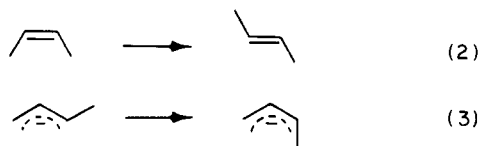


Decomposition of eq 1 into its component processes (eq 2 and 3) reveals that it is the difference in free energies of the neutral 2-butenes which provides the driving force. ($\Delta G^\circ = -0.7$ kcal/mol⁶ for eq 2 and $\Delta G^\circ = +0.2$ kcal/mol for eq 3)



In fact, it appears that *in the gas phase, the cis isomer of the 1-methylallyl anion is less stable than the trans*,¹⁵ although the free energy preference here is not as great as that for the neutral alkenes. It might be argued that, in comparison to the corresponding neutral olefins, the cis form of the 1-methylallyl anion is stabilized relative to the trans. Whether this small difference is simply a consequence of the reduction of vicinal H-H repulsions in *cis*-2-butene as a result of removal of a proton or of stabilization inherent to the anion in its *cis* geometry¹⁷ remains a matter for discussion.

The above caveats notwithstanding, what our experiments indicate, however, is that the preference for *cis* skeletal arrangements in the case of 1-methylallyl organometallics is not to be ascribed to the free anions. Rather it appears to arise because of differences in interaction energies among the allylic skeleton, the metal, and the solvent. Our data also suggest that the relative (*cis* vs. *trans*) stabilities of the organometallic compounds involving the most electropositive metals (e.g., potassium and cesium) do not mirror those of the free anions more closely than those of compounds involving the less electropositive metals (e.g., lithium and sodium).

References and Notes

- (a) H. Kloosterziel and J. A. A. van Drunen, *Recl. Trav. Chim. Pays-Bas*, **87**, 1025 (1968); (b) W. J. Glaze, J. E. Hanicak, J. Chaudhuri, M. L. Moore, and D. P. Duncan, *J. Organomet. Chem.*, **51**, 13 (1973), and earlier papers in this series; (c) D. A. Hutchinson, K. R. Beck, R. A. Benkeser, and J. B. Grutzner, *J. Am. Chem. Soc.*, **95**, 7075 (1973); (d) J. P. C. M. van Dongen and H. W. D. van Drunen, *Recl. Trav. Chim. Pays-Bas*, **93**, 29 (1974); (e) M. Schlosser, J. Hartmann, and V. David, *Helv. Chim. Acta*, **57**, 1567 (1974); (f) R. B. Bates and W. A. Beavers, *J. Am. Chem. Soc.*, **96**, 5001 (1974); (g) W. H. Glaze and D. P. Duncan, *J. Organomet. Chem.*, **99**, 11 (1975); (h) D. H. O'Brien, C. R. Russell, and A. J. Hart, *Tetrahedron Lett.*, 37 (1976); (i) M. Schlosser and J. Hartmann, *J. Am. Chem. Soc.*, **98**, 4674 (1976).
- Reviews: (a) H. F. Ebel, *Fortschr. Chem. Fortsch.*, **12**, 387 (1969); (b) L. A. Fedorov, *Russ. Chem. Rev.*, **39**, 655 (1970); (c) K. Vriese in "Dynamic Nuclear Magnetic Resonance Spectroscopy", L. M. Jackman and F. A. Cotton, Ed., Academic Press, New York, N.Y., 1975, Chapter 11; (d) M. Schlosser, "Polare Organometalle", Springer-Verlag, Berlin, 1973.
- Kinetic preferences for formation of *cis* alkyl allyl anions had been noted earlier: (a) W. O. Hoag and H. Pines, *J. Am. Chem. Soc.*, **82**, 387 (1960); (b) T. J. Prosser, *ibid.*, **83**, 1701 (1961); (c) C. C. Price and W. H. Snyder, *ibid.*, **83**, 1773 (1961); (d) A. Schriesheim, J. E. Hofmann, and C. A. Rowe, Jr., *ibid.*, **83**, 3731 (1961); (e) C. C. Price and W. H. Snyder, *Tetrahedron Lett.*, 69 (1962); (f) M. D. Carr, J. R. P. Clarke and M. F. Whiting, *Proc. Chem. Soc., London*, 333 (1963); (g) S. Bank, A. Schriesheim, and C. A. Rowe, Jr., *J. Am. Chem. Soc.*, **87**, 3244 (1965).
- Cis* skeletal preferences have also been noted for pentadienyl^{5a-c} and heptatrienyl^{5d} organometallics.
- (a) Z. G. J. Heiszwolf, J. A. A. van Drunen, and H. Kloosterziel, *Recl. Trav. Chim. Pays-Bas*, **88**, 1377 (1969); (b) W. T. Ford and M. Newcomb, *J. Am. Chem. Soc.*, **96**, 309 (1974); (c) H. Kloosterziel and J. A. A. van Drunen, *Recl. Trav. Chim. Pays-Bas*, **89**, 270 (1970); (d) H. Kloosterziel and J. A. A. van Drunen, *ibid.*, **88**, 1471 (1969).
- B. J. Zwolinski et al., "Selected Values of Thermodynamic Properties of Hydrocarbons and Related Compounds", American Petroleum Institute Research Project 44, Thermodynamics Research Center, Texas A&M University, College Station, Texas, 1975, section A.
- Trapped cell ion cyclotron resonance spectroscopy. Method: (a) R. T. McIver, Jr., *Rev. Sci. Instrum.*, **41**, 555 (1970); (b) J. D. Baldeschwieler and S. W. Woodgate, *Acc. Chem. Res.*, **4**, 114 (1971); (c) R. T. McIver, Jr., and R. C. Dunbar, *Int. J. Mass Spectrom. Ion Phys.*, **7**, 471 (1971). Representative applications to the studies of anions in the gas phase: (d) R. T. McIver, Jr., and J. R. Eyler, *J. Am. Chem. Soc.*, **93**, 6334 (1971); (e) R. T. McIver, Jr., and J. H. Silvers, *ibid.*, **95**, 8462 (1973); (f) R. T. McIver, Jr., and J. S. Miller, *ibid.*, **96**, 4323 (1974); (g) E. M. Arnett, L. E. Small, R. T. McIver, Jr., and J. S. Miller, *ibid.*, **96**, 5638 (1974).
- (a) H. H. Freedman, V. R. Sandel, and B. P. Thill, *J. Am. Chem. Soc.*, **89**, 1762 (1967); (b) V. R. Sandel, S. V. McKinley, and H. H. Freedman, *ibid.*, **90**, 495 (1968); (c) P. West, J. I. Purmort, and S. V. McKinley, *ibid.*, **90**, 797 (1968).

- (9) See, for example: J. F. Wolf, P. G. Harch, and R. W. Taft, *J. Am. Chem. Soc.*, **97**, 2904 (1975).
- (10) Calculations have been carried out using the STO-3G minimal basis set¹¹ and the GAUSSIAN 70 series of computer programs.¹²
- (11) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).
- (12) W. J. Hehre, W. A. Lathan, M. D. Newton, R. Ditchfield, and J. A. Pople, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind.
- (13) D. K. Bohme, E. Lee-Ruff, and L. B. Young, *J. Am. Chem. Soc.*, **94**, 5153 (1972).
- (14) For a discussion the consequences of the breakdown of the first and third assumptions (where reverse reaction of an ion leads to a neutral molecule which is different from its original precursor), see: S. K. Pollack, B. E. Levi, R. W. Taft, and W. J. Hehre, *J. Am. Chem. Soc.*, in press.
- (15) Ab initio calculations on the isomeric methylallyl anions have recently been performed.¹⁶ Although at the STO-3G minimal basis set level of the theory the *trans* structure is favored, in agreement with the experiments reported here, this prediction is reversed upon going to improved (extended basis set) calculations. The reason for the apparent discrepancy between theory and experiment is not obvious to us at this time.
- (16) P.v.R. Schleyer, J. D. Dill, J. A. Pople, and W. J. Hehre, *Tetrahedron*, to be submitted.
- (17) (a) R. Hoffmann and R. A. Olofson, *J. Am. Chem. Soc.*, **88**, 943 (1966); (b) I. Elphimoff-Felkin and J. Huet, *C.R. Acad. Sci., Ser. C*, **268**, 2210 (1969); (c) J. R. Grunwell and J. F. Sebastian, *Tetrahedron*, **27**, 4387 (1971); (d) N. D. Epictis, D. Bjorquist, L. Bjorquist, and L. Sarkanen, *J. Am. Chem. Soc.*, **95**, 7558 (1973).
- (18) Alfred P. Sloan Fellows: (a) 1974-1976; (b) 1973-1975; (c) 1975-1977.

John E. Bartmess, Warren J. Hehre*^{18a}
Robert T. McIver, Jr.,*^{18b} Larry E. Overman*^{18c}

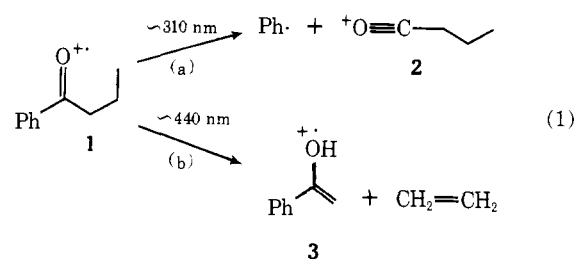
Department of Chemistry, University of California
Irvine, California 92717

Received August 26, 1976

Photodissociation of Butyrophenone Cation. Ionic Analogues of Norrish Type I and II Reactions

Sir:

The Norrish type I and II reactions of ketones are probably the most widely studied of photochemical processes.¹ We wish to report that the analogous reactions can be induced in molecular ions^{2,3} and that these reactions occur from specific excited states. Thus, butyrophenone cation **1** undergoes both photochemical α -cleavage (a) and elimination of ethylene (b), eq 1.



Relevant data² are presented in Figure 1, which indicates the total photoinduced disappearance of **1** as well as the appearance of **2** and **3**. The disappearance and total appearance spectra are not strictly congruent, since they have not been corrected for differences in ion trapping times and other mass effects. In addition, some photodecomposition of products also occurs.⁴ The possibility that both processes (a) and (b) arise from a common electronic state is essentially excluded by the data which show a sharp transition from (b) to (a) at about 3.3 eV. A possible broad distribution of initial energy states (vibrational or electronic) would also be unlikely to give these results, particularly since the photodissociation spectrum of **1** is independent of electron energy from 12 to 19 eV.

The photochemical onsets of (a) and (b) are well above the appearance potentials (A.P.'s) observed on electron impact.⁵ In fact, (a) is energetically feasible at 475 nm although pho-

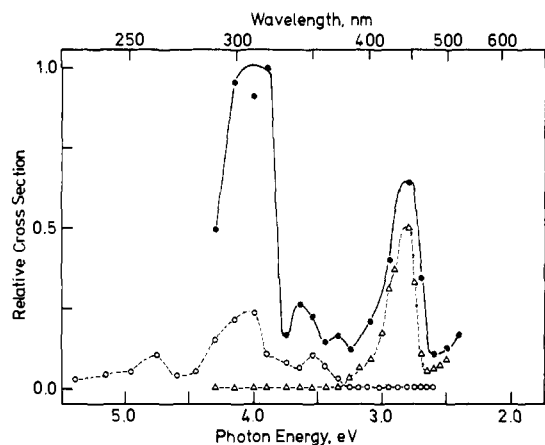


Figure 1. Relative cross sections for disappearance of **1** (●) and appearance of **2** (○), and **3** (Δ) (change in signal/photon flux). The magnitudes of the curves have not been corrected for trapping times or other mass effects. The fractional signal change at the maximum was about 8%, FWHM = 9.9 nm for all points except for **1**, 14.5 nm (380–520 nm).

toinduced appearance of **2** is not observed at that wavelength. The observed energy dependence of (a) and (b) is not consistent with a model in which energy is statistically equilibrated and selection is controlled by densities of vibrational states. Thus, fragmentation from these electronic states must occur prior to internal conversion to a common state.

It is possible that the observed photochemistry results from isomeric ions (e.g., **1** and an enol radical cation) with nonoverlapping chromophores, but this seems unlikely. If isomeric ions were important, **2** would be expected to arise exclusively from **1**, while **3** could come from the enol. The electronic transition observed at 440 nm corresponds to a band in the photoelectron spectrum of butyrophenone,⁶ suggesting strongly that this transition occurs in **1**. Since **3** is produced only in this wavelength region, we conclude that it arises from **1** also. (The photoelectron spectrum does not have a band corresponding to the photochemical process at 310 nm, suggesting that (a) occurs by excitation of an electron to a virtual orbital.) In addition, we have observed similar photochemical behavior with substituted ethyl benzoates, and substituents affect the positions of the two bands in a predictable way,⁷ also suggesting that isomeric ions are not important.

We are not aware of other examples in which direct photoexcitation of a positive ion leads to state specific reactions.^{8,9} Our results are particularly interesting in view of theoretical analyses which show that with ions¹⁰ as with neutrals,^{11,12} correlations exist between the electronic states of reactants and products, and reaction specificity may be expected depending on the nature of the excited state.

The relationship between our observations and those found in conventional mass spectrometry is not yet clear. The mass spectral decomposition patterns of **1** and related ions are highly characteristic and are among the best-studied examples in mass spectrometry.¹³ The behavior we observe strongly parallels the electron impact induced α -cleavage (a) and McLafferty (b) processes, eq 1. However, in contrast to the generally accepted picture that these reactions occur through a common electronic state with vibrational energy influencing decomposition rates (a Q.E.T. model),^{5,14} our results show that such decomposition can arise from isolated electronic states. The importance of isolated electronic states in the decomposition of ions formed by electron impact remains as an outstanding problem,¹⁵ and recent experimental work has shown that such states can be important.⁹

Interestingly, the spacing between the onsets for (b) and (a), ca. 1.2 eV, is quite close to the difference⁵ in electron impact A.P.'s of **3** and benzoyl cation, ca. 1.1 eV. However, the A.P.'s

occur ca. 2 eV closer to the ground state than do the photochemical onsets. It is not clear that Franck-Condon factors could account for such a result, although we do observe weak photodecomposition extending to ca. 700 nm (1.8 eV). The selection rules for excitation induced by electron impact are less restrictive than are optical selection rules,¹⁶ and lower lying optically forbidden states with differing chemistry may possibly be present in **1**.

In summary, we have demonstrated that the commonly observed photochemistry of neutral ketones also exists for these molecular ions, and part of the connection between the Norrish and McLafferty reactions is thus established. These wavelength dependent photoprocesses appear to occur from isolated electronic states rather than from a common one. Thus, while the conventional Q.E.T. model for mass spectral ketone decomposition cannot be excluded, the possibility that these electron impact reactions arise from more than one electronic state remains as an important alternative explanation.

Acknowledgments. We thank Professor D. A. Shirley and Dr. S. T. Lee for the photoelectron spectrum of butyrophenone. We are grateful to the National Science Foundation (CHE 76-02420), and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research, and to Bell Laboratories for fellowship support of R.G.

References and Notes

- (1) (a) J. D. Coyle and H. A. J. Carless, *Chem. Soc. Rev.*, **1**, 418 (1972); (b) N. J. Turro, J. C. Dalton, K. Dawes, G. Farington, R. Haulta, D. Morton, M. Niemczyk, and N. Schore, *Acc. Chem. Res.*, **5**, 92 (1972).
- (2) Experiments were carried out employing an arc lamp and grating monochromator with an ion cyclotron resonance (ICR) spectrometer as an ion trap and detector. See K. C. Smyth and J. I. Brauman, *J. Chem. Phys.*, **56**, 1132 (1972), for details. If the quantum yield is independent of wavelength, the cross section corresponds to an electronic absorption coefficient.^{3b} Ions were formed at an electron energy of 12.5 eV and trapped for 6–8 s at pressures of $3\text{--}5 \times 10^{-7}$ Torr. The ions present before irradiation and their approximate concentrations (% total ions) were **1**, 15.7%; **2**, 4.2%; **3**, 6.2%; m/e 133 (1–15), 16.2%; benzoyl cation, 50.5%; and phenyl cation, 7.2%.
- (3) For other photodissociation experiments, see, for example, (a) E. W. Fu, P. P. Dymerski, and R. C. Dunbar, *J. Am. Chem. Soc.*, **98**, 337 (1976); (b) B. S. Freiser and J. L. Beauchamp, *ibid.*, **98**, 3136 (1976).
- (4) Benzoyl cation, which is formed also by α -cleavage, photodissociates at $\lambda < 350$ nm,^{3b} and its extent of formation from **1** could not be determined in the region where **2** is formed. We see no evidence that it is formed in the region 350–600 nm.
- (5) (A.P.—I.P.) of **3** = 0.41 eV; benzoyl cation, 1.46 eV; P. Brown, *Org. Mass Spectrom.*, **3**, 1175 (1970).
- (6) The photoelectron spectrum of butyrophenone was measured by D. A. Shirley and S. T. Lee, University of California, Berkeley, unpublished results. The vertical ionization potential was 9.55 eV. The spectrum showed three broad bands, maximum 9.55 eV, relative height 4.8, width 1.2 eV; maximum 12.05 eV, relative height 5.7, width 3.1 eV; and maximum 14.40 eV, relative height 4.3, width 4.7 eV. The band at 12.05 eV may be the lowest allowed π - π excitation typically observed in the photoelectron spectra of mono-substituted benzenes, B. S. Freiser and J. L. Beauchamp, *Chem. Phys. Lett.*, **35**, 35 (1975).
- (7) N. C. Yang and R. L. Dusenberry, *J. Am. Chem. Soc.*, **90**, 5899 (1968).
- (8) Photodissociation and photodetachment can be competitive in negative ions, and these may be state specific also: J. H. Richardson, L. M. Stephenson, and J. I. Brauman, *J. Am. Chem. Soc.*, **96**, 3671 (1974).
- (9) State specific reactions in small ions (e.g., C_2F_6^+) induced by photoionization have recently been demonstrated: I. G. Simm, C. J. Danby, and J. H. D. Eland, *Int. J. Mass Spectrom. Ion Phys.*, **14**, 285 (1974).
- (10) C. Minot, N. T. Ahn, and L. Salem, *J. Am. Chem. Soc.*, **98**, 2678 (1976).
- (11) W. G. Dauben, L. Salem, and N. J. Turro, *Acc. Chem. Res.*, **8**, 41 (1975).
- (12) V. G. Plotkinov and V. K. Potapov, *Zh. Fiz. Khim.*, **40**, 192 (1966).
- (13) D. G. I. Kingston, J. T. Bursey, and M. M. Bursey, *Commun. Chem. Rev.*, **24**, 215 (1974).
- (14) D. H. Williams and R. G. Cooks, *Chem. Commun.*, 663 (1968).
- (15) (a) R. G. Cooks, I. Howe, and D. H. Williams, *Org. Mass Spectrom.*, **2**, 137 (1969); (b) M. E. Rennekamp and M. K. Hoffman, *ibid.*, **10**, 1067 (1976); (c) M. M. Bursey, D. G. Whitten, M. T. McCall, W. E. PUNCH, M. K. Hoffman, and S. A. Benezra, *ibid.*, **4**, 157 (1970).
- (16) A. Kupperman and L. M. Raff, *J. Chem. Phys.*, **37**, 2497 (1962).

Robert Gooden, John I. Brauman*

Department of Chemistry, Stanford University
Stanford, California 94305

Received July 27, 1976