xanthenone sensitization. Furthermore, in a methanol solution containing 0.01 N HCl, nitrosopiperidine quenches naphthalene fluorescence[19] with $k_q \cong 10^{10}$ M^{-1} sec^{-1}. The fact that naphthalene also sensitizes the photoreactions of N-nitrosopiperidine indicates that the transient is derived from a singlet state but not from a triplet state of N-nitrosopiperidine. This conclusion is also supported by the observation that conjugated dienes do not quench the nitrosamine photoreactions.[7]

The absorption spectrum of the above transient is very similar to that of the transient generated from flash photolysis of N-chloropiperidine in 0.01 N aqueous H_2SO_4 solution;[20] both exhibit increasing absorbance from the 450-nm region toward shorter wavelength and an apparent maximum at about 295 nm. The latter transient reacts with methanol with a second-order rate constant of 4.9×10^3 M^{-1} sec^{-1} in agreement with the rate constant of hydrogen abstraction by piperidinium radical (10^3–10^4 M^{-1} sec^{-1}) determined by the rotating sector method.[21] It is concluded that, in the photolysis of N-nitrosopiperidine, piperidinium radical derived from the lowest singlet excited state is the reactive transient which initiates elimination, reduction, and addition reactions. The absence of quenching in an oxygen-saturated solution (1.43×10^{-3} M of O_2)[22] places an upper limit of the rate constant for oxygen quenching at $\sim 1 \times 10^6$ M^{-1} sec^{-1}. This rate constant seems to be too low for triplet quenching in an aqueous solution[23] since the observed value is closer to those found for oxygen quenching of reactive radicals.[24]

The involvement of an aminium radical in the photoaddition of a nitrosamine to an olefin demands that the addition mechanism must be a stepwise radical process. It is indeed found that the photoaddition of N-nitrosopiperidine to both *trans*- and *cis*-2-butenes gives the same mixture of erythro and threo adducts.[25]

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[19] For emission studies, a high-pressure Hanovia xenon compact arc lamp (150 W) and a Farrand grating monochrometer were used for excitation and a Jarrell-Ash 82-810 monochromater with an EMI6256A photomultiplier tube was used as the detecting system.

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[22] Calculated from Henry's law using $K = 2.9 \times 10^7$ for the solubility of oxygen in water. The K is taken from "Handbook of Chemistry and Physics," 47th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1967.

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[26] Photoreactions of Nitroso Compounds in Solution. XVIII. For part XVII see: Y. L. Chow, R. A. Perry, and B. C. Menon, *Tetrahedron Lett.*, 1549 (1971).

[27] The author thanks the National Research Council of Canada and the President's Research Fund of Simon Fraser University for their generous support of this research.

[28] Issued as National Research Council Contribution No. 12084.

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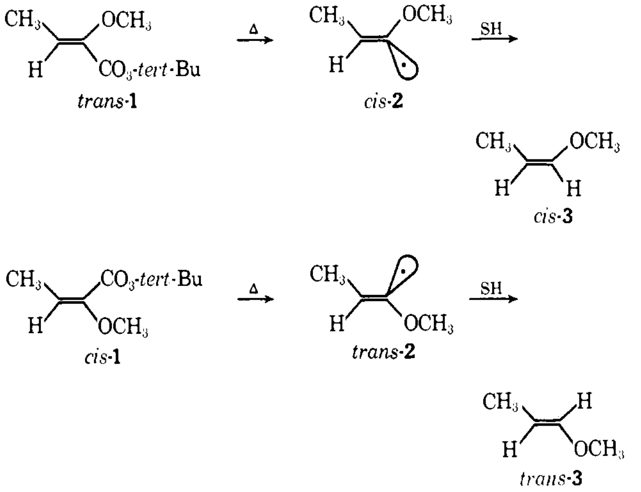
Received March 6, 1971

Vinyl Radicals. VI. The Configurational Stability of *cis*- and *trans*-1-Methoxy-1-propenyl Radicals

Sir:

We describe experiments which demonstrate the configurational stability of *cis*- and *trans*-1-methoxy-1-propenyl radicals. These radicals (*cis*- and *trans*-**2**) are prepared by the thermal decomposition of the corresponding *tert*-butyl *trans*- and *cis*-1-methoxy percrotonates (**1**) and are quenched by hydrogen transfer from cumene to give *cis*- and *trans*-methyl 1-propenyl ethers (**3**) with retention of stereochemistry.



trans-1-Methoxycrotonic acid is readily available as a crystalline solid (mp 60-61°) by the reaction of 2,3-dibromobutyric acid with NaOMe–MeOH.[1] The trans stereochemistry is assigned on the basis of the chemical shifts of the vinyl protons[2] (δ 6.35; calcd, 5.9) in the free acid and the corresponding methyl ester (δ 6.13; calcd, 5.67). A cis–trans mixture of the isomeric 1-methoxycrotonic acids (*ca.* c/t = 0.3) is obtained by the benzophenone-sensitized photoisomerization[3,4] (Pyrex filter) of the trans acid in acetonitrile. Further enrichment in cis acid is achieved by preferential removal of the trans isomer by crystallization from hexane, or by partial gas-chromatographic (gc) separation of the methyl esters followed by mild hydrolysis to the free acids. The cis stereochemical assignment is in accord with the chemical shifts of the vinyl protons[2] of the free acid (δ 5.35; calcd, 5.38) and the methyl ester (δ 5.12; calcd, 5.18).

The composition of any particular mixture of acids is determined by integration of the vinyl region of the nmr spectrum or by esterification with Ag_2O–MeI and gc assay of the cis–trans composition of the mixture of methyl esters. The corresponding *tert*-butyl peresters (**1**) are prepared by the sequential reaction of the free acids with N,N'-carbonyl diimidazole and *tert*-butyl hydroperoxide in THF at room temperature.[5] The peresters are purified by chromatography on Al_2O_3 and give satisfactory analyses, peroxide titers, and spectral data. The isomeric perester composition (*cis*-**1**/*trans*-**1**) of gross mixtures is established by in-

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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 (~75%), *cis*- and *trans*-methyl propenyl ethers (**3**) (~55%), acetone (~10%), and *tert*-butyl alcohol (~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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Received April 22, 1971

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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