preparation of a substrate-analogue-bound form and its properties described. Ligand exchange reactions with NaN_3 are being investigated to prepare the N_3^- analogue of 1 as a model of met-N_3-Hr. While met-Cl-Hr and met-N_3-Hr possess Cl^- and N_3^- at only one Fe center, other Fe biomolecules may well possess anion binding sites on both metals. For example, RR may contain a terminally coordinated OH^- at each Fe,[4d] and attempts are therefore in progress to replace the Cl^- ligands of 1 with OH^- and also with PhO^-, the latter to model PAP which is believed to possess Fe-OPh (tyrosine) linkages.[3] Also under investigation is the introduction at a Cl^- site of a peroxide or hydroperoxide (HO_2^-) group to yield a model of oxy-Hr and allow current thinking on the mode of O_2 binding to be assessed.

Note Added in Proof. We have now prepared and structurally characterized the $PhCO_2^-/N_3^-$ analogue of complex 1, viz Fe_2O-$(O_2CPh)_2(N_3)_2(bipy)_2$, corresponding to met-$N_3$-Hr.[22]

Acknowledgment. This work was supported by NSF Grant CHE-8507748 (G.C.), NIH Grant HL13652 (D.N.H.), and the Electric Power Research Institute under U.S. Department of Energy Contract No. DE-AC03-76SF00098 (R.H.F.). We thank the Bloomington Academic Computing Service for a gift of computer time.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, and bond distances and angles (8 pages). Ordering information is given on any current masthead page.

A Novel Type of Selectivity in Anionotropic Rearrangements

Vittorio Lucchini*

Dipartimento di Scienze Ambientali, Università di Venezia
Dorsoduro 2137, 30123 Venezia, Italy

Giorgio Modena* and Lucia Pasquato

Centro Meccanismi di Reazioni Organiche CNR
Dipartimento di Chimica Organica, Università di Padova
Via Marzolo 1, 35131 Padova, Italy

Received April 18, 1988

Anionotropic rearrangements (i.e., those where the migrating group moves with its electron pair)[1] prefer that geometric situation which maximizes orbital overlap in the transition state. When the rearrangment occurs under SN1 type conditions, the maximum overlap is obtained in the two configurations with zero dihedral angle between the vacant p-orbital and the migrating bond.[2,3] In SN2 type rearrangements the maximum overlap between the migrating bond and the bond associated with the leaving group occurs for antiperiplanar or synperiplanar geometries. The differences in configurational stability dictate a preference for the antiperiplanar rearrangement.[2] In this communication we wish to report about a novel restriction imposed to an SN2 type anionotropic rearrangement by the particular molecular asymmetry.

During our investigations[4] on the mechanistic details of the addition of sulfenyl halides to olefins and acetylenes, we have been concerned with the identification and isolation of thiiranium and thiirenium ions,[5] with their structure-stability relationships, their

reactivity toward nucleophiles,[6] and the alternative reaction paths, which are possible in long living ions (when the reactions with nucleophiles are suppressed).

Our search for stable ions led us to reconsider a rather old report[7] on the reaction of arenesulfenyl chlorides on (Z)-di-tert-butylethylene (1) (which gives a stable adduct) and on the E isomer 2 (with formation of an adduct which rearranges and eliminates HCl). In our hands the addition of methanesulfenyl chloride to 1 in CD_2Cl_2 gives instantaneously and quantitatively the stable adduct 3 (as monitored by NMR spectroscopy), while the adduct 4 from 2 is formed in about 1 h at room temperature and converts within 24 h into a series of decomposition products, which were not further investigated.

$$(1)$$

$$(2)$$
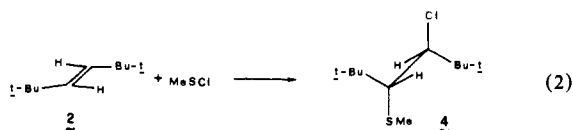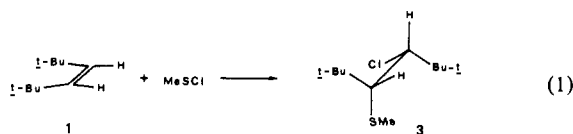
At first sight, the different stability of adducts 3 and 4 may be attributed to their conformational preference, as dictated by the steric repulsion of the two tert-butyl groups.[8] In conformer 4 the methylthio and chloride groups are antiperiplanar, thus favoring the formation of a thiiranium ion which may be supposed to mediate the rearrangement process. As a matter of fact, in a solvent such as sulfur dioxide, with strong solvolytic power toward saturated and unsaturated β-chlorosulfides,[9] the adduct 3 is indefinitely stable, while the adduct 4 converts instantaneously to thiiranium chloride 7, which then undergoes the slow rearrangement described below. This is however only an incomplete rationale for this process.

The hexachloroantimonate salts of thiiranium ions 6[8] and 7 can be easily prepared through the action of methylbis(methylthio)-sulfonium hexachloroantimonate (5) on 1 and 2.[5b] Their behavior demonstrates that the intermediacy of thiiranium ion is a necessary but not a sufficient condition for the occurrence of the rearrangement process. In fact at room temperature in CH_2Cl_2 thiiranium ion 6 is indefinitely stable, while thiiranium ion 7 converts quantitatively in about 5 days to thietanium ion 8.[10] The hexachloroantimonates of ions 6, 7, and 8 can be isolated and fully characterized.[11] The addition of chloride ion (from N-metyl-pyridinium chloride) to a solution of salt 8 in CH_2Cl_2 yields quantitatively the rearranged product 9.

At this stage of the investigation the other necessary condition can be tentatively proposed: only that antiperiplanar methide group can migrate, which belongs to the tert-butyl moiety syn to the S-methyl group. This condition is substantiated by the analysis of the rearrangement kinetics of the thiiranium ions 10 and 11

(1) March, J. Advanced Organic Chemistry; John Wiley and Sons: New York, 1985; Chapter 18.

(2) Delongchamps, P. Stereoelectronic Effects in Organic Chemistry; Pergamon Press: Oxford, 1983; Chapters 5 and 6.

(3) (a) Brouwer, D. M. Hogeveen, H. Recl. Trav. Chim. Pays Bas 1970, 89, 211. (b) Schleyer, P. v. R.; Lam, L. K. M.; Raber, D. J.; Fry, J. L.; McKervey, M. A.; Alford, J. R.; Cuddy, B. D.; Keizer, V. G.; Geluk, H. W.; Schlatmann, J. L. M. A. J. Am. Chem. Soc. 1970, 92, 5246.

(4) Capozzi, G.; Lucchini, V.; Modena, G. Rev. Chem. Intermediates 1979, 4, 347.

(5) (a) Pettitt, D. J.; Helmkamp, G. H. J. Org. Chem. 1963, 28, 2932. (b) Capozzi, G.; De Lucchi, O.; Lucchini, V.; Modena, G. Tetrahedron Lett. 1975, 2603. (c) Capozzi, G.; Lucchini, V.; Modena, G.; Scrimin, P. Tetrahedron Lett. 1977, 911. (d) Bolster, J.; Kellogg, R. M.; Meijer, E. W.; Wynberg, H. Tetrahedron Lett. 1979, 285. (e) Gybin, A. S.; Smit, W. A.; Krimer, M. Z.; Zefirov, N. S.; Novgorodtseva, L. A.; Sodovaya, N. K. Tetrahedron 1980, 36, 1361. (f) Gybin, A. S.; Smit, W. A.; Bogdanov, V. S.; Krimer, M. Z.; Kalyan, J. B. Tetrahedron Lett. 1980, 21, 383. (g) Lucchini, V.; Modena, G.; Valle, G.; Capozzi, G. J. Org. Chem. 1981, 46, 4720.

(6) Schmid, G. H.; Strukelj, M.; Dalipi, S.; Ryan, M. D. J. Org. Chem. 1987, 52, 2403.

(7) Dean, C. L.; Garratt, D. G.; Tidwell, T. T.; Schmid, G. H. J. Am. Chem. Soc. 1974, 96, 4958.

(8) Raynolds, P.; Zonnebelt, S.; Bakker, S.; Kellogg, R. M. J. Am. Chem. Soc. 1974, 96, 3146.

(9) Lucchini, V.; Modena, G.; Zaupa, T.; Capozzi, G. J. Org. Chem. 1982, 47, 590.

(10) For other observations of thietanium ions: (a) Trost, B. M.; Schinski, W. L.; Mantz, I. B. J. Am. Chem. Soc. 1969, 91, 4320. (b) Trost, B. M.; Schinski, W. L.; Chen, F.; Mantz, I. B. J. Am. Chem. Soc. 1971, 93, 676.
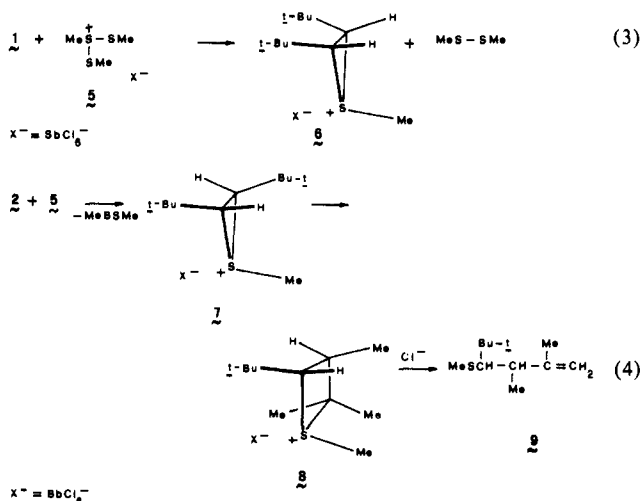
(11) The stereochemistry of hexachloroantimonate salts of 6, 7, 8, 10, 11, 12, and 13 was ascertained through NOE analysis in the differential mode.

(3)

(4)

obtained in equimolar ratio from the addition of **5** to (E)-*tert*-butyl-d_9-*tert*-butylethylene. Dimethyl disulfide, which can catalyze the interconversion between **10** and **11**, is removed through coprecipitation of the two salts. A substantial secondary kinetic isotope effect ($k_H/k_D = 1.32$) is measured for the migration (in CD_2Cl_2 at 25 °C) of CH_3 in **10** and of CD_3 in **11** (monitoring the nonisochronous NMR *tert*-butyl resonances of the unseparated isotopic isomers). The same ratio is constantly found between selected NMR resonances of the rearranged thietanium ions **12** and **13**. The identity between the ratio of reagent conversion rates and the ratio of product distribution is a strong evidence for the selectivity of the processes described in eq 5 and 6.[12]

(5)

(6)
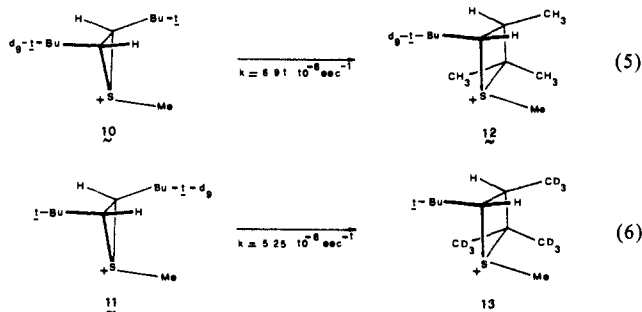
These experimental findings can be rationalized under the following assumptions.

(a) Methide migration and rupture of the C–S bond in thiiranium ion are concerted. A first step consisting in the nonassisted rupture of the C–S bond, i.e., a preequilibrium between thiiranium ion and corresponding open β-thiocarbocation, is inconsistent with the fact that thiiranium ions **6** and **7** do not interconvert and with the observed isotope effect. Furthermore, the methide migration at the level of open β-thiocarbocation would lead both to thietanium ion **8** and to the isomer with *tert*-butyl and migrated methyl on the same ring face.[13]

(b) The migration of methide group therefore occurs under SN2 type conditions. The restriction associated with this mechanism, i.e., the antiperiplanarity of migrating and leaving groups,[2] is not an exhaustive explanation for the observed specificity of the migration, which is limited to those units belonging to groups syn to the S-methyl group.

This novel type of selectivity may be associated with the fact that the leaving group, the methylthio moiety, lacks cylindrical symmetry around the bond to be broken, nor can it acquire this symmetry by rotation, which is hindered. This asymmetry is reflected in the region where the migration takes place. Alter-

natively, it may be argued that the methide migration can better assist the rupture of the weaker C–S bond, which is the one that supports the *tert*-butyl and S-methyl groups on the same side and hence is subjected to greater steric strain.

Further experimental and theoretical investigations aimed at the rationalization of the rearrangement mechanism are in progress.

Viable Geometries for T_1-S_0 ISC in Alkene Triplets

Richard A. Caldwell,*,† L. Carlacci,‡ C. E. Doubleday, Jr.,*,§
T. R. Furlani,*,⊥ H. F. King,*,‡ and J. W. McIver, Jr.*,‡

Departments of Chemistry, The University of Texas at
Dallas, Richardson, Texas 75080
State University of Buffalo
Buffalo, New York 14214
Calspan Advanced Technology Center
Buffalo, New York 14225

Acyclic alkenes, unless extensively conjugated, are expected to show energy maxima in the ground state and minima in the first triplet state at the perpendicularly twisted geometry (of symmetry D_{2d} for ethylene itself).[1-3] Since in this geometry the energies of S_0 and T_1 must be quite close, it has generally been assumed[4-8] that it represents the geometry at which T_1-S_0 intersystem crossing (isc) occurs if structural constraints do not prevent its attainment. There will be two factors, however, contributing to the rate of a radiationless process, of which energy gap is but one. The other is the intrinsic transition probability, in this case derived from the spin-orbit coupling (SOC) matrix element $\langle \Psi(T_1)|H_{so}|\Psi(S_0)\rangle$. The assumption that a minimized energy gap is the sole figure of merit by which isc rates as a function of geometry should be assessed is equivalent to the assumption of unchanging SOC in the range of feasible geometries. We have performed calculations of T_1-S_0 SOC for ethylene by the CAS-MCSCF technique previously described,[9] by using 2-in-2 CAS and the 3-21G basis set. Not only is the variation of SOC with geometry very large but also SOC *is nil at the D_{2d} geometry*. Since substitutions involving neither heavy atoms nor groups with lone pairs should not vitiate the qualitative trends of SOC with geometry we report here, we believe these results offer a useful framework for analysis of isc of olefin triplets more generally.

According to Salem,[10] T–S spin-orbit coupling in biradicals (we consider ethylene excited states as biradicaloids) requires both nonparallel orbitals and an ionic contribution to the singlet wave function, since with either parallel orbitals or a purely covalent

---

(12) Other investigations, which confirm the selectivity of these rearrangements, are in progress.

(13) This specificity was also invoked as evidence for an SN2 type mechanism in the rearrangement observed in the addition of Cl_2 to **2**: Fahey, R. C. *J. Am. Chem. Soc.* **1966**, *88*, 4681.

†UT–Dallas.
‡SUNY–Buffalo.
§Columbia University, New York, NY.
⊥Calspan Corp.
(1) Mulliken, R. S. *Phys. Rev.* **1932**, *41*, 751.
(2) Saltiel, J.; D'Agostino, J.; Megarity, E. D.; Metts, L.; Neuberger, K. R.; Wrighton, M.; Zafiriou, O. C. *Org. Photochem.* **1973**, *3*, 1.
(3) Buenker, R. J.; Peyerimhoff, S. D. *Chem. Phys.* **1976**, *9*, 75. Brooks, B. R.; Schaefer, H. F. *J. Am. Chem. Soc.* **1979**, *101*, 307.
(4) Saltiel, J.; Charlton, J. L. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; p 25.
(5) Caldwell, R. A. *Pure Appl. Chem.* **1984**, *56*, 1196.
(6) Caldwell, R. A.; Cao, C. V. *J. Am. Chem. Soc.* **1982**, *104*, 6174.
(7) Bonneau, R.; Herran, B. *Laser Chem.* **1984**, *4*, 151 and references therein.
(8) Goerner, H.; Schulte-Frohlinde, D. *J. Phys. Chem.* **1981**, *85*, 1835.
(9) Furlani, T. R.; King, H. F. *J. Chem. Phys.* **1985**, *82*, 5577. Carlacci, L.; Doubleday, C., Jr.; Furlani, T. R.; King, H. F.; McIver, J. W., Jr. *J. Am. Chem. Soc.* **1987**, *109*, 5323. To include all three triplet sublevels we report SOC = $[|SOC(m_s = 1)|^2 + |SOC(m_s = 0)|^2 + |SOC(m_s = -1)|^2]^{1/2}$. This quantity both is invariant to the coordinate frame in which the calculation is done (the components, of course, are not) and is that which would be used (subject to a statistical factor of $1/(3^{1/2})$) in a Golden Rule calculation of the rate of isc of an equilibrated set of triplet sublevels.
(10) Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92.