

2-Chloro-1,1-dimethyl-1*H*-cycloprop[*e*]azulene, the first cyclopropano-fused azulene

Alan D. Payne and Dieter Wege*

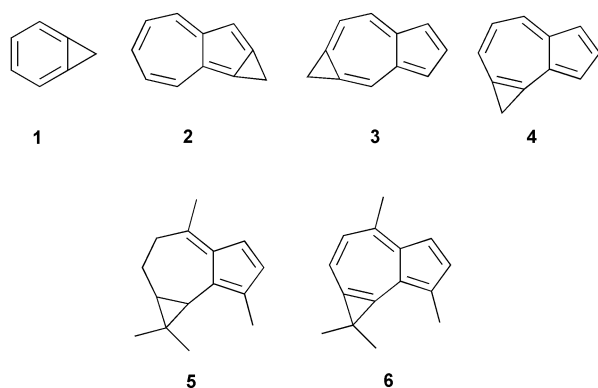
Department of Chemistry, University of Western Australia, 35 Stirling Highway, Crawley, 6009, Australia. E-mail: dw@chem.uwa.edu.au; Fax: 61 8 9380 1005

Received (in Cambridge, UK) 17th May 2001, Accepted 7th June 2001

First published as an Advance Article on the web 18th June 2001

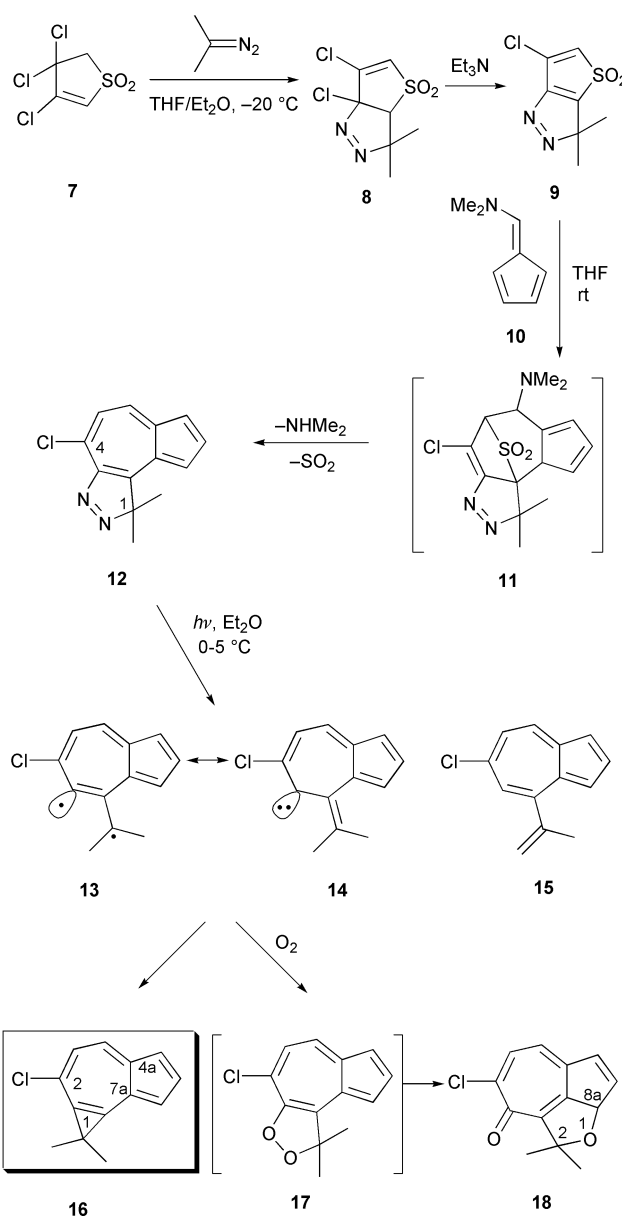
The title compound, 2-chloro-1,1-dimethyl-1*H*-cycloprop[*e*]azulene, **16** has been prepared by irradiation of the azulenopyrazole **12**.

The study of the chemistry of cycloproparenes, exemplified by the parent member benzocyclopropene **1**, has generated a wealth of fascinating information.¹ In contrast, our knowledge of nonbenzenoid cycloproparenes is very limited.² Particularly intriguing are the structural isomers **2–4** generated by cyclopropano-fusion to the azulene ring system. Geometric factors should result in **2** being more strained than a benzenoid cycloproparene and this may preclude its isolation, but compounds **3** and **4** possessing cyclopropano-fusion to the seven-membered ring should be capable of existence under normal laboratory conditions. The cycloprop[*e*]azulene skeleton of **4** is present in reduced form in members of the aromadendrene family of natural products,³ and the volatile yellow hydrocarbon fulfulvene **5**, isolated from the soft coral *Parerythropodium fulvum fulvum*,⁴ is only two double bonds short of the fully aromatic cyclopropazulene structure **6**. However, to date no aromatic cyclopropazulenes have been described. Herein we report the synthesis of the title compound **16**, the first example of such a system.



Addition of 2-diazopropane to the α,β -unsaturated sulfone **7**⁵ gave a product consisting mainly of the dehydrochlorinated adduct **8** (Scheme 1). The relatively high field absorption of the methine proton in **8** (δ 3.69) established that the cycloaddition had occurred in the sense shown. Treatment of **8** with triethylamine gave the unstable thiophene dioxide **9** which was then used in a Houk–Leaver azulene synthesis.⁶ Thus, addition of 6-(*N,N*-dimethylamino)fulvene (**10**) to a solution of **9** at room temperature gave the blue crystalline azulenopyrazole **12** as a single regioisomer in 48% yield. Irradiation of **12** in ether under nitrogen then afforded 2-chloro-1,1-dimethyl-1*H*-cycloprop[*e*]azulene **16** in 46% yield. If careful deoxygenation was not carried out, the tropone **18** was also formed, and this compound could be isolated in 22% yield [in addition to **16** (64%)] when the irradiation was carried out in ether saturated with oxygen. The formation of **18** can be rationalised in terms of interception of the diradical intermediate **13** by oxygen to give the cyclic peroxide **17**, a process well-documented in the

DOI: 10.1039/b104346n



Scheme 1

photonolysis of other cyclic azo compounds.⁷ Acid-catalysed or homolytic cleavage of the peroxide bond of **17** followed by cyclisation onto the reactive position of the five-membered ring of the azulene system would then deliver **18**. Significantly, the alkene **15**, resulting from intramolecular hydrogen atom transfer within intermediate **13** or **14**, was not detected. Such alkene formation is usually an important pathway in the photolysis of *gem*-dimethyl-substituted pyrazoles fused to six-membered aromatic rings,⁸ and the benzenoid cycloproparene is often the minor product or is not formed at all^{8b} in such

systems. In the present case, geometric and/or conformational factors are presumably responsible for the absence of H-transfer in intermediate **13/14**.

Although previous approaches to fully aromatic cyclopropazulenes have been unsuccessful,^{2,9} the present work shows that such a compound is accessible through the choice of an appropriate precursor. The presence of the chloro substituent in **16** conceals some potentially valuable ¹H NMR information but we note that the ¹³C resonance of C-7a, the carbon atom adjacent to the position of cyclopropa-fusion, is shifted upfield to 126.1 ppm compared to the value of 142.2 for C-4a. Such shielding is also observed for the analogous carbon in benzocyclopropene **1**.¹⁰

The synthesis of a less highly substituted crystalline cyclopropazulene, suitable for single crystal X-ray characterisation and more detailed NMR analysis, is the next challenge in this area. Experiments along these lines are in progress.

Experimental

6,6a-Dichloro-3,3-dimethyl-3a,6a-dihydro-3H-thieno[3,2-c]-pyrazole 4,4-dioxide **8** and 6-chloro-3,3-dimethyl-3H-thieno[3,2-c]pyrazole 4,4-dioxide **9**

A solution of 2-diazopropane¹¹ prepared from acetone hydrazone (4.5 g, 63 mmol) in Et₂O–THF (1 : 1, 20 ml) at –78 °C was added to a solution of **7**⁵ (1.00 g, 4.5 mmol) and the red solution was allowed to warm to –20 °C overnight. The resulting mixture was filtered and concentrated and subjected to silica gel filtration. Elution with EtOAc–petrol (5 : 95) gave a fraction (1.02 g) consisting mainly of **8**. A small sample crystallised from CH₂Cl₂–petrol as needles, mp 104–108 °C (decomp.) (C₇H₈Cl₂N₂O₂S requires C, 33.0; H, 3.2; N, 11.0; found: C, 33.1; H, 3.3; N, 11.1%). EI-MS (70 eV) *m/z* 163 (12%), 161 (11), 129 (15), 127 (51), 125 (18), 111 (12), 92 (14), 91 (100), 77 (14), 75 (11), 65 (21). δ_{H} (300 MHz, CDCl₃) 6.80 (s, 1H, vinyl), 3.69 (s, 1H, methine), 1.83 (s, 3H, CH₃), 1.66 (s, 3H, CH₃). δ_{C} (75.5 MHz, CDCl₃) 142.9 (C), 132.1 (CH), 107.7 (C), 95.0 (C), 72.5 (CH), 28.8 (CH₃), 21.2 (CH₃). ν_{max} (KBr) 1324, 1156 cm⁻¹ (S=O). Et₃N (0.82 ml, 1.2 eq.) was added to the remaining sample in anhydrous dichloromethane (20 ml) and the mixture was stirred at room temperature for 2 h. The solution was washed with 1 M HCl solution (1 × 20 ml), dried and concentrated to give a solid which was subjected to silica gel filtration. Elution with EtOAc–petrol (5 : 95) gave **9** as a solid of limited stability (505 mg, 59%). A sample crystallised from CH₂Cl₂–petrol as needles, mp 164–173 °C (decomp.). EI-MS (70 eV) *m/z* 138 (10%), 136 (28), 91 (100) [M⁺ – Cl – N₂ – SO₂], 75 (18), 74 (11), 65 (41), 63 (18). δ_{H} (300 MHz, CDCl₃) 6.71 (s, 1H, vinyl), 1.71 (s, 6H, 2 × CH₃). δ_{C} (75.5 MHz, CDCl₃) 157.6 (C), 154.4 (C), 134.9 (CH), 131.6 (C), 95.3 (C), 20.6 (2 × CH₃). ν_{max} (KBr) 1172, 1331 cm⁻¹ (S=O).

4-Chloro-1,1-dimethyl-1H-azuleno[5,4-c]pyrazole **12**

6-(*N,N*-Dimethylamino)fulvene (500 mg, 4.2 mmol) was added to a stirred solution of **9** (920 mg, 4.2 mmol) in THF (15 ml). The reaction was mildly exothermic and the black solution was stirred for 3 h at room temperature and then was adsorbed onto silica and subjected to silica gel filtration. Elution with EtOAc–petrol (2.5 : 97.5) gave **12** as blue crystals (460 mg, 48%) which crystallised from petrol as prisms, mp 146–148 °C (C₁₃H₁₁ClN₂ requires C, 67.7; H, 4.8; N, 12.1; found: C, 67.9; H, 5.0; N, 12.2%). EI-MS (70 eV) *m/z* 232 (10%) [M⁺ + 2], 230 (29) [M⁺], 202 (23) [M⁺ – N₂], 187 (19), 167 (58), 166 (25), 165 (64), 153 (14), 152 (100), 151 (26), 150 (12), 82 (17), 75 (11). δ_{H} (300 MHz, CDCl₃) 8.31 (d, *J* 10.4 Hz, 1H, 6-H), 8.00 (ddd, *J* 4.0, 4.0, 0.3 Hz, 1H, 8-H), 7.66 (dm, *J* 4.0 Hz, 1H, 9-H or 7-H), 7.60 (d, 1H, *J* 10.4 Hz, 1H, 5-H), 7.55 (dm, *J* 4.0 Hz, 1H, 7-H or 9-H), 1.77 (s, 6H, 2 × CH₃). δ_{C} (75.5 MHz, CDCl₃) 151.9 (C), 145.9 (C), 139.8 (C), 139.5 (C), 138.4 (CH), 135.1 (CH), 127.0 (C), 123.5 (CH), 122.7 (CH), 94.8 (C), 24.3 (CH₃). UV–Vis (Et₂O) λ_{max} /nm (ε/mol⁻¹ dm³ cm⁻¹) 256 (19500), 271 (21900), 278 (22400), 303 (25100), 313 (24500), 388 (3980), 405 (3800), 573 (537), 622 (490), 683 (263).

2-Chloro-1,1-dimethyl-1H-cycloprop[*c*]azulene **16**

A solution of **12** (88 mg, 0.38 mmol) in anhydrous Et₂O (250 ml) was flushed thoroughly with N₂ and then irradiated through Pyrex with a Philips HPK 125 W lamp at 0–5 °C under N₂ for 1.5 h. The solvent was evaporated and the residue subjected to radial chromatography on silica. Elution with petrol gave **16** as a blue oil [28 mg, 36%; 46% based on recovered starting material (19 mg)] (C₁₃H₁₁³⁵Cl requires M⁺ 202.0549; found: M⁺ 202.0553). EI-MS (70 eV) *m/z* 204 (16%) [M⁺ + 2], 202 (51) [M⁺], 187 (14), 167 (61), 166 (27), 165 (67), 153 (15), 152 (100), 151 (25), 150 (12), 83 (10), 82 (20), 75 (14), 71 (25), 70 (16), 69 (16), 68 (12), 63 (11), 57 (62), 56 (37). δ_{H} (500 MHz, CDCl₃) 8.11 (d, *J* 10.9 Hz, 1H, 4-H), 7.96 (dd, *J* 3.7, 3.7 Hz, 1H, 6-H), 7.45 (d, *J* 3.7 Hz, 1H, 5-H), 7.15 (d, *J* 3.6 Hz, 1H, H-7), 7.13 (d, *J* 10.9 Hz, 1H, 3-H), 1.78 (s, 6H, 2 × CH₃). δ_{C} (125.7 MHz, CDCl₃) 142.96 (C-7b), 142.40 (C-4a), 139.74 (C-6), 131.75 (C-2), 131.44 (C-4), 127.32 (C-1a), 126.13 (C-3), 126.09 (C-7a), 121.17 (C-5), 111.48 (C-7), 35.82 (C-1), 25.95 (2 × CH₃). These assignments were made with the aid of HSQC and HMBC experiments. UV–Vis (Et₂O) λ_{max} /nm (ε/mol⁻¹ dm³ cm⁻¹) 204 (9330), 245 (16200), 282 (53700), 329 (3310), 341 (4470), 566 (562).

4-Chloro-2,2-dimethyl-2,8a-dihydro-3H-azuleno[1,8-*bc*]-furan-3-one **18**

A solution of **12** (90 mg, 0.39 mmol) in anhydrous Et₂O (250 ml) was saturated with O₂ for 20 min, and then irradiated under O₂ for 3 h. The solvent was evaporated and the residue subjected to radial chromatography. Elution with petrol gave **16** as a blue oil (51 mg, 64%). Further elution with EtOAc–petrol (5 : 95) gave **18** as a colourless oil (22 mg, 22%) (C₁₃H₁₁O₂³⁵Cl requires M⁺ 234.0448; found: M⁺ 234.0441). EI-MS (70 eV) *m/z* 234 (6%) [M⁺], 178 (45), 177 (17), 176 (100) [M⁺ – C₃H₆O], 150 (25), 148 (70), 113 (38). δ_{H} (300 MHz, CDCl₃) 7.38 (s, 2H, 5-H and 6-H), 6.84 (dd, *J* 5.6, 2.0 Hz, 1H, 8-H or 7-H), 6.63 (dd, *J* 5.6, 2.0 Hz, 1H, 7-H or 8-H), 5.33 (dd, *J* 2.0, 2.0 Hz, 1H, 2a-H), 1.67 (s, 3H, CH₃), 1.49 (s, 3H, CH₃). δ_{C} (75.5 MHz, CDCl₃) 196.3 (C), 153.0 (C), 139.2 (C), 137.8 (CH), 133.1 (CH), 131.7 (CH), 129.3 (C), 126.7 (CH), 122.2 (C), 83.8 (C), 75.5 (CH), 27.0 (CH₃), 21.4 (CH₃). ν_{max} (film) 1696 cm⁻¹ (C=O). UV–Vis (Et₂O) λ_{max} /nm (ε/mol⁻¹ dm³ cm⁻¹) 220 (6460), 250 (5130), 320 (851).

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