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LETTERS

Bridged and Superbridged Cyclopropenylidene Iminium Salts

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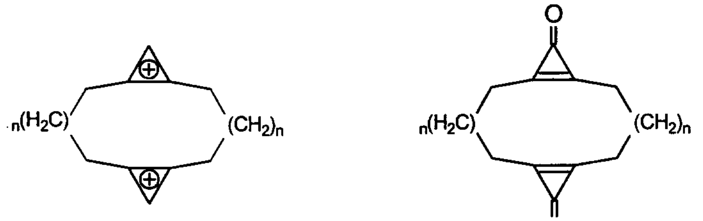
Abstract

The reaction of bridged cyclopropenones and doubly bridged biscyclopropenones with triethyloxonium fluoroborate and an amine led to the tetrafluoroborates of bridged and superbridged cyclopropenylidene iminium salts. © 1999 Elsevier Science Ltd. All rights reserved.

Key words: Iminium salts, cyclophanes, cyclopropenones

Cyclopropenylium salts[1] and cyclopropenones[1] are well known members of the family of the $(4n+2)\pi$ systems with n = 0. They are known since Breslow et al. have launched this field of chemistry.[2] The chemistry of cyclopropenones could be extended by O-alkylation to the alkoxycyclopropenylium salts[3] and by reaction with amines to the cyclopropenylideneiminium salts.[3,4] We have contributed to this field by preparing phanes which incorporate two cyclopropenylium or cyclopropenone rings, such as **1**[5,6] and **2**.[7]

Figure 1



1a, b, c n = 1,2,3 **2a, b, c** n = 1,2,3

Structural investigations on **1c**[6] and **2a**[7] demonstrated that in both phanes the ring systems face each other. The angle between the two planes of the three-membered rings amounts to 41° (**1c**)[6] and 95.5° (**2a**),[7] respectively. To find out if we could bridge both rings with a third tether via the bisiminium salts we investigated the possibility of preparing these species.

To transform the bicyclic species **3-5**[8] into the corresponding iminium salts we used the protocol shown in Scheme 1.

The cyclopropenones were treated with triethyloxonium tetrafluoroborate to yield the corresponding ethoxycyclopropenylium salts **6-8**. Subsequently, treatment of these species with a secondary amine yielded the corresponding iminium salts **9-11**.[9-11] The formation of **9-11** was accompanied by polymerization. We ascribe this to the abstraction of protons from the CH_2 groups in the α-position to the cyclopropenylium ring. To prevent this side reaction we have used **12**[12] as starting material (Scheme 2).

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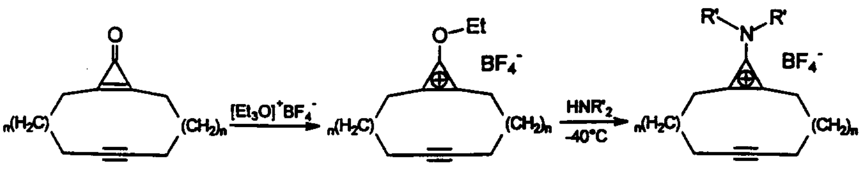
Scheme 1

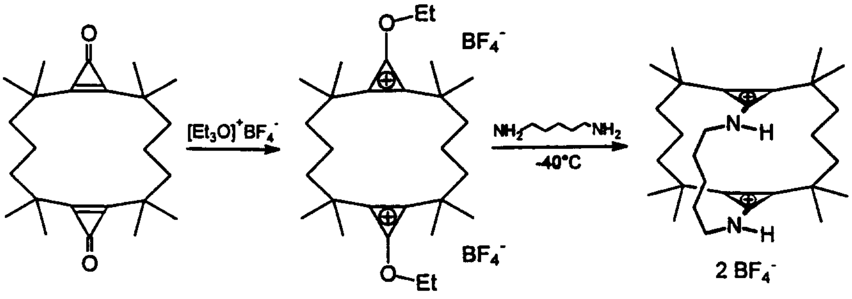


n = 1, 2, 3 | n = 1, 2, 3 | n = 1, 2, 3

3, 4, 5 | **6, 7, 8** | **9, 10, 11**

R' = **a** C_2H_5
b *i*-C_3H_7
c Phenyl

Scheme 2



12 **13** **14**

After generating the bisethoxycyclopropenylium phane **13**, we were able to tether both rings by reacting with 1.5-diaminopentane to yield the biscyclopropenylidene iminium salt **14**.[13] The isolation of single crystals of **14** enabled us to carry out X-ray diffraction studies.

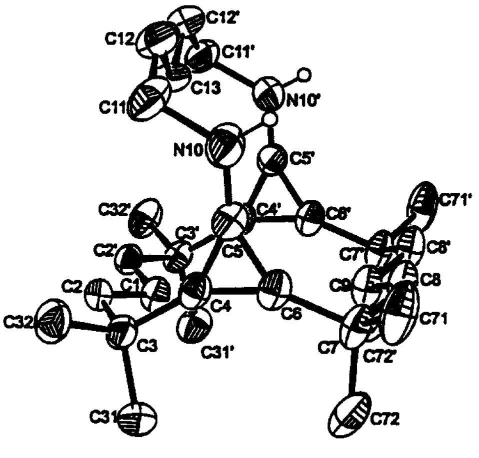


Figure 2. Molecular structure of **14**

The two cyclopropenyl rings are nearly perfectly parallel to each other with a negligible inclination angle of 0.2°. The distance between the rings amounts to 520 pm. The corresponding methyl groups (e.g. C32-C71) are nearly eclipsed with a maximum torsion angle of 1.2°. The bond lengths in the cyclopropenyl rings range from 134 pm (C4-C6) to 138 pm (C4-C5) thus indicating almost equal bond length in the three-membered ring. On the other side, the C5-N bond is about 128 pm long, a typical value of a C-N double bond.

Acknowledgements

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9. **9a**: $C_{15}H_{22}N$ [M(cation$^+$)], calc. 216.1752, found 216.1743. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 3.59 (q, 4H), 3.05 (m, 4H), 2.34 (pt, 4H), 1.92 (m, 4H), 1.34 (t, 6H). ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ = 149.5 (C-N), 146.5 (C_q), 81.6 ($C\equiv C$), 48.8 (CH_2-N), 24.9 (CH_2), 22.7 (CH_2), 19.2 (CH_2), 13.5 (CH_3).

   9b: $C_{17}H_{26}N$ [M(cation$^+$)], calc. 244.2066, found 244.2060. ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 3.91 (sep, 2H), 3.09 (m, 4H), 2.36 (pt, 4H), 1.96 (m, 4H), 1.83 (d, 12H). ^{13}C NMR (125.8 MHz, CD_2Cl_2): δ = 147.1 (C-N), 147.0 (C_q), 81.6 ($C\equiv C$), 54.8 (CH), 25.7 (CH_2), 22.6 (CH_2), 22.0 (CH_2), 19.1 (CH_3).

   9c: $C_{23}H_{22}N$ [M(cation$^+$)], calc. 312.1752, found 312.1749. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.41-7.19 (m, 10H), 3.00 (m, 4H), 2.34 (pt, 4H), 1.97 (m, 4H). ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ = 164.4 (C-N), 159.6 (C_q), 139.7 (C_q), 130.4 (CH), 126.5 (CH), 120.9 (CH), 81.7 ($C\equiv C$), 25.5 (CH_2), 22.5 (CH_2), 19.3 (CH_2).
10. **10a**: $C_{17}H_{26}N$ [M(cation$^+$)], calc. 244.2065, found 244.2108. ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 3.61 (q, 4H), 3.05 (t, 4H), 2.26 (pt, 4H), 2.03 (m, 4H), 1.62 (m, 4H), 1.36 (t, 6H). ^{13}C NMR (128.5 MHz, CD_2Cl_2): δ = 150.3 (C-N), 147.6 (C_q), 81.7 ($C\equiv C$), 48.9 (CH_2-N), 26.9 (CH_2), 25.2 (CH_2), 24.9 (CH_2), 18.1 (CH_2), 13.4 (CH_3).

    10b: $C_{19}H_{30}N$ [M(cation$^+$)], calc. 272.2379, found 272.2379. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 3.90 (sep, 2H), 3.06 (t, 4H), 2.28 (pt, 4H), 2.05 (m, 4H), 1.61 (m, 4H), 1.36 (d, 12H). ^{13}C NMR (75.5 MHz,

CD_2Cl_2): δ = 148.0 (C_q), 147.5 (C-N), 81.6 ($C\equiv C$), 55.2 (CH_2-N), 26.9 (CH_2), 25.8 (CH_2), 25.0 (CH_2), 21.8 (CH_2), 18.1 (CH_3).

10c: $C_{25}H_{26}N$ [M(cation$^+$)], calc. 340.2065, found 340.2059. ^1H NMR (300 MHz, CD_2Cl_2): δ = 7.48 (s, 10H), 3.02 (t, 4H), 2.24 (t, 4H), 2.03 (qui, 4H), 1.60 (m, 4H). ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ = 165.0 (C-N), 161.0 (C_q), 136.3 (C_q), 131.0 (CH), 130.9 (CH), 123.1 (CH), 81.8 ($C\equiv C$), 26.9 (CH_2), 25.3 (CH_2), 24.9 (CH_2), 14.4 (CH_2).

11. **11a**: $C_{19}H_{30}N$ [M(cation$^+$)], calc. 272.2378, found 272.2392. ^1H NMR (500 MHz, CD_2Cl_2): δ = 3.61 (q, 4H), 2.95 (m, 4H), 2.20 (m, 4H), 1.89 (m, 4H), 1.54 (m, 8H), 1.35 (t, 6H). ^{13}C NMR (125.8 MHz, CD_2Cl_2): δ = 150.8 (C-N), 146.8 (C_q), 81.0 ($C\equiv C$), 48.9 (CH_2-N), 28.6 (CH_2), 27.7 (CH_2), 25.6 (CH_2), 25.4 (CH_2), 18.4 (CH_2), 13.4 (CH_3).

    11b: $C_{21}H_{34}N$ [M(cation$^+$)], calc. 300.2691, 300.2697. ^1H NMR (500 MHz, CD_2Cl_2): δ = 3.91 (sep, 2H), 2.96 (t, 4H), 2.21 (m, 4H), 1.94 (m, 4H), 1.57 (m, 8H), 1.36 (d, 12H). ^{13}C NMR (125.8 MHz, CD_2Cl_2): δ = 148.1 (C-N), 147.1 (C_q), 81.0 ($C\equiv C$), 55.0 (CH_2-N), 28.9 (CH_2), 27.8 (CH_2), 26.8 (CH_2), 25.4 (CH_2), 21.8 (CH_2), 18.4 (CH_3).

    11c: $C_{27}H_{30}N$ [M(cation$^+$)], calc. 368.2379, found 368.2395. ^1H NMR (300 MHz, CD_2Cl_2): δ = 7.38-7.17 (m, 10H), 2.92 (t, 4H), 2.21 (m, 4H), 1.90 (m, 4H), 1.53 (m, 8H). ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ = 165.8 (C-N), 161.1 (C_q), 140.1 (C_q), 130.1 (CH), 125.7 (CH), 120.4 (CH), 80.9 ($C\equiv C$), 28.5 (CH_2), 27.6 (CH_2), 26.0 (CH_2), 24.9 (CH_2), 18.4 (CH_2).

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13. **14**: $C_{29}H_{47}N_2$ [M(cation^{2+}-H$^+$), calc. 423.3739, found 423.3731, $C_{29}H_{48}N_2{}^{10}BF_4$ [M([cation^{2+}]$^{10}BF_4^-$)], calc. 510.3883, found 510.3859, $C_{29}H_{48}N_2{}^{11}BF_4$ [M([cation^{2+}]$^{11}BF_4^-$)], calc. 511.3847, found 511.3848. $C_{29}H_{48}N_2B_2F_8$, M = 598.31, crystal dimensions 0.4x0.3x0.1 mm^3, crystal system orthorhombic, space group Pnma, Z = 4, a = 12.143(2) Å, b = 19.232(4) Å, c = 14.490(3) Å, V = 3384.0(10) Å^3, F(000) = 1272, $\rho_{calc.}$ = 1.174 g/cm^3, $2\Theta_{max.}$ = 49.28°. Radiation MoKα, λ = 0.71073 Å, 0.3° ω-scans with CCD area detector, T = 200(2) K, 5194 reflections measured, 2508 unique, 1226 observed ($I>2\sigma(I)$), intensities were corrected for Lorentz and polarisation effects, an empirical absorption correction was applied using SADABS[14] based on the Laue symmetry of the reciprocal space, μ = 0.098 mm^{-1}, $T_{min.}$ = 0.59, $T_{max.}$ = 0.92, structure solved by direct methods and refined against F^2 with a full matrix least squares algorithm using the SHELXTL Plus (5.03) software package,[15] 267 parameters refined. Hydrogen atoms were treated using appropriate riding models, except H10, which was refined isotropically. Final residual values R(F) = 0.068, wR(F^2) = 0.184, residual electron density 0.19 to -0.21 e/ Å^3. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number CCDC 133120.
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