

provide a rich source of intriguing problems. Hopefully, the present work establishes that the fascination extends beyond competing transition states to the physical properties of norbornyl derivatives in their ground states.

**Acknowledgments.** The authors are grateful for discussions with Professors E. M. Arnett, H. C. Brown, P. v. R. Schleyer, and R. A. Sneen. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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- (14) Complete geometric parameters calculated for the molecules in this work may be obtained from the authors upon request.
- (15) The MINDO/3 values for the heats of formation of norbornyl compounds are uniformly too high by  $\sim 20$  kcal/mol.<sup>9</sup>
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- methylcyclopentyl cation (164.3 kcal/mol), 1-methylcyclopentyl chloride ( $-34.8$  kcal/mol), and its protonated form (131.2 kcal/mol). Some of the values differ from Dewar's earlier reports,<sup>9</sup> presumably owing to improvements in the current MINDO/3 optimization procedures.
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- (32) The larger coefficient on the *exo*-3-H compared to the *endo*-3-H indicates stronger hyperconjugation with the former hydrogen. This is consistent with the more facile *exo* 3  $\rightarrow$  2 hydride shifts observed experimentally and theoretically for 2-norbornyl cations.<sup>3,4,12</sup>
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- (37) NOTE ADDED IN PROOF. Additional support can be found for the description of the 2-norbornyl cation by MINDO/3. Particularly, the agreement between the  $\Delta H_f$ s in eq 7 and 8 and Arnett's recent work<sup>31</sup> is good. In addition, the MINDO/3 value for the proton affinity of norbornene, 197.8 kcal/mol,<sup>38</sup> also compares well with the ICR value, 198.8 kcal/mol.<sup>39</sup> Thus, it appears that the strain in norbornyl derivatives is uniformly overestimated by MINDO/3.<sup>9</sup> However, the method's performance on the 7-norbornyl cation is still an anomaly<sup>40</sup> ( $\Delta H_f = 211.1$  kcal/mol<sup>38</sup> vs. 214.2 kcal/mol for 2-norbornyl<sup>12</sup>).
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## Molecular Asymmetry in *trans*-Thiacycloalkenes. 1. Interconversion of Diastereomeric *trans*-2-Methylthiacyclooct-4-enes

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**Abstract:** Rearrangement of the allyl sulfonium ylide derived from *cis*- and *trans*-1-ethyl-2-vinylthiolanium hexafluorophosphate gives three ring-expanded products, *cis*-2-methylthiacyclooct-4-ene (**2**) and two diastereomeric *trans*-2-methylthiacyclooct-4-enes, **3** and **4**. The existence of the latter two is evidence of the molecule possessing two elements of chirality, a chiral center ( $C_2$ ) and a plane, the diastereoisomers deriving their stability from restricted conformational inversion around the chiral plane. The two diastereoisomers are capable of thermal interconversion in what appears to be a purely unimolecular process ( $\Delta H^\ddagger = 29.7$  kcal/mol,  $\Delta S^\ddagger = -1$  eu) similar to that responsible for the racemization of *trans*-cyclooctene,<sup>4</sup> but considerably faster (a factor of  $10^3$ ). The greater ease of stereomutation of the heterocyclic olefin is discussed in relation to the conformational processes required for inversion around the chiral plane.

Medium- and large-size carbocycles ( $n \geq 8$ ) may incorporate a *trans* double bond. The resulting species are dissymmetric and give rise to enantiomeric conformations,<sup>1</sup> whose stability

appears to depend on ring size. For the larger rings ( $n \geq 10$ ) the enantiomeric conformers interconvert rapidly at room temperature and cannot be separated;<sup>2</sup> however, the rates of

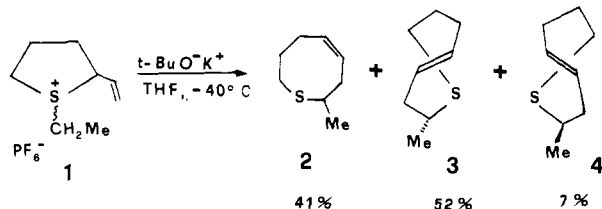
interconversion and the corresponding energy barriers can be obtained by dynamic NMR.<sup>3</sup> On the other hand, for the smaller ring sizes ( $n = 8, 9$ ) the conformers are stable enough to allow their interconversion to be studied by ordinary kinetic methods.<sup>1c,2,4</sup> The best known example is that of *trans*-cyclooctene, in which the barrier for chiral inversion is  $\sim 35$  kcal/mol, and the enantiomers are indefinitely stable at room temperature.<sup>4</sup>

Although, to the best of our knowledge, the resolution of heterocyclic *trans* olefins has never been reported, there is no reason why, given the appropriate ring size, they may not be separated in stable enantiomeric forms. In this paper we present evidence indicating that a sulfur-containing eight-membered cyclic olefin, *trans*-thiacyclooct-4-ene, is an intrinsically asymmetric molecule whose enantiomeric conformers most likely are capable of separate existence such as to allow chemical handling at ordinary temperatures.

## Results

The synthesis of diastereomeric 2-methylthiacyclooct-4-enes has been achieved through the Vedejs ring expansion procedure<sup>5</sup> (which involves the rearrangement of a phenacyl stabilized allylic sulfonium ylide) modified so as to adapt it to nonstabilized ylides.<sup>6</sup>

Ring expansion via rearrangement of the sulfonium ylide from a mixture of *trans*- and *cis*-1-ethyl-2-vinylthiolanium hexafluorophosphate (**1**) yielded a mixture of three sulfides, **2**, **3**, and **4**, roughly in the ratio 4:5:1 which were separated by preparative GLC and column chromatography.<sup>7</sup>



Sulfide **2** proved to be *cis*-2-methylthiacyclooct-4-ene. The major and minor products, **3** and **4**, appear to be the diastereomerically related (*SR,RS*)- and (*RR,SS*)-*trans*-2-methylthiacyclooct-4-ene, respectively.<sup>9,10</sup> The configurational assignment of **3** and **4** is tentative and could be inverted (see below).

The structural proofs are as follows: (1) The three sulfides give identical mass spectra,  $m/e$  142, indicating isomeric compounds which are converted to the same species upon electron impact. (2) Both **3** and **4** undergo irreversible thermal conversion to **2**. This isomerization takes place under very mild conditions ( $100^\circ\text{C}$ , several hours) and appears to occur via a radical process. Indeed, in the presence of an effective radical inhibitor, 2,6-di-*tert*-butylphenol, the conversion of **3** (or **4**) to **2** occurs negligibly even at  $120^\circ\text{C}$ . The direction of the isomerization, i.e., *trans*  $\rightarrow$  *cis*, agrees with the fact that in medium-sized cyclic olefins, the *cis* isomer is thermodynamically more stable.<sup>11</sup> (3)  $^1\text{H}$  NMR. The vicinal coupling constant of the olefinic protons provides evidence of the configuration of the double bond. For compound **2**  $^3J_{\text{HH(olefinic)}} = 9.5$  Hz, characteristic of a *cis* double bond,<sup>13</sup> while for both **3** and **4** the corresponding couplings are 15.5 Hz, a value typical of *trans* double bonds.<sup>13,5</sup> (4)  $^{13}\text{C}$  NMR. The olefinic carbons of **2** resonate closer together, and at relatively high field ( $\delta_{\text{Me}_4\text{Si}}$  131.0 and 128.5) than those of either **3** (136.6 and 131.7) or **4** (139.6 and 127.5). Moreover, the ring carbons of **2** resonate at higher field than those of both **3** and **4** (see Experimental Section). This behavior is consistent with the assigned structures, since in cyclic as well as acyclic alkenes, the *cis* olefinic carbons appear to resonate upfield with respect to the corresponding *trans* isomers.<sup>14</sup> Thus in *cis*- and *trans*-cyclooctene

**Table I.** Equilibration Rates of Diastereomeric *trans*-2-Methylthiacyclooct-4-enes in *n*-Octane at Various Temperatures

Temp, $^\circ\text{C}$	100.0	110.0	120.0	126.0
$10^4k, \text{s}^{-1}$	0.136	0.379	1.11	1.98

the olefinic carbons resonances occur at 130.4 and 134.0 ppm, respectively, while the  $\alpha$ ,  $\beta$ , and  $\gamma$  carbons resonate 9.5, 5.7, and 2.8 ppm more upfield in the *cis* than in the *trans* isomer.<sup>15</sup> (5) Definitive structural proof of **2** has been obtained by x-ray analysis of a platinum complex.<sup>16</sup> (6) Under conditions where the *trans*  $\rightarrow$  *cis* isomerization is prevented, another process can be observed, namely, the thermal interconversion  $\mathbf{3} \rightleftharpoons \mathbf{4}$ .

Of the two *trans* isomers, that which is formed more abundantly, **3**, appears to be the less stable thermodynamically, the equilibrium constant being  $[\mathbf{4}]/[\mathbf{3}] = 6.6 \pm 0.1$  at  $100^\circ\text{C}$ , the same value being reached starting from either side. The equilibrium constant decreases somewhat with increasing temperature:  $K = 6.1$  and  $5.6$  at  $124$  and  $150^\circ\text{C}$ , respectively, from which  $\Delta H \approx -1.0$  kcal/mol may be calculated.

We have measured the rate of equilibration,  $\mathbf{3} \rightleftharpoons \mathbf{4}$ , in *n*-octane solvent at four temperatures. The reaction appears to strictly obey a first-order law; the kinetics were normally run at  $3 \times 10^{-2}$  M initial concentration of the less stable isomer and followed through 80–90% completion. The run at  $110^\circ\text{C}$  was repeated twice at initial concentrations five times as large and ten times as small, respectively, without observing any significant specific rate change. The reaction rate appears to be unaffected by solvent polarity: on changing the solvent from octane to a much more polar solvent, methyl ethyl ketone, the rate was changed by less than 10%. Packing the vessel with glass beads had no appreciable effect on the rate of the reaction, which can be concluded to occur homogeneously.

The kinetic data are summarized in Table I. From these the "thermodynamic" parameters may be computed at  $110^\circ\text{C}$  to be  $\Delta H^\ddagger = 29.7 \pm 0.4$  kcal/mol,  $\Delta S^\ddagger = -1 \pm 1$  eu.

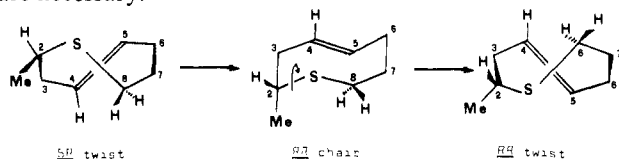
## Discussion

Although our synthesis of the thiacyclooctenes employs strongly basic conditions which might favor olefin isomerization, there can be little doubt that compounds **2–4** are not positional isomers and that the two *trans* olefins **3** and **4** are true diastereoisomers arising from the molecule having two elements of chirality. One is the chiral center at  $\text{C}_2$ ; the second is probably a chiral plane and the slow diastereomer interconversion is likely to arise from restricted conformational inversion.

The kinetic evidence is consistent with the diastereomer equilibration,  $\mathbf{3} \rightleftharpoons \mathbf{4}$ , being a reversible unimolecular process. The most likely mechanistic interpretation is that it involves epimerization through a conformational change which inverts the chirality around the chiral plane. The process would then be entirely comparable to the racemization of *trans*-cyclooctene,<sup>4</sup> with the only difference that, in the present case, the "conformers" are diastereomerically rather than enantiomerically related. Moreover, since the gross activation energy of the process would not depend on the presence of a Me group at  $\text{C}_2$ , it may be safely anticipated that *trans*-thiacyclooct-4-ene may be resolved into stable enantiomeric conformations.

The values of the activation parameters are fully consistent with this conclusion. The activation entropy in fact is close to zero in both *trans*-cyclooctene and *trans*-thiacyclooctene inversions while the enthalpy of activation is smaller for the latter by  $\sim 5$  kcal/mol, corresponding to a  $\sim 10^3$  rate increase. Without going into a detailed analysis of the various contributing factors (bond lengths and angles, bending and stretching force constants) the major single factor likely to be responsible for the greater ease of stereomutation of *trans*-thiacyclooctene

is the S heteroatom having only "phantom" ligands attached (other than the ring carbons). If the conformational changes are considered required for configurational inversion around the chiral plane, it will be realized that two distinct processes are necessary:<sup>3</sup>



In the step first depicted above the back side of the molecule, containing the  $sp^2$ -hybridized carbons, has to rotate through  $180^\circ$  around the pivot bonds  $C_3-C_4$  and  $C_5-C_6$  to produce the distorted chair conformation. In the second step a similar rotation of the front side of the molecule has to occur, the pivots now being the  $C_7C_8$  and  $SC_2$  bonds, which converts the chair into a twist conformation of inverted chirality.

The first process involves the passage of one of the olefinic hydrogens through the loop formed by the rest of the molecule and in so doing the H atom involved will suffer severe nonbonding interactions with the atoms across the ring, S and  $C_8$ , and the ligands thereon. Since, however, the heteroatom carries "phantom" ligands only, such interactions are likely to be less severe than in *trans*-cyclooctene, where both atoms across the ring carry H atoms. The second process is also likely to occur more favorably in the heterocyclic case. The "intermediate" chair conformation has two possible directions of rotation to complete the inversion. For the configuration depicted above, a clockwise rotation in the second step would bring the sulfur atom toward  $C_5$ , while a counterclockwise rotation would bring that of the H atom at  $C_8$  which projects inside, into very close proximity to the olefinic proton at  $C_5$ . Judging from models, the latter mode of rotation would appear to involve greater nonbonding interactions and the molecule will follow the former, easier route. Of course in *trans*-cyclooctene the molecule has no preferential direction of rotation, either direction being more or less equivalent to the higher energy route described for *trans*-thiacyclooctene.

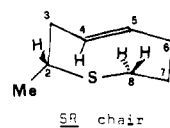
Thus no matter whether the first conformational change or the second determines the overall rate, it is quite reasonable that chiral inversion may occur more readily in the heterocyclic than in the carbocyclic case.

Although the above argument does not depend on whether the ground state has the twist conformation, as we have implicitly assumed so far, or the distorted chair, a brief discussion about the ground state conformation is in order. As we will see, this is related also to the question of configurational assignment of **3** and **4**.

As far as *trans*-cyclooctene is concerned, the more recent studies have definitely established the twist ground state conformation both in the gas phase (electron diffraction)<sup>19</sup> and in the solid state (x ray of derivatives).<sup>20</sup> However, reliable calculations indicate the chair form to be only 2.5<sup>21</sup> or 3.1<sup>22</sup> kcal/mol above. On this premise it is not at all certain that *trans*-thiacyclooct-4-ene should have the twist conformation as we have implicitly assumed.

We have sought to obtain conformational information from  $^1H$  NMR; unfortunately, however, the 270-MHz spectra of these multispin systems appear to be too complex to even afford partial solutions.<sup>23</sup> On the other hand,  $^{13}C$  NMR is not very suitable for conformational analysis in rings other than six membered.<sup>24</sup> It may be very valuable (particularly through the evaluation of  $\gamma$  shieldings)<sup>25</sup> for configurational assignments, provided, however, that the conformation is known. In the case at hand, the conformational possibilities are limited (twist or chair) and the configurational assignment may be attempted on the basis of the steric relations prevailing in each conformer.

From stereomodels of the four possible diastereomeric conformers (illustrated by the stereoforulas above and below)



the spatial relations of the Me group with respect to the two  $\gamma$  carbons,  $C_4$  and  $C_8$ , result as follows.

Conformer	$C_8$	H at $C_4$
<i>SR,RS</i> twist	Gauche	Same side as $CH_3$ , $\omega_{23} \approx 100^\circ$
<i>RR,SS</i> twist	Anti	Side opposite to $CH_3$ , $\omega_{23} \approx 140^\circ$
<i>RR,SS</i> chair	Gauche	Side opposite to $CH_3$ , $\omega_{23} \approx 100^\circ$
<i>SR,RS</i> chair	Anti	Same side as $CH_3$ , $\omega_{23} \approx 140^\circ$

On these bases and assuming that the  $\gamma$  shieldings are essentially steric in origin,<sup>25</sup> it can be predicted that, if the ground state adopts the twist conformation, both  $C_4$  and  $C_8$  should be upfield in one conformer, which may be assigned the *SR,RS* configuration. If instead the ground state adopts the distorted chair conformation, in one diastereomer (*RR,SS*)  $C_8$  must be upfield and  $C_4$  downfield with respect to the other diastereomer.

The comparison of the  $^{13}C$  NMR spectra of **3** and **4** shows that both  $C_4$  and  $C_8$  resonate ( $\delta_{Me_4Si}$  ( $CDCl_3$ )) upfield in **3** (127.7 and 25.9 ppm, respectively) with respect to **4** (131.8 and  $\geq 33.8$  ppm, respectively).<sup>26</sup> Therefore, on the basis of the arguments above, **3** and **4** may be tentatively assumed to have the twist conformation and assigned the *SR,RS* and *RR,SS* configuration, respectively.

We are fully aware, however, that such assignment is highly tentative and awaits further confirmatory evidence. We are currently synthesizing deuterium-labeled and methyl-substituted derivatives for conformational studies in solution, as well as solid derivatives for x-ray studies.

## Experimental Section

$^1H$  NMR spectra were recorded in  $CDCl_3$  at 60 MHz on a JEOL C-60 HL instrument and at 270 MHz on a Bruker WHF 270 instrument operating in the FT mode. Proton noise decoupled  $^{13}C$  spectra were recorded at 20.1 MHz on a Varian CFT-20 spectrometer by the FT technique. Single-frequency off-resonance spectra were obtained by irradiation with a continuous wave at about  $\delta -4$  in the proton spectrum. Mass spectra and exact mass determinations were obtained with a JEOL JMS-D100 instrument. Analytical GLC analyses and preparative GLC separations were carried out with a Hewlett-Packard 5700 and Perkin-Elmer F 21 gas chromatographs, respectively, equipped with flame ionization detectors.

Solvents were reagent grade. Tetrahydrofuran, dried over sodium and distilled, was redistilled from lithium aluminum hydride under nitrogen immediately before use. Methylene chloride and *tert*-butyl alcohol were distilled from calcium hydride.

**2-Vinylthiolane** was prepared by the procedure outlined by Vedejs,<sup>5</sup> 69% yield (lit.<sup>5</sup> 80%), bp 159–160  $^\circ C$  (760 mm). Anal. Calcd for  $C_6H_{10}S$ : C, 63.13; H, 8.84. Found: C, 63.25; H, 8.72. The  $^1H$  NMR spectrum was fully consistent with the title compound structure.

**1-Ethyl-2-vinylthiolanium Hexafluorophosphate (1)**. Triethyloxonium fluoborate (4.0 g, 21 mmol) was added rapidly to 2-vinylthiolane (2.3 g, 20 mmol) in dry  $CH_2Cl_2$  (20 mL) at 0  $^\circ C$ . After warming at room temperature, stirring was continued for 4 h. The residue after  $CH_2Cl_2$  evaporation was dissolved in  $H_2O$  (20 mL) and treated with an aqueous solution of  $NH_4PF_6$  (3.6 g, 22 mmol, in 8 mL). The precipitate was collected (4.3 g, 75%, mp 51–55  $^\circ C$ ) and the filtrate extracted with  $CH_2Cl_2$  gave an additional 0.3 g (5%), recrystallized from EtOH, mp 54–56  $^\circ C$ . Anal. Calcd for  $C_8H_{15}SPF_6$ : C, 33.33; H, 5.25. Found: C, 33.28; H, 5.32. The 60-MHz spectrum is consistent with the structure of the title compound:  $\delta_{Me_4Si}$  ( $CF_3COOH$ ) 5.5 complex multiplet extending over 1 ppm, 3 H, vinyl protons; 4.2 broad unresolved m, 1 H, methine proton at  $C_2$ ; 3.4 unresolved multiplet partially superimposed to a quartet,  $\delta$  3.2, 4 H overall, endo- and exocyclic  $S^+-CH_2$ 's; 1.52 and 1.45, triplets in a  $\sim 9:1$  ratio, 3 H overall, Me

groups. The latter resonances clearly indicate a mixture of isomers (*cis* and *trans*). No appreciable enrichment was obtained on further crystallization. Therefore the material was used as such in the subsequent ring expansion reaction.

#### Ring Expansion of 1-Ethyl-2-vinylthiolanium Hexafluorophosphate.

To a solution of the title sulfonium salt (5.76 g, 20 mmol) in dry THF-*t*-BuOH (10:1 v/v, 175 mL) at  $-40^{\circ}\text{C}$ , potassium *tert*-butoxide (2.88 g, 26 mmol) was added and stirred for 2 h. The dry ice bath was removed and, after warming to room temperature, the solution was quenched with  $\text{H}_2\text{O}$ , acidified with dilute HCl, and treated with aqueous  $\text{HgCl}_2$ . The mercuric chloride adduct<sup>27</sup> was collected and the sulfides regenerated by treatment with aqueous KI (40% w/w) under stirring, followed by pentane extraction. Removal of the solvent gave 1.8 g (62%) of a crude sulfide product which appeared to be made up of three products, **2** (41%), **3** (52%), and **4** (7%). The composition did not vary appreciably throughout several preparations.

The three products were obtained in pure form as follows.

**cis**-2-Methylthiacyclooct-4-ene (**2**). By heating the crude sulfide mixture ( $150^{\circ}\text{C}$ , 4.5 h), **3** and **4** were converted quantitatively to **2**, which was distilled, bp  $206^{\circ}\text{C}$  (760 mm). Exact mass, 142.081 53 (calcd for  $\text{C}_8\text{H}_{14}\text{S}$ , 142.081 55). The relevant  $^1\text{H}$  NMR features are (270 MHz)  $\delta$  5.70 and 5.58, 1 H, olefinic protons ( $^3J_{\text{HH}} = 9.5$  Hz); 2.80, broad m, 1 H, methine H at  $\text{C}_2$ ; 1.28 d,  $\text{CH}_3$ . The  $^{13}\text{C}$  NMR spectrum has  $\delta_{\text{Me}_4\text{Si}}$  131.0 ( $\text{C}_5$ ), 128.5 ( $\text{C}_4$ ), 41.7 ( $\text{C}_2$ ), 39.1 ( $\text{C}_3$ ), 30.5 and 28.0 ( $\text{C}_6$  and  $\text{C}_7$ , interchangeable), 23.8 ( $\text{C}_6$ ), 22.0 ppm ( $\text{CH}_3$ ); IR strong absorption at  $710\text{ cm}^{-1}$  (characteristic of *cis* olefins).

**trans**-2-Methylthiacyclooct-4-ene (**3**) has a tentative configurational assignment of *SR,RS* (see Discussion). Preparative GLC of the crude sulfide mixture ( $\frac{3}{8}$  in.  $\times$  3 m column, 10% XE-60 on Chromosorb W 60/80 mesh at  $100^{\circ}\text{C}$ ) allowed for the isolation of pure **3**. The mass spectrum was identical with that of **2**. The  $^1\text{H}$  NMR spectrum at 270 MHz is second order; however, the olefinic protons ( $\delta$  5.96 and 5.58) showing a 15.5-Hz coupling give unambiguous indication of a *trans* double bond. Other relevant features are 3.44 broad m, 1 H, methine H at  $\text{C}_2$ ; 1.43 d, 3 H,  $\text{CH}_3$ . It is remarkable how, with respect to the *cis* isomer, **2**, all the resonance are downfield.  $^{13}\text{C}$  NMR  $\delta_{\text{Me}_4\text{Si}}$  139.6 ( $\text{C}_5$ ), 127.5 ( $\text{C}_4$ ), 49.9 ( $\text{C}_2$ ), 41.8 ( $\text{C}_3$ ), 37.7 and 35.0 ( $\text{C}_6$  and  $\text{C}_7$  interchangeable), 25.9 ( $\text{C}_6$ ), 21.4 ppm ( $\text{CH}_3$ ). All the resonances occur downfield with respect to the *cis* isomer in agreement with a *trans* configuration.<sup>15,16</sup> IR strong absorption at  $960\text{ cm}^{-1}$  (characteristic of *trans* olefin).

**trans**-2-Methylthiacyclooct-4-ene (**4**) has a tentative configurational assignment of *RR,SS* (see Discussion). As sufficient separation from **2** could not be achieved by preparative GLC, pure **4** was obtained by column chromatography as follows: the crude sulfide mixture dissolved in *n*-octane was heated ( $150^{\circ}\text{C}$ , 2.5 h) in the presence of a radical inhibitor, di-*tert*-butylphenol (15% of the total sulfide). Under these conditions the *trans*  $\rightarrow$  *cis* isomerizations were slowed down enough to allow for the equilibration  $\mathbf{3} \rightleftharpoons \mathbf{4}$  to be achieved. The final mixture, enriched in **4** ( $\sim 40\%$ ), was chromatographed on a silica gel column with *n*-pentane eluent to yield pure **4**. The mass spectrum was identical with that of **2** and **3**. The  $^1\text{H}$  NMR spectrum at 270 MHz, although second order, clearly indicated a *trans* double bond as the olefinic protons ( $\delta$  5.84 and 5.36) show a 15.5-Hz coupling. Other relevant features are 3.00 broad m, 1 H, methine H at  $\text{C}_2$ ; 1.27 d, 3 H,  $\text{CH}_3$ . All the resonances are downfield with respect to the *cis* isomer **2** and upfield with respect to the *trans* isomer **3**. The  $^{13}\text{C}$  NMR spectrum has  $\delta_{\text{Me}_4\text{Si}}$  136.6 ( $\text{C}_5$ ), 131.7 ( $\text{C}_4$ ), 54.3 ( $\text{C}_2$ ), 44.9 ( $\text{C}_3$ ), 35.7, 34.8, and 33.8 ( $\text{C}_6$ ,  $\text{C}_7$ , and  $\text{C}_8$ , interchangeable), 21.2 ppm ( $\text{CH}_3$ ). In agreement with a *trans* double bond configuration, all the resonances are downfield with respect to the corresponding ones of the *cis* isomer **2**. IR strong absorption at  $960\text{ cm}^{-1}$ .

**Trans  $\rightarrow$  Cis Isomerization and Kinetics of the Thermal Interconversion of Diastereomeric *trans*-2-Methylthiacyclooct-4-enes.** Upon heating, **3** and **4**, either pure or in the crude sulfide mixture, undergo irreversible isomerization to **2**. The purified *trans* isomers appear to isomerize under milder conditions than the crude. The rate data, however, are completely erratic and we have not been able to standardize the reaction conditions. The addition of a radical chain inhibitor (di-*tert*-butylphenol) almost completely suppressed the *trans*  $\rightarrow$  *cis* isomerization, thus allowing for the observation of the thermal conversion of **3** to **4** and vice versa. The kinetics of equilibration were followed at four temperatures in *n*-octane. Pyrex glass ampules were cleaned with hot chromic acid solution, rinsed with water and ammonium hydroxide, and oven dried. The solution of the less stable isomer, **3**, and di-*tert*-butylphenol ( $3 \times 10^{-2}$  and  $3 \times 10^{-3}$  M in olefin

and phenol, respectively) was divided into 0.1-mL portions, placed in the ampules, and sealed in vacuo after three liquid  $\text{N}_2$  freezing-degassing cycles. The ampules were placed in a constant-temperature bath ( $\pm 0.1^{\circ}\text{C}$ ), removed at the appropriate time intervals, and quenched. The composition of the samples was determined by measuring the relative areas of the isomers peaks in the vapor phase chromatograms ( $\frac{1}{8}$  in.  $\times$  3 m column, 10% XE-60 on Chromosorb W 80/100 mesh). For each samples three to four chromatograms were obtained, the reproducibility in the measurement of the relative areas being better than 2%. For each kinetic run six to eight samples were withdrawn, the reaction being followed up to 80–90% equilibration. In two experiments at  $100^{\circ}\text{C}$  the initial concentration was raised to  $1.5 \times 10^{-1}$  and lowered to  $3 \times 10^{-3}$ , respectively (always in the presence of 10 mol % inhibitor). In another experiment at  $110^{\circ}\text{C}$  the surface to volume ratio was increased by approximately a factor of 25 by filling the vials with glass beads.

The equilibrium constants were determined after heating periods corresponding to 10–12 half lives on three independent samples. The determination at  $124^{\circ}\text{C}$  was repeated starting with either isomer.

**Acknowledgment.** Financial support by CNR, Rome, is gratefully acknowledged. We also thank Dr. G. Barbarella and Mr. D. Macciantelli for the high-field  $^1\text{H}$  NMR and the  $^{13}\text{C}$  NMR spectra, and Dr. C. M. Camaggi for the mass spectra.

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- (7) The dependence of product distribution on the stereochemistry of the starting material could not be established since we were unable to achieve separation of the isomeric starting sulfonium salts. There are, however, strong indications that the ring enlargement reaction is not stereospecific. The evidence rests upon the observation that a 1:1 equilibrium mixture of *cis*- and *trans*-1-methyl-2-vinylthiolanium hexafluorophosphates, subjected to ring expansion conditions, gives the same product distribution (85% *cis*- and 15% *trans*-thiacyclooct-4-ene) as given by the pure *trans* sulfonium salt.<sup>6</sup> Moreover, when ring expansion of the pure *trans*-1-methyl-2-vinylthiolanium cation was carried out with a defect of base, the unreacted sulfonium salt recovered was the 1:1 equilibrium mixture.<sup>6</sup> Apparently the reaction conditions promote relatively rapid isomerization of the starting material, presumably via reversible abstraction of the very acidic methine proton. There is no reason to believe that the 1-ethyl-2-vinylthiolanium cation would behave differently.
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- (9) In each pair of configurational descriptors, the first descriptor refers to the chiral plane and the second to the chiral center. This convention we will use throughout the paper. The formulas above show, of each diastereoisomer, only the first mentioned enantiomer.
- (10) It is remarkable that in the ring expansion of a carbonyl stabilized ylide, Vedje could detect in the product only one of the two possible *trans*-2-phenacylthiacyclooct-4-enes.<sup>5</sup>
- (11) The ring strain of *trans*-cyclooctene appears to be some 9.3 kcal/mol greater than that of the *cis* isomer.<sup>12</sup>
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- 130.4 and  $37.8 \geq \delta_{\text{C}_6} \geq 34.8$ , downfield with respect to **3**.<sup>8</sup>  
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## Preparation and Chemistry of Vinyl Triflates. 16. Mechanism of Alkylation of Aromatic Substrates<sup>1,2</sup>

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**Abstract:** The mechanism of electrophilic aromatic substitution with vinyl triflates was investigated. Alkylation of a series of monosubstituted benzenes gave a  $\rho$  value of  $-2.57$ , one of the lowest observed in any electrophilic aromatic substitution. Cyclooctenyl and cycloheptenyl triflates alkylated anisole, but cyclohexenyl triflate did not. All alkylations were carried out in the presence of 2,6-di-*tert*-butyl-4-methylpyridine, a sterically hindered nonnucleophilic base. These data are interpreted via a vinyl cation as the intermediate electrophile. From these results it is concluded that a number of other aromatic substitutions with unsaturated progenitors such as certain vinyl halides, vinyl esters, and alkynes may also proceed via the intermediacy of vinyl cations.

The familiar Friedel-Crafts alkylation of aromatic substrates has been known for a century.<sup>3</sup> The reaction is well known to involve electrophilic attack by trisubstituted carbonium ions or carbonium-ion-like species derived from a variety of precursors such as alkyl halides, alcohols, olefins, and others with the aid of various Lewis and/or Brønsted acids as catalysts.<sup>4</sup> Similarly, electrophilic substitution by disubstituted sp-hybridized ions like acylium and nitronium ions is well established.<sup>4</sup> These latter species of course derive their existence from the considerable stabilization provided to the cationic center by the adjacent heteroatom lone-pair electrons.

Considerable amount of work has also been done on aromatic alkylations with species derived from vinyl halides, vinyl esters, and alkynes catalyzed by Lewis or Brønsted acids. Shortly after the discovery of the Friedel-Crafts reaction Demole<sup>5</sup> and Anshütz<sup>6</sup> both reported the formation of 1,1-diphenylethene by alkylation of benzene with 1,1-dibromoethene and  $\text{AlCl}_3$ . Alkylation has also been reported with various other vinyl halides.<sup>7-10</sup> Similar alkylations have been observed with unsaturated esters such as Angelica lactone and vinyl acetates.<sup>11-14</sup> Alkynes and various mineral acids, both in the absence and presence of mercuric salts, have often been employed as precursors in aromatic alkylations.<sup>15-19</sup> In fact several efficient ring closures via alkylation, based upon protonation of alkynes, mostly by polyphosphoric acid, have been employed in the synthesis of certain heterocycles<sup>20,21</sup> as well as at least in one instance a steroid.<sup>22</sup>

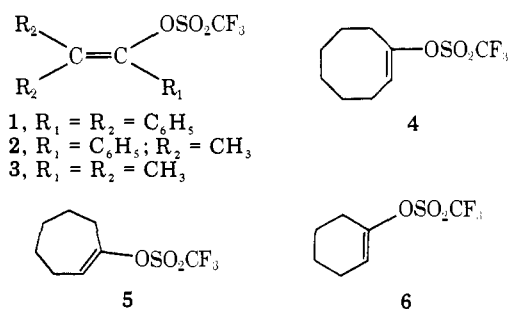
Despite the plethora of experimental data on aromatic alkylations with unsaturated precursors, very little is known about the mechanism of these reactions. Such alkylations could proceed via disubstituted sp-hybridized vinyl cations<sup>23</sup> analogous to acylations and nitrations or by a different, unknown process. Exact mechanistic interpretation of these reactions is difficult not only for lack of appropriate data but also due to complications arising from the use of heterogeneous catalysts and reaction conditions, the presence of acid, and the possibility of product rearrangements.

Hence, in order to unambiguously ascertain the feasibility of electrophilic aromatic substitution by vinyl compounds and

in particular to assess the possible involvement of vinyl cations and the exact mechanism of such reactions we undertook a careful and detailed study of Friedel-Crafts alkylation with vinyl sulfonate esters.

### Results and Discussion

It has long been known<sup>24-28</sup> that alkylations can be carried out in the absence of added Friedel-Crafts catalyst by use of alkyl sulfonate esters as carbonium ion precursors, thereby avoiding the usual complications due to heterogeneous reactions conditions. In order to increase the reactivity of normally lethargic vinylic compounds we prepared highly reactive vinyl triflates **1-6** as potential alkylating agents. Vinyl triflates **1-6**



were prepared in good yields from the appropriate ketones; in the case of **1** and **2** by trapping the KH-derived enolate<sup>29</sup> with triflic anhydride, and triflates **3-6** via known<sup>30</sup> literature procedures.

In order to avoid complications due to the acid liberated in all Friedel-Crafts alkylations, in the present case triflic acid, a base was sought that would neutralize the acid as rapidly as possible. To keep the reaction medium homogeneous, inorganic bases such as  $\text{NaH}$ ,  $\text{NaHCO}_3$ , and  $\text{Na}_2\text{CO}_3$  were avoided. Furthermore, to stop any interaction between potential electrophilic intermediates and base, thereby thwarting alkylation, sterically hindered nonnucleophilic bases were desirable. 2,6-Di-*tert*-butyl-4-methylpyridine (**7**) proved to be ideal owing to its ready availability,<sup>31</sup> deactivated aromatic ring, and