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SYNTHESIS AND PHOTOCHEMISTRY OF 2-CYCLOOCTENE-1,4-DIONE

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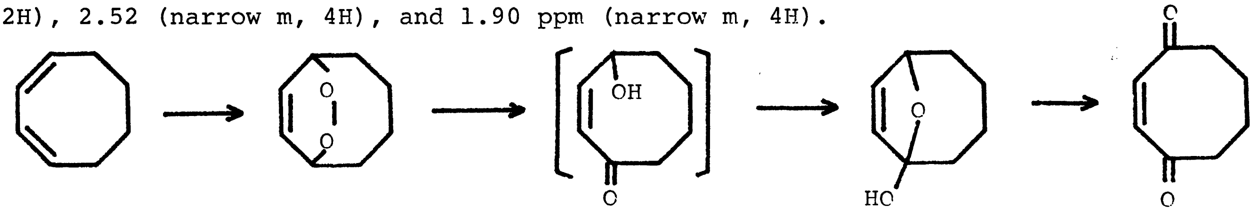
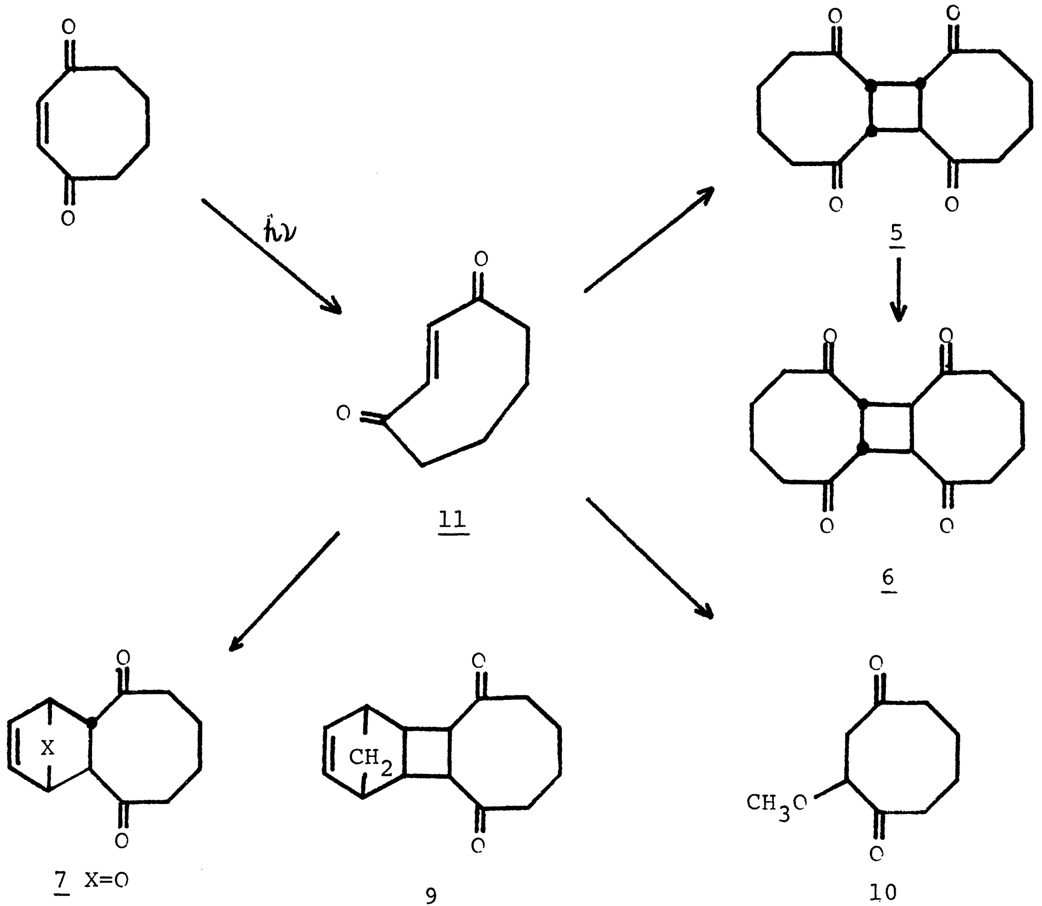
cis-2-Cyclooctene-1,4-dione 1 is prepared starting from 1,3-cyclooctadiene. Photoirradiation of 1 in ether gives a $[\pi 2s+\pi 2a]$ dimer, while irradiations in the presence of cyclic dienes give *trans*-[2+4]cycloadducts. The intermediacy of *trans*-2-cyclooctene-1,4-dione is suggested.

Eight-membered ring conjugated ketones have been found to undergo photochemical isomerization to strained *trans* forms which in turn undergo thermal dimerizations and cycloadditions[1a-f]. We have prepared previously unknown title compound 1 and found that 1 also isomerizes to the reactive *trans* form on irradiation.

Photo-oxygenation of 1,3-cyclooctadiene in acetone under irradiation (tungsten lamp) using hematoporphyrin as a sensitizer for one week gave the epidioxide 2, 9, 10-dioxabicyclo[4.2.2]deca-7-ene[2], in 52% yield after separation by silica-gel chromatography: mp 50.5-55.5°; ^{1}H-N.M.R.(CCl_4) δ 6.05 (dd, J=3.6 and 2.0 Hz, 2H), 4.06 (br. s, 2H), and 2.3-1.4 ppm (m, 8H). Heating to reflux of 2 with triethylamine in methylene chloride for 10 hrs gave 1-hydroxy-9-oxabicyclo[4.2.1]non-7-ene 4, mp 93-94° (lit. 92-93°[3]) in 80% yield, which may be formed from 4-hydroxycyclooctenone 3 by intramolecular cyclization. Oxidation of 4 with chromium trioxide in acetone[4] gave 1 in 63% yield: mp 36.5-37.5°; I.R.(KBr) ν 1672 and 1611 cm^{-1}; U.V.(EtOH) λ 221 (ε 9,150) and 327 nm (ε 190); ^{1}H-N.M.R.($CDCl_3$) δ 6.33 (s, 2H), 2.52 (narrow m, 4H), and 1.90 ppm (narrow m, 4H).



Irradiation of 1 in ether (0.04 M) using a 100W high pressure Hg lamp through a water cooled pyrex jacket repidly formed single dimer 5 in 70% yield: mp 156-161°; m/e 276 (M^+); I.R.(KBr)ν 1690 cm^{-1}. The ^{1}H-NMR spectrum (100 MHz, $CDCl_3$) exhibits the four-membered ring protons at δ 4.25 (dd, J=10.2 and 8.1 Hz, 1H), 4.21 (dd, J=11.0, 9.5 Hz, 1H), 3.79 (dd, J=10.2, 9.5 Hz, 1H) and 2.97 ppm (dd, J=11.0, 8.1 Hz, 1H) and other protons at 2.8-2.2 (m, 8H) and 2.2-1.4 ppm (m, 8H). The nonequivalency of the four four-membered ring protons indicates that the configuration around the four-membered ring is the least symmetric one, *i.e. cis-trans*, among the five possible isomers. Heating to reflux of 5 in toluene for 100 hrs resulted in a complete isomerization to a thermodynamically more stable symmetric isomer 6 (probably *cis*-anti-*cis*): mp 203.5-205°; m/e 276 (M^+); I.R.(KBr)ν 1687 cm^{-1}; ^{1}H-N.M.R.($CDCl_3$) δ 4.16 (s, 4H), 2.45 (m, 8H) and 1.96 ppm (m, 8H), the four-membered ring protons appearing as a sharp singlet. Therefore rather wide range (5°) of the melting point of 5 may be due to partial isomerization to 6 during the determination.



When 1 was irradiated (2 hrs) in the presence of excess furan, the *trans*-[2+4]cycloadduct 7 was obtained in 96% yield: mp 126-127°; I.R.(KBr) ν 1682 cm^{-1}; ^{1}H-N.M.R.($CDCl_3$) δ 6.63 (dd, J=5.8 and 1.5 Hz, 1H), 6.41 (dd, J=5.8, 1.7 Hz, 1H), 5.26 (dd, J=1.7, 1.2 Hz, 1H), 5.08 (ddd, J=4.0, 1.5, 1.2 Hz, 1H), 3.23 (dd, J=6.6, 4.0, Hz), 2.55 (d, J=6.6 Hz, 1H), 2.63 (m, 4H), and 1.95 ppm (m, 4H). The NMR data are consistent with the structure shown. With cyclopentadiene, 1 also produced the *trans*-[2+4]cycloadduct 8 in 82% yield on irradiation: mp 102-103°; ^{1}H-N.M.R.($CDCl_3$) δ 6.31 (ddd, J=5.5, 2.5 and 1 Hz, 1H), 6.08 (dd, J=5.5, 3.0 Hz, 1H), 2.99 (m, 3H), 2.55 (m, 5H), 1.87 (m, 4H), and 1.52 ppm (m, 2H). Thermal reaction of 1 with cyclopentadiene in the dark was very slow at room temperature and gave a symmetric *cis*-[2+4]cycloadduct 9: mp 54-56°; ^{1}H-N.M.R.($CDCl_3$) δ 6.20 (t, J=1.9 Hz, 2H), 3.35 (dd, J=1.8, 1.4 Hz, 2H), 3.11 (m, 2H), 2.07 (m, 4H), 1.78 (m, 4H), 1.50 (dt, J=8.3, 1.7 Hz, 1H), and 1.35 ppm (br. d, J=8.3 Hz, 1H).

Irradiation of 1 in methanol gave a methanol addition product, 2-methoxycyclooctane-1,4-dione 10, in 71% yield. A similar reaction has been reported with 2-cyclooctenone by Noyori[1b].

These results are well explained by the intermediacy of reactive *trans*-2-cyclooctene-1,4-dione 11. Irradiations of 1 in the presence of excess cyclohexenone or olefins did not give any adduct, but only the dimer 5. These results indicate that the dimer 5 arose from two molecules of 11, but not from each molecule of 1 and 11. For the photochemical dimerization of 2,4-cyclooctadienone which gives *cis*-*trans* and *trans*-*trans* dimers, Lange stated that the dimers must be formed from two molecules of *trans*, *cis*-2,4-cyclooctadienone in a two-step thermal process via a diradical[1f]. Since 1 gave a single dimer 5 stereospecifically on irradiation, we rather prefer the symmetry-allowed [π2s+π2a] process[5] for the dimerization of 11.

The photochemical cycloadditions of 1 may be of synthetic utility for *trans*-fused cyclooctane derivatives, because it gives rise to a single adduct with symmetric dienes.

References and Footnotes

* To whom all correspondences should be addressed.

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