

is strong indeed that the stabilities of these cations will not be greatly different in aqueous solution and, consequently, one needs rather small effects to account for the observed order of reactivities.

*Acknowledgment.* We are indebted to Professor Robert Taft, Jr., for critical comments concerning this work and for communication of pertinent data prior to publication.

## Mass Spectrometry in Structural and Stereochemical Problems. LXXIII.<sup>1</sup> The Negative Ion Mass Spectra of Some Simple Organic Compounds<sup>2</sup>

R. T. Aplin,<sup>3</sup> H. Budzikiewicz, and Carl Djerassi

*Contribution from the Department of Chemistry, Stanford University, Stanford, California. Received March 1, 1965*

*The negative ion mass spectra of alkylbenzenes, substituted benzenes, aliphatic acids, esters, nitriles, and ketones have been measured. The spectra are compared with their positive ion counterparts and with other work on negative ion mass spectrometry. The utility of this type of mass spectrometry under the experimental conditions used (20–70-e.v. electron energy) with respect to molecular weight and structure determination is considered to be only of limited value, at least as far as the compounds under discussion are concerned.*

### Introduction

In the last few years studies involving positive ion mass spectra have been applied to a great variety of organic compounds.<sup>4–6</sup> However, very little has been published with respect to negative ion mass spectrometry. There also appear to be discrepancies in the published experimental results, which demonstrate the need for further work. The most recent discussion of this subject is by Melton,<sup>7</sup> who classifies the formation of negative ions by electron bombardment under the following headings: (a) dissociative resonance capture,  $AB + e \rightarrow A\cdot + B^-$ ; (b) resonance capture,  $AB + e \rightarrow AB^-$ ; and (c) ion pair formation,  $AB + e \rightarrow A^+ + B^- + e$ .

In mechanisms a and b negative ions are formed exclusively by electron impact, whereas negative ion production by mechanism c may be induced by any ionizing radiation, e.g., photons,  $\alpha$  particles, etc., as

well as by electrons. Process a occurs when AB captures an electron and undergoes an electronic transition to give the negative ion  $B^-$  and the radical  $A\cdot$ . Process b is also initiated by electron capture. When AB captures a low-energy electron ( $<1$  e.v.), an excited negative species  $AB^{*-}$  is formed. This excited species may be stabilized by collision with a neutral molecule or by radiation; otherwise the captured electron is expelled. Dissociation into  $A\cdot$  and  $B^-$  will occur if the captured electron has sufficient energy to produce an electronic transition to a higher energy than that of the dissociation energy. In the generation of negative ions by process c the molecule after electron impact receives sufficient energy to dissociate into  $A^+$  and  $B^-$ , both of which may be in the excited state.

Under the normal operating conditions (50–70 e.v.) of a mass spectrometer, all three processes may occur. As they are pressure dependent in different ways, the relative intensities of negative ion mass spectra change with sample pressure. A further complication is the low yield of negative ions as compared with positive ions, generally by a factor of  $10^3$  lower. In an attempt to overcome these difficulties, Ardenne and his collaborators<sup>8</sup> have employed a gas discharge source (argon,  $10^{-2}$  mm.) with a sample partial pressure of approximately  $10^{-6}$  mm. The low-energy electrons created (2–4 e.v.) form negative ions by resonance capture (process b), which gives very little fragmentation. However, the high over-all source pressure ( $10^{-3}$ – $10^{-2}$  mm.) can cause ion–molecule reactions. For alcohols, species have been observed<sup>9</sup> corresponding to the combination of an alcoholate anion and a neutral molecule. This type of negative ion mass spectrometry has been employed in the determination of the molecular weights of steroids,<sup>10</sup> and natural products in general,<sup>11</sup> where the general absence of extensive fragment ions has been considered to be an advantage. However, recent

(1) For paper LXXII see A. M. Duffield, H. Budzikiewicz, and C. Djerassi, *J. Am. Chem. Soc.*, **87**, 2926 (1965).

(2) This study has been made possible by financial assistance from the National Institutes of Health (Grant No. AM-04257). The National Aeronautics and Space Administration (Grant No. NsG 81-60) provided funds for the purchase of the Atlas CH-4 mass spectrometer.

(3) The receipt of a Fulbright Travel Scholarship is gratefully acknowledged.

(4) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1964.

(5) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Structure Elucidation of Natural Products by Mass Spectrometry," Vol. I and II, Holden-Day, Inc., San Francisco, Calif., 1964.

(6) K. Biemann, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

(7) C. E. Melton in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press Inc., New York, N. Y., 1963, Chapter 4.

(8) M. v. Ardenne, *Z. Angew. Phys.*, **11**, 121 (1959).

(9) M. v. Ardenne, K. Steinfelder, and R. Tümmeler, *Z. physik. Chem. (Leipzig)*, **220**, 105 (1962); **221**, 240 (1963).

(10) M. v. Ardenne, K. Steinfelder, R. Tümmeler, and K. Schreiber, *Experientia*, **19**, 178 (1963).

(11) K. Schreiber, M. v. Ardenne, K. Steinfelder, and R. Tümmeler, 3rd International Symposium on Natural Products, Kyoto, Japan, April 1964.

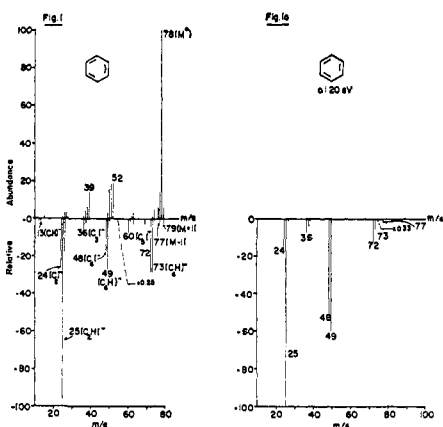


Figure 1. Positive and negative ion mass spectra of benzene.  
Figure 1a. 20-e.v. negative ion mass spectrum of benzene.

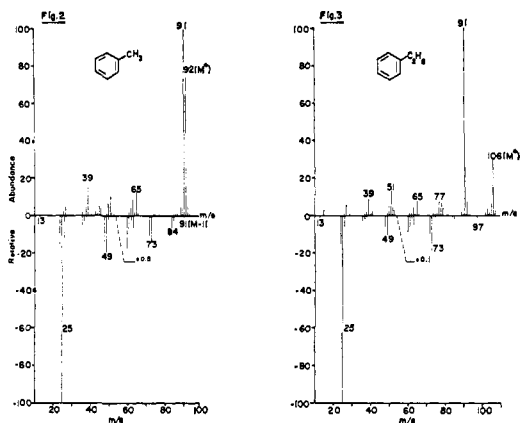


Figure 2. Positive and negative ion mass spectra of toluene.  
Figure 3. Positive and negative ion mass spectra of ethylbenzene.

experimental results<sup>12,13a</sup> show that fragmentation can occur. Thus, Huneck and Tümmeler have recently utilized the formation of major fragments by cleavage of ester linkages in this type of negative ion mass spectra in the determination of the structure of the trideside peltigerin.<sup>13b</sup> The relative ease of molecular weight determination is questionable since the spectra reported by Ardenne for condensed aromatic systems (see below) and steroids<sup>10</sup> exhibit  $M - 1$ ,  $M - 3$ ,  $(M - 1) + 16$ , and  $M + 16$  peaks. Unless one knows beforehand the approximate molecular weight, or the general behavior of the specific class to which the compound to be measured belongs, a decision as to which of the above peaks one is dealing with may be difficult.

Negative ion mass spectra at lower pressure ( $10^{-5}$ ) and high electron energy (50–70 e.v.) have been recorded for aliphatic hydrocarbons and alcohols by Melton and Rudolph,<sup>14</sup> the principal fragments corresponding to the acetylide anion ( $\text{HC}\equiv\text{C}^-$ ) and its higher analogs. An area in which negative ion mass spectra have been found to have certain advantages over positive ion mass spectra is in the investigation of

(12) M. v. Ardenne, R. Tümmeler, E. Weiss, and T. Reichstein, *Helv. Chim. Acta*, **47**, 1032 (1964).

(13) (a) K. Mothes, H. R. Schute, P. Müller, M. v. Ardenne, and R. Tümmeler, *Z. Naturforsch.*, **19B**, 1161 (1964); (b) S. Huneck and R. Tümmeler, *Ann.*, in press. We are indebted to Dr. Huneck for an advance copy of the manuscript.

(14) C. E. Melton and P. S. Rudolph, *J. Chem. Phys.*, **31**, 1485 (1959).

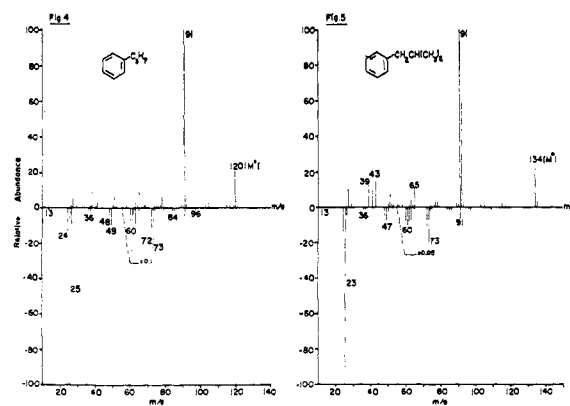


Figure 4. Positive and negative ion mass spectra of *n*-propylbenzene.  
Figure 5. Positive and negative ion mass spectra of isobutylbenzene.

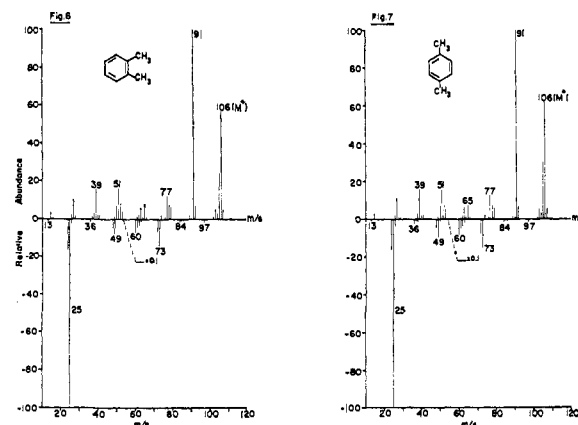


Figure 6. Positive and negative ion mass spectra of *o*-xylene.  
Figure 7. Positive and negative ion mass spectra of *p*-xylene.

polyhalogenated molecules, especially fluorocarbons,<sup>15</sup> where the tendency to form negative molecular ions is high compared with fragment ions.

**Tabulation of Results.** The spectra are presented in this paper in the "icicle fashion," with the relative abundance of the fragments plotted positive for the positive ion mass spectra and negative, to the same zero line, for the negative ion spectra (see Figures 1–35).

## Discussion

**1. Aromatic Compounds. A. Benzene and Alkylbenzenes.** The negative and positive ion<sup>16</sup> mass spectra of benzene, toluene, ethylbenzene, *n*-propylbenzene, *o*-xylene, and *p*-xylene are shown in Figures 1–7. The very large fragmentation observed in the negative ion mass spectra with their base peak at  $m/e$  25 ( $\text{HC}\equiv\text{C}^-$ ) is in marked contrast to their positive ion counterparts where the base peak is either the molecular ion (Figure 1) or the tropylium ion  $\text{C}_7\text{H}_7^+$ ,  $m/e$  91 (Figures 2–7). This difference is readily understood as the production of a negative molecular ion from benzene requires the insertion of an electron into a nonbonding orbital, the introduced instability being

(15) J. v. Hoene and W. H. Hickam, *ibid.*, **32**, 876 (1960).

(16) The positive ion mass spectra were taken from the "Catalog of Mass Spectral Data," American Petroleum Institute Research Project 44, Carnegie Institute of Technology, Pittsburgh, Pa., unless otherwise stated.

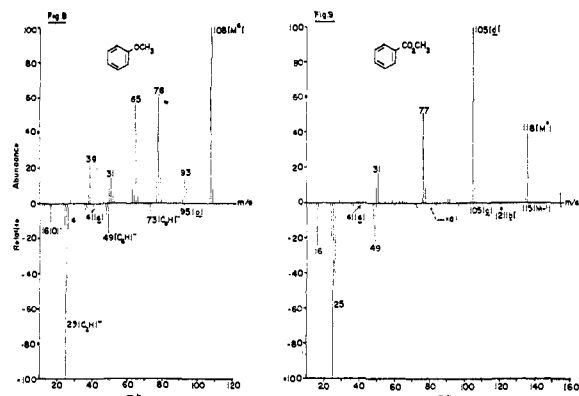


Figure 8. Positive (see C. S. Barnes and J. L. Occolowitz, *Australian J. Chem.*, **16**, 219 (1963)) and negative ion mass spectra of anisole.

Figure 9. Positive (see F. W. McLafferty and R. S. Gohlke, *Anal. Chem.*, **31**, 2076 (1959)) and negative ion mass spectra of methyl benzoate.

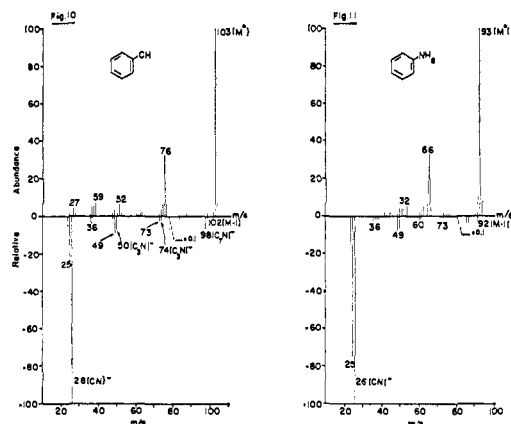


Figure 10. Positive and negative ion mass spectra of benzonitrile. Figure 11. Positive (see J. Momigny, *Bull. Soc. Roy. Sci. Liege*, **22**, 541 (1953)) and negative ion mass spectra of aniline.

released by extensive fragmentation. The most intense peaks ( $m/e$  25, 49, 73, and 97) in the spectra (e.g., Figure 3) correspond to a series of acetylide anions  $C_nH^-$  ( $n = 2, 4, 6$ , and  $8$ ). The remaining peaks ( $m/e$  24, 36, 48, 60, 72, 84, and 96—see, for instance, Figure 4) are due to  $C_n^-$  ( $n = 1$  to  $8$ ) and show a maximum for even values of  $n$ . These results are analogous to those reported<sup>14</sup> for the negative ion mass spectra of aliphatic hydrocarbons. The very weak  $M - 1$  peak observed for benzene (Figure 1) and toluene (Figure 2) is in contrast with the observations of Ardenne who reported<sup>17</sup> both  $M - 1$  and  $M - 3$  peaks for a number of condensed aromatic systems, but this apparent discrepancy is readily understood in view of the different experimental techniques (*vide supra*). In the other spectra (Figure 3–7) no peaks were detected in the molecular ion region. To check the effect of lowering the ionization potential on the intensity of the fragments the negative ion spectrum of benzene was repeated (Figure 1a) at 20 e.v. The intensity of the peaks at  $m/e$  48, 49, 72, and 73 is increased by a factor of 2–3 at the expense of the  $m/e$  24 and 25 peaks, although the intensity of the  $M - 1$  peak ( $m/e$  77) remains un-

(17) M. v. Ardenne, K. Steinfeld, and R. Tümmeler, *Angew. Chem.*, **73**, 136 (1961).

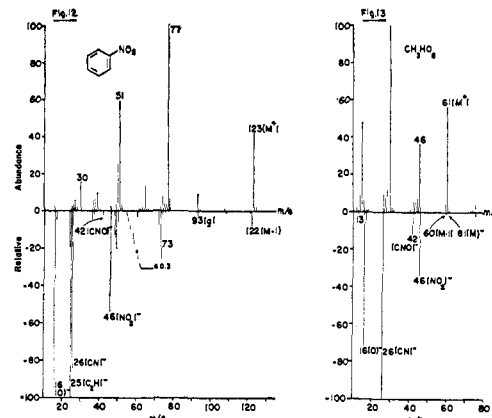
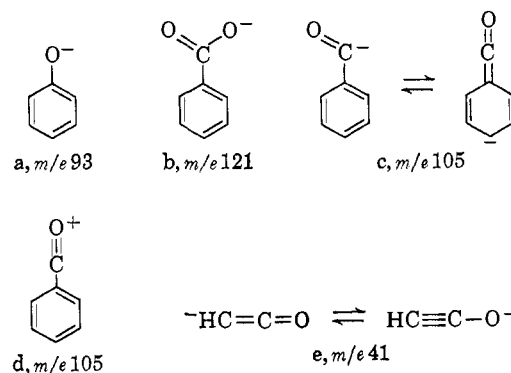


Figure 12. Positive and negative ion mass spectra of nitrobenzene. Figure 13. Positive (see J. Collin, *Bull. Soc. Roy. Sci. Liege*, **23**, 194 (1954)) and negative ion mass spectra of nitromethane.

changed, which indicates, as expected, that the complete fragmentation to  $HC\equiv C^-$  requires more energy than the formation of  $HC\equiv CC\equiv C^-$  ( $m/e$  49) and  $HC\equiv CC\equiv CC\equiv C^-$  ( $m/e$  73).

**B. Benzene Derivatives.** The negative ion mass spectra of anisole, methyl benzoate, benzonitrile, aniline, and nitrobenzene were measured for comparison with their positive ion spectra (Figures 8–12) and with the negative ion spectrum of benzene (Figure 1). In contrast to the alkylbenzenes, all of the derivatives, with the exception of anisole (Figure 8), show  $M - 1$  peaks. It is pertinent to note that the negative ion spectra again show evidence for considerable fragmentation as compared to their positive ion mass spectra. The negative ion mass spectra of anisole (Figure 8) and methyl benzoate (Figure 9), while being very similar to those of benzene (Figure 1) and toluene (Figure 2), exhibit additional peaks due to the presence of oxygen atom(s). Weak  $M - 15$  peaks ( $m/e$  93 and  $m/e$  121) correspond to the phenolate (a) and benzoate (b) anions while the  $m/e$  (c) peak in the spectrum of methyl benzoate is analogous to the  $m/e$  105 peak (d) in the positive ion spectrum. Two further oxygen-containing peaks, to which attention may be drawn (e.g., Figure 8), are those at  $m/e$  16 ( $O^-$ ) and  $m/e$  41 (e, the ketene anion).



The negative ion mass spectra of benzonitrile (Figure 10) and aniline (Figure 11) are again similar to those of benzene and toluene, but exhibit their base peak at  $m/e$  26 ( $CN^-$ ). This peak is also a very intense one in the spectrum (Figure 12) of nitrobenzene, which reflects

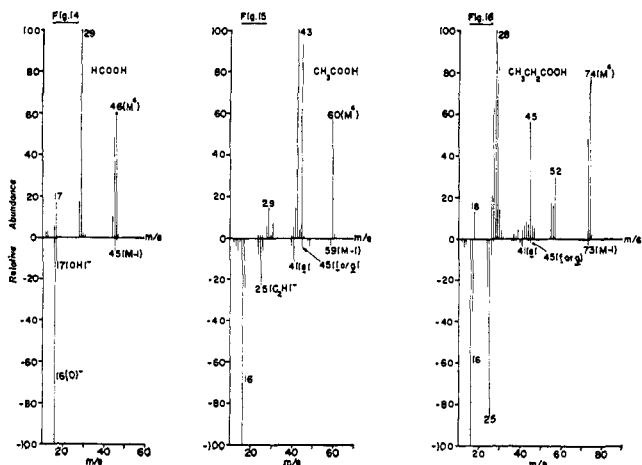


Figure 14. Positive and negative ion mass spectra of formic acid.  
 Figure 15. Positive and negative ion mass spectra of acetic acid.  
 Figure 16. Positive and negative ion mass spectra of propionic acid.

the greater stability of cyanide anion over the acetylide anion. The spectrum of nitrobenzene shows three further peaks worthy of mention, namely at  $m/e$  42 ( $-\text{CNO}$ ),  $m/e$  46 ( $-\text{NO}_2$ ), and  $m/e$  93, which corresponds to the loss of NO to give the phenolate anion  $a$ . A similar rearrangement has been observed in the positive ion mass spectra of aromatic nitro compounds.<sup>18</sup> It is interesting to note that the negative ion mass spectrum (Figure 13) of nitromethane shows marked similarities to that of nitrobenzene, even as far as the intensity of the common peaks is concerned.

2. *Aliphatic Compounds. A. Carboxylic Acids.* The negative ion mass spectra of formic acid, formic acid-*d* (HCOOD), and formic-*d* acid (DCOOH) have been studied by Ropp and Melton.<sup>19</sup> These workers showed that negative ion formation in this acid occurs predominantly by the loss of the hydroxyl hydrogen. Deuterium migration, although an observable process in the positive ion spectrum, was not noted in negative ion formation. Ropp and Melton<sup>19</sup> also showed that the relative ease of negative ion formation in the gas phase in three aliphatic acids (Table I) is roughly parallel to that of their ionic dissociation in aqueous solution.

Table I. Relative Abundance<sup>a</sup> of Carboxylate Anions in Negative Ion Mass Spectrometry<sup>b</sup>

| Acid                                 | Negative ion                                     | Relative abundance <sup>a</sup> |
|--------------------------------------|--|---------------------------------|
| HCOOH                                | HCOO <sup>-</sup>                                | 100                             |
| CH <sub>3</sub> COOH                 | CH <sub>3</sub> COO <sup>-</sup>                 | 40                              |
| CH <sub>3</sub> CH <sub>2</sub> COOH | CH <sub>3</sub> CH <sub>2</sub> COO <sup>-</sup> | 40                              |

<sup>a</sup> Per cent of base peak. <sup>b</sup> See Ropp and Melton, ref. 19.

The negative ion mass spectra (Figures 14–18) of formic, acetic, propionic, butyric, and isobutyric acids recorded in this study differ markedly from those reported by Ropp and Melton<sup>19</sup> in the intensity of the

(18) J. H. Benyon, R. A. Saunders, and A. E. Williams, *Ind. Chim. Belges*, 311 (1964).

(19) G. A. Ropp and C. E. Melton, *J. Am. Chem. Soc.*, **80**, 3509 (1958).

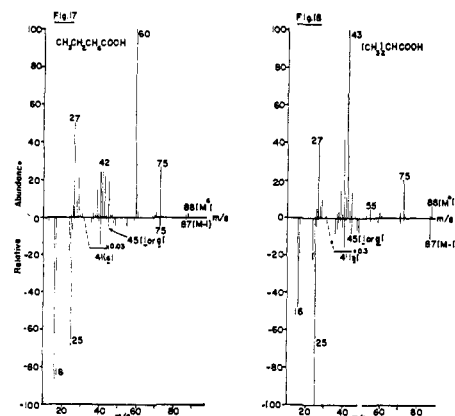


Figure 17. Positive and negative ion mass spectra of butyric acid.  
 Figure 18. Positive and negative ion mass spectra of isobutyric acid.

molecular ion region. We find the base peak for formic, acetic, propionic, and butyric acids to occur at  $m/e$  16 ( $\text{O}^-$ ), and at  $m/e$  25 ( $\text{HC}\equiv\text{C}^-$ ) for isobutyric acid (Figure 18). However, the ease of formation of the acid anion (Table II) for these five acids is again roughly parallel to that of their ionic dissociation in aqueous solution.

Table II. Relative Abundance ( $\Sigma_{12}$ ) of Carboxylate Anions in Negative Ion Mass Spectrometry<sup>a</sup>

| Acid   | Negative ion   | Relative abundance, $\Sigma_{12}$ |
|--|--|-----------------------------------|
| HCOOH  | HCOO <sup>-</sup>  | 5.88                              |
| CH <sub>3</sub> COOH                                 | CH <sub>3</sub> COO <sup>-</sup>                                 | 1.93                              |
| CH <sub>3</sub> CH <sub>2</sub> COOH                 | CH <sub>3</sub> CH <sub>2</sub> COO <sup>-</sup>                 | 1.06                              |
| CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> COOH | CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> COO <sup>-</sup> | 0.83                              |
| (CH <sub>3</sub> ) <sub>2</sub> CHCOOH               | (CH <sub>3</sub> ) <sub>2</sub> CHCOO <sup>-</sup>               | 1.73                              |

<sup>a</sup> Present work.

The quantitative discrepancies between our results and those of Ropp and Melton<sup>19</sup> do not appear to result from the difference in the ionizing voltage (70 vs. 50 e.v.<sup>19</sup>) as we have shown that changing from 70 (Figure 1) to 20 e.v. (Figure 1a) does not increase the relative intensity of the  $M - 1$  peak in the negative ion spectrum of benzene. It is more probable that differences in the ion source pressure ( $5 \times 10^{-7}$  vs.  $1 \times 10^{-5}$  mm.<sup>19</sup>) and in the geometry of the ion source are responsible for this lack of agreement, which again emphasizes the much greater sensitivity of negative ion mass spectrometry toward experimental variations as compared to positive ion mass spectrometry. Aside from the  $m/e$  41 peak (e), which is virtually ubiquitous in oxygen-containing compounds, the spectra (Figures 15–18) exhibit an  $m/e$  45 peak, which corresponds either to the formic acid anion f or the anion g.



B. *Esters.* The negative ion mass spectra (Figures 19–23) of ethyl formate, methyl acetate, ethyl acetate, *n*-butyl acetate, and methyl isobutyrate exhibit at least as much fragmentation as their corresponding positive ion counterparts. Besides the expected peaks (see

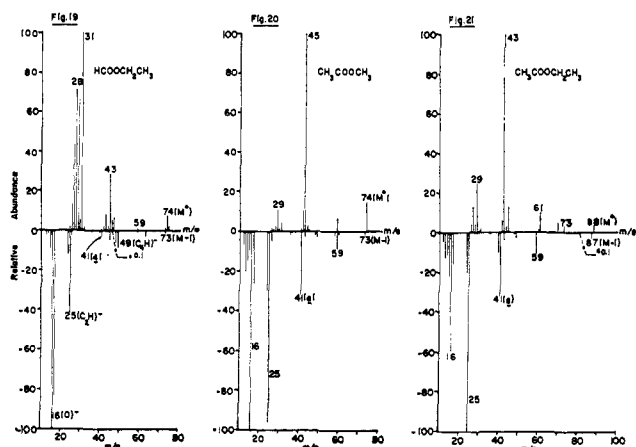


Figure 19. Positive and negative ion mass spectra of ethyl formate.  
 Figure 20. Positive and negative ion mass spectra of methyl acetate.  
 Figure 21. Positive and negative ion mass spectra of ethyl acetate.

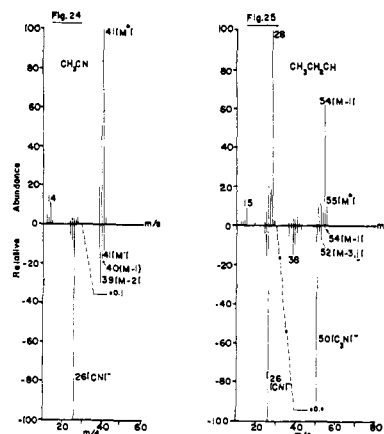


Figure 24. Positive and negative ion mass spectra of acetonitrile.  
 Figure 25. Positive and negative ion mass spectra of propionitrile.

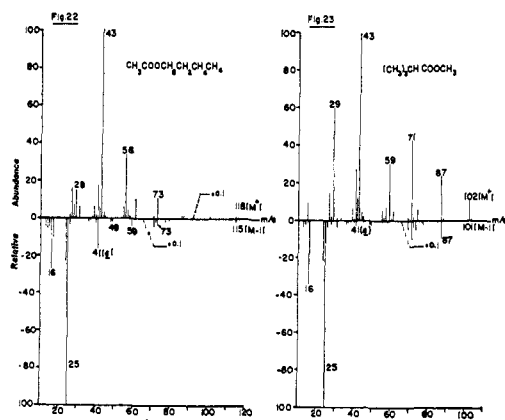


Figure 22. Positive and negative ion mass spectra of *n*-butyl acetate.  
 Figure 23. Positive (see J. H. Beynon, R. A. Saunders, and A. E. Williams, *Anal. Chem.*, **33**, 221 (1961)) and negative ion mass spectra of methyl isobutyrate.

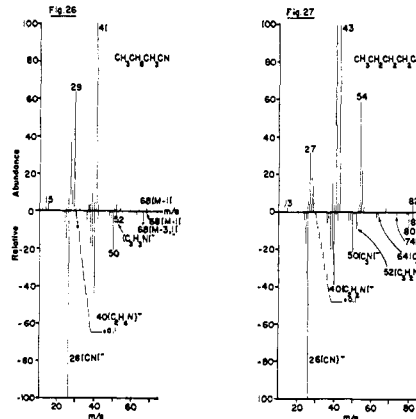
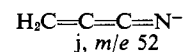
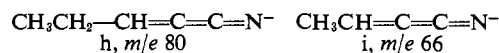


Figure 26. Positive and negative ion mass spectra of *n*-butyronitrile.  
 Figure 27. Positive and negative ion mass spectra of *n*-valeronitrile.

*m/e* 25, 49, and 73 in Figure 22) of the acetylide (C<sub>*n*</sub>H<sup>-</sup>) and ketene (e) anions all the spectra show peaks corresponding to O-alkyl cleavage at *m/e* 45 (Figure 19), *m/e* 59 (Figures 20–22), and *m/e* 87 (Figure 23), to give the acid anions (HCO<sub>2</sub><sup>-</sup>, CH<sub>3</sub>CO<sub>2</sub><sup>-</sup>, and C<sub>4</sub>H<sub>7</sub>CO<sub>2</sub><sup>-</sup>). The *m/e* 41 peak in methyl acetate (Figure 20) was shown to arise completely from the acid moiety, as this peak remained at *m/e* 41 in methyl-*d*<sub>3</sub> acetate.<sup>20</sup>

C. *Nitriles*. The negative ion mass spectra of acetonitrile, propionitrile, *n*-butyronitrile, and *n*-valeronitrile (Figures 24–27) display two series of peaks (e.g., Figure 27): C<sub>*n*</sub>N<sup>-</sup> (*n* = 1, 3, and 5) at *m/e* 26, 50, and 74, and C<sub>*n*</sub>H<sub>2</sub>N<sup>-</sup> (*n* = 2, 3, and 4) at *m/e* 40, 52, and 64. The former series (*n* = 1, 3, 5, and 7) is also present in the spectrum (Figure 10) of benzonitrile. The base peak in all cases is at *m/e* 26 (CN<sup>-</sup>), while the corresponding acetylide (HC≡C<sup>-</sup>) peak *m/e* 25 is comparatively weak in all cases. Besides showing reasonably intense *M* – 1 peaks, all the spectra except that (Figure 24) of acetonitrile display a stronger *M* – 3

peak which may be represented as h for valeronitrile, i for *n*-butyronitrile, and j for propionitrile.



D. *Ketones and Alcohols*. The negative ion mass spectra<sup>21</sup> of acetone (Figure 28) and methyl ethyl ketone (Figure 29) are virtually identical with those of isopropyl and *sec*-butyl alcohol (Figures 30 and 31) recorded by Melton and Rudolph<sup>14</sup> allowing for the difference in mass and the appearance of an intense *m/e* 17 peak (OH<sup>-</sup>) in the alcohol spectra. The utility of negative ion mass spectrometry among alcohols (notably for determination of molecular weight) has already been discussed.<sup>22</sup> A striking example is the mass spectrum of *t*-butyl alcohol, where the *M* – 1 peak in the negative ion mass spectrum can be seen without difficulty, while no peaks are found in the molecular ion region of the positive ion spectrum.

The negative ion mass spectra of acetone, methyl ethyl ketone, and the cyclic ketones, cyclobutanone, cyclopentanone, cyclohexanone, and cycloheptanone

(20) The authors thank Mr. H. Monteiro of this laboratory for a sample of methyl-*d*<sub>3</sub> acetate.

(21) For a discussion of positive ion mass spectra of ketones see ref. 4, Chapter 1.

(22) Reference 4, p. 45.

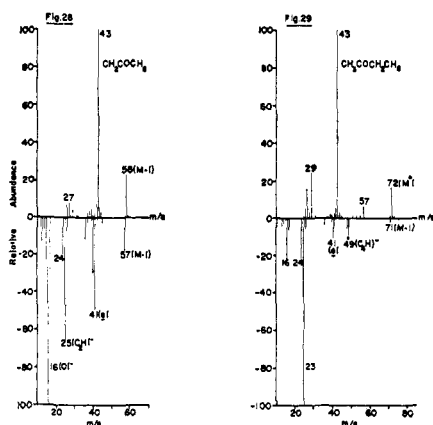


Figure 28. Positive and negative ion mass spectra of acetone.  
 Figure 29. Positive and negative ion mass spectra of methyl ethyl ketone.

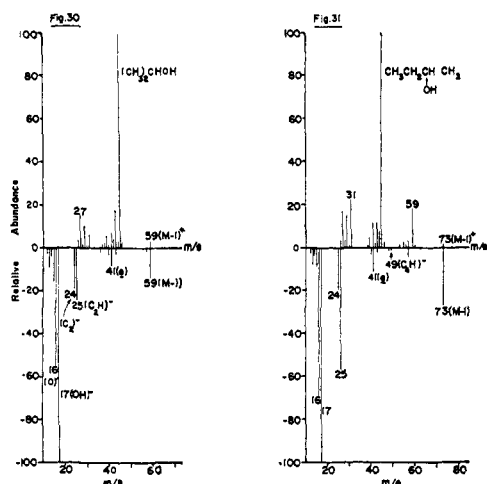


Figure 30. Positive and negative<sup>14</sup> ion mass spectra of isopropyl alcohol.  
 Figure 31. Positive and negative<sup>14</sup> ion mass spectra of *sec*-butyl alcohol.

(Figures 32–35), show the expected peaks at  $m/e$  16 ( $O^-$ ), 24 ( $C_2^-$ ), 25 ( $HC\equiv C^-$ ), and 41 (e) for oxygen-containing compounds. An additional peak in the spectra (Figures 34 and 35) of cyclohexanone ( $m/e$  69) and cycloheptanone ( $m/e$  83) corresponding to  $M - (1 + 28)$  may be analogous to the loss of 28 mass units ( $H_2C=CH_2$ ) from the molecular ion in their positive ion spectra.<sup>23</sup> The negative ion mass spectrum of cyclohexanone-2,2,6,6- $d_4$ <sup>24</sup> establishes the origin of the  $M - 1$ ,  $m/e$  41, and  $m/e$  25 peaks. The  $M - 1$  peak is shifted to  $M - 2$ , showing that an  $\alpha$ -hydrogen is lost in the formation of the  $M - 1$  ion; the  $m/e$  41 peak is moved quantitatively to  $m/e$  42, demonstrating that it corresponds to species e; the  $m/e$  25 peak is split almost equally between  $m/e$  25 and  $m/e$  26, which is in accord with its formulation as  $C_2H^-$ .

### Conclusion

It appears that negative ion mass spectra measured with a commercial instrument (Atlas CH-4) and the

(23) J. H. Beynon, R. A. Saunders, and A. E. Williams, *Appl. Spectry.*, **14**, 95 (1960).

(24) The authors thank Dr. P. Brown of this laboratory for a sample of this labeled ketone.

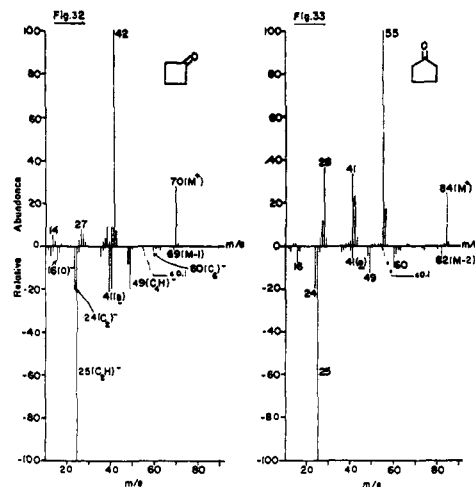


Figure 32. Positive (see H. J. Hofman, *Tetrahedron Letters*, **34**, 2329 (1964)) and negative ion mass spectra of cyclobutanone.  
 Figure 33. Positive and negative ion mass spectra of cyclopentanone.

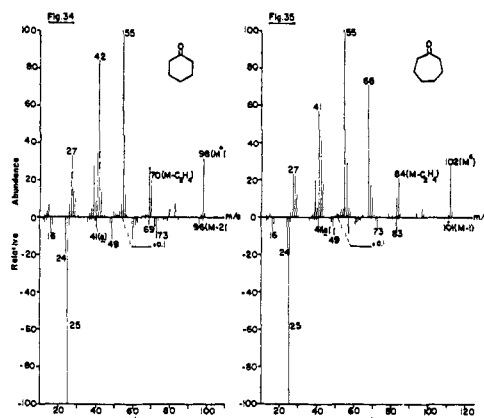


Figure 34. Positive and negative ion mass spectra of cyclohexanone.  
 Figure 35. Positive (see J. H. Beynon, R. A. Saunders, and A. E. Williams, *Appl. Spectry.*, **14**, 95 (1960)) and negative ion mass spectra of cycloheptanone.

electron energies used (20–70 e.v.) are not suitable either for molecular weight or for structure determination. With regard to the fragmentation observed, it is clear that hydrogen stripping of the organic compounds (at least of the type studied in our laboratory) to acetylide and polyacetylide anions occurs. If heteroatoms are present, abundant species corresponding to stable anions ( $OH^-$ ,  $CN^-$ , etc.) are formed. The over-all similarity of the spectra of alkylbenzenes and aliphatic hydrocarbons, alcohols, and ketones, acids and esters, etc., shows that the type of cleavage observed does not reflect the type of functional group, but only the nature of the heteroatom present in the molecule.

The technique used by Melton<sup>7</sup> seems to give similar results. There is, however, a marked contrast if one employs the operational technique developed by Ardenne.<sup>8</sup> In general, ions occur predominantly in the molecular weight region, and if fragmentation does proceed, it does not involve complete degradation of the molecules to acetylide, etc., species. However, since due to the high source pressure ion-molecule reactions

seem to be quite frequent, difficulties in the determination of molecular weights may be encountered. Nevertheless, the results obtained by Ardenne and his group combined with ours seem to indicate that negative ion mass spectrometry using low-energy electrons, but employing operating conditions where ion-molecule reactions are minimized, may lead to results useful for molecular weight and structure determination of organic compounds. Further research in this direction is certainly warranted.

### Experimental

This investigation was carried out using a standard Atlas CH-4 mass spectrometer equipped with an AN4 ion source fitted with a tungsten ribbon filament. All

the spectra were determined with an ionizing current of 40  $\mu$ a. and an ionizing energy of 70 e.v. (except for Figure 1a). The polarity of the collector ion lens was reversed to increase sensitivity and the electron multiplier was run at 2 kv. The source and sample reservoirs were maintained at a temperature of 80°. All the spectra were obtained with a source pressure between  $1 \times 10^{-7}$  and  $5 \times 10^{-7}$  mm. The mass of the individual peaks was determined using the "Masscontactor" of the instrument rather than the mass marker, which can only be employed for positive ion spectra.

*Acknowledgment.* The authors gratefully acknowledge the assistance of Dr. W. H. Nickels of Atlas Werke, Bremen, for his help in the initial stages of this study.

## Condensations of Carbonyl Compounds at the $\gamma$ -Position of $\beta$ -Ketoaldehydes by Means of Potassium Amide or Sodium Hydride<sup>1</sup>

Thomas M. Harris, Sandra Boatman, and Charles R. Hauser

Contribution from the Department of Chemistry, Duke University, Durham, North Carolina. Received February 25, 1965

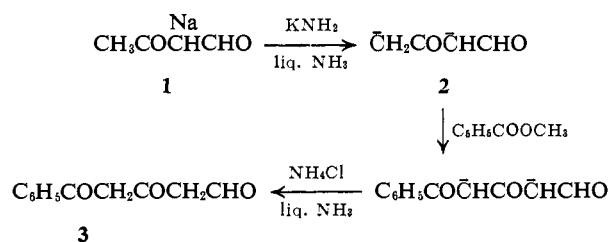
Condensations of carbonyl compounds at the  $\gamma$ -positions of  $\beta$ -ketoaldehydes were effected through the dicarbanions, which were prepared by means of potassium amide in liquid ammonia. The dicarbanions were aroylated with methyl benzoate and condensed with benzophenone and with chalcone in aldol-type and conjugate additions, respectively.  $\gamma$ -Aroylations of  $\beta$ -ketoaldehydes were also effected by means of sodium hydride. These three types of  $\gamma$ -condensations complement the earlier reported  $\gamma$ -alkylations and extend considerably the usefulness of  $\beta$ -ketoaldehyde dicarbanions in synthesis.

Previous papers have described alkylations at the  $\gamma$ -methyl,<sup>2</sup>  $\gamma$ -methylene,<sup>3</sup> and  $\gamma$ -methinyl groups of  $\beta$ -ketoaldehydes with alkyl halides. This novel mode of alkylation was effected through the  $\beta$ -ketoaldehyde dicarbanions, which were prepared by means of potassium amide in liquid ammonia.

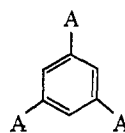
The present paper describes some examples of three other types of condensations at the  $\gamma$ -methyl or  $\gamma$ -methylene groups of appropriate  $\beta$ -ketoaldehydes with carbonyl compounds. Also another  $\gamma$ -alkylation is described.

*$\gamma$ -Aroylations.* Four  $\beta$ -ketoaldehyde dicarbanions were prepared and aroylated with methyl benzoate. The simplest dicarbanion (2) was prepared from mono-

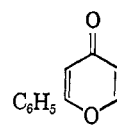
sodioacetoacetaldehyde (1)<sup>4</sup> and 1 molecular equiv. of potassium amide in liquid ammonia and benzoylated with 0.5 molecular equiv. of the ester to form diketoaldehyde 3 in 52% yield. Similar aroylations of  $\beta$ -diketone dicarbanions have been effected previously.<sup>5</sup>



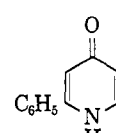
As might be expected, diketoaldehyde 3 readily underwent self-condensation, apparently to form 4. This reaction occurred in low (4%) yield even during the preparation (isolation) of 3, and in good yield on refluxing an ethereal solution of 3. Interestingly, this intermolecular reaction predominated over pyrone formation on treatment of 3 with sulfuric acid, 4 and 5 being obtained in yields of 67 and 25%, respectively. Similar treatment of a 1,3,5-triketone affords exclusively



4, A = COCH<sub>2</sub>COC<sub>6</sub>H<sub>5</sub>



5



6

(1) This investigation was supported by Public Health Service Research Grant No. USPHS CA 04455-06 and by National Science Foundation Research Grant No. NSF GP 2274.

(2) T. M. Harris, S. Boatman, and C. R. Hauser, *J. Am. Chem. Soc.*, **85**, 3273 (1963).

(3) S. Boatman, T. M. Harris, and C. R. Hauser, *ibid.*, **87**, 82 (1965).

(4) This sodio  $\beta$ -ketoaldehyde is readily prepared by acylation of acetone with ethyl formate by means of sodium methoxide; see R. P. Mariella, "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p. 210.