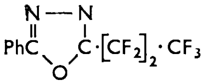
1264. *The Mass Spectra of Some Fluorine-containing 1,3,4-Oxadiazoles*

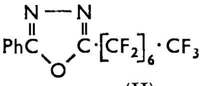
By J. L. COTTER

The electron-impact fragmentation patterns of 1-(2-phenyl-1,3,4-oxadiazol-5-yl)perfluoro-propane and -heptane, and 1,3-di-(2-phenyl-1,3,4-oxadiazol-5-yl)perfluoropropane have been obtained. Many of the principal ion-fragments have been correlated with probable structures and likely fragmentation paths. The ionisation potentials of these compounds are 9·8 ± 0·2, 9·9 ± 0·1, and 9·5 ± 0·1 ev, respectively.

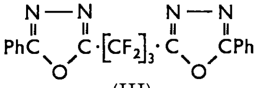
A PREVIOUS publication[1] dealt with the electron-impact fragmentations of 3,5-diphenyl-1,2,4-oxadiazole and 2,5-diphenyl-1,3,4-oxadiazole; this work has now been extended to



(I)



(II)



(III)

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[1] J. L. Cotter, *J.*, 1964, **5491**.

include the compounds (I)—(III), for which partial mass spectra are presented in Table 1 and ionisation and appearance potentials in Table 2.

TABLE 1

Partial mass spectra of compounds (I)—(III)

	Relative intensity (%)				Relative intensity (%)				Relative intensity (%)		
m/e	(I)	(II)	(III)	m/e	(I)	(II)	(III)	m/e	(I)	(II)	(III)
514		88·0		253			3·86	90	3·44	2·73	
495		10·7		204			10·5	89	11·4	7·45	7·95
440			11·2	195	7·26	28·2	1·54	77	100·0	77·5	77·5
363			15·4	176			24·2	76	7·14	5·40	11·9
337			14·8	145	89·0	100·0	28·7	69	10·6	18·8	15·7
335			7·45	119	2·59	7·30	2·73	63	13·8	7·12	9·30
314	98·0			105	28·1	35·8	100·0	51	12·1	6·28	8·38
323			3·82	103	22·5	16·6	38·8	50	6·21	2·73	3·84
295	4·10		3·82	92	2·60	2·12	7·16	39	7·65	3·90	5·46

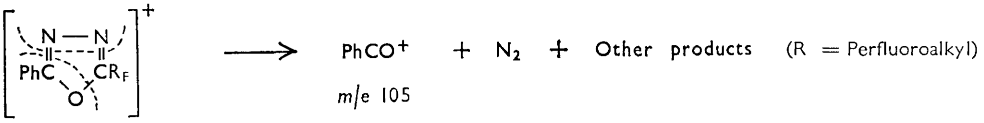
TABLE 2

Ionisation potentials of compounds (I)—(III), and the appearance potentials of some fragment ions

Molecule	m/e	Ionisation * or appearance † potential (ev)	No. of determinations
(I)	314	9·8 ± 0·2 *	5
(I)	145	11·8 ± 0·2 †	3
(II)	514	9·9 ± 0·1 *	3
(II)	145	12·1 ± 0·1 †	4
(III)	440	9·5 ± 0·1 *	2

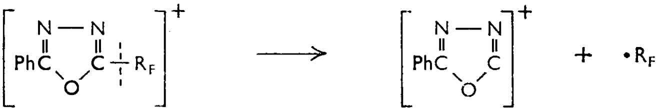
1-(2-*Phenyl*-1,3,4-*oxadiazol*-5-*yl*)*perfluoro-propane and -heptane,* (I) *and* (II).—Peaks at m/e 77 (Ph^+) are prominent in both spectra, and the presence of a metastable peak at m/e 56·4, $105^+ \longrightarrow 77^+ + 28$, in each of the spectra is evidence that this ion largely arises from the process $PhCO^+ \longrightarrow Ph^+ + CO$.

The relatively intense peaks at m/e 105 in both spectra might arise by the fragmentation processes



A similar fragmentation mechanism was suggested to account for the base peak at m/e 105 in the mass spectrum of 2,5-diphenyl-1,3,4-oxadiazole.[1]

The experimentally determined ratios of the isotopic ion-intensities at m/e 146 and 147 to the ion-intensity at m/e 145 were 0·0943 and 0·0065, respectively, in the spectrum of (I), and 0·0940 and 0·0059, respectively, in the spectrum of (II); in each spectrum these values are reasonably close to the calculated[2] ratios (0·0953 and 0·0061) for the atomic combination $C_8H_5N_2O$. If the oxadiazole ring structure is assumed to remain intact, then the formation of the ion at m/e 145 can be represented as



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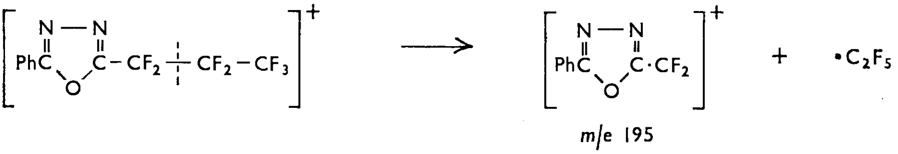
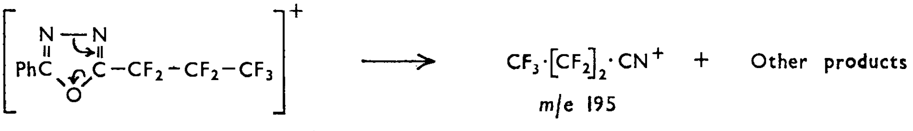
[2] J. H. Beynon and A. E. Williams, " Mass and Abundance Tables for Use in Mass Spectrometry," Elsevier, London, 1963.

Two fragmentation processes can be envisaged to account for the peak at *m/e* 195 in the spectrum of (I); the first is represented in Scheme 1, and the second in Scheme 2.



Scheme 1



Scheme 2

The ratios of the isotopic ion-intensities at *m/e* 196 and 197 to the ion-intensity at *m/e* 195 were 0·1340 and 0·0092, respectively. These values, although greater than the calculated[2] ratios (0·1061 and 0·0071) for the atomic combination $C_9H_5F_2N_2O$ (Scheme 1), are more consistent with them than the calculated[2] ratios (0·0470 and 0·0008) for the atomic combination C_4F_7N (Scheme 2). The corresponding isotopic ratios (0·0982 and 0·0076 in the spectrum of (II) are also consistent with the assignment of the ion at *m/e* 195 as in Scheme 1.

Ions at *m/e* 103 correspond to $PhCN^+$, and the presence of a metastable peak at *m/e* 33·9, $314^+ \longrightarrow 103^+ + 211$, in the spectrum of (I) establishes the molecular-ion as the immediate precursor; however, no direct evidence (in the form of metastable peaks) was found for similar transitions in the spectra of (II) and (III).

1,3-*Di*-(2-*phenyl*-1,3,4-*oxadiazol*-5-*yl*)*perfluoropropane* (III).—In common with the spectra of (I) and (II), the spectrum of (III) has prominent peaks at *m/e* = 145, 105, 103, and 77; however, the abundant ions of *m/e* 363, 337, 335, 204, and 176 have no counterparts in the spectra of (I) and (II). A further feature is that the molecular-ion of (III) is much less abudant than those of (I) and (II). The ion at *m/e* 363 is probably formed by the loss of the phenyl group from the molecular-ion, and the ion at *m/e* 335 might arise by the loss of either the benzoyl group, or the phenyl group together with molecular nitrogen from the molecular-ion, or by the loss of either molecular nitrogen or carbon dioxide from the ion at *m/e* 363. The ion at *m/e* 204 which formally differs from the ion at *m/e* 337 by 133 mass units might arise by the loss of the benzoyl group and molecular nitrogen from this ion.

EXPERIMENTAL

The compounds (I)—(III), m. p.s 29°, 56—57°, and 101—102°, respectively, were kindly made available by Dr. J. P. Critchley.

Mass spectra were obtained with 70-v electrons and an accelerating voltage of 1975 v, using an A.E.I. mass spectrometer M.S. 2-H. The temperature of the hot-inlet system was 178° with (I), 148° with (II), and 197° with (III). The molecular-ion intensities showed little or no variation over the time periods required for the determination of the spectra, showing that no thermal decomposition was taking place.

Ionisation and appearance potentials were obtained as described previously.[3]

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[3] J. L. Cotter, *J.*, 1965, 1520.