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Synthesis of Oxaspiropentene

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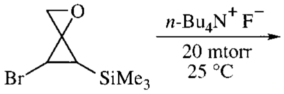
ABSTRACT



Epoxidation of either *cis*- or *trans*-1-methylene-2-bromo-3-(trimethylsilyl)cyclopropane by dimethyldioxirane followed by elimination of the epoxide over solid tetra-*n*-butylammonium fluoride using the vacuum gas–solid reaction procedure yields oxaspiropentene. The nuclear magnetic resonance spectrum of oxaspiropentene was recorded at –95 °C. Exact bond lengths were determined computationally.

Small-ring spiroconnected cycloalkenes can have, in principle, interesting properties resulting from spiro conjugation.[1] Although spiropentene (**1**)[2] and spiropentadiene (**2**)[3] have been synthesized recently and characterized spectroscopically, simple spirenes in which heteroatoms are part of the ring system have not been investigated. A derivative of oxaspiropentene, compound **3**, has been described,[4] but the parent compound **4** has not been reported. We report here the synthesis of oxaspiropentene via the vacuum gas−solid reaction procedure.[5]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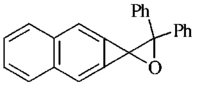
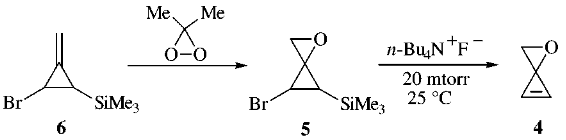


3

The synthesis of oxaspiropentene is illustrated as follows:



6 **5** **4**

The starting compound **5**[6] was prepared in nearly quantitative yield by oxidation of **6**[7] using dimethyldioxirane.[8] Elimination of trimethylsilyl bromide from the epoxide **5** using solid $(n\text{-Bu})_4N^+F^-$ adsorbed on glass helices as described previously[5] for other strained-ring compounds could be effected in vacuo at 25 °C.

Oxaspiropentene is stable below about −70 °C. The ^{1}H NMR spectrum, recorded in tetrahydrofuran-d_8 at −95 °C, exhibits singlets at δ 2.89 and 7.28. ^{13}C NMR signals observed at 116.73, 38.87, and 30.76 ppm are in agreement with ^{13}C chemical shifts calculated using the MP2/6-311G-(d,p) basis set at the MP2/6-311G(d,p) geometry (Figure 1).[9]

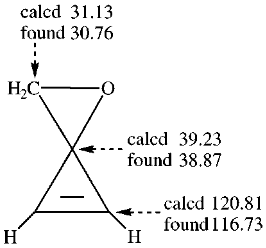


Figure 1. Experimental and calculated ^{13}C chemical shifts for **4**.

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[4] Halton, B.; Cooney, M. J.; Wong, H. *J. Am. Chem. Soc.* **1994**, *116*, 11574.

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[6] Spectral properties of *cis*-**5**: ^{1}H NMR δ 3.73 (d, 1H, J = 10.1 Hz), 3.34 (q, 2H, J = 4.9 Hz), 1.22 (d, 1H, J = 10.1 Hz), 0.17 (s, 9H); ^{13}C NMR 61.16, 49.98, 23.11, 12.75, −0.46 ppm; HRMS *m/e* calcd for $C_7H_{13}O^{79}Br$ 219.9911, found 219.9908, calcd for $C_7H_{13}O^{81}Br$ 221.9899, found 221.9985. Spectral properties of *trans*-**5**: ^{1}H NMR ($CDCl_3$) δ 3.29 (q, 2H, J = 5.9 Hz), 3.18 (d, 1H, J = 5.8 Hz), 1.04 (d, 1H, J = 5.8 Hz), 0.13 (s, 9H); ^{13}C NMR 61.34, 48.83, 19.13, 15.88, −1.82 ppm; CI HRMS *m/e* (m + 1) calcd for $C_7H_{14}O^{79}Br$ 220.9997, found 220.9994; calcd for $C_7H_{14}O^{81}Br$ 222.9978, found 222.9981.

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Molecular composition was provided by high-resolution mass spectroscopy: CI HRMS (m + 1) calcd for C_4H_5O m/e 69.0340, found 69.0343.

Optimized bond lengths for **4** calculated at the same level of theory are presented in Figure 2.

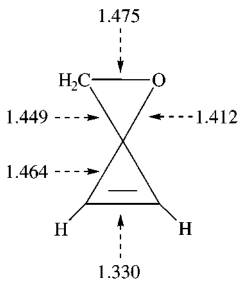
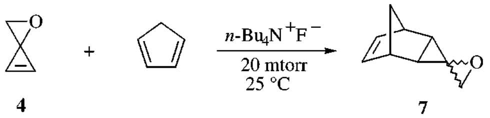


Figure 2. MP2/6-311G(d,p) geometry optimized bond lengths (Å).



4 **7**

The Diels–Alder adduct **7** could be isolated (one isomer) in 30% yield when **4** was condensed onto the surface of a cold trap coated with cyclopentadiene.[10] The ^1H NMR spectrum of **7** exhibits signals at δ 5.74 (t, 2H, $J = 2.1$ Hz), 3.01 (m, 2H), 2.94 (m, 2 H), 1.44 (s, 2H), 1.21 (dt, 1H, $J = 7.6, 1.5$ Hz), and 1.00 (d, 1H, $J = 7.6$ Hz). ^{13}C NMR signals were observed at 131.21, 63.17, 54.19, 47.87, 42.63, and 21.55 ppm. CI HRMS: (m + 1) calcd for $C_9H_{10}O$ m/e 135.0810, found 135.0816.

Studies on the X-ray crystal structure of **4** are planned.

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(10) The yield of **4** is probably somewhat higher than 30%.