acetate–hexanes) gave 48.7 mg (57%) of pure alcohol: R_f 0.15 (15% ethyl acetate–hexanes); IR (neat) 3330, 1439, 1049, and 1035 cm^{-1}; ^{1}H NMR δ 3.75 (m, 1 H), 2.16 (m, 1 H), 1.82–1.13 (complex pattern, 17 H), 0.94 (t, J = 6.90 Hz, 3 H); ^{13}C NMR δ 70.44 (*C*HOH), 46.66 (C(1)), 44.36 (C(7)), 43.57 (*C*H$_2$CHOH), 41.22 (CH(OH)*C*H$_2$), 36.68 (C(4)), 35.20 (C(2 or 6)), 34.83 (C(4 or 2)), 30.99 (C(3 or 5)), 30.56 (C(5 or 3)), 18.84 (*C*H$_2$CH$_3$), 14.09 (CH$_3$); HRMS calcd for $C_{12}H_{23}O$ (CI, MH$^+$) 183.1749, found 183.1745.

1-[(Methylthio)methyl]bicyclo[2.2.1]heptane. A solution of **3**, prepared from 109.6 mg (0.46 mmol) of **1**, was cooled to −78 °C, and 0.085 mL (0.93 mmol) of dimethyl disulfide was added in one portion. The reaction mixture was allowed to warm to room temperature and was then poured into 10 mL of brine. The organic phase was separated, the aqueous phase was extracted with fresh pentane, and the combined organic layers were dried (MgSO$_4$). Volatile components were removed by rotary evaporation to give 50.8 mg (70%) of pure product: ^{1}H NMR δ 2.76 (s, 2 H), 2.20–2.11 [overlapping patterns, i.e., 2.20–2.11 (m, 1 H), 2.15 (s, 3 H)], 1.75–1.17 (complex m, 10 H); ^{13}C NMR δ 48.64 (C(1)), 43.16 (C(7)), 41.74 (C(8)), 37.22 (C(4)), 34.42 (C(2,6)), 30.74 (C(3,5)), 17.78 (CH$_3$); HRMS calcd for $C_9H_{16}S$ 156.0973, found 156.0981.

1-[(Trimethylsilyl)methyl]bicyclo[2.2.1]heptane. A solution of **3**, prepared from 203.2 mg (0.86 mmol) of **1** via the general procedure described above, was cooled to −78 °C, and 0.22 mL (1.7 mmol) of freshly distilled chlorotrimethylsilane was added via syringe. The solution was allowed to warm to room temperature and worked up in the usual manner to afford the TMS derivative as an oil. Purification by chromatography on silica gel (*n*-pentane as eluent) gave 95.2 mg (61%) of the title compound: R_f 0.51 (pentane); IR (neat) 1451, 1413, 1239, and 837 cm^{-1}; ^{1}H NMR δ 2.10 (m, 1 H), 1.38–1.11 (m, 10 H), 0.89 (s, 2 H), 0.01 (s, 9 H); ^{13}C NMR δ 47.17 (C(7)), 46.01 (C(1)), 37.11 (C(2,6)), 36.80 (C(4)), 31.29 (C(3,5)), 24.52 (CH$_2$-TMS), 0.54 (CH$_3$); HRMS calcd for $C_{11}H_{22}Si$ 182.1492, found 182.1501.

Acknowledgment. This work was supported by a grant from the Humphrey Chemical Company, North Haven, CT, and by the Connecticut Department of Higher Education under Grant No. 90-630.

Registry No. 1, 129917-14-2; 1-methylbicyclo[3.3.1]heptane, 10052-18-3; (1-bicyclo[2.2.1]heptyl)acetic acid, 93980-80-4; ethyl 2-(3-oxocyclopentyl)acetate, 62457-60-7; ethyl 2-(3-methylenecyclopentyl)acetate, 129917-15-3; 2-(3-methylenecyclopentyl)ethanol, 113616-12-9; 1-[(2-mesyloxy)ethyl]-3-methylenecyclopentane, 129917-16-4; 1-bicyclo[2.2.1]heptylacetaldehyde, 129917-17-5; 2-(1-bicyclo[2.2.1]heptyl)ethanol, 129917-18-6; 1-(1-bicyclo[2.2.1]heptyl)propan-2-ol, 34298-82-3; 1-(1-bicyclo[2.2.1]heptyl)pentan-2-ol, 129917-19-7; 1-[(methylthio)methyl]bicyclo[2.2.1]heptane, 129917-20-0; 1-[(trimethylsilyl)methyl]bicyclo[2.2.1]heptane, 129917-21-1; acetaldehyde, 75-07-0; *n*-butyraldehyde, 123-72-8.

Supplementary Material Available: ^{1}H and ^{13}C spectra for all new compounds (16 pages). Ordering information is given on any current masthead.

---

^{13}C NMR Spectroscopic Study of γ-Substituted Tris(ethynyl)methyl Cations[1]

George A. Olah,* Ramesh Krishnamurti, and
G. K. Surya Prakash*

Donald P. and Katherine B. Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, Los Angeles, California 90089-1661

Received April 16, 1990

Introduction

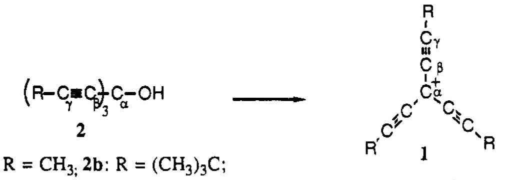
Over the years there has been considerable interst in the study of alkynylcarbocations (propargyl cations) (A)[2]. The positive charge in these cationic systems can be delocalized over the ethynyl system, thus giving rise to mesomeric allenyl cations (B). Such allenyl cations are of significant interest because they are structurally related to the elusive vinyl cations. We[2b] have earlier utilized ^{13}C NMR spectroscopy to study a number of alkylethynylmethyl cations. By choosing appropriate reference compounds, the relative contribution of the two mesomeric structures was estimated. In contrast to the mono(alkylethynyl)methyl cations, however, little is known about the bis- and tris(alkylethynyl)methyl cations.[3] Miller and co-workers[4] previously studied the tris(*tert*-butylethynyl)methyl cation by ^{1}H NMR spectroscopy. No ^{13}C data were, however, reported. Komatsu et al.[3b] prepared tris(phenylethynyl)methyl cation and studied its ^{13}C NMR parameters. They found that the degree of positive charge delocalization to C$_\gamma$ apparently increases as the number of ethynyl groups increases. However, no study, to date, has been reported in which the extent of charge delocalization in a series of γ-substituted tris(alkylethynyl)methyl cations was examined with regard to the C$_\gamma$-substituent.

A **B**

Results and Discussion

In our continued interest in persistent ethynylmethyl cations, we undertook a study of a series of γ-substituted tris(ethynyl)methyl cations.[2]

Ion **1a–d** were prepared by ionization of the corresponding γ-substituted tris(alkyl)methyl alcohols **2a–d** in FSO$_3$H–SO$_2$ClF solution at −78 °C.



2 **1**

2a: R = CH$_3$; **2b**: R = (CH$_3$)$_3$C;
2c: R = (CH$_3$)$_3$Si; **2d**: R = Ph;
2e: R = H

1a: R = CH$_3$; **1b**: R = (CH$_3$)$_3$C;
1c: R = (CH$_3$)$_3$Si; **1d**: R = Ph;
1e: R = H

Tris(propynyl)methyl alcohol **2a** was prepared by the reaction of propynyllithium (generated from 1-propyne and methyllithium) with diethyl carbonate. Similar, γ-(trimethylsilyl)propynyllithium and γ-phenylpropynyllithium were generated from the corresponding acetylene and treated with diethyl carbonate to afford **2c** and **2d**, respectively. Tris(3,3-dimethylbutynyl)methyl alcohol (**2b**) was prepared by the literature procedure.[4]

Carbon-13 NMR spectroscopy was used for the study of ions **1a–d** as carbon-13 chemical shifts give an indication of the charge densities at carbon atoms of similar hybridization and substitution.[2b,5] The ^{13}C NMR parameters

---

[1] Stable Carbocations. 279. Part 278, see: Olah, G. A.; Prakash, G. K. S.; Krishnamurti, R. *J. Am. Chem. Soc.*, in press.

[2] (a) Richey, H. G., Jr.; Richey, J. M. *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley Interscience: New York, 1970; Vol. 2. (b) Olah, G. A.; Spear, R. J.; Westerman, P. W.; Denis, J.-M. *J. Am. Chem. Soc.* **1974**, *96*, 5855. (c) Mayr, H.; Schneider, R. *Chem. Ber.* **1982**, *115*, 3470. (d) Prakash, G. K. S.; Krishnamurthy, V. V.; Olah, G. A.; Farnum, D. G. *J. Am. Chem. Soc.* **1985**, *107*, 3928. (e) Krishnamurthy, V. V.; Prakash, G. K. S.; Iyer, P. S.; Olah, G. A. *J. Am. Chem. Soc.* **1986**, *108*, 1575.

[3] (a) Richey, H. G., Jr.; Rennick, L. E.; Kushner, A. S.; Richey, J. M.; Philips, J. C. *J. Am. Chem. Soc.* **1965**, *87*, 4017. (b) Komatsu, K.; Takai, T.; Aonuma, S.; Takeuchi, K. *Tetrahedron Lett.* **1988**, *29*, 5157.

[4] Tseng, C. K.; Migliorese, K. G.; Miller, S. I. *Tetrahedron* **1974**, *30*, 377.

[5] (a) Spiesecke, H.; Schneider, W. G. *Tetrahedron Lett.* **1961**, 468. Olah, G. A.; Westerman, P. W. *J. Am. Chem. Soc.* **1973**, *95*, 7530.

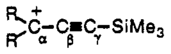
0022-3263/90/1955-6061$02.50/0

Table I. ^{13}C NMR Chemical Shifts[a] of Tris(ethynyl)methyl Cations (1a–d) and Their Precursor Alcohols (2a–d)

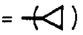
compd	C_α	C_β	C_γ	other carbons
1a	164.4	105.6	157.6	9.2
1b	162.6	105.3	164.1	33.1, 27.6
1c	166.3	101.3	144.9	−2.2
1d	140.7	110.5	137.9	118.9, 130.0 137.2, 137.5
1e[b]	–	–	–	–
2a	54.0	77.9	78.8	3.4
2b	54.5	78.2	90.4	27.2, 30.3
2c	54.7	88.1	101.6	−0.8
2d	55.6	83.1	86.6	121.5, 128.2 129.0, 132.0
2e	53.4	80.3	72.0	–

[a] In ppm, referenced to TMS. The spectra of cations **1a–d** were measured in SO_2ClF at −60 °C using $(CD_3)_2C{=}O$ (29.8 ppm) in a coaxial capillary tube. The spectra of the precursors were run in $CDCl_3$. [b] Attempts to generate this ion were unsuccessful (see text).

Scheme I



3

	chemical shift (ppm) of C_β
3a: R= 	98.3
3b: R= C_6H_5	111.3
3c: R= CH_3	126.3
1c: R= $Me_3SiC{\equiv}C$	101.3

of ions **1a–d** and their precursors **2a–d** are given in Table I.

Attempts to prepare the parent tris(ethynyl)methyl cation **1e** from the alcohol **2e**[6] using a variety of superacid systems (SbF_5–FSO_3H (1:1), FSO_3H, CF_3SO_3H) were so far unsuccessful. The data show that in all cases C_α and C_γ are deshielded more than C_β (relative to their precursor alcohols). This clearly indicates significant participation of resonance structures with allenyl cationic character. The positive charge is delocalized throughout the triethynyl framework to give a highly cross-conjugated cationic system. Another observation that is apparent from data of Table I is the relatively large shielding of C_γ in ion **1d** relative to those in **1a–c**. This shows that shielding of C_γ in **1d** is due to charge dispersal into the aromatic ring. In ions **1a** and **1b**, only hyperconjugative interaction is possible with the result that C_γ is relatively deshielded compared to **1d**. The trimethylsilyl-substituted ion **1c**, interestingly, shows C_γ significantly shielded relative to **1a** and **1b**. Also there is almost no deshielding of the C_β-carbon in **1c** relative to those in the other ions. Earlier observations on a series of trimethylsilyl-substituted ethynyl carbocations **3a–c** indicated that as the ability of the R group to delocalize positive charge increased, C_β became more shielded (Scheme I).[7] When the R group is a (trimethylsilyl)ethynyl group, C_β in the ion **1c** has a chemical shift of $\delta(^{13}C)$ 101.3. Comparing this value with those for C_β in **3a** and **3b** would appear to indicate that the delocalizing ability of the (trimethylsilyl)ethynyl group lies between those of the cyclopropyl and the phenyl group.

Attempts to prepare the parent tris(ethynyl)methyl cation **1e** using a variety of acid systems were unsuccessful presumably due to the highly reactive unsubstituted termini of the three ethynyl groups and resulting low kinetic stability. However, when one of the terminal acetylenic hydrogens in **2e** is replaced by methyl, phenyl, or cyclopropyl groups, stable carbocations have been obtained using fluorosulfuric acid in sulfur dioxide.[8]

In summary, a variety of stable γ-substituted tris(ethynyl)methyl cations were prepared under stable ion conditions in fluorosulfuric acid–sulfuryl chloride fluoride at low temperatures. The ^{13}C NMR chemical shifts of the studied ions **1** appear to indicate that electronic effects due to different γ-substituents are only marginal. The dominant stabilizing factor is due to delocalization of positive charge into the three ethynyl groups.

Experimental Section

General. Carbon-13 and proton NMR system were measured using a Varian Associates VXR-200 spectrometer. Chemical shifts are expressed in parts per million (ppm) and referenced to external capillary tetramethylsilane signal.

Tris(propynyl)methyl (**2a**),[6] tris(3,3-dimethylbutynyl)methyl (**2b**),[4] tris((trimethylsilyl)ethynyl)methyl (**2c**),[6] and tris(phenylethynyl)methyl (**2d**) alcohols[3b] were prepared using published procedures. Tris(ethynyl)methyl alcohol (**2e**) was prepared in 77% yield by desilylation of the trimethylsilyl derivative (**2c**) with aqueous KF (instead of ethanolic KOH,[6] which did not work satisfactorily).

Generation of the Carbocations (1a–d). General Procedure. To a cold (−78 °C) mixture of 40 mg of the alcohol (**2a–d**) in SO_2ClF was dropwise added a cold (−78 °C) solution of FSO_3H in SO_2ClF. The resulting solution was transferred to a 5-mm NMR tube, and ^1H and ^{13}C spectra were recorded at −85 °C (using capillary acetone-d_6 as the deuterium lock, as well as the reference). The chemical shifts of the ions and their precursors are summarized in Table I. Attempts to generate tris(ethynyl)methyl cation (**1e**) using FSO_3H, FSO_3H–SbF_5 (1:1), and CF_3SO_3H were unsuccessful and always led to decomposition.

Acknowledgment. Support of our work by the National Institutes of Health is gratefully acknowledged.

Registry No. **1a**, 129849-47-4; **1b**, 52917-33-6; **1c**, 129849-48-5; **1d**, 120758-25-0; **2a**, 52917-34-7; **2b**, 52917-32-5; **2c**, 118569-20-3; **2d**, 50428-40-5; **2e**, 27410-30-6.

---

[6] Alberts, A. H.; Wynberg, H. *J. Chem. Soc., Chem. Commun.* **1988**, 748.

[7] Olah, G. A.; Berrier, A. L.; Field, L. D.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1982**, *104*, 1349.

[8] Richey, H. G., Jr.; Rennick, L. E.; Kushner, A. S.; Richey, J. M.; Philips, J. C. *J. Am. Chem. Soc.* **1965**, *87*, 4017.