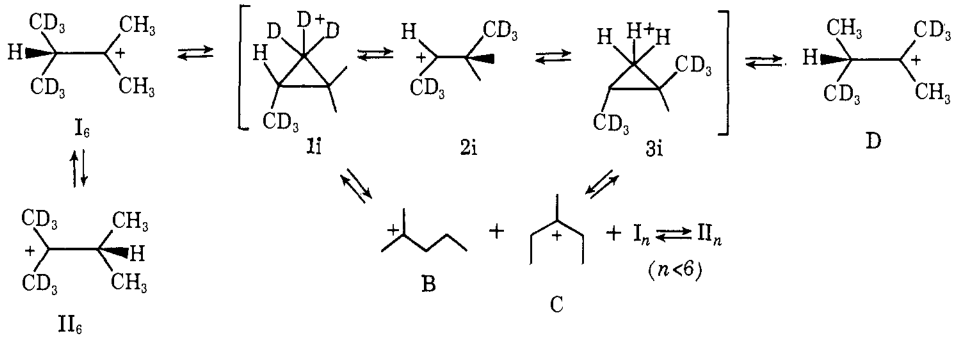

ion $I_1 \rightleftarrows II_1$ and unlabeled ion. The nmr spectrum of $I_1 \rightleftarrows II_1$ underwent temperature-dependent changes due to the methyl interchange process between −30 and +10°. A nmr line-shape analysis was performed to find the rate constant. The activation energy of the methyl interchange process was found to be 12.4–13.5 kcal/mol, log A = 12.5–13.5. In the nmr spectrum of $(I_6 \rightleftarrows II_6) \rightleftarrows D$ at equilibrium the measured area of the doublet at τ 7.07 ppm for D was 1.8 + 0.1 times the area of the doublet of the unsymmetrical ion $(I_6 \rightleftarrows II_6)$ at $T = -60$ to $-90°$.

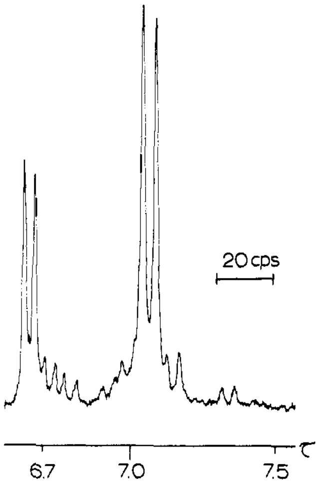

Figure 2. 100-MHz nmr spectrum of $I_6 \rightleftarrows II_6 \rightleftarrows D$ in SO_2ClF–SbF_5 at −60°. Due to incomplete labeling some $I_5 \rightleftarrows II_5$ and $I_4 \rightleftarrows II_4$ are present.

The deviation from the expected statistical ratio of 2 can be understood by considering that the isomer I_6, which has the six deuterium atoms away from the positive charge, is favored over II_6 $((I_6/II_6) = 2.584$ at $-79°)$. The average energy of the equilibrium mixture is lower than that of the symmetrical structure D. Introduction of this factor using a computer program written for this purpose yielded a predicted ratio of 1.8. We believe that this is the first observation of an equilibrium constant which is significantly affected by an isotope effect between isomers interconverted by a much more rapid process on one side of the equilibrium. This discrepancy from the statistical factor provides an independent method for obtaining the isotope effect. In this instance, it is less accurate than the use of isotopic splitting in the nmr spectrum, but in other cases it might be the only tool available.

No exchange between methyl and methine hydrogens was observed at $T < -50°$. On warming to −40°, the nmr peaks for the ions B and C appeared at a comparable rate as peaks at the positions of $I_5 \rightleftarrows II_5$ and $I_1 \rightleftarrows II_1$, and later at the positions of $I_4 \rightleftarrows II_4$ and $I_2 \rightleftarrows II_2$. This is consistent with a process accomplishing an overall pairwise interchange of the methine hydrogen with a hydrogen of *one* methyl group.[1] More deep-seated rearrangement could lead directly from $I_6 \rightleftarrows II_6 \rightleftarrows D$ to *any* isomer $I_n \rightleftarrows II_n$, $n < 6$. The mechanisms discussed would require two changes in branching level of the alkyl chain[8] where hydrogens from *two* methyl groups are converted to methylene and methine protons and scrambled before return to the starting material.

The observation that interchange of methyl groups $(I_6 \rightleftarrows II_6 \rightleftarrows D)$ is more rapid than any other process by a factor of 10–500 (at 0°) may be *most simply* explained by the supposition that the corner-protonated cyclopropane geometry **1i** or **3i** which is achieved in the course of methyl interchange is prevented from undergoing corner-to-corner proton migration by a barrier of several kilocalories/mole. This point of view suggests that the edge-protonated cyclopropane geometry may be less stable than the corner-protonated cyclopropane in this case.

Acknowledgment. We wish to acknowledge support of this work by the National Science Foundation and by the "Stiftung Fuer Stipendien auf dem Gebiete der Chemie, Basel, Switzerland."

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[8] M. Saunders and J. Rosenfeld, *J. Amer. Chem. Soc.*, **91**, 7756 (1969); H. Hogeveen and C. J. Gaasbeek, *Recl. Trav. Chim. Pays-Bas*, **88**, 1305 (1969); D. M. Brouwer, *ibid.*, **88**, 9 (1969).

Martin Saunders,* Pierre Vogel
Department of Chemistry, Yale University
New Haven, Connecticut 06520
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Cycloaddition Reactions of Alkenylidenecyclopropanes

Sir:

Several examples of the participation of the strained σ bonds of cyclopropane derivatives in cycloaddition reactions have been recently reported.[1-3] Bicyclo[1.1.0]butanes[2] and bicyclo[2.1.0]pentanes[1] react with reactive dienophiles in ${}_{\sigma}2 + {}_{\pi}2$ cycloaddition reactions *via* diradical intermediates. Examples of the participation of strained σ bonds of a cyclopropane in 4 + 2 cycloaddition reactions are less well known. α-Cyclo-

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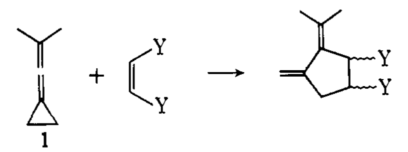
[1] P. G. Gassman and G. D. Richmond, *J. Amer. Chem. Soc.*, **92**, 2090 (1970); **90**, 5637 (1968); *Chem. Commun.*, 1630 (1968); P. G. Gassman and K. T. Mansfield, *J. Amer. Chem. Soc.*, **90**, 1524 (1968); *Chem. Commun.*, 391 (1965); P. G. Gassman, K. T. Mansfield, and T. J. Murphy, *J. Amer. Chem. Soc.*, **91**, 1684 (1969).

[2] A. Cairncross and E. P. Blanchard, Jr., *ibid.*, **88**, 496 (1966); M. Pomerantz, G. W. Gruber, and R. N. Wilke, *ibid.*, **90**, 5040 (1968).

[3] C. D. Smith, *ibid.*, **88**, 4273 (1966).



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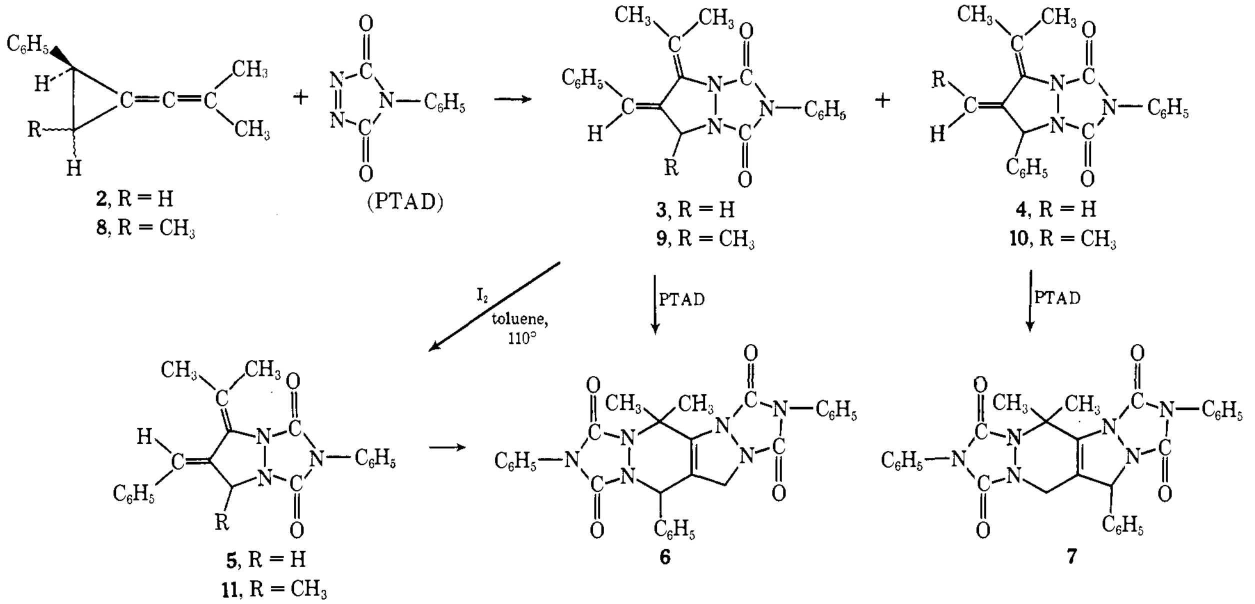


2, R = H
8, R = CH_3

(PTAD)

3, R = H
9, R = CH_3

4, R = H
10, R = CH_3

5, R = H
11, R = CH_3

6

7

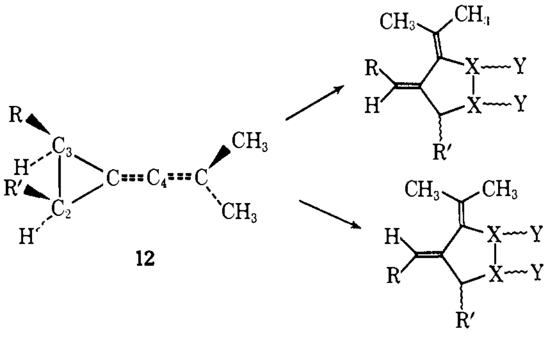
propylstyrene is reported to react with maleic anhydride to give 4-phenylcyclohept-4-ene-1,2-dicarboxylic anhydride,[4] and quadricyclane reacts with tetracyanoethylene in a $({}_{\sigma}2,{}_{\sigma}2) + {}_{\pi}2$ cycloaddition reaction.

We wish to report preliminary results on the cycloaddition reaction of alkenylidenecyclopropanes (**1**) which potentially provides useful synthetic procedures for the preparation of substituted bismethylenecyclopentanes.

The reaction of **2** with 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) in a 1:1 mole ratio in methylene chloride produces two 1:1 adducts and one 2:1 adduct. The reaction of **2** with PTAD is very rapid even at temperatures well below 25°. The 1:1 adducts are assigned structures **3** and **4** based on the following physical and chemical properties. Ozonolysis of **3** ($\lambda_{\max}$ 222 (4.31) and 268 nm (3.97)) in methylene chloride–pyridine solution produces benzaldehyde and acetone in a 1:1 mole ratio. Ozonolysis of **4** ($\lambda_{\max}$ 222 nm (4.35)) produces acetone but *no* benzaldehyde. **3** is *quantitatively* isomerized to **5** ($\lambda_{\max}$ 222.5 (4.38) and 274 nm (4.30)) with iodine in refluxing toluene. **3** and **5** both react with PTAD to produce identical 2:1 adducts of structure **6**;[5] however, **5** reacts at least 100 times faster than **3** with PTAD. **4** similarly reacts with PTAD to produce the 2:1 adduct **7**, identical with the 2:1 adduct isolated from the reaction mixture derived from **2** with PTAD. **4** also reacts at least 100 times faster than **3** with PTAD. Analysis of the nmr spectrum of the crude product mixture derived from **2** with PTAD showed the complete absence of the resonance peaks of **5** and **6**.

cis- and *trans*-**8** similarly react with PTAD to produce the 1:1 adducts **9** and **10**. Both **9** and **10** react more slowly with PTAD than does *cis*- or *trans*-**8** thus precluding extensive 2:1 adduct formation. **9** ($\lambda_{\max}$ 222.3 (4.35) and 268 nm (3.94)) is readily isomerized to **11** ($\lambda_{\max}$ 222 (4.35) and 273 nm (4.12)). **11** could not be detected in the product mixtures derived from *cis*- and *trans*-**8** with PTAD. **10** is resistant to isomerization in the presence of iodine in refluxing toluene, but does undergo isomerization on irradiation.

The formation of single stereoisomers of **3**, **9**, and **10** from **2** and **8**, with those being the least thermodynamically stable isomers, suggests that the 1:1 adducts are formed *via* concerted cycloaddition pathways. A two-step process involving the formation of a long-lived diradical or dipolar intermediate is not consistent with the present data. The concerted cycloaddition of a hypothetical dienophile Y—X=X—Y across carbon atoms 2 and 4 of **12** can occur in four different ways: (1) inversion at C-2 with rotation of the HC_3R plane such that R becomes syn to the isopropylidene group (syn rotation); (2) retention at C-2 with rotation of the HC_3R plane such that R becomes anti to the isopropylidene group (anti rotation); (3) inversion at C-2 with anti rotation about C_3; and (4) retention at C-2 with syn rotation about C_3. Processes 1 and 2 involve six-electron transition states, whereas processes 3 and 4 involve eight-electron transition states.[7] The



12

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[4] S. Sarel and E. Breuer, *J. Amer. Chem. Soc.*, **81**, 6522 (1959).

[5] The urazole ring in similar adducts of PTAD has been shown to be planar about the adjacent nitrogen atoms[6] thus resulting in the formation of a single adduct from both isomers.

[6] A. B. Evnin, D. R. Arnold, L. A. Karnishky, and E. Strom, *J. Amer. Chem. Soc.*, **92**, 6218 (1970).

[7] The six-electron processes involve only the electrons of the double bond exocyclic to the cyclopropane ring along with the σ electrons, whereas the eight-electron processes involve all four π electrons of the allene functional group along with the σ electrons.[8]

[8] The use of all four π electrons of the allene functional group is analogous with the use of all four π electrons of a ketene in ketene dimerizations.[9]

present data are consistent with product formation occurring only by processes 1 and/or 4. The theoretical and stereochemical aspects of these reactions will be discussed in detail in a later publication. Further studies are being directed toward the determination of the stereochemistry of attack at C_2, and the effect of the nature of R and R′ and the dienophile on the direction of the cycloaddition reaction.

(9) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, pp 163–168.

Daniel J. Pasto,* Albert Chen
Department of Chemistry, University of Notre Dame
Notre Dame, Indiana 46556

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Nuclear Magnetic Resonance Spectra of Tris[2,2,6,6-tetramethyl-3,5-heptanedionato] Complexes of the Lanthanides. Temperature Dependence of Shift Reagents

Sir:

Study of the tris[2,2,6,6-tetramethyl-3,5-heptanedionato] (tris(dpm)) chelates of the rare earth elements by nmr has been biased heavily toward the tris(dpm) derivative of europium,[1,2] which has enjoyed spectacular success as a deshielding shift reagent; the analogous derivative of praeseodymium, capable of displacing the signals of a sample to higher field with only a slight increase of line width, has also been studied,[3,4] and recent comparative studies have shown that the former complex displays superior magnetic[5] and solubility[6] properties. As tris(dpm) derivatives have been prepared[7] from the entire rare earth group (except cerium and promethium), we undertook to measure the nmr parameters of *tert*-butyl protons of these chelates, both alone and in the presence of potential ligands. Cyclohexanone or 1-hexanol as ligand produced approximately equal changes in chemical shift of the *tert*-butyl resonances of any given complex, although the magnitude and direction of such changes varied broadly from one central atom to the next (Table I). Table II details the concomitant alterations produced in the 100-MHz nmr spectrum of cyclohexanone. The direction of displacement is also a function of the central atom, and the magnitude of this effect, which varies from slight (Sm) to enormous (Dy, Ho), is nearly linear with the proportion[1,4,6] of complex present; the extent of broadening of signals is essentially a function only of the central atom. Direct measurements of relaxation times of the complexes are in progress. (Also under current investigation are the dipyridyl and 1,10-phenanthroline 1:1 adducts of the tris(dpm) compounds of the entire rare earth series[5] for the purpose of relaxation studies.)

Table I. Chemical Shifts and Line Widths (at Half-Height) of the *tert*-Butyl Proton Signals of $M(dpm)_3$ in CCl_4, in the Presence of Oxygen-Containing Species

	Ligand					
	None		Cyclohexanone		1-Hexanol	
M	Ppm[a]	Width[b]	Ppm[a]	Width[b]	Ppm[a]	Width[b]
Pr	0.6	40	2.8	2		
Nd	0.8	16	2.1	10		
Sm	1.08	7	1.2	6		
Eu	0.48	10	−0.5	5	−0.6	20
Gd	0.9	1500	1.8	800		
Tb	17.4	250	16.0	170	17.7	60
Dy	17.7	180	21.9	130	20.3	120
Ho	5.3	180	7.3	180	8.8	180
Er	−3.6	250	−6.2	70	−5.5	45
Tm	12.8	400	15.2	240	17.9	170
Yb	−0.3	60	−1.9	20		
Lu	1.14					

[a] Downfield from TMS. [b] In hertz, approximately.

Table II. Chemical Shifts and Line Widths (at Half-Height) of Signals of the α-, β-, and γ-Methylene Protons of Cyclohexanone (0.1 *M*) in a Saturated Solution[a] of $M(dpm)_3$ in CCl_4

	α		β		γ	
M	δ[b]	Width[c]	δ[b]	Width[c]	δ[b]	Width[c]
Pr	−8.8	(>20)[d]	−2.8	(~20)[d]	−2.0	(~20)[e]
Nd	−3.1	(>20)[e]	−0.4	(>20)	−0.1	(>20)
Sm[g]	~1.1	(>20)[e]	~1.1	(>20)	~1.1	(>20)
Eu	5.4	(~15)[d]	3.8	(~15)[d]	3.5	(~15)[e]
Gd[f]						
Tb	−23.8	(75)	−12.4	(32)	−9.2	(24)
Dy	−51.6	(85)	−21.2	(25)	−16.2	(21)
Ho	−49.0	(92)	−21.6	(29)	−16.4	(22)
Er	28.0	(61)	13.0	(>20)	10.5	(>20)
Tm[h]	−42.2	(90)	−17.3	(38)	−13.1	(34)
Yb	14.6	(23)	7.4	(>20)	6.1	(>20)
None	2.45(	~15)[d]		~2.00	1.70	

[a] Except Ho, which is much more soluble; $[M(dpm)_3]$ is slightly less than 0.1 *M*. [b] In parts per million. [c] In hertz. [d] Sufficiently resolved to permit identification of multiplicity. [e] Evidence of fine structure, but not resolved enough for identification. [f] Not observed; overlap possible as *tert*-butyl resonance is very broad. [g] These values were determined by adding cyclohexanone and observing emergence of resonances from beneath the *tert*-butyl signal. [h] These values are reversed in sign from analogous data reported by Hart, *et al.*,[3] for $Tm(ClO_4)_3[OP(NMe_2)_3]_4$ in acetonitrile, but similar reversals have been produced (E. R. Birnbaum and T. Moeller, *J. Amer. Chem. Soc.*, **91**, 7274 (1969)) by altering ligands in Pr and Nd complexes.

In general, the solubility of all 12 compounds in carbon tetrachloride is modest at best, and, as noted for the Eu analog, enhanced somewhat by the presence of a coordinating substrate; Ho and, to a lesser extent, Dy are slight exceptions in being rather less insoluble. Solutions of complexes in the present study were prepared by dissolving 15 ± 3 mg of the appropriate solid in 0.3 ml of warmed carbon tetrachloride that had been stored for at least 1 week over NaOH pellets.

It was found that the use of untreated CCl_4 as a solvent for such studies promoted decomposition of at least several of the complexes; the *tert*-butyl resonances of solutions of $Pr(dpm)_3$, $Nd(dpm)_3$, and $Sm(dpm)_3$ in untreated carbon tetrachloride were shown to diminish upon standing and/or dilution, with concurrent appearance of a second signal. During investigation of this phenomenon, it was further noted that these signals displayed substantial shifts of field

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(1) C. C. Hinckley, *J. Amer. Chem. Soc.*, **91**, 5160 (1969); *J. Org. Chem.*, **35**, 2834 (1970); P. V. DeMarco, T. K. Elzey, R. B. Lewis, and E. Wenkert, *J. Amer. Chem. Soc.*, **92**, 5734, 5737 (1970); G. M. Whitesides and D. W. Lewis, *ibid.*, **92**, 6979 (1970).

(2) J. K. M. Sanders and D. H. Williams, *Chem. Commun.*, 422 (1970); G. H. Wahl, Jr., and M. R. Peterson, Jr., *ibid.*, 1167 (1970).

(3) J. Briggs, G. H. Frost, F. A. Hart, G. P. Moss, and M. L. Staniforth, *ibid.*, 749 (1970).

(4) J. Briggs, F. A. Hart, and G. P. Moss, *ibid.*, 1506 (1970).

(5) D. R. Crump, J. K. M. Sanders, and D. H. Williams, *Tetrahedron Lett.*, 4419 (1970).

(6) J. K. M. Sanders and D. H. Williams, *J. Amer. Chem. Soc.*, **93**, 641 (1971).

(7) J. Selbin, N. Ahmad, and N. S. Bhacca, *Inorg. Chem.*, in press.