Table I
Rate Constants[a] for Decomposition and ^{18}O Scrambling at 130°
RCO_3-*t*-Bu

Solvent	k_o (R = CH_3)	k_s (R = CH_3)	$k_o + k_s$ (R = CH_3)	k_o (R = Ph)	k_s (R = Ph)	$k_o + k_s$ (R = Ph)	DSP,[b] atm
Hexane	50.8	13.1	63.9	3.72	0.16	3.88	0
Isooctane				3.36	0.20	3.56	288
Dodecane				3.08	(0.24)	3.42	534
60% hexane oil	44.3	16.6	60.9	3.39	(0.28)	3.67	263
30% hexane oil	38.0	19.3	57.1	3.04	(0.36)	3.40	571
Paraffin oil	31.3	20.8	52.1	2.33	(0.50)	2.83	1320

[a] × 10^5 sec^{-1}; values in parentheses are interpolated from Figure 1, ref 3b. [b] Empirical differential solvent pressures from Figure 1 of this work.

Table II
Activation Volumes from DSP for RCO_3-*t*-Bu

R	Rate constant	ΔV^*_{DSP}, cc/mol[a]	ΔV^*_{ext}, cc/mol[b]	Registry no.
C_6H_5	k_o[3b]	(+12.00)	+10.4, +12.9[11]	614-45-9
C_6H_5	$k_o + k_s$[3b]	+8.0		
CH_3	$k_o + k_s$[3a]	+5.0	(+5)[1,c]	107-71-1
$CH_3OC_6H_4CH_2$	k_o[13]	+3.0	+3.1[16]	27396-21-0
$C_6H_5CH_2$	k_o[13]	−2.0	+1.7[11]	3377-89-7
$(CH_3)_2CH$	k_o[14]	−1.0	+1.6[15]	109-13-7

[a] Using the empirical differential solvent pressures derived here. [b] Using external pressure variation. [c] The value for a simple one-bond process.

expectations from the external pressure studies of Neuman.[1]

It is possible to estimate the k_s values for the perbenzoate by comparison with the corresponding hyponitrite (ref 3b, Figure 1). These values, summed with the appropriate k_o, give an activation volume of +8 cc/mol for the O–O bond homolysis of the perbenzoate. Table II contains the activation volumes for all the compounds for which we have data. The agreement with external pressure measurements is quite good if the sign inversions for the phenylacetyl[11,13] and isobutyryl[14] compounds are attributed to differential solvation. Solvation effects have similarly been invoked to explain the nonlinearity of the external pressure plots for these systems.[15]

Finally, we note that the apparent activation volume for the *tert*-butyl *p*-nitrophenylperacetate, as estimated from cohesive energy densities of the hydrocarbon solvents and the rate data of Pryor and Smith,[4a] is very large (+15 cc/mol). This reinforces their suggestion that this compound may be in part a one-bond initiator. A large value of ΔV^* is an indication of reversibility and not of intrinsic differences in transition state structures for the one-bond compared to two-bond process. The k_o/k_s method of estimating fraction return is not subject to the complications of variable k_1. Ruling out 1,3-sigmatropism,[14,16] they give the best estimate of reversibility in peroxide decomposition.

References and Notes

(1) R. C. Neuman, Jr., *Accounts Chem. Res.*, **5**, 381 (1972).
(2) P. D. Bartlett and R. R. Hiatt, *J. Amer. Chem. Soc.*, **80**, 1398 (1958).
(3) (a) T. Koenig, J. Huntington, and R. Cruthoff, *J. Amer. Chem. Soc.*, **92**, 5413 (1970); (b) T. Koenig, M. Deinzer, and J. A. Hoobler, *ibid.*, **93**, 938 (1971).
(4) (a) W. A. Pryor and K. Smith, *J. Amer. Chem. Soc.*, **92**, 5403 (1970); (b) W. A. Pryor, E. Morkved, and H. Bickley, *J. Org. Chem.*, **37**, 1999 (1972).
(5) Neuman[6] has recently criticized studies of activation volumes through internal pressure on two grounds. The first was that the experimental data were compared with cohesive energy density rather than internal pressure. He showed that these two were not always correlated. Second, he showed negative correlations of some perester rates in solvents of rather different characteristics. He failed to point out the striking agreement of the difference in activation volumes for disproportionation and combination of ethyl radicals, observed by external pressure methods,[7] with that predicted previously from cohesive energy density correlations.[8,9] He also did not point out that a differential solvation energy of only 250 cal/mol completely swamps the effect of a differential internal pressure of 1000 atm for a reaction with an activation volume of 10 cc/mol. The latter comment applies to viscosity effects as well and our solvent series was chosen to minimize the differential solvation problem. Also, Figure 1 of ref 6 shows that internal pressure and cohesive energy density are related for hydrocarbons. In the original version of this work, correlations with calculated cohesive energy density were used. These gave essentially identical activation volumes, including the 12 cc/mol for the k_o values of the perbenzoate.
(6) R. C. Neuman, Jr., *J. Org. Chem.*, **37**, 495 (1972).
(7) C. M. Backman, S. Claesson, and M. Szwarc, *Trans. Faraday Soc.*, **66**, 3061 (1970).
(8) P. S. Dixon, A. P. Stefani, and M. Szwarc, *J. Amer. Chem. Soc.*, **85**, 2551 (1963).
(9) A. P. Stefani, *J. Amer. Chem. Soc.*, **90**, 1694 (1968); *J. Phys. Chem.*, **73**, 1257 (1969).
(10) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill, New York, N. Y., 1940.
(11) R. C. Neuman, Jr., and J. V. Behar, *J. Amer. Chem. Soc.*, **91**, 6024 (1969).
(12) We assumed the value to be 12.000 cc/mol, the rounded average of the two reported values.
(13) T. Koenig and R. Wolf, *J. Amer. Chem. Soc.*, **91**, 2574 (1969).
(14) T. Koenig and J. G. Huntington, *J. Amer. Chem. Soc.*, **96**, 592 (1974).
(15) R. C. Neuman and R. P. Pankratz, *J. Amer. Chem. Soc.*, **95**, 8372 (1973).
(16) M. Goldstein and H. Judson, *J. Amer. Chem. Soc.*, **92**, 4220 (1970).
(17) R. C. Neuman, Jr., and J. V. Behar, *J. Org. Chem.*, **36**, 654 (1971).

Structural Effects on Intramolecular Carbene Reactions. Δ^3-Cyclopentenylmethylcarbene

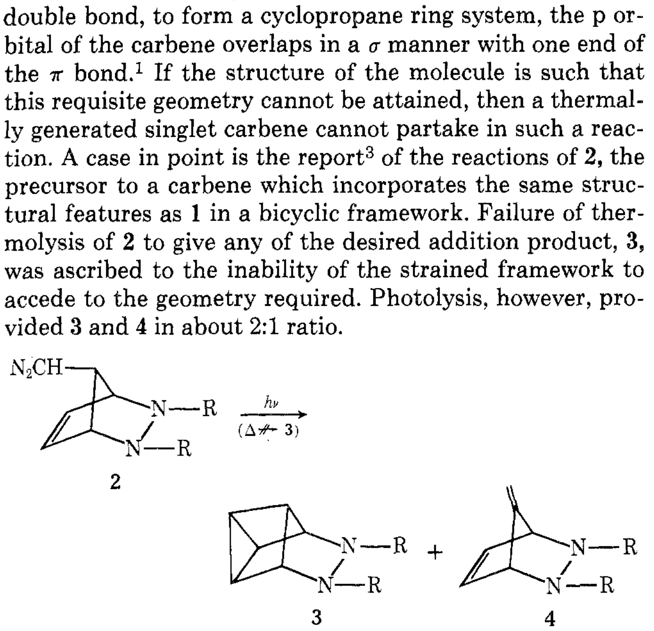
Alfred Viola,* Shyamala Madhavan, and Robert J. Proberb

Department of Chemistry, Northeastern University,
Boston, Massachusetts 02115

Received January 9, 1974

Intramolecular carbene insertions and cycloaddition reactions constitute a favorite route to small-ring polycyclic structures. Yet there is little information available from the literature concerning circumstances favorable to such approaches. This report deals with the behavior of Δ^3-cyclopentenylmethylcarbene (**1**), which bears upon this problem.

In the concerted cycloaddition of a singlet carbene to a double bond, to form a cyclopropane ring system, the p orbital of the carbene overlaps in a σ manner with one end of the π bond.[1] If the structure of the molecule is such that this requisite geometry cannot be attained, then a thermally generated singlet carbene cannot partake in such a reaction. A case in point is the report[3] of the reactions of **2**, the precursor to a carbene which incorporates the same structural features as **1** in a bicyclic framework. Failure of thermolysis of **2** to give any of the desired addition product, **3**, was ascribed to the inability of the strained framework to accede to the geometry required. Photolysis, however, provided **3** and **4** in about 2:1 ratio.



2

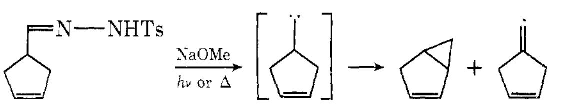
3

4

R = COOMe

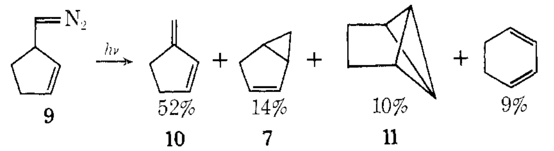
In the absence of the steric constraint inherent in the bicyclic framework of **2**, thermally generated singlet **1** might be expected to provide a route to tricyclo[2.2.0.0^{2,6}]hexane (**5**). Instead, the carbene, thermally generated from the tosylhydrazone **6**, afforded **7**[4] and **8**[5] in a 70:30 ratio, plus an unidentified, more volatile trace component.

5



6 1 7 8

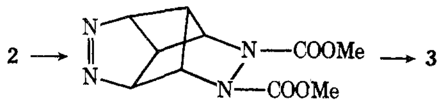
Photochemical decomposition of **6**, moreover, again afforded only **7** and **8** in a 70:30 ratio and again without any detectable amount[6] of **5**. These results differ substantially not only from those reported for **2**, but also from those reported[7] for **9**, the carbene from which is the Δ^2 analog of **1**.



9 10 7 11

We therefore conclude that neither singlet nor triplet carbene **1** can assume the requisite geometry for intramolecular cycloaddition and it follows that it is *not* the constraint inherent in the bicyclic framework which prevented thermal formation of **3** from **2**.

These results reinforce the suggestion of Trost and Cory[3] that the intermediate responsible for the formation of the cycloaddition product **3** is probably the 1,3-dipolar adduct **12** and an analogous process[8] may well account for the formation of **11**. The exaggerated puckering of the cyclopentene ring in the case of **2** places the diazo group closer to the double bond than is the case in the decomposition of **6**.



12

One further comment seems apropos. Photolysis of **9** is reported[7] to favor the formation of the 1,2-insertion product, **10**, over the 1,3-insertion product, **7**, by a factor of 4, as is normally the case. In the case of **1**, however, the preference is reversed, as **7** predominates over **8** by a 2.5:1 ratio. This difference in behavior may owe its origin to a hydrogen radical abstraction pathway for the 1,3-insertion, which in **1** leads to a stabilized allylic radical.[9] The same factor would favor the production of **10** from **9**. A similar process in **2**, leading to 1,3-insertion, is obviously ruled out by geometry of **2**.

In conclusion, preexisting strain, as in **2**, is not necessarily a deterrent to a formal intramolecular cycloaddition *via* carbenoid species and may indeed aid in achieving the requisite geometry for formation of the internal 1,3-dipolar adduct, a likely intermediate from photolytic decomposition of appropriate diazo compounds.

Experimental Section

Preparation of Δ^3-Cyclopentenecarboxaldehyde Tosylhydrazone (6). Δ^3-Cyclopentenecarboxaldehyde was prepared as previously reported[10] and was isolated and purified by preparative vapor phase chromatography (F & M Model 776 equipped with an 8 ft × 0.75 in. column packed with 20% Triton X-305 on Chromosorb P). The tosylhydrazone, **6**, was obtained quantitatively by addition of tosylhydrazine to an equimolar amount of the aldehyde dissolved in cold benzene. Addition of excess pentane precipitated the desired derivative. The tosylhydrazone proved surprisingly unstable and became tacky, with perceptible darkening, upon attempted recrystallization or drying. Consequently a freshly precipitated sample was subjected to analysis (Spang Microanalytical Laboratories, Ann Arbor, Mich.), mp 83–86°.

Anal. Calcd for $C_{13}H_{16}N_2O_2S$: C, 59.06; H, 6.10. Found: C, 58.86; H, 6.05.

Thermal and Photolytic Decomposition of Tosylhydrazone 6. Carbonium ion processes were avoided by use of "aprotic" conditions,[11] *i.e.*, freshly prepared $NaOCH_3$ and purified diglyme, and the participation of any such pathways is ruled out by the complete absence of any methoxy derivatives or any other products not ascribable to carbene insertions. A mixture of **6** with an excess of $NaOCH_3$ was heated, in diglyme, at 150–155° while the reaction vessel was vented with a stream of dry nitrogen which was then passed through a trap cooled with liquid nitrogen. The condensate consisted of methanol and a 35% yield of a 70:30 mixture (vpc, 10-ft column, 5% Apiezon on Chromosorp P) of bicyclo[3.1.0]hex-2-ene[4] (**7**), and 4-methylenecyclopentene[5] (**8**), which were identified by their characteristic nmr spectra. Photolysis was carried out on a similar mixture, with a 275-W sun lamp, while the mixture was maintained at room temperature. Prior to irradiation, the mixture was deoxygenated by sweeping it with a stream of dry nitrogen for a prolonged period. Irradiation was discontinued after evolution of nitrogen ceased and the remaining brown mixture was again flushed with nitrogen. The effluent, condensed in a trap cooled with liquid nitrogen, consisted of the same composition as that obtained from pyrolysis. That the observed reaction was indeed a photolysis, proceeding *via* the triplet carbene, is indicated by the fact that no visible reaction occurred when the deoxygenation step was omitted. The stability of products **7** and **8**, under these reaction conditions, was established by the fact that continued irradiation or heating, prior to flushing with nitrogen, failed to alter the product ratio or the amount produced.

Acknowledgment. We thank Professor J. M. Conia for the stimulating discussion which lead to this work.

Registry No.—**1**, 52123-97-4; **6**, 52123-98-5; **7**, 694-01-9; **8**, 14548-32-4; Δ^3-cyclopentenecarboxaldehyde, 20145-35-1; tosylhydrazine, 1576-35-8.

References and Notes

(1) Although this statement may be an oversimplification of the conclusions of ref 2, it reflects the commonly expressed interpretation thereof. (See, for example, ref 3.)

(2) R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968); N. Bodor, M. J. S. Dewar, and J. S. Wasson, *ibid.*, **94**, 9095 (1972).

(3) B. M. Trost and R. M. Cory, *J. Amer. Chem. Soc.*, **93**, 5572 (1971); B. M. Trost, R. M. Cory, P. H. Scudder, and H. B. Neubold, *ibid.*, **95**, 7813 (1973).

(4) P. K. Freeman, M. F. Grostic, and F. A. Raymond, *J. Org. Chem.*, **30**, 771 (1965); M. P. Schneider and R. J. Crawford, *Can. J. Chem.*, **48**, 628 (1970).

(5) W. D. Huntsman, J. A. DeBoer, and M. H. Woosley, *J. Amer. Chem. Soc.*, **88**, 5486 (1966).

(6) No vpc peaks ascribable to this compound were detectable nor were there any nmr bands in the region described for this compound. The stability of **5** under these reaction conditions seems assured by the more rigorous conditions utilized in its previously reported preparations: D. M. Lemal and K. S. Shim, *J. Amer. Chem. Soc.*, **86**, 1550 (1964); R. J. Roth and T. J. Katz, *ibid.*, **94**, 4770 (1972).

(7) D. M. Lemal and K. S. Shim, *Tetrahedron Lett.*, 3231 (1964).

(8) The pyrazoline intermediate has recently been isolated in a similar system: E. Piers, R. W. Britton, R. J. Keziere, and R. D. Smillie, *Can. J. Chem.*, **49**, 2623 (1971).

(9) It is surprising that thermally and photochemically generated carbene **1** produce identical isolatable product mixtures. However, a thermodynamic equilibration process is unlikely in the absence of Lewis acids (*e.g.*, Ag^+), as described by Roth and Katz.[6] Furthermore, more highly strained **3** survives more rigorous conditions in its preparation[3] than those described herein.

(10) A. Viola and J. H. MacMillan, *J. Amer. Chem. Soc.*, **90**, 6141 (1968).

(11) A. Nickon and N. H. Werstiuk, *J. Amer. Chem. Soc.*, **94**, 7081 (1972).

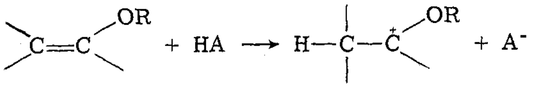
Structure and Reactivity of α,β-Unsaturated Ethers. XV.[1] The Acid-Catalyzed Hydrolysis of Alkyl Propenyl Ethers. The Relative Cis/Trans Reactivity

Tadashi Okuyama* and Takayuki Fueno

Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560, Japan

Received June 26, 1974

The acid-catalyzed hydrolysis of enol (α,β-unsaturated) ethers has widely been studied in recent years in the interest in its reaction mechanism.[2] It has been proved that the proton transfer to the unsaturated carbon is rate determining. This may be considered as a typical electrophilic addition reaction of the compounds of this class.



(1)

We already carried out kinetic studies on the hydrolysis and the cationic polymerization of a variety of α,β-unsaturated ethers from the viewpoint of the structure–reactivity relationship. It was found that the cis isomers of alkenyl alkyl ethers are generally more reactive than the corresponding trans isomers.[3-6] The greater reactivity of the former isomers was at first considered to be due to its lower stability in the ground state.[3,4] Similar discussion has been made to interpret the relative reactivity of cis and trans alkenes in terms of the strain relief on reaction.[7,8]

Later on, however, we have found that the cis isomers of β-chloro- and β-alkoxyvinyl ethers, which are more stable than the trans counterparts,[10] are also more reactive.[5,6] Explanation of these specific cases was made in terms of the polar nature of the reacting molecule; more polar cis isomers should more readily be attacked by an electrophile.[5,6] One example of this trend appearing in the earlier literature is the chlorination of a polar olefin, 1,2-dichloroethylene, in which the stable cis isomer[11] is more reactive.[12]

Nevertheless, we still feel it necessary to confirm the generality of the greater reactivity of cis olefins toward electrophiles. The most desirable for this purpose is to obtain reactivity data for a series of olefins structurally similar to each other but thermochemically different in terms of their geometrical stability. As such a class of olefins, we have chosen in the present study alkyl propenyl ethers; methyl and primary alkyl ethers are more stable in their trans form than in the cis form, while the reverse is the case for secondary and tertiary alkyl ethers.[10] The acid-catalyzed hydrolysis was studied as a typical reaction of these ethers. All the cis isomers were found to be more reactive than their trans counterparts, irrespective of the ground-state stability.

Results

The acid-catalyzed hydrolysis of unsaturated ethers was carried out in acidic 80% aqueous dioxane ([HCl] = 0.01–0.02 *M*). The reaction was followed by the gas chromatographic determination of ether concentrations.[3] Although ether was subjected to the kinetic measurements as an isomeric mixture, each geometric isomer showed excellent first-order decay separately, indicating the absence of concurrent geometrical isomerization of reactant isomers.[3] The reaction was first order in acid and an ether.

$$\text{rate} = k_2[\text{HCl}][\text{ether}] \qquad (2)$$

The rate measurements for methyl propenyl sulfide (**8**) was undertaken in the same way in 80% aqueous tetrahydrofuran. The kinetic features observed were much the same as those found for ethers.

Rate constants so obtained are summarized in Table I, together with some earlier results. The activation parameters, ΔH^* and ΔS^*, were calculated in the usual way (by plotting log k_2/T against $1/T$) and included in Table I. The final two columns of Table I give the thermodynamic data, $\Delta H°$ and $\Delta S°$, for the cis–trans isomerization equilibria.[10] Negative values of ΔH^0 indicate greater thermochemical stability of the cis isomer in the liquid phase.

The data given in Table I show that the cis isomers are more reactive than the trans isomers for all the ethers studied here. The activation enthalpies, ΔH^*, of the former isomers are smaller than those for the latter, irrespective of their $\Delta H°$ values for the isomerization equilibria.

Discussion

Substituent Effects on the Reactivity. The reactivity of alkyl propenyl ethers increases in the order $CH_3 < C_2H_5 < i\text{-}C_3H_7 < t\text{-}C_4H_9$ for both the cis and trans isomers. The same order of the reactivity regarding the α-alkoxy group was previously observed with alkyl vinyl ethers[13,14] and alkyl ethynyl ethers.[15] This reactivity order of alkyl vinyl ethers is opposite to that expected from the electron density on the β-carbon atom of the vinyl group, which is deduced from the nmr data.[16-18] Undoubtedly, the reactivity should be accounted for from the stability of the transition state. The transition state of the reaction of the present concern resembles an intermediate carbonium ion,[3] which would be stabilized by the inductive electron donation by an alkyl group.

The reactivity of methyl propenyl sulfide (**8**) is about one-thousandth that of methyl propenyl ether (**1**), though the reaction medium is somewhat different. The same order of reactivity difference between S and O analogs was