25.47 (t, cyclopropane CH$_2$), 36.49 (dd, *CH$_2$*C=), 41.41 (s, *C*Me$_3$), 44.36 (d, NCH), 59.68 (s, COH, 87.83 (d, *C*H=C), 163.32 (s, NC=), 203.73 (s, C=O); Mass spectrum, *m/e* (relative abundance) 267 (M$^+$, 5), 250 (5, OH·), 234 (15), 211 (10), 210 (85, *t*-Bu·), 192 (10), 188 (5), 182 (5), 168 (10), *t*-BuCOCH=C=N$^+$HiPr), 164 (10), 153 (10), 150 (8), 126 (100, *t*-BuCOCH=C=N$^+$H$_2$), 122 (10), 112 (10), 100 (15), 99 (30), 85 (15), 84 (30), 83 (15), 68 (8), 57 (90, *t*-Bu$^+$), 43 (15), 42 (15), 41 (35), 40 (10). Anal. Calcd: N, 5.23. Found: N, 5.11.

Condensation of 2,2-Dimethyl-3,5-heptanedione (12) with Isopropylamine. A magnetically stirred mixture of 1.55 g (0.01 mol) of 2,2-dimethyl-3,5-heptanedione (12) and 2.34 g (0.04 mol) of isopropylamine in 15 mL of benzene was treated dropwise either with 0.006 mol of titanium(IV) chloride (dissolved in 5 mL of pentane) or 0.03 mol of boron trifluoride etherate (dissolved in 5 mL of benzene). The reaction flask was protected with a calcium chloride tube. The reaction mixture was stirred for 1 h, after which it was poured into 150 mL of aqueous 2 N sodium hydroxide. The organic phase was isolated and the aqueous layer was extracted twice with ether. The combined organic phases were dried (Na$_2$CO$_3$) and evaporated in vacuo to afford enaminone 13 in 67% (using TiCl$_4$) or 87% (using BF$_3$·Et$_2$O) yield: bp 125–27 °C (15 mmHg); IR (NaCl) 1610–1560 cm^{-1} (broad strong band, $\nu_{C=O}$); ^{1}H NMR (CDCl$_3$) 1.13 (9 H, s, *t*-Bu), 1.22 (6 H, d, *J* = 6 Hz, Me$_2$), 1.1 (3 H, covered by *t*-Bu signal, CH$_3$), 2.26 (2 H, q, *J* = 7.5 Hz, CH$_2$C=), 3.71 (1 H, m, NCH), 5.06 (1 H, s, CH=), 10.8 (1 H, broad signal, NH); ^{13}C NMR (CDCl$_3$) 13.08 (q, Me), 24.22 (q, Me$_2$), 25.23 (t, CH$_2$), 28.12 (q, Me$_3$), 41.25 (s, *C*Me$_3$), 44.06 (d, NCH), 87.91 (d, CH=), 167.50 (s, NC=), 203.34 (s, C=O); mass spectrum, *m/e* (relative abundance) 197 (M$^+$, 8), 140 (100), 122 (8), 93 (39), 57 (17), 56 (17), 55 (8), 44 (15), 43 (23), 42 (16), 41 (35), 40 (9), 39 (8).

Reaction of Enaminone 2 with Sodium Methoxide in Methanol. A solution of 50 mg (0.18 mmol) of enaminone 2 in 0.4 mL of 1 N sodium methoxide in methanol was refluxed for 1 h, after which the reaction mixture was poured into water and extracted three times with dichloromethane. The extracts were dried (sodium carbonate) and evaporated under vacuo to give a clear liquid residue. Although the product was more than 95% pure, an additional purification by preparative TLC (hexane/ether 80:20, silica gel GF$_{254}$ (Merck)) provided an analytical sample of compound 14 (40 mg, 90% yield): mp 54 °C; ^{1}H NMR (CDCl$_3$) 1.10 (9 H, s, *t*-Bu), 1.20 (9 H, s, *t*-Bu), 1.20 (6 H, d, *J* = 6.5 Hz, Me$_2$), 3.43 (2 H, s, CH$_2$), 3.2–3.7 (1 H, m, NCH), 4.92 (1 H, s, *C*H=C), 10.4 (1 H, broad, NH); ^{13}C NMR (CDCl$_3$) 24.06 (q, Me$_2$), 27.46 (q, Me$_3$), 27.96 (q, Me$_3$), 40.66 (t, CH$_2$), 41.31 (s, *C*Me$_3$), 44.99 (s, *C*Me$_3$), 45.37 (d, NCH), 90.86 (d, =CH), 158.76 (s, =CN), 203.69 (s, O=CC=C), 209.50 (s, CH$_2$C=O); IR (NaCl) 1722 ($\nu_{t\text{-BuCOCH}_2}$), 1605 (br, $\nu_{t\text{-BuCOCH=CN}}$), 3320 cm^{-1} (w, ν_{NH}); MS, *m/e* (relative abundance) 267 (M$^+$, 2), 211 (3), 210 (27), 126 (6), 58 (8), 57 (100), 45 (10), 44 (5), 43 (14), 42 (8), 41 (27), 40 (22). Anal. Calcd: N, 5.23. Found: N, 5.15.

Modification of the Catalytic Activity of Zinc Chloride. A Kinetic Investigation in Zinc Chloride–Ether–Dichloromethane Mixtures

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The addition reaction of chlorodiphenylmethane with 2-methyl-1-pentene was studied kinetically in order to characterize the catalytic activities of ZnCl$_2$/Et$_2$O/CH$_2$Cl$_2$ mixtures of different composition. The activity of the heterogeneous ZnCl$_2$/CH$_2$Cl$_2$ system is raised by 3–4 orders of magnitude when 0.5 equiv of ether are added. At –70 °C the system is homogeneous for [Et$_2$O]/[ZnCl$_2$] > 1.1, and the catalytic activity decreases with increasing ether/zinc chloride ratio. At [Et$_2$O]/[ZnCl$_2$] ratios greater than 2, the reaction rate depends on the ether/zinc chloride ratio and is almost independent of the absolute concentration of the catalyst.

Zinc chloride is usually considered to be a weak Lewis acid.[1] This view is essentially based on experiments carried out either under homogeneous conditions in donor solvents or under heterogeneous conditions in solvents like chlorinated hydrocarbons. In previous work we have found that addition reactions of chloroalkanes with alkenes, which are not efficiently catalyzed by zinc chloride in either dichloromethane or ether, readily take place in a mixture of these two solvents.[2,3] In order to quantify this observation, we determined the rates of the zinc chloride catalyzed reactions of chlorodiphenylmethane (1) with 2-methyl-1-pentene (2) in dichloromethane–ether solutions of variable composition.

Experimental Section

Zinc chloride (commercial product, MERCK) was heated 48 h at 160 °C (0.01 mmHg) and stored in a nitrogen atmosphere.

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Figure 1. Decrease of [1] during the $ZnCl_2$–Et_2O catalyzed reaction of 1 with 2.

Diethyl ether was predried over alumina (WOELM B Super I), refluxed over a sodium wire (15 h), and distilled in a nitrogen atmosphere. **Dichloromethane** was refluxed over P_2O_5 (20 h) and distilled. Traces of phosphoric acid were removed by refluxing over a Pb/Na alloy (20 h) and subsequent distillation. The purified solvent was stored over molecular sieves (4 Å). **Chlorodiphenylmethane.** Since commercial samples are usually contaminated by benzophenone, 1 was prepared by bubbling HCl into a suspension of diphenylmethanol (60 g) in petroleum ether (100 mL). **2-Methyl-1-pentene.** The commercial product (>99%, FLUKA) was used without further purification.

3-Chloro-3-methyl-1,1-diphenylhexane (3). 1.5 g of $ZnCl_2$ was dissolved in 1.8 mL of ether cooled at −78 °C and diluted with 50 mL of CH_2Cl_2. After addition of 4.05 g (20.0 mmol) of 1, 1.78 g (20.8 mmol) of 2 were added dropwise with stirring within 1 h. The mixture was stirred for 1 h at −78 °C, washed with aqueous ammonia, and dried with $CaCl_2$. The solvent was evaporated and the remaining oil was distilled to give 5.5 g (96%) of 3: bp (bath) 155–160 °C (0.05 mmHg); mp 46–47 °C; ^1H NMR (60 MHz, internal Me$_4$Si) δ 0.78 (br t, J = 6 Hz, 3 H), 1.30 (s, 3 H), 1.03–1.97 (m, 7 H), 2.58 (d, J = 6 Hz, 2 H), 4.33 (t, J = 6 Hz, 1 H), 7.27 (s, 10 H); mass spectrum (70 eV), m/e (relative intensity) 288, 286 (1.9, 5.6, M⁺), 167 (100). Anal. Calcd for $C_{19}H_{23}Cl$: C, 79.56; H, 8.08. Found: C, 79.04; H, 8.16.

Kinetic Experiments. Typical Procedure. A solution of $ZnCl_2$ (1.00 g, 7.34 mmol) in ether (1.61 g, 21.7 mmol) was diluted with CH_2Cl_2 to give 5 mL. This solution was placed in a 100-mL flask and cooled at −70.0 ± 0.2 °C with nitrogen protection. A CH_2Cl_2 solution (25 mL) of nitrobenzene (27.0 mg, HPLC standard), a CH_2Cl_2 solution (20 mL) of 2 (2.10 g, 25.0 mmol), and 30 mL of CH_2Cl_2 were added and stirred until equalization of temperature took place (~15 min). Finally, a solution of 1 (0.500 g, 2.47 mmol) in 1 mL of CH_2Cl_2 was injected into the vigorously stirred solution. The volume of this solution decreased by 11% when cooled at −70 °C.

At certain intervals, ~0.5 mL of the solution were drawn into a syringe containing 2–3 mL of concentrated aqueous ammonia and shaken vigorously to destroy the catalyst. The two phases were allowed to separate in the syringe, and the organic layer was analyzed by HPLC (NUCLEOSIL 5 NO_2, 5-μm particles, isooctane–ether = 98:2 (v/v), 100 bar, flow 1.12 mL/min, detection at 254 nm) to yield the composition of the reaction mixture as a function of time. If NaOH was utilized instead of NH_3, the Lewis acid was not quenched instantaneously as indicated by deviations of individual points from the concentration/time correlation.

As shown in Figure 1, ln [1] gives a linear correlation with time and the pseudo-first-order rate constant $k_{1\psi}$ can be evaluated from the slope of the straight line.

Results and Discussion

Homogeneous solutions of zinc chloride in ether can be obtained at 20 °C if the molar ratio $Et_2O/ZnCl_2$ is greater than 1.1. Solutions with a $Et_2O/ZnCl_2$ ratio between 1.1 and 1.5 are very viscous and their preparation requires several hours of shaking. Precipitation of $ZnCl_2$, which takes place when solutions with a $Et_2O/ZnCl_2$ ratio ≲2 are diluted with CH_2Cl_2 at room temperature, can be avoided if the $ZnCl_2$–ether complex is cooled at −70 °C prior to the addition of CH_2Cl_2.

Table I. Influence of Water on the Rate of the $ZnCl_2$–Et_2O Catalyzed Reaction of 1 with 2[a]

H_2O, mmol	$k_{1\psi}$, s^{-1}
0.00	4.96 × 10^{-4}
1.00	4.10 × 10^{-4}
2.50	2.56 × 10^{-4}
4.00	1.72 × 10^{-4}

[a] 7.34 mmol of $ZnCl_2$ (105 mmol/L), 21.7 mmol of Et_2O (311 mmol/L), 2.47 mmol of 1, and 25.0 mmol of 2.

All kinetic studies of reaction 1 in homogeneous $ZnCl_2$–Et_2O–CH_2Cl_2 systems gave linear ln [1]/t plots when 2 was employed in large excess over 1. A first reaction order of 1 is thus indicated. Similarly a first reaction order of 2 can be derived from linear ln [3]/t plots, when 1 was used in great excess over 2. In both cases, however, the reaction order of the excess compound was smaller than 1 and decreased with increasing concentration. Therefore, k_2 values cannot be calculated by dividing $k_{1\psi}$ by the concentration of the excess compound. Comparable pseudo-first-order reaction constants were usually obtained by keeping the concentration of the major compound constant within a series of experiments.

The Effect of Moisture. Reproducibility of Rate Constants. The effect of water in Lewis acid catalyzed reactions seems to be rather obscure. Traces of water have been reported to be necessary in some Friedel–Crafts reactions whereas the catalyst is destroyed by larger amounts of water.[1b,c,4] Quantitative data for the "water effect" in the zinc chloride–ether system were obtained by studying the rate of the model reaction (1) in the presence of definite amounts of water.

Table I shows that water somewhat retards the reaction. The effect of more than 4 mmol of H_2O was not determined because the mixture became inhomogeneous. Comparison of Tables I and II shows that the addition of water causes a similar retardation as the addition of equimolar amounts of ether. We, therefore, conclude that replacement of ether by water in the zinc complexes does not significantly influence their catalytic activity.

These data furthermore indicate that traces of water cannot considerably adulterate the reaction rates in homogeneous $ZnCl_2/Et_2O/CH_2Cl_2$ systems. Consequently, we were able to reproduce the $k_{1\psi}$ values within ±7%. Deviations up to ±23% were observed, however, with $ZnCl_2$ from different batches though identical drying procedures have regularly been applied. Deviations of $k_{1\psi}$ values in different tables can be explained by that effect. Within each series of experiments, the same batch of $ZnCl_2$ has been used. Zinc chloride, prepared from zinc and hydrogen chloride in anhydrous ether,[5] was 10% more active than the best commercial product used.

Variation of the $Et_2O/ZnCl_2$ Ratio. Table II and Figure 2 show that the rate of the model reaction 1, catalyzed by a constant amount of $ZnCl_2$ (102 mmol/L), strongly depends on the ratio [Et_2O]/[$ZnCl_2$]. For [Et_2O] = 0, i.e., heterogeneous $ZnCl_2$–CH_2Cl_2 mixtures, nonlinear ln [1]/time plots were obtained, in contrast to the situation with ether containing systems. In three independent experiments with ether free systems, the slopes of the ln [1]/time plots increased by factors of 2.4–2.8 during the course of the reaction. Furthermore, the activity of $ZnCl_2$ samples with different pretreatment differed up to a factor of 3 as indicated by the uncertainty region at the left edge of Figure 2.

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**Table II. Influence of Ether on the Rate of the ZnCl₂
Catalyzed Reaction of 1 with 2**[a]

Et₂O, mmol	[Et₂O]/[ZnCl₂⁻]	$k_{1\psi}$, s⁻¹
0.0	0.0[b,c]	7.45 × 10⁻⁶[d]
		(2.01 × 10⁻⁵)[d]
0.0	0.0[b,c]	2.29 × 10⁻⁵[d]
		(6.39 × 10⁻⁵)[d]
0.0	0.0[b,c]	1.02 × 10⁻⁵[d]
		(2.43 × 10⁻⁵)[d]
1.61	0.22[b]	1.73 × 10⁻²[e]
3.67	0.50[b]	6.61 × 10⁻²[e]
7.34	1.00[b]	4.80 × 10⁻²[e]
8.09	1.10	3.95 × 10⁻²[e]
10.8	1.47	1.82 × 10⁻²[e]
11.6	1.58	8.88 × 10⁻³[e]
13.5	1.84	5.35 × 10⁻³[e]
16.2	2.21	1.66 × 10⁻³
18.9	2.57	7.05 × 10⁻⁴
21.7	2.96	4.96 × 10⁻⁴
24.4	3.32	2.98 × 10⁻⁴
27.1	3.69	1.27 × 10⁻⁴
28.4	3.87	9.82 × 10⁻⁵
29.8	4.06	8.61 × 10⁻⁵
32.5	4.43	4.72 × 10⁻⁵
35.2	4.79	3.27 × 10⁻⁵
40.6	5.53	1.73 × 10⁻⁵
56.8	7.73	4.59 × 10⁻⁶

[a] 7.34 mmol of ZnCl₂ (0.102 mol/L), 2.47 mmol of 1, and 25.0 mmol of 2. [b] Heterogeneous system. [c] ZnCl₂ was stirred in CH₂Cl₂ for 24 h at 20 °C before the reactants were added. [d] These additions give nonlinear ln [1]/time plots. The first $k_{1\psi}$ value corresponds to the slope at the initial stage of the reaction and the $k_{1\psi}$ value in parentheses corresponds to the final stage. [e] Experiments were carried out with 1.23 mmol of 1 and 12.5 mmol of 2. The reported $k_{1\psi}$ values are corrected.
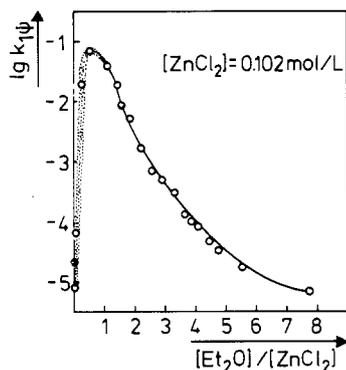

Figure 2. Rates of reaction 1 at constant zinc chloride concentration and variable [Et₂O]/[ZnCl₂] ratio.

Small amounts of ether raise the solubility of zinc chloride, resulting in a dramatic increase of the catalytic activity. The most active catalyst system ([Et₂O]/[ZnCl₂] ≈ 0.5), is 10³ to 10⁴ times more effective than the ether free ZnCl₂–CH₂Cl₂ mixture. The exact position of the reactivity maximum cannot be determined since the system is heterogenous in this region.

More ether deactivates ZnCl₂ by complexation, and at a ratio of [Et₂O]/[ZnCl₂] ≳ 4 the activity drops below that of the ether free system.

Variation of the ZnCl₂–Et₂O Concentration at Constant [Et₂O]/[ZnCl₂] Ratios. At a constant [Et₂O]/[ZnCl₂] ratio of 1.84, the pseudo-first-order rate constant $k_{1\psi}$ increased by a factor of 1.7 when the ZnCl₂ concentration was raised from 0.1 to 0.3 mol/L (Table III). If the [Et₂O]/[ZnCl₂] ratio was kept constant at values between 2.5 and 4, variation of the total concentration of the catalyst over a wide range did not affect the reaction rates. For [Et₂O]/[ZnCl₂] = 2.57 the zinc chloride concentration was varied from 10.3 to 206 mmol/L, while $k_{1\psi}$
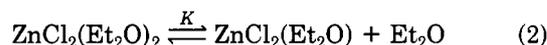
**Table III. Variation of the Catalyst Concentration at
Constant [Et₂O]/[ZnCl₂] Ratio**

Et₂O, mmol	ZnCl₂, mmol	[Et₂O]/[ZnCl₂]	$k_{1\psi}$, s⁻¹
13.5	7.34	1.84	3.61 × 10⁻³[a]
27.0	14.7	1.84	4.62 × 10⁻³[a]
40.5	22.0	1.84	6.04 × 10⁻³[a]
10.9	3.67	2.96	5.24 × 10⁻⁴[b]
21.7	7.34	2.96	5.26 × 10⁻⁴[b]
43.4	14.7	2.96	5.26 × 10⁻⁴[b]
65.1	22.0	2.96	5.55 × 10⁻⁴[b]
86.8	29.4	2.96	6.69 × 10⁻⁴[b]
29.4	7.34	4.00	9.12 × 10⁻⁵[b]
58.7	14.7	4.00	7.92 × 10⁻⁵[b]
88.1	22.0	4.00	8.68 × 10⁻⁵[b]
1.88	0.73	2.57	2.25 × 10⁻³[c]
4.72	1.83	2.57	2.36 × 10⁻³[c]
9.44	3.67	2.57	2.39 × 10⁻³[c]
18.9	7.34	2.57	2.18 × 10⁻³[c]
28.3	11.0	2.57	2.11 × 10⁻³[c]
37.8	14.7	2.57	2.39 × 10⁻³[c]
75.5	29.4	2.57	5.07 × 10⁻³[c]

[a] 1.23 mmol of 1 and 12.5 mmol of 2. [b] 2.47 mol of 1 and 25.0 mmol of 2. [c] 24.7 mmol of 1 and 2.50 mmol of 2.

was constant at $(2.25 \pm 0.15)10^{-3}$ s⁻¹. A further increase of the catalyst total concentration accelerated the reaction.

Presently we are unable to give an unequivocal interpretation of these findings because of the multiplicity of complex equilibria conceivable in this catalyst system. Since tetracoordination is of great importance in zinc chemistry, the following equilibrium may play a central role.

$$ZnCl_2(Et_2O)_2 \overset{K}{\rightleftharpoons} ZnCl_2(Et_2O) + Et_2O \qquad (2)$$

Our findings can be explained with the assumption that K is relatively small and that the tricoordinated complex $ZnCl_2(Et_2O)$ is the catalytically active species. On these premises, zinc chloride is almost completely tetracoordinated for $[Et_2O]_0/[ZnCl_2]_0 > 2$, i.e.,

$$[ZnCl_2(Et_2O)] \text{ very small}$$

$$[ZnCl_2(Et_2O)_2] \approx [ZnCl_2]_0$$

$$[Et_2O] \approx [Et_2O]_0 - 2[ZnCl_2]_0$$

with

$$[ZnCl_2(Et_2O)] =$$

$$K\frac{[ZnCl_2(Et_2O)_2]}{[Et_2O]} = K\frac{[ZnCl_2]_0}{[Et_2O]_0 - 2[ZnCl_2]_0}$$

one can derive

$$k_{1\psi} \sim \frac{K}{\dfrac{[Et_2O]_0}{[ZnCl_2]_0} - 2} \qquad (3)$$

These considerations rationalize that at Et₂O/ZnCl₂ ratios greater than 2 the reaction rates depend on the ratio Et₂O/ZnCl₂ but not on the absolute ZnCl₂ concentration. The zeroth order of [ZnCl₂] over a wide range of concentrations can thus be understood.

If the ether/zinc chloride ratio is altered (e.g., Table II) the relative importance of different complex equilibria changes. At low ether/zinc chloride ratios binuclear complexes, at high ratios, pentacoordinated complexes may become important. Equation 3 can, therefore, not be expected to cover the whole range of Table II. Though not very significant because of the small number of points, it is satisfactory that a linear correlation of $k_{1\psi}$ with 1/([Et₂O]₀/[ZnCl₂]₀ - 2) is found for the three values with 2 < [Et₂O]/[ZnCl₂] < 3.

Table IV. Pseudo-First-Order Rate Constants of ZnCl$_2$-Catalyzed Reactions of 1 with 2 in Dichloromethane (–70 °C) in the Presence of Different Donors^a

donor	$k_{1\psi}$, s^{-1}	k_{rel}
diethyl ether	1.02×10^{-3}	1.00
ethyl acetate	2.99×10^{-4}	0.29
acetone	2.49×10^{-5}	0.024
tetrahydrofuran	1.17×10^{-6}	0.0011
tetrahydropyran^b	4×10^{-6}–4×10^{-7}	$\sim 10^{-4}$
dimethyl sulfoxide	no reaction	
pyridine	no reaction	

^{a} 7.34 mmol of ZnCl$_2$ (0.103 mol/L), 18.9 mmol of donor, 2.47 mmol of 1 and 25.0 mmol of 2. ^{b} No first-order kinetics.

Other Donor Solvents. Some other ZnCl$_2$ donor complexes which are soluble in CH$_2$Cl$_2$ have been examined with respect to their catalytic activity. At a donor/ZnCl$_2$ ratio of 2.57, the ether complex exhibited the greatest relative catalytic activity (Table IV). The Me$_2$SO and pyridine complexes are so stable that no reaction was observed at –70 °C.

Conclusion. Addition of ether increases the solubility of ZnCl$_2$ in dichloromethane and thus enhances the catalytic activity of the Lewis acid. In systems with [Et$_2$O]/[ZnCl$_2$] $\approx$ 0.5 the reactivity is 10^3–10^4 times higher than in ether free systems. Reactions, which take more than 6 weeks in ZnCl$_2$–CH$_2$Cl$_2$ systems, are complete within 1 h if 0.5 equiv of ether are added! More ether reduces the catalytic activity of ZnCl$_2$ because of complexation. The little sensitivity of the ZnCl$_2$–Et$_2$O system toward moisture facilitates its synthetic applications. Since a zeroth reaction order of [ZnCl$_2$] is found at [Et$_2$O]/[ZnCl$_2$] = 2.5–4.0 over a wide range of concentrations, an increase of the ZnCl$_2$–Et$_2$O quantity is usually not helpful to accelerate a reaction.

Notes

Concerning the Mechanism of Isomerization of cis-Azoalkanes

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The mechanism of thermal decomposition of azoalkanes has been the subject of many investigations in recent years. Much of the discussion has focused on the unresolved question of whether a synchronous, two-bond cleavage process (k_s) or a two-step, one-bond cleavage process via short-lived diazenyl radicals ($k_f < k_\beta + k_d > k_r$) is operative (Scheme I).[2,3] Neuman and co-workers[4,5] have employed high pressure techniques to determine the volumes of activation for such processes and consider the latter to be a good mechanistic discriminator. They[4,5] found typical values of between +12 and +20 cm^3 mol^{-1} for a two-step radical formation mechanism, compared to values of between +2 and +5 cm^3 mol^{-1} for synchronous two-bond scission processes. Preliminary investigations in our laboratories[6] on the pressure dependence of the thermal deazatization reactions of a series of trans-azoalkanes resulted in volumes of activation which fitted well into the two categories mentioned above, viz., C$_6$H$_5$N=NC(CN)$_2$-

Scheme I

v – inversion   r – radical pair recombination
s – synchronous   f – radical pair formation
d – diffusion   c – cis
                 t – trans

CH$_3$, $\Delta V^\ddagger$ = +11.9 ± 0.8; C$_6$H$_5$C(CH$_3$)(C$_2$H$_5$)N=NC(CH$_3$)(C$_2$H$_5$)CH$_3$, $\Delta V^\ddagger$ = +12.8 ± 2.3; NCC(CH$_3$)(C$_2$H$_5$)N=NC(CH$_3$)(C$_2$H$_5$)CN, $\Delta V^\ddagger$ = +2.9 ± 0.5 cm^3 mol^{-1}. Recently, the possible participation of cis-azoalkanes during the deazatization of trans-azoalkanes has been suggested.[7-10] Theoretical MNDO calculations[11] on the thermal decomposition of cis- and trans-azoethane and 1,1-diethyldiazene not only suggest that the step-wise mechanism is preferred to the synchronous two-bond cleavage process but also indicate that the cis transition state is common to both the cis and trans isomers, i.e., trans-azoethane first isomerizes and then looses N$_2$. Similarly the mechanism by which cis-azoalkanes isomerize thermally is a subject of great controversy.[12] Various

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