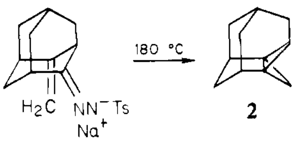
6862 J. Am. Chem. Soc. 1980, 102, 6862-6863

[3.1.1]Propellane[1]

Sir:

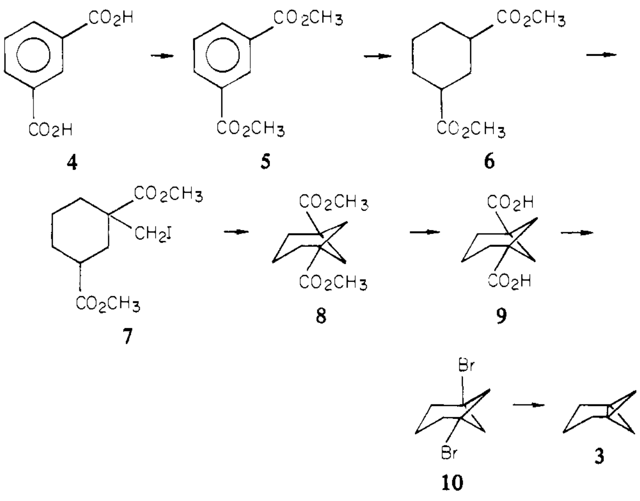
Recent years have witnessed extensive theoretical[2] and experimental[3] interest in the small propellanes.[4] Because of our previous involvement in the area[3a] and our extensive interest in derivatives of bicyclo[1.1.0]butane,[5] we were intrigued with the possibility of studying the synthesis and reactions of the [*n*.1.1]propellanes. Shortly after the initiation of our studies in this area, reports of the synthesis of complex derivatives of the [4.1.1]propellane system appeared.[6] Quite recently, the conversion of **1** into **2** has been reported.[7] It was this report which prompted us to disclose our results on the synthesis and reactions of the parent hydrocarbon, [3.1.1]propellane (**3**).



1 **2**

The synthesis of **3** originated with isophthalic acid (**4**) (Scheme I) which was converted into the corresponding dimethyl ester, **5**,[8] in 87% yield with methanol and *p*-toluenesulfonic acid. Catalytic reduction of **5** over 5% rhodium on alumina with hydrogen at 50 psi in a Parr hydrogenator gave 85% of **6**.[9] Treatment of **6** with 1 equiv of lithium diisopropylamide followed by 1 equiv of methylene iodide at −78 °C, stirring for 1 h, and warming to 25 °C gave a 66% yield of **7**:[10] ^{1}H NMR (CDCl$_3$) δ 3.70 (3 H, s), 3.63 (3 H, s), 3.25 (2 H, br s), 2.7–0.8 (9 H, m); ^{13}C NMR (CDCl$_3$) δ 174.84 (s), 172.66 (s), 51.75 (q), 51.17 (q), 47.07 (s), 39.74 (d), 35.84 (t), 33.97 (t), 27.93 (t), 22.55 (t), 15.71 (t). Refluxing a tetrahydrofuran solution of **7** with 2 equiv of potassium hydride[11] for 2 days gave a 46% yield of **8**: bp 78–79 °C (0.05 mmHg); ^{13}C NMR (CDCl$_3$) δ 175.28 (s), 51.58 (q), 42.12 (s), 37.85 (t), 29.35 (t), 15.78 (t). Saponification of **8** with potassium hydroxide in aqueous methanol followed by acidification gave a 90% yield of **9**: mp 210–215 °C dec; ^{13}C NMR (Me$_2$SO-d_6) δ 176.16 (s), 41.46 (s), 37.40 (t), 29.11 (t), 15.54 (t).

Scheme I



The conversion of **9** into **10** was particularly difficult. Numerous attempts conducted under a wide variety of conditions failed to yield the desired dibromide. Finally, a modified version of the Cristol–Firth modification[12] of the Hunsdiecker reaction[13] gave the desired dibromide. Treatment of **9** with 1.6 equiv of red mercuric oxide and 2.1 equiv of anhydrous magnesium sulfate in dibromomethane[14] at reflux for 1 h, cooling to 25 °C, and addition of 2.1 equiv of bromine gave 28% of **10**, mp 28.0–28.5 °C, after purification by alumina chromatography and molecular distillation: ^{13}C NMR (CDCl$_3$) δ 55.51 (t), 51.71 (s), 37.77 (t), 20.33 (t). This ^{13}C NMR spectrum can be compared with that of bicyclo[3.1.1]heptane (**11**):[15] ^{13}C NMR (CDCl$_3$) δ 34.13 (d), 33.15 (t), 29.31 (t), 15.90 (t).

The debromination of **10** to produce **3** proved to be a relatively clean reaction when carefully base-washed equipment was used and the reaction mixture and products were maintained under an inert atmosphere. Slow addition of a solution of **10** in triglyme to a refluxing slurry of sodium in triglyme resulted in the distillation of **3** directly into a trap at −78 °C. When 11 equiv of sodium were used, a 75% yield of clear, colorless **3** was obtained: M$^+$/*e* calcd for $C_7 10_{10}$, 94:0782; found, 94.0782. When warmed to room temperature, this material turned into a white solid which was sparingly soluble in common solvents and appeared to be of high molecular weight.

NMR data on **3** could be obtained by condensing the product of the debromination of **10** directly into toluene-d_8. The ^{1}H NMR spectrum was very complex, while the ^{13}C NMR was extremely simple; ^{13}C NMR δ 53.83 (t), 42.84 (t), 31.25 (t), 25.37 (s).[16] After the sample was allowed to remain for 2 weeks at 25 °C, the ^{1}H NMR spectrum was again measured and found to be essentially unchanged. Thus, while **3** appears to be quite unstable when concentrated, it can be stored in solution.

Condensation of **3** into methanol at −78 °C led to trace amounts of **11**[15,17] in addition to three methyl ethers. Considerable amounts of nonvolatile material were also formed. The hydrocarbon **11** was identified through comparison with an authentic sample.[15] The structure of **12** was based on its exact mass molecular weight

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(1) The "propellane" nomenclature will be used throughout this report. An alternate name for the title compound is tricyclo[3.1.1.0^{1,5}]heptane.

(2) (a) M. D. Newton and J. M. Schulman, *J. Am. Chem. Soc.*, **94**, 773 (1972); (b) W. D. Stohrer and R. Hoffmann, *ibid.*, **94**, 779 (1972); (c) M. D. Newton and J. M. Schulman, *ibid.*, **94**, 4391 (1972); (d) J. J. Dannenberg and T. M. Prociv, *J. Chem. Soc., Chem. Commun.*, **291** (1973); (e) E. M. Engler, J. D. Andose, and P. von R. Schleyer, *J. Am. Chem. Soc.*, **95**, 8005 (1973); (f) M. L. Herr, *Tetrahedron*, **33**, 1897 (1977).

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(10) Satisfactory elemental analyses and/or exact mass molecular weights were obtained on all new compounds.

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(16) This spectrum was measured at −78 °C. At 10 °C, slight shifts were noted: ^{13}C NMR δ 53.27 (t), 42.46 (t), 30.92 (t), 24.88 (s).

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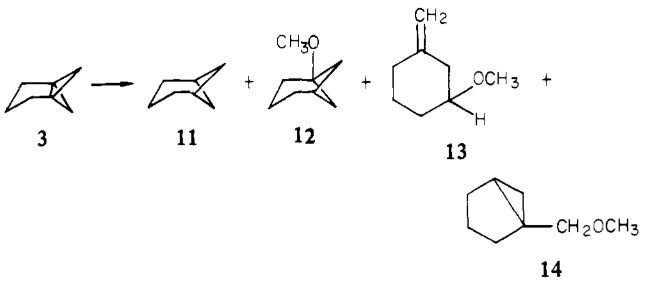

(M^+/e calcd for $C_8H_{14}O$, 126.1044; found, 126.1043) and NMR spectral data: ^{1}H NMR ($CDCl_3$) δ 3.17 (3 H, s), 2.0–1.5 (11 H, br m); ^{13}C NMR (CD_3CN) δ 50.02, 37.21, 33.60, 28.33, 26.63, and 18.07.[18] The ^{13}C NMR spectrum of **12** was very similar to those of other bicyclo[3.1.1]heptane derivatives. Compound **13** could not be obtained free of **14**. Thus, it was identified through comparison with an authentic sample of **13**[19] which showed the following data: ^{13}C NMR (CD_3CN) δ 147.92 (s), 109.43 (t), 79.85 (d), 55.77 (q), 41.22 (t), 35.09 (t), 31.84 (t), 24.72 (t). Unfortunately, we were unable to obtain **14** as a pure compound. However, the presence of absorptions in the ^{1}H NMR spectrum at δ 0.45–0.25 and in the ^{13}C NMR spectrum at δ 58.49 (q), coupled with the complete absence of absorptions which could be attributed to olefinic carbons, suggests that this compound might be the cyclopropylcarbinyl methyl ether **14**. This analysis was confirmed through comparison of **14** with an authentic sample which was synthesized via Simmons–Smith cyclopropanation[20,21] of 1-hydroxymethylcyclopentene[22] followed by methylation of the alkoxide anion with methyl iodide.

In summary, [3.1.1]propellane has been synthesized and found to be stable in solution at room temperature. Our results counter the pessimism of those who questioned whether **3** would be a stable entity.[2f,23] We are continuing to investigate the chemical properties of **3** and of related small propellanes.

Acknowledgment. We are indebted to the National Science Foundation for Grant CHE78-10231 which supported this investigation.

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(18) Only six of the expected seven signals were observed. Relative intensities suggest that the signal due to C-1 is missing.

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(24) National Science Foundation Fellow, 1976–1979.

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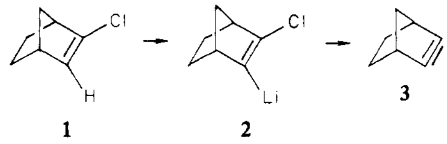
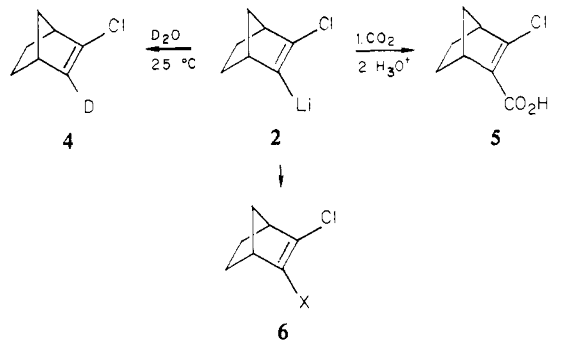
Synthesis and Reactions of 2-Lithio-3-chlorobicyclo[2.2.1]hept-2-ene. Generation of the Trimer of Bicyclo[2.2.1]hept-2-yne

Sir:

In a detailed study of the mechanism of the reaction of 2-chlorobicyclo[2.2.1]hept-2-ene (**1**) with *n*-butyllithium, Gassman and Valcho[1] convincingly demonstrated that **1** underwent an acid–base reaction with *n*-butyllithium to produce **2**. Spontaneous loss of lithium chloride under the reaction conditions (large excess of organolithium) then produced bicyclo[2.2.1]hept-2-yne (**3**) as a highly reactive intermediate which immediately added the excess *n*-butyllithium. As part of a program designed to explore the chemistry of highly strained acetylenes, we desired to generate **3** in the absence of excess organolithiums. We now report on the synthesis and reactions of **2**, including its conversion to **3** and the subsequent trimerization of **3**.



Treatment of **1** with 1 equiv of *tert*-butyllithium in 1:1 tetrahydrofuran–pentane at −45 °C gave 2-lithio-3-chlorobicyclo-[2.2.1]hept-2-ene (**2**) as the exclusive product.[2] We found that **2** was quite stable when generated in this manner. No detectable decomposition of **2** was noted when the solution of **2** was warmed to 25 °C and maintained at that temperature for 12 h. This was demonstrated through conversion to **4** in 70% yield with deuterium oxide, and carbonation of **2** to give **5** in 60% yield.[3] The stability of **2** made it an attractive intermediate for the preparation of a variety of sustituted derivatives of bicyclo[2.2.1]hept-2-ene of general formula **6**. Thus, **2** reacted with (a) trimethylsilyl chloride, (b) carbon tetrachloride, (c) 1,2-dibromoethane, and (d) methyl iodide to give **6a** (40%), **6b** (34%), **6c** (50%), and **6d** (47%), respectively.



6a, X = $Si(CH_3)_3$
6b, X = Cl
6c, X = Br
6d, X = CH_3

The stability of **2** at 25 °C can be compared with the reported stabilities of other 1-lithio-2-halocycloalkenes. 1-Lithio-2-bromocyclohexene, 1-lithio-2-bromocyclopentene, and 1-lithio-2-bromoacenaphthene are reported to lose lithium bromide at <−120 °C,[4] 25 °C,[5] and 100 °C,[6] respectively. 1-Lithio-2-fluorobenzene was reported to yield benzyne at −65 °C[7] while 2-lithio-1-chloro-3,3-dimethylindene was stable to 25 °C.[8] Thus, it was of interest to establish the temperature at which **2** would lose lithium chloride. Heating of the solution of **2** to 45 °C for 4 h resulted in the complete disappearance of **2**. In addition to a large amount of high molecular weight, intractable gum, the reaction gave 9–11% of a white solid, mp 162–164 °C. The UV spectrum of this material showed λ_{max} (ethanol) 269 nm (ϵ 242). This, coupled with the absence of any aromatic or olefinic protons in the NMR spectrum, was diagnostic of a hexasubstituted benzene derivative.[9] ^{13}C NMR spectra indicated the presence of two components. This 2:1 mixture of **7** and **8** was separated by preparative VPC on a 10% SE-30 on 60:80 Chromasorb W column at 220 °C. The major component, mp 165–168 °C,

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(1) P. G. Gassman and J. J. Valcho, *J. Am. Chem. Soc.*, **97**, 4768 (1975).

(2) In contrast, when a similar reaction was carried out at 25 °C, **1** gave 38% of bicyclo[2.2.1]hept-2-ene, 44% of 3-*tert*-butyltricyclo[2.2.1.0^{2,6}]heptane, and only 5% of **1** after hydrolysis.

(3) Satisfactory elemental analyses and/or exact mass molecular weights were obtained on all new compounds.

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