trans-Tricyclo[5.1.0.0^{1,3}]octane

Thomas Miebach and Udo H. Brinker*

Department of Chemistry, State University of New York at Binghamton, Binghamton, New York, 13902-6000

Received June 16, 1993

Introduction

The construction of highly strained compounds containing a spiropentane subunit has often been achieved successfully through intramolecular addition of cyclopropylidenes (or the related carbenoids) to suitably positioned double bonds.[1] As has been shown in the accompanying publication,[2] however, this methodology fails for the preparation of tricyclo[5.1.0.0^{1,3}]octane (4). Although one highly substituted compound has been mentioned in the literature,[3] the parent hydrocarbon 4 is unknown.

Results and Discussion

In principle, it should be possible to synthesize 4 starting from 1,4-disubstituted dihalospiropentanes followed by introduction of an *n*-propano bridge through coupling reactions with properly substituted propane segments. This strategy should afford either *cis*- or *trans*-tricyclo[5.1.0.0^{1,3}]octane (4). We chose, however, a different four-step sequence for the synthesis of 4. Tricyclo[5.1.0.0^{1,3}]oct-3-ene (3),[4] a direct precursor to 4, had been prepared from 1,5-hexadiene by two-fold dibromocarbene addition to give bisadduct 1.[5] Treatment of 1 with 2 mol equiv of methyllithium at −78 °C afforded 7-methylenetricyclo[4.1.0.0^{1,3}]heptane (2).[5] One molar equivalent of methyllithium generates a cyclopropylidene which rearranges to form a terminal allene. The second molar equivalent generates a second cyclopropylidene which adds to the inner double bond of the allene. Thermolysis of 2[4] at 250 °C provided 3 in an isolated yield of 19%. The methylenecyclopropane–methylenecyclopropane rearrangement 2 → 3 is only a minor reaction pathway of 2.[4] Compound 3 was separated by preparative GC and obtained in a purity of >75% according to ^{1}H NMR with 2 being the main impurity. Hydrogenation of 3 at 0 °C with freshly prepared diimide[6] afforded 4 in 53% yield after GC separation.

The hydrogenation 3 → 4, in principle, could lead to *trans*- and/or *cis*-tricyclo[5.1.0.0^{1,3}]octane (4). According to our AM1 calculations,[7] ΔH_f of the *cis*-compound is about 24 kcal mol^{-1} higher than ΔH_f of *trans*-4. This trend is also reflected in a higher calculated strain energy (SE) of about 97 kcal mol^{-1} for *cis*-4.[8] The ^{13}C NMR spectrum of 4 reveals the five signals expected for a compound with C_2 symmetry, i.e., *trans*-4. In contrast, due to its C_1 symmetry, the spectrum of *cis*-4 should display 8 signals. In general, a double bond is approached by diimide at its less sterically hindered side.[9] Molecular modeling (AM1) of 3 reveals a methylenecyclopropane subunit which is slightly bent down in regard to the six-membered ring. Obviously, in the transition state diimide has easier access to the double bond when entering from the *same* side of the second cyclopropane ring leading to the formation of less strained *trans*-4. AM1 calculations of 4 reveal an angle at the quaternary carbon C1 (C2–C1–C8) of 150.1°. The corresponding angle C2–C1–C7 in *trans*-tricyclo[4.1.0.0^{1,3}]-heptane (5)[5] containing an ethano linkage connecting the three-membered rings of the spiropentane unit has been determined by X-ray crystallography[10] to be 158.2° (AM1, 161.8°). Therefore the additional CH_2 group in 4 causes a decrease of the C2–C1–C8 angle by about 12°. The strain energy for 5 has been calculated using *ab initio* methods and strainless group increments to be 80 kcal mol^{-1}.[11] Our AM1 calculations for 5 arrive at SE = 87 kcal mol^{-1} and ΔH_f = 63.5 kcal mol^{-1} (59 kcal mol^{-1} [11]). The same method calculates the energy for 4 to be SE = 73 kcal mol^{-1} and ΔH_f = 43.5 kcal mol^{-1}. Thus, when compared with 5, the additional CH_2 group in 4 reduces the strain energy by about 14 kcal mol^{-1}.

Studies of the reactive behavior of 4 are under investigation.

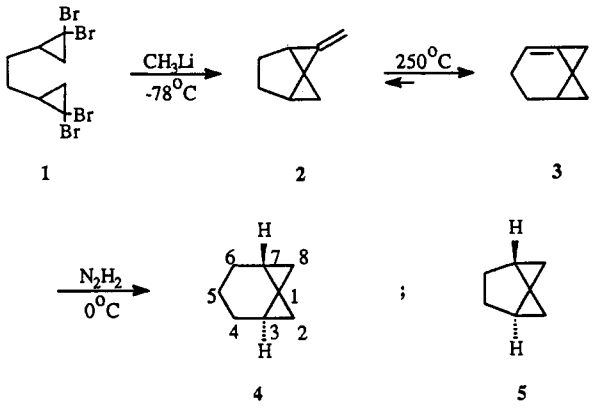

Figure 1.

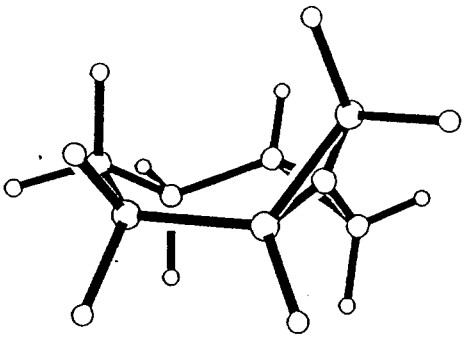

Figure 2. Structure of *trans*-tricyclo[5.1.0.0^{1,3}]octane (4) (AM1 calculation).

Experimental Section

General (See Preceding Paper in This Issue). Tricyclo[5.1.0.0^{1,3}]oct-3-ene (3). An amount of 1.24 g (11.7 mmol) of 2 was thermolyzedby injecting 25-μL portions into the injector of

(1) For a review see: Backes, J.; Brinker, U. H. In *Houben-Weyl, Methoden der Organischen Chemie*; Regitz, M., Ed.; Thieme: Stuttgart, 1989; Vol. E19, p 391.
(2) Miebach, T.; Wüster, H.; Brinker, U. H. Preceding paper in this issue.
(3) Köbrich, G.; Baumann, M. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 52.
(4) Roth, W. R.; Erker, G. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 505. Grimme, W.; Rother, H.-J. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 505.
(5) Skattebøl, L. *J. Org. Chem.* **1966**, *31*, 2789.
(6) Nagendrappa, G.; Devaprabhakara, D. *Tetrahedron Lett.* **1970**, 4243.
(7) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.
(8) Van Vechten, D.; Liebman, J. F. *Isr. J. Chem.* **1981**, *21*, 105.
(9) Pasto, D. J.; Taylor, R. T. *Org. React. (N.Y.)* **1991**, *40*, 91.
(10) Boese, R.; Bläser, D.; Gomann, K.; Brinker, U. H. *J. Am. Chem. Soc.* **1989**, *111*, 1501.
(11) Wiberg, K. B. *J. Org. Chem.* **1985**, *50*, 5285.

0022-3263/93/1958-6524$04.00/0

a preparative GC heated at 250 °C. The equilibrium mixture of **2** and **3** was separated on the attached column (6 ft, 20% TCEP on Chromosorb HP, 30 °C, 175 mL He/min). An amount of 158 mg (13%) of **3** was obtained, and 611 mg (49%) of **2** was recovered. The ^{1}H NMR spectrum indicated the purity to be >75%. The main impurity could be determined to be **2**. The yield based on 635 mg (5.98 mmol) of reacted **2** is calculated to be >19% (119 mg of pure **3**): ^{1}H NMR ($CDCl_3$, >75%, 360 MHz) δ 0.91 (t, 1H), 1.18–1.22 (m, 2H), 1.52–1.59 (m, 1H), 1.84–1.96 (m, 3H), 2.01–2.11 (m, 1H), 2.48–2.56 (m, 1H), 5.71–5.77 (m, 1H, H_{C4}); ^{13}C NMR ($CDCl_3$, >75%, 90.6 MHz) δ 9.5 (t, C8), 13.6 (t, C2), 14.1 (s, C1), 15.7 (d, C7), 22.9 (t, C5 or C6), 24.5 (t, C5 or C6), 109.0 (d, C4), 130.6 (s, C3).

Tricyclo[5.1.0.0^{1,3}]octane (4). An amount of 154 mg (purity >75%, 1.09 mmol) of the above-obtained **3** and 232 mg (7.25 mmol, 228 μL) of anhydrous hydrazine were dissolved in 3 mL of methanol, and 1 drop of a 1% aqueous copper(II) sulfate was added. After cooling to 0 °C, 272 mg (8 mmol, 907 μL) of a 30% solution of hydrogen peroxide was carefully added within 10 min. The solution was stirred for an additional 30 min. After dilution with 10 mL of water, the aqueous layer was extracted several times with pentane. Analytical GC showed the presence of three compounds (one main compound 94%). The pentane was carefully distilled off over a 20-cm vigreux column and the residue separated by preparative GC (10 ft, OV 101 on Chromosorb W HP, 30 °C, 50 mL He/min). Three fractions could be separated. First fraction: yield 63 mg (53%), purity 100% (GC). **3**: ^{1}H NMR ($CDCl_3$, 360 MHz) δ 0.59 (dd, 2H, $1H_{C2,syn}$, $1H_{C8,syn}$, J = 4.2 Hz), 0.85 ("septet", ddd, 2H, H_{C3}, H_{C7}), 1.01 (ddd, 2H, $1H_{C4}$, $1H_{C6}$) 1.07–1.18 (m, 4H, $H_{C2,anti}$, $H_{C8,anti}$, $2H_{C5}$), 1.72 ("sextet", 2H, $1H_{C4}$, $1H_{C6}$); ^{13}C NMR ($CDCl_3$, 90.6 MHz) δ 10.8 (d, 2C, J_{C-H} = 160 Hz, C3, C7), 12.5 (t, 2C, J_{C-H} = 160 Hz, C2, C8), 12.7 (s, C1), 21.3 (t, J_{C-H} = 126 Hz, C5), 24.4 (t, J_{C-H} = 127 Hz, C4, C6); FT IR ($CDCl_3$) 3693, 3604, 3050, 2988, 2924, 2852, 2656, 1601, 1516, 1446, 1409, 1333, 1319, 1258, 1192, 1148, 1137, 1095, 1064, 1037, 999, 840, 828, 568 cm^{-1}; HRMS m/z 108.0935 (calcd for 108.0939); MS m/z 108 (11, M^+), 107 (13), 106 (15), 105 (19), 94 (11), 93 (100), 91 (72), 80 (26), 79 (69), 78 (20), 77 (32). Second fraction: 5 mg (4%); probably 7-methyltricyclo[4.1.0.0^{1,3}]heptane. Third fraction: 2 mg (2%) of a compound of unknown structure.

Acknowledgment. T.M. thanks the Studienstiftung des deutschen Volkes for a dissertation fellowship and the Quadrille Ball Committee of the Germanistic Society of America for a supplementary fellowship.