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ELECTRON-IMPACT STUDIES—L:*

SKELETAL-REARRANGEMENT FRAGMENTS IN THE MASS SPECTRA OF DIPHENYLPYRAZOLES AND -ISOXAZOLES

B. K. SIMONS, R. K. M. R. KALLURY† and J. H. BOWIE
Department of Organic Chemistry, University of Adelaide,
South Australia 5001

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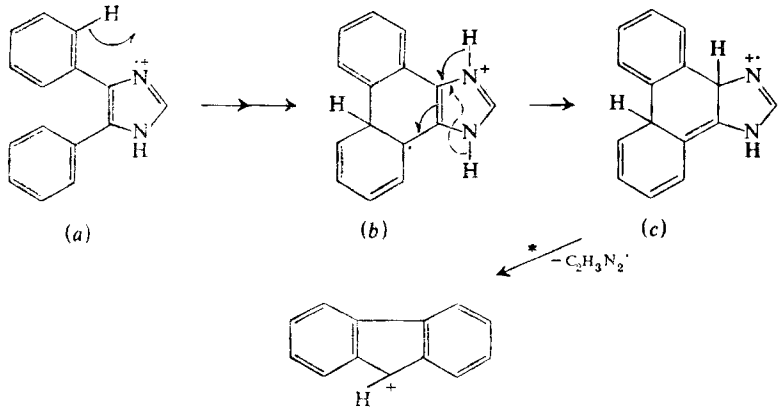
Abstract—The mass spectra of all diphenylpyrazoles and -isoxazoles contain rearrangement peaks at *m/e* 165 $[C_{13}H_9]^+$. In addition, the spectra of 3,5-diphenylisoxazoles contain peaks at *m/e* 180 $[C_{13}H_{10}N]^+$, which are produced by specific phenyl migrations. The mechanisms of both rearrangement processes have been studied by deuterium labelling.

THE EXTENSIVE rearrangement processes which occur in the mass spectra of aryl and alkyl-imidazoles,[2] oxazoles,[2 to 5] thiazoles[2] and isoxazoles[6] have been discussed. A report[7] of the formation of *m/e* 165 in the spectra of diphenylpyrazoles has appeared, but the mechanism of the rearrangement was not studied by deuterium labelling. The differences between the spectra of oxazoles and isoxazoles have been outlined[6] and it has been suggested[6,8,9] that the molecular ion interconversions [isoxazole]$^{+\cdot} \rightleftarrows$ [azirine]$^{+\cdot} \rightarrow$ [oxazole]$^{+\cdot}$ may account for many fragment ions in the mass spectra of substituted isoxazoles. The formation of *m/e* 165 by rearrangement processes is also noted in the spectra of 2,5-diphenyl-1,2,4-oxadiazole,[10] 4,5-diphenyl-2-pyrone,[11] 3,4-diphenyl-4,5-epoxy-2-cyclopenten-1-one,[13] stilbene and related compounds,[2,12,13,14] 9,10-dihydrophenanthrene[12,15] and benzyl phenyl ketone derivatives.[1]

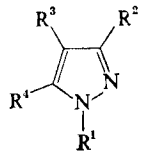


We have previously shown[2] that a double hydrogen transfer and randomization of hydrogens within each phenyl ring precedes the formation of *d*(*m/e* 165) from the

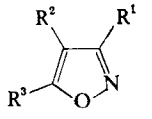
* For Part XLIX, see Ref. 1.

† Present address: Osmania University, Hyderabad, India.

molecular ion of 4,5-diphenylimidazole. One possible mechanism for this rearrangement is $a \rightarrow d$.[2] Similar rearrangements in the spectra of diphenylpyrazoles and -isoxazoles were noted previously[2] and the present investigation (outlined below) was planned in order to (a) investigate the scope of the rearrangement in pyrazoles and isoxazoles and (b) to determine the mechanism of the rearrangement for the unsymmetrical 3,4-diphenylpyrazole and the corresponding isoxazoles.



	R^1	R^2	R^3	R^4
(I)	H	C_6H_5	C_6H_5	H
(II)	D	C_6H_5	C_6H_5	H
(III)	H	C_6D_5	C_6H_5	H
(IV)	H	C_6H_5	C_6D_5	H
(V)	H	C_6H_5	H	C_6H_5
(VI)	D	C_6H_5	H	C_6H_5



	R^1	R^2	R^3
(VII)	C_6H_5	C_6H_5	H
(VIII)	C_6H_5	H	C_6H_5
(IX)	C_6H_5	D	C_6H_5
(X)	C_6H_5	I	C_6H_5
(XI)	H	C_6H_5	C_6H_5
(XII)	H	C_6H_5	C_6D_5
(XIII)	C_6H_5	C_6H_5	C_6H_5
(XIV)	$C_6H_2D_3$	C_6H_5	C_6H_5
(XV)	C_6H_5	$C_6H_2D_3$	C_6H_5

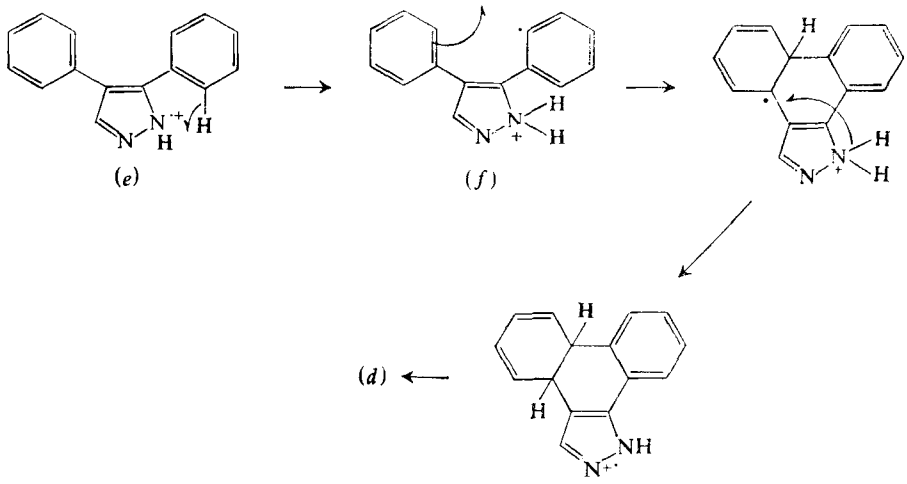
Selected mass spectra of I to XV are illustrated in Figs. 1 to 8, and the abundances of rearrangement peaks are summarized in Table 1. The compositions of all ions produced by skeletal-rearrangements in the spectra of the unlabelled compounds have been established by exact mass measurements. The presence of an appropriate metastable peak is depicted by an asterisk in either a figure or the text.

It can be seen from Table 1 that the abundance of $d(m/e\ 165)$ is large when the

TABLE 1. RELATIVE ABUNDANCES (%) OF m/e 165 (d) IN THE SPECTRA OF DIPHENYLPYRAZOLES AND -ISOXAZOLES

Compound	% d	Compound	% d
(I)	21	(X)	2
(IV)	7	(XI)	36
(VII)	42	(XIII)	20
(VIII)	4		

two phenyl groups are adjacent and minimal when they are 1,3 to each other. This is in accord with previous observations of diphenylimidazoles and oxazoles.[2] The spectra of 3,4-diphenylpyrazole (I) and the labelled derivatives (II to IV) are illustrated in Figs. 1 to 3. It was anticipated that transfer of a hydrogen atom would proceed to charged nitrogen and that back transfer of either hydrogen on nitrogen to some radical centre in the hydrophenanthrene unit should follow the cyclization process (e.g. $e \rightarrow d$), but that because 3,4-diphenylpyrazole is unsymmetrical (unlike 4,5-diphenylimidazole) that the hydrogen transferred to nitrogen should come specifically from the 3-phenyl ring, viz. $e \rightarrow f$.



There are several possibilities which may either preclude or make unrecognizable the specific transfer of hydrogen or deuterium from the 3-phenyl system in a labelled derivative. First, the 3,4-diphenylpyrazole molecular ion may rearrange to the 4,5-diphenylimidazole molecular ion. Second, hydrogen/deuterium randomization on the two phenyl rings may precede the transfer. Third, hydrogen transfer may proceed from both the 3- and 4-phenyl rings.

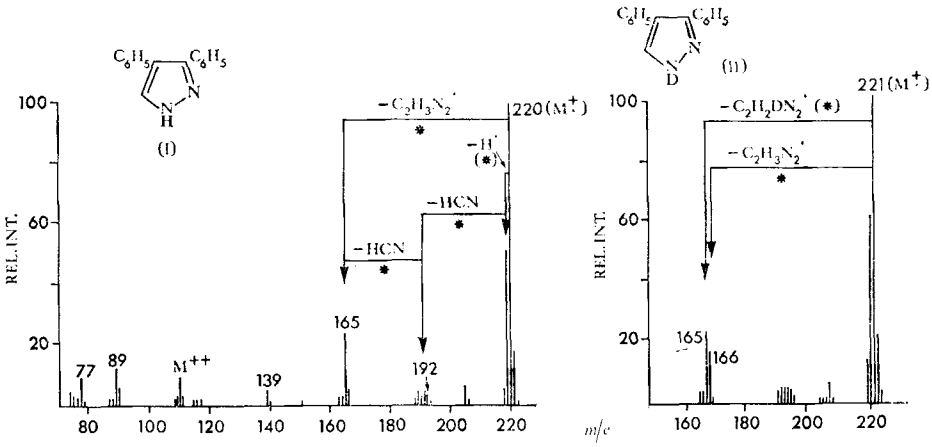


FIG. 1

Careful analysis of the spectra of the labelled derivatives allow certain proposals to be made. The ratio of the abundances (corrected for ^{13}C isotope peaks) of the *m/e* 165/166 ions in the spectrum of II is 1·37:1 at 15 eV. The theoretical ratio obtained, assuming hydrogen transfer to nitrogen followed by back transfer of either hydrogen or deuterium is 1·22:1. Ratios obtained for (a) the double hydrogen transfer process, but with scrambling of the H and D on nitrogen with the hydrogen at C-5 before the back transfer, and (b) for completely random loss of three hydrogens/deuterium are

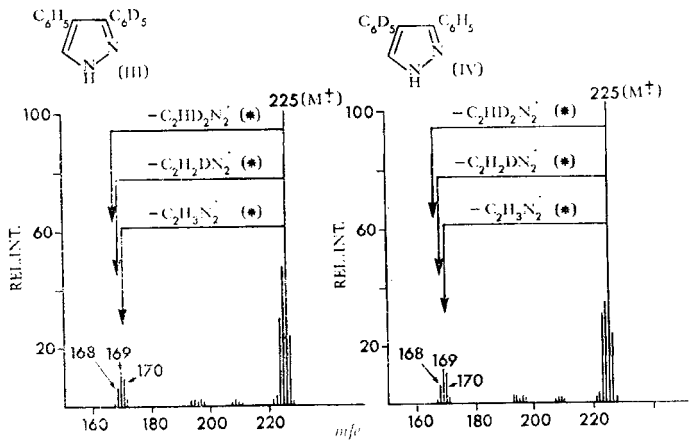


FIG. 2

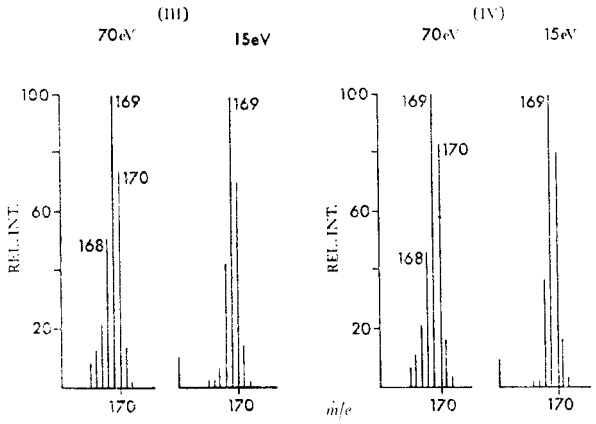


FIG. 3

2·3:1·0 and 3·0:1·0 respectively. These ratios show that after the initial hydrogen transfer to nitrogen that specific back transfer occurs. No randomization of the hydrogen/deuterium on nitrogen with any other hydrogen is observed. This is in accord with previous observations of diphenyloxazoles labelled with deuterium on the oxazole ring.[2]

The spectra (Figs. 2 and 3) of III and IV also show that the double hydrogen transfer does occur. The peaks in the *m/e* 168 to 170 region in the spectra of III and IV are qualitatively similar, indicative of either a symmetrical molecular ion, or of considerable randomization of the ten hydrogens/deuteriums of the phenyl rings, or of hydrogen transfer from either phenyl ring. There are two processes producing *m/e* 165 in the spectrum of I. A concerted process, substantiated by a metastable peak, produces the rearrangement ion directly from the molecular ion. A second process, M—H·—HCN—HCN, produces *m/e* 165 in a stepwise manner. At 70 eV both processes occur, but at 10 to 15 eV the stepwise process becomes minor in comparison to the concerted

process. Our arguments concerning abundance ratios will consequently be restricted to measurements at 15 eV, where it is assumed that the concerted formation of *m/e* 165 is the major process.

A detailed study* of the metastable peak shapes for the 220 → 165 and stepwise 220 → 219 → 192 → 165 processes in the spectra of I and 4,5-diphenylimidazole, and of the ratios of the abundances of the metastable ion at *m/e* 123·7 (220 → 165) and *m/e* 165, and *m/e* 168·3 (219 → 192) and *m/e* 192, shows that the daughter ions in the spectra of I do not have the properties of those in the spectrum of 4,5-diphenylimidazole. It is concluded that if the conversion $e \rightarrow a$ does occur, then it is only a minor process.

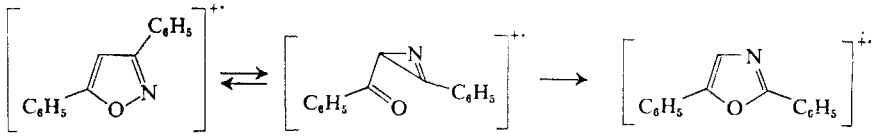
TABLE 2. RATIOS OF ABUNDANCES (CORRECTED FOR ^{13}C ISOTOPES) OF *m/e* 168 TO 170 IN THE SPECTRA OF (III) AND (IV) AT 15 AND 70 eV

eV	(III) Observed	Calculated 168:169:170	(IV) Observed 168:169:170
70	35:100:71	19:100:72	29:100:83
15	46:100:60		40:100:70

The ratios of the abundances of the *m/e* 168, 169 and 170 peaks in the spectra of III and IV are recorded in Table 2. If we now assume that the rearrangement process involves complete randomization of the five hydrogens and five deuterium atoms (cf. scrambling of the hydrogens in stilbene[14] and diphenyl[21]), followed by transfer of a hydrogen/deuterium atom to nitrogen (cf. *e*–also ignoring possible deuterium isotope effects) followed by specific back transfer of hydrogen/deuterium to the rearrangement centre ($f \rightarrow d$), with specific loss of HCN and random loss of HCN/DCN, a theoretical value of 19:100:72 for the [M—C_2HD_2N], [M—C_2H_2DN] and [M—C_2H_3N] concerted processes of III and IV is obtained (these values are the same as those which should be observed if hydrogen is transferred equally from both phenyl rings). The observed ratios are outlined in Table 2. Bearing in mind that the stepwise process does occur (especially at 70 eV), these ratios are not inconsistent except that the process [M—C_2HD_2N] is more pronounced than expected. This may indicate the operation of a small deuterium isotope effect. Computer calculations show that the observed ratios deviate more from the theoretical when the amount of initial randomization is less than 90%. Nevertheless, complete randomization does not occur, as the observed ratios (Table 2) and abundances (Fig. 3) show that the process [M—C_2H_3N·] is slightly more pronounced (and [M—C_2HD_2N·] less pronounced) in the spectrum of IV than in that of III. This must mean that at least *some* preferential hydrogen transfer occurs from the 3-phenyl substituent. Recalculation of the abundance ratios in the 15 eV spectrum of 4,5-di(2,4,6-d_3-phenyl)imidazole[2] also shows that complete randomization does not occur, and that some preferential transfer of the four *ortho* deuteriums occurs. We conclude that when 3,4-diphenylpyrazole is

* The theoretical background of this method has been described,[16,17] and its application widely used.[1,18,19,20] An analogous method to that used for this determination has been described.[1] The results have not been tabulated as no information can be gained from the figures except that there is no correlation of peak ratios. In all cases cited in this paper the abundance ratios of metastable and daughter ions being compared in various spectra were in error by a factor of more than 1:1·5.

subjected to electron-impact, that either unspecified (and incomplete) randomization of hydrogens of both phenyl rings precedes preferential hydrogen transfer to nitrogen from the 3-phenyl ring, with the further transfer and eliminations proceeding as outlined above, or alternatively that no hydrogen scrambling occurs between the phenyl rings but that hydrogens may be transferred from both the 3- and 4-phenyl rings with a slight preference for transfer from the 3-phenyl group. Of the two possibilities, we prefer the former.



(*g*) (*h*) (*i*)

The rearrangement processes in the spectra of di- and triphenylisoxazoles are illustrated in Figs. 4 to 8, and are analogous to those observed in the spectra[2] of the corresponding diphenyloxazoles. It has been proposed[9] that the isoxazole → oxazole conversion, (e.g. *g* → *i*) may account for the formation of *d* in the spectrum of 3,5-diphenylisoxazole. There is a qualitative correlation between the rearrangement ions in the spectra of the corresponding diphenylisoxazoles and -oxazoles (viz. 3,4-diphenylisoxazole–2,4-diphenyloxazole, 4,5-diphenylisoxazole and -oxazole, and 3,5-diphenylisoxazole–2,5-diphenyloxazole) but the application of metastable characteristics to the spectra of each pair of compounds does not substantiate the proposed

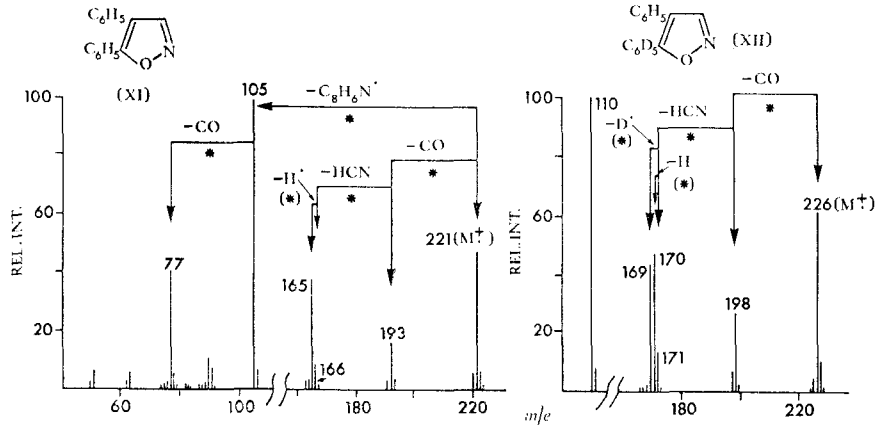


FIG. 4

molecular ion interconversions. The rearrangements are complex, occurring by both concerted and stepwise mechanisms in certain diphenyloxazole spectra,[2] but only by stepwise* elimination in those of the diphenylisoxazoles.

Although we consider it unlikely that major conversion to a diphenyloxazole species precedes the formation of *d*(*m*/*e* 165) in the spectra of VII, VIII, XI and XIII it is not possible to completely unequivocate such an isomerization.

* No appropriate metastable peaks substantiate the processes $[M]^{+\cdot} \rightarrow 166$ (cf.[3]).

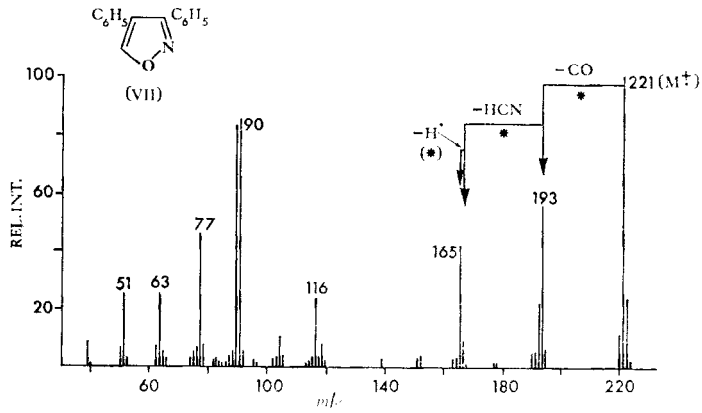


FIG. 5

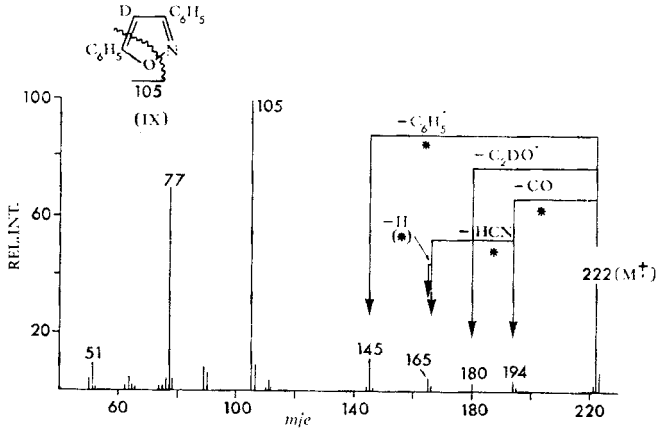


FIG. 6

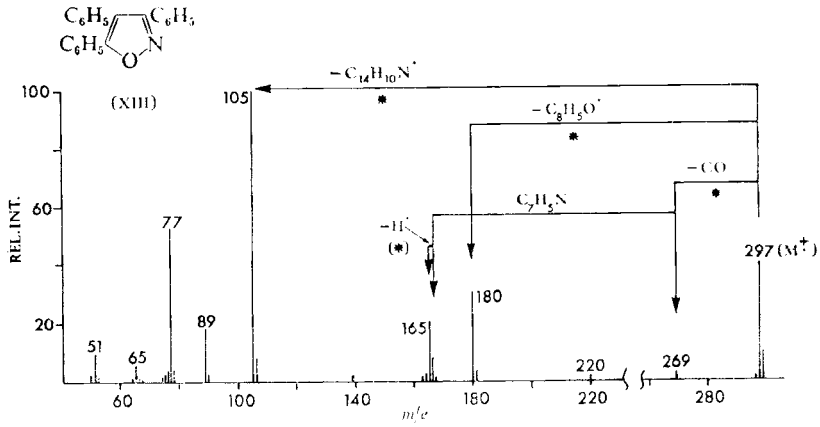


FIG. 7

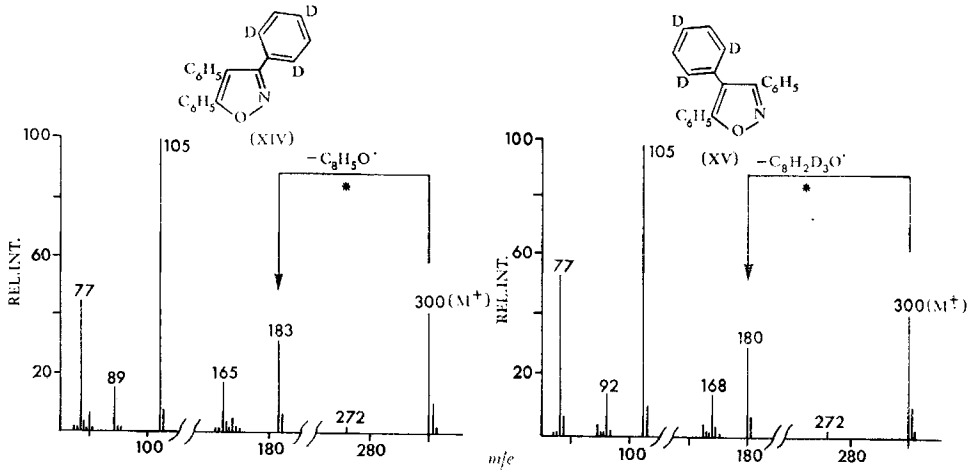
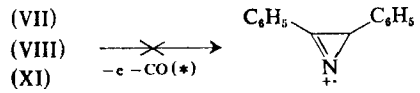


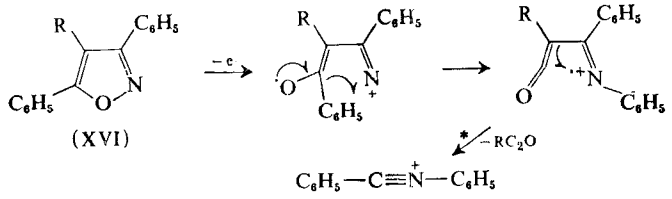
FIG. 8

A plausible structure for the [M — CO] species in the spectra of VII, VIII and XI is the 2,3-diphenyl-2--2-H-azirine radical ion (*j*). The metastable characteristics of the *m/e* 193 → 166 decompositions were compared in the spectra of the azirine, VII, VIII and XI. In no case was any correlation of peak shapes or abundance ratios obtained. Another important feature of the spectra of the diphenylisoxazoles is that a hydrogen attached to an isoxazole ring does not randomize with phenyl hydrogens (see Fig. 6). It is not possible to ascertain whether the hydrogen transfer process (which occurs for 3,4-diphenylpyrazole) or a phenyl migration accounts for the formation of *m/e* 165 in the spectra of diphenylisoxazoles. The 'normal' fragmentations of substituted isoxazoles have been described, and are best rationalized by breakdown of an acylazirine intermediate[6,8,9] (cf. *h*).



(*j*) *m/e* 193

The spectra of 3,5-diphenylisoxazole derivatives contain an ion at *m/e* 180 $[C_{13}H_{10}N]^+$ which is produced by a specific skeletal-rearrangement. The abundances of this ion in the spectra of VIII, X and XIII are 3, 10 and 32% respectively. The rearrangement ion is most pronounced in the spectrum (Fig. 7) of triphenylisoxazole; where it is more abundant than *d*(*m/e* 165). This rearrangement does not occur



(*k*) *m/e* 180

when 2,5-diphenyl and triphenyloxazole are subjected to electron-impact. Figure 8 shows that the 5-phenyl group is the migrating species, and that although hydrogen scrambling within a phenyl ring occurs, cross hydrogen randomization between the 5-phenyl hydrogens and the hydrogens of either the 4-phenyl or 4-H groups does not occur. A possible mechanism for this rearrangement is (XVI) → *k*, and the stability of *m/e* 180 is compatible with the properties of the Schiff's base cation *k*.[22]

EXPERIMENTAL

All mass spectra were determined with an Hitachi Perkin–Elmer RMU-6D double focusing mass spectrometer operating at 70 eV. Samples were introduced both through the all glass heated inlet system at 150° and 'direct insertion' at 70 to 80°. In all cases the two spectra were very similar except for very small differences in relative abundances of certain ions. The spectra recorded in Figs. 1 to 8 were all obtained after introduction of the samples through the heated inlet system. Exact mass measurements were performed at a resolution of 10,000 (40% valley definition) using heptacosafluorotributylamine to provide reference masses.

All compounds were recrystallized and checked for purity by n.m.r. and mass spectrometry. Light petroleum refers to the fraction b.p. 40 to 60°. All melting points were determined with a Gallenkamp melting point apparatus and are uncorrected.

The following compounds were prepared by reported procedures: I,[23] V,[24] VII,[25] VIII,[26] X,[27] XI[28] and XIII.[29]

Labelled compounds

The spectra of II and VI were obtained by introducing I and V directly into the source with deuterium oxide.[30]

3-(d_5-*Phenyl*)-4-*phenylpyrazole* (III)

(a) The reaction between d_6-benzene (4·0 g) and acetylchloride (4·0 g) in tetrachloroethane (25 cc) with aluminium chloride (10·0 g) gave d_5-acetophenone (2·6 g, 58%) b.p. 201 to 202°.

(b) d_5-Acetophenone (2·5 g) was converted[31] into 1-(d_5-*benzoyl*)-2-*phenylethylene* (4·6 g, 96%) m.p. 54 to 55° from ethanol.

(c) The reaction[32] of 1-(d_5-*benzoyl*)-2-*phenylethylene* (2·08 g) in methanol (25 cc) with hydrogen peroxide (7·0 cc, 15%) and aqueous sodium hydroxide (4 N, 3·5 cc) gave 1-(d_5-*benzoyl*)-2-*phenylethylene oxide* (2·0 g, 95%), which crystallized as white plates from ethanol, m.p. 90 to 91°.

(d) 1-(d_5-*benzoyl*)-2-*phenylethylene oxide* (1·09) was converted into d_5-*benzoylphenylacetaldehyde* (0·28 g, 28% m.p. 112 to 113°) by a reported procedure.[33] Purification of the product was achieved by chromatography over silicic acid (Mallinckrodt, 100 mesh) eluting with light petroleum/diethylether (97:3).

(e) Treatment[23] of d_5-*benzoylphenylacetaldehyde* (0·102 g) with hydrazine hydrate (0·3 g, 50%) in glacial acetic acid (1 cc) gave 3-(d_5-*phenyl*)-4-*phenylpyrazole* (0·120 g, 60%) which crystallized from diethylether/light petroleum (1:1) as colourless needles, m.p. 154 to 155°.

3-*Phenyl*-4-(d_5-*phenyl*)*pyrazole* (IV)

(a) d_8-Toluene (2·09 g) was converted[34] into d_7-benzyl bromide (2·6 g, 70%) b.p. 97 to 100°/35 mm Hg.

(b) The reaction[35] between d_7-benzyl magnesium bromide [from d_7-benzyl bromide (2·6 g) and magnesium (0·36 g)] and benzaldehyde (1·51 g) in ether (6 cc) gave 2-d_2-2-(d_5-*phenyl*)-1-*phenylethanol* (1·4 g, 70%), b.p. 134 to 140°/1 mm Hg.

(c) 2-d_2-2-(d_5-*phenyl*)-1-*phenylethanol* (1·1 g) in acetone (10 cc) was heated under reflux for 15 minutes with Jones reagent (1·6 cc). Water (10 cc) was added, and the solution extracted with ether (3 × 10 cc), the ether extract dried (Na_2SO_4), evaporated, and distillation of the residue gave d_7-*benzyl phenyl ketone* (1·0 g, 91%), b.p. 120 to 122°/0·1 mm Hg.

(d) d_7-*Benzyl phenyl ketone* (1·0 g) was added at 0°, with stirring, to a solution of sodium ethoxide [from sodium (0·12 g) and ethanol (2 cc)] and ethylformate (0·33 g) which had previously been kept at 0° for 2 hours. The resultant solution was maintained at 4° for three days, then poured into water (10 cc), acidified with dilute sulphuric acid, and extracted with ether (3 × 10 cc). The combined

ether extract was washed with water, and dried (Na_2SO_4). After removal of the solvent, the residue was chromatographed over silicic acid, eluting with benzene/light petroleum 1:1 to yield *benzoyl-(d_5-phenyl)-acetaldehyde* (0·184 g, 23%) as a pale yellow solid, m.p. 111 to 112°.

(e) *Benzoyl-(d_5-phenyl)acetaldehyde* (100 mg) was treated[34] with hydrazine hydrate (0·15 g, 50%) to yield *3-phenyl-4(d_5-phenyl)pyrazole* (0·03 g, 30%) which crystallized (as above) as colourless needles, m.p. 155 to 156°.

4-d-3,5-*Diphenylisoxazole* (IX)

To a solution of *n*-butyl lithium (1·0 g) in dry ether (50 cc) was added a suspension of 3,5-diphenyl-4-iodo-isoxazole (0·5 g) in ether (25 cc) with stirring, at −50°, under nitrogen, over a period of 15 minutes. After addition of deuterium oxide (1·5 cc), the ether layer was separated, dried (Na_2SO_4) and evaporated. The residue was crystallized from ethanol to yield (IX) as colourless needles, m.p. 178 to 179°. Yield 0·3 g (45%).

4-Phenyl-5-(d_5-phenyl)isoxazole (XII)

Treatment[28] of d_5-*benzoylphenylacetaldehyde* (0·029 g) with hydroxylamine hydrochloride (0·1 g) gave *4-phenyl-(5-d_5-phenyl)isoxazole* (0·011 g, 50%) which crystallized from ethanol as colourless needles, m.p. 68 to 69°.

3-(d_3-*Phenyl*)-4,5-*diphenylisoxazole* (XIV)

d_3-Benzaldehyde[36] (0·5 g) was converted[37] into d_3-benzaldoxime (0·50 g, 83%), m.p. 30 to 31° d_3-Benzaldoxime (0·50 g) was converted[29] into d_3-benzohydroxamyl chloride (0·5 g, 80%). The crude chloride (0·5 g) was treated[29] with aqueous sodium hydroxide to produce d_3-benzonitrile oxide to which was added trans-stilbene (0·80 g) to yield colourless needles of trans-3-d_3-*phenyl*-4,5 *diphenylisoxazoline* (0·61 g, 45%), m.p. 140 to 141° (white needles from ethanol). Treatment[29] of the isoxazoline (0·55 g) with N-bromosuccinimide and sodium methoxide, gave 3-d_3-*phenyl*-4,5-*diphenylisoxazole* (0·31 g, 56%) which was crystallized from ethanol as colourless needles, m.p 210 to 212°.

3,5-*Diphenyl*-4-(d_3-*phenyl*)*isoxazole* (XV)

To a solution of phenylnitromethane (0·5 g) and d_3-benzaldehyde[36] (0·4 g) in ethanol (2 cc) was added a saturated solution of ammonia in ethanol (0·5 cc). After standing at room temperature for 12 hours, the solid was filtered off and heated under reflux with aqueous potassium hydroxide (1 N, 5 cc). On cooling, XV was filtered and crystallized from ethanol as colourless needles, m.p. 211 to 213°. Yield 0·52 g (51%).

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