

cloalkanes. The cyclic diphosphines were readily oxidized by warming with an excess of hydrogen peroxide in water-acetone at 60° for 3 hr. In each case, removal of the solvent at reduced pressure afforded a white solid which was found to be completely isomerically pure from tlc and had a R_f value similar to that of the isomeric cyclic bis(phosphine oxide) from which the diphosphine was obtained. The solid, when dried at 120° under low pressure (0.1 mm) for 12 hr, gave a melting point close to that of the original isomeric cyclic bis(phosphine oxide).

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Notes

Indications of Stereospecific Loss of Water from Bicyclic Ketones during Chemical Ionization Mass Spectrometry

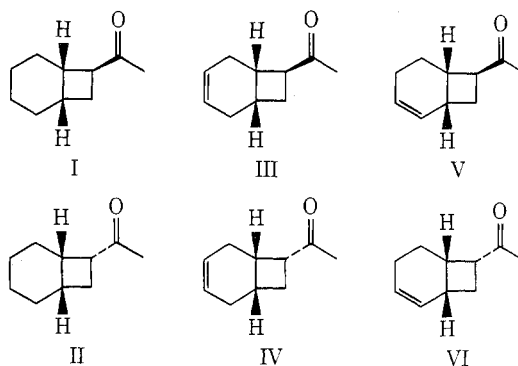
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The application of mass spectrometry to studies of the stereochemistry of cyclic and acyclic molecules is of continuing interest.¹ In a recent example, the stereochemistry of two deuterated bicyclo[3.3.1]nonanols was unequivocally determined by electron ionization (EI) mass spectrometry.² The application of chemical ionization (CI) mass spectrometry to stereochemical problems has been studied only to a limited extent, but promising initial results have been obtained.³ The loss of H₂O from ketones⁴ and aldehydes⁵ has been examined by both methods of ionization. For ketones, a ten-member transition state was proposed. Aldehydes were reported to lose H₂O *via* a five-membered transition state under both EI^{5a,e} and CI^{5e} conditions. One EI study suggested the presence of six-membered or even eight-membered transition states.^{5b} In a CI study of labeled heptanals, scrambling of deuterium was noted.^{5d} Migration of allylic hydrogens to carbonyl groups in the EI spectra of polycyclic cyclohexenediones has been related to the distance between the hydrogens and the carbonyl oxygens.⁶

During a mass spectrometric examination of six bicyclic ketones of established⁷ structure I-VI we observed marked differences between the isobutane CI spectra of isomers. Salient portions of the EI and CI spectra obtained are given in Tables I and II.⁸ These show the relative intensities (as fractions of the total sample ionization⁹) of the



peaks at $(M + 1)^+$, M^+ , $(M - 1)^+$, $(M + 1 - 18)^+$, and $(M - 18)^+$ in the EI and CI spectra.

The EI spectra show very weak $(M - 18)^+$ peaks, all of similar intensity. While there are intensity differences in the M^+ ions of the EI spectra, these differences are small and involve peaks of low intensity.

The CI spectra of the isomeric saturated ketones I and II are very similar. We have no explanation for the difference between the $(M - 1)^+$ intensities in these isomers. The CI spectra of the exo isomers of the unsaturated ketones, compounds III and V, are similar to the CI spectrum of the exo isomer I. We infer that the similar intensities of $(M + 1)^+$ and $(M + 1 - 18)^+$ in these three compounds arise from similar mechanisms for loss of H₂O. We have examined Dreiding models of these compounds, and find that in all three exo isomers the carbonyl group is isolated from hydrogens on the bicyclic system.

The two endo unsaturated ketones IV and VI have strong $(M + 1 - 18)^+$ ions [respectively 9 and 12 times stronger than $(M + 1 - 18)^+$ of their exo isomers III and V]. The models show that in all three endo isomers the carbonyl oxygen can closely approach hydrogens of the six-membered ring. In the endo isomer II transfer of aliphatic hydrogen to the carbonyl oxygen could occur *via* a

Table I
Relative Intensities of Selected Ions in the EI Spectra

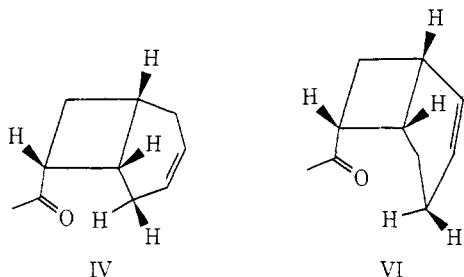
Compd	I	II	III	IV	V	VI
Stereochemistry	Exo	Endo	Exo	Endo	Exo	Endo
M ⁺	0.039	0.008	0.032	0.002	0.042	0.012
(M - 18) ⁺	0.001	0.004	0.010	0.002	0.009	0.005

Table II
Relative Intensities of Selected Ions in the Isobutane CI Spectra

Compd	I	II	III	IV	V	VI
Stereochemistry	Exo	Endo	Exo	Endo	Exo	Endo
(M + 1) ⁺	0.540	0.402	0.633	0.575	0.724	0.562
M ⁻	0.021	0.019	0.016	0.002	0.016	0.006
(M - 1) ⁺	0.051	0.145	0.005	0.011	0.007	0.016
(M + 1 - 18) ⁺	0.026	0.032	0.015	0.131	0.012	0.144
(M - 18) ⁺	0.002	0.002	0.004	0.001	0.003	0.002
(M - 1 - 18) ⁺	0.008	0.001				

six-membered transition state. Hydrogen transfer to the carbonyl group of the unsaturated endo isomers IV and VI could involve the allylic hydrogens of the cyclohexene ring. This suggests that the ready loss of water in the CI spectra of IV and VI reflects the weakness of the allylic C-H bond. The greater aliphatic C-H bond strength results in the weak (M + 1 - 18)⁺ ion of compound II.

It is usually assumed in CI experiments that protonation of aldehydes or ketones occurs on the carbonyl oxygen.^{5e} The evidence presented above indicates that the second proton of the departing H₂O molecule comes from the allylic hydrogens in IV and VI. This means that the loss of water in IV must involve a six-membered transition state, while in VI a seven-membered transition state is required, as shown below. Labeling studies will be necessary to establish these conclusions concerning mechanism with rigor. However, our experimental observations already provide further evidence that CI mass spectrometry can reflect stereochemical differences.¹⁰



Experimental Section

Ketones I-VI were prepared as previously described⁷ and purified by preparative vapor phase chromatography before use.

Mass spectra were obtained with a Du Pont 21-492 mass spectrometer at resolution 2000 or 10,000, source temperature 200°, and at 100 eV ionizing potential for electron ionization and 220 eV for chemical ionization. Samples were introduced via a glass batch inlet system at 200°. Isobutane reactant was Matheson Instrument Grade gas. The repellers were used to optimize the ion current, and were typically zero voltage for CI spectra. The pressure of the source could not be measured, but was about 0.5-1.0 Torr for CI spectra, based on prior experience.

The combined CI-EI source was designed and built in our laboratory under license from Scientific Research Instruments Corp., Baltimore, Md.

The intensities reported have not been corrected for ¹³C isotope contributions. The CI spectra have been corrected for contributions from the reactant gas. Data were obtained with an AEI DS-30 data system to which our own CI programs have been added. A peak with relative intensity 0.001 would typically be three times stronger than the computer threshold level.

Registry No.—I, 24112-75-2; II, 34969-29-4; III, 51222-29-8; IV, 51222-30-1; V, 51222-31-2; VI, 51222-32-3.

Supplementary Material Available. Tabulation of these spectra and high-resolution results will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JOC-74-1752.

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- This fraction is calculated by dividing the intensities of the peak by the total intensity of all sample peaks above *m/e* 40 for EI and above *m/e* 60 for CI spectra. The intensities of peaks of the CI reactant gas are not included. The intensities reported are averages of duplicate spectra.
- W. C. A. and R. A. C. acknowledge the partial support of this research by the donors of the Petroleum Research Fund, administered by the American Chemical Society; F. H. F. and D. V. B. thank the Rockefeller Foundation for purchase of the mass spectrometer through a grant to research in reproductive biology.

Synthetic Organic Photochemistry. VI. The Photochemical Ring Expansion of an α-Hydroxy-β,γ-Unsaturated Ketone

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We have recently provided examples of two-carbon photochemical ring expansions of 2-alkenyl- and 2-alkynylcycloalkanes^{2,3} and three-atom photochemical ring expansions of 2-cyclopropyl- and 2-(2-oxiranyl)cycloalkanes.^{4,5} Of these unique methods for ring-size modification, the photochemical ring expansions of 2-alkenylcyclo-