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†

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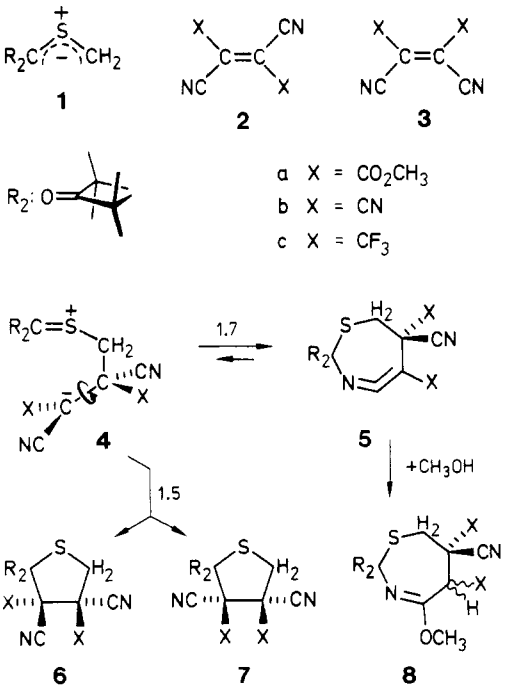
Summary: The [3 + 4] cycloaddition of 1,1,3,3-tetramethylindane-2-thione *S*-methylide (**11**) and 2,3-bis(trifluoromethyl)fumaronitrile (**2c**) afforded 86% of the ketene imine **14**, the X-ray structure of which revealed a strained ring; the thermolysis to thione **9** + cyclopropane **18** constitutes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

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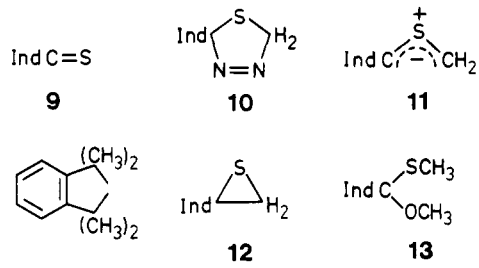
from **10** proceeded at 50 °C in xylene with $t_{1/2}$ = 68 min and in acetonitrile with $t_{1/2}$ = 148 min. The thione *S*-methylide **11** set free in C_6D_6 (**10**, 16 h, 50 °C) cyclized to give thiirane **12** quantitatively (NMR analysis with weighed standard, 3-H_2 s δ 2.54). When **11** was generated in methanol at 60 °C, the *O*,*S*-dimethyl acetal **13** (73%, bp 100–110 °C/0.01 Torr, SCH_3 δ_H 2.04, OCH_3 3.54), a 1,3 adduct of methanol, was isolated.

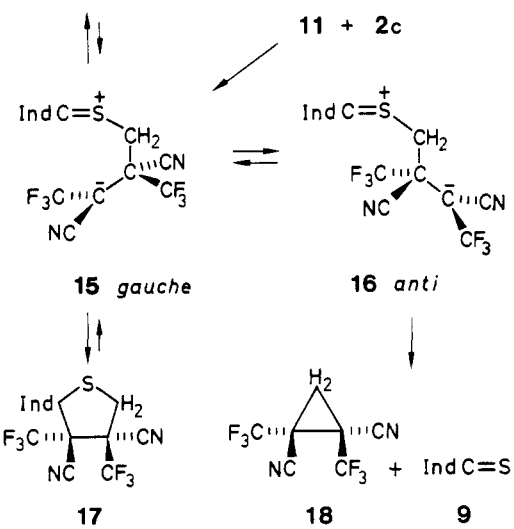


9 **10** **11**

12 **13**

Elimination of N_2 from **10** in the presence of 1.1 equiv of trans acceptor olefin **2c**[7] in [D_{12}]cyclohexane (7.5 h, 50 °C) gave rise to 86% of ketene imine **14** (^{1}H NMR analysis), whereas the ^{19}F NMR spectrum indicated 83% **14**, 4% thiolane **17**, and 4% cyclopropane **18**. The reaction with the cis olefin **3c** provided nearly the same product mixture under conditions where the cis → trans isomerization **3c** → **2c** was slow.

14



11 + **2c**

15 *gauche* **16** *anti*

17 **18** **9**

The lemon-yellow crystals of **14**, mp 88–89 °C, are moderately stable on exposure to air. The AB spectrum of 7-H_2 occurs at δ 3.15 and 3.48 with 16 Hz ($CDCl_3$); the ^{13}C signals, δ 185.7 for C-4 and 61.7 for C-5 (q, $J_{C,F}$ = 39 Hz), agree with those of **5c**[4] and open-chain ketene imines.[8] The IR absorption of the cumulated bond system at 2019 cm^{-1} (CCl_4) is the strongest in the spectrum.

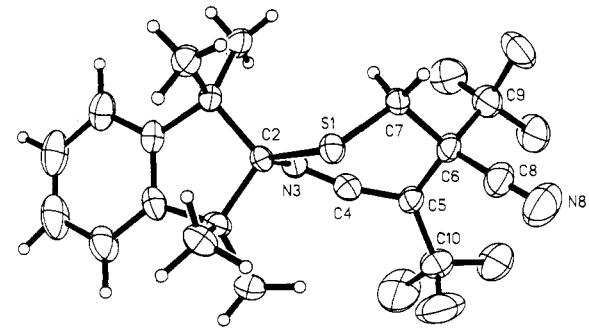


Figure 1. ORTEP drawing of the X-ray structure of ketene imine **14** (thermal ellipsoids represent a 30% probability level).

The X-ray analysis (Figure 1)[9] confirmed the seven-membered ring structure of **14**. Bond lengths of 133 and 120 pm for the cumulated system C=C=N hardly deviate from those of diphenylketene *p*-tolylimine (133 and 121 pm)[10] or *o*-tolylimine (136 and 121 pm).[11] The involvement of the allenic type bond system into a seven-membered ring creates strain. The C=C=N bond system is not linear but rather bent to 163.8 °C.[12] The N–C single bond should form a 90° angle with the plane of the olefinic C-atom (C5), an expectation fulfilled, e.g., in diphenylketene *o*-tolylimine.[11] However, in **14** the dihedral angle C6–C5–N3–C2 has shrunk to 58 °C. Furthermore, the bond system at C5 is not planar; its deviation —C5 is located 13 pm above the plane of C4, C6, C10—signals another deformation caused by ring strain.

So far, the smallest ring harboring a ketene imine group was the eight-membered 3,8-dibenzyl-1-azacycloocta-1,2-diene.[13] With two stereocenters, i.e., C-6 and the ketene imine system, two diastereoisomers of **14** are conceivable. Only one species appears to be formed although a few percent of a second isomer in the mother liquor cannot be excluded. A fast N-inversion (NMR time scale) as observed for open-chain ketene imines[14] appears improbable for **14** since inversion is slow for the eight-membered cyclic representative[13] and should be even more hindered for the seven-membered ring. In fact, the thermal ellipsoid of N3 (Figure 1) is normal and does not suggest a preinversion mode.

The rearrangement of ketene imine **5c** to the thiolane

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(9) Crystallographic data: $C_{20}H_{18}F_6N_2S$, mol wt 438.4, orthorhombic, a = 30.444 (14), b = 10.659 (4), and c = 6.217 (2) Å, space group $Pna2_1$, Z = 4, D_c = 1.443 g cm^{-3}, $F(000)$ = 888.0, T = 213 K, μ(Mo K_α) = 2.12 cm^{-1}. Data collection: Syntex R3 diffractometer, crystal (size 0.31 × 0.35 × 0.45 mm) mounted in a glass capillary, cell constants from 25 centered reflexions, Mo Kα radiation, graphite monochromator, λ = 0.71069 Å, ω scan with profile fitting, scan rate variable 1.8–29.3° min^{-1} for <150 to >2500 counts s^{-1}, scan ranges 0.4, 0.4°, background/scan ratio 0.5, intensity of two standard reflexions checked after every 48 intensity measurements, 2θ range 2–45° for all h +/−k +/−l, 4233 reflexions measured, 129 rejected (3 with too high an intensity, 122 with spikes, 4 asymmetric), data corrected for Lorentz and polarization effects as well as changes in standard's intensities (<1.5%), 3808 unique reflexions, 3567 considered as observed with $I > 3\sigma(I)$. Structure solution and refinement: direct methods of the SHELXTL program package (Nicolet version 4.1), non-hydrogen atoms refined anisotropically, hydrogen atoms isotropically with fixed U_i = 0.05, blocked matrix refinement. Final R and R_w values were 0.051 and 0.054, respectively ($R = \sum|\Delta F|/\sum|F_o|$ and $R_w = (\sum|\Delta F|w^{1/2})/(\sum|F_o|w^{1/2})$ with $1/w = \sigma^2(F) + 0.00143\,(F)^2$). GOOF = 1.435, final mean Δ/σ = 0.05, ρ_{max} = 0.43 e Å^{-3}. The final difference map was featureless for 314 refined variables.
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(11) Jochims, J. C.; Lambrecht, J.; Burkert, U.; Zsolnai, L.; Huttner, G. *Tetrahedron* **1984**, *40*, 893.
(12) X-ray results on open-chain ketene imines show 170–175 °C for C=C=N. An energy minimum was calculated for 175° by SCF with STO-3G basis set.[11]
(13) Firl, J.; Schink, K.; Kosbahn, W. *Chem. Lett.* **1981**, 527. The ketene imine was an unstable oil that was not obtained analytically pure.
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6c at 60 °C is 850 times faster in acetonitrile than in cyclohexane,[5] suggesting the gauche zwitterion **4** as an intermediate. The half-life of **14** at 40 °C amounted to 138 h in CS_2 and 35 h in $CDCl_3$. Products were the *trans*-thiolane **17** and the *trans*-cyclopropane **18** in the time-independent ratio of 78:22 (kinetic control); in addition, the ^1H NMR spectrum showed the methyl singlet of thione **9**. An equilibration of the gauche zwitterion **15** with anti conformation **16** is assumed. The cyclopropane formation is interpreted by an intramolecular nucleophilic substitution of **16**, thione **9** being the leaving group. The preference for the trans structures of **17** and **18** may result from steric factors.

In contrast to **4c** → **6c**, the ring closure **15** → **17** is reversible. In benzonitrile at 80 °C, **17** is converted to **18** + **9** with a half-life of 13 h. The thermodynamic preference of **18** + **9** must be due to the loss of steric strain in the indane-spiro-thiolane **17** and the entropy factor (two molecules from one), thus outweighing the ring strain of cyclopropane **18**.

The isolation of **17**, mp 113 °C, required removal of **18** + **9** by distillation. The CF_3 groups of **17** appear at δ_F -58.2 and -63.9 ($J_{F,F}$ = 11.6 Hz), less different than in **14** (-55.6, -73.7). After thermolysis of **17** (140 °C, neat), cyclopropane **18**, mp 58-59 °C, was sublimed at 40-50 °C. The singlet of 3-H_2 at δ 2.46 is broadened by H,F coupling. The CF_3 groups form a singlet at δ -66.2 in the ^1H-decoupled ^{19}F NMR spectrum.

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Stereospecific Telluride-Mediated Conversion of Glycidols to Allyl Alcohols: An Extension of the Sharpless Kinetic Resolution

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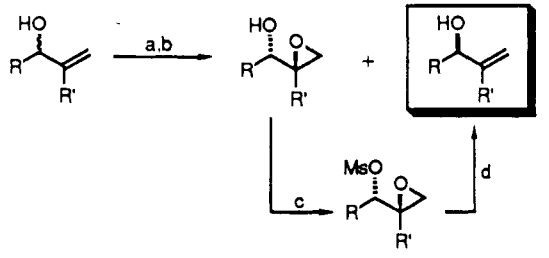
Summary: Treatment of methanesulfonate esters of terminal glycidols obtained by epoxidation in the Sharpless kinetic resolution (SKR) of 1-substituted 2-propenols (secondary allyl alcohols) with telluride ion (Te^{2-}) converts the glycidols to allyl alcohols of the same stereochemical configuration as the unreacted enantiomer from the SKR.

The Sharpless kinetic resolution (SKR) of secondary allyl alcohols,[1] like all resolutions, is limited to a theoretical yield of 50% of one enantiomer from the racemic mixture. In the Sharpless procedure, one enantiomer of the allyl alcohol is converted to a glycidol, leaving the slower reacting enantiomer virtually untouched. The mixture is easily separated, and the allyl alcohol and the glycidol of high optical purity can be obtained when the relative rates of epoxidation of the two enantiomers are sufficiently different. We report that the glycidol, whose carbinol carbon atom has a configuration opposite to that of the allyl alcohol, can be converted to the same allyl alcohol obtained in the kinetic resolution. The process involves an application of telluride chemistry used in our earlier, general synthesis of allyl alcohols.[2] This combination of the SKR and our telluride method effects a conversion of a racemic allyl alcohol to a single enantiomer, the theoretical yield being 100%. The inversion of configuration that occurs in the telluride-mediated reactions that we have studied is complete, and the yields of allyl alcohol in this process are generally high (typically 87-93%, although in one case a 69% yield was obtained). Combined yields of allyl alcohol from both the kinetic resolution and telluride steps range from 75-88%.[3]

The glycidol product in the SKR is converted to the methanesulfonate ester by the action of methanesulfonic anhydride and pyridine, followed by treatment with telluride ion generated by the in situ reduction of the element by sodium hydroxymethanesulfinate dihydrate (Rongalite).[4] The overall transformation that occurs is the deoxygenation of the epoxide with concurrent inversion of the carbinol center to give the desired allyl alcohol. Deoxygenations by tellurium reagents of epoxides that do not bear proximate leaving groups have been reported previously.[5,6]



(1)[7]

(a) Ti(O-*i*-Pr)$_4$, TBHP, (+)- or (-)-DIPT, CH_2Cl_2; (b) chromatographic separation (silica gel); (c) $(CH_3SO_2)_2O$, pyridine, DMAP, CH_2Cl_2; (d) Te (1.1 equiv), $HOCH_2SO_2Na{\cdot}2H_2O$ (3 equiv based on tellurium), NaOH (5 equiv based on tellurium, 1 N), 50 °C, 2 h; cool to room temperature; add mesylate in THF.

Although there are a number of methods for inverting carbinol carbon centers, we know of no single-step procedure to deoxygenate an epoxide and invert an adjacent carbinol center. Furthermore, the tellurium from these reactions is recovered and may be reused. If the epoxy alcohol is desired, the allyl alcohol from the SKR may be epoxidized, inverted via the telluride method, and re-epoxidized under the conditions for the Sharpless asymmetric epoxidation.[1a]

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(2) Polson, G.; Dittmer, D. C. *Tetrahedron Lett.* **1986**, *27*, 5579-5582.

(3) The deviation from 100% ee is the result of the kinetic resolution step and depends on the relative rates of epoxidation of the two enantiomers of the allyl alcohol. The overall yields suffer both in the epoxidation step and in the telluride step. However, no attempts were made to optimize them.

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