Hydrogen and Carbon Scrambling in the Molecular Ions of Diphenylmethane Derivatives[1]

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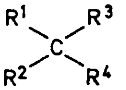
Summary Hydrogen and carbon scrambling precedes the losses of methyl radicals from *m/e* 168 and 167 in the spectra of diphenylmethane and its derivatives.

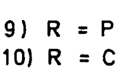
THE mass spectra of diphenylmethane derivatives have been reported previously.[2–7] Two suggestions, based on deuterium labelling data, which pertain to the loss of a methyl radical from *m/e* 167 ($C_{13}H_{11}^+$) are:—(i) that the methyl radical is formed from the central CH unit together with two *ortho*-hydrogens,[4] and (ii) that the elimination is preceded by complete hydrogen scrambling.[5] We have examined the abundances of fragment ions and metastable ions (formed in the first field-free region of the double focussing mass spectrometer[8,9]) in the spectra of (**1**)—(**10**) in order to clarify both this and other fragmentations.



	R^1	R^2	R^3	R^4
(1)	Ph	Ph	H	H
(2)	C_6D_5	Ph	H	H
(3)	Ph	Ph	H	Br
(4)	Ph	Ph	D	Br
(5)	$C_6H_2D_3$	Ph	H	Br
(6)	C_6D_5	Ph	H	Br

$Ph_2\,{}^{13}CH{-}R$

(7) R = H
(8) R = Br



(9) R = Ph
(10) R = C_6D_5

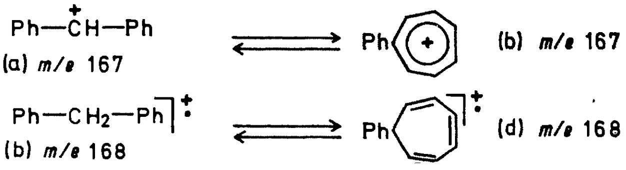
The results listed in Table 1 confirm the earlier suggestion[5] that complete hydrogen scrambling precedes the elimination of a methyl radical from *m/e* 167. The ratio of the metastable ions for the processes *m/e* 168 → 153 and *m/e* 168 → 152 ($m^* = 139{\cdot}5$ and $137{\cdot}5$ respectively) in the spectrum of (**8**) is 13 : 1 at 70 ev, and 15·1 at 15 ev. The calculated value for random loss is 12 : 1.

TABLE 1

Abundances of $[(M - Br\bullet) - CH_xD\bullet_{3-x}]$ *ions*[a] *for* (**4**)—(**6**) *at* 25 ev

Compound	$(M - Br\bullet) - CH_3\bullet$	$- CH_2D\bullet$	$- CHD_2\bullet$	$-CD_3\bullet$	$(M - Br\bullet) - CH_3\bullet$	$- CH_2D\bullet$	$- CHD_2\bullet$	$-CD_3\bullet$
	Found				Calculated			
(**4**)	70	30			73	27		
(**5**)	34	49	15·5	1·5	34	49	15	2
(**6**)	14	42	34·5	9·5	15	41	34	10

[a] The ratios obtained for fragment ions and metastable ions are almost identical.



At 70 ev the processes $M - Me^\bullet$ and $(M - H^\bullet) - Me^\bullet$ produce *m/e* 153 and 152 respectively in the spectra of (**1**) and (**9**). The latter process does not occur at 15 ev. The incorporation of ^{13}C in the molecular ion of (**7**) is 60·1%, and the 15 ev spectrum of this compound shows an incorporation of 55·3% for the $M - Me^\bullet$ ion (complete randomisation 55·5%). The metastable ions for the processes *m/e* 169 → 154 and 169 → 153 occur in the ratio 15 : 1 (randomisation 12 : 1) at 15 ev. The data in Table 2 show that hydrogen randomisation occurs, (*cf.* ref. 6) and the similarity between the values of (**2**) and (**10**) support the suggestion[5] that (d) may be implicated in the rearrangement. The enhanced loss of deuterium from the even-electron species is similar to that observed for the losses of Me• from the 9,10-dihydrophenanthrene[10,11] and stilbene[11] molecular ions.

The hydrogen and carbon scrambling which precedes the losses of Me• from *m/e* 167 and *m/e* 168 can be explained by the reversible processes (a) → (b) and (c) → (d)[5,12] with the central carbon unit (together with its substituents) inserting randomly into each C–C bond of the phenyl ring. This is likely to be accompanied by independent scrambling of the hydrogens of the seven and six carbon units during each cycle [*e.g.* (a) → (b)]. Our carbon scrambling observations are analogous to results obtained for (α,1-$^{13}C_2$]toluene,[13] and should be contrasted with loss of Ph• from the diphenylmethane 1-^{13}C molecular ion, which occurs with no loss of the label (*cf.* ref. 6). We also suggest that ^{13}C labelling data for the losses of Me• from the *o*-terphenyl[14] and triphenylmethane[12] molecular ions are consistent with complete carbon scrambling.

TABLE 2

Abundances of $M - CH_xD\bullet_{3-x}$ *for* (**2**) *and* (**10**) *at* 15 ev

Compound	$M - CH_3\bullet$:	$- CH_2D\bullet$:	$- CHD_2\bullet$:	$- CD_3\bullet$				
	Found				Calculated			
(**2**)	21	38	31·5	9·5	15	48	32	5
(**10**)	20	37	33	10				

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[1] Previous paper in this series, *Org. Mass Spectrometry*, in the press.

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