Some Novel Eliminations of Neutral Fragments from Ions in Mass Spectrometry

Part II. Loss of Non-Terminal Carbon Atoms as Methyl Radicals *

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(Z. Naturforschg. **21 a**, 604—608 [1966]; received 27 November 1965)

The loss of methyl radicals from diphenylmethyl, 1,2-diphenylethyl and stilbene ions in the mass spectrometer has been studied by means of ^{2}H and ^{13}C labelling. Mechanisms by which these methyl radicals are eliminated have been proposed.

A possible mode of fragmentation of ions in mass spectrometry is as follows:

$$\mathrm{A-B-C^+ \rightarrow A-C^+ + B}\,.$$

Recently such elimination of the neutral molecules CO, HCN, C_2H_4, N_2H_2, HNCO from non-terminal positions in open-chain ions in the mass spectrometer has been reported[1–4], but the similar loss of methyl radicals has only recently been observed[5, 6].

The work described here concerns the loss of a non-terminal carbon atom as a methyl radical first observed during a study of the mass spectra of some sulphoxides. It was found that the 1,2-diphenylethyl ion produced by fragmentation of 1,2-diphenylethyl methyl sulphoxide showed a considerable loss of a methyl radical. It was found, too, that the diphenylmethyl ion produced from diphenylmethyl bromide loses methyl, as does the parent ion from stilbene.

The three processes may be represented formally as:

$$\begin{aligned}
&\mathrm{C_6H_5-CH_2-{}^+CH-C_6H_5} &&\rightarrow \mathrm{C_{13}H_{10}}^{+\cdot} + \mathrm{CH_3}^{\cdot}\\
&\mathrm{C_6H_5-{}^+CH-C_6H_5} &&\rightarrow \mathrm{C_{12}H_8}^{+\cdot} + \mathrm{CH_3}^{\cdot}\\
&\mathrm{C_6H_5-{}^{\cdot}CH-{}^+CH-C_6H_5} &&\rightarrow \mathrm{C_{13}H_9}^{+} + \mathrm{CH_3}^{\cdot}
\end{aligned}$$

the overall reaction paths being verified by metastable ions.

In order to elucidate the mechanism for this unusual process, experiments have been carried out on ^{2}H- and ^{13}C-labelled 1,2-diphenylethyl chloride (I) (a more convenient source of the 1,2-diphenylethyl ion), diphenylmethyl bromide (II), and stilbene (III). The mass spectra of the unlabelled compounds are shown in Fig. 1. The base peak in the chloride (I) is formed by the tropylium ion at *m/e* 91, but the ion of *m/e* 166 due to loss of a methyl radical from the 1,2-dimethylethyl ion itself has an intensity 5% of the base peak.

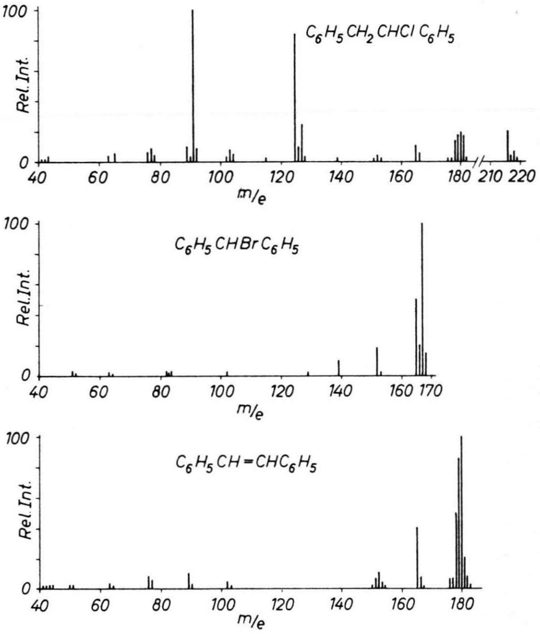

Fig. 1.

The bromide (II) shows no parent ion and the base peak in the spectrum is due to the diphenyl-

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* Part I, J. Chem. Soc. 1966, (C), 358.

[1] R. A. W. JOHNSTONE and B. J. MILLARD, J. Chem. Soc. 1966, (C), 358.

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methyl ion. The ion at *m/e* 152 produced by loss of a methyl radical from the base peak has an intensity 10% of the base peak.

The loss of a methyl radical from stilbene (III) is much more important than from parent ions produced by (I) and (II). In this case the *M*-15 ion is 40% of the intensity of the parent ion (also the base peak). As this loss of a methyl radical is such an important mode of fragmentation, the energy involved in the process is of considerable interest. The difference in appearance potentials between the stilbene parent ion and the *M*-15 ion was measured in the usual manner and found to be (4.10 ± 0.05) eV.

The energy required to expel a methyl radical from stilbene must contain an energy term (E_1) for the decomposition of an ion-radical at the final stage, and also an energy term (E_2) required to form this ion-radical.

Thus, $E_1 + E_2 = 4.1$ eV.

From the ionisation potentials for ethylbenzene and the benzyl radical (9.12 and 7.76 eV respectively [7, 8]), and the $C_6H_5CH_2-CH_3$ bond energy (2.73 eV) [9], it is calculated that only 1.37 eV is required to release the methyl radical from the ethylbenzene ion-radical.

For the process (i)

$$C_6H_5CH_2-CH_3^{\cdot+} \rightarrow C_6H_5CH_2^{+} + CH_3^{\cdot}, \quad E_1 = 1.37\ \text{eV},$$

and for the process (ii)

$$C_6H_5CH_3^{\cdot+} \rightarrow C_6H_5^{+} + CH_3^{\cdot}, \quad E_1 = 4.88\ \text{eV}\ ^{10}.$$

As energy must be needed to rearrange the stilbene ion, the value of 4.1 eV is consistent with the methyl radical being lost from an alkyl side chain as in process (i), rather than from an aromatic ring, as in process (ii). The mechanism described later utilises this fact.

The energy required to rearrange the stilbene ion-radical to the final structure from which the methyl radical is lost is given by:

$$E_2 = 4.10 - 1.37 \cong 2.7\ \text{eV}.$$

The metastable peak for the process of losing a methyl radical is quite narrow and not flat-topped, so it is deduced that the departing methyl radical does not carry away a large amount of kinetic energy [11].

In the mass spectrum of diphenylmethyl bromide, the ion formed by elimination of a methyl radical occurs at *m/e* 152. The intensities of the peaks about *m/e* 152 are shown in Table 1, for diphenylmethyl bromide (II), 1-^{2}H-phenyl-1-phenylmethyl bromide (IV), and 1-phenyl-1-(2,4,6-^{2}H-phenyl) methyl bromide (V), the intensities having been corrected for naturally occurring ^{13}C isotopes.

m/e	(II)	(IV)	(V)
155	–	–	69.5
154	–	–	100.0
153	–	100.0	38.4
152	100.0	89.0	–

Table 1. Partial mass spectra of diphenylmethyl bromides (II, IV and V).

It can be seen that substitution with one ^{2}H atom in the ortho position causes the ion of *m/e* 152 to split into two parts at *m/e* 152 and *m/e* 153. The ion at *m/e* 153 is due to the loss of a CH_3 radical and that at *m/e* 152 to loss of a $CH_2{}^2H$ radical from the diphenylmethyl ion, showing that ortho hydrogen atoms of the benzene rings are involved in the loss of the methyl group. The ratio (0.89) of the intensities of the ions of *m/e* 152 and *m/e* 153 is in excellent agreement with the generally accepted figure of 0.88 for the isotope effect involved in a transfer of ^{2}H atoms as compared with ^{1}H atoms [12]. If the central CH unit is lost, two hydrogen atoms must be provided from the phenyl rings to form a methyl group. These hydrogen atoms could either come from the two ortho positions of one phenyl ring or one ortho position of each ring. Examination of the relevant peaks in the mass spectrum of the ^{2}H-labelled compound (V) shows that the radical lost has the composition CH_3, 33.4%; $CH_2{}^2H$, 48.1; $CH{}^2H_2$, 18.5%. If an ortho position in each ring is involved, only the $CH_2{}^2H$ radical should be lost, and if two ortho positions in the same ring are involved, only CH_3 and $CH{}^2H_2$ radicals can be lost. In fact, the observed values mean that both mechanisms operate simultaneously:

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[7] R. I. Reed, Ion Production by Electron Impact, Academic Press, New York 1962, p. 28.

[8] Ibid., p. 7.

[9] Ibid., p. 274.

[10] Ibid., p. 41.

[11] J. H. Beynon, R. A. Saunders, and A. E. Williams, Z. Naturforschg. **20 a**, 180 [1965].

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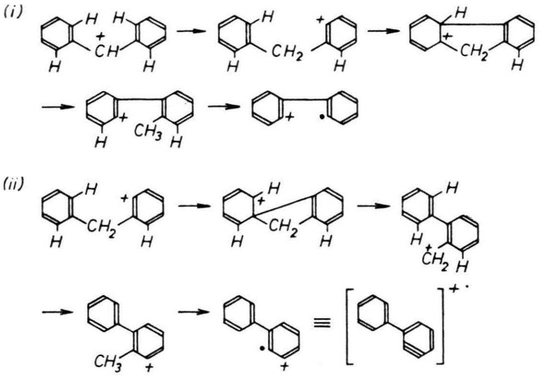


Table 2 shows the partial mass spectra of stilbene (III) and 2,2′-^{2}H-stilbene (VI), corrected for naturally occurring ^{13}C isotopes.

The two aromatic rings in the labelled stilbene (VI) had different isotopic contents. One ring contained 62.5% of ^{2}H in the ortho position and the other ring 85.5% in the ortho position. The values in Table 2 are not corrected for unlabelled material.

m/e	(III)	(VI)
167	—	86.4
166	—	100.0
165	100.0	24.7

Table 2.

Consider first the removal of ^{1}H or ^{2}H from an ortho position in the ring which is 62.5% labelled. Then,

$$\frac{\text{loss of } ^1\text{H}}{\text{loss of } ^2\text{H}} = \frac{137.5}{62.5 \times 0.88} = 2.5 : 1$$

(the factor 0.88 is included to allow for the isotope effect), and similarly, in the other ring,

$$\frac{\text{loss of } ^1\text{H}}{\text{loss of } ^2\text{H}} = \frac{114.5}{85.5 \times 0.88} = 1.52 : 1\,.$$

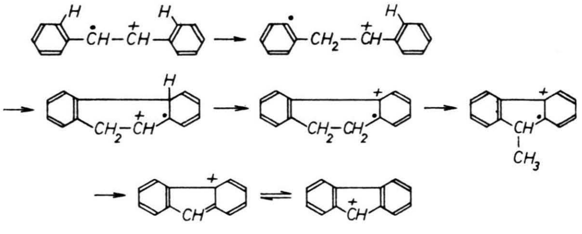
If the parent ion from the stilbene (VI) lost a central CH unit and one ortho hydrogen atom from each ring, the radical lost would have the composition

$$CH_3,\quad 2.5 \times 1.52 = 3.8\,,$$
$$CH_2\,^2H,\quad (2.5 \times 1) + (1.52 \times 1) = 4.02\,,$$
$$CH\,^2H_2,\quad 1 \times 1 = 1$$

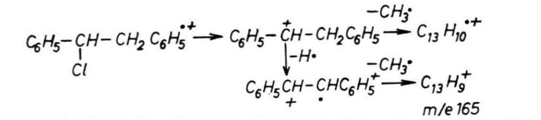
that is,

$$CH_3,\ 43.1\%;\quad CH_2\,^2H,\ 45.6\%;\quad CH^2H_2,\ 11.3\%.$$

It is found from the values given in Table 2 that the actual composition of the radical lost is CH_3, 40.9%; $CH_2\,^2H$, 47.4%; CH^2H_2, 11.7%, in excellent agreement with the calculated figures. The molecule does therefore lose one ortho hydrogen atom from each ring along with a central CH unit. The slight discrepancy in the figures is probably due to some measure of randomisation of the hydrogen atoms over the whole molecule. A possible mechanism is shown:



The elimination of a methyl radical from the 1,2-diphenylethyl ion produced from 1,2-diphenylethyl chloride (I) gives rise to an ion of m/e 166.



The partial spectra of 1,2-diphenylethyl chloride (I), 1-^{13}C-1,2-diphenylethyl chloride (VII), 1-^{2}H-1,2-diphenylethyl chloride (VIII) and 1-phenyl-2-(2-^{2}H-phenyl)-ethyl chloride (IX) are shown in Table 3, corrected for natural ^{13}C isotopes and unlabelled material.

m/e	(I)	(VII)	(VIII)	(IX)
167	—	41.9	25.7	24.9
166	34.2	100.0	100.0	100.0
165	100.0	43.0	52.4	36.4

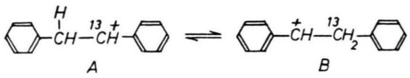
Table 3.

In the mass spectrum of the ^{13}C labelled compound (VII), the stilbene ion initially formed has the structure $(C_6H_5CH - {}^{13}CHC_6H_5)^{+\cdot}$, and ignoring the small isotope effect due to the ^{13}C atom, the methyl group lost from this ion will be half ^{12}C-methyl and half ^{13}C-methyl. Thus the peak of intensity 43.0 at m/e 165 due to loss of a methyl group from stilbene means that 43.0 units of the 100 units of intensity at m/e 166 also arise from the labelled stilbene. The remaining 57.0 units of intensity at m/e 166 are due to the loss of a ^{13}C-methyl radical from the diphenylethyl ion-radical, while the peak at m/e 167 of intensity 41.9 units is due to the loss of a ^{12}C-methyl radical from the diphenylethyl ion. Hence,

$$\frac{\text{loss of }^{13}\text{C-methyl}}{\text{loss of }^{12}\text{C-methyl}} = \frac{57.0}{41.9}$$

i. e. 57.7% of the ^{13}C-label is lost.

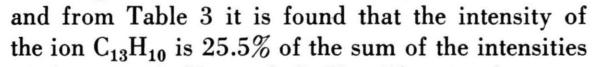
The fact that the label is neither completely retained nor completely lost means that considerable hydrogen migration occurs:



If complete equilibrium were attained, this ion would be 50% A and 50% B, and 50% of the label would be lost as a methyl group. If there was no hydrogen migration and the ion was 100% of form A, then loss of the CH_2 unit plus one ring hydrogen would involve no loss of label. If the CH unit plus two ring hydrogen atoms were lost, none of the label would remain. As the actual figure of 57.7% lies between 100% and 50%, the CH unit must be ejected along with two ring hydrogens, and the amount of equilibration of forms A and B which has occured equals $\frac{100-57.7}{50} \times 100\% = 84.5\%$.

As expected, studies at low electron volts show an increase in the amount of equilibration which occurs.

In the spectrum of the 1-^{2}H compound (VIII) the following possibilities arise:



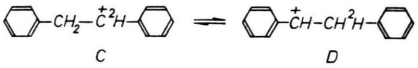
Comparison with the unlabelled compound (I) enables a calculation to be made of the proportion of the peak at m/e 166 due to the ion-radical $C_{13}H_{10}$. In the spectrum of the unlabelled compound (I), fragment ions are formed at m/e 165 and 166, and from Table 3 it is found that the intensity of the ion $C_{13}H_{10}$ is 25.5% of the sum of the intensities of the ions $C_{13}H_{10}$ and $C_{13}H_9$. Thus in the mass spectrum of the labelled compound (VIII) the sum of the intensities of the ions $C_{13}H_{10}$ and $C_{13}H_9{}^2H$ will be 25.5% of the total intensities of the ions at m/e 165, 166 and 167, that is

$$\frac{25.5}{100}(25.7 + 100.0 + 52.4) = 45.4 \text{ units.}$$

The intensity of the ion-radical at m/e 167, due to $C_{13}H_9{}^2H$ is 25.7 units, so that the intensity of the ion-radical $C_{13}H_{10}$ at m/e 166 is $45.4 - 25.7 = 19.7$ units.

$$\text{Thus,}\ \frac{\text{loss of } CH_2{}^2H}{\text{loss of } CH_3 + CH_2{}^2H} = \frac{19.7}{45.4} \times 100.0\% = 43.4\%$$

As in the ^{13}C compound, migration of hydrogen occurs:



and from the loss of 43.4% of ^{2}H the amount of equilibration which has occurred can be calculated as follows.

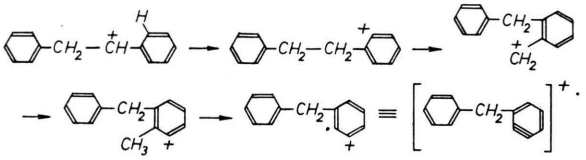
If complete equilibration was attained between ions C and D, one third of the ^{2}H atoms would appear on the CH and two thirds on the CH_2 parts of the ion. As the ^{13}C-labelled compound shows that the CH unit is lost as methyl, 33.3% of the ^{2}H content should be lost at the same time. If there was no hydrogen migration and the ion was exclusively of form C, 100% of the ^{2}H content would be lost, thus the amount of equilibration which has occurred is,

$$\frac{100-43.40}{100-33.33} \times 100\% = 84.9\%,$$

a value in excellent agreement with that (84.5%) calculated above for the ^{13}C-labelled compound, adding further support for the mechanism.

Similarly, from the mass spectrum of the labelled compound (IX) it can be shown that the methyl group lost contains 39.6% of its ^{2}H content. The previous calculations have shown that two ring hydrogen atoms are ejected in the methyl radical, giving rise to three possibilities:

(i) two ortho hydrogen atoms from both ortho positions of ring a; (ii) two ortho hydrogen atoms of ring b; (iii) one ortho hydrogen atom from each ring. If complete equilibration between E and F was attained, all three cases would result in a loss of 46.7% of the ^{2}H content, the isotope effect of 0.88 being included. If no hydrogen migration took place, and the ion was 100% form E, case (i) would give 100% loss, case (ii) zero loss and case (iii) 46.7% loss of ^{2}H. The calculated value of 39.6% loss means that case (ii) is the situation obtaining, because loss of ^{2}H would be zero if no equilibration occurred and 46.7% if complete equilibrium was attained. The actual value of 39.6% gives a degree of equilibration of: $(39.6/46.7) \times 100 = 84.7\%$, compared with the values of 84.5% and 84.9% found above. The fact that (VII), (VIII) and (IX) give equilibrium values in such excellent agreement provides sound support for the mechanism of methyl radical loss as involving the loss of the CH unit plus two ortho hydrogen atoms from one aromatic ring possibly as shown:



Furthermore, there can be no formation of a benzyl tropylium ion as this would lead to randomisation of the ^{2}H label over the whole molecule.

Experimental

All mass spectra were recorded on an A.E.I. M.S. 9 mass spectrometer with a source temperature of 200° and using a direct inlet system (except for appearance potential measurements made in a hot inlet system). The labelled compounds were prepared by well-established literature methods for the preparation of the unlabelled compounds as indicated.

2-^{2}H-Benzaldehyde. By the thermal decomposition of 2-^{2}H-phenylmethyl methyl sulphoxide [13].

2,4,6-^{2}H-Bromobenzene. Prepared by diazotisation of 2,4,6-^{2}H-aniline [14], and reaction with cuprous bromide and 50% hydrobromic acid [15].

2-^{2}H-Phenylmethyl bromide. From N-bromosuccinimide and 2-^{2}H-toluene in carbon tetrachloride.

Diphenylmethyl bromides. Prepared from the corresponding alcohol with phosphorus tribromide in pyridine.

1-Phenyl-1-(2-^{2}H-phenyl)methanol. By treatment of 2-^{2}H-benzaldehyde with phenyl magnesium bromide. Similarly, benzaldehyde and 2,4,6-^{2}H-phenyl magnesium bromide afforded *1-phenyl-1-(2,4,6-^{2}H-phenyl)-methanol.*

1,2-Diphenylethyl chlorides. Prepared by the action of thionyl chloride on the corresponding alcohol.

α-^{13}C-benzaldehyde. Prepared from α-^{13}C-benzoic acid by the McFadyen–Stevens reaction [16].

1-^{13}C-1,2-Diphenylethanol. By reacting α-^{13}C-benzaldehyde and benzyl magnesium bromide. Similarly, 2-^{2}H-phenylmethyl magnesium bromide and benzaldehyde gave *1-phenyl-2-(2-^{2}H-phenyl)ethanol,* and 2-^{2}H-phenylmethyl magnesium bromide and 2-^{2}H-benzaldehyde afforded *1,2-di-(2-^{2}H-phenyl)ethanol.*

1-^{2}H-1,2-diphenylethanol. By reduction of benzyl phenyl ketone with lithium aluminium deuteride in ether.

2,2'-^{2}H-Stilbene. Prepared by the action of ethanolic potassium hydroxide on 1,2-di-(2-^{2}H-phenyl)ethyl chloride.

All labelled compounds were checked against the unlabelled compounds by melting point (where appropriate), thin-layer chromatography, infra-red spectroscopy and mass spectrometry.

The authors wish to thank the Science Research Council for financial support.

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