has made these adducts very suitable for the photocage reaction, illustrative of which are the conversions (1) → (2),[2] (3) → (4),[3,4] and (5) → (6).[5]



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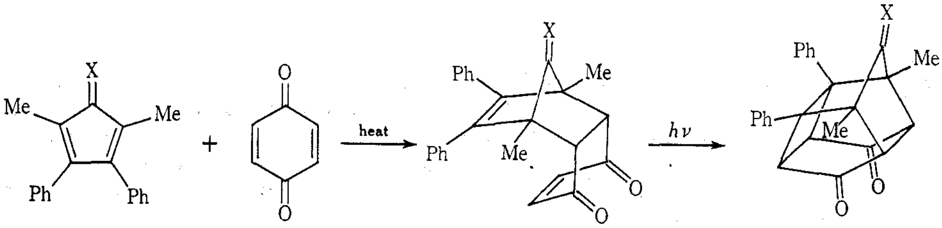
[1] Onishchenko, A. S., 'Diene Synthesis' (Oldbourne Press: London 1965).
[2] Filipescu, N., and Menter, J. M., *J. Chem. Soc. B*, 1969, 616.
[3] Cookson, R. C., Crundwell, E., Hill, R. R., and Hudec, J., *J. Chem. Soc.*, 1964, 3062.
[4] Cookson, R. C., Crundwell, E., and Hudec, J., *Chem. Ind. (London)*, 1958, 1003.
[5] Barborak, J. C., Watts, L., and Pettit, R., *J. Am. Chem. Soc.*, 1966, **88**, 1328.

As part of a program[6,7] involving the cycloadditions of 2,5-dimethyl-3,4-diphenylcyclopenta-2,4-dienone (7), and the related 1,4-dimethyl-2,3-diphenylcyclopenta-1,3-diene (11), we prepared the *p*-benzoquinone adducts of each of these dienes. The cyclopentadienone (7) readily formed an adduct on reaction with *p*-benzoquinone (8) in refluxing chloroform solution for 3 h. The yellow-coloured adduct (9), formed in high yield, showed the typical high frequency carbonyl stretch in the i.r. at 1778 cm^{-1} characteristic of bridged ketones, as well as the enedione carbonyl stretching frequency at 1670 cm^{-1}. The n.m.r. spectrum was fully consistent with the assigned structure, displaying a singlet methyl resonance at δ 1·53, a singlet at 3·30 for the methine protons, another sharp singlet at 6·82 for the vinylic protons and a multiplet for the aromatic protons. The *endo* stereochemistry was confirmed by irradiation in the *solid state* to form a single product (10), m.p. 270°.



(7) X = O (8) (9) X = O (10) X = O

(11) X = H_2 (12) X = H_2 (13) X = H_2

Here the cage structure was supported by its n.m.r. spectrum where the two sets of methine protons at δ 2·94 and 3·68 are indicative of the newly formed cyclobutyl group. In addition the infrared carbonyl absorptions at 1755 and 1740 cm^{-1} confirm the presence of the two types of ring-strained carbonyl groups present in the symmetrical (C_s symmetry) cage product (10).

The cyclopentadiene (11) was far less reactive than the dienone (7) towards *p*-benzoquinone, the reaction requiring heating under reflux in benzene for 15 h to yield the single yellow-coloured adduct (12). In this case the infrared showed only the enedione carbonyl stretching frequency at 1665 cm^{-1}, while the n.m.r. spectrum again showed singlet resonances for the methyl groups (δ 1·56), the methine protons (3·22) and the olefinic protons (6·61), together with an AB pattern for the bridging methylene protons centred at 1·67 and 1·89 with a coupling constant of 9 Hz. Here again the symmetry of the adduct was reflected in its n.m.r. spectrum. This is important for this case since it showed that bond migration had not occurred in the diene prior to adduct formation.

The cage compound (13) was formed in quantitative yield by long-wavelength and ultraviolet irradiation of (12) both in the solid state and in benzene solution. The compound (13) retained the same symmetry as its precursor (12), since its n.m.r. spectrum displayed a single resonance for the methyl groups.

However, the irradiation of the bridged ketone adduct (9) *in benzene solution* formed not only the caged compound (10) but also a second compound which was isolated by chromatography. The latter compound has no clear melting point and

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[6] Anderson, C. M., Bremner, J. B., McCay, I. W., and Warrener, R. N., *Tetrahedron Lett.*, 1968, 1155.

[7] McCay, I. W., Honours B.Sc. Thesis, Australian National University, 1967.

decomposed on heating at about 180°. Analytical data confirmed that it was isomeric with its progenitor, a conclusion which was further supported by the strong peak in the mass spectrum at *m/e* 368. The n.m.r. spectrum (Fig. 1) clearly shows that it has lost the characteristic symmetry associated with other compounds in this series. Further, there are two sharp carbonyl stretching frequencies in the infrared at 1660, 1765 cm^{-1}, which indicates that at least two carbonyl groups have been retained in the product. The oxetan structure (14) is assigned to this product.

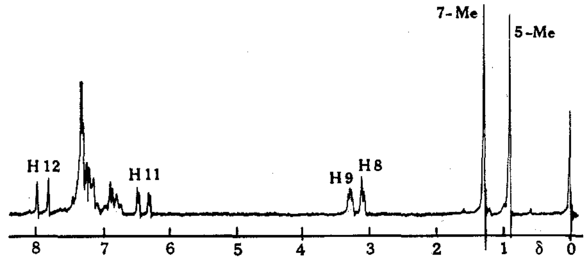

Fig. 1. 60-MHz n.m.r. spectrum of the caged oxetan (14) in $CDCl_3$.

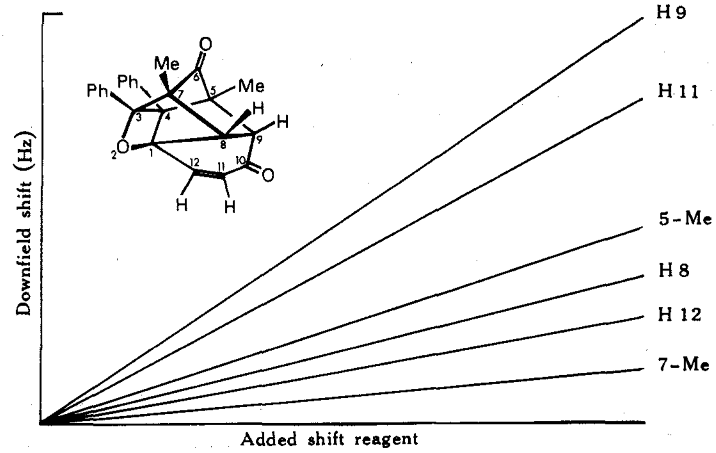

Fig. 2. Lanthanide shift, Eu(fod[D_9])$_3$, on the caged oxetan (14).

The n.m.r. spectrum of the oxetan was assigned after consideration of a lanthanide-induced-shift spectroscopic study, and spin-decoupling information. The lanthanide-induced-shift study is shown diagrammatically in Fig. 2. As expected the europium coordinated onto the 10-keto group, rather than at the strained 6-ketone.[8,9] This distinguishes the adjacent protons at δ 3·30 and 6·40 respectively. It also allows an assignment to be made to the methyl resonances, the higher field one at 0·90 is shifted significantly more than the other and is logically assigned to the 5-methyl group.

Spin-decoupling experiments confirmed the quoted couplings. In particular, irradiation at δ 6·4 (H 11) was especially informative since it caused the doublet at 7·9 (H 12; $J_{11,12}$ 11·0 Hz) to collapse into a singlet, and H 9 (3·30) and H 8 (3·10) to appear as a pair of doublets ($J_{8,9}$ 3·0 Hz). The coupling between H 9 and H 11 was confirmed by irradiation at δ 7·90 (H 12): H 11 appeared as a finely split doublet ($J_{9,11}$ 1·8 Hz).

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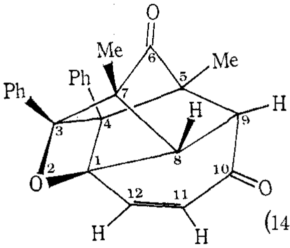
[8] Sanders, J. K. M., Hanson, S. W., and Williams, D. H., *J. Am. Chem. Soc.*, 1972, **94**, 5325.

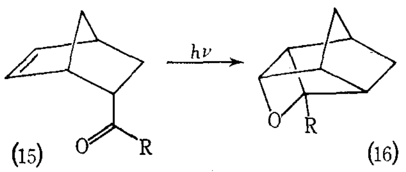
[9] Sievers, R. E., 'Nuclear Magnetic Resonance Shift Reagents' (Academic Press: New York 1973).

Although there are several precedents for intramolecular oxetan formation involving keto groups, for example (15) → (16),[10–13] the corresponding reaction involving an enedione group is rare.[14] That (9) forms the oxetan (14) in solution but not in the solid state presumably reflects the ease with which (9) may achieve the appropriate conformation for this reaction mode.

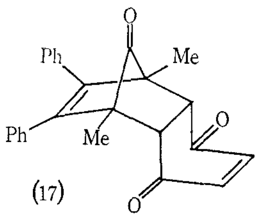


(14)

For reasons of efficient packing the enedione must adopt the 'folded' conformation as shown in (9) and (12). Thus the cyclohexenedione ring is puckered in such a way as to place the two olefinic bonds in close proximity to one another. This conformation is hardly conducive to oxetan formation. However, molecular models suggest that the cyclohexenedione ring is quite flexible and that another stable conformation, the 'extended' form (17), might be present in solution. In this conformation the carbonyl group is well located for oxetan formation.



(15) (16)



(17)

However, the conformational requirement is not a sufficient condition for oxetan formation since the related adduct (12), which should also be able to adopt the 'extended' conformation in solution, does not produce any oxetan. Therefore the 11-substituent in the adduct of type (9) plays a significant role in this respect but whether it is electronic or geometric in origin is a point yet to be determined.*

Experimental

General

Microanalyses were carried out by the A.N.U. Microanalytical Service under the direction of Miss B. Stevenson and Dr J. E. Fildes.

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* A referee has pointed out that the failure to isolate an oxetan adduct from (12) may indicate that this reaction is a reversible one like that observed by Scheffer and Jennings.[14] However, even after only 30 min irradiation, conversion of (12) into (13) was quantitative with no trace of the presence of any oxetan. Under these conditions the oxetan (14) is photostable.

[10] Sauers, R. R., and Henderson, T. R., *J. Org. Chem.*, 1974, **39**, 1850.

[11] Sauers, R. R., and De Padis, A. M., *J. Org. Chem.*, 1973, **38**, 639.

[12] Sauers, R. R., and Kelly, K. K., *J. Org. Chem.*, 1970, **35**, 498.

[13] Sauers, R. R., and Whittle, J. A., *J. Org. Chem.*, 1969, **34**, 3579.

[14] Scheffer, J. R., and Jennings, B. M., *J. Chem. Soc., Chem. Commun.*, 1975, 609.

Melting points were determined on a Kofler hot-strip apparatus, which was calibrated against standard materials.

Infrared spectra were recorded on a Unicam SP200G spectrophotometer, as Nujol mulls between sodium chloride discs, unless otherwise stated. Polystyrene was used as a reference.

Ultraviolet spectra were recorded on a Unicam SP800 spectrophotometer, using holmium as a reference. All spectra were run in 90% ethanol solutions in matched silica cells of path length 1 cm.

Mass spectra were recorded on a Varian MAT CH7 instrument having a direct inlet system and operating at 70 eV.

Proton magnetic resonance spectra were recorded on a 100-MHz Jeol Minimar spectrometer, or on a 60-MHz Perkin–Elmer R10 spectrometer, in $CDCl_3$ with tetramethylsilane as internal standard. The 100-MHz instrument was used for all variable temperature studies or spin-decoupling experiments.

Preparative layer chromatography (p.l.c.) was carried out on glass plates (100 by 20 cm) with silica gel (Merck$_{256+366}$) as adsorbent.

All photolyses were carried out in an inert atmosphere of nitrogen.

endo-*1,8-Dimethyl-9,10-diphenyltricyclo[6,2,1,0^{2,7}]undeca-4,9-diene-3,6,11-trione (9)*

2,5-Dimethyl-3,4-diphenylcyclopenta-2,4-dienone (7) (as its dimer)[15] (1·85 g, 3·6 mmol) and *p*-benzoquinone (8) (389 mg, 3·6 mmol) were heated together in benzene, under reflux, for 1·25 h. The reaction mixture was cooled and filtered to afford the title *adduct* (9), as a yellow crystalline solid (1·93 g, 74%), m.p. 214°. Recrystallization from benzene/chloroform raised the m.p. to 220° (Found: C, 81·2; H, 5·5; O, 13·2. $C_{25}H_{20}O_3$ requires C, 81·5; H, 5·5; O, 13·0%). ν_{max} 1778 (bridge carbonyl), 1670 (enedione) cm^{-1}; δ 1·53 (s, 6H, methyl); 3·30 (s, 2H, H2,7); 6·82 (s, H4,5), 6·65–7·30 (m, aromatics, integrating for protons).

Irradiation of Enedione (9)

(i) *Solution photolysis.*—The adduct (9) (1 g, 2·82 mmol) was dissolved in benzene (130 ml) and irradiated at 40° through a Pyrex filter with an Hanovia 450-W high-pressure mercury lamp (type L) for 1·5 h. The solution was evaporated to dryness. The p.m.r. spectrum showed the presence of the pentacyclic triketone (10) and a second photoproduct (14). The mixture was chromatographed on a column of silica gel (100 g) and eluted with chloroform. The photoproduct (14) eluted first and was followed by trione (10).

Recrystallization from a mixture of chloroform and hexane gave *3,5-dimethyl-2,6-diphenylpentacyclo[5,4,0,0^{2,6},0^{3,10},0^{5,9}]undecane-4,8,11-trione* (10), m.p. 270° (Found: C, 80·1; H, 5·5; O, 13·9. $C_{25}H_{20}O_3,0\cdot33H_2O$ requires C, 80·2; H, 5·6; O, 14·2%). ν_{max} 1755 and 1740s (br, carbonyl), 1600w, 1578m, 1230m, 1068m (br), 973m, 960m, 815m, 780m, 770s, 756m, 703s cm^{-1}; λ_{max}, no absorption band above 210 nm; δ 1·06 (s, 6H, methyl); 2·94, 3·68 (m, m, 2H, 2H, H1,7,9,10); 6·70–7·25 (m, 10H, aromatics). The minor photoproduct was recrystallized from ethanol to yield *5,7-dimethyl-3,4-diphenyl-2-oxapentacyclo[6,4,0,0^{1,4},0^{3,7},0^{5,9}]dodec-11-ene-6,10-dione* (14) (214 mg, 21%), m.p. *c.* 225°, with some prior decomposition at *c.* 180° (Found: C, 81·7; H, 5·4. $C_{25}H_{20}O_3$ requires C, 81·5; H, 5·5%). ν_{max} 1765s (bridge carbonyl), 1660s (α,β-unsaturated ketone), 1600w, 1500m, 1391m, 1240m, 1160m, 1059m, 972m, 938m, 907m, 870m, 806m, 758m, 733s, 700s cm^{-1}; λ_{max} ($CHCl_3$) 262 (ε 6000), 349 nm (ε *c.* 150); for n.m.r. spectrum, see Fig. 1; *m/e* 368 (M, 95%), 340 (M −CO, 63%), 258 (51), 235 (31), 105 (100).

(ii) *Solid state irradiation.*—Irradiation of a thin film of enedione (9) in a Pyrex flask with sunlight yielded the pentacyclic triketone (10), identical with that obtained from solution photolysis.

endo-*1,8-Dimethyl-9,10-diphenyltricyclo[6,2,1,0^{2,7}]undeca-4,9-diene-3,6-dione (12)*

A solution of 1,4-dimethyl-2,3-diphenylcyclopentadiene (11)[16] (492 mg, 2 mmol) and freshly sublimed *p*-benzoquinone (216 mg, 2 mmol) in benzene (15 ml) was heated under reflux for 15 h. The solution was evaporated to dryness and the resulting glass taken up in hot ethanol (10 ml). Yellow crystals of the *adduct* (12) (566 mg, 80%) separated on cooling, m.p. 158° (Found: C, 84·5;

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[15] Allen, C. F. H., and Van Allan, J., *J. Am. Chem. Soc.*, 1942, **64**, 1260.

[16] Bladon, P., McVey, S., Pauson, P. L., Broadhead, G. D., and Horspool, W. M., *J. Chem. Soc. C*, 1966, 306.

H, 6·3; O, 9·3. $C_{25}H_{22}O_2$ requires C, 84·7; H, 6·3; O, 9·0%). ν_{max} 1665s (br, enedione), 1610m, 1571w, 1494m, 1486m, 1380m, 1296m, 1288m, 1269m, 1157w, 1110m, 1080m, 1039s, 1009w, 949w, 863s, 771m, 750s, 718m, 701s, 695m cm^{-1}; δ 1·56 (s, 6H, methyl); 1·67, 1·89 (AB pattern, *J c.* 9 Hz, 2H, H11); 3·22 (s, 2H, H2,7); 6·61 (s, 2H, H4,5); 6·72–7·25 (m, 10H, aromatics).

3,5-Dimethyl-2,6-diphenylpentacyclo[5,4,0,0^{2,6},0^{3,10},0^{5,9}]undecane-8,11-dione (13)

A solution of the adduct (12) (400 mg, 1·32 mmol) in benzene (130 ml) was irradiated through Pyrex with an Hanovia high-pressure mercury lamp (type L). After 30 min, conversion into the title compound was found to be quantitative from the p.m.r. spectrum. The solution was evaporated to dryness and the residue crystallized from ethanol to give colourless crystals of the title *dione* (13) (150 mg, 37·5%) (low yield due to reaction with ethanol), m.p. 235° (Found: C, 84·4; H, 6·5; O, 9·3. $C_{25}H_{22}O_2$ requires C, 84·7; H, 6·3; O, 9·0%). ν_{max} 1740s (br, carbonyl), 1600m, 1500m, 1271m, 1242m, 1072m, 759m, 751m, 700s cm^{-1}; δ 1·05 (s, 6H, methyl); 2·17, 2·88 (dd, AB pattern, *J c.* 12 Hz, H4); 2·80, 3·42 (m, m, 2H, 2H, H1,7,9,10); 7·09 (s, 10H, aromatics).

Solid state photolysis of (12) by an identical procedure as that described for the corresponding enedione (9) gave only the pentacyclic dione (13).

Acknowledgments

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