tegration of the areas of the vinyl proton signals in the nmr spectrum (*cis*-**1**, δ 5.18; *trans*-**1**, δ 6.60). These ratios correspond to the cis–trans acid composition, as determined by nmr, and to the results of the gc assay by way of the methyl esters, indicating retention of stereochemistry in the esterification and peresterification steps. The perester from trans acid shows no nmr absorption due to cis perester at δ 5.18 (limit of detectability, 4%). The methyl ester assay of the same sample of starting trans acid indicates 0.2% cis ester; the perester composition is, therefore, taken as >99% *trans*-**1**.

Preparative scale decomposition of the peresters (*cis*- and *trans*-**1**) in cumene at 110° for 4 hr gives CO_2 ($\sim$75%), *cis*- and *trans*-methyl propenyl ethers (**3**) ($\sim$55%), acetone ($\sim$10%), and *tert*-butyl alcohol ($\sim$70%) as volatile products. 1-Methoxycrotonic acids are not detected as reaction products; the stability of the trans acid to the perester decomposition conditions is assured by a control experiment. The olefins, acetone, and *tert*-butyl alcohol are characterized by nmr and gc retention times; yields are determined by gc. Authentic samples of the olefins were prepared by the acid-catalyzed pyrolysis[6] of 1,1-dimethoxypropane and are characterized as *cis*- and *trans*-**3** by the olefinic coupling constants of 6 and 12 Hz, respectively.

The stereochemical consequences of the thermal decompositions of mixtures of *cis*- and *trans*-**1** in deoxygenated cumene are presented in Table I. The olefinic product compositions are determined by gc analysis. The olefin yields (and CO_2 yields) from perester mixtures of very different compositions are similar, indicating that the isomeric peresters are equally efficient sources of vinyl radical products. The gross stability of the olefins to the reaction conditions is independently demonstrated by decomposing *trans*-**1** in the absence and in the presence of a mixture of *cis*- and *trans*-**3**. The yield of *cis*-**3** in the reference reaction (*i.e.*, from *trans*-**1**) plus the amount of *cis*-**3** added represents the expected amount of *cis*-**3** in the doped reaction. Since *trans*-**1** gives only trivial amounts of *trans*-**3**, the anticipated amount of *trans*-**3** in the doped reaction is equal to the *trans*-**3** added. Analysis of the doped mixture indicates 93 and 99% of the anticipated amounts of *cis*- and *trans*-**3**, respectively. The small discrepancies between perester and olefin compositions in Table I are assigned to isomerization of the olefins under the reaction conditions.[7] The conclusion to be derived from the data in Table I is that the anticipated vinyl radical products, *cis*- and *trans*-**3**, are formed as major products with retention of initial perester stereochemistry. This result is most simply interpreted in terms of intermediate, isomeric 1-methoxypropenyl radicals (*cis*- and *trans*-**2**) which are scavenged by cumene more rapidly than they interconvert. No other carbon radical is known which can survive comparable treatment with clean retention of stereochemistry.

Table I. Decomposition of *cis*- and *trans*-**1**[a]

[**1**], *M*	*t*, min	% *trans*-**1**[b]	% *cis*-**3**[c]	% yield, **3**
0.063[d]	240	10	13[e]	
0.098	240	29	32	52
0.115[d]	240	61	60[e]	
0.096	240	68	67	54
0.204	240	>99[f]	95	44
0.088	240	>99[f]	99	55
0.095[g]	120	>99[f]	>99	54
0.095[g]	80	>99[f]	>99	50
0.095[g]	40	>99[f]	>99	41

[a] In cumene at 110°. [b] [*trans*-**1**/(*cis*-**1** + *trans*-**1**)] × 10^2. [c] [*cis*-**3**/(*cis*-**3** + *trans*-**3**)] × 10^2. [d] Preparative scale decomposition. [e] Composition by nmr and gc. [f] Composition by gc assay of the methyl esters of the starting acid (see text). [g] Undecomposed perester is destroyed by triphenylphosphine before gc analysis; controls demonstrate the efficiency of this quench.

Previous studies clearly demonstrate that the interconversion of 1-alkylvinyl radicals is much faster than hydrogen transfer from cumene and suggest that the processes are competitive for 1-chlorovinyl radicals.[8] A spectrum of behavior therefore exists. Although the experimental results reflect the ratios of the rates of isomerization and capture of the vinyl radicals, it seems reasonable to propose that the main effect is in the rate of configurational change and that there is considerable variation in the rate of inversion of vinyl radicals as a function of the nature of the 1-substituent. It is our current thought that these differences in rate of inversion are controlled by the electronegativities[9] of the 1-substituent (Me < Cl < OMe).[10,11]

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[6] W. L. Howard, E. C. Jacobsen, and R. A. Newton, *J. Org. Chem.*, **26**, 3574 (1961).

[7] The thermodynamic mixture of isomeric olefins, *trans*-**3**/*cis*-**3** $\cong$ 53/47 at 25°, is established by equilibration with thiophenol.

[8] Previous studies of vinyl radicals are critically reviewed by W. G. Bentrude, *Annu. Rev. Phys. Chem.*, **18**, 300 (1967), and by L. A. Singer in "Selective Organic Transformations," Vol. II, B. S. Thyagarajan, Ed., Wiley, New York, N. Y., in press.

[9] P. R. Wells, *Progr. Phys. Org. Chem.*, **6**, 111 (1968).

[10] H. A. Bent, *Chem. Rev.*, **61**, 275 (1961).

[11] This work was supported by the National Science Foundation, Grant No. GP-13475.

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Geometrical Isomerization of Allylic Radicals

Sir:

The geometrical isomerization of allylic radicals has long been a subject of interest to chemists,[1] and the configurational stability of the cis and trans butenyl radicals has been observed at 40° in solution.[1a] We wish to report our observations on the isomerization of butenyl radicals in the gas phase.

Recently we demonstrated that allyl radicals are produced upon the thermolysis of 3,3′-azo-1-propene, and that these radicals dimerize to produce 1,5-hexadiene.[2] The absence of any significant amount of hydrogen abstraction by the allylic radicals, and of any chain-induced decomposition, suggested that a study of azo compounds **1**, **2**, and **3** would present an opportunity to test the geometrical stability of such radicals. To this end we have synthesized (*E*,*E*)-4,4′-azo-2-

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[1] (a) C. Walling and W. Thaler, *J. Amer. Chem. Soc.*, **83**, 3877 (1961); (b) D. B. Denney, R. M. Hoyte, and P. T. MacGregor, *Chem. Commun.*, 1241 (1967); (c) D. M. Golden, *Int. J. Chem. Kinet.*, **1**, 127 (1969); (d) J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, **90**, 7157 (1968).

[2] B. H. Al-Sader and R. J. Crawford, *Can. J. Chem.*, **48**, 2745 (1970).

butene (**1**) and (*Z,Z*)-4,4′-azo-2-butene (**2**)[3] using the hydrazo dicarboxylate method described previously.[2] The synthesis of 3,3′-azo-1-butene (**3**) was achieved by the low-yield, pot-luck, direct diallylation of hydrazine, using 3-chloro-1-butene, followed by oxidation with mercuric oxide and analysis of the various fractions separated on a preparative gas chromatograph.[4]

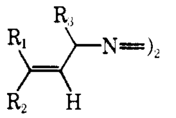
Gas-phase thermolysis of the azo compounds gave only the dienes **6–11** with less than 1% of butadiene and butenes. The proportions of dienes from the azo compounds are listed in Table I. The peaks were identified in the same manner as that used by Doering and Roth.[5] The gc analyses were carried out using a 150-ft capillary column (i.d. 0.01 in.) coated with β,β′-oxydipropionitrile and utilizing a Hewlett Packard 3370A electronic integrator. The mixture of isomeric dienes, **6–11**, is well suited to precision gc analysis, and the azo compounds **1**, **2**, and **3** are cleanly separated on the same column.

Table I. Product Composition from the Thermolysis of **1**, **2**, and **3**[a]

Azo compd	% yield[b]					
	6[c]	**7**	**8**	**9**	**10**	**11**
1	16.99	28.31	18.59	11.91	17.67	6.54
s (11)	0.21	0.06	0.08	0.03	0.11	0.07
2	17.20	28.66	18.36	12.20	17.47	6.12
s[d] (10)[e]	0.28	0.15	0.17	0.17	0.21	0.06
3	17.05	28.83	18.48	11.94	17.64	6.08
s (12)	0.19	0.08	0.07	0.07	0.13	0.01

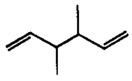
[a] At 125.7 ± 0.1°, 100 Torr of N_2 added in a 1200-ml glass vessel. [b] Values are not rounded off for computational purposes; initial concentration of azo compounds 2.0×10^{-5} *M*. [c] Two peaks of essentially equal size (meso + racemic). [d] Standard deviation. [e] Number of analyses.

At 60% completion a sample of **1** was recovered unchanged as judged by gc and nmr analysis.[6] Similarly, when an aliquot of **2** was added to **11** and then allowed to react, **11** was observed to be stable under the reaction conditions. Analysis of samples of **1** thermolyzed in cumene gave a 2.4:1 ratio of **8**:**7**.[8] We conclude that the radicals, **4** and **5**, are interconverting and that the products arise from a "nearly equilibrated" reservoir of butenyl radicals. That the mixture of dienes from **1** has a greater proportion of **8** and **11** than does the mixture of dienes from **2** or **3** is confirmed statistically at the 99% confidence level by use of the *t test*.[10] The rates of thermolysis of **1**, **2**, and **3** at 125.7° are 1.37×10^{-4} sec^{-1}, 1.48×10^{-4} sec^{-1}, and 10.7×10^{-4} sec^{-1}.[11]

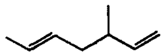


1, $R_1 = CH_3$; $R_2 = R_3 = H$
2, $R_1 = R_3 = H$; $R_2 = CH_3$
3, $R_1 = R_2 = H$; $R_3 = CH_3$

4 **5**



6 (meso + rac)



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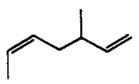

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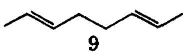

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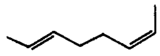

10

11

Using a value of k_{comb} for the allyl radicals of 8.5×10^9 l. mol^{-1} sec^{-1} derived from the data of van den Bergh and Callear[12] and estimating from the data in Table I that the reversible isomerization of **4** to **5** has completed 8–10 half-lives we can, by use of the steady-state approximation, calculate values of k_{tc}, k_{ct}, and $\Delta G_{tc}^{\ddagger}$ of 11 sec^{-1}, 16 sec^{-1}, *and 21 ± 3 kcal mol*$^{-1}$ at 398.9°K.

Wall effects cannot be responsible for the isomerization since during the mean lifetime, $\tau = 0.20$ sec, the radicals will have diffused[13] 0.76 cm before recombining. The radius of the vessel used was 7.2 cm. It is of interest to note that by using a value of $K = 1.45$ and because the primary centers in **4** and **5** are more reactive than the secondary centers by a factor of 1.48 the product proportions of **6**:**7**:**8**:**9**:**10**:**11** on a statistical basis would be 16.2, 28.5, 19.6, 12.5, 17.2, and 6.0% which compares favorably with those observed from **3**. Such a statistical condition would only hold if the activation energy for recombination is considerably less than that for geometrical isomerization.

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(3) The nomenclature used for the azo compounds described herein was kindly prescribed by Dr. K. L. Loening, Nomenclature Director, Chemical Abstracts; see J. E. Blackwood, C. L. Gladys, K. L. Loening, A. E. Petraria, and J. E. Rush, *J. Amer. Chem. Soc.*, **90**, 509 (1968).

(4) All new compounds gave satisfactory elemental analysis and appropriate nmr, ir, and uv spectra.

(5) W. von E. Doering and W. R. Roth, *Tetrahedron*, 18, 67 (1962).

(6) The nmr spectrum of the recovered **1** showed no signal at δ 4.32 corresponding to the allylic methylene group of **2**. This implies that a reversible azo to diazene[7] rearrangement cannot be isomerizing the reactant at these temperatures. The products, **6–11**, undergo a Cope rearrangement[5] at 200–240° and thus are stable at these temperatures.

(7) J. E. Baldwin, J. E. Brown, and G. Hoyle, *J. Amer. Chem. Soc.*, 93, 788 (1971).

(8) In decalin using galvinoxyl as a scavenger the ratio of **8**:**7**, starting from **1**, was found to be 6.0:1 and that of **11**:**9** was found to be 19:1. However, it was observed that the galvinoxyl was decomposing under the reaction conditions and inducing[9] the thermolysis of **1**. As yet we have not been able to scavenge all of those radicals which escape the solvent cage.

(9) P. D. Bartlett and S. T. Purrington, *J. Amer. Chem. Soc.*, 88, 3303 (1966).

(10) C. J. Brooks, I. G. Betteley, and S. M. Loxston, "Mathematics and Statistics for Chemists," Wiley, London, 1966, Chapter 13.

(11) Compound **3** is actually a mixture of meso and racemic as indicated by gc. The rates were measured using a sample of approximately 40:60 proportion. That isomer which was the slower moving on the gc column reacted 1.2 times faster than the other. Such steric factors upon the rate of thermolysis of azo compounds have been observed before. See S. E. Scheppele and S. Seltzer, *J. Amer. Chem. Soc.*, **90**, 358 (1968).

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(14) Counseil des Arts de Canada Fellow, 1968–1969.