ORGANIC LETTERS
2004
Vol. 6, No. 22
4017−4020

# $C_6H_4$ Valence Bond Isomers: A Reactive Bicyclopropenylidene

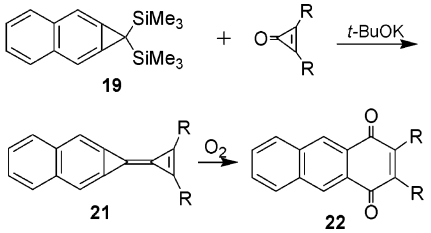
**Brian Halton,*,† Mark J. Cooney,† Carissa S. Jones,† Roland Boese,*,‡ and Dieter Bläser‡**

*School of Chemical & Physical Sciences, Victoria University of Wellington,*
*P.O. Box 600, Wellington, New Zealand, and Institute for Inorganic Chemistry,*
*Duisburg-Essen University, Universitaetsstrasse 3-5, 45117 Essen, Germany*

*brian.halton@vuw.ac.nz; roland.boese@uni-essen.de*

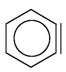
Received August 24, 2004

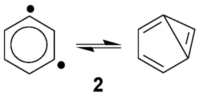
## ABSTRACT

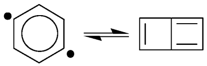


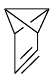
**The simple bicyclopropenylidene derivative 21b, stabilized by fusion into naphthalene, results from reaction of dimesitylcyclopropenone 20b with the 1-trimethylsilyl-1*H*-cyclopropa[*b*]naphthalenyl anion. Although unstable in air, the molecule survives ambient conditions long enough for separation and mass spectral characterization. Aerial oxidation of 21b leads to 2,3-dimesitylanthracene-1,4-dione 22b whose X-ray crystal structure has been determined. While diphenylcyclopropenone 20a does not give identifiable products, the di-*tert*-butyl analogue 20c gives quinone 22c but in lower yield.**

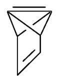
The $C_6H_4$ energy surface has been recognized for more than a century[1] with *o*-benzyne **1** and a number of its valence bond isomers characterized by chemical trapping, spectroscopy, and more recently, matrix isolation.[2] Compared to benzene, benzyne **1** is strained and reactive, but its ready accessibility has provided a cornerstone in the development of modern physical organic chemistry.[3] There can be little doubt that *m*-**2** and *p*-**3** benzyne exist,[4] especially from the isolation of the perfluoro derivatives of **1**−**3** by Sander and his group.[5] There is no report of benzvalyne **4**, but diene isomer **5** is involved in dehydrobenzvalene chemistry.[6] More recently, attention has been directed toward the remaining unknown $C_6H_4$ valence bond isomer, bicyclopropenylidene (triafulvalene) **6**.[7]

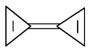

**1**


**2**


**3**


**4**


**5**


**6**

Two derivatives of the triafulvalene ring system have been recorded by way of the heavily substituted, crystalline bicycloproparenylidenes **7**, prepared from dimerization of the carbenoid that results from reaction of the relevant *gem*-

---

[†] Victoria University of Wellington.

[‡] Duisburg-Essen University.

(1) Stormer, R.; Kahlert, B. *Ber. Dtsch. Chem. Ges.* **1902**, *35*, 1633−1640.

(2) (a) Wenk, H. H.; Winkler, M.; Sander, W. *Angew. Chem., Int. Ed.* **2003**, *42*, 502−527. (b) Halton, B. *Chem. N.Z.* **2001**, *65*, 28−32.

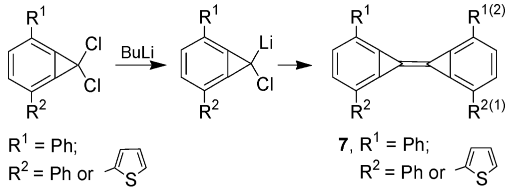
(3) Warmuth, R. *Eur. J. Org. Chem.* **2001**, 423−437.

(4) (a) Luis, S. V.; Gavina, F.; Ferrer, P.; Safont, V. S.; Torres, M. C.; Burguete, M. I. *Tetrahedron* **1989**, *45*, 6281−6296. (b) Lockhart, T. P.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 4091−4096. (c) Lockhart, T. P.; Commita, P. B.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 4082−4090. (d) Washburn, W. N.; Zahler, R.; Chen, I. *J. Am. Chem. Soc.* **1978**, *100*, 5863−5874.

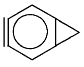
(5) (a) Wenk, H. H.; Balster, A.; Sander, W.; Hrovat, D. A.; Borden, W. T. *Angew. Chem., Int. Ed.* **2001**, *40*, 2295−2298. (b) Wenk, H. H.; Sander, W. *Chem.*−*Eur. J.* **2001**, *7*, 1837−1844.

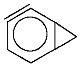
10.1021/ol048307g CCC: $27.50

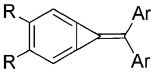
**Scheme 1**



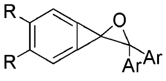
dichlorocyclopropabenzene with BuLi (Scheme 1).[8] These compounds illustrate that annulation of cyclopropene into an aromatic core provides compounds significantly more stable than their nonaromatic congeners. From our own studies, we have noted (i) that the highly strained benzynes **8** and **9**[9] can be intercepted at ambient temperature, (ii) that the exocyclic alkenes **10** are exceptionally stable compounds,[10,11] and (iii) that epoxides **11** survive at 0 °C,[12] while parent **12** is stable only to −50 °C.[13]


**8**

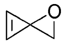

**9**



**10**, R = H or RR = benzo

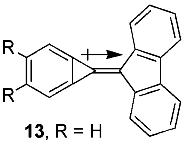


**11**, R = H or RR = benzo

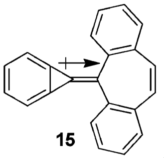


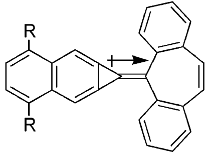
**12**

Polar fulvalenes have been prepared in the cycloproparene series as illustrated by **13**−**16**. Calculations[14] show the polarity to be directed *away* from the cycloproparene and *toward* the cross-conjugated moiety, even in **15** and **16**; these last compounds distort from planarity to prevent the formation of an 8$\pi$ 7C antiaromatic ring.[15] The *only* cycloproparene hydrocarbons predicted to have polarity directed *toward* the cycloproparene unit are the triafulvalenes **17** and **18** ($\mu_{calcd}$ 2.6 and 4.4 D, respectively[14]); they are also expected to be *less stable* than cyclopentadienyl and cycloheptatrienyl analogues and the unknown parent methylidene compounds.[14] Thus, kinetically stabilized derivatives of **17** and/or **18** would be the simplest bicyclopropenylidenes so far recorded. We now provide evidence to support the formation of the simple bicyclopropenylidene derivatives **21** as easily oxidized reactive molecules.

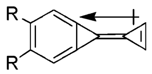


**13**, R = H
**14**, RR = benzo


**15**



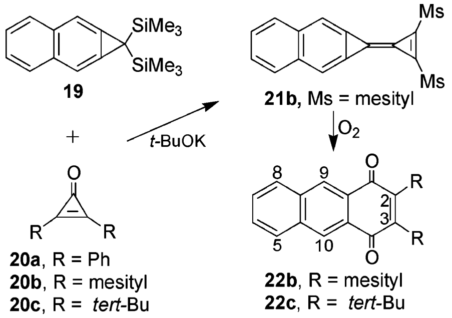
**16**, R = H or OMe



**17**, R = H, $\mu_{calc}$ 2.6 D,
**18**, RR = benzo, $\mu_{calc}$ 4.4 D

Our approach to **17** and **18** follows the established route to the alkylidenecycloproparenes that employs Peterson olefination of the 1,1-bis(trimethylsilyl)cycloproparene.[10] However, the exceedingly foul odor of cyclopropabenzene has dictated that all work involve the anion derived from cyclopropa[*b*]naphthalene derivative **19**.[16] Initial attempts to effect reaction between disilane **19** and diphenylcyclopropenone **20a** led to much decomposition and the formation of a plethora of largely inseparable reaction products. By employing the sterically more demanding 2,3-dimesitylcyclopropenone **20b** less decomposition occurred, but the products were still difficult to separate. Repeated radial chromatography provided an orange crystalline solid identified as 2,3-dimesitylanthracene-1,4-dione **22b** (8%) (Scheme 2) from its spectroscopic data and confirmed by single-crystal X-ray diffraction analysis.[17]

**Scheme 2**



The $^1$H NMR spectrum of **22b** shows singlets for the equivalent H9/H10 protons of the anthracene core and the *meta/meta′* hydrogens of the pendant mesityl groups. The *o*/*o′*- and *p*/*p′*-methyl groups appear as 2:1 singlets, and H5−H8 give rise to the expected AA′BB′ pattern; the protonated aromatic carbon atoms resonate in the narrow 128.4−130.1 ppm range, and the absence of shielded methine carbons signifies the loss of the cycloproparene core.[10] Figure 1 is an ORTEP plot of **22b** at 50% probability and shows the quinone to exist as two independent molecules with slightly differing interplanar angles of the mesityl rings with respect to the anthracene system [molecule A (lower): 76.8° and

---

(6) Schlueter, A. D.; Belzner, J.; Heywang, U.; Szeimies, G. *Tetrahedron Lett.* **1983**, *24*, 891−894.

(7) (a) Huwyler, V. R.; Al-Dulayymi, A.; Neuenschwander, M. *Helv. Chim. Acta* **1999**, *82*, 2336−2347. (b) Lang, C.; Muhlebach, M.; Neuenschwander, M. *Helv. Chim. Acta* **1997**, *80*, 2124−2136.

(8) Neidlein, R.; Poignee, V.; Kramer, W.; Glueck, C. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 731−734.

(9) (a) Apeloig, Y.; Arad, D.; Halton, B.; Randall, C. J. *J. Am. Chem. Soc.* **1986**, *108*, 4932−4937. (b) Halton, B.; Randall, C. J. *J. Am. Chem. Soc.* **1983**, *105*, 6310−6311.

(10) (a) Halton, B. *Chem. Rev.* **2003**, *103*, 1327−1370. (b) Halton, B.; Stang, P. J. *Synlett* **1997**, 145−158.

(11) Dixon, G. M.; Halton, B. *Eur. J. Org. Chem.* **2004**, 3707−3713.

(12) (a) Bickers, P. T.; Halton, B.; Kay, A. J.; Northcote, P. T. *Aust. J. Chem.* **1999**, *52*, 647−652. (b) Halton, B.; Cooney, M. J.; Wong, H. *J. Am. Chem. Soc.* **1994**, *116*, 11574−11575.

(13) Billups, W. E.; Litosh, V. A.; Saini, R. K.; Daniels, A. D. *Org. Lett.* **1999**, *1*, 115−116.

(14) Apeloig, Y.; Boese, R.; Bläser, D.; Halton, B.; Maulitz, A. H. *J. Am. Chem. Soc.* **1998**, *120*, 10147−10153.

(15) Halton, B.; Jones, C. S. *Eur. J. Org. Chem.* **2004**, 138−146.

(16) Halton, B.; Cooney, M. J.; Davey, T. W.; Forman, G. S.; Lu, Q.; Boese, R.; Bläser, D.; Maulitz, A. H. *J. Chem. Soc., Perkin Trans. 1* **1995**, 2819−2827.

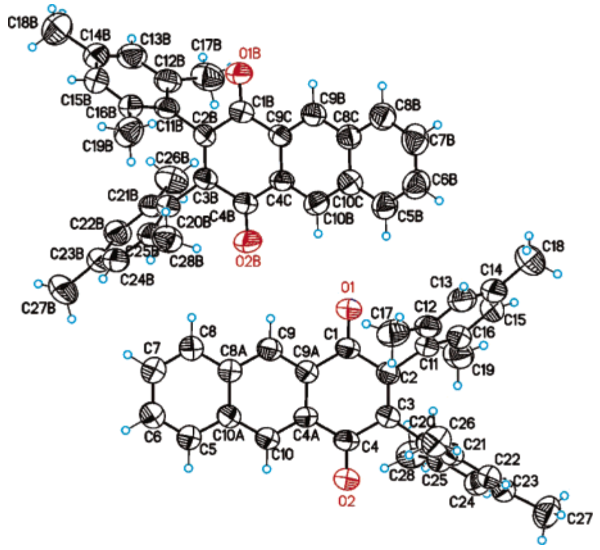
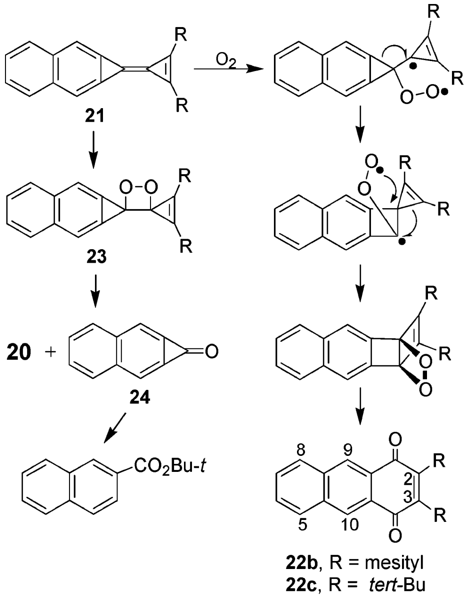


**Figure 1.** ORTEP plot of quinone **22b** at 50% probability. The two independent molecules have differing interplanar angles of the mesityl rings with respect to the anthracene system (see text).

99.2° toward and molecule B (upper): 78.4° and 114.8° against]. In both cases, the anthracene core is not strictly planar but slightly distorted at the 1,4-positions (molecule A: C9A−C1−C2−C3, 7.0° and C2−C3−C4−C4A, 14.1°; molecule B: C9C−C1B−C2B−C3B, 1.5° and C2B−C3B−C4B−C4C, 10.1°). There is no obvious C−H····O hydrogen bond and the difference of the molecular geometries is a consequence of close packing. Accordingly, we expect only small differences in the molecular energies.

Analogous reaction of di-*tert*-butylcyclopropenone **20c** provides yellow anthraquinone **22c**, but in only 6% yield.[18] This compound displays proton singlets for H9/H10 and the *tert*-butyl protons, and has its carbon resonances for the anthraquinone moiety in agreement with those from **22b**; accurate mass measurement (electrospray) provided a protonated molecular ion for **22c** in accord with expectation.[18]

**Scheme 3**



The reaction products from **19** and **20b** gave rise to a small (∼2 mg) sample of pale yellow compound from careful repeated chromatography; it had limited stability and slowly transformed into quinone **22b**. The electron-impact mass spectrum of this yellow solid prior to its decomposition provided a molecular ion $M^{\bullet +}$ as base peak at *m*/*z* 412 with fragment ions at *m*/*z* 397 (11) $[M - 15]^+$, 382 (24) $[M - 30]^{\bullet +}$ and 367 (30) $[M - 45]^+$. A contaminant at *m*/*z* 502 with 11% relative abundance was also recorded (see below). It is our view that the reactive solid is the sought after annulated bicyclopropenylidene **21b** ($M_r$ 412) arising from the expected Peterson olefination (Scheme 2). The aerial oxidation of **21b** into quinone **22b** responsible for the color change can be explained by capture of molecular oxygen by the reactive exocyclic double bond (Scheme 3). In this regard, the behavior of the bicyclopropenylidene is analogous to the instability of cyclobutadienes in air;[19,20] tetraphenylcyclobutadiene adds oxygen to give a dioxetane intermediate that opens to (*Z*)-tetraphenylbut-2-ene-1,4-dione,[20] while the catalyzed addition of oxygen leads to a furan.[21]

Despite many variations in the reaction conditions, no experiment has provided **21b** in anything other than trace quantities, but they have given a large number of essentially

---

(17) **22b:** orange-red crystalline solid (22 mg, 8%); mp 173−5 °C (dichloromethane−light petroleum, 1:1); IR $\lambda_{max}$/cm$^{-1}$ (KBr) 3055, 2960, 2919, 1662, 1612, 1585, 1460, 1398, 1343, 1277, 1187, 1058, 1026; UV $\lambda_{max}$ (acetonitrile)/nm 235 (4.66), 271 (3.77), 289 (3.78), 299 (3.78), 356 (3.23), 397 (log $\epsilon$ 3.27); $\delta_H$ (80 MHz; $CDCl_3$) 2.00 (s, 12H), 2.23 (s, 6H), 6.75 (s, 6H), 7.69−7.71 (AA′, 2H, H6/7), 8.08−8.11 (BB′, 2H, H5/8), 8.73 (s, 2H, H9/10); $\delta_C$ (20 MHz; $CDCl_3$) 20.9 (C12/16-**Me**), 21.1(5) (C14-**Me**), 128.4 (C13/15), 128.8(5) (C4a/9a), 129.1 (C9/10), 129.4 (C6/7), 130.1 (C5/8 + C11), 135.1 (C8a/10a), 136.0(5) (C12/16), 137.7 (C14), 150.1 (C2/3), 184.1 (C1/4). Anal. Calcd: C, 86.4(5); H, 6.3(5). Found: C, 86.2; H, 6.5. **Crystal structure determination of 22b:** $C_{32}H_{28}O_2$, $M_r$ 444.54, mp 174−5 °C, red plate dimensions 0.25 × 0.13 × 0.11 mm measured on a Siemens P4 four circle diffractometer with Mo Kα radiation, *T* 293(2) K, cell dimensions $a = 11.3439(17)$ Å, $b = 14.390(2)$ Å, $c = 16.389(3)$ Å, $\alpha = 100.405(14)°$, $\beta = 108.679(13)°$, $\gamma = 95.758(13)°$, $V = 2456.6(7)$ Å$^3$, triclinic crystal system, Z = 4, $d_{calcd}$ 1.202 g/cm$^3$, $\mu = 0.073$ mm$^{-1}$ space group *P*-1, data collection of 5241 intensities, 5025 independent ($R_{int} = 0.0118$, Θ 1.75−22.50°), 3285 observes [$F_o \geq 2\sigma(F)$]; structure solution and refinement on $F^2$ (Bruker AXS SHELXTL 5.10) 614 parameters, the hydrogen atoms as Riding model on idealized geometries with the 1.2-fold (1.5-fold for methyl groups) isotropic displacement parameters of the equivalent $U_{ij}$ of the corresponding carbon atom. Crystallographic data (excluding structure factors) for this structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 245990. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax +44-(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk) or from www.ccdc.cam.ac.uk/conts/retrieving.html.

(18) **22c:** yellow solid (6.5 mg, 6%); MS (electrospray) $[M + H]^+$ *m*/*z* 321.18647 amu, $C_{22}H_{25}O_2^+$ requires 321.18491, Δ 4.9 ppm; $\delta_H$ (300 MHz; $CDCl_3$) 1.58 (s, 9H), 7.64−7.68 (AA′, 2H, H6/7), 8.02−8.07 (BB′, 2H, H5/8), 8.44 (s, 2H, H9/10); $\delta_C$ (75 MHz; $CDCl_3$) 32.0(5) (Me), 39.1 (**C**$Me_3$), 126.9(5) (C9/10), 128.8 (C6/7), 129.3 (C4a/9a), 129.8 (C5/8), 135.1 (C8a/10a), 163.6 (C2/3), 188.7 (C1/4).

(19) Krebs, A.; Kemper, R.; Kimling, H.; Klaska, K. H.; Klaska, R. *Liebigs Ann. Chem.* **1979**, 473−483.

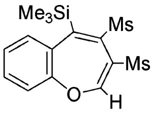
(20) Cava, M. P.; Mitchell, M. J. *Cyclobutadiene and Related Compounds*; Academic Press: New York, 1967.

(21) Omerod, R. M.; Lanmbert, R. M. *Catal. Lett.* **1990**, *6*, 121−129.

inseparable products, not least that appearing as a contaminant at $m/z$ 502 in the mass spectrum of **21b**. Of these compounds, cyclopropa[*b*]naphthalene and *tert*-butyl 2-naphthoate have been identified by comparison of their spectral data with literature values. The former is an anticipated product when unreacted silyl anion reacts with water,[22] and the presence of naphthoate is easily understood from ring opening of naphthalenone **24** (Scheme 3).[23] Ketone **24** is to be expected from dioxetane metathesis following oxygen addition across the central double bond of **21** in analogy to the reaction of $Ph_4C_4$ with $O_2$.[20]

The product with $m/z$ 502, and an isomer of it also obtained in trace amounts, is less easy to account for. Without imposing undue speculation, we tentatively assign benzoxepin structure **25** ($m/z$ 502) to this compound as it can arise from initial 1,2-addition to **20b** with subsequent rearrangement and protonation on workup. Furthermore, 1,4-conjugate addition of the anion to cyclopropenone **20b** accounts for isomeric **25** in which the proton and the trimethylsilyl groups are reversed.

These experiments indicate that room temperature isolation of a kinetically stabilized bicyclopropenylidene is likely only with markedly better steric protection than that offered by *tert*-butyl or mesityl groups. In this context, the use of the sterically very demanding 2,6-diisopropylphenyl (Dip) or 2,4,6-tris-[bis(trimethylsilyl)methyl]phenyl (Tbt) so effectively used by Tokitoh and co-workers is attractive.[24] We leave others to explore such possibilities.



**25**, Ms = mesityl

**Acknowledgment.** We thank Professor Manfred Regitz (Kaiserslautern University) for a generous sample of cyclopropenone **20c**. Financial assistance from Victoria University by way of a postdoctoral fellowship (to M.J.C.) and Curtis-Gordon scholarships (to C.S.J.) and from the Deutsche Forschungs-gemeinschaft and the Fonds der Chemischen Industrie (in Germany) is gratefully acknowledged.

OL048307G

---

(22) Halton, B.; Jones, C. S. *J. Chem. Soc., Perkin Trans. 2* **1998** 2505−2508, **1999**, 387.

(23) Buckland, S. J.; Halton, B.; Stang, P. J. *Aust. J. Chem.* **1988**, *41*, 845−854.

(24) (a) Tajima, T.; Sasaki, T.; Sasamori, T.; Takeda, N.; Tokitoh, N.; N. *Chem. Commun.* **2004**, 402−403. (b) Tajima, T.; Hatano, K.; Sasaki, T.; Sasamori, T.; Takeda, N.; Tokitoh, N.; Takagi, N.; Nagase, S. *J. Organomet. Chem.* **2003**, *686*, 118−126.