acteristic ratio is strongly negative.[55] (d) The characteristic ratio is solvent dependent.[36] (e) The characteristic ratios are higher than those found for most polymers.[62] (f) The α calculated in the conventional manner are close to unity.[62] It is reasonable that the explanations for the hydrodynamic behavior would be similar.

In a previous study[17] of poly-L-proline of M_W up to 16,300, the hydrodynamics were interpreted as reflecting the conformation of a somewhat flexible rod based on the *a priori* assumption of the Schimmel-Flory conformational map,[19] which leads to such structures at low molecular weight. Based on the studies of the high molecular weight polymer we now find from Figure 7 SCC has an $\langle r^2\rangle_0^{1/2}$ which is 58% that of the completely extended chain and 68% that of a rigid helix with the Φ and ψ determined for poly-L-proline form II in the solid state.[4,5] The coiling in this case is of such a low degree that spherical symmetry would not be attained. This offers an alternate, more consistent interpretation of hydrodynamic properties with molecular weight.

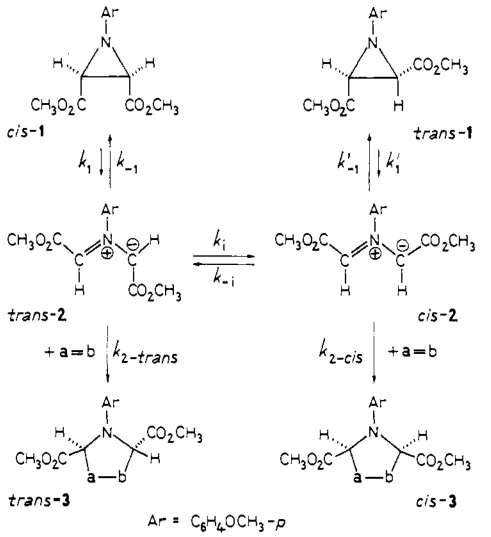
Communications to the Editor

Azomethine Ylide from Dimethyl 1-(*p*-Methoxyphenyl)aziridine-2,3(*cis*)-dicarboxylate. Kinetics of the Thermal Ring Opening

Sir:

The cis–trans isomeric aziridines **1** on heating establish equilibria with small concentrations of the azomethine ylides **2** by conrotatory ring opening as had been shown earlier.[1] The cyclic and the ring-opened structures are isoelectronic with cyclopropyl anions and allyl anions, respectively. The azomethine ylides **2** are 1,3 dipoles; *trans*-**2** combines stereospecifically even with weak dipolarophiles, while in the case of the less reactive *cis*-**2** the isomerization to *trans*-**2** competes with the 1,3-dipolar cycloaddition except for dipolarophiles of highest activity (see Scheme I).[2]

Scheme I



Dilatometric measurements of the reaction of *cis*- and *trans*-**1** with an increasing excess of tetracyanoethylene revealed that this very active dipolarophile does not enter into the rate equation.[3] The fast cycloaddition is preceded by the rate-determining electrocyclic ring opening with the rate constants k_1 or k_1', respectively, while the ring closures with the constants k_{-1} and k_{-1}' as well as the isomerization with k_i and k_{-i} are completely suppressed.

The blue color of the solution of **1** and TCNE in ethyl acetate is due to a charge-transfer complex which suggests an alternative explanation for the dilatometric rate constants being independent of the concentration of TCNE. If the association constants of the CT complexes of *cis*- and *trans*-**1** with TCNE are sufficiently high, the rate of a one-step reaction of **1** and TCNE should become virtually independent of a further excess of TCNE. However, on the basis of this one-step model the stereospecific formation of *trans*-**3** from *cis*-**1** and of *cis*-**3** from *trans*-**1** would hardly be conceivable.

This alternative interpretation can now be discarded. No charge-transfer interaction can be detected between *cis*- or *trans*-**1** and diethyl fumarate by uv spectrophotometry. Nevertheless, dilatometric rate measurements[4] in ethyl acetate at 119° furnish first-order constants (k_d) for *cis*-**1** which are independent of the concentration of fumaric ester and are identical with the ones obtained with TCNE (Table I). Thus, k_d must be identical with k_1.

On treating *cis*-**1** with less active dipolarophiles, the recyclization *trans*-**2** → *cis*-**1** can compete with the cycloaddition. Still $k_{2\text{-trans}}[D]$ (where [D] is the dipolarophile concentration) is large compared with the isomerization constant k_i; k_i can, therefore, be ignored. The cycloadditions are thus stereospecific. Using the symbols of the formula scheme, steady-state treatment with respect to *trans*-**2** leads to eq 1 for the dilatometric

$$k_d = \frac{k_1 k_{2\text{-trans}}[D]}{k_{-1} + k_{2\text{-trans}}[D]} \qquad (1)$$

rate constant k_d. This can be transformed into eq 2 of a straight line.

$$k_d = k_1 - \frac{k_{-1}k_d}{k_{2\text{-trans}}[D]} \qquad (2)$$

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(1) R. Huisgen, W. Scheer, and H. Huber, *J. Amer. Chem. Soc.*, **89**, 1753 (1967).

(2) R. Huisgen, W. Scheer, H. Mäder, and E. Brunn, *Angew. Chem., Int. Ed. Engl.*, **8**, 604 (1969).

(3) R. Huisgen, W. Scheer, and H. Mäder, *ibid.*, **8**, 602 (1969).

(4) Method and apparatus: R. Huisgen, H. Seidl, and I. Brüning, *Chem. Ber.*, **102**, 1102 (1969).

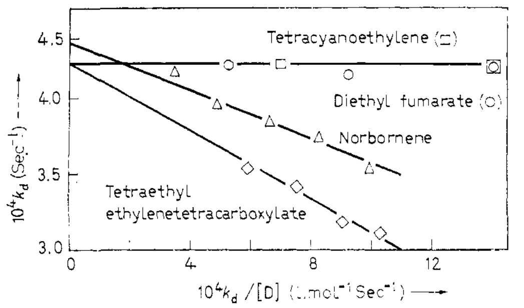


Figure 1. Dilatometric rate constant k_d for cycloadditions of *cis*-**1** as a function of k_d/[D].

The rate constants for the reactions of *cis*-**1** with norbornene or tetraethyl ethylenetetracarboxylate (Table I) are nonlinear functions of the dipolarophile concentration. However, on plotting k_d *vs.* k_d/[D] in Figure 1, straight lines were obtained which possess a common intercept within the limits of error. This intercept is the valence isomerization constant k_1 which is independent of the nature of the trapping dipolarophile. For TCNE and diethyl fumarate, $k_{2\text{-trans}}[D]$ is much larger than k_{-1}; therefore, $k_d = k_1$ in eq 2. Thus, all the kinetic results prove that a *reversible first-order reaction* of *cis*-**1** (interpreted as ring scission to *trans*-**2**) precedes the combination with the dipolarophile.

Table I. Dilatometric Rate Constants for Cycloadditions of the Aziridines **1** (40 mmol l.$^{-1}$) in Ethyl Acetate at 119°

1	Dipolarophile	mmol l.$^{-1}$	10^4k_d, sec^{-1}
cis-	Tetracyanoethylene	301	4.21
cis-	Tetracyanoethylene	601	4.22
cis-	Diethyl fumarate	300	4.22
cis-	Diethyl fumarate	451	4.16
cis-	Diethyl fumarate	800	4.22
cis-	Norbornene	355	3.54
cis-	Norbornene	450	3.73
cis-	Norbornene	583	3.84
cis-	Norbornene	808	3.96
cis-	Norbornene	1200	4.17
cis-	Tetraethyl ethylenetetracarboxylate	300	3.10
cis-	Tetraethyl ethylenetetracarboxylate	350	3.17
cis-	Tetraethyl ethylenetetracarboxylate	450	3.40
cis-	Tetraethyl ethylenetetracarboxylate	600	3.54
trans-	Tetracyanoethylene	600	3.75
trans-	Diethyl fumarate	200	2.23
trans-	Diethyl fumarate	300	2.36
trans-	Diethyl fumarate	447	2.48
trans-	Diethyl fumarate	550	2.54
trans-	Diethyl fumarate	600	2.56
trans-	Diethyl fumarate	701	2.62

Cycloadditions of the aziridine *trans*-**1** to less active dipolarophiles proceed with a lower degree of stereospecificity because $k_{2\text{-cis}}$ is smaller than $k_{2\text{-trans}}$; the geometrical isomerization *cis*-**2** → *trans*-**2** with k_{-i} becomes the more prominent the less active the dipolarophile.[2] The rather complex formal kinetics have so far been solved only for the case of diethyl fumarate where $k_{2\text{-trans}}[D] \gg k_{-1}, k_i$. The rate of adduct formation (eq 3) now contains two terms. Steady-state treatment for *cis*-**2** and *trans*-**2** yields eq 4 and 5. Substituting eq 4 and 5 into 3 gives expression 6 for k_d which can be transformed into the straight-line correlation of eq 7. k_1' is known from the dilatometric

$$\frac{d[\mathbf{3}]}{dt} = -\frac{d[trans\text{-}\mathbf{1}]}{dt} = k_d[trans\text{-}\mathbf{1}] = k_{2\text{-cis}}[cis\text{-}\mathbf{2}][D] + k_{2\text{-trans}}[trans\text{-}\mathbf{2}][D] \tag{3}$$

$$[cis\text{-}\mathbf{2}] = \frac{k_1'[trans\text{-}\mathbf{1}]}{k_{-1}' + k_{-i} + k_{2\text{-cis}}[D]} \tag{4}$$

$$[trans\text{-}\mathbf{2}] = \frac{k_{-i}[cis\text{-}\mathbf{2}]}{k_{2\text{-trans}}[D]} \tag{5}$$

$$k_d = \frac{k_1'k_{2\text{-cis}}[D] + k_1'k_{-i}}{k_{-1}' + k_{-i} + k_{2\text{-cis}}[D]} \tag{6}$$

$$\frac{1}{k_1' - k_d} = \frac{k_{-1}' + k_{-i}}{k_1'k_{-1}'} + \frac{k_{2\text{-cis}}[D]}{k_1'k_{-1}'} \tag{7}$$

measurements of the reaction of *trans*-**1** + TCNE (Table I and ref 3). Using k_d values measured for *trans*-**1** + diethyl fumarate (Table I) in the plot of $1/(k_1' - k_d)$ *vs.* [D], a straight line is indeed obtained (Figure 2). Thus, the requirements of the kinetic system above are met. Knowledge of k_1' and k_{-1}' [5] allows the calculation of the addition constant of diethyl fumarate from the slope of the straight line, $k_{2\text{-cis}}$ at 119° = 31 l. mol^{-1} sec^{-1}.

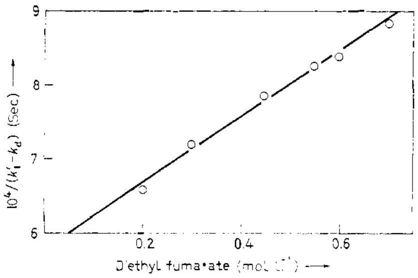
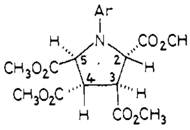


Figure 2. Dilatometric rate measurements for the reaction of *trans*-**1** with diethyl fumarate; $1/(k_1' - k_d)$ as a function of [D].

Distillation of the aziridine at 160–180° (0.001 mm) afforded a 23:77 equilibrium mixture of *cis*-**1** and *trans*-**1**. The cumbersome separation by thick-layer chromatography[1] was replaced by a more convenient procedure. *trans*-**1** crystallized from methanol; the mother liquor was evaporated and its ethereal solution yielded crystals of *cis*-**1**.



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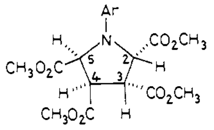

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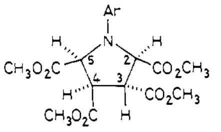

6

Ar = $C_6H_4OCH_3$-*p*

On heating *cis*-**1** with 8 equiv of dimethyl fumarate for 18 hr at 140°, a quantitative yield of the pyrrolidines **4** and **5** in a ratio of 63:37 was obtained. **4**, mp 118–119°, and **5**, mp 95–96°, were separated by chromatography. The structural assignment was possible by nmr; both adducts showed AA'BB' spectra for the pyrrolidine ring protons in accordance with the C_2 symmetry of **4** and **5**. Under the same conditions, *trans*-**1** combined with dimethyl fumarate to give 93%

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(5) H. Hermann, R. Huisgen, and H. Mäder, *J. Amer. Chem. Soc.*, **93**, 1779 (1971).

of an adduct mixture which contained 86% of **6** (mp 114–115°, ABCD spectrum for ring protons) and 14% of **4** + **5**. Dehydrogenation of this adduct mixture by chloranil to tetramethyl 1-(*p*-methoxyphenyl)-pyrrole-2,3,4,5-tetracarboxylate and the independent synthesis of this pyrrole have been described earlier.[6]

(6) R. Huisgen, W. Scheer, G. Szeimies, and H. Huber, *Tetrahedron Lett.*, 397 (1966).

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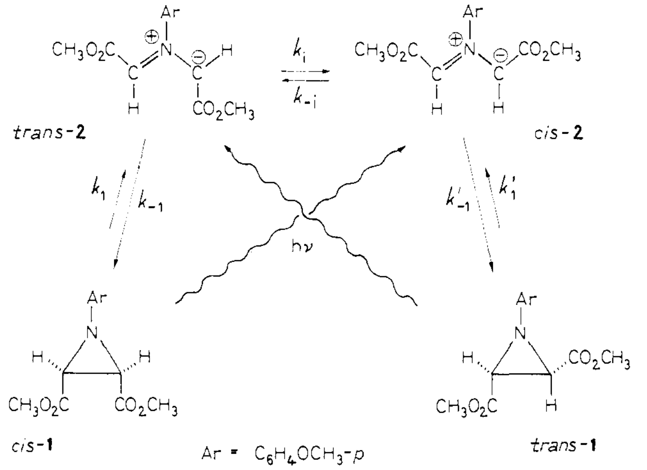
Azomethine Ylides by Photolysis of Isomeric Dimethyl 1-(*p*-Methoxyphenyl)aziridine-2,3-dicarboxylates. Elaboration of the Total Energy Profile

Sir:

The title compounds *cis*-**1** and *trans*-**1** maintain thermal equilibria with small concentrations of the isomeric azomethine ylides, *trans*-**2** and cis-**2**. The rate of cycloaddition to very active dipolarophiles is only determined by the first-order electrocyclic ring scission *cis*-**1** → *trans*-**2** and *trans*-**1** → *cis*-**2**.[1,2] The Eyring parameters of the ring-opening reactions have been evaluated. Kinetic measurements of the net isomerization rate *cis*-**1** $\rightleftarrows$ *trans*-**1** in the absence of dipolarophiles provided additional information; two out of three molecules of *cis*-**1** which overcome the ring-opening barrier at 120° and arrive in the energy trough of *trans*-**2** will roll back to *cis*-**1**, while the third makes the next pass which leads to *cis*-**2**. The corresponding *cis*-**2** is partitioned in the ratio 9:2 between *conrotatory* ring closure to *trans*-**1** and geometrical isomerization to *trans*-**2**.[3]

Scheme I



Only the depths of the energy troughs which belong to the open-chain intermediates **2** are still missing. We earlier[4] established that uv light induces *disrotatory* ring opening of **1**. If one succeeded in generating a high population of the azomethine ylides **2** by flash photolysis, then it would be possible to measure the rate of thermal cyclization **2** → **1**.

Dilute dioxane solutions of *cis*- and *trans*-**1** (10^{-4} *M*, 5 cm quartz cell) were exposed to a 25-J flash generated with an argon-filled quartz tube, whereby a species with λ_{max} 420 mμ was formed; *cis*-**1** absorbs at 286 mμ, *trans*-**1** at 288 mμ. Photometry (halogen lamp, 377.5-mμ interference filter to prevent noticeable photochemical conversion by the monitoring light) allowed one to measure the first-order kinetics of thermal disappearance of the intermediates to which we ascribe structures *trans*-**2** and *cis*-**2**. The half-lives of *trans*-**2** → *cis*-**1** and of *cis*-**2** → *trans*-**1** at 25° were found to be 5.4 and 7.8 sec, respectively. The corresponding $\Delta G^{\ddagger}$ values were 18.7 and 18.9 kcal mol^{-1}. Measurements at different temperatures enabled activation enthalpies and entropies to be calculated (Table I).

Table I. Kinetics of Thermal Reversion of the Cis–Trans Isomeric Azomethine Ylides **2** to the Aziridines **1** after Flash Photolysis in Dioxane

trans-**2** → *cis*-**1**		*cis*-**2** → *trans*-**1**	
Temp, °C	k_{-1}, sec^{-1}	Temp, °C	k_{-1}', sec^{-1}
24.6	0.136	27.1	0.106
26.1	0.143	36.4	0.183
41.8	0.291	44.1	0.400
42.4	0.291	51.4	0.517
51.4	0.465	67.4	1.45
67.7	1.12		
$\Delta H^{\ddagger}$ = 9.1 ± 0.7[a]		12.7 ± 0.8 kcal mol^{-1}	
$\Delta S^{\ddagger}$ = −32 ± 2[a]		−21 ± 2 eu	

[a] Eyring parameters were computed with the program ARRHEY assuming a ±10% range of error for the rate constants and ±0.5° for temperature. So far we have no explanation for the high negative entropies of activation and a systematic error cannot be excluded.

After the flash photolysis of **1**, a second-order reaction in the millisecond range was observed besides the slow first-order reaction which we dealt with above. How can one be sure that the rate data of Table I refer to the electrocyclic ring closure, **2** → **1**? The previously mentioned absorption maximum of 420 mμ made it possible for the first time *to see the colored intermediate.* On irradiating rather concentrated solutions of *cis*-**1** and *trans*-**1** in dioxane (0.07–0.2 *M*) with a medium-pressure mercury arc for 5 sec at room temperature, a yellow color appeared which faded within *ca.* 20 sec. Extinction measurements at 380 and 420 mμ led to rate constants which roughly corresponded to the ones of Table I. On addition of a drop of diethyl fumarate, an active dipolarophile,[2] the yellow color of the solution disappeared suddenly. The result was especially striking with the deep-yellow solution which we obtained by irradiating **1** in acetone at −30°. *Thus, the yellow intermediate must be the 1,3 dipole, the azomethine ylide* **2**.

Combination of all the rate data and their extrapolation to 120° permits the construction of the free-energy profile of the four-component system (Figure 1).[5] The troughs of the azomethine ylides **2** are of re-

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(1) R. Huisgen, W. Scheer, and H. Mäder, *Angew. Chem., Int. Ed. Engl.*, **8**, 602 (1969).

(2) R. Huisgen and H. Mäder, *J. Amer. Chem. Soc.*, **93**, 1777 (1971), preceding communication.

(3) The somewhat different ratios given elsewhere[1] are based on the simplified assumption of an undisturbed ring-opening equilibrium. The correct treatment requires a rather cumbersome rate equation.

(4) R. Huisgen, W. Scheer, and H. Huber, *J. Amer. Chem. Soc.*, **89**, 1753 (1967).

(5) The rate data for ring opening and geometrical isomerization refer to measurements in ethyl acetate solutions while k_{-1}' and k_{-1} were measured in dioxane.