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PHOTOISOMERIZATION OF THE 1,4-NAPHTHOQUINONE--CYCLOPENTADIENE ADDUCT. A NOVEL INTRAMOLECULAR [6 + 2] CYCLOADDITION.[1]

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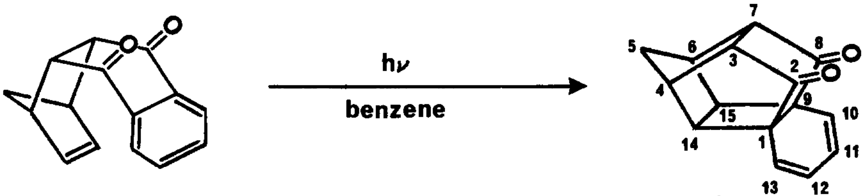
Intramolecular photoisomerizations involving a benzene ring to give [6 + 2] cycloadditions have been reported.[2,3,4] In these cases, the 6π electron system of the benzene ring is regenerated. We wish to report the first example of an intramolecular [6 + 2] photocycloaddition in which the 6π electron system of the benzene ring is not regenerated.[5,6]

When a 1% solution of the 1,4-naphthoquinone--cyclopentadiene adduct (1) in benzene[7,8] is irradiated for sixty minutes under a nitrogen atmosphere,[9] hexacyclo-$[7.4.2.0^{1,9}.0^{3,7}.0^{4,14}.0^{6,15}]$pentadeca-10,12-diene-2,8-dione (2)[10] is obtained in 80% yield along with 15% of recovered (1) and 5% of a white, insoluble solid.



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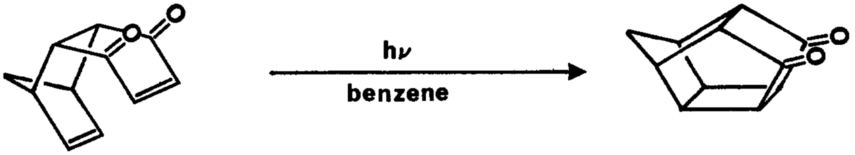
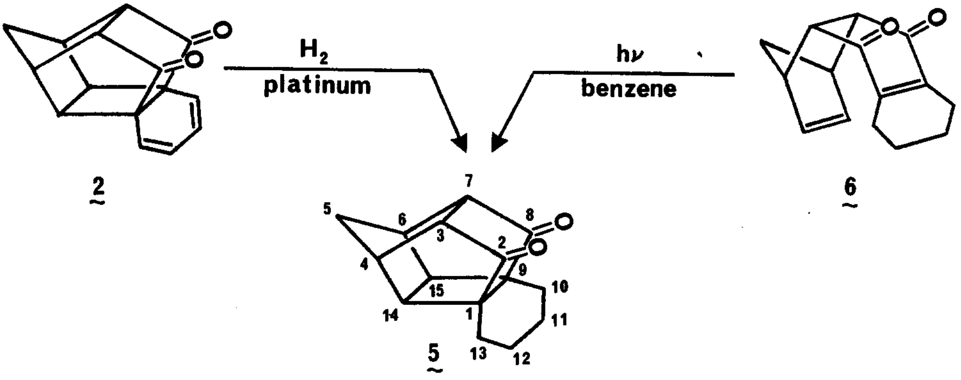


3 4

This observed photochemical process while analogous to the well documented [2 + 2] photochemical cyclization of the p-benzoquinone--cyclopentadiene adduct (3)[11] to pentacyclo-$[6.2.1.0^{2,7}.0^{4,10}.0^{5,9}]$undeca-3,6-dione (4),[12] is unusual in that it occurrs with destruction of an aromatic ring.

When recrystallized from n-heptane, 2 is found to be an off-white, needle-like crystalline material with a melting point of 111-112°.[13] Spectral data are in full agreement with the assigned structure: ir (KBr pellet) 3045 (m, $=$CH— stretch), 1745 (vs, C$=$O stretch), 1650 (w, —CH$=$CH—CH$=$CH— stretch), 1575 (m, —CH$=$CH—CH$=$CH — stretch), 715 cm^{-1} (s, cis$=$CH — bend); nmr ($CDCl_3$, 60 MHz) δ1.92 (2 H, two asymmetric doublets, J = 5.5 Hz, H-5), 2.85 and 3.00 (4 H, two broad singlets with small shoulders, H-3,7,14,15), 3.40 (2 H, broad singlet, H-4,6), 5.42 and 6.05 ppm (4 H, a set of symmetrical multiplets, H-10,11,12,13); uv max (cyclohexane) 287 nm (ε 1800), 219 nm (ε 1700).[14]

Hydrogenation of 2 [15] gave hexacyclo$[7.4.2.0^{1,9}.0^{3,7}.0^{4,14}.0^{6,15}]$pentadeca-2,8-dione (5) mp 68-69° (from heptane), which was identical to authentic 5 prepared by the photochemical ring closure of the 1,2,3,4-tetrahydro-5,8-naphthoquinone--cyclopentadiene adduct (6).[16,17] Spectral data support the assigned structure for 5: ir (CCl_4 solution) 2925, 2840 (s, —CH_2— stretch), 1750, 1730 (s, C$=$O stretch), 725 cm^{-1} (s, —CH_2— rock); nmr (CCl_4, 60 MHz) δ2.20 - 1.05 (10 H, broad complex multiplet, H-5,10,11,12,13), 2.75 (2 H, singlet, H-4,6), 2.85 ppm (4 H, singlet, H- 3,7,14,15).



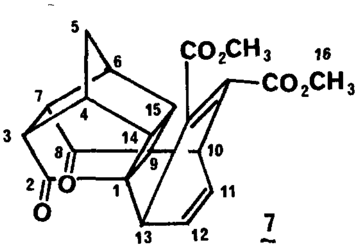
2

6

5

Compound 2 when treated with dimethyl acetylenedicarboxylate forms a crystalline adduct, 7 or 8, mp 275-278° (from benzene), which indicated the presence of the 1,3-diene moiety in

2.[18,19,20] Spectral data support the assignment of structure 7 or 8 to the adduct: ir (KBr pellet) 3070 (w, =CH— stretch), 1750, 1730, 1705 (s, C=O stretch), 1070 (m, methyl ester), 760 cm^{-1} (m, =CH— bend); nmr ($CDCl_3$, 60 MHz) δ1.95 (2 H, broad singlet, H-5), 3.05 -- 2.60 (6 H, complex multiplet, H-3,4,6,7,14,15), 3.82 (6 H, singlet, H-16), 4.05 and 4.12 (2 H, two doublets, J ≈ 1.5 Hz, H-10,13), 6.66 and 6.73 ppm (2 H, two doublets, J = 1.5 Hz, H-11,12). Spin decoupling studies indicate that the two sets of protons, H-10,13 and H-11,12 are coupled.



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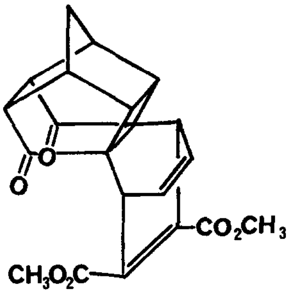

Work designed to learn more about the chemistry of this system is now in progress.

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REFERENCES

(1) A preliminary report of part of this work was presented at the Third Central Regional Meeting of the American Chemical Society, Cincinnati, Ohio, June 1971.

(2) G. R. Ziegler and G. S. Hammond, J. Amer. Chem. Soc., **90**, 513 (1968).

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(4) R. B. Woodward and R. Hoffmann, Angew. Chem. Intern. Ed., **8**, 781 (1969)

(5) Intermolecular [6 + 2] photoaddition involving a benzene ring in which the 6π electron system of the benzene ring is not regenerated has been reported.[6]

(6) J. G. Atkinson, D. E. Ayer, G. Büchi, and E. W. Robb, J. Amer. Chem. Soc., **85**, 2257 (1963).

(7) 1,4,4a,9a-Tetrahydro-9,10-dioxo-1,4-methanoanthracene.

(8) W. Albrect, Justus Liebigs Ann. Chem., **348**, 31 (1906).

(9) A 450 watt high pressure Hanovia lamp in a quartz irradiation cell was used.

(10) Compound 2 is isolated using a silica gel chromatography column (Silicar, Mallinckrodt Chemical Works).

(11) 1,4,9,10-Tetrahydro-5,8-dioxo-1,4-methanonaphthalene.

(12) R. C. Cookson, E. Crundwell, R. R. Hill, and J. Hudec, J. Chem. Soc., 3062 (1964).

(13) Elemental analyses consistent with the structures of all new compounds were obtained.

(14) The uv spectrum is similar to that found for compound **4** as well as to that found for a 1,3 cyclohexadiene ring containing compound. See reference 12, also, V. Henri and L. W. Pickett, J. Chem. Phys., **7**, 439 (1939).

(15) Hydrogenation was performed using the Brown^{2} Hydrogenator (Delmar Scientific Labs). Two moles of hydrogen were necessary for complete hyrogenation of **2**.

(16) 1,4,4a,5,6,7,8,9a-Octahydro-9,10-dioxo-1,4-methanoanthracene.

(17) 1,2,3,4-Tetrahydro-5,8-naphthoquinone was prepared according to the procedure of R. T. Arnold and H. E. Zaugg, J. Amer. Chem. Soc., **63**, 1317 (1941). The cyclopentadiene adduct was prepared using a method similar to that given in reference 8.

(18) Compound **2** also forms a Diels-Alder adduct with maleic anhydride. This adduct proved difficult to characterize because of its insolubility; however, it did give an elemental analysis in agreement with the expected structure.

(19) 10,14-(1,2-Dimethylcarboxy)ethenohexacyclo$[7.4.2.0^{1,9}.0^{3,7}.0^{4,14}.0^{6,15}]$pentadeca-11-ene-2,8-dione.

(20) While it is felt that **7** is the more probable structure for the Diels-Alder adduct, **8** can not be eliminated on the basis of data now in hand. Molecular models indicate a preference for attack from the side opposite the carbonyl moieties by the dimethyl acetylenedicarboxylate molecule.