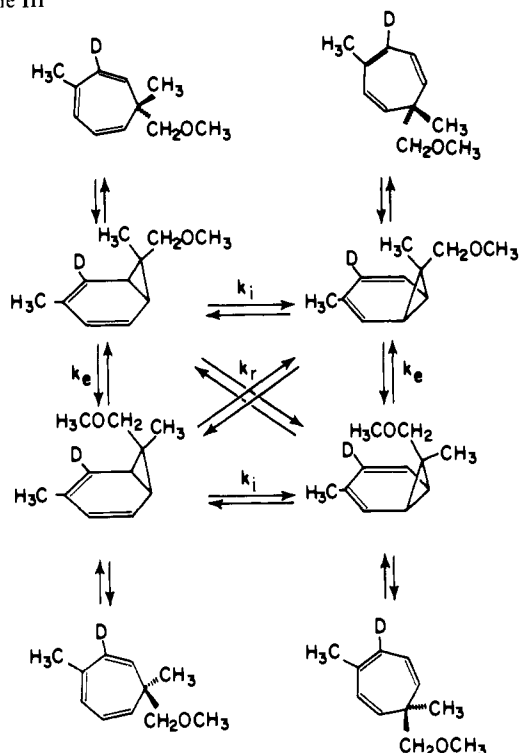


Scheme III



The kinetic work was done at 223.4 °C using degassed solutions of substrate in toluene; after thermolysis starting material and its degenerate isomers were reisolated by preparative GLC and analyzed by polarimetry and by NMR using the optically active shift reagent tris[3-(heptafluoropropylhydroxymethylene)-*d*-camphorato]europium(III)⁸ in C₆D₆, which shifted apart H-C(4) doublets in the (+) and (-) isomers. The extent of deuterium scrambling was determined by converting the trienes to TCNE adducts followed by NMR comparisons of the relative intensities of vinyl to adjacent bridgehead protons.

The experimental results made possible definition of the time dependence of all four isomers of Scheme III and derivation of the rate constants k_e , k_i , and k_r using exact solutions to the required kinetic expressions. An 11-point linear plot of \ln (optical purity) vs. time gave $2(k_e + k_i) = (1.00 \pm 0.04) \times 10^{-5} \text{ s}^{-1}$. An 8-point linear plot of $\ln \{[(2-d) - (4-d)] / [(2-d) + (4-d)]\}$ against time revealed that $2(k_i + k_r) = (0.68 \pm 0.04) \times 10^{-5} \text{ s}^{-1}$. Finally, experimental values of $[(+)-2-d + (+)-d_0] / [(-)-2-d + (-)-d_0]$ allowed calculation of all concentrations and $2(k_e + k_r) = (1.48 \pm 0.15) \times 10^{-5} \text{ s}^{-1}$. A comparison of calculated and observed mol percent concentrations is provided in Table I.

The racemization is dominated by a direct isomerization of one antipode to the other without a concomitant [1,5] carbon shift, and the [1,5] shift occurs predominantly with retention of stereochemistry at the migrating carbon.

These results demonstrate a sigmatropic [1,5] carbon shift with allowed stereochemistry in a type of molecule previously thought to isomerize according to a "forbidden" least-motion stereochemical route, and they provide an instance in which one-centered epimerization in a cyclopropane does not involve a simple diradical intermediate, for $k_e \neq k_i$.

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References and Notes

- (1) J. A. Berson and M. R. Willcott, III, *J. Am. Chem. Soc.*, **87**, 2751, 2752 (1965); **88**, 2494 (1966). J. A. Berson, *Acc. Chem. Res.*, **1**, 152 (1968).
- (2) F.-G. Klärner, *Angew. Chem., Int. Ed. Engl.*, **13**, 268 (1974).

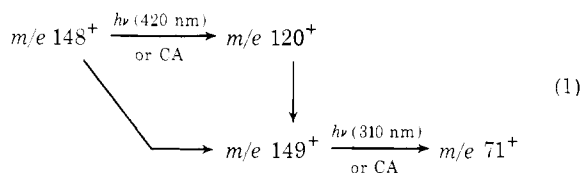
- (3) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 2511 (1965); "The Conservation of Orbital Symmetry", Verlag Chemie/Academic Press, New York, N.Y., 1970.
- (4) W. W. Schoeller, *J. Am. Chem. Soc.*, **97**, 1978 (1975).
- (5) R. T. Hansen, Ph.D. Thesis, Yale University, Dec 1976; *Chem. Abstr.*, **87**, 101708p (1977); *Diss. Abstr. Int. B*, **37**, 6130 (1977).
- (6) Inter alia, J. E. Baldwin and K. E. Gilbert, *J. Am. Chem. Soc.*, **98**, 8283 (1976); J. E. Baldwin and C. Carter, *ibid.*, **100**, 3942 (1978).
- (7) R. Howe, F. J. McQuillin, and R. W. Temple, *J. Chem. Soc.*, 363 (1959).
- (8) H. L. Goering, J. N. Eikenberry, and G. S. Koerner, *J. Am. Chem. Soc.*, **93**, 5913 (1971); H. L. Goering, J. N. Eikenberry, G. S. Koerner, and C. J. Latimer, *ibid.*, **96**, 1493 (1974).

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Fragmentation of Butyrophenone Ions

Sir:

We have investigated the unimolecular dissociation of butyrophenone molecular ion and protonated molecular ion, using the complementary techniques of ion photodissociation in the ICR spectrometer¹ and collisional activation (CA) in the double focussing mass spectrometer.² Photodissociation and CA dissociation of both species were observed, and the unimolecular and ion-molecule chemistry in this system was elucidated as summarized in eq 1. This fuller understanding

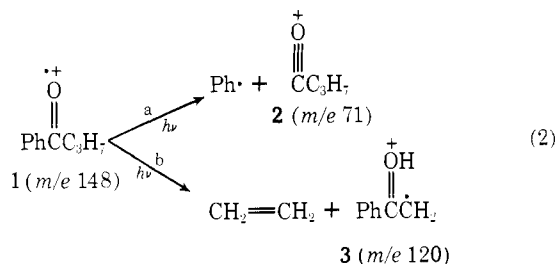


of the chemistry provides a satisfactory alternative explanation for the observations which led Gooden and Brauman³ to propose state-specific, noncompetitive photodissociation of butyrophenone molecular ion.

The fragmentation of polyatomic molecular ions in mass spectrometry has been a subject of theoretical and experimental investigation for a long time. In most cases, quasi-equilibrium theory⁴ (QET) has been successfully used to explain the internal energy dependence of the relative abundances of various fragment ions formed from competing processes. It is usually assumed in application of the theory that the ions produced in excited electronic states undergo fast radiationless transition to a common electronic state, presumably the ground state, prior to decomposition. Decompositions from excited states, so-called state-specific reactions, have been observed in very few cases⁵ in violation of this assumption.

Accordingly, instances of demonstrable noncompetitive fragmentation in ions are of some interest, and the recent report by Gooden and Brauman³ of possible highly state-specific reactions in the photodissociation of butyrophenone molecular ion has received substantial attention. The chemistry shown in eq 2 was reported.

A sharp transition from dissociation path b to path a was reported to occur at a photon energy near 3.3 eV, indicating state-specific reactions. However, the failure of Kim and



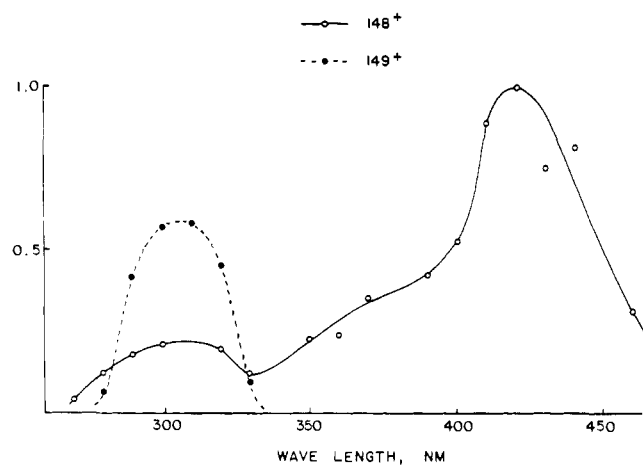


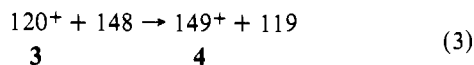
Figure 1. Photodissociation spectra of butyrophenone molecular ion (148^+) and protonated ion (149^+). The y axis is the relative cross section for the photodissociation. A cross section of 1.0 on this scale corresponds to an absolute cross section of $\sim 4 \times 10^{-18} \text{ cm}^2$.

Table I. CA Mass Spectra of Butyrophenone Parent and Protonated Parent Ions

m/e	Precursor ions	
	148	149 ^a
71	<0.05	23
77	12	14
91	24	18
105	47	34
120	100	<i>b</i>
121	<i>b</i>	100
130	15	<i>b</i>
131	<i>b</i>	45

^a Produced under CI conditions. Approximately 20% is the isotopic contribution of the molecular ion. ^b Unresolved.

McLafferty⁶ to observe **2** ion using the CA technique, which is known to deposit a rather broad range of excitation energies in the dissociating ions,⁷ was unexpected and difficult to reconcile. We decided to re-examine the photochemistry of this ion using our pulsed ICR system:⁸ our unsatisfactory experience using steady-state photodissociation techniques similar to those of ref 3 has led us increasingly to turn to the pulsed-ICR technique in systems of complex photochemistry. In fact we found this system to be rather rich in chemistry: specifically the production of protonated parent ion by ion-molecule chemistry, and its photodissociation, are important features of this system's photochemistry. Even at low pressure ($\sim 2 \times 10^{-8}$ Torr), low electron energy (11–15 eV), and residence times of a few seconds, protonated parent butyrophenone ion (**4**) was abundant.⁹ Double resonance ejection¹⁰ of m/e 120 (eq 3) shows that the process



accounts for much of the **4** ions formed, and the rate constant of this protonation reaction, measured at several pressures, was estimated to be $2.5 \times 10^{-9} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

Photodissociation (disappearance) spectra of ions **1** and **4** are shown in Figure 1: it is evident that the photodissociation of **1** at 310 nm is much weaker than at visible wavelengths, but that **4** is strongly dissociated at 310 nm. **2** ion was formed at 310 nm as previously reported.³ Using double resonance, protonated **4** ion was found to be the precursor of **2**, as shown in Figure 2: photoformation of **2** at 310 nm decreased substantially upon double resonance ejection of **4**, while ejection of **1** had no effect.

As a further check on the indication that **2** is a product of

PHOTOFORMATION OF 71^+ AT 310 NM

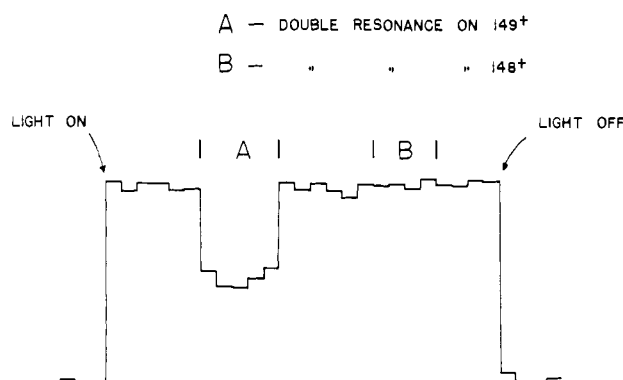


Figure 2. Double resonance spectrum of **2** ion (71^+). **2** ion was photoformed at 310 nm. In A, **4** ion (149^+) was removed from the cell by double resonance. In B, **1** (148^+) was removed.

protonated parent ion dissociation, the CA spectrum of **4** was recorded,¹¹ as shown in Table I. While the CA spectrum of butyrophenone parent ion showed no formation of **2**, this ion (**2**) was a major CA product of protonated parent.

We also studied the photoformation (or nonphotoformation) of **3** ion at 310 nm, since the previous observation that **3** was not formed with this photon energy was one of the bases of the argument for state-specific reaction. Unfortunately, we found that **3** ion also dissociates at 310 nm, and it could not be decided whether this ion was photoformed from **1** ion or not at this wavelength.

The present results give a consistent and reasonable picture of butyrophenone ion photochemistry, and an assumption of state-specific reactions does not seem necessary.

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References and Notes

- (1) (a) F. W. McLafferty, "Chemical Applications of High Performance Mass Spectrometry," M. L. Gross, Ed., American Chemical Society, Washington, D.C., 1978; (b) Karsten Levsen and Helmut Schwarz, *Angew. Chem.*, **15**, 509 (1976).
- (2) R. C. Dunbar in "Interactions Between Ions and Molecules", P. Ausloos, Ed., Plenum Press, New York, N.Y., 1975.
- (3) Robert Gooden and John I. Brauman, *J. Am. Chem. Soc.*, **99**, 1977 (1977).
- (4) (a) H. M. Rosenstock, M. B. Wallenstein, A. L. Wahrhaftig, and H. Eyring, *Proc. Natl. Acad. Sci. U.S.A.*, **38**, 667 (1952); (b) P. J. Robinson and K. A. Holbrook, "Unimolecular Reactions", Wiley, New York, N.Y., 1972.
- (5) See for example, for benzene ions, (a) B. Andlauer and Ch. Ottinger, *J. Chem. Phys.*, **55**, 1471 (1971); (b) R. D. Smith and J. H. Futrell, *Org. Mass. Spectrom.*, **11**, 445 (1976); (c) J. H. D. Eland, R. Frey, H. Schulte, and B. Brehm, *Int. J. Mass. Spectrom. Ion Phys.*, **21**, 209 (1976); (d) M. L. Gross, D. H. Russell, R. J. Aernl, and S. A. Bronczyk, *J. Am. Chem. Soc.*, **99**, 3603 (1977).
- (6) Myung S. Kim and F. W. McLafferty, *J. Phys. Chem.*, **82**, 501 (1978).
- (7) Myung S. Kim and F. W. McLafferty, *J. Am. Chem. Soc.*, in press.
- (8) R. C. Dunbar, E. W. Fu, and G. A. Olah, *J. Am. Chem. Soc.*, **99**, 7502 (1977).
- (9) The intensity of protonated ion was about twice that of molecular ion.
- (10) L. R. Anders, J. L. Beauchamp, R. C. Dunbar, and J. D. Baldeschwieler, *J. Chem. Phys.*, **45**, 1062 (1966).
- (11) In order to obtain a sufficient abundance of protonated ion, the mass spectrometer source was operated under chemical ionization conditions, with a source pressure of 10^{-3} Torr.

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