eq 1 should be more competitive at low electron energies. Under these conditions [a] ≥ [b], despite the unfavorable entropy of the transition state for a formation. This would suggest that ΔH_f(a) is at least 5–10 kcal/mol less than ΔH_f(b); however, ΔH_f(b) derived by Lossing[7] from $CH_3S\cdot$ suggests this is an upper limit to the difference. Molecular orbital calculations (MINDO/3;[12] ab initio, to be reported in the full paper) are in general agreement with such relative stabilities.[16]

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(16) NOTE ADDED IN PROOF. A detailed study of the effect of ionizing electron energy shows that [b]/[a] reaches a maximum value at ∼17 eV, suggesting that higher energy b ions isomerize to a.

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Impact of Methyl Imidate Functionality upon Cope Rearrangements. The Heteroatomic *cis*-1,2-Divinylcyclopropane Example[1]

Sir:

The irreversible thermal isomerization of *cis*-divinylcyclopropane (**1**) to 1,4-cycloheptadiene (**2**) has played a pivotal role in the development of our understanding of the Cope rearrangement. Although the pioneering efforts of Doering[2] and Vogel[3] did not result in the actual isolation of **1**, their findings set the stage for rapid development of this field in many directions. More recent work by Brown[4] and Schneider[5] has led to the successful preparation of **1** and permitted quantitative
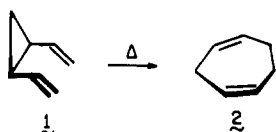
measurement of its electrocyclic conversion to **2**. From the experimentally determined activation parameters ($\Delta H^{\ddagger} = 19.4$ kcal/mol; $\Delta S^{\ddagger} = -5$ eu), an appreciation is quickly gained of the driving force provided by release of strain in the three-membered ring.

In the present study, we consider whether the ground-state

Table I. Kinetic Data and Activation Parameters for the Reversible Conversion of **4** to **5** ($Cl_2C=CCl_2$ solution)

| T, °C	k_f (×10⁵), s⁻¹	k_r (×10⁵), s⁻¹	Mol fraction of **5**[a]
110.0[b]	3.03	0.978	0.76
110.0	3.1	0.98	0.76
120.0	7.7	2.7	0.74
120.0	8.3	3.0	0.74
130.0	17.7	6.88	0.72
130.0	17.3	6.08	0.74
	$\Delta H^{\ddagger} = 26.0 \pm 0.7$ kcal/mol $\Delta S^{\ddagger} = -12 \pm 2$ eu	$\Delta H^{\ddagger} = 28 \pm 1$ kcal/mol $\Delta S^{\ddagger} = -8 \pm 3$ eu	

[a] At equilibrium. [b] Experiments were conducted in sealed NMR tubes placed in a thermostated oil bath (±0.1 °C) and the progress of reaction was monitored by ^1H NMR (at ambient temperature).

destabilization intrinsic to such molecules as **1** can be used to advantage in the assessment of the magnitude of resonance stabilization available to simple diatomic structural units of the type M=N, or, in this specific instance, the *O*,*N*-dimethyl imidate moiety
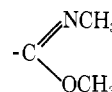

Our interest in this question arose from past studies of 2-methoxyazabullvalene (**3**)[6] where the activation energy for conversion of **3a** to **3b** (12 kcal/mol) was found to be significantly lower than that required for isomerization to **3c** (15–20 kcal/mol) where deconjugation of the imino ether necessarily occurs.[7]
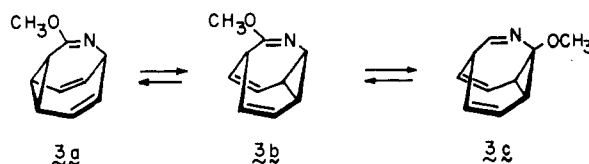
The principal compound of interest, **4**, was prepared conveniently from *cis*-2-vinylcyclopropanecarboxylic acid[8] by adaptation of a procedure developed earlier for the desvinyl system:[9] ν_{max}^{neat} 1670 cm⁻¹; ^1H NMR (CCl_4, δ) 5.4–4.75 (m, 3), 3.65 (s, 3), 2.98 (s, 3), 2.0–1.6 (m, 2), and 1.4–0.75 (m, 2).[10] At temperatures below 100 °C, **4** did not rearrange sufficiently rapidly for kinetic purposes. Under somewhat more forcing conditions, however, this cyclopropyl imidate was converted to **5** with a rate profile accommodated nicely by the differential rate expression

$$\frac{d[\mathbf{5}]}{dt} = k_f[\mathbf{4}] - k_r[\mathbf{5}]$$

indicative of a first-order reversible reaction (Table I). Although the exact ratio of **5:4** at equilibrium was somewhat temperature dependent, the value was seen to border on 3:1.
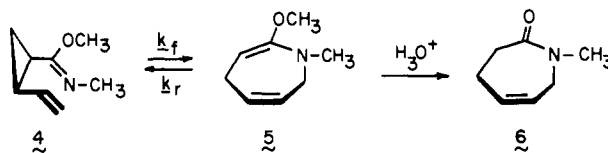
Dihydroazepine **5** whose ring protons generate a characteristic ^1H NMR pattern ((C_6D_6, δ) 6.0–5.3 (m, 2), 4.03 (t, $J = 7$ Hz, 1), 3.37 (m, 2), and 2.80 (m, 2)) proved expectedly to be extremely air and moisture sensitive. For characterization purposes, a tetrachloroethylene solution of the equilibrium

mixture was carefully added to 1 N hydrochloric acid and tetrahydrofuran.[11] The unsaturated lactam so produced (**6**) was catalytically hydrogenated to give *N*-methylcaprolactam, spectroscopically identical with an authentic sample.
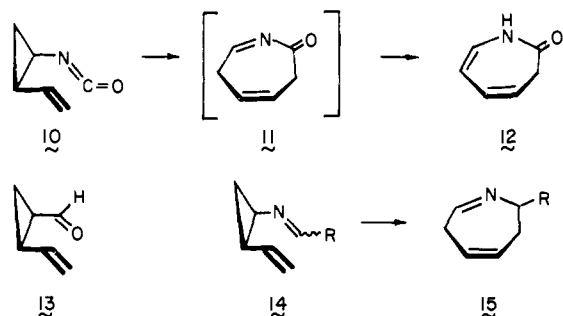
The kinetic data, which were handled by nonlinear least-squares methods[12] (Hewlett-Packard 9830A programmable calculator), permit determination of the reverse rate constants (k_r) as well (Table I). When comparison is made of the enthalpies of activation for the Cope rearrangements of **1** and **4**, the added barrier imposed by deconjugation of a methyl imidate relative to a carbon–carbon double bond is seen to be 7 kcal/mol.[13] This value is in good agreement with that observed for the formation of **3c** from **3b**. It likewise conforms closely with Beak's conclusion[14] that an imidate is ~14 kcal/mol less stable than the structurally related amide, whose functional group is generally considered to possess a resonance energy of 21 kcal/mol.[15] Equally significant is the finding that the return reaction (**5 → 4**) proceeds with a closely comparable, albeit slightly larger, activation enthalpy. The free energies of activation for the isomerizations of **4** and **5** at 80 °C are computed to be 30 and 31 kcal/mol, respectively, values substantially in excess of that previously determined for **1** at the same temperature (21 kcal/mol).[4,5] The latter process also differs in being an essentially irreversible rearrangement.

The behavior of **4** constitutes an interesting example of a reversible divinylcyclopropane-type Cope rearrangement in which the double bonds are not contained within an additional ring as in bicyclo[5.1.0]octa-2,5-diene, semibullvalene, or bullvalene.[16] Clearly, the resonance energy of the imidate fragment has almost completely counterbalanced the strain energy of the cyclopropane ring. Thus, the relatively unconstrained seven-membered ring of **5** which contains the deconjugated imidate is merely 1 kcal/mol or so more stable than **4**.

We have also examined the thermolysis of **7** and have found this trans imidate to be stable to 200 °C for prolonged periods. Unfortunately, heating of **7** above this temperature led only to polymerization. This behavior can be contrasted to that of **8** which underwent the Chapman rearrangement[17] to give **9** when heated to 350 °C or above in diphenyl ether solution (5.5 h for complete conversion).
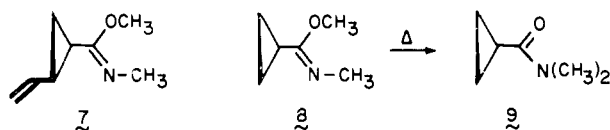
The kinetic procedure detailed herein appears suited to analysis of the thermal chemistry of other select *cis*-2-vinyl-cyclopropyl-M≡N systems. In suitable cases, such methodology could prove simpler than other alternatives capable of providing quantitative information on the relative stability of the M≡N substituent at C_1. The conversion of **10** to **11** would comprise another prototypical example if the isocyanate could be obtained in a pure state (rather than in situ under Curtius conditions);[8] the subsequent prototropic shift in **11** to deliver **12** might thereby be adequately retarded and permit obser-

vation of reversibility. Aldehyde **13** is ideally suited to scrutiny in this fashion,[16] despite an earlier claim to the contrary.[18] In contrast, imines such as **14** are unsuitable, since their isomerization serves to generate a new imine subunit, thereby again permitting relief of cyclopropyl strain to dominate heavily. The latter phenomenon has in fact contributed to the widespread success of the diaza-Cope rearrangement.[19,20]

In any case, it is now quite clear that imidates do not enter into electrocyclic rearrangements with a facility equal to their isoconjugate olefinic counterparts.[21] This information is used to mechanistic advantage in the accompanying communication.[22]

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Thermal Isomerization of Homoazocines[1]

Sir:

Recent years have seen major attention directed toward elucidation of the precise pathway by which *cis*-bicyclo[6.1.0]nona-2,4,6-trienes undergo thermal isomerization to *cis*-8,9-dihydroindenes.[2] While some of these investigations have established what the mechanism is not, none have conclusively established what it is. While there now remains little doubt that thermolysis proceeds preferably by way of a