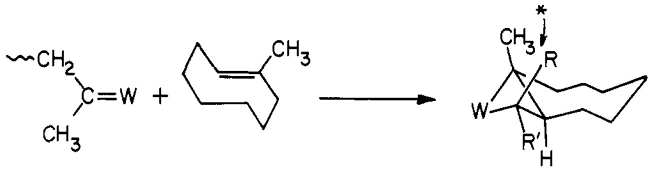
as a single carbon resonance, reaction 1a occurs at least 50 times as often as reaction 1b.

The percentages of *E* and *Z* isomers, measured by the intensities of the $^{13}$C NMR signals[18] of carbons 2, 8, and 9, was 76 ± 1% *E* and 24 ± 1% *Z*. This measurement, as well as the structure of the polymer, is confirmed by the proton NMR spectrum, which exhibits five peaks;[20] the intensities of those (at $\delta$ 1.57 and 1.67) assigned to the methyls in the *E* and *Z* isomers[21] are 73:27.

While the directional specificity may be a consequence of carbenium ion stabilization by alkyl substituents, the stereochemical selectivity for forming the *E* stereoisomer may reflect the lesser 1,3-diaxial interaction, indicated in structure I, of a methyl group with another that is unsubstituted.[22]



R = CH$_3$, R′ = chain or vice versa

I

A significant characteristic of the polymer is its absorption in the ultraviolet spectrum with a maximum at 245 nm. This is where 1,1-diphenyl-1-propene exhibits its ultraviolet absorption maximum ($\epsilon$ 14 000) and the intensities indicate one diphenylethene for every 70 methylcyclooctenes. Since the number average molecular weight measured by gel permeation chromatography is 6800 (the weight av mol wt is 15 500),[23,26] the average chain has, according to these figures, just under one diphenylethene attached to it (6800/(70 × 124) = 0.8). This is one of the best indications that the mechanism of olefin metathesis is a chain reaction in which a metal-carbene is the chain carrier.[2b,27]

Also that, as demonstrated above, an isolable metal-carbene without cocatalysts induces olefin metathesis is in accord with this hypothesis. The generality of this phenomenon is indicated by the discovery that metatheses of disubstituted olefins can be induced similarly by small amounts of (diphenylcarbene)-pentacarbonyltungsten[7,28] and by (phenylmethoxycarbene)-pentacarbonyltungsten.[29]

**Acknowledgment.** We are grateful to Iwao Miura for the NMR spectra.

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(23) The molecular weights measured assuming the polymer to be polystyrene, the calibration standard, were multiplied by 0.45. This factor was the estimated ratio of the unperturbed dimensions, $\langle L_0^2\rangle/M$, for polystyrene and poly(1-methyl-1-octene-1,8-diyl). The factor was used by analogy with the work of Dawkins et al.[24] The estimate was made assuming $[\langle L_0^2\rangle/M]^{1/2}$ to be 0.92 Å for *cis*-polyisoprene and 1.07 Å for polyethylene.[25]

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## New Mechanistic Criterion for Early and Late Transition States

*Sir:*

Sauer et al.[1] have measured the rates of Diels–Alder reactions of polycyanoolefins as dienophiles. On going from acrylonitrile to tetracyanoethylene (TCNE), one observes a 4 × 10$^7$-fold increase of the rate constant towards cyclopentadiene and a 1.5 × 10$^{10}$-fold increase vs. 9,10-dimethylanthracene (Table I).

We compared the rate constants of 2 + 2 cycloadditions of polycyanoolefins to isobutenyl methyl ether (**1**) with the above-mentioned 4 + 2 cycloadditions. Cyclobutanes **4** were formed virtually quantitatively from 1,1-dicyano-, tricyano-,

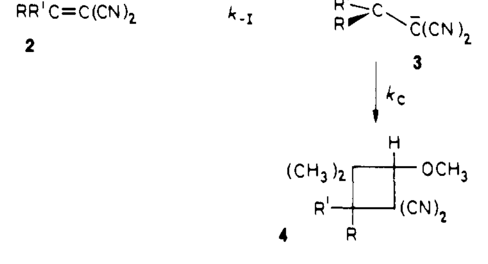


**Table I.** Comparison of Rate Constants of 4 + 2 and 2 + 2 Cycloaddition Reactions with Polycyanoethylenes

| | Diels–Alder reactions (dioxane, 20 °C)[a] | | 2 + 2 cycloadditions (benzene, 25 °C) | | |
|---|---|---|---|---|---|
| | Cyclopentadiene $10^5k_2$, l. mol$^{-1}$ s$^{-1}$ | Dimethylanthracene $10^5k_2$, l. mol$^{-1}$ s$^{-1}$ | Isobutenyl methyl ether (**1**) $10^5k_2$, l. mol$^{-1}$ s$^{-1}$ | $k_{rel.}$ | Diene **5** $10^5k_2$, l. mol$^{-1}$ s$^{-1}$ |
| Acrylonitrile | 1.04 | 0.89 | 0[b] | | |
| Fumaronitrile | 81 | 139 | 0[b] | | |
| 1,1-Dicyanoethylene | $4.55 \times 10^4$ | $1.27 \times 10^5$ | 31.6[c] | 16.0 | 147,[d,e] 169[f,e] |
| Tricyanoethylene | $4.80 \times 10^5$ | $5.90 \times 10^6$ | 2.39[g] | 1.2 | 560[h,i] |
| Tetracyanoethylene | $4.30 \times 10^7$ | $1.30 \times 10^{10}$ | 3.97[j] | 1.0[k] | 1450[h] |

[a] Photometric method, ref 1. [b] Immeasurably slow. [c] After evaporation NMR analysis of **4,** R = R′ = H, by singlets at $\tau$ 9.00 and 9.40 (toluene as internal standard). [d] Stopping of reaction with tetramethoxyethylene, NMR analysis of 1,1-dicyano-2,2,3,3-tetramethoxycyclobutane. [e] Ene reaction. [f] Photometry of CT complex at 340 nm. [g] Photometry at 450 nm, orange-red CT complex. [h] Photometry of CT complex at 420 nm. [i] Ene reaction + cycloaddition. [j] Photometry at 550 nm, dark red charge transfer complex. [k] Divided by statistical factor of 2.

and tetracyanoethylene with the enol ether **1** in benzene at room temperature, whereas acrylonitrile and fumaronitrile did not react. Tricyanoethylene afforded cis–trans isomeric cyclobutanes.

Whereas the 4 + 2 cycloaddition constants are accelerated $10^3$- and $10^5$-fold, respectively, in the sequence 1,1-dicyano- < tricyano- < tetracyanoethylene, the 2 + 2 cycloaddition constants (Table I) differ little, even decrease by a factor of 16. What is the reason for these divergent substituent effects?

The concerted Diels–Alder reaction has an early transition state which resembles the two-plane orientation complex of the reactants; e.g., 86% of the $\Delta G^{\ddagger}$ for TCNE + 9,10-dimethylanthracene (benzene, 25 °C)[2] is due to the entropy term, while only 14% for $\Delta H^{\ddagger}$ signifies little change in bond energy. The early transition states make the application of MO perturbation theory to reactivity sequences in Diels–Alder reactions successful.[3,4]

The additions of polycyanoolefins to cyclopentadiene and dimethylanthracene belong to the "normal" Diels–Alder reactions,[1] which are HO(diene) – LU(dienophile) controlled. The successive introduction of cyano groups lowers the HO and LU energies of ethylene. The diminishing frontier orbital separation corresponds to a greater energy gain in the transition state. The log $k_2$ of the two Diels–Alder reactions of Table I are linearly dependent on

$$(\mathrm{IP_{diene}} - \mathrm{EA_{cyanoalkene}})^{-1\ 5}$$

the difference of ionization potential and electron affinity should be proportional to the orbital energy distance, which constitutes the denominator of the perturbation equation.

In contrast, the slow step of the 2 + 2 cycloaddition of **1** and **2** is the reversible[6] formation of the zwitterion **3**, the intermediate **3** being partitioned between cyclization and dissociation:

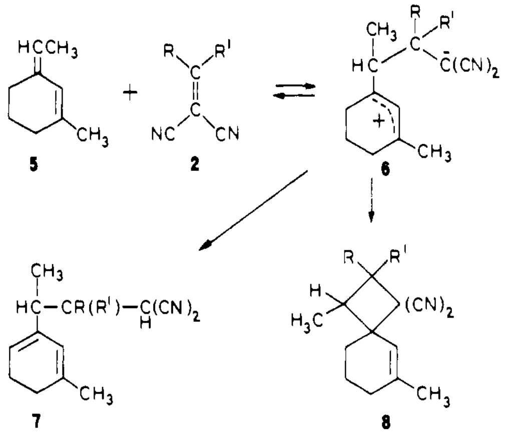
$$k_2 = k_1k_C/(k_{-1} + k_C) \qquad (1)$$

The sequence of $k_2$ in Table I is probably mainly due to variation of $k_1$; the structure–rate relationship of 2 + 2 cycloadditions of TCNE and enol ethers[7] and the linear dependence of log $k_2$ on the solvent polarity parameter $E_T$[8] testify that at least $k_1$ and the partition coefficient in eq 1 vary systematically.

Why do the rate constants of the dicyano-, tricyano-, and tetracyanoethylene cycloaddition to **1** not show the steep increase expected for a HO(enol ether) – LU(cyanoethylene) control of zwitterion formation? The late transition state of the endothermic **3** formation bears a structural similarity to the zwitterion rather than to the reactants. The MO energies of the reactants suffer gross changes before the transition state is reached; perturbation theory which inspects the first infinitesimal part of the reaction becomes useless.

The same two cyano groups contribute to the stabilization of the anionic charge in the zwitterions **3** from **1** with 1,1-di-, tri-, and tetracyanoethylene. Acrylonitrile and fumaronitrile are unreactive to **1,** since the zwitterion would be insufficiently stabilized by only one nitrile group. Cyano groups at the other carbon atom decelerate the cycloaddition somewhat. The influence of the orbital energies of the reactants on the transition state is overcompensated by: (a) steric screening of the carbon atom which forms the first bond; (b) loss of ground-state conjugation energy between C≡N and C=C when this olefinic carbon atom becomes tetrahedral in **3.**

Recently, Houk and Munchausen[9] defined "two-bond" and "one-bond" electrophilicities of cyanoethylenes, which should reflect reactivities in concerted 4 + 2 and stepwise 2 + 2 cycloadditions. No numerical data were available on "one-bond" electrophilicities. Table I offers the first two sets.



The second set consists of rate data for the reaction with the trans-fixed diene **5.** Whereas TCNE yielded the spirocyclobutane **8,** R = R′ = CN,[10] the ene reaction with 1,1-dicyanoethylene furnished the cyclohexadiene **7** and its Diels–Alder adduct with a second mole of 1,1-dicyanoethylene. In the case of tricyanoethylene, 2 + 2 cycloaddition and ene reaction are competing. The small range of relative reactivities of polycyanoethylenes vs. **1** and **5** suggests the allylic zwitterion **6** to be the intermediate for ene reaction as well as 2 + 2 cycloaddition. Concerted and stepwise mechanisms have been proposed for ene reactions.[11] The assumption that the electron-deficient enophile **2** prefers the zwitterionic path is the more justified, as all of the ene reactions described for TCNE[10,12] concern *conjugated* dienes which can form stable cationic intermediates.

The rate constants of the Diels–Alder reactions in Table I are many powers of ten larger than those of the 2 + 2 cycloadditions; the concerted 4 + 2 addition avoids the high-energy intermediate, which must be passed in the 2 + 2 cycloaddition due to the "forbiddenness" of the process [$_{\pi}2_s$ +

$_{\pi}2_s$].[13,14] Thus, the reactivity sequences of Table I offer indirectly via early and late transition states a highly valuable criterion for the presence or absence of concertedness.

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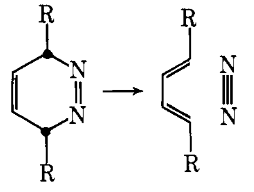
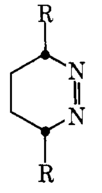
## Concerted Cycloreversion in Solution: Medium Influence on Nitrogen Extrusion

*Sir:*

The thermal deazetation of azoalkanes **1** provides a striking contrast to the behavior of the saturated derivatives **2**. For the former, nitrogen extrusion is rapid, stereospecific, and product specific never leading to ring closure products. Berson and co-workers have suggested that these reactivity traits be adopted as basic criteria for concerted cycloreversion.[1]



**1**



**2**

Replacement of the carbon-carbon double bond in **1** by an anti-fused cyclopropane ring as in **3** also leads to product specificity and enormous rate enhancements for $N_2$ loss (up to $10^{17}$).[2,3] Unlike the unsaturated species cyclopropanated azoalkanes are stable enough to permit kinetic evaluation of the decomposition rates. The results have led Allred and colleagues to propose a fourth measure for concertedness, namely, a negative activation entropy.[2a,b] The four polycyclic derivatives on which the suggestion was based (**3–6**) have been associated with $\Delta S^{\ddagger}$ (25 °C) = −21, −13, −5, and −6 eu, respectively. A $\Delta S^{\ddagger} = -8$ eu has likewise been recorded for the benzo derivative **7**.[4] With few exceptions[5-10] other kinetic measurements on the decomposition of cyclic and acyclic azoalkanes yield positive $\Delta S^{\ddagger}$ values. For these reactions radicals are the generally accepted intermediates.[9,11]

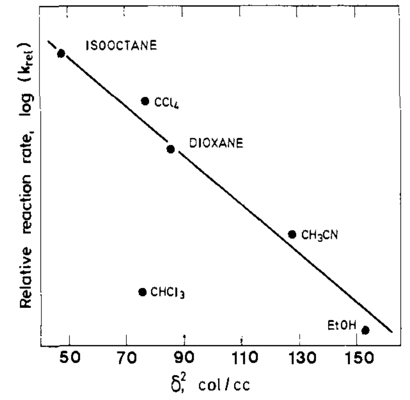
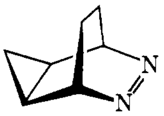
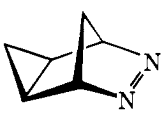


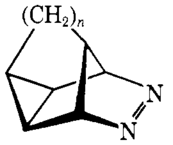
**Figure 1.** Log ($k_{\text{rel}}$) for the cycloreversion of azo **3** at 25 °C in various solvents plotted against the internal solvent pressure, $\delta^2$.



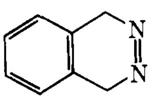
**3**



**4**



**5**, $n = 2$
**6**, $n = 3$



**7**

Negative and low positive activation entropies have been observed for the concerted, thermal decomposition of acyclic peresters and interpreted in terms of restricted internal rotations in the transition state.[12] A similar rationale for the rigid bicyclic azo structures is not easily constructed. We speculated that a possible clue to understanding the phenomenon might reside in the fact that $-\Delta S^{\ddagger}$'s have been reported *only* for azo decompositions in solution. Positive values are consistently found in the gas phase.[11] To test the effect of solvent on the behavior of a reasonably well-established cycloreversion as well as the source of the unusual activation parameters, we have reinvestigated the kinetics of compound **3** in media of widely differing polarity.

The substrate was isolated from its cuprous bromide complex and recrystallized from hexane below 0 °C (best mp 29.5-30.0°, lit.[13] 25-30 °C; NMR (−5 °C, $CDCl_3/Me_4Si$, 90 MHz) 5.47 (2 H, s, hw = 8.3 Hz), 1.58-0.42 ppm (8 H, m); uv, $\lambda_{\max}$(isooctane) ($\epsilon_{\min}$) 366 (80), 377 nm (180)). Gradual

Table I. Relative Rates, Activation Parameters and Error Limits for the Cycloreversion of Cyclopropylazoalkane **3**[a]

| Solvent | $10^3k$, $s^{-1}$ | $k_{\text{rel}}$ | $\Delta G^{\ddagger}$, kcal/mol | $E_a$, kcal/mol[b] | ln $A$ | $\Delta S^{\ddagger}$, eu[b] | Confidence limits for $\Delta S^{\ddagger}$[c] 95% | Confidence limits for $\Delta S^{\ddagger}$[c] 99% |
|---|---|---|---|---|---|---|---|---|
| Isooctane | 8.5 | 14.9 | 20.3 | 22.1 ± 0.4 | 32.5 | 4.1 ± 1.1 | ±3.0 | ±4.2 |
| $CCl_4$ | 4.5 | 7.9 | 20.7 | 22.6 ± 0.2 | 32.8 | 4.7 ± 0.8 | ±2.5 | ± 3.7 |
| Dioxane | 3.1 | 5.4 | 20.9 | 22.9 ± 0.3 | 32.9 | 4.9 ± 0.7 | ±2.1 | ±3.0 |
| Pyridine | 2.4 | 4.2 | 21.0 | 24.3 ± 0.4 | 34.9 | 8.9 ± 1.3 | ±3.2 | ±4.6 |
| $CH_3CN$ | 1.4 | 2.4 | 21.4 | 23.0 ± 0.2 | 32.3 | 3.6 ± 0.5 | ±1.4 | ±2.1 |
| $CHCl_3$ | 0.94 | 1.6 | 21.6 | 24.1 ± 0.3 | 33.6 | 6.3 ± 0.9 | ±2.0 | ±3.0 |
| EtOH (96%) | 0.57 | 1.0 | 21.9 | 23.5 ± 0.1 | 32.2 | 3.4 ± 0.8 | ±0.8 | ±1.2 |

[a] At 25 °C. [b] Error limits represent the standard deviation from the least-squares line. [c] Cf. E. S. Swinbourne, "Analysis of Kinetic Data", Thomas Nelson and Sons Ltd., London, 1971, pp 40–43.