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.
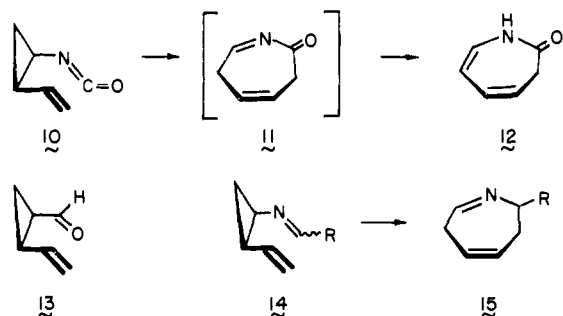
The kinetic data, which were handled by nonlinear least-squares methods[12] (Hewlett-Packard 9830A programmable calculator), permit determination of the reverse rate constants (k_r) as well (Table I). When comparison is made of the enthalpies of activation for the Cope rearrangements of 1 and 4, the 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).
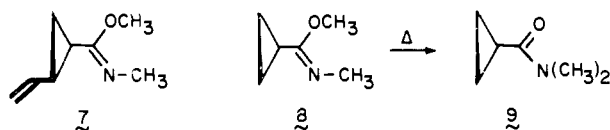
The kinetic procedure detailed herein appears suited to analysis of the thermal chemistry of other select *cis*-2-vinylcyclopropyl-M=N systems. In suitable cases, such methodology could prove simpler than other alternatives capable of providing quantitative information on the relative stability of the 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
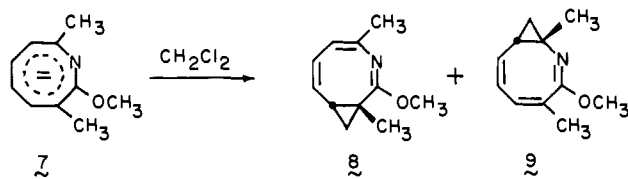
Table I. Kinetic Data

Compd	T, °C	$k \times 10^5$, s^{-1}	Thermodynamic parameters
8	70.0	1.05 ± 0.01	
	70.0	1.16 ± 0.02	
	80.1	3.38 ± 0.05	$\Delta H^{\ddagger} = 28.3 \pm 0.7$ kcal/mol
	80.4	3.61 ± 0.07	$\Delta S^{\ddagger} = -1 \pm 2$ eu
	80.5	3.99 ± 0.08	
	90.9	12.6 ± 0.2	
	90.9	12.8 ± 0.2	
9	50.0	4.4 ± 0.9	
	50.0	5.0 ± 0.2	
	60.0	14.8 ± 0.4	$\Delta H^{\ddagger} = 26.6 \pm 0.7$ kcal/mol
	60.0	17.2 ± 0.5	$\Delta S^{\ddagger} = 0.7 \pm 2$ eu
	70.0	53 ± 1	
	70.0	56 ± 1	
	70.0	57.8 ± 0.6	

folded rather than an extended molecular conformation,[3] the difficulties have consisted in reconciling stereochemical and kinetic fact with orbital symmetry theory and in disregarding the several other nonrelevant structural changes which operate concurrently. Thus, the established capability of **1** for reversible isomerization to *c,t,c,c*-cyclonona-1,3,5,7-tetraene (**2**),[4] *cis*-bicyclo[5.2.0]nona-2,5,8-triene (**3**),[5] and the cis,anti,cis diene (**4**),[6] as well as for epimerization at C_9,[7] appears to have seriously obfuscated solution of the problem. Further, despite independent demonstration of the facile and efficient cyclization of **5** to **6**,[2f,8] the formation of **5** from **1** has not been proven and remains but an inference.
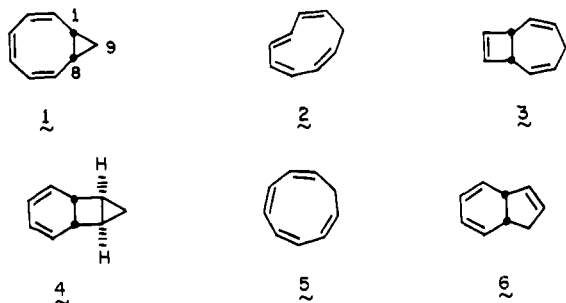
Quantitative measurements[2j] have confirmed a kinetic dependence on the π donor (acceleration) or π acceptor (deceleration) characteristics of an anti-C_9 substituent as required of C_1–C_8 bond cleavage at or before the rate-determining step. However, we see that, notwithstanding whether this cross-link is ruptured to give **2–5** or *cis*[3],*trans*-cyclonona-1,3,5,7-tetraene, π-bond shifting must operate throughout the remainder of the medium ring. Replacement of at least one double bond in **1** with an imidate function should significantly deter any such valence isomerizations.[1,9] We were therefore led to prepare the homoazocines **8** and **9** and to conduct a detailed analysis of their thermal rearrangement. The findings which are recorded herein are believed to have a direct bearing on current thinking regarding the thermolysis of **1**.

The bicyclic heterocycles **8** and **9** were synthesized by reaction of azocinyl dianion **7**[10] with dichloromethane and sep-

arated by column chromatography on basic alumina at −40 to −60 °C. None of the 5,6-cyclopropanated isomer was detected. The more dominant product was identified as **8** chiefly on the basis of its ^{1}H NMR spectrum which shows the char-

acteristic high field olefinic absorption due to H_7 (δ 4.9–4.7 (m, 1))[11] amid the other expected signals (δ (CDCl$_3$) 5.8–5.3 (m, 2), 3.53 (s, 3), 1.96 (br s, 3), 1.11 (s, 3), and 1.4–0.4 (m, 3)). The spectrum of **9** (δ (CDCl$_3$) 6.0–5.5 (m, 3), 3.53 (s, 3), 1.97 (br s, 3), 1.10 (s, 3), and 1.5–0.2 (m, 3)) was equally confirmatory of structure.[12]

Heating a degassed tetrachloroethylene solution of **8** at 100 °C for 6 h causes clean quantitative isomerization to **10** (VPC analysis). The progress of reaction can be easily monitored by integration of the singlet NMR signals of the methoxyl protons in both compounds. Noteworthy features of its ^{1}H NMR spectrum (δ (CDCl$_3$) 5.7–5.35 (m, 2), 4.85 (d, $J = 3.5$ Hz, 1), 3.64 (s, 3), 3.0 (m, 1), 2.85 (br d, $J = 16$ Hz, 1), 2.3 (br d, $J = 16$ Hz, 1), 1.82 (br s, 3), and 1.2 (s, 3)) are the high-field olefinic absorption characteristic of a hydrogen in conjugation with the imino ether nitrogen (see **8**), the presence of a bisallylic proton at 3.0, and the appearance of the sp^3-bound methyl signal as a very sharp singlet ($W_{h/2} = 0.45$ Hz). The latter pattern is taken as an indication that there exists no efficient coupling to the bridgehead proton as would be present if the ring fusion were trans and the protons in question could attain the W-planar arrangement necessary for long-range spin interaction.[13,14] In agreement with this stereochemical assignment, **10** undergoes cycloaddition to TCNE at 0 °C to give an adduct[15] which has not survived attempts at chromatographic


purification. Although [4 + 2] adducts of imidates are not frequently encountered, the Diels–Alder nature of **10·TCNE** follows from its spectral features, particularly the chemical shifts of the methyl group α to nitrogen (δ 2.1 (s, 3 H)).

Similar treatment of **9** led efficiently to **11**, the ^{1}H NMR spectrum of which parallels closely that of **10** (δ (CDCl$_3$) 5.72 (m, 2), 5.48 (m, 1), 3.58 (s, 3), 2.88 (m, 1), 2.43 (m, 2), 1.74 (m, 3), and 1.24 (s, 3)). Here again, the high-field methyl signal is seen as a very sharp singlet ($W_{h/2} = 0.39$ Hz).[14] Additionally, that olefinic proton conjugated with the C terminus of the imidate moiety is not displaced upfield as it is when the functional group is reversed in orientation.[16]

Careful monitoring of these isomerizations showed them to follow first-order kinetics and to be governed by thermodynamic parameters (Table I) remarkably comparable with those exhibited by **1** ($\Delta H^{\ddagger} = 26$ kcal/mol; $\Delta S^{\ddagger} = -5$ eu)[2i,j] and its anti 9-substituted derivatives.[2j] As with the parent hydrocarbon,[6] the connectivities of the nine ring atoms in **8** and **9** remain intact during bond relocation. Given the well-established sensitivity of **1** → **6** conversions to substituent influences,[2j] an increase in energy requirements of ∼7 kcal/mol[1,9] can logically be expected for the homoazocine rearrangements if imidate resonance energy is temporarily disrupted. However, such effects are clearly not observed. On this basis we conclude that **8** and **9** do *not* experience electronic reorganization by any of the π disruptive reaction channels previously considered for **1**.

Rather, the facile rearrangements of **8** and **9** and the unique "labeling" features provided by these homoazocines can be explained in terms of a regiospecific vinylcyclopropane rearrangement. Operationally, the incursion of [1,3]-sigmatropic shift either along concerted lines or mediated by biradicals **12** and **13** serves uniquely to insulate the imidate from possible deconjugation. According to conventional thinking, the energetics of thermochemical vinylcyclopropane → cyclopentene isomerizations are prohibitively high[17] for application to the

12 13
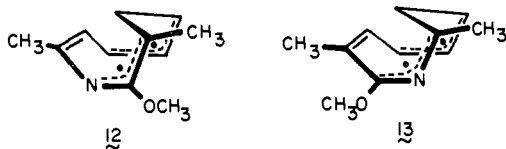
present circumstances. However, it is conceivable that more extended conjugation is able to provide stabilization modes unavailable to simpler molecules. Although this facet of [1,3] sigmatropy seems not to have been purposefully investigated, the reported conversion of **14** to **15** (E_a = 26.3 kcal/mol)[18] serves to illustrate our conceptual analysis. An imidate group is merely the nitrogen analogue of a carboxylate ester and should be capable of comparable stabilization.

14 15
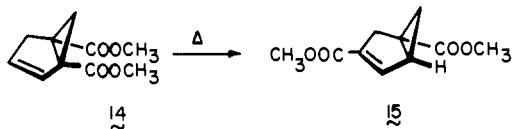
What causes **9** to be somewhat more reactive that **8**? A formal possibility derives from the earlier work of Richey and Schull[19] who have demonstrated that a tertiary nitrogen atom exerts an accelerating effect on the [1,3]-sigmatropic behavior of vinylcyclopropanes.

We cannot claim knowledge of the precise extent, if any, to which [1,3] sigmatropy contributes to the thermal bond relocation of **1**, but such a process must now be given explicit consideration.

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i ii
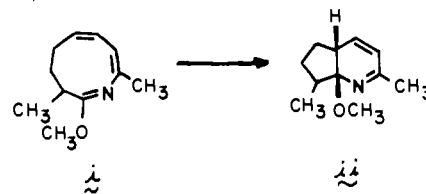
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A Molecular Chlorine Complex of Cobalt(II). The Crystal Structure of a Dichlorine Sorption Complex of Dehydrated Cobalt(II)-Exchanged Sodium Zeolite A, Co_4Na_4-A·$4Cl_2$

Sir:

Chlorine gas at ~300 Torr and at 24 (1) °C was sorbed into a single crystal of partially cobalt(II)-exchanged vacuum-dehydrated Co_4Na_4-A.[1] A crystallographic analysis indicates that four chlorine molecules are present within the unit cell of the zeolite, each complexed at one end to a cobalt(II) ion and associated at the other to a Na^+ ion. A nearly identical structure was found using diffraction data gathered at −165 (3) °C. The results show that the Cl_2 molecule behaves as a Lewis base to complex strongly, in a bent manner, to the "hard" acid cobalt(II).

The sorption of dichlorine onto cobalt(II)-exchanged zeolite A was initially done to extend work on the Br_2 and I_2 complexes[2] of partially cobalt(II)-exchanged zeolite A. It was anticipated that Cl_2, like Br_2 and I_2, would form a linear charge-transfer complex with oxide ions of the zeolite framework.[2,3]

An 85-μm single crystal of partially cobalt(II)-exchanged zeolite A, prepared by methods described before,[4] was lodged in a thin-walled Pyrex capillary and was dehydrated for 2 days at 5×10^{-5} Torr and 350 °C. After it was allowed to cool to 24 °C, the dry crystal was exposed to ~300 Torr of Cl_2 gas (Matheson, 99.96%) for 1 h. The crystal, still in the chlorine atmosphere, was then sealed in its capillary by torch. It retained the deep blue color of dehydrated Co_4Na_4-A.

The space group $Pm3m$ (no systematic absences) was used throughout this work for reasons discussed previously.[5] Preliminary crystallographic experiments and subsequent data collection were performed with an automated, four-circle Syntex $P\bar{1}$ diffractometer, equipped with a graphite monochromator and a pulse-height analyzer. Molybdenum radiation was used for all experiments ($K\alpha_1$, λ = 0.70930 Å; $K\alpha_2$, λ = 0.71359 Å). The cubic unit cell constant, as determined by a least-squares refinement of 15 intense reflections for which 20° < 2θ < 24°, is 12.103 (2) Å at 24 (1) °C and 12.099 (7) Å at −165 (3) °C. The 879 unique reciprocal lattice points for which 2θ < 70°, were examined at 24 (1) °C. Of these only the 333 reflections for which $I > 3\sigma(I)$ were used for structure