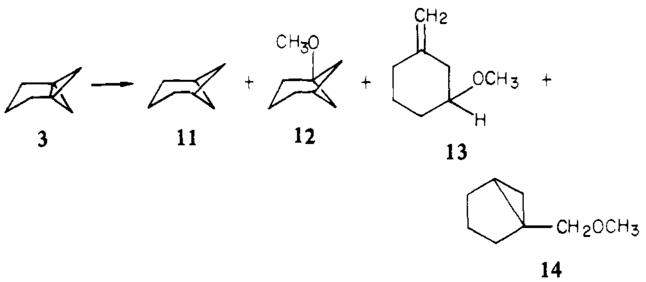


($M^+/e$ calcd for $C_8H_{14}O$, 126.1044; found, 126.1043) and NMR spectral data: $^1$H NMR ($CDCl_3$) δ 3.17 (3 H, s), 2.0–1.5 (11 H, br m); $^{13}$C NMR ($CD_3CN$) δ 50.02, 37.21, 33.60, 28.33, 26.63, and 18.07.[18] The $^{13}$C NMR spectrum of **12** was very similar to those of other bicyclo[3.1.1]heptane 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.

---

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

(19) J. B. Lambert and R. R. Clikeman, *J. Am. Chem. Soc.*, **98**, 4203 (1976).

(20) H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **81**, 4256 (1959).

(21) S. Winstein and J. Sonnenberg, *J. Am. Chem. Soc.*, **83**, 3235 (1961).

(22) M. J. Bullivant and G. Pattenden, *J. Chem. Soc., Perkin Trans. 1*, 249 (1976).

(23) J. F. Liebman and A. Greenberg, *Chem. Rev.*, **76**, 311 (1976).

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

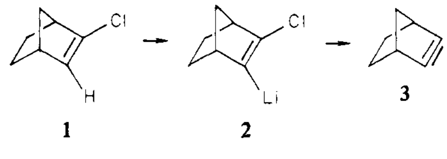
**Paul G. Gassman,* Gary S. Proehl**[24]
*Department of Chemistry, University of Minnesota*
*Minneapolis, Minnesota 55455*

*Received July 16, 1980*

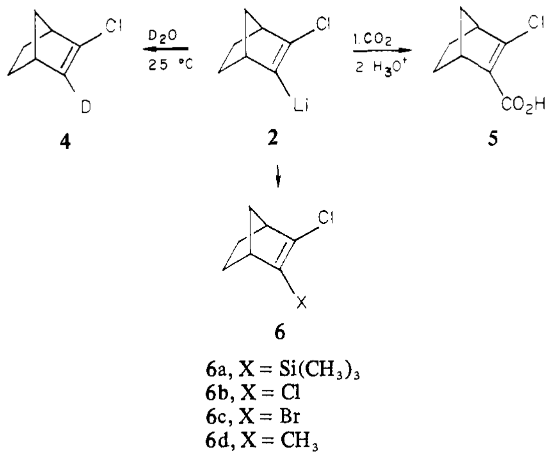
## Synthesis and Reactions of 2-Lithio-3-chlorobicyclo[2.2.1]hept-2-ene. Generation of the Trimer of Bicyclo[2.2.1]hept-2-yne

*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 $\lambda_{max}$ (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,

---

(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.

(4) G. Wittig and U. Mayer, *Chem. Ber.*, **96**, 329 (1963).

(5) G. Wittig, J. Weinlich, and E. R. Wilson, *Chem. Ber.*, **98**, 458 (1965).

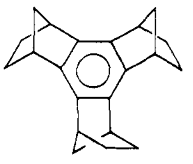
(6) K. Rasheed, *Tetrahedron*, **22**, 2957 (1966).

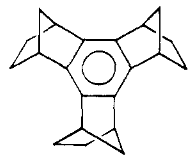
(7) H. Gilman and R. D. Gorsich, *J. Am. Chem. Soc.*, **78**, 2217 (1956).

(8) G. Wittig and H. Heyn, *Chem. Ber.*, **97**, 1609 (1964).

(9) The UV spectrum of the trimer of cycloheptyne showed $\lambda_{max}$ 274 nm (ε 262): R. Breslow, L. Altman, A. Krebs, E. Mohasci, I. Murata, R. A. Peterson, and J. Posner, *J. Am. Chem. Soc.*, **87**, 1326 (1965).

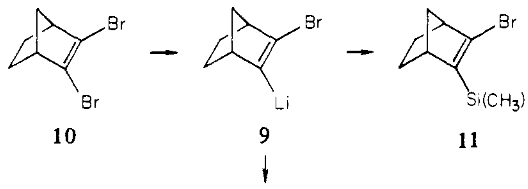
showed four sets of peaks in its $^{13}$C NMR spectrum at 136.2 and 123.72 (s), 48.69 and 48.44 (t), 41.21 and 41.11 (d), and 27.43 and 27.12 (t) ppm, indicating that it was the syn–anti–syn isomer, **7**.[10] The $^{13}$C NMR spectra of the minor isomer, mp 175–180 °C, showed only four absorptions at 136.19 (s), 48.91 (t), 41.05 (d), and 27.09 (t) ppm, indicating that it was the all-syn isomer, **8**.


**7**


**8**

The formation of trimers, in yields ranging from 2–44%, has been used as evidence for the formation of cyclooctyne,[11] cycloheptyne,[9,12] cyclohexyne,[9] and cyclopentyne.[5] We suggest that the isolation of **7** and **8** provides equally strong evidence for the transitory existence of bicyclo[2.2.1]hept-2-yne (**3**). We believe that this is the most strained acetylene derivative prepared thus far.

The results above raised the question of why **2** appeared to decompose at 25 °C under the conditions of excess *n*-butyllithium[1] but was stable at 25 °C when prepared as described above. We felt that the decomposition of **2** might be promoted by excess organolithium reagents. This was substantiated by the observation that addition of *tert*-butyllithium, methyllithium, or *n*-butyllithium to **2** promoted its dehydrohalogenation at 25 °C. Both *tert*-butyllithium and methyllithium promoted the conversion of **2** into high molecular weight oligomers and a mixture of **7** and **8**. In contrast, *n*-butyllithium promoted the conversion of **2** to 2-*n*-butylbicyclo[2.2.1]hept-2-ene which was the major product identified previously.[1]



**10** **9** **11**

**7** + **8**

Lastly, we examined the stability of **9**. Unfortunately, **9** could not be prepared through an acid–base reaction of 2-bromobicyclo[2.2.1]hept-2-ene with an organolithium reagent due to the propensity of the bromide to undergo halogen–metal exchange reactions. Thus, **10** was used as the precursor.[13] Treatment of **10** with *n*-butyllithium in tetrahydrofuran–hexane at −78 °C gave **9**. When a solution of **9** was warmed quickly to 25 °C, only intractable material was formed. In contrast, addition of (chlorotrimethyl)silane to a solution of **9** at −78 °C, gave a 90% yield of **11**, which substantiated the intermediacy of **9**.[14] Since acetylene trimerization is known to be catalyzed by certain transition-metal complexes,[15] we questioned whether the addition of such complexes to a solution of **9** at −78 °C followed by warming would produce **7** and **8**. When a solution of **9** was treated with nickelocene[16] and allowed to warm to room temperature, a 37% yield of a mixture of **7** and **8** was obtained. Other transition-metal derivatives which promoted formation of the trimer of bicyclo[2.2.1]hept-2-yne were nickel(II) chloride, iron(III) chloride, copper(I) iodide, copper(II) chloride, and cyclopentadienylbis(triphenylphosphine)cobalt.[15]

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

**Paul G. Gassman,* Irene Gennick**[17]
*Department of Chemistry, University of Minnesota*
*Minneapolis, Minnesota 55455*

*Received June 30, 1980*

---

[10] Theoretically, one would expect three separate resonances for the bridgehead carbons, three different aromatic carbons, three different ethanobridge carbons, and two different methanobridge carbons. However, in view of the small chemical shift differences within the sets, some degeneracy might be expected.

[11] G. Wittig and S. Fischer, *Chem. Ber.*, **105**, 3542 (1972).

[12] G. Wittig and J. Meske-Schüller, *Justus Liebigs Ann. Chem.*, **711**, 65 (1968).

[13] The synthesis of **10** will be reported elsewhere: P. G. Gassman and I. A. Gennick, *J. Org. Chem.*, in press.

[14] In a similar manner, treatment of **9** with iodine gave a 60% yield of 2-bromo-3-iodobicyclo[2.2.1]hept-2-ene.

[15] K. P. C. Vollhardt, *Acc. Chem. Res.*, **10**, 1 (1977).

[16] W. L. Jolly and D. J. Chozan, *Inorg. Synth.*, **11**, 122 (1968).

[17] National Science Foundation Predoctoral Fellow, 1975–1978; Louise T. Dosdall Graduate Fellow, 1978–1979; Lubrizol Foundation Fellow, Summer 1979.

---

## Mixed Valence and Magnetically Coupled Vanadate Domains in Heteropoly Tungstate Anions

*Sir:*

The analogy between heteropoly anions and metal oxide lattices vis-à-vis structures and catalytic properties has been recognized for several years.[1] Partially reduced polyanions ("heteropoly blues")[2] are of considerable interest because, in principle, they provide insight into electron mobility (semiconduction) and magnetic exchange interactions in metal-oxide-like environments. Analysis of such processes in heteropoly blues and oxides has been complicated by the existence of numerous "intramolecular" pathways for electron transfer and magnetic coupling. We have recently developed stereospecific syntheses of certain mixed-metal polyanions and can use these to explore electronic interactions between a small number of adjacent metal atoms in a polyanion. We report here the first ESR and magnetic data for complexes of this sort in which unpaired electrons are restricted to two or three oxygen-bridged vanadium atoms.

The complexes are $\alpha$-1,2-$SiV_2W_{10}O_{40}^{6-}$ (**1**) and $\alpha$-1,2,3-$SiV_3W_9O_{40}H^{6-}$ (**2**) and their reduced forms. It is believed that the vanadium atoms in **1** and **2** occupy adjacent corner-sharing "octahedral" sites in the Keggin structure (Figure 1).[3] Controlled potential reduction of **1** and **2** yields green $\alpha$-$SiV^{IV}V^{V}W_{10}O_{40}^{7-}$ (**1a**) and $\alpha$-$SiV^{IV}V_2^{V}W_9O_{40}H_x^{8-x}$ (**2a**) with the ESR spectra shown in Figure 2. The 15-line spectrum ($g = 1.966$, $a = 51$ G) for **1a** is consistent with an electron interacting with two equivalent vanadium-51 nuclei ($I = {}^7/_2$)[4] and stands in contrast to the spectrum of a mixture of isomers of $\alpha$-$PV^{IV}V^{V}W_{10}O_{40}^{6-}$ which consists of both 8- and 15-line components.[5] The ESR spectrum of **2a** consists of more than 40 equally spaced hyperfine lines ($g = 1.960$) and has been interpreted according to the stick diagram shown in Figure 2. The interpretation assumes a spectrum of eight equally intense lines ($a_1 = 68$ G) each one of which is split into

---

[1] Baker, L. C. W. In "Advances in the Chemistry of Coordination Compounds"; Kirschner, S., Ed.; Macmillan: New York, 1961; p 604.

[2] Pope, M. T. In "Mixed Valence Compounds in Chemistry, Physics and Biology"; Brown, D. B., Ed.; Reidel: Amsterdam, 1980.

[3] The complexes are prepared as potassium salts from $\alpha$-$SiW_9O_{34}H^{8-}$ and $VO_3^-$ (**2**) or partially hydrolyzed $\alpha$-$SiW_{12}O_{40}^{4-}$ and $VO^{2+}$ (**1b** and subsequent oxidation to **1**). Details will be given in forthcoming publications. Analyses: K, Si, V, W, $H_2O$. $^{51}$V FT NMR spectra (24 and 71 MHz) consist of a single symmetrical line for each complex. At 80 °C, pH 2, chemical shifts from $VOCl_3$ and line widths are **1**, −536 ppm, 66 Hz; **2**, −566 ppm, 130 Hz. On the basis of the structure of the precursor ion, the vanadium atoms in **1** and **2** occupy the sites shown in Figure 1. Alternative structures in which the vanadium atoms occupy adjacent edge-shared octahedra would also be consistent with the data of the present paper, but are considered unlikely.

[4] To our knowledge, the only other example of a 15-line mixed-valence vanadium ESR spectrum was recently reported for $\mu$-oxybis(nitrilotriacetato)oxovanadate(IV,V): Nishizawa, M.; Hirotsu, K.; Ooi, S.; Saito, K. *J. Chem. Soc., Chem. Commun.* **1979**, 707. We are unable to say with present data whether the electron is delocalized or rapidly hopping in these cases.

[5] Pope, M. T.; O'Donnell, S. E.; Prados, R. A. *J. Chem. Soc., Chem. Commun.*, **1976**, 85.

0002-7863/80/1502-6864$01.00/0