that it is a relatively slow process. Obviously, any structural feature, such as the double bond in lycorine (XXIII), which serves to stabilize the final carbonium ion, will greatly facilitate a sequence such as XXX and increase the relative abundance of the resulting fragment ion.

Loss of methanol from aliphatic methyl ethers is presumably a completely analogous process but in molecules such as haemanthidine (XXIV), which contains a methoxyl group and a hydroxyl group, the activating proton is presumably carried away with whichever function is lost and the charge left behind is stabilized by some other feature of the molecule so there is less tendency for a second fragment to be lost. Thus is observed the loss of 32 or 18 mass units from the QM^+ ion of XXIV, but there is no ion at *m/e* ($QM^+ - 50$).

In the light of the data reported here, methane CI mass spectrometry would appear to have great promise as a method for the mass spectrometric investigation of functional groups in organic molecules. Information regarding those groups that are more labile under conditions of electron bombardment may well be available by this technique and the complementary nature of the two types of spectra increased the value of both techniques.

Chemical Ionization Mass Spectrometry of Complex Molecules. III.[1] The Structure of the Photodimers of Cyclic α,β-Unsaturated Ketones

H. Ziffer, H. M. Fales, G. W. A. Milne, and F. H. Field

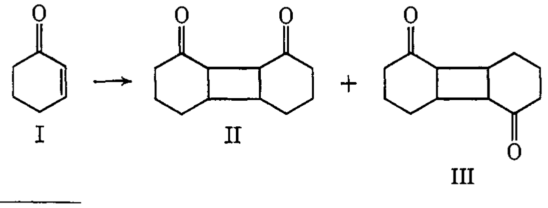
Contribution from the Laboratory of Physical Biology,
National Institute of Arthritis and Metabolic Diseases, and Molecular Disease Branch, National Heart Institute, Bethesda, Maryland 20014, and the Corporate Research Laboratory, Esso Research and Engineering Company.

Received August 8, 1969

Abstract: The chemical ionization mass spectra of several pairs of head-to-head and head-to-tail photodimers of α,β-unsaturated cycloalkenones have been examined. The most abundant ion in the spectra of the head-to-head dimers is the quasimolecular ion while in the spectra of the head-to-tail dimers the ion at *m/e* $((M/2) + 1)^+$ is the most abundant ion. These results have been rationalized in terms of possible fragmentation paths of the protonated photodimers.

It has long been known[2] that irradiation of cyclic α,β-unsaturated ketones leads to dimerization with the formation of the so-called "photodimers."

A number of isomeric dimers is possible; however, these can be divided into two groups, head-to-head (h–h) and head-to-tail (h–t), which differ in that the former is a 1,4-diketone while the latter is a 1,5-diketone. Several isomers are frequently isolated from the irradiation of cyclohexenones,[3] cyclopentenones,[4] and cycloheptenones.[5] Cyclohexenone (I) for example, gives the h–h dimer (II) and the h–t dimer (III). Determination of the structure and stereochemistry about the cyclobutane ring is difficult. An unequivocal assignment of the structure greatly facilitates the remaining stereochemical assignments. Only in special cases do physical measurements such as ir or nmr spectroscopy aid in distinguishing between the two groups of dimers.[6,7] Since chemical ionization (CI) mass spectrometry has been shown[8] to be of value in differentiating between isomeric structures, the CI spectra of a series of h–h and h–t dimers were examined.



Experimental Section

In all the chemical ionization mass spectra reported here, the reactant gas was methane, at an ion chamber pressure of approximately 0.8 mm.[1] Thus the major protonating species are[9] CH_5^+ and $C_2H_5^+$. Samples of the photodimers were admitted to the source *via* a direct insertion probe with a source temperature of 50–100° except where otherwise noted.

---

[1] Part II: H. M. Fales, H. A. Lloyd, and G. W. A. Milne, *J. Amer. Chem. Soc.*, **92**, 1590 (1970).

[2] N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1965, p 194.

[3] (a) D. Valentine, N. J. Turro, and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 5202 (1964); (b) H. Ziffer, submitted for publication; (c) O. L. Chapman, *Rec. Chem. Progr.*, **28**, 167 (1967).

[4] P. E. Eaton, *J. Amer. Chem. Soc.*, **84**, 2344 (1962).

[5] P. E. Eaton, private communication.

[6] H. Ziffer, N. E. Sharpless, and R. D. Kan, *Tetrahedron*, **22**, 3011 (1966).

[7] We have also found that gas chromatography may be used to differentiate the isomers. The h–h isomer is always retained longer than its h–t counterpart on a nonpolar OV-1 phase. Thus Rt (h–h)/(h–t) for II/III = 1.14; VI/VII = 1.70; V/IV = 1.15; VIII/IX = 1.54; VIII/X = 2.12; XVI/XV = 1.43. The results are reasonable in view of the increased dipole moment of the h–h isomer and as expected, the effect is magnified on the more polar XE-60 phase, the above ratios becoming 1.34, 2.52, 2.78, 2.25, 3.21, and 2.19, respectively.

[8] J. D. Baty, G. W. A. Milne, and H. M. Fales, unpublished work.

[9] F. H. Field and M. S. B. Munson, *J. Amer. Chem. Soc.*, **87**, 3289 (1965).

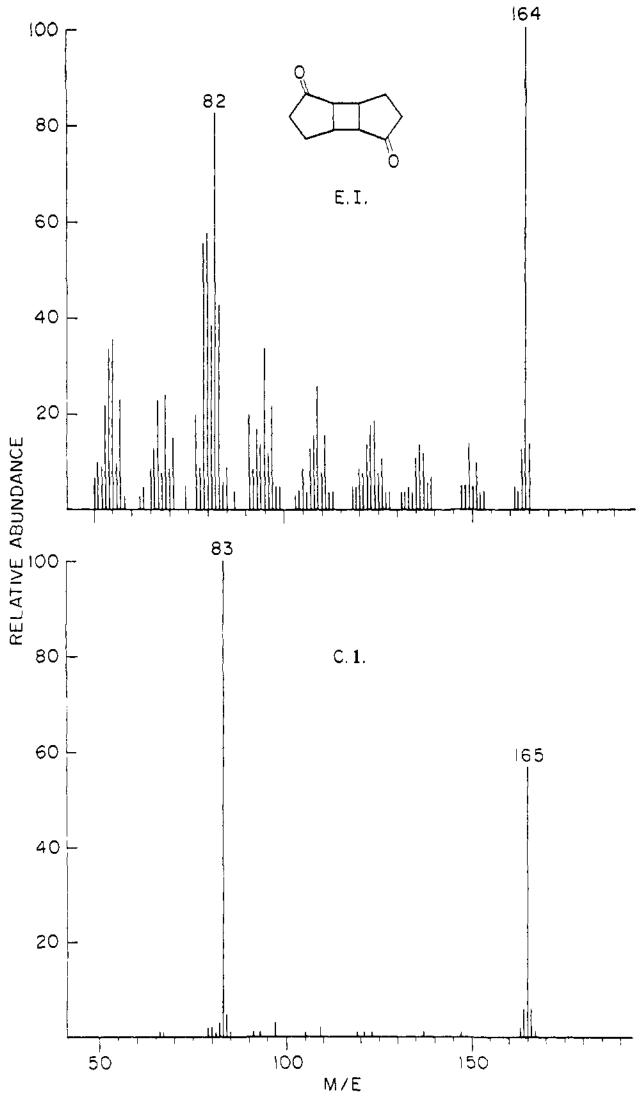


Figure 1. Mass spectra of IV.

The dimers employed in this study were prepared by published procedures as indicated in Table I. The dimers are all thermally stable at temperatures below 300° and can in fact often be purified by distillation at this temperature.

Table I

Dimer	Mp, °C	Reported mp, °C	Ref
V	69–70	66–67	*a*
IV	126–126.5	125–126.5	*a*
III	51–52	53–55	*b*
II	77–78	79–80	*b*
VII	146–147	146–147	*c*
VI	68–69	68–69	*c*
VIII	188.5–190	188.5–190	*d*
IX	(*syn*) 112–113.5	112–113.5	*d*
X	(*anti*) 211–213	211–213	*d*
XV	286–288	293	*e*
XVI	229	225–226	*f*

[a] Reference 4. [b] Reference 3a. [c] Reference 3b. [d] Reference 3c. [e] E. H. White and H. C. Dunathan, *J. Amer. Chem. Soc.*, **78**, 6055 (1956). [f] J. Bowyer and Q. N. Porter, *Aust. J. Chem.*, **19**, 1455 (1966).

Results and Discussion

The CI mass spectrum of the h–t dimer of cyclopentenone (IV) is shown in Figure 1. As has generally been observed[10] the CI mass spectrum consists predominantly of even electron ions and is considerably less complex than the corresponding electron impact (EI) spectrum which is also shown in Figure 1. The CI mass spectrum of IV consists mainly of two ions, *viz* the quasimolecular ion (QM^+) at *m/e* 165 $(M + 1)^+$ and the base peak at *m/e* 83 (*i.e.*, *m/e* $((M/2) + 1)^+$). The loss of the elements of cyclopentenone from the molecular ion in the EI spectrum of IV is also an important process, leading in this case to the ion at *m/e* 82. In the EI mass spectra, this cleavage of the dimer into its respective monomer parts takes place equally readily with both the h–t and h–h systems but in the CI mass spectra, the two types of compounds behave quite differently. Thus the CI mass spectrum of the h–h isomer (V) of the cyclopentenone dimer, shown in Figure 2, has a QM^+ ion at *m/e* 165 (100%) and a considerably less abundant ion (11%) at *m/e* 83, in contrast to the h–t isomer (IV) where these ions have abundances of 57 and 100%, respectively. This difference in behavior between the h–h and h–t systems is also observed in the spectra of the cyclohexenone dimers VI–X and appears without exception. In Table II are presented the relative abundances of these two peaks in each of the spectra.

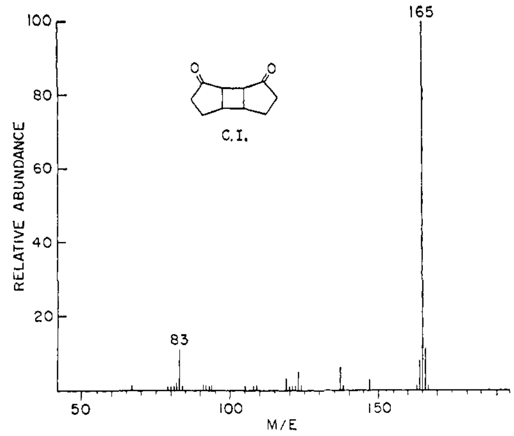
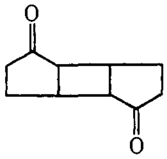
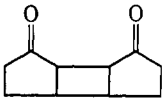


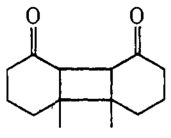
Figure 2. CI mass spectrum of V.



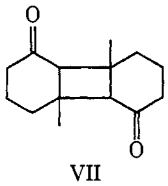
IV



V



VI

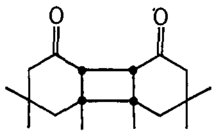


VII

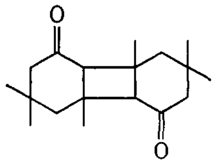
From these data, it can be seen that the QM^+ ions formed by protonation of the h–t dimers are less stable than those derived from the corresponding h–h dimers. Since both isomers should be protonated with roughly equal facility this difference in behavior of the QM^+

---

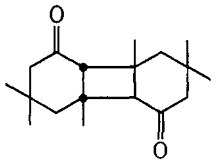
(10) H. M. Fales, G. W. A. Milne, and M. L. Vestal, *J. Amer. Chem. Soc.*, **91**, 3682 (1969).



VIII



IX



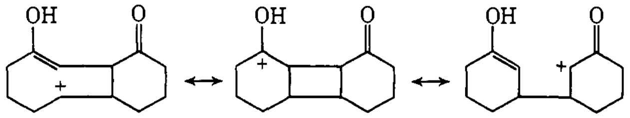
X

ions must be related to the fact that the h-h dimers are 1,4-diketones while the h-t dimers are 1,5-diketones.

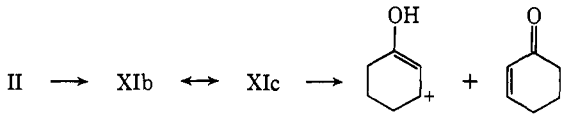
Protonation of an h-h dimer such as II gives a QM$^+$ ion which can have three resonance forms XIa–c. Of these, XIc is destabilized by the proximity of the formal positive charge to the carbon of the carbonyl group and since XIc is an obligatory intermediate in the formation of XII from XIb, collapse of XIb to XII (*m/e* ((M/2) + 1)$^+$) and cyclohexenone will not be a facile process.

Table II. Relative Abundances of Ions in the CI Mass Spectra of Dimers

Compd	Series	QM$^+$; *m/e* (relative abundance)	((M/2) + 1)$^+$; *m/e* (relative abundance)
II	h-h	193 (100)	97 (4)
III	h-t	193 (100)	97 (55)
IV	h-t	165 (57)	83 (100)
V	h-h	165 (100)	83 (11)
VI	h-h	221 (100)	111 (12)
VII	h-t	221 (5)	111 (100)
VIII	h-h	277 (100)	139 (27)
IX	h-t	277 (4)	139 (100)
X	h-t	277 (5)	139 (100)
XIV	h-h	305 (100)	153 (11)
XV	h-t	261 (64)	131 (100)
XVI	h-h	261 (100)	131 (58)
XVII	h-h	405 (100)	203 (65)
XVIII	h-h	435 (1)	218 (100)

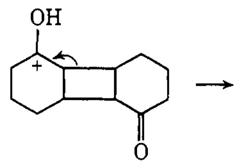


XIa XIb XIc

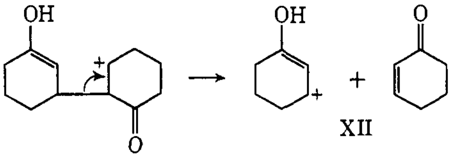


XII

In the case of the h-t isomer (III), on the other hand, there is no such difficulty attending the collapse of the QM$^+$ ion (XIII) to XII and cyclohexenone.



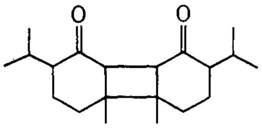
XIII



XIIIa XII

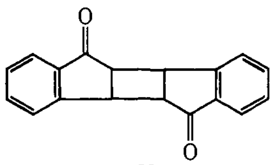
Support for this line of reasoning may be found in the observation that the presence of a methyl group β to the carbonyl group (*e.g.*, in VII, IX, and X) leads to more extensive collapse of the QM$^+$ ion to the ion of *m/e* ((M/2) + 1)$^+$ by stabilization of the carbonium ion corresponding to XIIIa. The corresponding h-h isomers, VI and VIII, however, fragment no more markedly than does the cyclohexenone h-h dimer II itself.

The cyclopentenone h-t dimer (IV) gives a QM$^+$ ion which collapses to the ion at *m/e* ((M/2) + 1)$^+$ more readily than does the QM$^+$ ion from III and this is consistent with the greater stability of a carbonium ion in a five rather than a six-membered ring.[11] Furthermore, the CI mass spectrum of the piperitone dimer XIV shows a QM$^+$ ion at *m/e* 305 (100%) with very little breakdown to the ion at *m/e* 153 (11%), consistent with its previous formulation[6] as an h-h dimer.

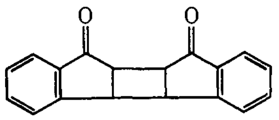


XIV

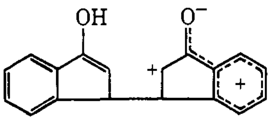
The two indenone dimers XV and XVI show similar behavior, but compared to the nonaromatic h-h dimers, XVI gives a relatively unstable QM$^+$ ion. This is presumably because the dipole of the carbonyl group is to some extent dispersed over the aromatic system with correspondingly less destabilization of the carbonium ion XVIa.



XV



XVI



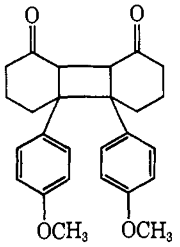
XVIa

Finally, the two h-h dimers XVII and XVIII were studied.[12] The slightly higher temperature (~150°) required for these two compounds certainly contributed to the higher rates of fragmentation compared to the simple dimers, but the differences in behavior between XVII and XVIII were of interest. The QM$^+$ ion from XVIII (*m/e* 435, 1%) was very unstable, collapsing rapidly to the ion at *m/e* 218 (100%). That from XVII on the other hand (*m/e* 405, 100%) fragmented far less

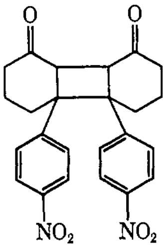
---

(11) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 266–267.

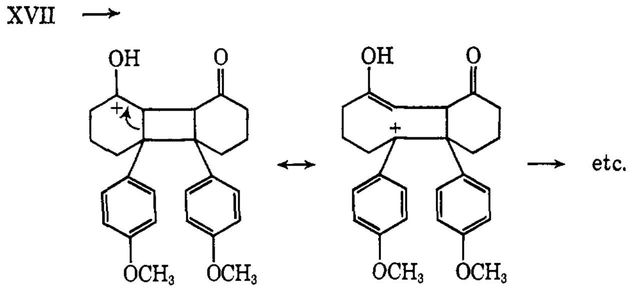
(12) A. N. Ege and P. Yates, *Can. J. Chem.*, **45**, 2933 (1967).



XVII



XVIII



XVIIa XVIIb

readily to the ion at m/e 203 (65%) and this is undoubtedly due to the stabilization, by the p-anisyl group, of the resonance form XVIIb of the QM$^+$ ion. Such stabilization is not present in the QM$^+$ ion derived from XVIII.

The studies of the aliphatic photodimers demonstrate that it is possible to assign an h-h or h-t structure to an unknown photodimer from an examination of its methane CI spectrum. Clearly in correlations of this type factors such as an aromatic ring that significantly affect the stability of the carbonium ions must be taken into account in structural assignments.

Acknowledgments. We thank Dr. O. L. Chapman for samples of the isophorone photodimers and Dr. P. Yates for samples of XVII and XVIII.

Chemical Ionization Mass Spectrometry. XI. Reactions of Methoxymethyl Formate and Methoxymethyl Acetate with Methane and Isobutane

D. P. Weeks and F. H. Field

Contribution from the Department of Chemistry, Seton Hall University, South Orange, New Jersey 07079, and the Corporate Research Laboratory, Esso Research and Engineering Company, Linden, New Jersey 07036.

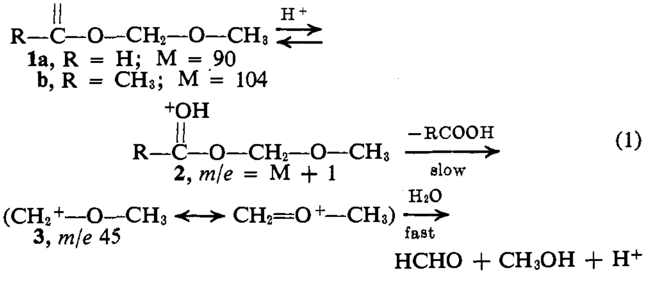
Received August 11, 1969

Abstract: The chemical ionization mass spectra of methoxymethyl formate and methoxymethyl acetate have been determined at several temperatures using isobutane and methane as reactants. The major ions observed in the isobutane spectra are the protonated molecule ions and an ion with m/e 101, which is formed by displacement of the carboxylic acid by t-butyl cation. No methoxymethyl cation is observed. In the methane spectra the methoxymethyl cation is by far the most abundant ion. Rate constants for its formation from the two esters were determined at several temperatures. At 300°K the rate constant for the formation of this ion from methoxymethyl formate is a factor of two higher than that for the formation of the ion from methoxymethyl acetate, which is in agreement with the relative rates found in solution. Activation energies and frequency factors are given, but the significance of the magnitudes obtained for these quantities is not understood.

Chemical ionization mass spectrometry[1] is a process wherein organic substances may be ionized by reaction with a set of reactant ions in the ionization chamber of a mass spectrometer. In many cases the reactions which are observed in these experiments are analogous to those which the organic substances undergo in acidic solution.[2,3]

The acid-catalyzed hydrolysis of simple partial acylals has been studied by Salomaa and his coworkers,[4] and that of more complex partial acylals by one of us.[5] Thus, it appeared that a study of the behavior of methoxymethyl formate (**1a**) and methoxymethyl acetate (**1b**) in the acidic plasmas generated in chemical ionization mass spectrometry would provide a comparison of the gaseous and solution phase chemistry of these simple partial acylals.

Methoxymethyl formate and methoxymethyl acetate undergo hydrolysis in aqueous acid by an $A_{Al}1$ mechanism[5] (eq 1). One would expect this mechanism to be



$$\mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}O{-}CH_2{-}O{-}CH_3} \underset{}{\overset{H^+}{\rightleftarrows}}$$

1a, R = H; M = 90
b, R = CH_3; M = 104

$$\mathrm{R{-}\overset{^+OH}{\overset{\|}{C}}{-}O{-}CH_2{-}O{-}CH_3} \xrightarrow[\text{slow}]{-\mathrm{RCOOH}} \qquad (1)$$

2, m/e = M + 1

$$(\mathrm{CH_2{}^+{-}O{-}CH_3} \longleftrightarrow \mathrm{CH_2{=}O^+{-}CH_3}) \xrightarrow[\text{fast}]{\mathrm{H_2O}} \mathrm{HCHO + CH_3OH + H^+}$$

3, m/e 45

---

[1] M. S. B. Munson and F. H. Field, *J. Amer. Chem. Soc.*, **88**, 2621 (1966).

[2] F. H. Field, *Accounts Chem. Res.*, **1**, 42 (1968).

[3] F. H. Field, *J. Amer. Chem. Soc.*, **91**, 2827 (1969).

[4] P. Salomaa, *Acta Chem. Scand.*, **11**, 132 (1957); **14**, 586 (1960).

[5] D. P. Weeks, A. Grodski, and R. Fanucci, *J. Amer. Chem. Soc.*, **90**, 4958 (1968); D. P. Weeks and G. W. Zuorick, *ibid.*, **91**, 477 (1969).