Synthesis and Properties of 4,4'-Bi(cyclopentene)-3,3',5,5'-tetraone

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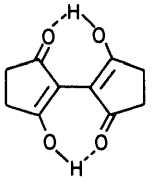
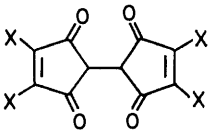
The title compound (2) has been prepared both from cyclopent-4-ene-1,3-dione and from 5,5'-bi(cyclopentadiene). The spectral data indicate the exclusive existence of (2) in the keto-form.

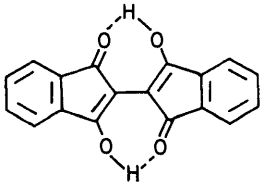
BI(CYCLOPENTANE)-2,2',5,5'-TETRAONE (1) exists completely in the enol form owing to stabilisation by intramolecular hydrogen bonding.[1] It was of interest to discover whether the conjugated analogue (2) similarly exists in the enol form (2b), in spite of the fact that this would comprise two antiaromatic cyclopentadienone units. Although the preparation of the tetrahydroxy-derivative (3) has been described, no mention was made of enolisation.[2] Cyclopent-4-ene-1,3-dione[3] does not enolise; nor do other simple cyclopentenediones[4] and cyclopentanetriones[5] enolise in such a way as to produce cyclopentadienone structures. The dibenzo-derivative (4) is however known to exist in the enol form;[6] this can be ascribed mainly to the greatly reduced anti-aromatic character of indenone. We describe here two methods of synthesis of compound (2) and show that it exists preferentially in the keto-form (2a).



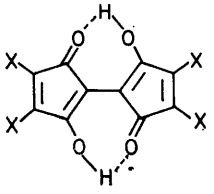
(1)



(2a) X = H
(3a) X = OH

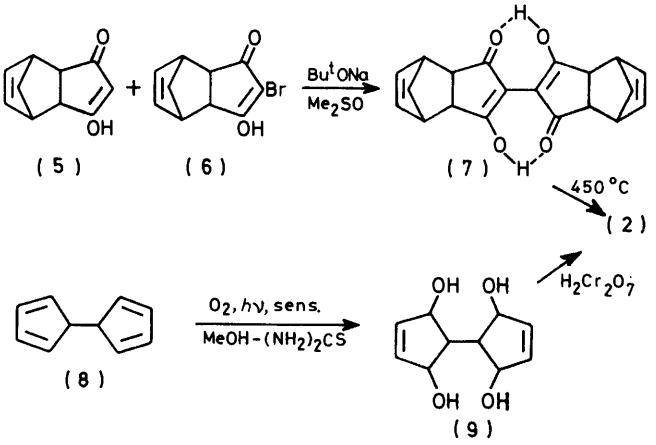


(4)



(2b)
(3b)

The reaction of the Diels–Alder adduct (5) of cyclopent-4-ene-1,3-dione and cyclopentadiene[3] with its monobromide (6) in dimethyl sulphoxide, with sodium t-butoxide as base, afforded the coupling product (7) in 15—19% yield. The broad i.r. absorption at 1 500 cm^{-1} and the appearance of n.m.r. signals for two protons at very low field (δ 16.6) indicate the existence of (7) in the enol form. The mass spectrum shows a fragment at $M - 132$, corresponding to the molecular ion of (2), as the base peak, which led us to expect the pyrolytic conversion of (7) into (2). Indeed, pyrolysis of (7) at



450 °C *in vacuo* gave compound (2) by a retro-Diels–Alder reaction in 60% yield.

Alternatively, photosensitised oxygenation of 5,5'-bi(cyclopentadiene) (8)[7] in methanol at −40 °C in the presence of thiourea,[8] followed by evaporation, and extraction of the residue with water, afforded an aqueous solution of the tetraol (9). Treatment of the solution with chromic acid provided the product (2) as the sole chloroform-extractable material in 4% overall yield from cyclopentadiene.

Compound (2) is stable in the solid state and in neutral aprotic solution, but it is unstable towards bases, as is cyclopent-4-ene-1,3-dione.[3] The i.r. spectrum shows carbonyl absorptions at 1 740 and 1 700 cm^{-1}, and no hydroxy-absorption. U.v. absorption maxima (in acetonitrile) are at 215 (ε 24 000), 317sh (355), 328.5 (370), 347.5 (345), and 374 nm (400), very similar to those of cyclopent-4-ene-1,3-dione (except for the nearly doubled

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[3] C. H. Depuy and E. F. Zwaeski, *J. Amer. Chem. Soc.*, 1959, **81**, 4920.
[4] (*a*) A. Roedig and H. Ziegler, *Chem. Ber.*, 1961, **94**, 1800; (*b*) L. va Wijnsberghe and M. Vandewalle, *Bull. Soc. chim. belges*, 1970, **79**, 699; (*c*) H.-W. Wanzlick and W. Sucrow, *Chem. Ber.*, 1958, **91**, 2727; (*d*) C. Maignan and F. Rouessac, *Bull. Soc. chim. France*, 1971, 3041.
[5] J. A. Elvidge and R. Stevens, *J. Chem. Soc.*, 1965, 2251.
[6] H. Wittmann, A. Miller, and Z. Ziegler, *Monatsh.*, 1970, **101**, 1389.
[7] L. A. Paquette and M. J. Wyvratt, *J. Amer. Chem. Soc.*, 1974, **96**, 4671.
[8] C. Kaneko, A. Sugimoto, and S. Tanaka, *Synthesis*, 1974, 876.

intensities). The ^1H n.m.r. spectrum exhibits two singlets in 2 : 1 integral ratio at δ 7.33 and 3.47 in $CDCl_3$ and at δ 7.57 and 3.76 in $(CD_3)_2SO$. No hydrogen-bonded hydroxy-proton signal was observed.

Compound (2) does not respond to the iron(III) chloride test. On treatment with cyclopentadiene, it gives the Diels–Alder adduct (7) in high yield.

In conclusion, compound (2) exists exclusively in the keto-form (2a) in the crystalline form and in neutral solutions. Therefore the destabilisation of enol form (2b) by its antiaromatic nature is greater than its stabilisation by intramolecular hydrogen bonding.

EXPERIMENTAL

I.r. spectra were recorded with a Hitachi 215 grating spectrometer, u.v. spectra with a Hitachi 323 spectrometer, and ^1H n.m.r. spectra with a Varian A-60A or JEOL-PMX 60 spectrometer. Mass spectra were obtained with a Hitachi RMU 60 spectrometer at 25 eV.

Bromination of the Cyclopent-4-ene-1,3-dione–Cyclopentadiene Diels–Alder Adduct (5).—To a solution of the adduct (5) [3] (1.62 g, 10 mmol) and sodium acetate (1.23 g, 15 mmol) in acetic acid (20 ml) was added a solution of bromine (1.68 g, 10.5 mmol) in acetic acid (3 ml) at room temperature. After stirring for 1 h, the solution was evaporated, water (10 ml) was added, and the mixture stirred for 30 min at room temperature. The separated crystals of 4-*bromo*-endo-*tricyclo*[5.2.1.$0^{2,6}$]*dec*-8-*ene*-3,5-*dione* (6) (2.3 g, 98%) were washed with a small amount of cold water and dried *in vacuo*. Recrystallisation (MeOH–EtOAc) gave prisms, m.p. 216—217 °C (decomp.), $\nu_{max.}$ (KBr) 3 200—2 300, 1 550, and 1 400 cm^{-1}; $\lambda_{max.}$ (MeOH) 263 nm (log ε 4.05); δ(CD_3OD) 1.58br (1 H, d, *J* 9.0 Hz), 1.83 (1 H, dt, *J* 9.0 and 1.4 Hz), 3.18br (4 H, s), and 5.96br (2 H, s) (Found: C, 49.6; H, 3.8. $C_{10}H_9BrO_2$ requires C, 49.8; H, 3.75%).

Coupling of Compounds (5) *and* (6).—A mixture of compounds (5) (4.86 g, 30 mmol) and (6) (7.23 g, 30 mmol) and sodium t-butoxide (3.46 g, 36 mmol) in dried dimethyl sulphoxide (120 ml) was stirred at 110 °C under nitrogen for 48 h. The mixture was poured into ice–water (200 ml); the resulting solution was adjusted to pH *ca.* 3 with 6N-hydrochloric acid and extracted with chloroform (4 × 100 ml). The combined extracts were washed with water, dried, and evaporated. The residue was chromatographed on silica gel [elution with PhH–EtOAc (95 : 5)] to give 4,4′-*bi*(*tricyclo*[5.2.1.$0^{2,6}$]*dec*-8-*ene*)-3,3′,5,5′-*tetraone* (7) (1.84 g, 19%). Recrystallisation ($CHCl_3$–CCl_4) afforded prisms, m.p. 270—272 °C; $\nu_{max.}$ (KBr) 1 500, 840, 790, and 735 cm^{-1}; $\lambda_{max.}$ (MeOH) 253 (log ε 4.12), 263 (4.13), 273sh (4.13), 282 (4.15), and 288sh nm (4.12); δ ($CDCl_3$) 1.51br (2 H, d, *J* 9.5 Hz), 1.78 (2 H, d, *J* 9.5 Hz), 3.18br (8 H, s), 6.00br (4 H, s), and 16.6 (2 H, s); *m/e* 322 (M^+, 30%), 256 (M − 66, 68), and 190 (M − 132, 100) (Found: C, 74.4; H, 5.8. $C_{20}H_{18}O_4$ requires C, 74.5; H, 5.65%). Yields from several runs were in the range 15—19%.

Pyrolysis of Compound (7).—The vapour of (7) (644 mg, 2 mmol) was passed through a preheated column (1 × 20 cm) packed with Pyrex chips at 450 °C and 0.1 mmHg. The vapour was produced by heating a probe containing (7) at 250 °C and 0.1 mmHg. The pyrolysate was collected in a flask cooled in solid CO_2–acetone. After cooling to room temperature the column was washed with acetonitrile, and the solution concentrated to leave orange solids (280 mg). Recrystallisation from acetonitrile gave (220 mg, 60%) of 4,4′-*bi*(*cyclopentene*)-3,3′,5,5′-*tetraone* (2) as pale yellow needles, m.p. 235—236 °C (decomp.); $\nu_{max.}$ (KBr) 3 150vw, 3 090w, 1 740m, 1 700s, 1 568w, 1 310m, 1 227m, and 867m cm^{-1}; *m/e* 190 (M^+, 100%), 162(8), 136(12), 108(28), and 82(27) (Found: C, 63.2; H, 3.3. $C_{10}H_6O_4$ requires C, 63.15; H, 3.2%).

Preparation of Compound (2) *from* 5,5′-*Bi*(*cyclopentadiene*).—A mixture of crude 5,5′-bi(cyclopentadiene) (26 g, 0.2 mol) (prepared as reported [7]), thiourea (30.5 g, 0.4 mol), and Rose Bengal (1 g) in methanol (3 l) was irradiated at −40 °C with a 400 W high-pressure mercury lamp through a Pyrex filter while oxygen was bubbled steadily through the solution for 12 h. The mixture was then stirred in the dark at room temperature for 12 h, and evaporated; water (300 ml) was added, and the mixture was stirred for 1 h, then washed with chloroform (2 × 100 ml). The aqueous solution was added dropwise to chromic acid [CrO_3 (200 g) in 8N-H_2SO_4 (1.2 l)] at −5 °C, and the product was extracted with chloroform (4 × 300 ml). Evaporation left nearly pure (2) (1.5 g, 4% from cyclopentadiene).

We thank Daiseru Co. Ltd. for a sample of cyclopent-2-ene-1,4-diol.

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