maxima (and log ϵ values) of the former occur at 233 (4.25), 280 (3.91), 315 (3.38), and 400 mμ (3.43), while for the latter cation they appear at 234 (4.30), 282 (4.74), 338 (3.54), and 426 mμ (3.25).[11,12]

Evidence therefore suggests that cation VI does possess a homoaromatic structure; however, as might be expected, the presence of the benzene ring strongly dampens the extent of the homoallylic interaction.

(11) H. H. Rennhard, E. Heilbronner, and A. Eschenmoser, *Chem. Ind.* (London), 415 (1955).

(12) The resemblance to the uv spectrum of the benzotropylium cation is closer than that which is shown by the bicyclo[5.4.1]dodecapentaenylium cation: W. Grimme, H. Hoffmann, and E. Vogel, *Angew. Chem.*, 77, 348 (1965).

(13) We thank the National Science Foundation, the U. S. Army Research Office (Durham), and the Robert A. Welch Foundation for financial support. We also thank Badische Anilin und Soda Fabrik and General Aniline and Film Corporation for generous gifts of cyclooctatetraene and iron carbonyl, respectively.

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Concerning the Structure of "Isomeric" Molecular Ions of Unsaturated Hydrocarbons

Sir:

One of the more intriguing problems connected with electron-impact fragmentation mechanisms is concerned with the nature of "isomeric" molecular ions. *cis-trans* isomeric olefins often give essentially identical mass spectra, and the view has been expressed that the isomerism is eliminated in the ionized molecules due to rotation about the electron-deficient π bond.[1] In addition it has been observed that the relative abundances of the molecular ions of *cis* olefins are smaller than those of the corresponding *trans* isomers when the latter are more stable by at least 2–3 kcal/mole.[1c] This was explained on the basis of the disappearance of the isomerism in the molecular ion; the energy resulting from steric hindrance in the *cis* isomer would thereby be released and used in the decomposition processes.[1c] However, these data are not incompatible with the decomposition of molecular ions which maintain the geometric integrity of the un-ionized molecules. More recently Smith and Thornton have studied the retro-Diels–Alder (RDA) reaction of 4-vinylcyclohexene; the possibility of isomeric activated complexes (*e.g.*, *s-cis* and *s-trans*) was considered.[2] We wish to present evidence that the conformation of an olefinic side chain can markedly influence the course of the RDA fragmentation of cyclohexene derivatives.

The compounds chosen for study were *trans-* and *cis*-1-propenylcyclohexenes (**1** and **2**, respectively).[3] Dreiding models clearly indicate that large nonbonded repulsions exist in conformations of **2** in which the double bonds are coplanar. Strong evidence for a more twisted *s-trans* conformation in the *cis* isomer than in the *trans* isomer is provided by the ultraviolet spectra; **1** has

(1) (a) K. Biemann, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 151; (b) J. Momigny, *Nature*, 191, 1089 (1961); (c) P. Natalis in "Mass Spectrometry," R. I. Reed, Ed., Academic Press Inc., New York, N. Y., 1965, p 379, and references cited therein.

(2) E. P. Smith and E. R. Thornton, *J. Am. Chem. Soc.*, 89, 5079 (1967).

(3) All new compounds have been fully characterized; syntheses will be published at a later time.
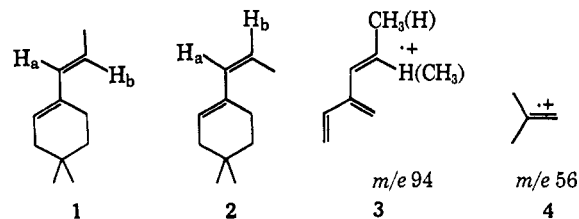
λ_{max} 232.5 mμ (ϵ 19,200), whereas **2** has λ_{max} 224.5 mμ (ϵ 13,700) (both in hexane).[4] In addition, the nmr doublet for H_a, located at τ 3.88 and 4.15 for **1** ($J_{ab} = 16.0$ Hz), is shifted upfield to τ 4.21 and 4.40 for **2** ($J_{ab} = 11.5$ Hz); the two nmr spectra are virtually identical in all other respects. This shift is interpreted as resulting from H_a in the *cis* isomer being affected less by the anisotropy of the endocyclic π bond due to the fact that it is twisted farther out of the nodal plane of the bond.[5] The infrared spectra provide further evidence for these relative conformations; the *trans* isomer shows a sharp unsymmetrical doublet at 1650 and 1625 cm^{-1} due to vibrational coupling of the double bonds[6] while the *cis* isomer shows only a single broadened peak at 1638 cm^{-1}, the coupling having been largely eliminated by the twisting.

Another manifestation of the twisted equilibrium conformation of **2** is the free energy of isomerization of 3.0 $\pm$ 0.25 kcal/mole at 25.0° for the conversion **1** → **2**. This was determined by equilibrium studies (starting from each side of the equilibrium mixture) in solutions of 0.5 N potassium *t*-butoxide in hexamethylphosphoramide.[7] This result constitutes further evidence for a significant π delocalization energy in dienes[8] since the nonbonded repulsions can be greatly reduced by twisting the propenyl group, but only at the expense of decreased π overlap.

The greater stability of the *trans* isomer is, as expected, reflected in the greater relative abundance ($\% \Sigma_{27}$) of its molecular ion (8.20) relative to that of the *cis* isomer (6.72).[9] In addition, these dienes display the expected odd-electron fragments at m/e 94 (the base peak) and 56 which result from the RDA reaction.[10]

Since Hückel molecular orbital calculations indicate that the π-electron energy of ion **3** decreases to a greater extent with twisting of the propenyl group than does that of the corresponding neutral fragment,[11] the degree of departure from coplanarity of the propenyl group in the activated complexes for the respective RDA reac-

(4) A λ_{max} of 232 mμ is predicted for these dienes using empirical rules: R. B. Woodward, *J. Am. Chem. Soc.*, 64, 72 (1942). For a closely related pair of isomers see E. N. Marvell and J. Tashiro, *J. Org. Chem.*, 30, 3991 (1965).

(5) J. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Inc., New York, N. Y., 1959, p 129.

(6) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1964, p 40.

(7) S. Bank, A. Schriesheim, and C. A. Rowe, Jr., *J. Am. Chem. Soc.*, 87, 3244 (1965).

(8) (a) S. W. Staley, *ibid.*, 89, 1532 (1967); (b) P. S. Carleton, Ph.D. Thesis, Yale University, 1966. The study by Carleton (and W. von E. Doering) involved sterically hindered styryl derivatives.

(9) These values (corrected for isotopes) were obtained at 70 eV using an LKB 9000 mass spectrometer. A Varian M-66 instrument (utilizing a different geometry) gave very similar results.

(10) (a) H. Budzikiewicz, J. I. Brauman, and C. Djerassi, *Tetrahedron*, 21, 1855 (1959); (b) T. J. Kinstle and R. E. Stark, *J. Org. Chem.*, 32, 1318 (1967).

(11) The π-electron energies of the ions were calculated using the ω technique (A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p 115) and utilizing a computer program written by J. P. Erdman of this laboratory.

tions will be reflected in the ratios of m/e 94:56 (3:4). This ratio is 30.3 for the *cis* isomer and 49.2 for the *trans* isomer, in accord with the postulation of a more twisted *cis* activated complex. Such an analysis is tenuous, however, because it fails to take into account further decomposition pathways. Alternatively an analysis may be made using the kinetic approach of Bursey and McLafferty.[12] Thus the effect of the local molecular environment on the absolute rate of a decomposition reaction can be compared for two similar reactions using the ratio of the abundance of a common product ion to that of its precursor ion if the product ion is formed with the same energy distribution from each molecular ion. The ratio of m/e 56:150 is 0.024 for the *trans* isomer and 0.039 or 1.62 times as great for the *cis* isomer;[13] thus the conformation of the propenyl group in the un-ionized molecule is reflected in the relative energies of the activated complexes for the RDA reaction. Since the rate of decomposition of the molecular ion of the *cis* isomer is only 1.24 times as great as that of the *trans* isomer we feel that these data suggest (but do not demand) that the greater rate of formation of m/e 56 in the *cis* isomer is due (at least in part) to the maintenance of the stereochemical integrity of the exocyclic double bond upon ionization. It should be noted, however, that the π bond order will be greater in the conjugated dienes studied by us than in simple olefins, thus restricting isomerization to a greater extent.[14]

(12) M. M. Bursey and F. W. McLafferty, *J. Am. Chem. Soc.*, **88**, 529 (1966).

(13) The assumption that the m/e 56 ions are formed with equal energy distribution from each molecular ion actually sets a lower limit on the higher ratio value for the *cis* isomer since this isomer is the one which is more likely to possess excess energy and thus to have product ions which undergo further decomposition.

(14) Excess vibrational energy would aid in overcoming the barrier to internal rotation about the essential single bond of the diene moiety and may thereby reduce the *cis–trans* difference.[12]

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## A New General Synthesis of Macrocyclic Compounds

Sir:

We wish to report the discovery of a general method for the synthesis of macrocyclic compounds from inexpensive and readily available starting materials. The procedure is extremely simple, involving only photolysis or thermolysis of an appropriate ketone peroxide. The desired macrocyclic compound is generated directly in good yield. In this communication we report the synthesis of carbocyclic hydrocarbons and macrocyclic lactones. We shall report subsequently on extension of the method to substituted carbocycles and heterocycles. The reactions of cyclohexanone diperoxide (1)[1] serve to illustrate.

Photolysis of **1** (12 g) in methanol (4.5 l.) or in benzene using a standard quartz Hanovia apparatus with a 450-w lamp for 3 hr followed by solvent removal with a rotary evaporator yields cyclodecane (2; 14%), 11-undecanolactone (3;[2] 10%), and cyclohexanone ($\sim$20%).[3]

Thermolysis of **1** gave the same products but in appreciably higher yield. Heating solid peroxide **1** in an evacuated and sealed ampoule for 30 min at 150° yields as the major product cyclodecane (2; 44%) along with the lactone (3; 23%) and cyclohexanone (21%).[4] Provided the necessary peroxide is available (usually the peroxide is quickly and easily prepared from the appropriate ketone with hydrogen peroxide), the procedure becomes almost trivial, particularly since we have also found that thermolysis of most peroxides can be carried out using a gas-chromatograph injection inlet and/or column heated to about 180°. Pyrolysis occurs instantaneously, and excellent separation of the products is obtained. A variety of chromatographic columns may be used.
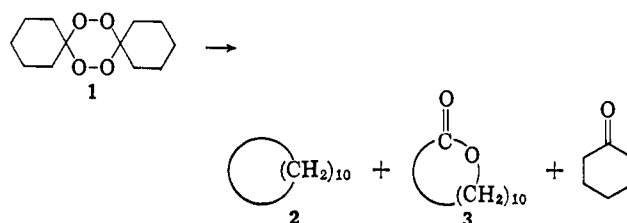
Trimeric cyclohexanone peroxide (4)[5] reacts in similar fashion to yield cyclopentadecane (5), 16-hexadecanolactone (dihydroambrettolide; 6),[2,6] and cyclohexanone.
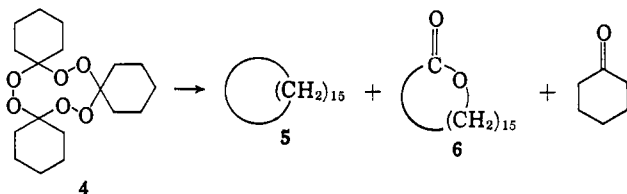
The reaction is not limited to six-membered ring ketones. The dimeric peroxide of cycloheptanone,[7] for example, on thermolysis gives cyclododecane in 22% yield. Using appropriately substituted cyclic ketones it appears likely that almost any macrocyclic compound can be synthesized, provided the necessary peroxide percursor can be obtained. The generality and utility of the reactions are illustrated by the data in the tables. We have not yet attempted to maximize the yields; a study of reaction variables is under way.

The thermal or photochemical decomposition of ketone peroxides is most reasonably interpreted as proceeding through homolysis of an oxygen–oxygen bond as indicated here for cyclohexanone diperoxide (1). The cleavage should be analogous to that of alkyl

(1) R. Criegee and G. Lohaus, *Ann.*, **583**, 6 (1953); M. S. Kharasch and G. Sosnovsky, *J. Org. Chem.*, **23**, 1322 (1958).

(2) L. Ruzicka and M. Stoll, *Helv. Chim. Acta*, **11**, 1159 (1928); M. Stoll and W. Scherrer, *ibid.*, **13**, 142 (1930).

(3) Products were identified by infrared, nmr, and mass spectral analyses.

(4) Caution! Some peroxides will occasionally explode with considerable violence. Generally if a small amount of solvent such as methanol or benzene is left in the solid, explosions can be avoided.

(5) R. Criegee, W. Schnorrenberg, and J. Becke, *Ann.*, **565**, 7 (1949).

(6) S. D. Sabnis, H. H. Mathur, and S. C. Bhattacharyya, *J. Chem. Soc.*, 4580 (1965).

(7) T. Ledaal, *Acta Chem. Scand.*, **21**, 1656 (1967).