

Interrelations between the Mass Spectrometry and Photochemistry of Organic Molecules. I. Ketene Dimers and Other Small Ring Compounds

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An attempt has been made to establish a relationship between the unimolecular reactions of ions produced in the mass spectrometer and the photochemical behavior of a number of small ring compounds. A correlation is found between some of the primary processes which occur in the mass spectrometer (especially at low voltages) and in the photochemical decomposition of several ketene dimers (1, 3, and 4), benzylcyclopropane (5), and nortricyclanone (6).

Introduction

The interrelationship of the factors which determine mass spectrometric and photochemical decomposition paths poses an intriguing problem. McLafferty¹ has pointed out that useful empirical correlations exist between the unimolecular reactions induced by electron impact and by nonionizing ultraviolet radiation. Although a quantitative theory of the mass spectral decomposition processes has not appeared, it is clear that well-established structure-reactivity relationships are adequate for the empirical interpretation of the majority of mass spectra of organic molecules.^{1,2} However, consideration of the factors which determine the course of reactions of organic molecules in solution (energy and steric requirements, stabilities of reactants and products, etc.) must be modified somewhat when interpreting mass spectra, since in the latter case one is dealing with the unimolecular reactions of an unsolvated positive ion. Unfortunately, the structures and reactions of ions of organic molecules are largely unknown, and more familiar systems must be used as a guide. Thus, correlations between the extent of photochemical decompositions and mass spectrometric cracking patterns may serve as a useful guide for the interpretation of mass spectra. Furthermore, such correlations imply that mass spectrometry will provide an important tool for predicting and interpreting photochemical reactions.

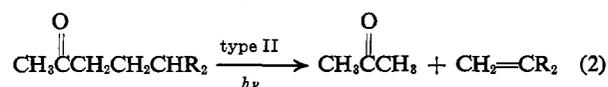
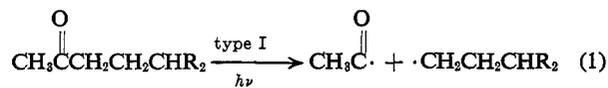
Pitts³ and Nicholson⁴ have shown that the photo-

(1) (a) F. W. McLafferty, *Anal. Chem.*, **31**, 821 (1959); (b) "Mass Spectrometry of Organic Ions," Academic Press Inc., New York, N. Y., 1963, p. 309; in "Determination of Organic Structures by Physical Methods," Vol. II, F. C. Nachod and W. D. Phillips, Ed., Academic Press Inc., New York, N. Y., 1962, p. 93.

(2) (a) J. H. Beynon, "Mass Spectrometry and Its Applications to Organic Chemistry," Elsevier Publishing Co., New York, N. Y., 1960; (b) K. Biemann, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962; (c) H. Budzikiewicz, C. Djerassi, and D. W. Williams, "Interpretation of the Mass Spectra of Organic Compounds," Holden-Day, San Francisco, Calif., 1964.

(3) (a) J. N. Pitts, Jr., Conference on Photochemistry, Rochester, N. Y., 1954; (b) T. W. Martin and J. N. Pitts, Jr., *J. Am. Chem. Soc.*, **77**, 5465 (1955); (c) J. N. Pitts and A. D. Osborne, "Symposium on Chemical Reactions in the Upper and Lower Atmosphere," John Wiley and Sons, Inc., New York, N. Y., 1961, p. 129; (d) J. N. Pitts, Jr., *J. Chem.*

chemical type-I radical split (eq. 1) and type-II rearrangement (eq. 2) of methyl alkyl ketones have analogy in the mass spectrometer.



The vapor phase quantum yields for the type-I process correlate with the appearance of an intense fragment at m/e 43 (CH_3CO^+) in the mass spectra of methyl ketones.³ A correlation also exists^{3,4} between the quantum yields for the type-II process and the (normalized) sensitivity of the mass spectrometric peak at m/e 58 ($\text{CH}_3\text{COCH}_3^+$). Furthermore, only those ketones with γ -hydrogens give acetone and an olefin³⁻⁵ and also a peak at m/e 58. It appears that a number of other correlations⁵⁻⁸ are possible.

These previous results encourage the hope that extrapolation from one technique to the other may be possible. It is very important to determine the scope and theoretical foundations of such correlations. The studies reported here were made with these notions in mind.

Mass Spectra of Ketene Dimers

The photochemistry of a number of ketene dimers has been the subject of considerable recent study.⁹⁻¹⁴ Compounds 1, 2, 3, and 4 were chosen for initial studies (see Tables I and II).

Educ., **34**, 112 (1957); (e) J. N. Pitts, Jr., J. K. Foote, and J. K. S. Wan, *Photochem. Photobiol.*, in press; (f) J. N. Pitts and A. D. Osborne, *J. Am. Chem. Soc.*, **83**, 3011 (1961).

(4) A. J. C. Nicholson, *Trans. Faraday Soc.*, **50**, 1067 (1954).

(5) F. W. McLafferty, *Anal. Chem.*, **28**, 306 (1956).

(6) D. T. Coyle, *J. Phys. Chem.*, **67**, 1800 (1963); S. Meyerson, *ibid.*, **68**, 968 (1964); P. P. Manning, *J. Am. Chem. Soc.*, **79**, 5151 (1957); S. Meyerson and P. N. Ryland, *ibid.*, **79**, 1058 (1957).

(7) The type II process in ester photolysis and mass spectra follows a pattern similar to that mentioned above for ketones: see R. Ryhage and E. Stenhagen in ref. 1b, p. 399; P. Ausloos, *J. Am. Chem. Soc.*, **80**, 1310 (1958); **83**, 1053 (1961).

(8) The elimination of a ring carbon to form substituted cyclopentadienyl compounds is demonstrated in the flash photolysis [G. Porter and B. Ward, *Proc. Chem. Soc.*, 288 (1964)] and mass spectra² of substituted benzenes.

(9) N. J. Turro, G. W. Byers, and P. A. Leermakers, *J. Am. Chem. Soc.*, **86**, 955 (1964).

(10) P. A. Leermakers, G. Vesley, N. J. Turro, and D. C. Neckers, *ibid.*, **86**, 4213 (1964).

(11) R. C. Cookson, M. J. Nye, and G. Subrahmanyam, *Proc. Chem. Soc.*, 144 (1964).

(12) H. G. Richey, Jr., J. M. Richey, and D. C. Clagett, *J. Am. Chem. Soc.*, **86**, 3906 (1964).

(13) I. Haller and R. Srinivasan, *ibid.*, **87**, 1144 (1965).

(14) N. J. Turro, P. A. Leermakers, H. R. Wilson, D. C. Neckers, G. W. Byers, and G. F. Vesley, *ibid.*, **87**, 2613 (1965).

Table I. Partial Mass Spectra of Ketene Dimers^a

| Fragment | 1 | 2 ^b | 3a | 3b | 3c | 4 |
|---------------------|-------|----------------|------|-----|------|-------|
| M ⁺ | 12 | 11.0 | 7.6 | 3.0 | ~1 | ~1 |
| M ⁺ - 28 | 1.0 | 1.0 | ~1 | ~1 | ~1 | 1.3 |
| M ⁺ - 56 | 9.0 | 4.3 | ~1 | ~1 | ~1 | 4.0 |
| M ⁺ /2 | 100.0 | 90.0 | 97.0 | 100 | 98.2 | 100.5 |

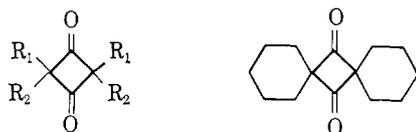
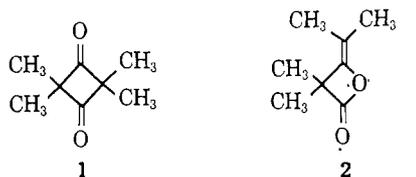
^a At 75 v., % of base peak. ^b An important peak at *m/e* 96 (M⁺ - 44, 15%) also appears in this spectrum.

Table II. Partial Mass Spectra of Ketene Dimers^a

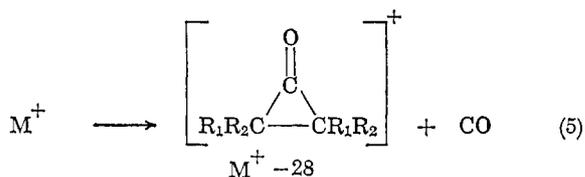
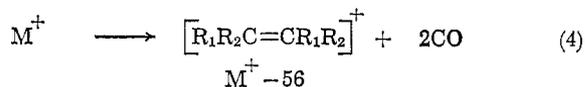
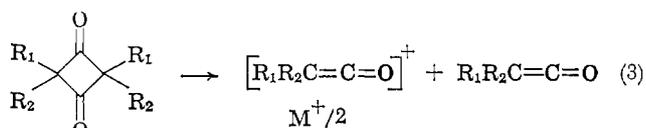
| Fragment | 1 | 2 | 4 |
|---------------------|-----|-----|-----|
| M ⁺ | 30 | 48 | 16 |
| M ⁺ - 28 | 3.0 | ~0 | ~1 |
| M ⁺ - 56 | 27 | 12 | 12 |
| M ⁺ /2 | 100 | 100 | 100 |

^a At 10 v., % of base peak.

The dione dimers (1, 3, 4) studied all undergo the following fragmentation processes in the mass spectrometer at an ionization voltage of 75 e.v.¹⁵



3a, R₁ = R₂ = C₂H₅
 b, R₁ = CH₃; R₂ = C₃H₇
 c, R₁ = R₂ = C₆H₅

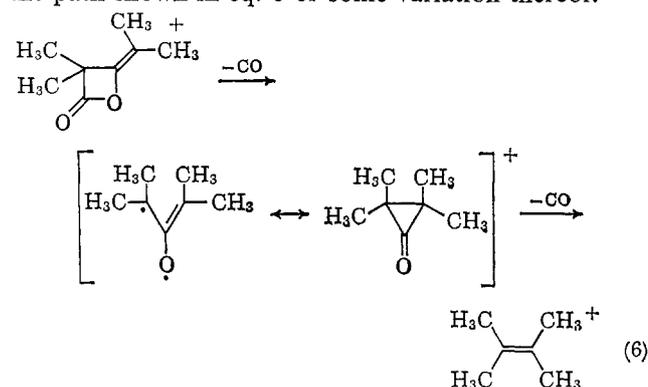


As the ionization voltage is lowered, process 4 (which may occur in one or two steps) increases in importance. A metastable peak at *m/e* 50.5 (M⁺ → M⁺ - 56) appears in the spectrum of 1 at 75 and 10 e.v. This result demands^{1,2} that at least a fraction of the molecular ions of 1 which are formed decompose to lose two molecules of carbon monoxide in one step.

The relatively important peak at *m/e* 84 in the spectrum of 2 is of special interest because it can be reason-

(15) Elimination of carbon monoxide from a molecular ion followed by a specific rearrangement has been shown to be important in the mass spectra of a number of organic molecules: J. H. Beynon, G. R. Lester, and A. E. Williams, *J. Phys. Chem.*, 63, 1861 (1959).

ably assigned only to the fragment C₆H₁₂⁺, perhaps by the path shown in eq. 6 or some variation thereof.



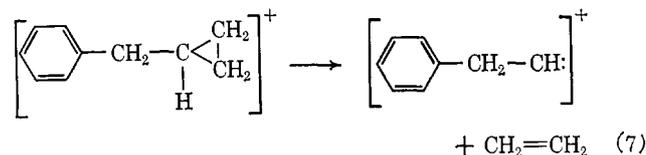
Mass Spectra of Nortricyclanone and Benzylcyclopropane

The mass spectra of benzylcyclopropane (5) at 75 and 10 e.v. are given in Table III. A metastable peak

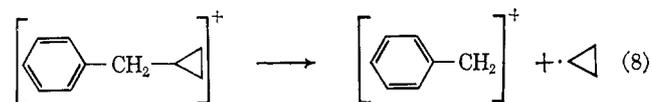
Table III. Partial Mass Spectrum of 5 at 75 and 10 E.v. (% of Base Peak)

| <i>m/e</i> | 75 e.v. | 10 e.v. |
|---|---------|---------|
| 132 (M ⁺ , C ₁₀ H ₁₂) | 38 | 100 |
| 104 (M ⁺ - 28, C ₈ H ₈) | 55 | 50 |
| 91 (M ⁺ - 41, C ₇ H ₇) | 100 | 50 |

at *m/e* 82 (M⁺ → M⁺ - 28) appears in the spectrum at both voltages. This transformation is assigned to the loss of ethylene as shown in eq. 7. The other important decomposition leading to the peak at *m/e* 91



is assigned to the loss of a cyclopropyl radical as shown in eq. 8.

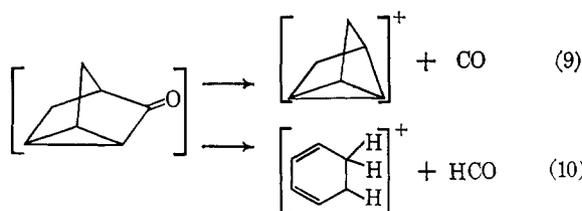


The partial mass spectrum of nortricyclanone (6) is given in Table IV. The two important decomposition

Table IV. Partial Mass Spectrum of 6 at 75 and 10 E.v. (% of Base Peak)

| <i>m/e</i> | 75 e.v. | 10 e.v. |
|--|---------|---------|
| 108 (M ⁺ , C ₇ H ₈ O) | 35 | 70 |
| 80 (M ⁺ - 28, C ₆ H ₈) | 55 | 100 |
| 79 (M ⁺ - 29, C ₆ H ₇) | 100 | 100 |

paths for the molecular ion appear to be loss of masses 28 and 29 as shown in eq. 9 and 10.



Relationship between the Mass Spectra and Photochemistry of the Compounds Investigated

The values reported in Tables I-IV at low voltage are the only significant peaks (except for the metastable peaks reported in the text) which appear in the mass spectra of compounds 1-6 when the molecular ion of these compounds is produced with a minimum amount of excess energy. These, therefore, are the processes we wish to compare to the photolyses results. It is striking that the primary processes described by eq. 1-3 have been proposed to explain the analogous photochemistry of 1 in the vapor phase and in inert solvents.⁹⁻¹⁵ The photochemistry of compounds 3 and 4 has not been studied as extensively as that of compound 1, but preliminary results indicate that the photochemistry of the ketene dione¹⁴ dimers follow the same paths as 1.

The paths of decomposition induced by ultraviolet radiation and electron bombardment of compounds 5 and 6 are also probably related.^{16,17} An important process in the vapor photolysis of 5 is believed to be¹⁶ the loss of ethylene in one step from an electronically excited state of 5. This process corresponds nicely with the process given in eq. 5 and the metastable peak at m/e 82 in the low voltage mass spectrum of 5. Furthermore, cyclopropane and toluene are significant products from vapor photolysis of 5; this photoprocess correlates with the mass spectrometric process given in eq. 6.

Compound 6 yields tricyclo[2.2.0.0^{2,6}]hexane and benzene when the nortricyclanone is irradiated in the vapor phase.¹⁷ The mass spectrum of 6 at low voltage shows only peaks at m/e 80 and 79, in addition to the molecular ion. The peak at m/e 80 presumably corresponds to loss of carbon monoxide as shown in eq. 7, but may correspond to loss of ethylene.¹⁸ The peak at m/e 79 corresponds to protonated benzene.

Discussion

Let us consider a comparison of the decomposition paths of the molecular ion and the electronically excited state of the same molecule. Since the molecular ion is generated in the vapor state, we may expect any correlation between the chemistry of the molecular ion and the electronically excited state to be most apparent in a comparison of the vapor phase photochemistry and the mass spectrometric cracking processes. Yet, with appropriate allowances for the differences expected from the chemistry of ionized vs. neutral molecular species, one may make extensions of such correlations to the solution photochemistry of the molecules under study (and also to the chemistry produced by ionizing radiation on solution³). At low ionization voltages, when the molecule is ionized, the most loosely bound electrons are removed preferentially (on the average). When the molecule contains a functional group, this group may dominate the fragmentation process and lead to a relatively few selective (low energy) processes. In the case of carbonyl compounds, the n -electrons (nonbonding electrons on oxygen) are selectively removed with low energy electrons.¹⁹ After

formation of the molecular ion, the height of a peak in the mass spectrum of a molecule is determined not only by the rates of formation of ions from the parent ion but also by the rates of destruction of the ions so formed.¹

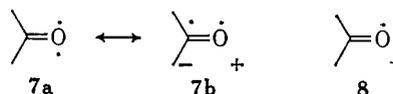
It is important to note that the photochemistry of carbonyl compounds, like the lowest energy ionization processes, often involves n -electrons.²⁰ The theoretical foundation of correlations such as those presented here and by other workers^{1,3,4} may stem therefore from similarities in the structures of excited states produced by electron bombardment and by absorption of nonionizing ultraviolet radiation. Thus, although photochemical excitation is more selective than ionization by electron bombardment, at low voltages the details of the decomposition paths of the molecular ion are crudely similar to the decomposition paths of the electronically excited states. Since correlations can be found for molecules which do not possess heteroatoms (e.g., 5), clearly n -electrons are not a unique prerequisite for such a correlation.

One must be careful in the evaluation of correlations of the type described here to make due allowance for special reactions expected for positive ions and for the effect of transition from the vapor phase to solution on the photochemistry of organic molecules.²¹

For example, the peak at m/e 79 in the mass spectrum of 6 may be correlated with the formation of benzene in the photochemistry of 6, because the protonated form of benzene is more stable in the mass spectrometer than benzene positive ion.

Conclusion

It appears that the study of the relationship between mass spectrometry and photochemistry, and thereby the use of each technique to study the other, may be quite valuable. To date such studies have been largely empirical, but correlations such as those reported here and earlier^{1,3,4} imply that attempts to extract the theoretical foundations of such correlations should be fruitful. The n, π^* state, which is presumably responsible for much of the photochemistry of carbonyl compounds, has been described in terms of contributing forms which indicate an electron deficiency at the oxygen atom (7b). This exaggerated valence form may be compared to the classical valence form 8 which crudely indicates a similarity between the electronic structures of the molecular ions and the n, π^* states of carbonyl compounds.



Experimental

Chemicals. Tetramethyl-1,3-cyclobutanedione (1), Eastman Kodak White Label, was used as received. Compounds 2, 3, and 4 were kindly supplied by Dr. Kent C. Brannock of Tennessee Eastman. Benzylcyclopropane (5), Aldrich, was used as received (purity

(16) P. A. Leermakers and G. F. Vesley, *J. Org. Chem.*, **30**, 539 (1965).

(17) D. M. Lemal and K. Shim, *J. Am. Chem. Soc.*, **86**, 1550 (1964).

(18) High resolution spectra are being run by Professor F. W. McLafferty of Purdue University in order to remove these ambiguities.

(19) R. S. Mulliken, *J. Chem. Phys.*, **3**, 564 (1935).

(20) (a) G. S. Hammond and N. J. Turro, *Science*, **142**, 1541 (1964); (b) P. A. Leermakers and G. F. Vesley, *J. Chem. Educ.*, **41**, 535 (1964); (c) N. J. Turro, "Molecular Photochemistry, W. A. Benjamin, Inc., New York, N. Y., in press.

(21) R. Srinivasan, *Advan. Photochem.*, **1**, 83 (1964).

greater than 99% by v.p.c. analysis). Nortricyclanone was prepared by the procedure of Meinwald.²²

Mass Spectra. All spectra were taken on a Hitachi Model RMU-6D spectrometer with source temperature of 250° and inlet system at 150°. Variation of the

(22) J. Meinwald, J. Crandall, and H. E. Hymans, *Org. Syn.*, submitted. We wish to thank Professor Meinwald for a preprint of this procedure.

inlet temperature between 50 and 250° did not cause the spectra to change significantly.

Acknowledgments. The authors wish to thank the Petroleum Research Fund (G-216) and the National Science Foundation (GP-4280 and GP-2848) for their generous support of this work. N. J. T. was a visiting scientist, Dow Chemical, summer 1964, and thanks them for their support.

Reactions in Frozen Solutions. II. Base-Catalyzed Decomposition of *t*-Butylperoxy Formate in Frozen *p*-Xylene

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Contribution from the Department of Chemistry, University of British Columbia, Vancouver 8, British Columbia. Received June 8, 1965

The 2,6-lutidine-catalyzed decomposition of *t*-butylperoxy formate (TBF) to yield carbon dioxide and *t*-butyl alcohol in *p*-xylene is accelerated at 0° by factors of 30 to 400 (depending on initial concentrations) when the solution is frozen. The reaction rate does not depend on the manner in which solutions are frozen. The frozen solution reaction, which is first order in TBF, is first order in base catalyst at low base concentration but becomes zero order in base at high base concentration. The reaction has a maximum rate at ca. 2° and occurs to as low a temperature as -30°. The presence of any soluble compound such as benzene, *o*-xylene, *m*-xylene, carbon tetrachloride, or heptane results in the same decrease per mole in observed rate constant. The results indicate that the reaction occurs in liquid regions, present in the frozen solutions, which contain a constant total concentration of solutes. Assuming ideal solutions, the dependency of the observed, first-order rate constants on the concentration of reactants, on temperature, and on the presence of impurities is given by the relationship $k_{obsd} = k_2 C_h (B_0 / (B_0 + P_0 + I_0))$ where k_2 is the normal, second-order rate constant for reaction in solution, C_h is the total solute concentration of liquid regions in the frozen solution, and B_0 , P_0 , and I_0 are the initial solution concentrations of base, peroxide, and impurities. Several general aspects of reactions in frozen solutions are discussed.

A bimolecular reaction which occurs in solution at low reactant concentrations would not generally be expected to proceed when the solution is frozen.¹ The greatly decreased mobility of the solid state should prevent the necessary mutual approach of the reaction components. Recent reports,²⁻⁴ however, have in-

(1) For reviews and discussions of reactions in organic solids see, e.g., H. Morawetz, "Physics and Chemistry of the Organic Solid State," Vol. 1, D. Fox, M. M. Labes, and A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p. 287; Vol. 2, 1965, p. 853; J. E. Lefter and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, p. 403; C. E. H. Bawn, "Chemistry of the Solid State," W. E. Garner, Ed., Butterworth and Co. (Publishers) Ltd., London, 1955, p. 254.

(2) (a) T. C. Bruice and A. R. Butler, *J. Am. Chem. Soc.*, **86**, 313 (1964); (b) *ibid.*, **86**, 4104 (1964).

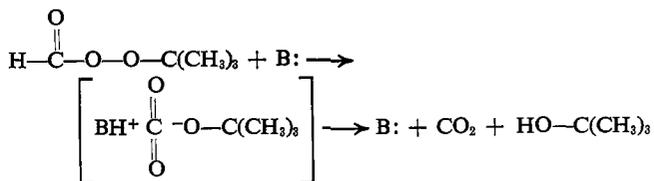
(3) N. H. Grant, D. E. Clark, and H. E. Alburn, *ibid.*, **83**, 4476 (1961).

dicated that some bimolecular reactions in dilute aqueous solutions may occur, and are even accelerated, when the solution is frozen. Bruice and Butler² in a study of the acid- and base-catalyzed hydrolysis of acetic anhydride in water and in ice have presented evidence that in frozen solutions the reaction components are gathered together in regions which remain liquid. The greater concentrations of reactants in these pockets of liquid result in an acceleration of the reaction. Other striking effects were also observed,^{2b} as in the reaction of some thiolactones with morpholine where freezing of aqueous solutions causes a change in kinetic order as well as an acceleration of the reaction.

As has been pointed out,²⁻⁴ rather special effects might appear with reactions in ice, but accelerated reactions have also been observed when dilute organic solutions are frozen.⁵ In inert organic solvents, which are not involved in the stoichiometry of the reaction, the results are so far adequately explained by the concentration effect. The reactions are not actually solid-state reactions but involve highly concentrated solutes present in liquid regions among the crystalline solid. In this paper, the details of the pyridine- and 2,6-lutidine-catalyzed decomposition of *t*-butylperoxy formate in frozen *p*-xylene solutions are presented and the general features of such "frozen state" reactions are discussed.

Results

In organic solutions the base-catalyzed decomposition of *t*-butylperoxy formate (TBF) is a simple bimolecular reaction involving attack by base on the formate hydrogen.⁶ A dipolar transition state is formed and



(4) W. H. Prusoff, *Biochim. Biophys. Acta*, **68**, 302 (1963).

(5) R. E. Pincock and T. E. Kiovsky, *J. Am. Chem. Soc.*, **87**, 2072 (1965).

(6) (a) R. E. Pincock, *ibid.*, **86**, 1820 (1964); (b) *ibid.*, **87**, 1274 (1965).