

Electron Impact Studies. Part LXXVI.¹ Scrambling Processes in Ions derived from Diphenylmethane Derivatives

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The loss of a methyl radical from the ion $C_{13}H_{11}^+$ [derived from the molecular ions of Ph_2CHX ($X = Br, OMe, \text{ and } OH$)] occurs with complete hydrogen and carbon scrambling, with all the C-H bonds breaking and re-forming in a statistical manner. A similar loss of methyl occurs from the molecular ion of diphenylmethane, but in this case the scrambling is not complete, and the molecular ions of 7-phenylcyclohepta-1,3,5-triene and *o*-methylbiphenyl may be implicated in the rearrangement. The loss of a phenyl radical from the molecular ions of Ph_2CHX ($X = H \text{ and } OH$) proceeds with partial hydrogen scrambling, but carbon scrambling does not occur.

THE study of the properties of the ion $C_7H_7^+$, derived by loss of a hydrogen atom from the toluene molecular ion, has been the subject of controversy for nearly 20 years. The classical studies of Grubb and Meyerson²

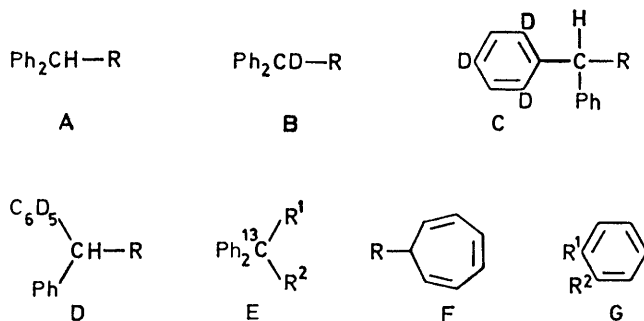
showed the $C_7H_7^+$ ion to have (or to have passed through) a higher symmetry than a benzyl structure, and therefore presumably to correspond to the tropylium cation. The application of ^{13}C labelling techniques has recently

¹ Part LXXV, J. H. Bowie and A. J. Blackman, *Austral. J. Chem.*, 1972, **25**, 1335.

² H. M. Grubb and S. Meyerson, in 'Mass Spectrometry of Organic Ions,' ed. F. W. McLafferty, Academic Press, New York, 1963.

shown^{3,4} that all the carbon atoms in the $C_7H_7^+$ species have lost their positional identity either before or during further decomposition, and that the insertion-cyclisation processes must be complex.⁴

The investigation of toluene prompted a study of the ions formed from the related diphenylmethane system.⁵⁻¹¹ The major ions observed in the spectrum of diphenylmethane are: $(M - H^+)^+$ ($C_{13}H_{11}^+$, m/e 167), $(M - H^+ - H_2)^+$ ($C_{13}H_9^+$, m/e 165), $(M - Me^+)^+$ ($C_{12}H_9^+$, m/e 153), $(M - H^+ - Me^+)^+$ ($C_{12}H_8^+$, m/e 152), and $(M - Ph^+)^+$ ($C_7H_7^+$, m/e 91). The losses of methyl radicals from both the molecular and $M - 1$ ions of diphenylmethane have been noted by many authors.⁵⁻⁹ Johnstone and Millard⁷ suggested that the loss of methyl from $C_{13}H_{11}^+$ came from the central CH unit together with loss of *ortho*-hydrogens, and that the *o*-methylbiphenyl cation may be an intermediate in the reaction. Williams⁸ and Meyerson⁹ and their co-workers showed that the losses of Me^+ from $C_{13}H_{11}^+$ and $C_{13}H_{12}^{+*}$ occurred with complete randomisation of hydrogen, and scrambling through a phenyltropylium cation was suggested for $C_{13}H_{11}^+$.⁸ In order to clarify this situation we prepared a series of 2H - and ^{13}C -labelled derivatives of diphenylmethane and 7-phenyl-1,3,5-cycloheptatriene, and our preliminary results¹² confirmed both the hydrogen scrambling previously observed for the $M - Me^+$ and $M - H^+ - Me^+$ processes, the possible intermediacy of a phenyltropylium ion, and showed that both eliminations occur with complete carbon randomisation. This paper now amplifies and extends the previous report, and considers the method of scrambling and possible intermediates in the



reaction pathways. The compounds used, together with the isotopic incorporation of the labelled compounds, are listed in Table 1.

DISCUSSION

The Loss of Me^+ from $C_{13}H_{11}^+$.—A study of the decompositions of $C_{13}H_{11}^+$ produced from the molecular

* The values obtained for the labelled derivatives of (2) and (4) are not listed, as they are identical with those reported¹² for (3). The ratio recorded¹² for the calculated losses of CH_3^+ , CH_2D^+ , CHD_2^+ , and CD_3^+ from $C_{13}H_9D_5^+$ is in error, and should read 12 : 45 : 36 : 7.

³ K. L. Rinehart, A. C. Buchholz, G. E. Van Lear, and H. L. Cantrell, *J. Amer. Chem. Soc.*, 1968, **90**, 2983.

⁴ A. S. Siegel, *J. Amer. Chem. Soc.*, 1970, **92**, 5277.

⁵ S. Meyerson, H. Drews, and E. K. Fields, *J. Amer. Chem. Soc.*, 1964, **86**, 4964.

ion of diphenylmethane is complicated by scrambling reactions which occur for the $M - H^+$ process, and by competing fragmentation of the molecular ion. The ion was therefore produced by loss of X^+ from the molecular

TABLE 1

Structure	R = H	OH	Br	OMe	Incorporation
A	(1)	(2)	(3)	(4)	[2H_1] = 100% [2H_2] = 3, [2H_3] = 97% [2H_5] = 100%
B		(5)	(6)	(7)	
C	(8)	(9)	(10)	(11)	
D	(12)	(13)	(14)	(15)	
		R ¹	R ²		Incorporation
E	(16)	H	H	[^{13}C] = 60.1%	[^{13}C] = 62.1, [2H_2] = 100% [^{13}C] = 60.1% [^{13}C] = 62.1%, [2H_2] = 100% [^{13}C] = 60.1% [^{13}C] = 62.1%, [2H_1] = 100%
	(17)	D	D		
	(18)	H	OH		
	(19)	D	OD		
	(20)	H	Br		
	(21)	D	Br		
F	(22)	R = Ph			[2H_5] = 100%
	(23)	R = C_6D_5			
G	(24)	R ¹	R ²		[2H_5] = 100% [2H_3] = 100%
	(25)	Ph	Me		
	(26)	C_6D_5	Me		

ions of Ph_2CHX ($X = OH, Br,$ and OMe) and metastable defocusing¹² of the spectra of the appropriate labelled compounds (above) show that the ion is statistically scrambled before or during elimination of Me^+ .

The doubly-labelled ions $C_{12}H_{10}^{13}CD^+$ were produced from the molecular ions of compounds (19) and (21) respectively, and the scrambling processes are identical

TABLE 2

The losses of CH_3^+ , CH_2D^+ , $^{13}CH_3^+$, and $^{13}CH_2D^+$ from $C_{12}H_{10}^{13}CD^+$		Product ion m/e 154 : 153 : 152	
Decomposing ion [from (21)]	Type	Found	Calculated (randomisation)
$C_{12}H_{10}^{13}CD$ (62.1%)	a	39 : 46 : 15	40 : 49 : 11
$C_{13}H_{10}D$ (37.9%)			
		- CH_3^+ : -($^{13}CH_3^+$ + CH_2D^+) : - $^{13}CH_2D^+$	
$C_{12}H_{10}^{13}CD^+$	b	68 : 29 : 3	Calculated
	c	65 : 33 : 2	67 : 30.5 : 2.5

* Daughter ion. ^b Defocused metastable ions; first field-free region. ^c Metastable ions; second field-free region.

in both cases. The losses of Me^+ and its labelled analogues are listed in Table 2, and the data show that all the C-H bonds in $C_{13}H_{11}^+$ have broken and re-formed

⁶ J. H. D. Eland and C. J. Danby, *J. Chem. Soc.*, 1965, 5935.

⁷ R. A. W. Johnstone and B. J. Millard, *Z. Naturforsch.*, 1966, **21a**, 604.

⁸ D. H. Williams, R. S. Ward, and R. G. Cooks, *J. Chem. Soc. (B)*, 1968, 522.

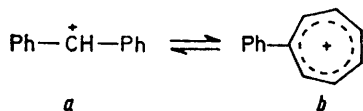
⁹ S. Meyerson, H. Hart, and L. C. Leitch, *J. Amer. Chem. Soc.*, 1968, **90**, 3419.

¹⁰ J. Lesko, V. Vesely, and S. Korcek, *Coll. Czech. Chem. Comm.*, 1969, **34**, 2836.

¹¹ H. Budzikiewicz, J. Rullkotter, and H. M. Schiebel, *Org. Mass Spectrometry*, 1972, **6**, 251.

¹² T. K. Bradshaw, J. H. Bowie, and P. Y. White, *Chem. Comm.*, 1970, 537.

statistically before (or during) elimination of the methyl radical. The mechanism of the scrambling process will be complex (*cf.* ref. 4), but it may involve cyclisation



through a phenyltropylium cation⁸ (*e.g.*, $a \rightleftharpoons b$). Computer calculations based on this model show that at least 2000 bond-breaking-re-forming reactions must occur to account for the independent scrambling of C and H, irrespective of the precise nature of the cyclisation-contraction processes. This result is not incompatible with recent theories¹³ concerning the rates and time scales of deep-seated rearrangement reactions and other low-energy decompositions.

The Loss of Me[•] from C₁₃H₁₂⁺.—The field-ionisation mass spectrum of diphenylmethane, measured through the courtesy of Professor H. D. Beckey, shows no field-induced dissociation peak ($\tau = 10^{-14}$ – 10^{-12} s), no fast metastable peak ($\tau = 10^{-12}$ – 10^{-7} s), but shows the presence of a normal metastable peak ($\tau = 10^{-7}$ – 3×10^{-3} s) for the elimination of a methyl radical from the molecular ion.¹⁴ This reveals that the elimination is a slow process, probably produced from a low-energy molecular ion (*i.e.*, a reaction of low activation energy and frequency factor). These are conditions favourable to scrambling reactions.¹³

The processes $M - \text{Me}^{\bullet}$ and $(M - \text{H}^{\bullet}) - \text{Me}^{\bullet}$ both occur in the electron-impact induced mass spectrum of compound (1) at 70 eV, but at 15 eV ions are only

TABLE 3

Metastable abundances for the processes $M - \text{CH}_x\text{D}_{3-x}^{\bullet}$ from compounds (8), (12), (23), (25), and (26) (at 15 eV)

Compound	Metastable type	Found †				Calculated (randomisation)			
		$M - \text{CH}_3^{\bullet}$	$-\text{CH}_2\text{D}^{\bullet}$	$-\text{CHD}_2^{\bullet}$	$-\text{CD}_3^{\bullet}$	$M - \text{CH}_3^{\bullet}$	$-\text{CH}_2\text{D}^{\bullet}$	$-\text{CHD}_2^{\bullet}$	$-\text{CD}_3^{\bullet}$
(12)	<i>a</i>	21	38	31.5	9.5	15	48	32	5
	<i>b</i>	17	44	32	7				
(23)	<i>a</i>	20	37	33	10				
(25)	<i>a</i>	18	39	32	11				
(8)	<i>a</i>	43	44.5	11	1	1.5	38	49	12
	<i>b</i>	41	46	11	1				
(26)	<i>a</i>	42	44	12	2				

a Defocused metastable ions; first field-free region. Metastable ions; second field-free region.

† Ratios are an average of five measurements, and are correct to within 0.5%.

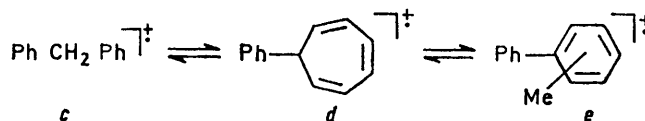
observed for the former process. Metastable defocusing of compounds (12) and (16) at 15 eV shows¹² that the elimination of a methyl radical proceeds with hydrogen and carbon scrambling. The metastable ratios for (8)

* Slightly more loss of label comes from the phenyl rings than that calculated for complete scrambling, a situation analogous to that observed for the loss of Me[•] from the stilbene molecular ion.¹⁶

¹³ I. Howe, 'Energetics, Kinetics and Ion-Structures,' in 'Mass Spectrometry, Specialist Reports,' ed. D. H. Williams, The Chemical Society, 1970, pp. 38–66, and references therein.

and (12) (Table 3) show, in contrast to those observed for the process $\text{C}_{13}\text{H}_{11}^+ - \text{Me}^{\bullet}$, that the decompositions in the first and second field-free regions occur with differing amounts of hydrogen randomisation. Computer calculations, based on a variety of possible mechanisms, indicate that those molecular ions undergoing decomposition in the first field-free region (*i.e.*, after 5×10^{-5} s¹⁵) are *ca.* 85–90% scrambled with respect to hydrogen,* while those fragmenting in the second field-free region (*i.e.*, after 10^{-4} s¹⁶) are *ca.* 95% scrambled. This is understandable, since the elimination is occurring from an odd-electron species, whereas the corresponding loss from $\text{C}_{13}\text{H}_{11}^+$ involves the more stable (longer lived) even-electron ion. The fragmentations of the ion $\text{C}_{12}\text{H}_{10}^{13}\text{CD}_2^{+\bullet}$ [*viz.*, the molecular ion of (17)] show that the eliminations also involve the cleavage and re-formation of C–H bonds, *i.e.*, the ratio of defocused metastable species for the eliminations $M - \text{CH}_3^{\bullet} : M - (\text{CH}_2\text{D}^{\bullet} + {}^{13}\text{CH}_3^{\bullet}) : M - (\text{CHD}_2^{\bullet} + {}^{13}\text{CH}_2\text{D}^{\bullet}) : M - {}^{13}\text{CHD}_2^{\bullet}$ is 47:40.5:12:0.5 at 15 eV (calculated 50.5:42:7:0.5).

It is possible that the scrambling processes may be explained by the conversion $c \rightleftharpoons d$ (*cf.* $a \rightleftharpoons b$) and



that the elimination of Me[•] could be originating from a methylbiphenyl species (*cf.* ref. 7). The spectra of diphenylmethane, 7-phenylcyclohepta-1,3,5-triene, and *o*-methylbiphenyl are very similar, and the process $M - \text{Me}^{\bullet}$ can be studied at 15 eV. The labelled derivatives (23), (25), and (26) were prepared to test whether *d* and *e* undergo scrambling before loss of Me[•], and the remarkable correspondence between the metastable ratios of compounds (12), (23), and (25), and (8) and (26) (see Table 3) proves that all three species are scrambled to the same extent, and suggests that they are all decomposing through the same intermediate. No information is available to suggest a structure for the decomposing species.

The Loss of C₆H₅[•] from the Molecular Ions of Diphenylmethane and Diphenylmethyl Alcohol.—Meyerson⁹ and Williams⁸ and their co-workers have reported that partial randomisation of hydrogen precedes the loss of a phenyl radical from the molecular ions of diphenylmethane⁹ and diphenylmethyl alcohol.⁸ For example, the ratio of the daughter ions (no metastable ion observed) produced by the cleavages $M - \text{C}_6\text{H}_5^{\bullet}$, $-\text{C}_6\text{H}_4\text{D}^{\bullet}$, $-\text{C}_6\text{H}_3\text{D}_2^{\bullet}$, and $-\text{C}_6\text{H}_2\text{D}_3^{\bullet}$ (*m/e* 94:93:92:91) from the molecular ion of Ph-CH₂-C₆H₂D₃ (8) are 43:9:8:40 (70 eV) and 35:18:20:27 at 20 eV (calculated for scrambling 16:47.5:32:4.5). In marked contrast, the

¹⁴ H. J. Beckey, personal communication.

¹⁵ J. Seibl and E. Tajima, *Internat. J. Mass Spectrometry and Ion Phys.*, 1969, **3**, 245.

¹⁶ J. H. Bowie and P. Y. White, *Org. Mass Spectrometry*, 1972, **6**, 135.

spectra of the labelled derivatives (16) and (18) show retentions of ^{13}C of 97.5 and 98.0% respectively in the two $M - \text{Ph}^*$ ions at 20 eV. The spectrum of diphenylmethyl alcohol⁸ also shows the eliminations ($M - \text{Ph}^*$) - CO and ($M - \text{C}_6\text{H}_7^*$) - CO. The spectrum of (18) exhibits metastable transitions in the first field-free region of the mass spectrometer for the processes ($M - \text{Ph}^*$) - ^{13}CO and ($M - \text{Ph}^*$) - CO in the ratio 95:5, while the process ($M - \text{C}_6\text{H}_7^*$) - ^{13}CO occurs exclusively. This demonstrates that the losses of CO involve the central carbon atom. The decompositions considered above are examples of reactions which occur with partial hydrogen scrambling, but with no randomisation of carbon between the methylene (or methine) group and the phenyl rings. In the case of diphenylmethane, the loss of Ph^* cannot originate from the low-energy species which eliminates the methyl radical, and it is likely that the cleavage occurs from a high-energy precursor ion which has no time to undergo ring expansion before decomposition.

EXPERIMENTAL

All mass spectra were determined with an Hitachi-Perkin-Elmer RMU 6D double-focusing mass spectrometer operating at 70 eV (unless otherwise specified), and equipped with a metastable-defocusing device operating on the electrostatic sector.^{17,18} Samples were introduced through a glass inlet system maintained at 100 °C.

All samples were distilled and their purity confirmed by v.p.c. Compounds (22)–(26) were further purified by preparative v.p.c.

7-Phenylcyclohepta-1,3,5-triene (22) and 7- $^{2}\text{H}_5$]phenylcyclohepta-1,3,5-triene (23) were prepared (in 60% yield) by the reaction¹⁹ between 7-methoxycyclohepta-1,3,5-triene and phenyl-lithium or $^{2}\text{H}_5$]phenyl-lithium respectively.

The unlabelled and singly-labelled ^2H - and ^{13}C -diphenylmethane derivatives (1)–(16), (18), and (20) were prepared

¹⁷ A. H. Struck and H. W. Major, paper presented to the ASTM E14 Meeting, May 18–23, 1969, Dallas, Texas.

¹⁸ J. H. Bowie and T. K. Bradshaw, *Austral. J. Chem.*, 1970, **23**, 1431.

¹⁹ C. Jutz and F. Voithenleitner, *Chem. Ber.*, 1964, **97**, 29.

²⁰ D. Seebach, B. W. Erickson, and G. Singh, *J. Org. Chem.*, 1966, **31**, 4303.

²¹ J. Ronayne, D. H. Williams, and J. H. Bowie, *J. Amer. Chem. Soc.*, 1966, **88**, 4980.

²² L. I. Smith and M. Bayliss, *J. Org. Chem.*, 1941, **6**, 437.

²³ J. Morton and H. Gilman, *Org. Reactions*, 1946, **8**, 286.

from benzaldehyde, $[\alpha\text{-}^2\text{H}_1]$ benzaldehyde,²⁰ $[2,4,6\text{-}^2\text{H}_3]$ benzaldehyde,²¹ $^{2}\text{H}_5$]benzaldehyde,²² and $[\alpha\text{-}^{13}\text{C}_1]$ benzaldehyde. The reaction²³ between the appropriate benzaldehyde and phenyl-lithium gave the diphenylmethyl alcohol (70% yield), which upon treatment²⁴ with phosphorus tribromide in carbon tetrachloride yielded the diphenylmethyl bromide (65%), which was converted into the diphenylmethyl methyl ether (95%) by heating under reflux with methanolic sodium methoxide for 2 h. Hydrogenation of the alcohol (above) with Raney nickel in ethanol²⁵ gave the appropriate diphenylmethane in 70% yield.

The reaction²⁶ between lithium $[\alpha\text{-}^{13}\text{C}]$ benzoate and phenyl-lithium gave a mixture, which after chromatography over silicic acid (Mallinckrodt) in light petroleum (b.p. 60–80 °C)–benzene (1:3) yielded $[\alpha\text{-}^{13}\text{C}]$ benzophenone (56% yield). Reduction of the benzophenone with lithium aluminium deuteride in diethyl ether followed by work up with deuterium oxide gave the alcohol (19) (98% yield), which was converted (see above) into the $[\alpha\text{-}^{13}\text{C}_1, \alpha\text{-}^2\text{H}_1]$ diphenylmethyl bromide (21) (65% yield). The reaction between the bromide and lithium aluminium deuteride in diethyl ether followed by work up with deuterium oxide yielded $[\alpha\text{-}^{13}\text{C}_1, \alpha\alpha\text{-}^2\text{H}_2]$ diphenylmethane (17) (85% yield).

o-Methylbiphenyl was produced by the reaction between 2-methylcyclohexanone and phenylmagnesium bromide (*cf.* ref. 27) followed by dehydration of the alcohol,²⁸ and aromatisation.²⁹ The $^{2}\text{H}_5$]derivative (25) was prepared as above using $^{2}\text{H}_5$]phenylmagnesium bromide, and *o*-methyl- $^{2}\text{H}_5$]biphenyl (26) was prepared from 2-methyl- $^{2}\text{H}_3$]cyclohexanone.³⁰

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²⁴ J. F. Norris, R. Thomas, and B. M. Brown, *Ber.*, 1910, **43**, 2959.

²⁵ R. Mazingo, *Org. Synth.*, 1955, **3**, 181.

²⁶ H. Gilman and P. R. van Ess, *J. Amer. Chem. Soc.*, 1933, **55**, 1258.

²⁷ R. G. Cooks, I. Howe, S. W. Tam, and D. H. Williams, *J. Amer. Chem. Soc.*, 1968, **90**, 522.

²⁸ W. N. Haworth, *J. Chem. Soc.*, 1913, **103**, 1242.

²⁹ R. T. Arnold and C. J. Collins, *J. Amer. Chem. Soc.*, 1939, **61**, 1407; R. T. Arnold, C. J. Collins, and W. Zenk, *ibid.*, 1940, **62**, 983.

³⁰ H. O. House, W. L. Roelofs, and B. M. Trost, *J. Org. Chem.*, 1966, **31**, 646.