

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

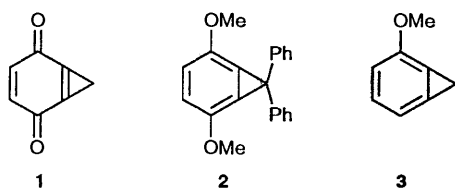
Brian Halton,* Andrew J. Kay and Zha Zhi-mei

Department of Chemistry, Victoria University of Wellington, P.O. Box 600, Wellington, New Zealand

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.

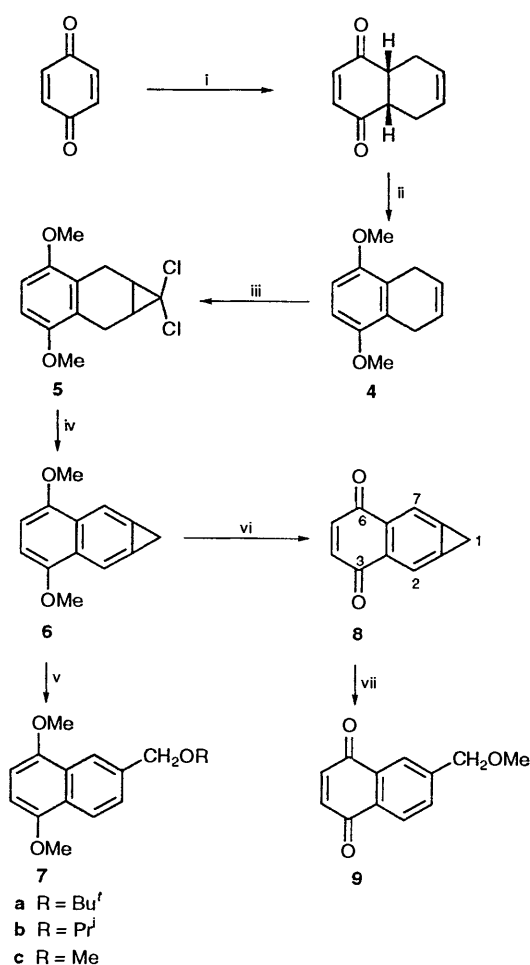
In recent times the chemistry of highly strained molecules has experienced an upsurge of interest.¹ Our own studies continue to address fundamental aspects of the class of compounds known as the cycloproparenes² and we now report upon the synthesis of 1*H*-cyclopropa[*b*]naphthalene-3,6-dione **8**.

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 proposed⁴ 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

The approach to naphthalenedione **8** is depicted in Scheme 1. Thus, controlled⁶ 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) catalysed⁹ 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



Scheme 1 Reagents and conditions: i, butadiene, 40 °C, 4 days⁶; ii, K₂CO₃/Me₂SO₄⁷; iii, :CCl₂; iv, Bu^tOK; v, Ag^I/ROH; vi, CAN_(aq), MeCN/CH₂Cl₂, (3:2), room temp., 30 min, 85%; vii, Ag^I/MeOH

cerium(IV) ammonium nitrate¹¹ 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 known¹² quinone ether **9**.

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 (>CH₂), 6.95 (4-H/5-H) and 7.90 (2-H/7-H), respectively, while the ¹³C 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

† 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; CDCl₃; Me₄Si) 3.46 (s, CH₂), 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 (ε/dm³ mol⁻¹ cm⁻¹ 40 800), 327 (61 300). The NMR assignments [δ_H(300 MHz; CDCl₃; Me₄Si), 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 cm³), at room temperature, was added in small portions (2–3 cm³) cerium(IV) ammonium nitrate (4.30 g, 7.84 mmol) in water (20 cm³). 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 cm³). The combined extracts were washed with water (3 × 30 cm³), dried (MgSO₄) 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. C₁₁H₆O₂ requires C, 77.6; H, 3.6%).

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Paper 3/04464E

Received 27th July 1993

Accepted 10th August 1993