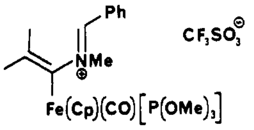
provided the corresponding acyl **6b**[8] (93%). Dehydration of **6a** and **6b** according to the Hughes procedure using

$[(MeO)_3P](Cp)(OC)FeCOCHR'_2$

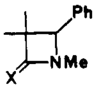
6

a R' = H
b R' = Me

trifluoromethanesulfonic anhydride[9] gave the cationic iron vinylidenes **5a** (used directly in situ) and **5b** (85%) as yellow and peach colored solids, respectively. Vinylidene **5a** reacted with the imine PhCH=NMe[10] in dichloromethane at room temperature over 24 h to give the complex **3d** (R^2 = Ph; 14% from **6a**). Alternatively PhCH=NMe reacted with **5b** rapidly in dichloromethane solution at −78 °C to produce the acyclic adduct **7**. This material was slowly converted into the azetidinylene complex **8a** on standing (NMR) or preferably by brief reflux in 1,2-dichloroethane in the presence of anhydrous Amberlyst A21 resin. Thus, addition of PhCH=NMe to a 1,2-dichloroethane solution of **5b** at room temperature followed by refluxing for 3 h gave **8a** in good yield (66%) as a mixture of diastereoisomers (1.5:1). Recrystallization from methanol gave the *R*(*S*),*R*(*S*) diastereoisomer.[11] Oxidation of **8a** with iodosobenzene in ethanol solution gave the corresponding β-lactam **8b** (36%).[12]



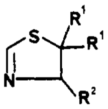
7



8

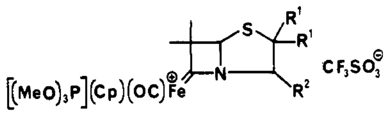
a X = $Fe^{\oplus}(Cp)(CO)[P(OMe)_3]$ $CF_3SO_3^{\ominus}$
b X = O

The stepwise cycloaddition methodology was extended to the 2-thiazoline derivatives **9a–c**[13-15] to provide the corresponding complexes **10a** (82%), **10b** (72%), and **10c** (51%). Again these materials were obtained as mixtures of two diastereoisomers [**10a** (15:1), **10b** (8:1), and **10c** (6:1)]. While we have not unambiguously identified the stereochemistries of the principal adducts, it is reasonable to assume that their azetidinylidene ligands have the exo stereochemistry.[16] This is consistent with the known chemistry of 2-thiazolines.[14] Additional support for this contention was obtained when oxidation of **10b** with iodosobenzene in ethanol gave **11** (52%). The stereochemistry of this material was assigned as the exo configuration since treatment with catalytic base caused no epimerization.



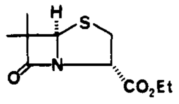
9

a $R^1 = R^2 = H$
b $R^1 = H$, $R^2 = CO_2Et$
c $R^1 = Me$, $R^2 = CO_2Me$



10

a $R^1 = R^2 = H$
b $R^1 = H$, $R^2 = CO_2Et$
c $R^1 = Me$, $R^2 = CO_2Me$



11

Clearly the phosphite cationic iron vinylidenes are efficient reagents for the synthesis of both monocyclic and bicyclic β-lactams with the penicillin framework from simple imines. The methodology complements the synthesis of β-lactams from the oxidative cyclization of β-amino acyl compounds previously reported by Rosenblum,[17] Liebeskind,[18] Davies,[19] and Ojima.[20]

Acknowledgment. We thank the National Science Foundation (CHE-8500890) for the generous support of this program, the Midwest Center for Mass Spectrometry, an NSF Regional Instrument Facility (CHE-8211164), for obtaining mass spectral data, and both the NIH (RR-01672) and the NSF (CHE-8300958) for providing the Enraf-Nonius CAD$_4$ single-crystal diffractomer.

---

(8) All new compounds were fully authenticated by spectral data and microanalyses or FAB high resolution mass spectra except for the vinylidenes **7a** and **7b**, which were characterized by NMR and IR spectra only.

(9) Boland-Lussier, B. E.; Churchill, M. R.; Hughes, R. P.; Rheingold, A. L. *Organometallics* **1982**, *1*, 628.

(10) Cromwell, N. H.; Babson, R. D.; Harris, C. E. *J. Am. Chem. Soc.* **1943**, *65*, 312.

(11) X-ray crystallographic structure: Sabat, M. unpublished results. Assignment of configuration was based on the following order of priority; $P(OMe)_3$ > CO > carbene > Cp.

(12) Rogalska, E.; Belzecki, C. *J. Org. Chem.* **1984**, *49*, 1397.

(13) Ito, Y.; Inubushi, Y.; Zenbayashi, M.; Tomita, S.; Saegusa, T. *J. Am. Chem. Soc.* **1973**, *95*, 4447.

(14) Bose, A. K.; Manhas, M. S.; Chib, J. S.; Chawla, H. P. S.; Dayal, B. *J. Org. Chem.* **1974**, *39*, 2877.

(15) Bell, M. R.; Carlson, J. A.; Oesterlin, R. *J. Org. Chem.* **1972**, *37*, 2733.

(16) Exo refers to the stereochemistry of the alkoxycarbonyl group on the 4-thia-1-azabicyclo[3.2.0]heptylene ligand.

(17) Wong, P. K.; Modhavarao, M.; Marten, D. F.; Rosenblum, M. *J. Am. Chem. Soc.* **1977**, *99*, 2823.

(18) Liebeskind, L. S.; Welker, M. E.; Goedken, V. *J. Am. Chem. Soc.* **1984**, *106*, 441. Liebeskind, L. S.; Welker, M. E.; Fengl, R. W. *Ibid*, **1986**, *108*, 6328.

(19) Broadley, K.; Davies, S. G. *Tetrahedron Lett.* **1984**, *25*, 1743. Davies, S. G.; Dordor-Hedgecock, I. M.; Sutton, K. H.; Walker, J. C.; Jones, R. H.; Prout, K. *Tetrahedron* **1986**, *42*, 5123.

(20) Ojima, I.; Kwon, H. B. *Chem. Lett.* **1985**, 1327.

Anthony G. M. Barrett,* Michael A. Sturgess
Department of Chemistry
Northwestern University
Evanston, Illinois 60201

Received March 6, 1987

Dynamic NMR Study of Dimethyl Trithiocarbonate[1]

Summary: Low-temperature proton NMR spectra of dimethyl trithiocarbonate show that the populations of the *E,Z* and *E,E* conformations are 0.52 and 0.48, with free energy barriers to interconversion at −138 °C of 6.9_4 and 6.9_7 kcal/mol.

Sir: Although dialkyl carbonates and the various possible sulfur-substituted derivatives comprise a large class of compounds, no successful[2] dynamic NMR studies of these

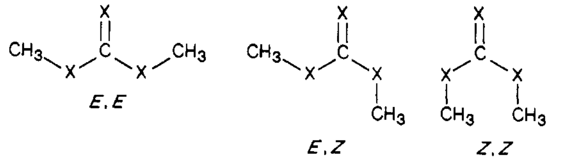
---

(1) (a) This work was supported by the National Institutes of Health (Grant No. S06RR08047). (b) Presented at the 192nd National Meeting of the American Chemical Society, Anaheim, Ca, September 12, 1986.

(2) Methyl *tert*-butyl carbonate was reported[3] to exist as a mixture of conformations, but the slow-exchange spectrum was not observed, and the evidence for the conformational equilibrium is not conclusive.

0022-3263/87/1952-3941$01.50/0

compounds have been reported. Three planar conformations are possible for symmetrically substituted compounds of this type, as shown below for dimethyl carbonate (**1**) and dimethyl trithiocarbonate (**2**).



1, X = O
2, X = S

The *E,E* and *Z,Z* conformations both possess twofold rotational axes, and the identical methyl groups of either conformation would show only a single peak in the proton NMR spectrum. The diastereotopic methyl groups of the *E,Z* conformation would show two peaks of equal intensity under conditions of slow topomerization ($EZ \rightleftharpoons ZE$), while a single peak would be observed if rotation about the C–O or C–S bonds is rapid. Thus, only the *E,Z* conformation could, by itself, show changes in the NMR spectrum as the temperature is lowered and the rate of rotation is slowed.

Studies of **1** in the gas phase[4] and in the condensed phase[5-7] indicate that the *E,E* conformation predominates. Katon and Cohen[6] have assigned peaks in the Raman and infrared spectra of liquid dimethyl carbonate to the *E,Z* conformation and estimated an enthalpy difference of 2.6 ± 0.5 kcal/mol for the *E,Z* and *E,E* conformations. The *Z,Z* conformation is expected to be destabilized by steric repulsion between the methyl groups, and the population of this isomer should be small; in one study,[7] ΔH for the *Z,Z* and *E,E* conformations was estimated to be 4.1 ± 0.5 kcal/mol.

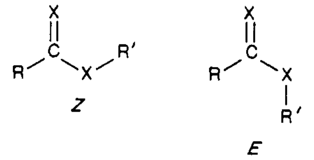
Dipole moments of 0.23, 1.69, and 3.03 D for the *E,E*, *E,Z*, and *Z,Z* conformations were predicted[5] for **1** by vector addition of bond moments. Experimental values range from 0.55 to 1.07 D;[8] for example, a dipole moment of 0.86 D was found[5] for a solution in carbon tetrachloride. This value is consistent with the *E,E* conformation, with smaller populations of the *E,Z* and *Z,Z*.

Similar dipole moments of 0.17, 2.46, and 4.17 D were obtained[9] from HMO calculations for the *E,E*, *E,Z*, and *Z,Z* conformations of **2**. The experimental value of 1.33 D for a benzene solution is intermediate between the values expected for the *E,E* and *E,Z* forms and was interpreted in terms of a mixture of these two conformations. The IR spectra[9] in several solvents also indicated the presence of the two conformations, and the authors concluded that the *E,E* conformation predominates. The results of an electron diffraction study[10] of **2** in the gas phase were interpreted in terms of the *E,E* conformation only, although the possible presence of small amounts of the *E,Z* isomer could not be excluded.

The NMR spectrum (90.02 MHz) of **2** in $CHClF_2$/$CHCl_2F$ (3.4:1) at 21 °C shows a single peak for the methyl protons at δ 2.72. At lower temperatures, the peak broadens and splits into two lines of unequal intensity separated by 10.8 Hz at −150 °C. The peak heights are in a ratio of 4.17:1 (upfield:downfield). The finding of two signals of unequal intensity at slow exchange cannot be interpreted in terms of any single conformation but can readily be explained if a mixture of *E,Z* and *E,E* conformations is present, with the upfield peak of the *E,Z* isomer overlapping with the signal from the *E,E* conformation. The population of the *Z,Z* conformation is assumed to be negligibly small.

Populations of 0.52 and 0.48 for the *E,Z* and *E,E* conformations and rate constants of 16.3 s^{-1} ($E,E \rightarrow E,Z$) and 15.0 s^{-1} ($E,Z \rightarrow E,E$) were determined at −138 °C by using the DNMR program of Binsch and Kleier.[11] The corresponding free energy barriers are 6.9_4 and 6.9_7 kcal/mol at −138 °C.

Most esters of carboxylic acids, and the related sulfur compounds, have a strong preference for the *Z* conformation, in which *R′* and C=X are cis to each other.[12] For example, the population of the *E* isomer of methyl formate is only 0.3% at −83 °C in DMF/acetone,[13] and no evidence for the *E* isomer of methyl dithioacetate was found.[9] The reasons for this conformational preference have been discussed,[14] and for methyl formate probably include three factors: (1) more favorable dipole–dipole interactions for the *Z* isomer; (2) stabilization of the *Z* isomer by lone pair ("ether" oxygen) $-\sigma^*$ (C=O) interaction, and (3) "aromaticity" of the *Z* conformation. Studies of compounds related to **2** are in progress to clarify the reasons for the large population of the *E,Z* conformation of this compound.



---

(3) Oki, M.; Nakanishi, H. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 3419.

(4) Mijlhoff, F. C. *J. Mol. Struct.* **1977**, *36*, 334.

(5) Chia, L. H. L.; Kwan, K. J.; Huang, H. H. *Aust. J. Chem.* **1981**, *34*, 349.

(6) Katon, J. E.; Cohen, M. D. *Can. J. Chem.* **1975**, *53*, 1378.

(7) Thiebaut, J.-M.; Rivail, J.-L.; Greffe, J.-L. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 2024.

(8) McClellan, A. L. *Tables of Experimental Dipole Moments*; Rahara Enterprises: El Cerrito, 1974; Vol. 2.

(9) Herzog, K.; Steger, E.; Rosmus, P.; Scheithauer, S.; Mayer, R. *J. Mol. Struct.* **1969**, *3*, 339.

(10) Almenningen, A.; Fernholt, L.; Seip, H. M.; Henriksen, L. *Acta Chem. Scand., Ser. A.* **1974**, *28*, 1037.

(11) Binsch, G.; Kleier, D. A. *QCPE* **1969**, *11*, 140.

(12) For a review, see: Jones, G. I. L.; Owen, N. L. *J. Mol. Struct.* **1973**, *18*, 1.

(13) Grindley, T. B. *Tetrahedron Lett.* **1982**, *23*, 1757.

(14) Noe, E. A.; Sanders, T.; Garahi, M.; Hosseini, H.; Young, R. *J. Am. Chem. Soc.* **1985**, *107*, 4785 and references cited therein.

Masood Garahi, Felicia Badelle, Eric A. Noe*
Department of Chemistry
Jackson State University
Jackson, Mississippi 39217

Received May 20, 1987

Samarium-Promoted, Stereocontrolled Cyclopropanation Reactions[1]

Summary: Samarium-based carbenoids have been found to be highly efficient cyclopropanation reagents for allylic alcohol substrates. Hydroxyl-directed cyclopropanations occur under very mild conditions with a high degree of selectivity.

Sir: Cyclopropanes play an important role in many aspects of organic chemistry. This structural unit is found in a number of significant natural products (for example chrysanthemic acid derivatives), as well as in synthetic

---

(1) Lanthanides in Organic Synthesis. 7.