1955

Some Novel Eliminations of Neutral Fragments from lons in Mass Spectrometry. Part III.* Fragmentation of the 1,3-Diphenylpropene Ion-radical

By R. A. W. Johnstone and B. J. Millard

The loss of methyl, ethyl, and vinyl radicals from the 1,3-diphenylpropene ion-radical in the mass spectrometer has been studied by means of ²H- and ¹³C-labelling and appearance-potential measurements. Mechanisms have been suggested for these unusual eliminations.

RECENTLY many examples have been reported of the elimination of such neutral molecules as CO, HCN, $C_{2}H_{4}$, $N_{2}H_{2}$, and HNCO from the non-terminal positions of open-chain ions,¹ in a process of the type

The loss of alkyl radicals from such positions has only been reported for long-chain esters ² and three other ions,

* Part II. R. A. W. Johnstone and B. J. Millard, Z. Naturforsch., 1966, 21a, 604.

namely diphenylmethyl,^{3,4} 1,2-diphenylethyl,⁴ and stilbene.3,4 Cyclic molecules such as cyclohexane and

¹ A. Bhatti, R. A. W. Johnstone, and B. J. Millard, J. Chem. A. Bnatti, R. A. W. Johnstone, and B. J. Millard, J. Chem.
Soc. (C), 1966, 358; B. J. Millard, Tetrahedron Letters, 1965, 34, 3041; J. H. Bowie, R. Grigg, S.-O. Lawesson, G. Schroll, and D. H. Williams, Chem. Comm., 1965, 403; J. H. Beynon, G. R. Lester, and A. E. Williams, J. Phys. Chem., 1959, 63, 1864.
² R. Ryhage and E. Stanhagen in "Mass Spectrometry of Organic Ions," ed. F. W. McLafferty, Academic Press, New Werk, 1969.

York, 1963.

³ C. J. Danby and J. H. D. Eland, *J. Chem. Soc.*, 1965, 5935, ⁴ R. A. W. Johnstone and B. J. Millard, *Z. Naturforsch.*, 1966, 21a, 604.

J. Chem. Soc. (C), 1966

cyclopentane lose alkyl radicals, but this loss occurs at the end of the open-chain form of the parent ion.⁵ The present work shows that the 1,3-diphenylpropene ionradical loses methyl, vinyl, and ethyl radicals.

The 1,3-diphenylpropene ion-radical can be generated in the mass spectrometer from the parent hydrocarbon, from 1,3-diphenyl-1-chloropropane, and from 1,3-diphenyl-2-chloropropane, since the chloro-compounds calculations the figures in the Table have not been corrected to a base peak of 100.

The three processes investigated can be written as

There is also an ion-radical C₁₄H₁₀ mainly derived from

	Partial	Partial mass spectra of $1,3$ -diphenylpropene ions at 70 eV (corrected for natural 13 C)				
		PhCH ₂ ·CH=CHAr				
	PhCH ₂ ·CH=CHPh	PhCH ₂ •CH=C ² HPh	PhCH ₂ ·C ² H=CHPh	$\left(Ar = \underbrace{\overset{^{2}H}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}$	Ph·13CH ₂ ·CH=CHPh	PhCH₂·CH=¹³CHPh
m e	(I)	(II)	(III)	(IV)	(V)	(VI)
165	17.0	12.0	8.0			6.55
166	2.6	10.3	$6 \cdot 9$	3.35		13.0
167	13.3	5.7	4.5	8.5		8.05
168	1.9	3.6	$5 \cdot 2$	7.78		7.15
169				$4 \cdot 5$		
170				$9 \cdot 3$		
171				1.4		
178	25.0	15.5	11.0			
179	30.1	39.6	21.3	7.5	25.0	25.0
	(100.0)	(28.3)	(45.6)			
180		35.5	13.6	31.5	30.0	30.0
		(71.7)	$(54 \cdot 4)$		(100.0)	(100.0)
181				$54 \cdot 9$ (36 $\cdot 0$)	<u> </u>	
182				50·7 (64·0)	_	

TABLE 1

The figures in parentheses indicate values obtained at 14 ev.

both eliminate hydrogen chloride by an electron impactinduced mechanism (metastable peaks at $m/e \ 163 \cdot 6$ and $612 \cdot 1$) in contrast with 1,2-diphenylethyl chloride which loses a chlorine radical.⁴ The Figure shows the mass



spectra of 1,3-diphenylpropene and 1,3-diphenyl-1chloropropane, showing that the portions of the mass spectra discussed in this work are identical. Table 1 gives the partial mass spectra of 1,3-diphenylpropene, [1-¹³C]-1,2-diphenyl-1-chloropropane, [3-13C]-1,2-diphenylprop-1-ene, 1,3-diphenyl[2-2H]prop-1-ene, 1,3-diphenyl-[1-2H]-1-chloropropane, and 1-[2,4,6-2H3]phenyl-3-phenylprop-1-ene at 70 and 14 ev. To facilitate

the ion $C_{14}H_{11}$ by loss of a hydrogen atom, but some derived by the alternative process

$$C_{6}H_{5} \cdot CH = CH \cdot CH_{2}C_{6}H_{5}^{+} \cdot \underbrace{-H}_{C_{6}H_{5}} \cdot CH = CH \cdot \underbrace{C_{6}H_{5}}_{+} \cdot CH = CH \cdot \underbrace{C_{13}H_{10}}_{+} \cdot C_{13}H_{10}^{+} \cdot C_{13}H_{10}^{+$$

At 14 ev the last process no longer takes place and the ion-radical C₁₄H₁₀ is removed from the spectrum, making calculations of the deuterium content of C14H11 ions simpler.

Consideration of the loss of a methyl radical from the diphenylpropene ion-radical in process (i) shows that the ¹³C-labelled compounds lose none of the label, proving that the 1- and 3-carbon atom of the propene chain are not involved. Thus either the 2-carbon atom of the propene chain, or a carbon atom from an aromatic ring, must be eliminated as methyl. Since compound (III), with deuterium at the 2-position, loses 45.6% of its deuterium during the loss of a methyl radical (Table 1) this constitutes very strong evidence that the 2-carbon atom is eliminated, as a ring carbon atom would be unlikely to take this amount of deuterium with it. Proof of this conclusion was obtained by appearance-potential measurements (Table 2). Only 3.65 ev are required to remove the methyl radical from 1,3-diphenylpropene whereas the removal of a methyl radical from an aromatic ring is unimportant and requires much more energy.

⁵ B. J. Millard and D. F. Shaw, J. Chem. Soc., (B), 1966, 664.

The benzene ion-radical, for example, requires 7.3 ev to effect the loss of methyl.

Table 1 shows that compound (IV) loses the methyl radical as CH_2^2H (36%) and CH_3 (64%) with no loss of

TABLE 2

Appearance potentials of 1,3-diphenylpropene and derived ions

		App.	Energy to form ion from
Ion	m e	potl. (ev)	parent ion
C ₆ H ₅ ·CH=CH·CH ₂ ·C ₆ H ₅ +•	194	8.30	
$C_{6}H_{5} \cdot CH = CH \cdot CH^{+} \cdot C_{6}H_{5} \dots$	193	11.65	3.35
$C_{14}H_{11}^+$	179	11.95	3.65
$C_{14}H_{10}^{-+}+$	178	15.05	6.75
$C_{13}H_{11}^{+}$	167	12.40	4.10
$C_{13}H_{0}^{+}$	165	13.75	5.65
Benzene, C _s H _s ⁺ •	78	9.25	
Benzene — methyl, C ₅ H ₃ +	63	16.55	7.30

 $CH^{2}H_{2}$. These figures are explained by an equilibrium as shown between A and B.



Such an equilibrium has been noted in the 1,2diphenylethyl ion,⁴ and additional evidence for its occurring here is the fact that the tropylium ion produced in the fragmentation of the labelled diphenylpropene (IV) appears in two parts, 75% at m/e 91 and 25% at m/e 94, with no tropylium ion at m/e 92 and 93. This result implies an equilibrium of 75% of A and 25% of B for tropylium fragmentation, which is not necessarily the same quantitatively for the other fragmentations under consideration.

As loss of methyl is not 100% CH₂²H, a process involving loss of the central CH unit plus one ortho hydrogen from each ring cannot occur. There is also no loss of $CH^{2}H_{2}$, so that a process involving loss of the central CH unit plus two ortho hydrogens from the same ring cannot operate. The ejection of the methyl radical then must involve the central CH unit, a hydrogen atom transferred from the CH₂ group and a hydrogen atom from the ortho position of ring b. The proportions of the two forms (A, B) in the equilibrium (E_1) calculated from the figures in Table 1, with use of an isotope effect of 0.88 for deuterium transfer,⁶ are A, 61% and B, 39%. As complete equilibrium would give A, 50% and B, 50%, percentage equilibration = $(39/50) \times 100 = 78\%$.

The ²H-labelled diphenylpropenes (II, III) at low electron voltages show the following losses of label as methyl:

(II)
$$C_6H_5 \cdot C^2H = CH \cdot CH_2C_6 \cdot H_5 \longrightarrow CH_3(71 \cdot 7\%)$$
 and $CH_2^2H(28 \cdot 3\%)$
(III) $C_6H_5 \cdot CH = C^2H \cdot CH_2 \cdot C_6H_5 \longrightarrow CH_3(54 \cdot 5\%)$ and $CH_2^2H(45 \cdot 6\%)$

These figures are in good qualitative agreement with the central CH unit's being lost. The equilibration between A and B probably takes place by a series of 1,2shifts of hydrogen: 7

$$C_{6}H_{5}$$
 $\stackrel{+}{\subset}H^{+}$ $\stackrel{+}{\leftarrow}H^{+}$ $C_{6}H_{5}$ $\stackrel{+}{\leftarrow}C_{6}H_{5}$ $\stackrel{+}{\leftarrow}H^{+}$ $\stackrel{+}{\leftarrow}H^{+}$ $C_{6}H_{5}$ $\stackrel{+}{\leftarrow}H^{+}$ $\stackrel{+}{$

The methyl radical can be lost any time the central ionradical is formed, and a large amount of the ²H originally present on the central atom of compound (III) will be lost with it. However, several 1,2 shifts are necessary to put ²H atoms on the central carbon atom in compound (II), so less ²H will be lost as methyl. The figures of 28.3 and 45.6% of CH22H lost from compounds (II) and (III), respectively, are in excellent qualitative agreement with this argument.

A possible mechanism for the removal of the metal radical from the diphenylpropene molecular ion is shown. The initial ionisation depicted is the most reasonable on consideration of the ionisation potentials of benzene and styrene which are 9.24 ev 8 and 8.86 ev,7 respectively:



The carbon atoms involved in the loss of vinyl and ethyl radicals were determined by considering the spectra of the unlabelled and 13 C-labelled hydrocarbons (I, VI). The loss of C₂H₃ from the molecular ion of the diphenylpropene (I) gives an ion at m/e 167, whereas this ion in the spectrum of the ¹³C-labelled compound (VI) arises from the loss of ${}^{13}CCH_3$. The ion at m/e 167 in the spectrum of compound (VI) would have intensity 13.3 if the label were lost completely, but the intensity was actually

⁸ K. Watanabe, J. Chem. Phys., 1957, 26, 542.

⁶ P. H. Groggins, R. H. Nagel, and A. I. Stirton, *Ind. Eng. Chem.*, 1934, **26**, 1313, 1317. ⁷ J. D. Morrison and A. J. Nicholson, *J. Chem. Phys.*, 1952,

²⁰, 1021.

8.05, so that 60.4% of the label had been lost. Again, this is evidence of the equilibrium shown (cf. E_1):

$$\begin{array}{c} \begin{array}{c} & & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & \\ & \\ \end{array} \begin{array}{c} + \cdot \\ & \\ & \\ & \\ \end{array} \begin{array}{c} \\ & \\ & \\ & \\ \end{array} \begin{array}{c} \\ \\ & \\ \end{array} \begin{array}{c} \\ \\ & \\ \end{array} \begin{array}{c} \\ \\ & \\ \end{array} \begin{array}{c} \\ \end{array} \begin{array}{c} \\ \\ \end{array} \begin{array}{c} \\ \end{array} \begin{array}{c} \\ \\ \end{array} \begin{array}{c} \\ \end{array} \end{array}$$
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The results show that carbon atoms 1 and 2 are lost as C_2H_3 , and that the extra hydrogen atom required comes from the aromatic rings (Table I; I, IV). The peak at m/e 167 in the spectrum of compound (I) is due to the loss of a C_2H_3 radical. In the ²H-labelled compound (IV), this appears at m/e 170 or 169, depending on whether C_2H_3 or $C_2H_2^2H$ is lost. If only $C_2H_2^2H$ were ejected, the peak would appear completely at m/e 169, and would have intensity 13·3. However, the peak at m/e 169 had intensity 4·5, and the remaining 8·8 was due to loss of C_2H_3 , giving a percentage loss of $C_2H_2^2H$ of $33\cdot9\%$. Again this implies an equilibrium between C and D, as for the ¹³C-labelled compound, with the extra hydrogen atom coming from the *ortho* position of ring b.

2. .

The equilibrium values of C and D calculated from the above figures, have closely similar values to those calculated for the ¹³C-labelled compounds. Thus, for the equilibrium (E_3) , $C/(100-C) \times 0.88 = 66 \cdot 1/33 \cdot 9$ giving $C(63 \cdot 3\%)$ and $D(36 \cdot 7\%)$. It being borne in mind that this loss of a C_2H_3 radical is a higher-energy process $(4 \cdot 10 \text{ ev})$ than the loss of the methyl radical $(3 \cdot 65 \text{ ev})$, the mechanism for the process may be:



In the spectrum of the unlabelled compound (I), the peak at m/e 165 is due to the loss of C_2H_5 , and in the case of the ¹³C-labelled compound (VI) this peak is due to the loss of the labelled radical ¹³CCH₅. The peak at m/e 165 would have intensity 17.0 if the label were lost completely, but its intensity was actually 6.55 (Table 1), so that $(6.55/17.0) \times 100 = 38.5\%$ was ejected as ¹³CCH₅. Again there is an equilibrium (E_4) .

Consideration of this equilibrium shows that carbon atoms 2 and 3 are lost as C_2H_5 . Since these atoms carry only three hydrogen atoms, a further two hydrogen atoms are required, and these come from the aromatic rings (Table 1; compounds I, IV). The peak at m/e 165 in the spectrum of the hydrocarbon (I) is due to loss of C₂H₅. In the ²H-labelled compound (IV), this peak appears at m/e 168, 167, or 166, depending on whether H₂, H²H, or ²H₂ are removed from the rings. If only $^{2}\mathrm{H}_{2}$ were removed, the peak at m/e 166 would have intensity 17.0, but the intensity was actually 3.32, so the amount of ${}^2\mathrm{H_2}$ lost was $(3{\cdot}32/17{\cdot}0)\times100=19{\cdot}5\%.$ The peak at m/e 168 due to loss of H₂ had intensity 7.78, giving $(7.78/17) \times 100 = 45.8\%$ loss of H₂. This means that the remainder (34.7%) was due to the loss of H²H. The ethyl group lost from the ²H-labelled compound (IV) therefore has the composition C_2H_5 , 45.8%; $C_2H_4^2H$, 34.7%; C₂H₃²H₂, 19.5%, and two mechanisms must operate. In one, $C_2H_4^2H$ can be lost by elimination of carbon atoms 2 and 3 of the propene chain plus one orthohydrogen atom from each ring. In the other, both C_2H_5 and $C_2H_3^2H_2$ radicals are lost by elimination of carbon atoms 2 and 3 of the propene chain plus two ortho hydrogen atoms from ring b. These figures give, for the equilibrium (E_4) , E (64.5%) and F (3.5%), again in close agreement with the equilibrium results for the 13C-labelled compounds.



The processes leading to loss of an ethyl radical can be represented as



The ¹³C-labelled compounds were prepared from available 55% enriched [1-¹³C]acetic acid. Friedel-Crafts

reactions with benzene afforded methyl phenyl [13C]ketone which was condensed with benzaldehyde to give benzylideneacetophenone. Reduction with lithium aluminium hydride gave 1,3-diphenyl[1-13C]-1-hydroxypropane and further treatment with thionyl chloride gave the corresponding chloro-compound. Condensation of 1,3-diphenyl[1-13C]-1-oxyprop-2-ene with ethanedithiol yielded 1,1-bis-(2-mercaptoethanethio)-1,3-diphenylprop-2-ene and not the expected ethanedithioketal. The ¹³C-label was switched to the other end of the diphenylpropene chain by reduction of the thioketal to give 1,3-diphenyl[3-13C]propene. The ²H-labelled compounds were obtained by reduction of the corresponding ketones with lithium aluminium [2H]hydride.

EXPERIMENTAL

All spectra were measured on an A.E.I. MS. 9 mass spectrometer through a direct inlet at a source temperature of 200°. The appearance-potential measurements were obtained by the "1% ionisation" method. All the compounds prepared are known, except the thioketal. The labelled compounds were purified by thin-layer chromatography and compared with the unlabelled compounds.

1,3-Diphenyl[1-13C]-1-chloropropene.—Treatment of benzene with [1-13C]acetic acid and anhydrous aluminium chloride at 80° for 24 hr. gave methyl phenyl [13C]ketone (85% yield).⁸ Condensation of the ketone with benzaldehyde afforded 1,3-diphenyl[1-13C]-1-oxyprop-2-ene (90%) yield).9 Reduction with lithium aluminium hydride gave 1,3-diphenyl-[1-13C]-1-hydroxypropane.10 Treatment with

⁹ Organic Syntheses, Coll. Vol. I, 78.
¹⁰ Gaylord, "Reduction with Complex Metal Hydrides," 10 Gaylord, Interscience, New York and London, 1956.

¹¹ L. F. Fieser, J. Amer. Chem. Soc., 1954, 76, 1945.

thionyl chloride yielded 1,3-diphenyl[1-13C]-1-chloropropane.

1,3-Diphenyl[3-13C]propene. Condensation of 1,3diphenyl[1-13C]-1-oxyprop-2-ene with ethanedithiol 11 gave 1,1-bis-(2-mercaptoethanethio)-1,3-diphenylprop-2-ene, 2550 cm.⁻¹, τ : 7.69, 7.65 (SH); 7.15-6.40 (CH₂); 2.87(C₆H₅); 2·45, 2·37 (CH=CH) (Found: C, 60·59; H, 5·67; S, 33.90. $C_{19}H_{22}S_4$ requires C, 60.31; H, 5.86; S, 33.83%). Reduction of this with deactivated Raney nickel 12 gave 1,3-diphenyl[3-13C]propene.

[2,4,6-2H₃]Bromobenzene.—This was prepared by the Sandmeyer reaction from [2,4,6-2H3]aniline.13

1-[2,4,6-2H3]Phenyl-3-phenyl-1-chloropropane.—This was prepared by the action of thionyl chloride on the corresponding alcohol obtained by reacting the Grignard reagent from [2,4,6-2H₃]bromobenzene with 3-phenylpropionaldehvde.

1,3-Diphenyl[2-2H]-2-chloropropane.—This was prepared by the action of thionyl chloride on the corresponding alcohol obtained by reduction of dibenzyl ketone¹⁴ with lithium aluminium deuteride.¹⁰

1,3-Diphenyl[1-2H]-1-chloropropane.--Prepared by the action of thionyl chloride on the corresponding alcohol obtained by reduction of benzylacetophenone 15 with lithium aluminium deuteride.10

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¹² G. B. Spero, A. V. McIntosh, jun., and R. H. Levin, J. Amer. Chem. Soc., 1948, 70, 1907.

¹³ A. P. Best and C. L. Wilson, J. Chem. Soc., 1946, 242.

14 C. D. Hurd and C. L. Thomas, J. Amer. Chem. Soc., 1936, **58**, 1240.

¹⁵ Org. Synth., Coll. Vol. I, 101.