Table I. Photonitration of Phenols by Tetranitromethane in Cyclohexane[a]

reactant	product	quantum yield
phenol	4-nitrophenol	0.12
	2-nitrophenol	0.17
	3-nitrophenol	1.2×10^{-3}
p-chlorophenol	4-chloro-2-nitrophenol	0.27
o-chlorophenol	2-chloro-4-nitrophenol	0.15
	2-chloro-6-nitrophenol	0.12
p-cresol	4-methyl-2-nitrophenol	0.15
o-cresol	2-methyl-6-nitrophenol	0.31
	2-methyl-4-nitrophenol	0.19
o-nitrophenol	none	*c*

[a] At 20 °C; solutions of TNM (0.167 M) and the phenol (0.167) were stirred magnetically during photolysis. See footnote 9 and the text. [b] None detected; upper limit to quantum yield. [c] None detected after 24 h of irradiation under the conditions given in the text.

phenols when irradiated at wavelengths where neither free TNM nor the free phenol absorb in cyclohexane. Irradiation was carried out with light from 500-W tungsten–halogen lamp filtered through either a Corning 3-69 or 3-71 filter.[8] All nitrated phenols were identified by comparison of their HPLC elution volumes (2 × 250 mm silica gel, 10 μm/CH_2Cl_2, detection at 280 nm) with those measured for authentic materials and additionally, in some cases, by the NMR and UV spectra of the products isolated from preparative TLC. Yields were determined by integration of the peaks in the chromatographic trace and by comparison with standards. Quantum yields were determined by sampling light intensities between 440 and 500 nm in steps of about 20 nm by passing the light through narrow band-pass filters while the energy of the transmitted light was measured with a thermopile.[9] These measurements together with the absorption curves of the complexes, the transmission curves of the filters, and the yields of products lead to the result that the quantum yields for *o*- and *p*-nitrophenol are 0.17 and 0.12, respectively. *m*-Nitrophenol was not detected; $\Phi \leq 1.2 \times 10^{-3}$. One molecule of nitroform is produced per molecule of nitrophenol formed.[10] Photonitration of *o*- and *p*-cresol and *o*- and *p*-chlorophenol under the same conditions leads to similar results (Table I). Here too, meta nitration cannot be detected. It is noteworthy that a TNM-*o*-nitrophenol complex is not detected spectroscopically when the two components are present together in cyclohexane at concentrations where similar complexes of TNM with phenol and methyl- and chloro-substituted phenols are readily detected. That TNM fails to nitrate *o*-nitrophenol when a mixture of the two are present and irradiated under the conditions stated provides further evidence that prior formation of a ground-state donor–acceptor complex is necessary for reaction to occur.

Further study is required before the scope of this reaction is fully understood, but at the present time the results presented above suggest the following mechanism. TNM and the substitued phenol associate to form a donor–acceptor complex (eq 3), which can

$$\mathrm{C(NO_2)_4 + X\text{-}PhOH \rightleftharpoons \underset{\text{D–A complex}}{X\text{-}PhOH \cdots C(NO_2)_4}} \tag{3}$$

be observed by the new characteristic absorbance. The D–A complex upon absorption of a photon is converted to an excited-state charge-transfer complex (CTC′, eq 4) where there is greater

$$\text{D–A complex} \xrightleftharpoons{h\nu} (\mathrm{CTC'})^* \tag{4}$$

electron donation from the phenol to TNM than in the ground-state complex.[7] It is probable that the excited state can revert back to the ground-state D–A complex, which would account for the quantum yield of less than unity. In competition with decay is electron transfer to form the TNM radical anion and the phenol radical–cation pair (eq 5). The TNM radical anion is expected

$$(\mathrm{CTC'})^* \rightarrow \mathrm{X\text{–}PhOH^{+}\cdot\ C(NO_2)_4{}^{-}\cdot} \tag{5}$$

to fragment rapidly to yield nitroform anion and NO_2 radical in close proximity to the phenol radical cation (eq 6). which could

$$\begin{aligned}\mathrm{X\text{-}PhOH^{+}\cdot C(NO_2)_4{}^{-}\cdot} &\rightarrow \mathrm{[NO_2\cdot + X\text{–}PhOH^{+}\cdot + C(NO_2)_3{}^{-}]} \\ &\rightarrow \mathrm{[NO_2\cdot + X\text{–}PhO\cdot + HC(NO_2)_3]}\end{aligned} \tag{6}$$

combine to yield ortho- or para-nitrated phenols. It should be noted that if nitrophenols are produced by combination of phenoxy and NO_2 radicals as suggested then the almost exclusive formation of *o*- and *p*-nitrophenols are to be expected since the transition states leading to these products would be expected to be at lower energy than that leading to *m*-nitrophenol.[11]

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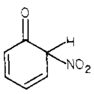
[8] Transmission is 1% or less for the 3-71 filter at $\lambda \leq 460$ nm and for the 3-69 filter at $\lambda \leq 515$ nm.

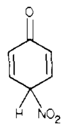
[9] Narrow band-pass filters having their maxima at 600, 580, 560, 550, 520, 500, 480, 450, and 440 nm were used. On the average these had a width of 10 nm at half-height. The thermopile was a product of the Eppley Laboratory, Newport, RI 02840. We thank Drs. N. Sutin, R. Weston, and B. Brunschwig for furnishing this apparatus.

[10] [Nitroform]/([*o*-nitrophenol] + [*p*-nitrophenol]) = 0.91. The phenol–TNM photolysate (3 mL), after a 33-fold dilution with a 50–50 mixture of CH_2Cl_2–cyclohexane, was extracted with 0.01 M H_2SO_4 (3 × 15 mL). The optical densities at 350, 400, and 415 nm of the aqueous extract, adjusted to pH 13, were measured to obtain the concentrations of nitroform and *o*- and *p*-nitrophenols. All operations were carried out in dim red light.

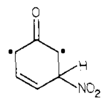
[11] Combination of phenoxy and NO_2 radicals would yield *o*- and *p*-dienone intermediates (I and II). Addition of NO_2 radical to the meta position of the phenoxy radical would yield a 1,3-diradical (e.g., III) and if the diradical is a singlet could lead to a bicyclic intermediate (e.g., IV). Both III and IV are expected to be considerably less stable than I and II. It should be emphasized that the isomer distribution produced from a radical–radical coupling reaction[12a] is expected to be clearly different from that observed from the more frequently encountered homolytic aromatic substitution.[12b]



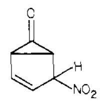
I



II



III



IV

[12] (a) Fleming, I. "Frontier Orbitals and Organic Chemical Reactions"; Wiley: New York, 1976; pp 195–200, 202–207. We thank Dr. Philip B. Shevlin for calling our attention to this reference. (b) Lowry, T. H.; Richardson, K. S. "Mechanism and Theory in Organic Chemistry"; 2nd ed.; Harper and Row: New York, 1981; pp 730–733.

β-Alkyl Transfer in a Lanthanide Model for Chain Termination

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The chemistry of lutetium–isobutyl complex **1**, described herein, delineates a number of reaction pathways that are energetically accessible to organolanthanide complexes. In particular, *β-alkyl elimination* has now been observed directly. We note that fundamental reactions of lanthanide–alkyl complexes are not well documented. Products obtained from attempted preparations of homoleptic alkyl complexes implicate α-hydrogen abstraction as a viable reaction,[1-3] and β-hydrogen elimination can also apparently constitute a major decomposition route.[4,5] Both β-hy-

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[1] Vollershtein, E. L.; Yakoulev, V. A.; Tinyakova, E. I.; Dolgoplosk, B. A. *Dokl. Akad. Nauk. SSSR* **1980**, *250*, 365–366.

[2] Guzman, I. Sh.; Chigir, N. N.; Sharaev, O. V.; Bondarenko, G. N.; Tinyakova, E. I.; Dolgoplosk, B. A. *Dokl. Akad. Nauk. SSSR* **1979**, *249*, 860–862.

[3] Schumann, H.; Müller, J. *J. Organomet. Chem.* **1979**, *169*, C1–C4.

[4] Schumann, H.; Genthe, W.; Bruncks, N. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 119–120.

[5] Evans, W. J.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L. *J. Chem. Soc., Chem. Commun.* **1981**, 292–293.

0002-7863/82/1504-6471$01.25/0

drogen elimination from lanthanide–alkyls (e.g., eq 1 forward)

$$\underset{\mathbf{1}}{\mathrm{Lu}(\eta^5\text{-}C_5Me_5)_2CH_2CH(CH_3)_2} \rightleftarrows \underset{\mathbf{2}}{\mathrm{Lu}(\eta^5\text{-}C_5Me_5)_2H} + CH_2{=}C(CH_3)_2 \quad (1)$$

$$\mathrm{Lu}(\eta^5\text{-}C_5Me_5)_2CH_2CH(CH_3)_2 \rightleftarrows \underset{\mathbf{3}}{\mathrm{Lu}(\eta^5\text{-}C_5Me_5)_2CH_3} + CH_2{=}CH(CH_3) \quad (2)$$

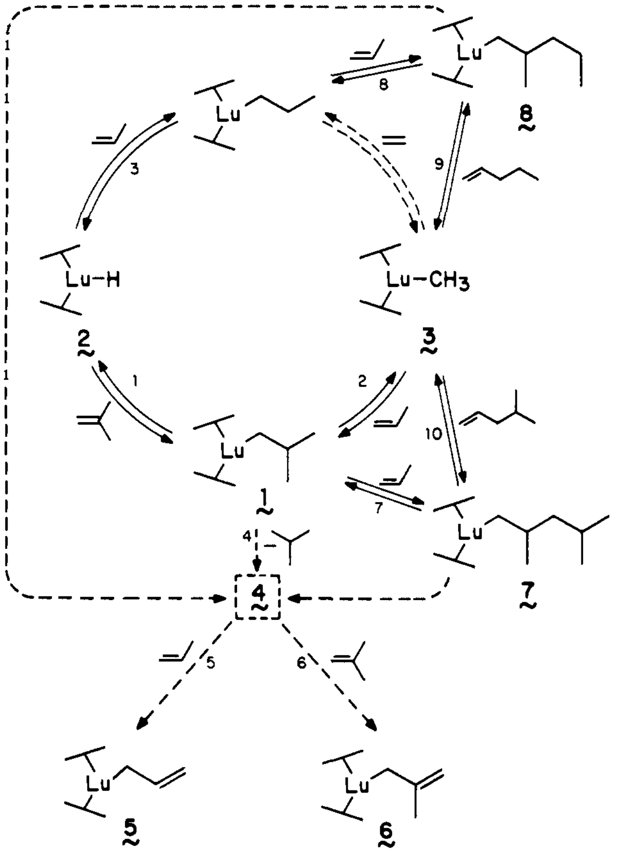
and olefin insertion into both lanthanide–alkyl and -hydride bonds (e.g., eq 1 and 2 reverse) are important, observable reactions in our model for Ziegler–Natta polymerization.[6] We now report β-alkyl elimination[7] (eq 2 forward), so called by analogy with β-hydrogen elimination. Both β eliminations lead to thermal decomposition of the isobutyl complex **1**, providing a model for chain termination occurring during propene oligomerization[8] using $Lu(C_5Me_5)_2R$ catalysts.

Reactions of methyl complex **3** were previously investigated[6] by using the labile diethyl ether adduct $Lu(\eta^5\text{-}C_5Me_5)_2CH_3{\cdot}Et_2O$. Formation of **1** from $Lu(\eta^5\text{-}C_5Me_5)_2CH_3{\cdot}Et_2O$ and excess propene is retarded by the presence of ether. The coordinately unsaturated complex **3** has now been prepared[9] and found to react rapidly and stoichiometrically with 1 equiv of propene.[10] Solutions of **1** (characterized previously[6,11]) are therefore very clean and suitable for mechanistic study.

Decomposition of isobutyl complex **1** (monitored by ^1H NMR) shows first-order kinetics over at least 4 half-lives. A typical reaction mixture[11] equimolar in methyl complex **3** and propene shows essentially complete conversion to **1** within 0.2 h followed by slow first-order decomposition of **1** with a half-life of 3.4 h ($k_{obsd} = 5.2 \times 10^{-5}$ s^{-1}). Despite these observations, the decomposition is not mechanistically simple but results from the summation of several processes, all of which appear first order in **1** and at least one of which is irreversible. These processes, which rearrange the isobutyl fragment, are outlined in Scheme I (eq 1–10). It is emphasized that the general features noted below for reactions of **1** are also observed when **1** is prepared from the hydride[12] $Lu(\eta^5\text{-}C_5Me_5)_2H$ and isobutene rather than from $Lu(\eta^5\text{-}C_5Me_5)_2CH$ and propene.

Evidence for the mechanisms outlined (refer to the scheme) derives from several sources: (a) ^1H and ^{13}C NMR observation of the time-dependent formation and decay of the postulated intermediates; (b) independent synthesis, ^1H and ^{13}C NMR identification of lutetium–alkyl species (other than **4**); (c) identification of the lutetium–allyl products via hydrolysis followed by GC–MS analysis; (d) observation and isotopic analysis of the lutetium–methyl complex **3** formed by methyl group transfer from several β-methylalkyl–lutetium complexes; (e) computer simulation of the time-dependent concentration profiles of the various intermediates.

Scheme I. Rate Constants for Equilibria, k_n, Are Designated in the Text as Negative ($-k_n$) for the Bimolecular Insertion Process and Positive ($+k_n$) for the Unimolecular Deinsertion Reaction



Major final products[13] from decomposition of **1** are the allyl complexes $Lu(\eta^5\text{-}C_5Me_5)_2C_3H_5$ (**5**) and $Lu(\eta^5\text{-}C_5Me_5)_2C_4H_7$ (**6**) (50–80%), the methyl complex **3** (20–40%), and isobutane (40–60%). Minor products include isobutene (0–3%), $Lu(\eta^5\text{-}C_5Me_5)_2$-2,4-dimethylpentyllutetium (**7**, 0–5%), and $Lu(\eta^5\text{-}C_5Me_5)_2$-2-methylpentyllutetium (**8**, 0–5%); **7** and **8** also decompose to give the corresponding C_7 and C_6 alkanes.

Irreversible reactions account for the highest rate loss of **1** and generate isobutane in addition to species **5** and **6**.[14] The reversible processes involved in decomposition of **1**, β-hydrogen and β-alkyl elimination, lead the system into a manifold of insertion–deinsertion equilibria (scheme). β-Alkyl elimination results in the regeneration of the methyl complex **3**, while the propene released is initially taken into higher oligomers. β-Hydrogen elimination (eq 1) is less readily observed. The lutetium hydride formed reacts

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(6) Watson, P. L. *J. Am. Chem. Soc.* **1982**, *104*, 337–339.

(7) Formation of trimethylaluminum and isobutene from trineopentylaluminum is, to our knowledge, the only previously reported example of this type of reaction: Pfohl, W. *Ann. Chem.* **1960**, *629*, 207–210, 210–221.

(8) Propene oligomerization (rather than polymerization) occurs because the rate of chain termination (essentially unimolecular decomposition of $Lu(\eta^5C_5Me_5)_2CH_2CH(CH_3)R$ species ($k \sim (5\text{–}9) \times 10^{-5}$ s^{-1} at 22 °C)) is comparable with the biomolecular rate of chain propagation ($k = 2 \times 10^{-2}$ M^{-1} s^{-1}, by use of the reaction of **1** with propene as a model). Thus, even in liquid propene (12 M) the maximum propagation/termination ratio is 250–500. With ethylene, chain propagation is faster by a factor of $>10^3$, and polymerization is observed. Chain termination in the two cases should be mechanistically and kinetically comparable.

(9) Under vacuum NEt_3 is removed stoichiometrically from $Lu(\eta^5\text{-}C_5Me_5)_2CH_3{\cdot}NEt_3$ leaving **3** as a white solid: ^1H NMR (0.075 M in C_6D_{12}) δ 1.98 (30 H), –0.96 (3 H). Anal. Calcd for $C_{21}H_{33}Lu$: C, 54.77; H, 7.22; Lu, 38.00. Found: C, 54.44; H, 7.19; Lu, 37.10. A rapid monomer–dimer equilibrium ($\Delta G°$ dissociation, 25 °C, = 2.9 kcal/mol) is observed for this complex in hydrocarbon solution. ^1H NMR (–90 °C) shows the dimer to have one bridging and one terminal methyl group and mutually perpendicular $Lu(C_5Me_5)_2$ units.

(10) Chemistry of the analogous paramagnetic ytterbium complex is also under investigation.

(11) Solutions (0.05–0.075 M in C_6D_{12}, 22 °C) were monitored by using a Nicolet 360-MHz spectrometer. **1**: ^1H NMR (C_6D_{12}) δ 0.17 (d, 2 H, J_{HH} = 8.28 Hz), 0.82 (d, 6 H, J_{HH} = 6.59 Hz), 1.97 (s, 30 H) (decoupling experiments show the tertiary isobutyl hydrogen to lie under the C_5Me_5 resonance); ^{13}C NMR (C_6D_{12}) δ 10.9 (C_5Me_5) 29.2 (CH), 29.4 (CH_3), 49.3 (CH_2), 118.3 (C_5Me_5).

(12) The highly reactive hydride $Lu(\eta^5\text{-}C_5Me_5)_2H$ (**2**) was prepared by reaction of **3** with hydrogen at 20 °C in hexane and has been fully characterized: ^1H NMR (0.03 M in C_6D_{12}) δ 2.12 (s, 30 H), 9.27 (s, 1 H). Anal. Calcd for $C_{20}H_{31}Lu$: C, 53.81; H, 7.00; Lu, 39.18. Found: C, 53.15; H, 6.90; Lu, 38.90. ^1H NMR (–95 °C) confirms an asymetric structure analogous to the methyl dimer.[9] $\Delta G°$ (25 °C) for dissociation is less than 2 kcal/mol.

(13) Samples were examined 24 h after formation of **1** in a sealed NMR tube. Hydrogenation of the decomposition mixtures gave 80–85% $Lu(\eta^5\text{-}C_5Me_5)_2H$, indicating at least this amount of lutetium was present as complexes of the general type $Lu(\eta^5\text{-}C_5Me_5)_2R$.

(14) LuC_3H_5 and LuC_4H_7 species are identified by hydrolysis and, then GC measurement of the propene and isobutene released. Time-dependent ^{13}C NMR of decomposiing [1-, 2-, and 3-^{13}C]**1** show product $Lu(\eta^5\text{-}C_5Me_5)_2C_3H_5$ to have a CH peak at δ 163 and CH_2 at δ 68, suggesting a *fluxional* σ-allyl structure. Independent synthesis is in progress.

(15) Theoretical kinetics were calculated by using the Gear integration package HAVCHEM: Stable, R. N.; Chesick, J. *Int. J. Chem. Kinet.* **1978**, *10*, 461–469.

(16) Biomolecular rate constants (C_6D_{12}, 22 °C) are k_{-1} = 5.9 M^{-1} s^{-1}, k_{-2} = 0.21 M^{-1} s^{-1}, and k_{-7} = 0.001 M^{-1} s^{-1}.

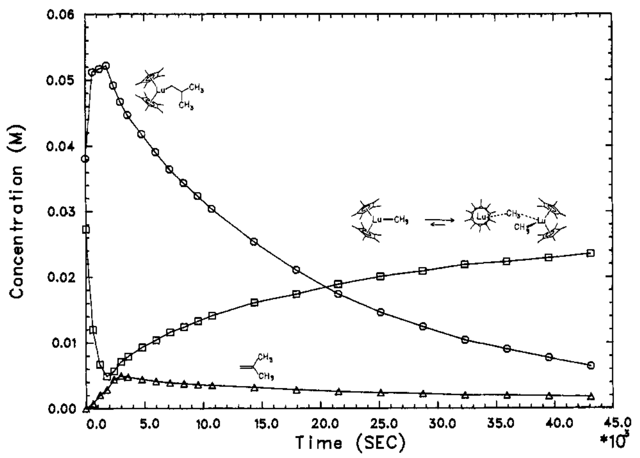

Figure 1. Lutetium–isobutyl rearrangement and decomposition: Time-dependent concentration of three species observed during decay of **1** at 22 °C in C_6D_{12}. In situ preparation of **1** was from **3** and propene in equimolar amounts. Lines drawn merely connect experimental points and are not calculated profiles. All species were monitored by 360-MHz ^{1}H NMR over a 12-h period.

rapidly with propene to give C_3 and C_6 lutetium–alkyl species. Isobutylene is observable since it is too sterically hindered to undergo insertion reactions into the lutetium–carbon bonds of **3** or **1**.

To account for the final allyl products **5** and **6**, we postulate the intermediacy[17] of $\overline{\mathrm{Lu}(\eta^5\text{-}C_5Me_5)\eta^5\text{-}C_5Me_4CH_2}$ (**4**), which reacts with olefins generated by β-alkyl and β-hydrogen elimination. Alternative pathways, such as direct reaction of **1** via vinylic C–H bond activation (eq 11) or reaction of **1** and olefin

$$\mathbf{1} + CH_2{=}CH(CH_3) \rightarrow \mathbf{5} + C_4H_{10} \tag{11}$$

$$\mathbf{2} + CH_2{=}CH(CH_3) \rightleftharpoons \mathbf{5} + H_2 \tag{12}$$

$$\mathbf{1} + H_2 \rightarrow \mathbf{2} + C_4H_{10} \tag{13}$$

via the hydride (eq 12–13)[18] are vitiated as major pathways by isotopic analysis of isobutane formed from $Lu(\eta^5\text{-}C_5Me_5)_2CD_2CD(CD_3)(CH_3)$ in cyclohexane-d_{12}. Primarily $C_4D_6H_4$ was produced, indicating that neither vinylic C–H bonds nor solvent were the major direct source of reducing hydrogen. Further clarification of this process is necessary.

β-Alkyl transfer is evidenced by the formation of **3** during decomposition of all three β-methyl complexes, **1**, **7**, and **8**. Additionaly, the complex $Lu(\eta^5\text{-}C_5Me_5)_2CD_2CD(CD_3)(CH_3)$ produced both $LuCD_3$ and $LuCH_3$ species as shown by hydrolysis, which gave the methanes CD_3H and CH_4 (approximately equal amounts). We propose a concerted four-center transition state for the β-alkyl transfer reaction. Radical processes are not considered reasonable since the microscopic reverse, olefin insertion into the Lu–C bond, is a concerted addition.[19]

Data for the changes in concentration of three principal solution species are illustrated in Figure 1.[15] The rate constants k_{-1}, k_{-2}, and k_{-7} (see scheme) were determined independently[16] while the others have been estimated to provide a consistent fit with observed data. Although further refinement is necessary, it is clear that β-hydrogen and β-alkyl elimination reactions have rate constants of $\sim 5 \times 10^{-5}$ and $\sim 1.5 \times 10^{-4}$ s^{-1}. The equilibrium constant for eq 1 is thus $\approx 10^{-3}$ and for eq 2 is $\approx 10^{-5}$. Work is in progress to provide independent experimental evdience for rate constants k_1 and k_2.

In conclusion, we have detailed a number of important reactions and products observed during decomposition of lutetium–alkyl species. We expect such chemistry to show generality for the lanthanide elements and early transition metals. A critical and interesting feature of the lutetium–isobutyl decomposition is that although β-hydrogen and β-alkyl elimination are energetically accessible reactions, they are readily observable only when coupled to processes that remove olefin from the system. We are currently investigating the generality of the intriguing β-alkyl transfer reaction.

Acknowledgment. The excellent technical assistance of R. Swiatek is gratefully acknowledged. Comments from Drs. F. N. Tebbe and J. E. Bercaw are also most appreciated.

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[17] We have no direct evidence for this structure at the present time. The structure suggested is akin to bercaw's zirconium "tuck-in" intermediates: Bercaw, J. E. *Adv. Chem. Ser.* **1978**, *No. 167*, 136–148.

[18] It should be noted that reactions analogous to eq 12 and 13, but with propene replaced by aromatics such as benzene or toluene, are rapid at 22 °C. Thus, $Lu(\eta^5\text{-}C_5Me_5)_2H$ is a true catalyst for the conversion of $Lu(\eta^5\text{-}C_5Me_5)_2R$ (R = alkyl) to $Lu(\eta^5\text{-}C_5Me_5)_2C_6H_5$ in benzene solution, via the hydrogenolysis mechanism: Watson, P. L., these results will be published in detail later.

[19] Addition of 1,2-*cis*-propene-d_2 to **1** initially gives only one diastereomer of labeled **7**. These results will be reported fully elsewhere.

Limits on the Activation Parameters for Automerization of Cyclobutadiene-*1,2*-d_2

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In this communication we report temperature and concentration dependence studies on the trapping of vicinally dideuterated cyclobutadiene in dichloromethane solution. The results allow limits to be placed on the activation parameters for automerization of cyclobutadiene.

The source of cyclobutadiene-d_2 was the azo compound **1**, whose preparation we have described previously.[1]

If one assumes that decomposition of **1** produces only one isomer of the labeled cyclobutadiene (depicted to be cyclobutadiene-*1,4*-d_2 in Figure 1, although we have no evidence on this point) then the ratio of S:U products should be given by

$$[S]/[U] = 1 + k_2[A]/k_1$$

where the products that are symmetrically labeled with respect to the bicyclo[2.2.0]hexene skeleton are designated S and those that are unsymmetrically labeled are designated U (see Figure 1). A is the alkene trapping reagent (methyl (*Z*)-3-cyanoacrylate).

To test this hypothesis, we investigated the concentration dependence of the S:U ratio at −9 °C. The products were converted to iodolactones and analyzed by ^{1}H NMR as described previously.[1] Figure 2 shows the graph of ([S]/[U]) − 1 vs. [A]. We take the linearity of this plot ($r^2 = 0.9987$) to be good support for the hypothesis.[2]

The next step of the investigation was to determine how the ratio k_2/k_1 varied with temperature. This was achieved by nonlinear least-squares[3] optimization of the parameters $\Delta\Delta H^{*}$ and $\Delta\Delta S^{*}$ in the equation

$$[S]/[U] = 1 + [A]\exp(\Delta\Delta H^{*}/RT - \Delta\Delta S^{*}/R)$$

$\Delta\Delta H^{*}$ is defined as $\Delta H^{*}{}_1 - \Delta H^{*}{}_2$ (i.e., ΔH^{*}(automerization) − ΔH^{*}(trapping)). $\Delta\Delta S^{*}$ is defined similarly. For display purposes only, Figure 3 shows a plot of ln (k_2/k_1), vs. $10^3/T$, which should be linear.

Measurements were made at −9 °C (four concentrations), −17 °C (three concentrations), −40 °C (one concentration), and −50

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[1] Whitman, D. W.; Carpenter, B. K. *J. Am. Chem. Soc.* **1980**, *102*, 4272–4274.

[2] The gradient of this line gives k_2/k_1. The result (0.35 ± 0.01 L/mol) is smaller than that estimated from our previous work.[1] This presumably is caused by the change in solvent from Me_2SO to dichloromethane.

[3] Wentworth, W. E. *J. Chem. Educ.* **1965**, *42*, 96–103.