1*H*-Cyclopropa[*b*]naphthalene-3,6-dione

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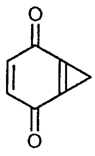
Cerium ammonium nitrate demethylation and oxidation of 3,6-dimethoxy-1*H*-cyclopropa[*b*]-naphthalene **6** provides 1*H*-cyclopropa[*b*]naphthalene-3,6-dione **8** as the first stable cyclopropaquinone.

In recent times the chemistry of highly strained molecules has experienced an upsurge of interest.[1] Our own studies continue to address fundamental aspects of the class of compounds known as the cycloproparenes[2] and we now report upon the synthesis of 1*H*-cyclopropa[*b*]naphthalene-3,6-dione **8**.

To the best of our knowledge only three cycloproparenes carrying an oxygen substituent have been recorded. The cyclopropaquinone **1** has been generated by Oda *et al.* using flash pyrolysis methods but the compound defied isolation.[3] Its presence as a reaction product was adduced by interception with anthracene to give the product of Diels–Alder addition across the strained 'cyclopropene' double bond. In comparison to the quinone, the dimethoxy derivative **2** was proposed[4] as a reactive molecule in solution. Its instability results from phenyl participation in opening of the three-membered ring and not from the presence of the methoxy groups.[2] The only stable oxygen-containing cycloproparene hitherto reported is 2-methoxybicyclo[4.1.0]hepta-1,3,5-triene **3** that was obtained by Arad.[5]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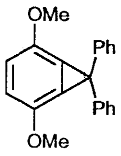
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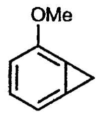
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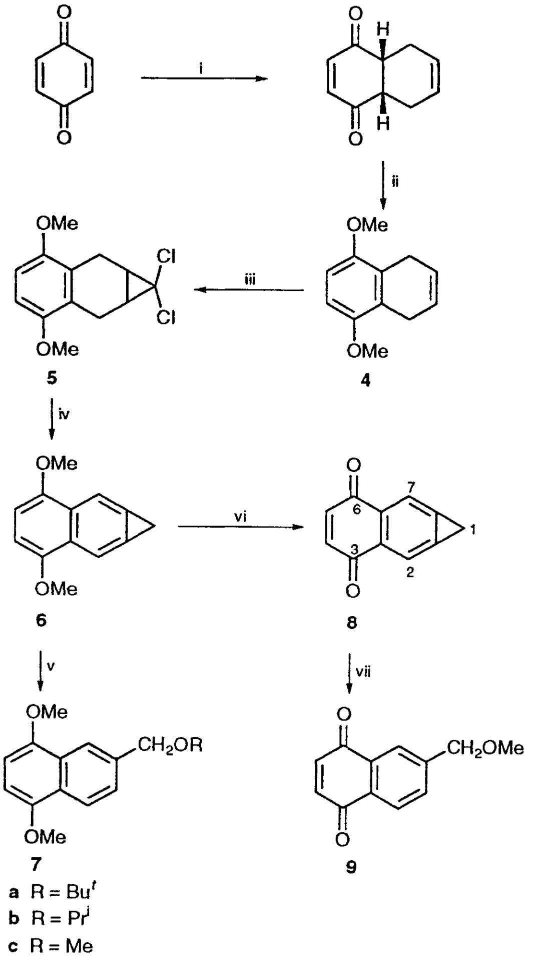
The approach to naphthalenedione **8** is depicted in Scheme 1. Thus, controlled[6] addition of buta-1,3-diene to benzoquinone followed by methylation and oxidation gives the diether **4**.[7] In analogy to the addition of dibromocarbene to **4**,[8] dichlorocyclopropanation gives the bicycle **5** in 72% yield.† Didehydrochlorination of **5** with *tert*-butoxide affords the dimethoxycycloproparene **6** in 39% yield in accord with expectation,[2] but as somewhat air-sensitive crystals.‡ In addition to **6**, the ring-opened triether **7a** is isolated in 34% yield. While this is not the first report of such a side-product,[9,10] the yield is notably higher perhaps because of the oxygen functionalities. Silver(I) catalysed[9] ring-opening of **6** gives the ethers **7a–c** depending upon the alcohol used. The transformation of 1,4-dimethoxy aromatics into 1,4-quinones has been effected with a variety of reagents, but particularly mild conditions were deemed appropriate in the present case. In the event, **6** when stirred with cerium(IV) ammonium nitrate[11] gave the quinone **8** in 85% yield as air-sensitive bright yellow needles.§ Treatment of quinone **8** with Ag^I/methanol results in ring-opening to the known[12] quinone ether **9**.



Scheme 1 *Reagents and conditions:* i, butadiene, 40 °C, 4 days[6]; ii, K_2CO_3/Me_2SO_4[7]; iii, :CCl_2; iv, Bu^{t}OK; v, Ag^I/ROH; vi, CAN$_{(aq)}$, $MeCN/CH_2Cl_2$, (3:2), room temp., 30 min, 85%; vii, Ag^I/MeOH

The structure of **8** is assigned with confidence from the spectroscopic data and confirmed by X-ray analysis.[13] The ^1H NMR spectrum shows three equal intensity singlets at δ 3.36 (>CH_2), 6.95 (4-H/5-H) and 7.90 (2-H/7-H), respectively, while the ^{13}C NMR spectrum displays three protonated and three quaternary carbon resonances. The methylene signal (δ 19.1) is unequivocal and the higher field methine signal (δ 112.8) is shielded as expected[3,14] for C-2/C-7 of a cycloproparene; C-4/C-5 of **8** (δ 138.1) match C-2/C-3 of naphthoquinone. Of the quaternary carbon resonances that at 185.2 ppm is due to the quinone carbonyl groups, but differentiation

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[†] All new compounds were fully characterised from microanalytical and spectroscopic data.

[‡] Selected data for **6**: m.p. 130–131.5 °C; δ_H(300 MHz; $CDCl_3$; Me_4Si) 3.46 (s, CH_2), 6.72 (s, 4-H/5-H) and 8.01 (s, 2-H/7-H); δ_C(75 MHz) 18.1 (C-1), 55.9 (2 × OMe), 103.4 (C-4/C-5), 106.8 (C-2/C-7), 123.4 (C-1a/C-7a), 128.9 (C-2a/C-6a) and 150.5 (C-3/C-6).

[§] Selected data for **8**: m.p. 130–132 °C; ν_{max}/cm^{-1} 1659; λ_{max}(MeCN)/nm 287.5 ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ 40 800), 327 (61 300). The NMR assignments [δ_H(300 MHz; $CDCl_3$; Me_4Si), δ_C(75 MHz)] discussed in the text are fully consistent with heteronuclear correlation spectroscopy results.

of the remaining pair (135.4, 132.5 ppm) between C-1a/C-7a and C-2a/C-6a is not obvious. However, heteronuclear multiple bond connectivity (HMBC) experiments unequivocally show that the lower field quaternary at δ 132.5 is due to C-1a/C-7 as it correlates with *both* the methylene and 2-H/7-H proton signals; that at δ 135.4 correlates only with 2-H/7-H and is thus due to C-2a/C-6a. Particularly notable here is the marked downfield shift of the C-1a/C-7a signal from its position in both **6** and cyclopropa[*b*]naphthalene (123.4 ppm). We ascribe the *ca.* 9 ppm deshielding to polarity within the quinone whereby C-1a and C-7a attain a degree of cationic character. Further physicochemical properties of this interesting molecule will be reported in subsequent publications.

Experimental

1H-*Cyclopropa*[b]*naphthalene*-3,6-*dione* **8**.—To a stirred solution of the dimethoxycyclopropanaphthalene **6** (0.520 g, 2.60 mmol) in acetonitrile–dichloromethane (3:2; 25 cm^3), at room temperature, was added in small portions (2–3 cm^3) cerium(IV) ammonium nitrate (4.30 g, 7.84 mmol) in water (20 cm^3). The addition was performed in such a way as to minimise, but to observe, a transient blue–black colouration which rapidly changed to orange. The resultant orange solution was then stirred for a further 30 min, after which it was extracted with dichloromethane (2 × 30 cm^3). The combined extracts were washed with water (3 × 30 cm^3), dried ($MgSO_4$) and then evaporated to dryness under reduced pressure. The brown residue (0.675 g) was purified by column chromatography over silica gel (eluent dichloromethane–hexanes, 1:1) to afford **8** (0.375 g, 85%) as bright yellow needles, m.p. 130–132 °C (decomp.) (dichloromethane–hexanes, 1:2; −40 °C) (Found: C, 77.4; H, 3.6. $C_{11}H_6O_2$ requires C, 77.6; H, 3.6%).

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