Evidence for 2-fold Hyperconjugation in the Solvolysis of 5-(Trimethylsilyl)- and 5-(Trimethylstannyl)-2-adamantyl Sulfonates

W. Adcock,*[,1a] Janet Coope,[1b] V. J. Shiner, Jr.,*[,1b] and Neil A. Trout[1a]

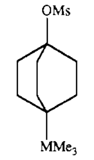
Department of Chemistry, Indiana University, Bloomington, Indiana 47405, and the School of Physical Sciences, The Flinders University of South Australia, Adelaide, Australia 5001

Received November 10, 1989

Summary: We wish to report that 5-trimethylsilyl and 5-trimethylstannyl substituents cause unexpectedly large accelerations of the solvolysis of 2-adamantyl *p*-bromobenzenesulfonate esters and that these observations confirm the importance of long-range hyperconjugative interactions.

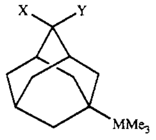
There has been considerable recent interest in the modes of transmission of electronic effects of substituents across rigid saturated bicyclic carbon skeletons and particularly in the "double hyperconjugation" type interaction. Adcock et al.[2] have shown that ^{19}F substituent chemical shifts (SCS) of 4-X-bicyclo[2.2.2]oct-1-yl fluorides are strongly regulated by a "through-three-bond" electron delocalization interaction that couples the C–X and C–F bonds through the intervening C–C single bonds. This "double hyperconjugation" had earlier been invoked by Grob et al.[3] to explain the accelerative effects of electrofugal substituents including hydrogen on the solvolysis rates of 4-substituted bicyclooctyl *p*-nitrobenzenesulfonates.

In a recent study of the effects of metalloidal substituents in the 4-position on the solvolysis rates of bicyclo[2.2.2]octyl methanesulfonate esters **1** we found acceleration factors approaching 50 and 3000 for the $Si(CH_3)_3$ and $Sn(CH_3)_3$ groups, respectively.[4] In extending these observations we had already found similarly large solvolytic accelerations with these metalloidal substituents in the 5*E* position of 2-adamantyl brosylates **2** when a report by Xie and le Noble[5] appeared claiming that the 5-trimethylstannyl substituent caused only modest accelerations of the solvolysis of 2-adamantyl tosylate and that the factor for the Z isomer (15×) was larger than that for the *E* isomer (10×).



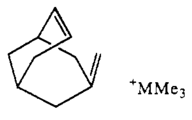
M = Si or Sn

1



M = Si or Sn
E: X = OBs, Y = H
Z: X = H, Y = OBs

2



M = Si or Sn

3

Table I. Solvolysis Rate Constants for 5-X-2-adamantyl Brosylates and Ratios Relative to 2-Adamantyl Brosylate at 25 °C

	97T[a]		70E[a]		80E[a]		90E[a]	
X	k^b	$k_{rel}{}^c$	k	k_{rel}	k	k_{rel}	k	k_{rel}
(*E*)-Me_3Sn	3200[d]	7000			17.99	1160	4.423	1373
(*Z*)-Me_3Sn	44.83	98	1.27	27	0.527	34	0.160	50
(*E*)-Me_3Si	23.13	51	0.656	14				
(*Z*)-Me_3Si	3.69	8	0.13	3				

[a] 97T is 97 wt % trifluoroethanol –3 wt % water;, 70E, 80E, and 90E are 70, 80 and 90 vol % ethanol –30, 20, and 10 vol % water. [b] Units are 10^{-5} s^{-1}. [c] Ratio of the rate constant of 5-X-2-adamantyl OBs to 2-adamantyl OBs. [d] Extrapolated from rates measured at lower temperatures.

Solvolysis rate constants determined by using the conductance method described previously,[4,6] along with the ratios of these rates relative to that of 2-adamantyl brosylate, are in Table I. The accelerations for the (*E*)-trimethylsilyl and especially for the (*E*)-trimethylstannyl substituents are large and very similar to the corresponding substituent effects in the bicyclooctyl series.[4] This similarity of the substituent effects is striking and significant because the substituent groups and the reaction centers are separated by the same number of bonds in both cases but their spatial separations and orientations are different; the conclusion that the effects are transmitted through *bonds* rather than through *space* is thus strongly reinforced. Also it is clear that the hyperconjugating bonds do not all have to lie in the same plane as they are in the bicyclooctyl compounds; the central bond in the adamantyl compounds hyperconjugates with each end bond through two different planar arrangements oriented at an angle of 120° to each other. This is in accord with the stereoelectronic requirements of the through-bond interaction model put forward by Hoffmann et al., which has received much experimental verification.[7,8]

The major product (70–90%) obtained from the (*E*)-stannyl-substituted isomer in all solvents is 7-methylenebicyclo[3.3.1]non-2-ene, formed by a five-bond heterolytic fragmentation. This observation graphically illustrates the importance of the through-bond interaction.[9] The (*Z*)-stannyl isomer gives 85% of the fragmentation product in 97T and 30% in 90E; the remaining products for both isomers are exclusively the *E* alcohol and ether. No fragmentation was detected for either silyl isomer; both gave predominately the *E* alcohol and ether.

le Noble's analysis[5,10] of the 5-substituent effects on reactivity of the 2-adamantyl compounds in terms of hy-

---

(1) (a) The Flinders University. (b) Indiana University.

(2) Adcock, W.; Iyer, V. S. *J. Org. Chem.* **1988**, *53*, 5259–5266, and references cited therein.

(3) (a) Grob, C. A.; Rich, R. *Helv. Chim. Acta* **1979**, *62*, 2793–2801. (b) Bielman, R.; Grob, C. A.; Küry, D.; Yao, G. W. *Helv. Chim. Acta* **1985**, *68*, 2158–2164, and references cited therein.

(4) Adcock, W.; Coope, J.; Duggan, P. J.; Ensinger, M. W.; Krstic, A. R.; Shiner, V. J., Jr. *J. Am. Chem. Soc.*, in press.

(5) Xie, M.; le Noble, W. J. *J. Org. Chem.* **1989**, *54*, 3839–3841.

(6) Shiner, V. J., Jr.; Ensinger, M. W.; Huffman *J. Am. Chem. Soc.* **1989**, *111*, 7199–7205.

(7) Hoffmann, R.; Imamura, A.; Hehre, W. J. *J. Am. Chem. Soc.* **1968**, *90*, 1499–1509. Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1.

(8) Krijnen, B.; Beverloo, H. B.; Verhoeven, J. W.; Reiss, C. A.; Goubitz, K.; Heijdenrijk, D. *J. Am. Chem. Soc.* **1989**, *111*, 4433–4440, and references cited therein.

(9) The formation of the fragmentation product also confirms Grob's view that hyperconjugation merges with fragmentation when the electron-donor group is strongly electrofugal; see ref 3a.

(10) Lin, M.-H.; Cheung, C. K.; le Noble, W. J. *J. Am. Chem. Soc.* **1988**, *110*, 6562–6563, and references cited therein.

0022-3263/90/1955-1411$02.50/0

perconjugation serves quite adequately to explain the behavior of the *E* isomers provided it is modified to include stabilization of the pyramidal *E* cation by double hyperconjugation as denoted by canonical structure **3**. However, the significant accelerations found for the *Z* isomers are not directly predicted from any earlier considerations. Here we postulate that the accelerations are due to isomerization of the (pyramidal) *Z* cation[11] to the more stable *E* cation, thereby reducing internal return. Evidence for this mechanism comes from preliminary findings of the lack of sulfonyl oxygen scrambling in ^{18}O-labeled 5(*Z*)-(trimethylstannyl)-2-adamantyl brosylate that was recovered after 1 half-life of solvolysis.[12] We are currently attempting to confirm or reject this explanation by examination of α-deuterium isotope effects. An alternative explanation is that hyperconjugation is transmitted through the intervening five C–C bonds having a less than optimal orientation.[13]

Acknowledgment. We thank F. P. Wilgis and Thomas Schuster for their assistance in obtaining 500-MHz spectra. Support of the work at Indiana University from the National Science Foundation, Grants No. CHE-85-06682 (project support) and CHE-81-05004 and CHE-85-13707 (NMR Instrumentation), and at the Flinders University from the Australian Research Council is gratefully acknowledged.

Supplementary Material Available: Preparation, physical constants, and spectral data of the compounds used (8 pages). Ordering information is given on any current masthead page.

---

[11] Finne, E. S.; Gunn, J. R.; Sorensen, T. S. *J. Am. Chem. Soc.* **1987**, *109*, 7816–7823.

[12] The minimum fraction of return $(k_{eq}/(k_{eq} + k_t))$ for 2-adamantyl brosylate under similar conditions is 0.54.

[13] Accelerative effects in a stereoelectronically unfavorable arrangement have been observed in solvolyses of 4-bromo-1-azaadamantane and have been ascribed to hyperconjugation. Grob, C. A.; Bolleter, M.; Kunz, W. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 708–709.

A Crystalline Seven-Membered Cyclic Ketene Imine from a Thiocarbonyl *S*-Methylide[†]

Rolf Huisgen* and Elke Langhals

Institut für Organische Chemie der Universität München, Karlstr. 23, D-8000 München 2, FRG

Heinrich Nöth*

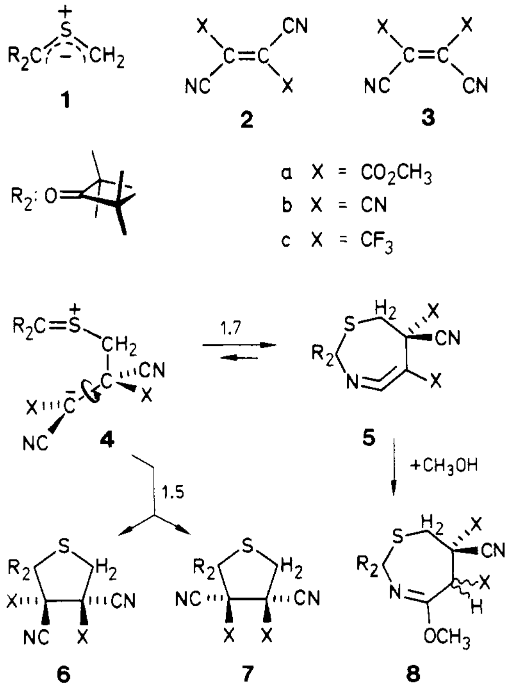
Institut für Anorganische Chemie der Universität München, D-8000 München 2, FRG

Received December 13, 1989

Summary: The [3 + 4] cycloaddition of 1,1,3,3-tetramethylindane-2-thione *S*-methylide (**11**) and 2,3-bis(trifluoromethyl)fumaronitrile (**2c**) afforded 86% of the ketene imine **14**, the X-ray structure of which revealed a strained ring; the thermolysis to thione **9** + cyclopropane **18** constitutes a novel reaction course.

A great difference between the π-MO energies of 1,3-dipole and dipolarophile as well as steric hindrance of the concerted process are prerequisites to the two-step pathway of cycloaddition. The nonstereospecific combination of the nucleophilic thiocarbonyl ylide **1** with the electrophilic ethylenes **2a** and **3a**, both giving thiolanes **6a** *and* **7a**, suggested the zwitterionic intermediate **4**.[1,2] Furthermore, the zwitterion **4b** generated in THF + 2 vol % methanol in the presence of **2b** furnished lactim ether **8b** and thiolane **6b** in a 65:35 ratio;[3] a reversible 1,7 recombination of **4b** affording the cyclic ketene imine **5b** was conjectured.

The reaction of **1** with the cis acceptor olefin **3c** provided 71% of the ketene imine **5c**, 16% of *trans*-thiolane **6c**, and 10% *cis*-thiolane **7c**;[4] **5c** was stable at room temperature, but rearranged to **6c** at 60 °C.[5] Ketene imine **5c** was crystalline, but single crystals suitable for X-ray analysis were not obtained. We are reporting on the crystal structure of a related ketene imine and its novel course of thermolysis.



1,1,3,3-Tetramethylindan-2-one was converted to the thione **9** (red crystals, mp 41–42 °C); addition of diazomethane in pentane at −20 °C gave 82% of the colorless thiadiazoline **10**, mp 84 °C.[6] The first-order N_2 extrusion

---

[†] Dedicated to Professor Wang Yu, Shanghai, on the occasion of his 80th birthday.

[1] Huisgen, R.; Mloston, G.; Langhals, E. *J. Am. Chem. Soc.* **1986**, *108*, 6401.

[2] Mloston, G.; Langhals, E.; Huisgen, R. *Tetrahedron Lett.* **1989**, *30*, 5373.

0022-3263/90/1955-1412$02.50/0