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ELECTRON IMPACT STUDIES—XXIX[1]

THE $C_{13}H_9$ SKELETAL-REARRANGEMENT FRAGMENT IN THE MASS SPECTRA OF HETEROCYCLIC SYSTEMS CONTAINING DIPHENYL SUBSTITUENTS. A DEUTERIUM LABELLING STUDY

J. H. BOWIE, P. F. DONAGHUE, H. J. RODDA and B. K. SIMONS

Department of Organic Chemistry, The University of Adelaide, South Australia 5001

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Abstract—The *m/e* 165 ion ($C_{13}H_9$) has been noted in the mass spectra of a variety of heterocyclic systems containing two (or more) phenyl substituents. This skeletal-rearrangement fragment is most prominent in the spectra of particularly substituted oxazoles, imidazoles and thiazoles. Deuterium-labelling studies have allowed probable mechanistic formulations in the case of the 4,5-diphenylimidazoles, and the detection of two alternate rearrangement pathways in the spectrum of 2,4,5-triphenyloxazole. A comparison is made between the formation of *m/e* 165 in the spectrum of stilbene and 9,10-dihydrophenanthrene.

DURING a study of the mass-spectral fragmentations of substituted imidazoles,[2] it was observed that the spectra of 4,5-diphenylimidazoles exhibited pronounced skeletal-rearrangement fragments at *m/e* 165 ($C_{13}H_9^+$, high resolution). This ion is formed directly from the molecular ion, and its formation demands a Ph migration. Similar phenomena are observed[3] in the spectra of the isomeric diphenyloxazoles, and tentative mechanisms have been proposed for the genesis of the rearrangement ion. The $C_{13}H_9$ ion is also observed in the spectra of 2,5-diphenyl-1,2,4-oxadiazole

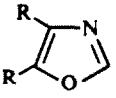
TABLE 1. RELATIVE ABUNDANCE OF *m/e* 165. FRAGMENTS IN THE MASS SPECTRA OF DIPHENYL HETEROCYCLES

Compound	Abund. of *m/e* 165 (%)	Compound	Abund. of *m/e* 165 (%)
4,5-Diphenylimidazole	42	2,4-Diphenylthiazole	1
2-Isopropyl-4,5-diphenylimidazole	26	3,5-Diphenylisoxazole	4
2,4,5-Triphenylimidazole	100	3,5-Diphenylpyrazole	7
4,5-Diphenyloxazole	75	3,4-Diphenylpyrazole	21
2-Methyl-4,5-diphenyloxazole	86	2,5-Diphenylfuran	3
2-Ethyl-4,5-diphenyloxazole	100	5-Methyl-2,3-diphenylpyrrole	2
2-*n*-Pentyl-4,5-diphenyloxazole	73	2,3-Diphenylthiophen	7
2,4,5-Triphenyloxazole	80	2,4-Diphenylthiophen	5
2,5-Diphenyloxazole	53	2,5-Diphenylthiophen	2
4,5-Diphenylthiazole	85	2-Chloro-5,6-diphenylpyrazine	2
2-Amino-4,5-diphenylthiazole	45	3,6-Diphenylpyridazine	0

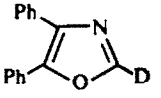
(53% of the base peak),[4] 4,5-diphenyl-2-pyrone (18%),[5] 3,4-diphenyl-4,5-epoxy-2-cyclopenten-1-one (21%)[5] diphenylmethane (29%),[6] stilbene (30%)[7] and 9,10-dihydrophenanthrene (30%).[8]

As a knowledge of skeletal-reorganization processes in mass spectrometry is extremely important,[9] it was decided to investigate (a) whether the presence of a prominent $C_{13}H_9$ peak is characteristic of all compounds containing the Ph—C=C—Ph unit, and (b) to study the genesis of the rearrangement ion in the spectra of the 4,5-diphenyloxazoles, the 4,5-diphenylimidazoles, stilbene and 9,10-dihydrophenanthrene, by deuterium-labelling studies. This paper deals primarily with these problems.

The relative abundances of the $C_{13}H_9$ fragments in the mass spectra of some heterocyclic compounds are summarized in Table 1. It can be clearly seen that the rearrangement fragment is pronounced in the spectra of 4,5-diphenyloxazoles (where in several cases it constitutes the base peak of the spectrum), 4,5-diphenylimidazoles, 4,5-diphenylthiazoles and 2,5-diphenyloxazoles. In the case of the 5-membered heterocycles containing one heteroatom, and with adjacent Ph substituents, the rearrangement peak is less than 10% of the base peak,* while the *m/e* 165 peak is either small or absent in the spectra of the two 6-membered compounds. Therefore, a pronounced $C_{13}H_9$ peak is not characteristic of the Ph—C=C—Ph moiety, but is generally confined to 5-membered heterocyclic systems containing two heteroatoms (normally in 1,3 positions), and to isolated instances, including diphenylmethane, stilbene and dihydrophenanthrene.



1: R = Ph



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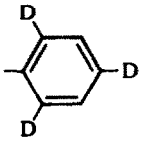
2: R =



The mass spectra of 4,5-diphenyloxazole **1** and the two labelled derivatives **2** and **3** are recorded in Figs 1–3. It has been shown previously that hydrogens on aromatic rings become equivalent upon electron impact[10,11] and that randomization does not occur for isolated hydrogen substituents attached to the oxazole nucleus.[12] This situation has also been apparent throughout this study, and consequently, even though the benzene rings are specifically labelled with deuterium, fragmentations involving loss of deuterium and/or hydrogen atoms from the benzene rings of **2** will occur in the ratio 3:2 (D:H) (ignoring possible isotope effects). In the spectrum (Fig. 1) of 4,5-diphenyloxazole **1**, *m/e* 165 may be formed by two pathways: viz.

* The skeletal-rearrangement fragments observed in the mass spectra of isoxazoles, pyrazoles, 2,5-diphenyl-furan, -pyrrole and -thiophen, will be the subject of a future publication.

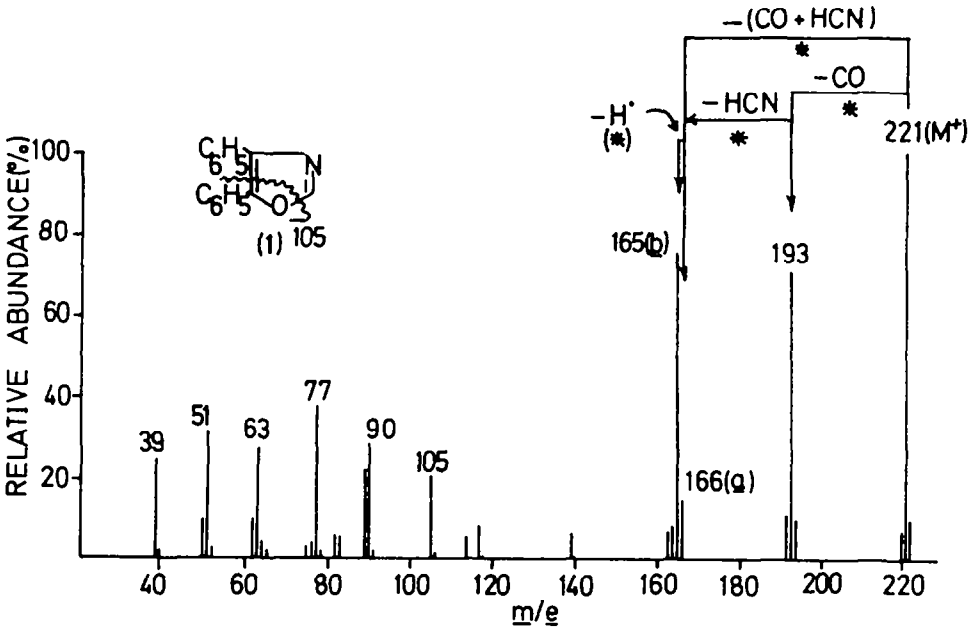

—(CO + HCN)
—CO
—HCN
—H·
(*)
221(M+)
165(b)
193
166(a)
(1) 105
RELATIVE ABUNDANCE(%)
m/e
39
51
63
77
90
105

FIG. 1.

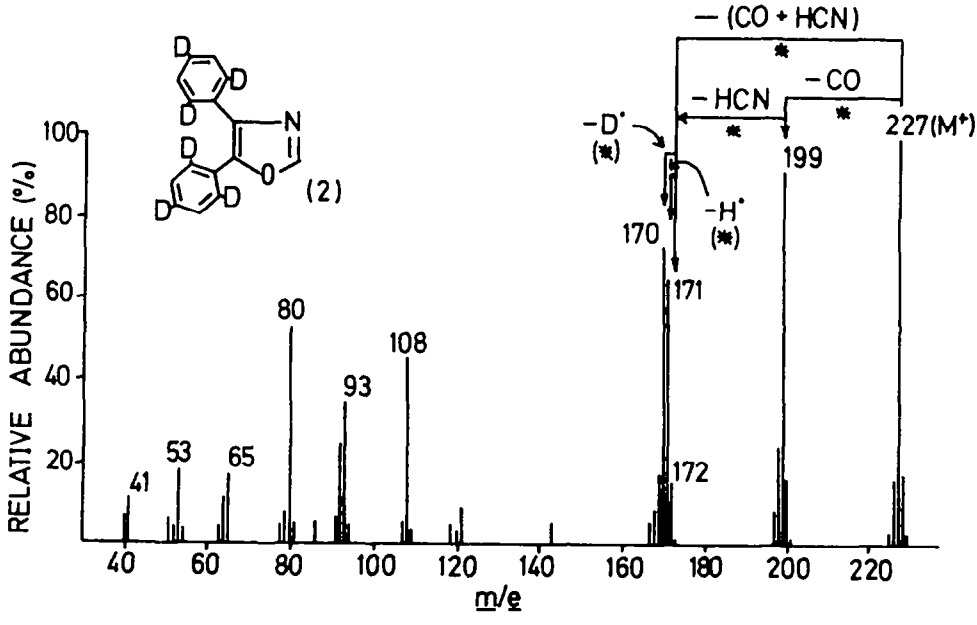

— (CO + HCN)
— HCN
— CO
-D·
(*)
-H·
(*)
227(M+)
199
170
171
172
(2)
RELATIVE ABUNDANCE (%)
m/e
41
53
65
80
93
108

FIG. 2

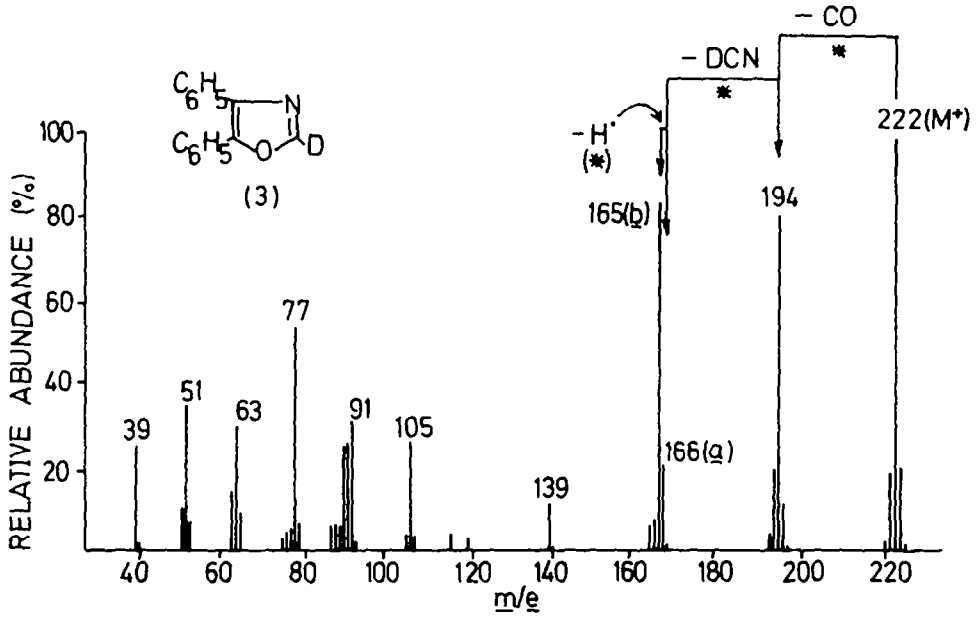
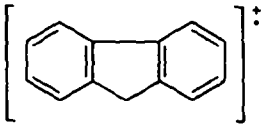
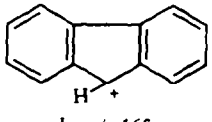


FIG. 3.

(a) M—(CO + HCN)—H· and (b) M—CO—HCN—H· [appropriate metastable ions (denoted by an asterisk in the Figs) substantiate all processes]. These processes are modified in the spectra of all the 2-substituted 4,5-diphenyloxazoles to M—(CO + RCN)—H· and M—CO—RCN—H·. When the energy of the electron beam is reduced to 10 eV, the process M → *m/e* 166 is always pronounced, with *m/e* 165 being the minor component. Even though structures drawn for fragment ions are nominal only, it is argued that the most plausible structures for *m/e* 166 and 165, correspond to the fluorene radical ion (*a*) and cation (*b*), respectively, although this does not preclude the possibility of more extensive rearrangement.



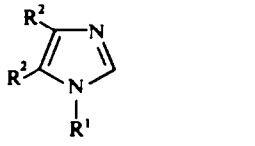
a: *m/e* 166



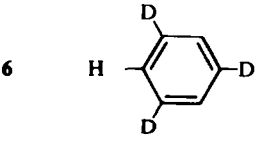
b: *m/e* 165

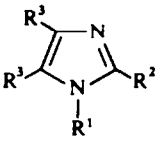
The spectra (Figs 2 and 3) of the labelled compounds **2** and **3** show that the two Ph rings are involved in the formation of the fluorene cation [i.e. the processes M—CO—HCN—H· or M—CO—HCN—D· produce *m/e* 171 or 170 respectively (Fig. 2)], and that the deuterium at C-2 in (**3**) is specifically lost in the initial process, and plays no part in the formation of the rearrangement ion. The latter observation negates the earlier mechanistic proposal[3] for the formation of *m/e* 165 from 4,5-diphenyloxazole, as this mechanism invokes the participation of the hydrogen at

C-2 in the transformation. Nevertheless, the above observations still do not allow unequivocal proposals to be advanced for the mechanism.

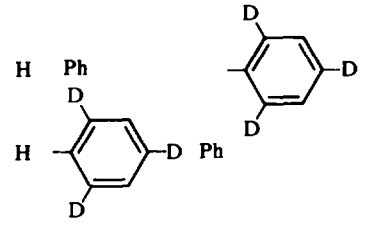


	R^1	R^2
4	H	Ph
5	D	Ph





	R^1	R^2	R^3
7	H	Ph	Ph
8	D	Ph	Ph



However, the spectra of the imidazoles **4–10** permits conclusions to be reached concerning the genesis of the ion *b*. The spectra (Figs 4 and 6) of 4,5-diphenylimidazole (**4**) and 2,4,5-triphenylimidazole (**7**) are different from that of 4,5-diphenyloxazole (**1**), as in these spectra, *b* (*m/e* 165) is formed directly from the molecular ions (concerted losses of $C_2H_3N_2^{\cdot}$ and $C_8H_7N_2^{\cdot}$ respectively). Metastable ions substantiate these processes, which, although concerted, do not necessarily occur by one-step processes.[13] The spectra (e.g. Fig. 6) of the N–d_1 derivatives **5** and **8** show incorporation of deuterium into the rearrangement peaks, and after a calculation (which is approximate because of M-1 and M-2 peaks) to allow for incomplete labelling, a value of $50 \pm 10\%$ is obtained for the incorporation of deuterium into the rearrangement ions (now *m/e* 165, 166 and 167). Such a value is much too high to be accounted for by randomization of the label, and a specific transfer process is indicated. It is of interest to note that the spectrum (Fig. 7) of **10** shows that the phenyl substituent at C-2 is not involved in the rearrangement process.

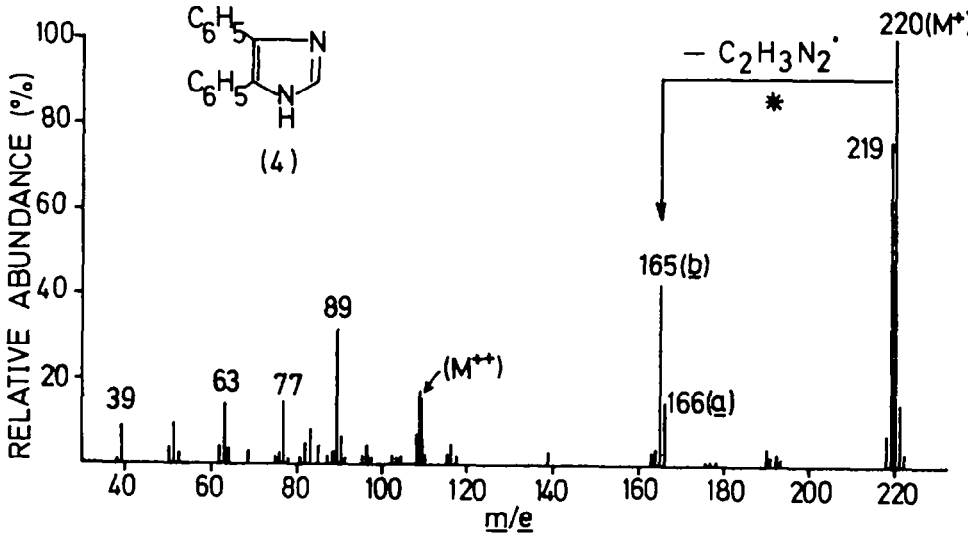

RELATIVE ABUNDANCE (%)
m/e
(4)
220(M+)
− C2H3N2·
219
165(b)
166(a)
89
(M++)
39
63
77

Fig. 4.

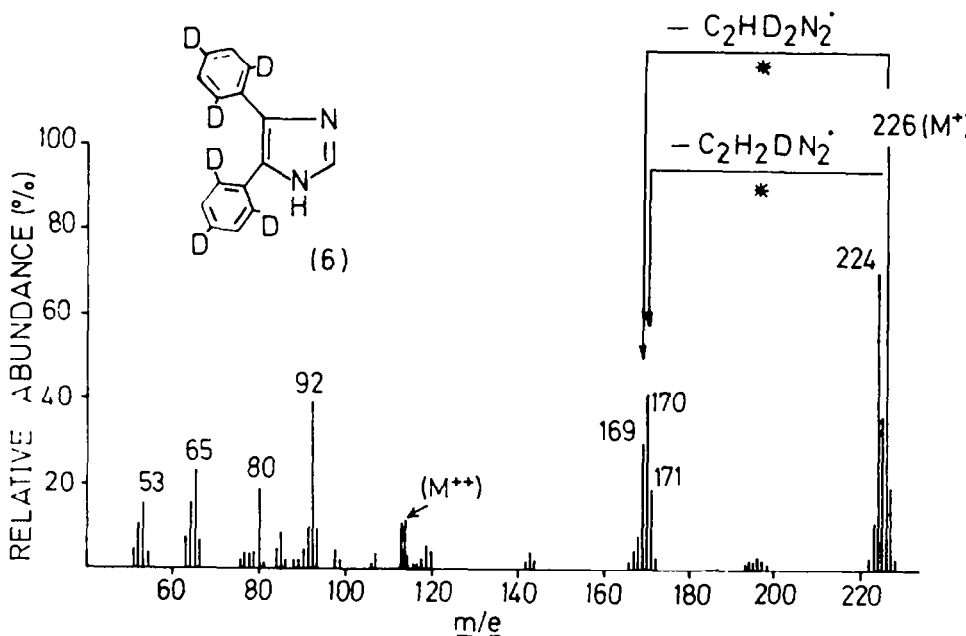

RELATIVE ABUNDANCE (%)
m/e
(6)
− C2HD2N2·
− C2H2DN2·
226(M+)
224
92
65
80
53
(M++)
169
170
171

Fig. 5.

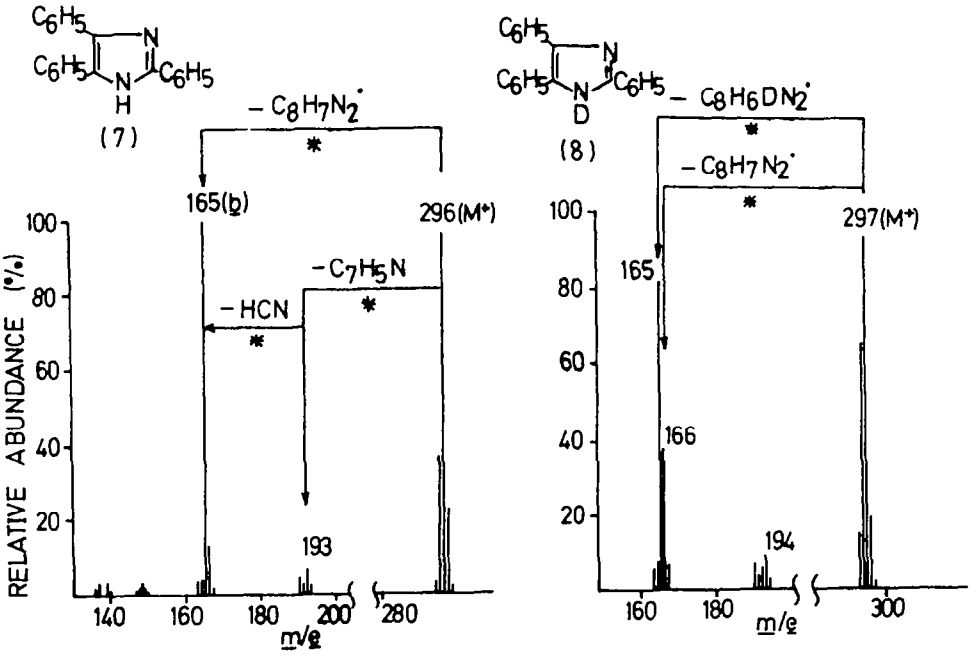

(7)
(8)
$-C_8H_7N_2^{\cdot}$
$-C_8H_6DN_2^{\cdot}$
165(b)
296(M⁺)
297(M⁺)
$-C_7H_5N$
-HCN
193
194
166
RELATIVE ABUNDANCE (%)
m/e

FIG. 6.

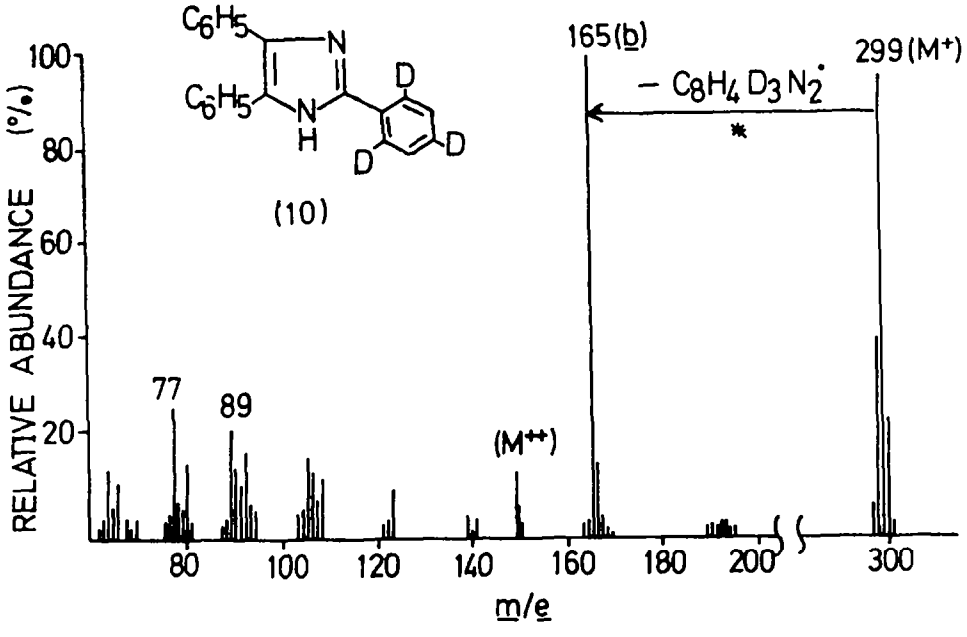
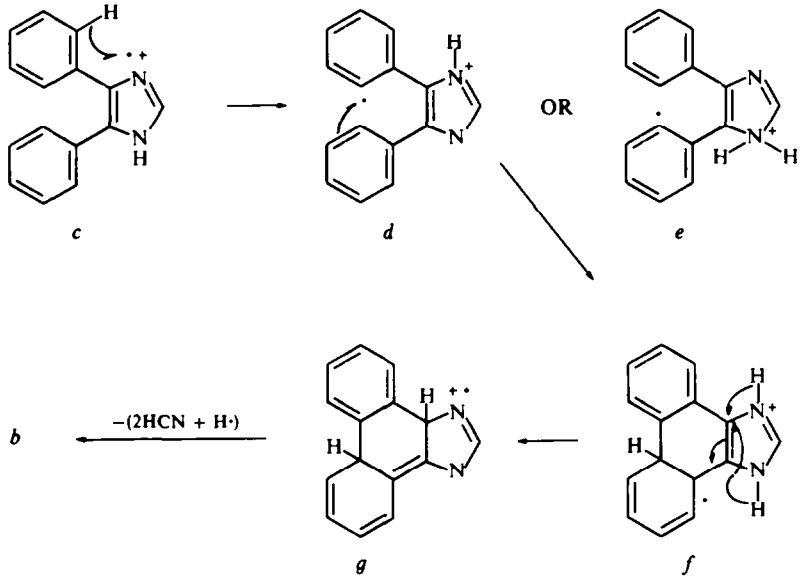

(10)
165(b)
299(M⁺)
$-C_8H_4D_3N_2^{\cdot}$
77
89
(M⁺⁺)
RELATIVE ABUNDANCE (%)
m/e

FIG. 7.

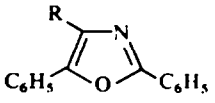
The spectra of the d_6-derivatives **6** and **9** demonstrate the participation of a second hydrogen-transfer process. The spectrum of **6** is illustrated in Fig. 5, and it should be noted that the ratios of *m/e* 169:170:171 are identical in the spectra of **6** and **9**, although the relative abundances of the peaks are not the same in the two spectra. Two concerted eliminations are noted, viz. in Fig. 5, M—$C_2H_2DN_2$· (to *m/e* 170) and M—$C_2HD_2N_2$· (to *m/e* 169). The presence of the second process can only mean that a deuterium has migrated from a Ph ring to the imidazole ring in order to allow the loss of the second D atom in the rearrangement. This migration must of course involve both D and H atoms in the ratio 3:2. To explain this double hydrogen rearrangement, Scheme 1 is proposed for the formation of *b*. Migration of a H atom to either nitrogen, produces *d* or *e*, which cannot be distinguished (we have a marginal preference for *d* because it forms symmetrical intermediates). The production of *d* (or *e*) provides an electron-deficient centre on one of the aromatic rings to which the other may migrate (e.g. *d* → *f*). In order for the rearrangement to proceed, either hydrogen on nitrogen must migrate back to the "fluorene-centre". There is an equal probability of either hydrogen migrating, as *f* may be considered as a symmetrical intermediate, and although the acceptor-site of the rearrangement is not known, a possible formulation is *g* (it is possible that the imidazole ring may have opened by this stage), which may now readily fragment to the fluorene cation.

SCHEME 1

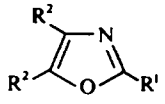


Although this rationale is speculative, it explains the hydrogen rearrangements, and may be correlated with the ratios of *m/e* 169:170:171 in the spectra of **6** and **9**. A simple calculation assuming deuterium/hydrogen rearrangement to nitrogen in the ratio 3:2, followed by 50% back exchange of each atom (H or D) on nitrogen together with the possible eliminations to produce the rearrangement ions, gives a calculated ratio for the *m/e* 169, 170 and 171 peaks as 1·0:2·1:1·2. When isotopic corrections,

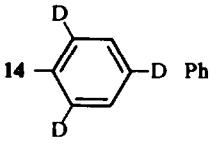
and approximate corrections due to incomplete labelling are made, the observed ratios are 1·0:1·5:0·9. These ratios are not inconsistent when the approximations inherent in the calculations are considered, and also as possible isotopic effects have been ignored. If one argues by analogy, a similar mechanism could apply to the formation of *b* in the spectra of the 4,5-diphenyloxazoles and -thiazoles, although it is recognized that this double-hydrogen rearrangement could not occur in such cases.



11: R = H
12: R = D



13 Ph Ph



14

The formation of the fluorene cation (*b*) in the spectrum of 2,5-diphenyloxazole (**11**) has been noted previously,[3] and a mechanism has been proposed for its formation. We wished to compare this rearrangement with that observed in the spectrum of 4,5-diphenyloxazole. The spectra of **11** and **12** are illustrated in Fig. 8, and it can be seen that the hydrogen at C-4 is not involved in the formation of *b*. Apart from the fact that Ph migration must occur, no concrete proposal can be presented for the mechanism, but it is noteworthy that the formation of *b* in the spectrum of 2,4-diphenyloxazole occurs only to the extent of 5%.[3] It has already been shown (*vide supra*) that the 2-phenyl group of 2,4,5-triphenylimidazole is not involved in the formation of *b*,

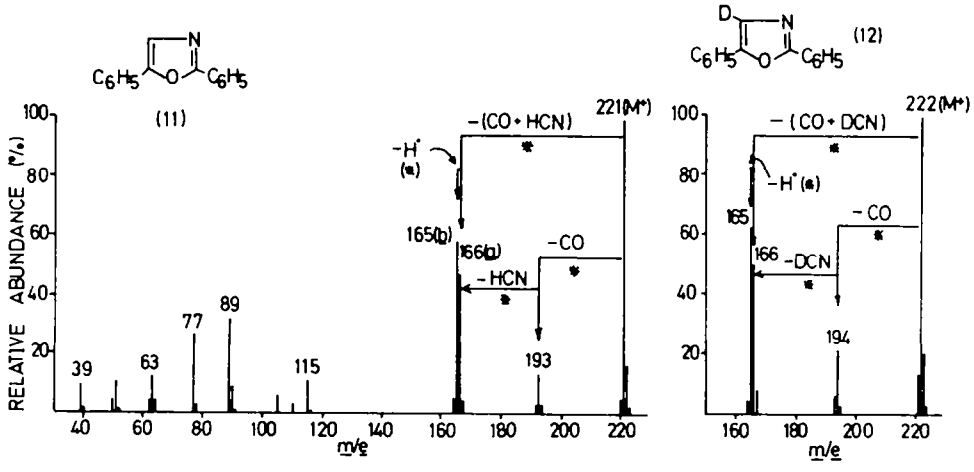
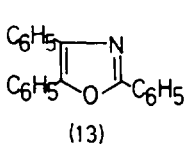
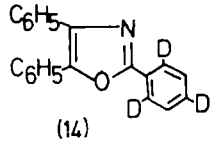


FIG. 8.

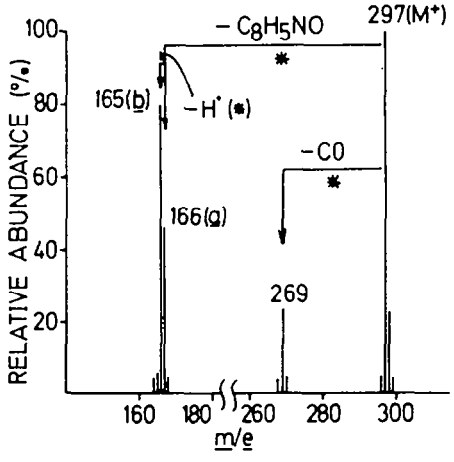
but because of the pronounced rearrangement occurring in the spectrum of 2,5-diphenyloxazole, the spectra (Fig. 9) of 2,4,5-triphenyloxazole (**13**) and **14** were examined. Fig. 9 shows the occurrence of two distinct processes, *viz.* (a) the formation of *b* from the 4,5-Ph groups via the normal pathway (60%), and (b) formation of the



(13)



(14)



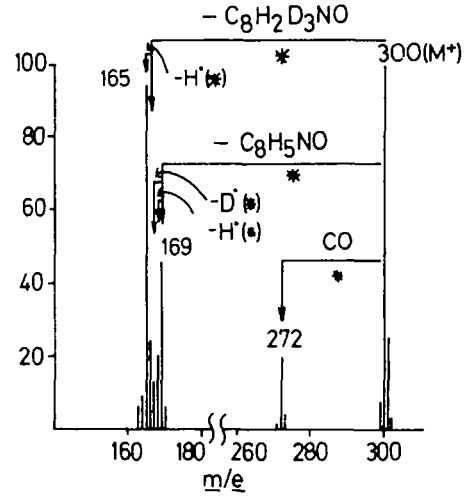
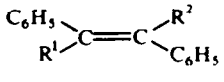
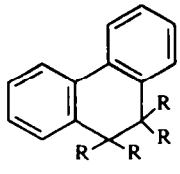


FIG. 9.

d_3-fluorene radical ion (*m/e* 169) from the 2,5-phenyl substituents (40%). This ion (*m/e* 169) may either lose a H atom (to *m/e* 168) or a D atom (to *m/e* 167). When the energy of the electron beam is reduced to 10 eV, only two ions are observed in the *m/e* 165–170 region; *m/e* 166 and 169 in the ratio 2:3. This implies that the formation of the fluorene radical ion (*a*) from the 2 and 5 Ph groups is more energetically favourable than its formation from the 4 and 5 Ph substituents. It is assumed that bond formation does not occur between the 2 and 4 Ph substituents, because of the small relative abundance of *b* in the mass spectrum of 2,4-diphenyloxazole. The loss of carbon monoxide from the molecular ions of 2,4,5-trisubstituted oxazoles has been reported previously.[12]



	R^1	R^2
15	H	H
16	H	D
17	D	D



18: R = H

19: R = D

Finally, it was of interest to examine the almost identical spectra of stilbene[7] and 9,10-dihydrophenanthrene,[8] which both lose a Me radical from their molecular ions to form *m/e* 165 (*b*, 30% of the base peak). In order to examine this feature, **17** was required. The synthesis of this compound was approached by equilibration of desoxybenzoin with MeOD/Na, then reduction with LAD followed by elimination of D_2O. Unfortunately, the initial step gives only 65% of the d_2 species, any further equilibration then results in deuteration of the aromatic system. As the final product contains only ca. 75% d_2, compound **16** was used for this study. The partial spectra of the stilbenes **15** and **16** are illustrated in Fig. 10. The ratios of the 165/166 peaks

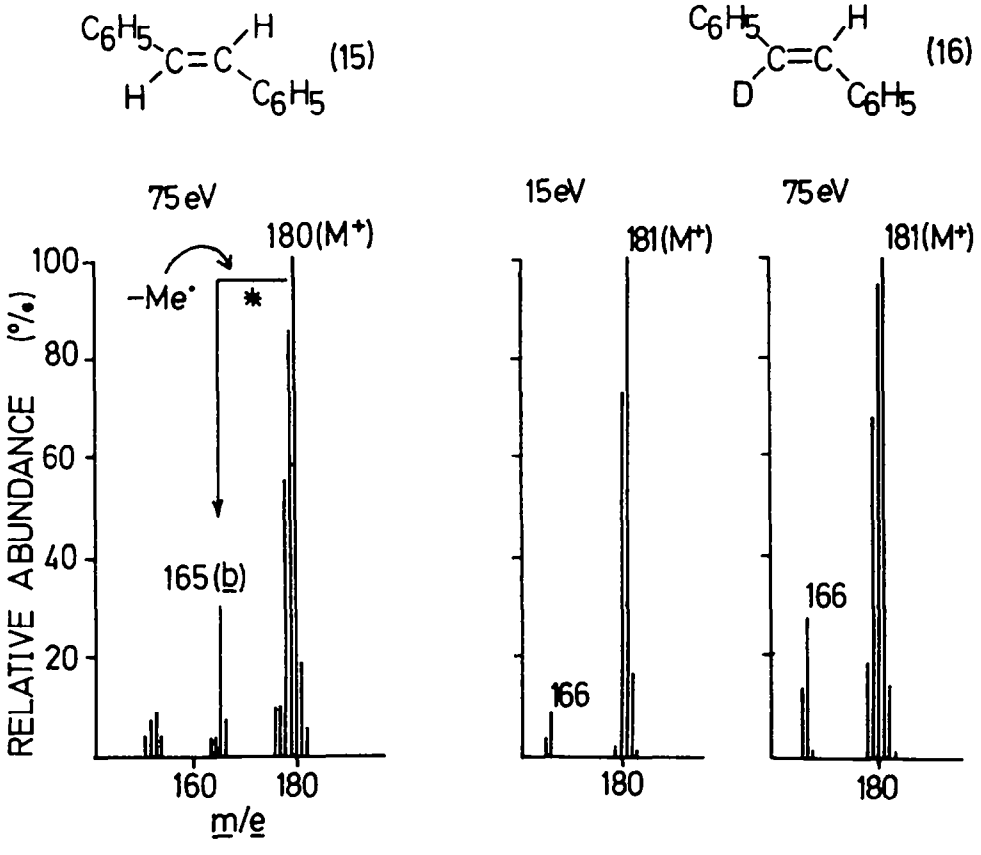
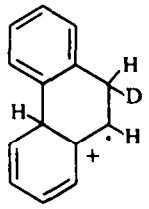


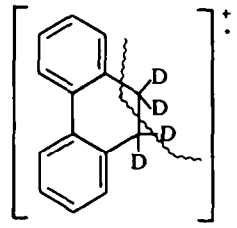
FIG. 10

in the spectrum of **16** are unchanged at 75, 20, 15 and 10 eV and each spectrum shows 34% relative loss of $CH_2D\cdot$ and 66% of $CH_3\cdot$. This cannot be explained by randomization of the hydrogen (or deuterium) on the olefinic link with the aromatic hydrogens, nor can it be explained by an intermediate of the type *h*, which would be the species obtained from an adaptation of the mechanism outlined in Scheme 1 (the participation of such an intermediate is unlikely in any case, as it has been demonstrated above that the heteroatoms play a significant part in the mechanism

outlined in Scheme 1). Further rearrangement of *h* has been previously used to explain the loss of a methyl radical from the stilbene molecular ion.[14] Although the mechanism for the loss of Me· from the stilbene molecular ion is not clear, it seems that at least

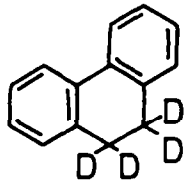


h: *m/e* 181



i: *m/e* 184

two processes may be involved. The loss of a methyl radical from 9,10-dihydrophenanthrene (**18**) is even more difficult to explain. The spectrum (Fig. 11) of the d_4-derivative (**19**) might be expected to exhibit loss of CD_3· (see *i*). However, the



(19)

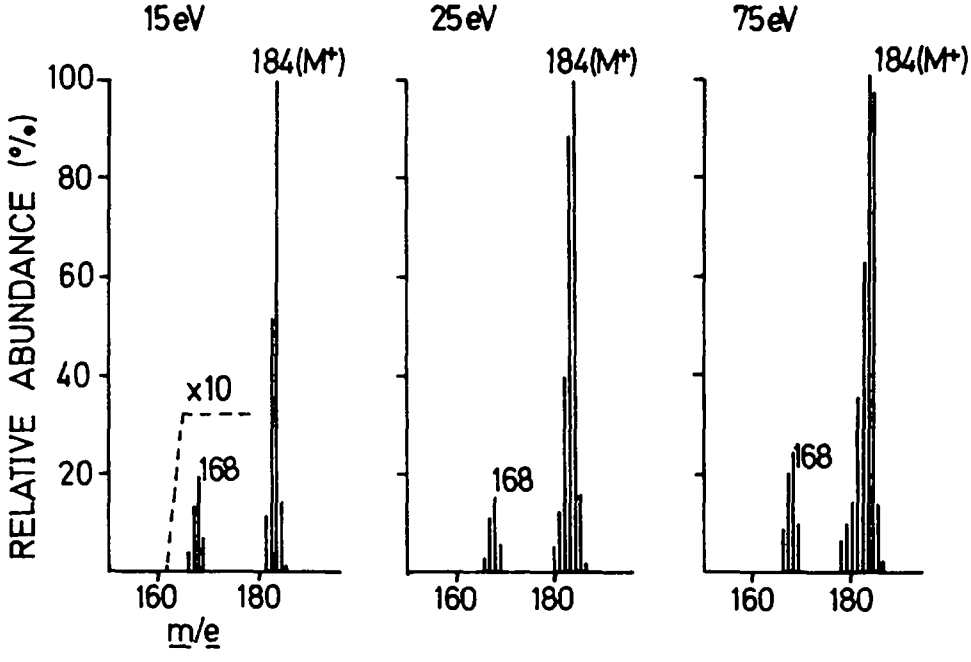


FIG. 11.

loss of CD_3· is minor, the major losses being CH_2D· and CD_2H·. Again, the *m/e* 166, 167, 168, 169 ratio is not markedly affected by decreasing the energy of the electron beam (see Fig. 11), and it appears that little randomization of deuterium occurs. In a previous paper[8] it was assumed that hydrogen lost in the M—H_2 process [to produce the phenanthrene molecular ion (*m/e* 178)] originated from the 9,10 positions of 9,10-dihydrophenanthrene. This is not the case, as the major loss in the spectrum of **19** is H_2 and not D_2, and probably indicates considerable rearrangement of the molecular ion. Although the losses of Me· from stilbene and 9,10-dihydrophenanthrene are complex, there is little doubt that the formation of *b* proceeds differently in these cases than it does for 4,5-diphenylimidazole.

These studies demonstrate yet again that extreme caution must be exercised when postulating mass-spectrometric mechanisms without the aid of the spectra of suitably labelled derivatives.

EXPERIMENTAL

All mass spectra were determined with an Hitachi Perkin–Elmer RMU 6D double focussing mass spectrometer operating at 75 eV (unless otherwise specified) with a source temp of approximately 150° and an inlet temp between 50° and 200°.

All samples used in this study were routinely checked for purity by nuclear magnetic resonance and mass spectrometry.

4,5-Diphenylimidazole, 2-isopropyl-4,5-diphenylimidazole and 2,5-diphenyloxazole were purified commercial samples. The following compounds were prepared by reported procedures: 2,4,5-triphenylimidazole,[15] 4,5-diphenyloxazole,[16] 2-methyl-4,5-diphenyloxazole,[17] 2-ethyl-4,5-diphenyloxazole,[18] 4,5-diphenyl-2-n-propyloxazole,[18] 2-n-pentyl-4,5-diphenyloxazole,[12] 2,4,5-triphenyloxazole,[17] 4,5-diphenylthiazole,[19] 2-amino-4,5-diphenylthiazole,[21] 2,4-diphenylthiazole,[22] 3,5-diphenylisoxazole,[23] 3,5-diphenylpyrazole,[23] 3,4-diphenylpyrazole,[24] 2,5-diphenylfuran,[25] 2,5-diphenylpyrrole,[26] 5-methyl-2,3-diphenylpyrrole,[27] 2,3-diphenylthiophen,[28] 2,4-diphenylthiophen,[29] 2,5-diphenylthiophen,[29] 2-chloro-5,6-diphenylpyrazine,[30] and 3,6-diphenylpyridazine.[31]

The spectra of 5 and 8 were obtained by introducing 4 and 7 into the source with deuterium oxide.[32]

Labelled compounds

2,4,6-d_3-*Benzaldehyde.* Prepared from 2,4,6-d_3-aniline by the method of Williams *et al.*[11]

2,4,6-d_3-*Benzoylchloride.* Prepared in quantitative yield by oxidation of 2,4,6-d_3-benzaldehyde with $KMnO_4$aq, followed by treatment of 2,4,6-d_3-benzoic acid with $SOCl_2$.

2,4,6,2',4',6'-d_6-*Benzoin.* Prepared from 2,4,6-d_3-benzaldehyde by the benzoin condensation.

2,4,6,2',4',6'-d_6-*Benzil.* Prepared in quantitative yield by HNO_3 oxidation of 2,4,6,2',4',6'-d_6-benzoin. (d_5 = 4%, d_6 = 96%).

2-d-4,5-*Diphenyloxazole* (**3**). 4,5-Diphenyloxazole (0·58 g) in dry ether (10 cc) was added to a soln of n-BuLi [from Li (0·086 g) and n-BuBr (0·69 g)] in dry ether (20 cc) at −65°, under dry O_2-free nitrogen. After stirring for 30 min, D_2O (5 cc) was added, the ethereal soln was separated, dried (Na_2SO_4) and evaporated. The product was purified by preparative VPC (30% SE30, 12'). The NMR spectrum lacked the singlet at 2·19 τ indicative of the 2-H of 4,5-diphenyloxazole.[20]

4,5-*Di*(2,4,6-d_3-*phenyl*)*oxazole* (**2**). Prepared from d_6-benzoin by the method of Theilig.[18] Purified by preparative VPC (see above) b.p. 190–194°/14 mm Hg.

2-(2,4,6-d_3-*Phenyl*)4,5-*diphenyloxazole* (**14**). 2,4,6-d_3-Benzoylchloride (1·3 g) and benzoin (2·1 g) were warmed on a water bath for 1 hr. The benzoin-d_3-benzoate was cyclized to 14 by the method of Davidson *et al.*[17] The crude product was chromatographed over alumina in ether, and crystallized from EtOH as colourless prisms, m.p. 115–116°.

4-*Bromo*-2,5-*diphenyloxazole.* To a soln of 2,5-diphenyloxazole (4·4 g) in glacial AcOH (100 cc), boiling under reflux, was added a soln of Br_2 (3·2 g) in AcOH (15 cc) over a period of 1 hr. The mixture was cooled and a solid ppt removed. The filtrate was poured onto ice (800 g), extracted with ether (3 × 100 cc), and the combined extracts washed with Na_2CO_3aq, water, and then dried (Na_2SO_4). Removal of the ether left a solid which was chromatographed over alumina in light petroleum:ether (92:8) to give

4-bromo-2,5-diphenyloxazole (1·1 g, 31%), which crystallized from light petroleum as colourless needles, m.p. 70–71°. (Found: C, 60·2; H, 3·5; N, 4·6; Br, 26·3. $C_{15}H_{10}BrO$ requires: C, 60·5; H, 3·4; N, 4·7; Br, 26·6%). The NMR spectrum lacks the singlet at 2·68 τ attributed to the 4-H of the oxazole system.[20]

3-d_1-2,5-*Diphenyloxazole* (**12**). To 4-bromo-2,5-diphenyloxazole (0·3 g) in dry ether (10 cc) was added soln of n-BuLi [from Li (0·07 g) and n-BuBr (0·68 g)] in ether (20 cc), at −65°, for 1 hr, decomposed with D_2O (4 ml) and worked up as for 3. The product (0·2 g) was purified by sublimation, followed by preparative VPC (see above), m.p. 72–73°. The NMR spectrum completely lacked the characteristic singlet at 2·68 τ in the spectrum of 2,5-diphenyloxazole.[20]

4,5-*Di*(2,4,6-d_3)*phenylimidazole* (**6**). Prepared from d_6-benzil, formaldehyde and formamide (cf. Ref. 15). Crystallized from aqueous EtOH as colourless needles, m.p. 232–233°, yield 61%.

2-*Phenyl*-4,5-di(2,4,6-d_3)*phenylimidazole* (**9**). Prepared from d_6-benzil, benzaldehyde and formamide (cf. Ref. 15). Crystallized from aqueous EtOH as colourless needles, m.p. 270–272°, yield 60%.

2-(2,4,6-d_3)*Phenyl*-4,5-*diphenylimidazole* (**10**). Prepared from benzil, 2,4,6,-d_3-benzaldehyde and formamide as for 9, m.p. 273–274°.

d_1-*Stilbene* (**16**). Reduction of desoxybenzoin with LAD gave 1-d_1-1,2-diphenylethanol, which was dehydrated in DMSO to give d_1-stilbene, m.p. 124–125° (cf. Ref. 33). This was purified by preparative VPC. The NMR spectrum indicated quantitative incorporation of D (>99% d_1).

9,10-d_2-9,10-*Dideuterophenanthrene* (**19**). Reduction of the dimethyl ester of diphenic acid with LAD gave 2,2'-(d_2-hydroxymethyl)diphenyl, which was converted to 19 by the method of Hall *et al.*[34] Purification by preparative VPC gave 19, b.p. 174°/17 mm Hg. The NMR spectrum indicated quantitative incorporation of D (>99% d_4).

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