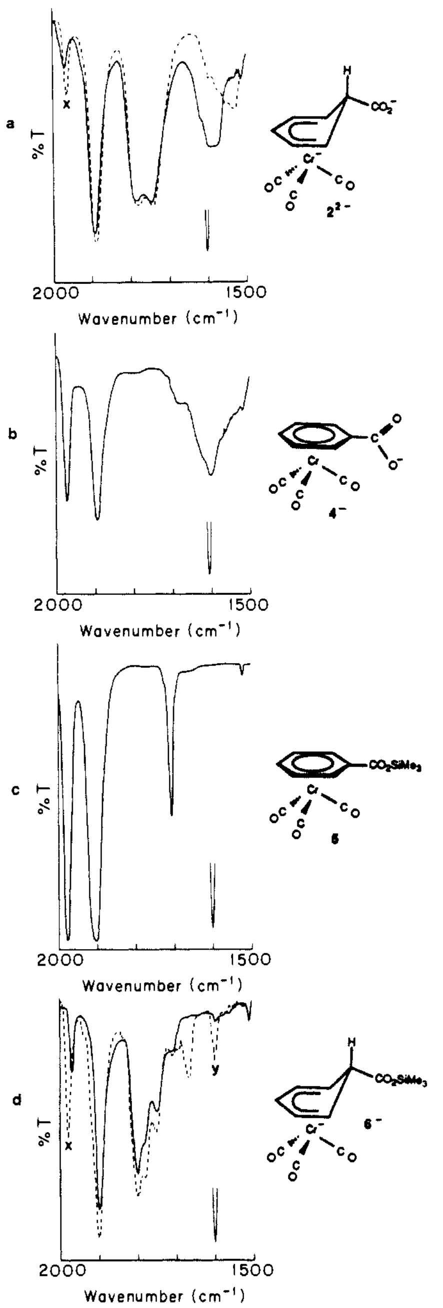

Figure 1. Solution IR spectra (%T) in C≡O and C=O stretching region of the principal CO_2 adducts and derivatives in Scheme I. Peaks marked x correspond to **1** impurities. Spectra of samples prepared from $^{12}CO_2$ are indicated by solid lines, and those of $^{13}CO_2$-derived samples are indicated by dashed lines. Control experiments using $^{12}CO_2$ have established that the peak marked y arises from the presence of excess carbon dioxide in the labeled run.

Direct carboxylation of an arene under mild conditions, without initial deprotonation by a strong base such as an alkyllithium, would appear to be unprecedented except for the mechanistically complex[13] and commercially important[14] Kolbe–Schmitt carboxylation of phenolates. Our results suggest that the carboxylation of reductively activated ligands, including arenes, may provide an attractive general strategy for the incorporation of CO_2 into useful organic molecules, and further experiments along these lines are being pursued in our laboratory.

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Registry No. $1^{2-}2K^+$, 113303-46-1; $2^{2-}2K^+$, 125666-44-6; $2^{2-}2K^+$ ($^{13}CO_2$ labeled), 125666-48-0; 3^-K^+, 113303-48-3; 4^-K^+, 125666-45-7; 5, 125666-46-8; 6^-K^+, 125666-47-9; 6^-K^+ ($^{13}CO_2$ labeled), 125666-49-1; $[Cr(\eta^5\text{-}C_6H_6CO_2SiMe_2Bu\text{-}t)(CO)_3]K$, 125666-50-4; $[Cr(\eta^5\text{-}C_6H_6CO_2SiPh_3)(CO)_3]K$, 125666-51-5; CO_2, 124-38-9.

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Solvolytic Acceleration Accompanying (Trimethylsilyl)methyl Migration

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It has been reported that a γ-silyl substituent enhances the solvolytic reactivity of secondary alkyl sulfonate esters by factors of $10–10^2$.[1] The carbocation involved is stabilized by interaction with the back lobe of the silicon–carbon bond in either a "W" or an "endo-Sickle" conformation.[2] Products of unrearranged substitution and minor yields of cyclopropanes from 1,3-deoxysilylation were found in each instance in which one of these conformations is possible.

As shown in Table I, the solvolysis rates for **1** and **2** are larger than those for the analogous neopentyl and pinacolyl esters by factors of 400–21 800. These accelerations are the largest ever attributed to a single γ-silyl group.[3]

As outlined in Scheme I, the products from the solvolysis in 80E of both esters derive exclusively (for **1**) or predominately (for **2**) from the intermediate tertiary ion **4**, which is formed by migration of the (trimethylsilyl)methyl group. Products were isolated from both the deuterated and undeuterated sulfonate esters in order to distinguish between methyl and (trimethylsilyl)methyl migration. The alkenes formed with loss of Me_3Si^+ were isolated by vacuum transferring the volatiles into NMR tubes containing $CDCl_3$. The alkenes that retained the TMS group were identified as the alcohols resulting from the hydroboration/oxidation of a pentane-extracted reaction mixture.

Interestingly, *none of the products are derived from methyl migration* even though the carbocation so formed would be not only tertiary but also β-silyl stabilized. The ability of γ-silicon to direct carbon and hydrogen rearrangements to yield β-silyl carbocation intermediates is well documented.[4] In the present examples, it is clear that the stability of that potential intermediate does not control the rearrangement; our results show that $(CH_3)_3SiCH_2$ has a far greater migratory aptitude than CH_3. Preferences for (trimethylsilyl)methyl migration over methyl migration[5a] and over ring expansion[5b,c] have been reported.

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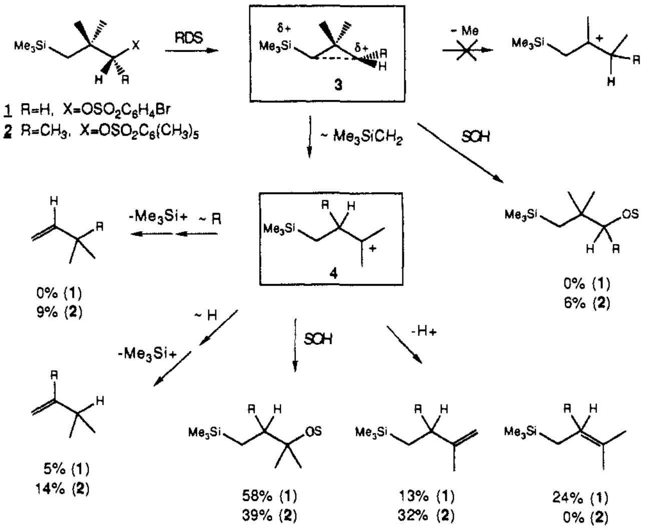
Table I. Rate Constants and Deuterium Kinetic Isotope Effects for Solvolysis at 25 °C

				isotope rate effects		
	solvent[a]	k, 10^{-5} s^{-1}	k_{rel}[b]	α-d_1	γ-d_6[c]	γ-d_2[d]
1	80E	0.5411		1.105	0.927	0.972
	50E	4.766	2500			
	97T	14.370	21800	1.106	0.931	0.985
2	90E	2.218	500	1.119	0.985	0.985
	80E	5.936	400	1.130	0.977	0.985
	97T	707	4600			

[a] 90E, 80E, and 50E are 90, 80, and 50 vol % aqueous ethanol, respectively; 97T is 97% 2,2,2-trifluoroethanol–3% water. [b] The rate constants for the primary substrate are expressed relative to Me_3CCH_2OBs; those for the secondary substrate are relative to $Me_3CCHMeOPms$[9] (estimated OBs/OPms = 43).[10] [c] Deuteration of both γ-methyl groups. [d] Deuteration at the γ-methylene position.

Scheme I. General Mechanistic Scheme for Product Formation and Percent Yields in 80E



However, since deuterium substitution at the *γ-methylene position slows solvolysis* (Table I), the $(CH_3)_3SiCH_2$ group *does not migrate in the rate-determining step*.[6] Further, the fact that **2** produces some unrearranged substitution, while the pinacolyl ester does not, means that the substitution reaction is also accelerated by the γ-silyl group. These facts can be accommodated by the mechanism proposed in Scheme I which involves rate-determining formation of the intermediate (**3**) which is stabilized by the same type of percaudal interaction of the $Si–C_\gamma$ bond previously identified.[1] This interaction is favored by methyl substitution at C_β, as is evident from the stepwise increase in reaction rate with methyl substitution at C_β of 1:12:65 (97T) for **1** and 1:7:57 (80E) for **2**, which can be attributed to the Thorpe–Ingold or the *gem*-dimethyl effect.[7] *gem*-Dimethyl substitution serves to make the rearrangement of the intermediate **3** to the tertiary ion **4** by Me_3SiCH_2 migration, faster than nucleophilic attack on carbon or silicon. Nevertheless, the bridged ion does give a small fraction of substitution in the secondary case. In intermediate **3**, the $C_\beta–C_\gamma$ bond is optimally oriented for rearrangement, whereas methyl migration would involve bond rotation which would break the silyl stabilization.[8]

Acknowledgment. Support from the National Science Foundation, Grant No. CHE-85-06682 (project support) and CHE-81-05004 and CHE-85-13707 (NMR instrumentation), is gratefully acknowledged.

Supplementary Material Available: Information about the preparation, physical constants, and spectra of the compounds used (**1–24**) and the isolation and identification of the products (**106–111** and **123–126**) (17 pages). Ordering information is given on any current masthead page.

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(8) The γ-silyl-stabilized carbocation may be formed in preference to concerted rearrangement to a β-silyl-stabilized carbocation because the latter reaction is retarded by steric interactions which hinder the "U" conformation, in which the orbitals of the C_α–X bond, the C_β-methyl bond, and the C_γ–Si bond are all parallel.

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Electron Spin Resonance Evidence for the 1,4-Bishomobenzene Structure of the C_{2v} Ring-Opened Semibullvalene (Bicyclo[3.3.0]octa-2,6-diene-4,8-diyl)[†] Radical Cation

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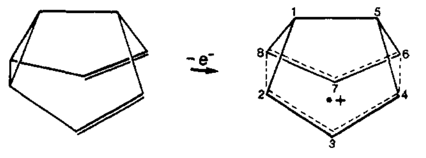
The remarkable fact that semibullvalene (**1**)[1] undergoes a rapid degenerate Cope rearrangement on the NMR time scale at −150 °C has prompted efforts to lower the activation energy of only 4.8 kcal mol^{-1} for the parent molecule[2] to a negative value by appropriate substitution.[3,4] This exciting goal where the expected 1,4-bishomobenzene transition structure[3] would be stabilized relative to the localized semibullvalene structures has not hitherto been realized, however, even for purposely designed derivatives.[4] In contrast, we now report that radiolytic oxidation of **1** in Freon matrices generates the delocalized bicyclo[3.3.0]octa-2,6-diene-4,8-diyl radical cation $\mathbf{2}^{\bullet+}$ as *a stable species*.



1 $\mathbf{2}^{\bullet+}$

Bishomoaromatic radical cations of this generic type were first suggested by Roth and Abelt[5a] as the precursors responsible for the CIDNP patterns observed from the neutral recombination products in photoinduced electron transfer reactions between a series of bridged bicyclo[5.1.0]octa-2,5-dienes, exemplified by barbaralane, and various electron acceptors. Such NMR evidence[5] of radical cation structure is, of course, indirect and we are not aware of any previous *direct* spectroscopic measurements on a bishomobenzene radical cation derived from two strongly inter-

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[†] The diyl parent of the radical cation may also be named bicyclo[3.3.0]-octa-3,7-diene-2,6-diyl, these two equivalent valence-bond structures reflecting its bisallyl character.

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