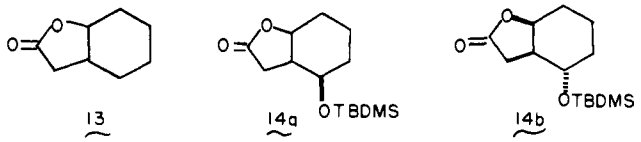
chemistry was obtained from the complete reduction of products **10**, **12a**, and **12b** with Raney nickel. This transformation yielded the known *cis*-butyrolactone **13** and the isomeric lactones **14a** and **14b**.



13 14a 14b

On the basis of the stereoselectivity of this new cyclization process, we propose the following polar mechanism as shown in Scheme I. The highly electrophilic ketene molecule is sufficiently reactive to acylate the sulfoxide oxygen atom to generate the zwitterion **15**. Through a highly ordered transition state, we envisage a rearrangement initiated by the carbanion of **15** leading to a Pummerer-type[9] intermediate **16**. This latter species can be intramolecularly trapped by the carboxylate anion to produce the observed lactone products.[10] We believe that the rearrangement of zwitterion **15** to the lactones is the first example of an intramolecular and stereoselective addition of a carbanion to a vinyloxysulfonium cation. The lower yields of lactones using the triethylamine method B can be rationalized by the fact that the byproduct triethylammonium chloride protonates **15** and prevents the formation of **16**. The greater solubility of ammonium chlorides in methylene chloride also explains why ether is a better solvent for the reaction.

The utilization of vinylacyloxysulfonium intermediates in stereocontrolled formation of carbon–carbon bonds offers new strategies in the synthetic chemistry of vinyl sulfoxides and their precursors, vinyl sulfides. We are currently exploring the generality of this rearrangement/cycloaddition process and its applications to natural products synthesis.

(9) For an example of a vinylogous Pummerer rearrangement via an unsaturated (phenylthio)carbonium ion, see: Kosugi, H.; Uda, H.; Yamagawa, S. *J. Chem. Soc., Chem. Commun.* **1975**, 192.

(10) Scheme I only represents a simplified picture of the bond-forming process from **15** → **16** → lactone products. For Scheme I to apply, **16** must cyclize faster than it rotates about a carbon-carbon bond.

(11) Brady, W. T. *Synthesis* **1977**, 155.

Azocyclopropane

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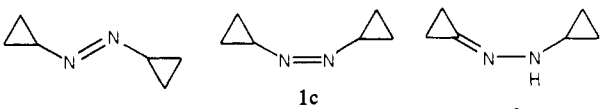
The stability of *trans*-azoalkanes toward loss of nitrogen depends primarily on the nature of the incipient alkyl radicals.[1] Although the same factor is prominent in *cis*-azoalkane chemistry, the cis–trans energy difference, which is a function of alkyl group size, is known to be equally important. When only poor alkyl radicals can be formed, *cis*-azoalkanes isomerize to trans at a rate determined by alkyl group size.[2]

The small size of cyclopropyl groups coupled with their high reactivity as free radicals[3,4] suggest that azocyclopropane (**1**) ought to be especially stable. We report here the first preparation of both the trans (**1t**) and the cis (**1c**) isomers of this simple but unusual azoalkane.[5] Tautomerism to the hydrazone (**2**), a troublesome side reaction in many azoalkanes, is not observed in **1** because of the high strain energy of methylenecyclopropanes[8] and presumably of iminocyclopropanes.

Table I. Properties of *trans*- and *cis*-Azocyclopropane

compd	bp (mp), °C	λ_{max}, nm	ϵ	$\Delta H^{\ddagger}$, kcal mol^{-1} [a]	$\Delta S^{\ddagger}$,[a] eu
1t	139	335	50	39.7 ± 0.7	−1.1 ± 1.4
1c	(38–39.5)	345	279	36.2 ± 0.5	−3.3 ± 1.1

[a] In hexadecane.



1t 1c 2

The synthesis of **1t**[9] was achieved by Si_2Cl_6 reduction[10] of the known azoxycyclopropane.[11] Irradiation of **1t** at 313 nm gave partial conversion to **1c**,[12] the mixtures being conveniently analyzed by HPLC on silica gel. After purification by chromatography on alumina (CH_2Cl_2/hexane), **1c** proved to be a solid (cf. Table I), not a very surprising result in view of the high dipole moment of *cis*-azoalkanes.[13] The UV spectrum of both isomers was unusual in that λ_{max} was lower than that of any previously reported azoalkanes; moreover, the difference between the isomers was only 10 nm, even smaller than the 16-nm separation between *cis*- and *trans*-azomethane. Since this UV band is normally attributed to an n,π^* transition, the cyclopropyl groups must stabilize the n orbital or raise the π^* energy. These possibilities are being evaluated by photoelectron spectroscopy.[14]

The most striking property of both isomers of **1** is their extraordinarily high thermal stability. The kinetics for disappearance of **1t** and **1c** were monitored by UV spectroscopy at five temperatures between 200 and 235 °C, giving the activation parameters shown in Table I.[15] While rearrangement of **1t** was a clean first-order process, disappearance of **1c** was treated as sequential first-order reactions with allowance for strongly overlapping UV absorption bands of the two isomers. A nonlinear least-squares computer program and the known rate constants for **1t** were used to extract rate constants for **1c**. Nitrogen evolution was not observed from **1c**, the exclusive reaction being isomerization to **1t**. The even more unreactive trans isomer underwent a vinylcyclopropane rearrangement to **4**[16] in strong preference to deazatization (<1%). 1,1′-Diphenylazocyclopropane exhibits the same behavior but at a lower temperature ($\Delta H^{\ddagger}$ = 31.6 kcal mol^{-1}, $\Delta S^{\ddagger}$ = −5.5 eu).[4] The observed 8.1 kcal mol^{-1} stabilization by phenyl is consistent with, but of course does not prove, a diradical mechanism for the rearrangement.[17] Because the observed $\Delta H^{\ddagger}$

(1) Engel, P. S. *Chem. Rev.* **1980**, *80*, 99.

(2) Chae, W. K.; Baughman, S. A.; Engel, P. S.; Bruch, M.; Özmeral, C.; Szilagyi, S.; Timberlake, J. W. *J. Am. Chem. Soc.* **1981**, *103*, 4824.

(3) For a recent review, see Walborsky, H. M. *Tetrahedron* **1981**, *37*, 1625.

(4) Bonnekessel, J.; Rüchardt, C. *Chem. Ber.* **1973**, *106*, 2890.

(5) Only three *trans*-azocyclopropyl compounds and no cis isomers have been reported previously.[4,6,7] As the parent compound of all azocycloalkanes, azocyclopropane is nearly as fundamental as azomethane.

(6) Chakravorty, K.; Pearson, J. M.; Szwarc, M. *J. Phys. Chem.* **1969**, *73*, 746.

(7) Rosenkranz, H. J.; Schmid, H. *Helv. Chem. Acta* **1968**, *51*, 1628.

(8) Greenberg, A.; Liebman, J. F. "Strained Organic Molecules"; Academic Press: New York, 1978; p 94.

(9) Properties of **1t**: NMR ($CDCl_3$) δ 1.08 (m, 2 H), 1.26 (m, 2 H) 3.38 (m, 1 H); MS, *m/e* (rel intensity) 110 (1), 109 (2), 68 (8), 54 (19), 41 (90), 40 (46), 39 (89), 38 (43), 28 (50), 27 (100), 26 (45). Anal. Calcd for $C_6H_{10}N_2$: 110.0844. Found: 110.0845.

(10) Greene, F. D.; Gilbert, K. E. *J. Org. Chem.* **1975**, *40*, 1409. Snyder, J. P.; Lee, L.; Bandurco, V. T.; Yu, C. Y.; Boyd, R. J. *J. Am. Chem. Soc.* **1972**, *94*, 3260.

(11) Iversen, P. E. *Chem. Ber.* **1971**, *104*, 2195.

(12) Properties of **1c**: NMR ($CDCl_3$) δ 1.08 (m, 2 H), 1.28 (m, 2 H), 3.60 (m, 1 H). MS, *m/e* (rel intensity) 110 (1), 109 (3), 68 (15), 54 (30), 41 (90), 40 (91), 39 (100), 38 (73), 27 (57), 26 (60).

(13) Stevens, J. F.; Curl, R. F.; Engel, P. S. *J. Phys. Chem.* **1979**, *83*, 1432.

(14) Houk, K. N.; Rozeboom, M. L.; Engel, P. S., work in progress.

(15) Rate data for azocyclopropane, temperature (°C), 10^5k (**1t** → **4**, s^{-1}), 10^5k (**1c** → **1t**, s^{-1}): 200.16, 0.264, 3.43; 209.95, 0.654, 7.97; 219.56, 1.51, 17.4; 230.04, 3.30, 36.3; 235.52, 5.55, 54.0.

(16) Properties of **4**: NMR ($CDCl_3$) δ 0.65 (m, 4 H), 2.1 (m, 1 H), 2.60 (distorted t, 2 H), 3.05 (distorted t, 2 H), 6.80 (m, 1 H); IR ($CDCl_3$) 3090, 3015, 2920, 2850, 1580 (C=N), 1020 cm^{-1}; MS, *m/e* (rel intensity) 110 (7), 109 (6), 83 (26), 68 (29), 55 (44), 54 (59), 41 (87), 40 (59), 39 (85), 28 (29), 27 (100), 26 (72). Anal. Calcd for $C_6H_{10}N_2$: 110.0844. Found: 110.0845.

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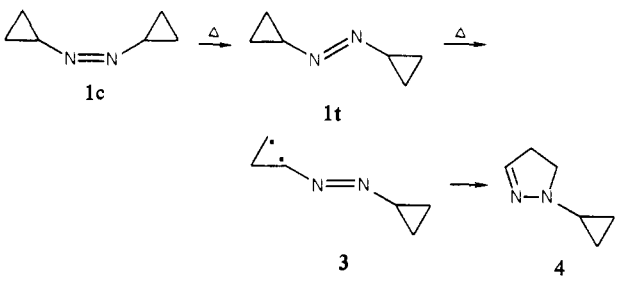
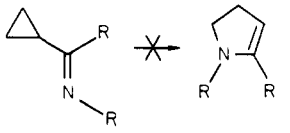


1c 1t 3 4

for **1t** is 8.8 kcal mol^{-1} below that reported for rearrangement of vinylcyclopropane ($\Delta H^{\ddagger}$ = 48.5 kcal mol^{-1}),[18] we suggest that α-azo radicals **3** might be especially stable. The extra stabilization is not that of 1-azaallyl vs. allyl because cyclopropylimines (**5**) do not undergo purely thermal rearrangement.[19] Instead, the



5

odd electron α to nitrogen appears to be resonance stabilized by the adjacent lone pair, analogous to the effect in α-azo cations.[20] It is conceivable that the distant cyclopropane stabilizes **3** by conjugation, a point which could be tested by comparison of activation parameters for vinylcyclopropane and 1,2-dicyclopropylethylene. Although the latter compound is known,[21] its rearrangement has not been reported. However, 1-cyclopropylbutadiene rearranges only 5.1 kcal mol^{-1} more readily than vinylcyclopropane.[22] Since a cyclopropyl group should be less effective than the additional double bond in stabilizing the radical, most of the 8.8 kcal mol^{-1} difference between **1t** and vinylcyclopropane is attributed to the above-mentioned three-electron stabilization.[23] Independent evidence for this effect is adduced from the lower E_a for abstraction of H· from azomethane than from ethane.[24]

Compound **1c** isomerizes over three orders of magnitude slower than the most stable cis acylic azoalkane reported to date, 1-azobicyclo[2.1.1]hexane[2] ($\Delta H^{\ddagger}$ = 30.3 kcal mol^{-1}, $\Delta S^{\ddagger}$ = 0.8 eu). Since we have found previously[2] that the transition-state free energy for azoalkane isomerization is constant at 42.1 kcal mol^{-1}, we can deduce the cis–trans ground-state energy difference for **1** as 42.1–37.8[27] = 4.3 kcal mol^{-1}. This energy difference is even smaller than the 7 kcal mol^{-1} estimated for azoisopropane.[2,28] One explanation for the low strain energy of **1c** is stabilization by cyclopropyl groups and another is reduction of alkyl group steric repulsion by "tying back" the methyls of azoisopropane. Although we have previously assumed that the cis–trans energy gap in azoisopropane would be close to the "inherent" value, the severe crowding found in *cis*-azomethane[13] suggests that values below 7 kcal mol^{-1} are possible. Unfortunately, the potentially enlightening experimental determination of activation parameters for *cis*-azomethane isomerization is rendered difficult by its facile tautomerization. Theoretically calculated cis–trans gaps are of little help because they span a broad range[1].

In summary, we have found that both cis- and trans-azocyclopropane are extraordinarily stable azoalkanes. While heating **1c** at >200 °C causes isomerization to **1t**, thermolysis of **1t** gives mostly diazavinylcyclopropane rearrangement. The activation enthalpy for this rearrangement suggests three-electron stabilization of α-azo alkyl radicals. Finally, the cis–trans energy gap (4.3 kcal mol^{-1}) estimated for azocyclopropane is the lowest discovered to date.

Acknowledgment. We thank the National Science Foundation and the Robert A. Welch Foundation for financial support.

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(23) 2,2′-Dimethoxy-2,2′-azopropane decomposes 6.4 kcal mol^{-1} more readily than 2,2′-azopropane, suggesting three-electron stabilization by the methoxyl groups. Bandlish, B. K.; Garner, A. W.; Hodges, M. L.; Timberlake, J. W. *J. Am. Chem. Soc.* **1975**, *97*, 5856. See also: Malatesta, V.; Ingold, K. U. *J. Am. Chem. Soc.* **1981**, *103*, 609.

(24) E_a is about 7.9 kcal mol^{-1} for methyl plus azomethane[25] but is 11.8 kcal mol^{-1} for methyl plus a primary C–H bond.[26] See also: Cher, M. *J. Phys. Chem.* **1964**, *68*, 1316.

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(27) This figure is $\Delta G^{\ddagger}$ (490 K) calculated from data in Table I. Free energies are used for consistency with our earlier work.[2]

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Vanadium-Catalyzed Epoxidations. 2. Highly Stereoselective Epoxidations of Acyclic Homoallylic Alcohols Predicted by a Detailed Transition-State Model[1]

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The area of stereoselective synthesis of acyclic molecules has been expanding rapidly in recent years to meet the considerable challenges posed by such complex natural products as the ionophore, macrolide, and ansamycin antibiotics.[2] Epoxidations of straight-chain olefinic alcohols have been crucial to the successful completion of a number of these synthetic efforts,[3] and the exceptional versatility of the epoxide functionality in synthesis makes further advances in stereoselective acyclic epoxidations of particular interest. Recently, a remarkably enantioselective epoxidation of allylic alcohols has been reported.[4] Although mechanistic details are yet to be established, it is now possible to unequivocally predict the direction of asymmetric induction in this system irrespective of substrate substitution. Surprisingly, the same is *not* true for the widely used vanadium/*tert*-butyl hydroperoxide procedure (V^{5+}/TBHP) when applied to acyclic systems. Although "preferred-angle" proposals have been made for some open-chain allylic alcohols,[5] a general solution applicable to all acyclic olefinic alcohols has been lacking. In a recent paper[6]

(1) This work was presented at the First IUPAC Symposium on Organometallic Chemistry Directed toward Organic Synthesis at Ft. Collins, CO, on Aug 4, 1981.

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