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MASS SPECTROMETRIC BEHAVIOUR OF SOME 5,5-DIPHENYLGLYCOCYAMIDINE AND -HYDANTOIN DERIVATIVES†‡

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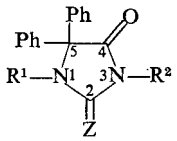
Abstract—The mass spectra and main fragmentation pathways are presented for thirteen 1- and 3-substituted 5,5-diphenylglycocyamidine and -hydantoin derivatives. The principal decomposition routes of these compounds are also of diagnostic value for ascertaining positional isomerism when the substituents are eliminated in the initial stage of fragmentation.

INTRODUCTION

IN AN earlier paper[1] it was shown that the structure of 1,5,5- and 3,5,5-triphenylhydantoins, -thiohydantoins and -glycocyamidines can be unambiguously deduced from their mass spectra, in a similar manner as for the 1- and 3-methylhydantoin[2] and dithiohydantoin[3] derivatives.

In this paper we wish to demonstrate, by means of model compounds (Table 1), that correlations suitable for unambiguous structure assignment also exist between mass spectra and structure in cases where substituents that are attached to the N atoms in positions 1 and/or 3 are lost in the initial fragmentation.

TABLE 1. COMPOUNDS INVESTIGATED



Compound	R^1	R^2	Z
(I)	H	*t*-Bu	NH[a]
(II)	Me	*t*-Bu	NH
(III)	Et	*t*-Bu	NH
(IV)	CH_2Ph	*t*-Bu	NH
(V)	*t*-Bu	*t*-Bu	NH
(VI)	*t*-Bu	H	NH[a]
(VII)	*t*-Bu	Et	NH
(VIII)	*t*-Bu	CH_2—Ph	NH
(IX)	*t*-Bu	H	N-*t*-Bu[a]
(X)	H	*t*-Bu	N-*t*-Bu[a]
(XI)	*t*-Bu	Et	0
(XII)	*t*-Bu	CH_2—Ph	0
(XIII)	*t*-Bu	*t*-Bu	0

[a] Potentially tautomeric compounds.

† Hydantoins, thiohydantoins, glycocyamidines—Part XLII.

‡ For Part XLI, see Ref. 5.

TABLE 2. MONOISOTOPIC MASS SPECTRA OF COMPOUNDS I TO XIII

m/e	(I)	(II)	(III)	(IV)	(V)	(VI)	(VII)	(VIII)	(IX)	(X)	(XI)	(XII)	(XIII)
398												16[M]$^{+\cdot}$	
397				13[M]$^{+\cdot}$				67[M]$^{+\cdot}$					
383												32	
382				0,2				18					
364													2,1[M]$^{+\cdot}$
363					3,1[M]$^{+\cdot}$				42[M]$^{+\cdot}$	52[M]$^{+\cdot}$			
349													2,2
348									0,5	0,4			
342				5,2				4,0				14	
341				12				18				0,6	
340				4,1				15					
336											4,5[M]$^{+\cdot}$		
335			17[M]$^{+\cdot}$				31[M]$^{+\cdot}$						
321		12[M]$^{+\cdot}$									45		
320			0,6				40						
308													0,7
307	18[M]$^{+\cdot}$				9,0	13[M]$^{+\cdot}$			15	51			0,1
306		0,6			1,0				14	6,1			
293													3,7
292	0,4				1,6	3,1							
280			15								2,5		
279	1,5		70				5,0				0,2		
278							6,1						

TABLE 2 (*continued*)

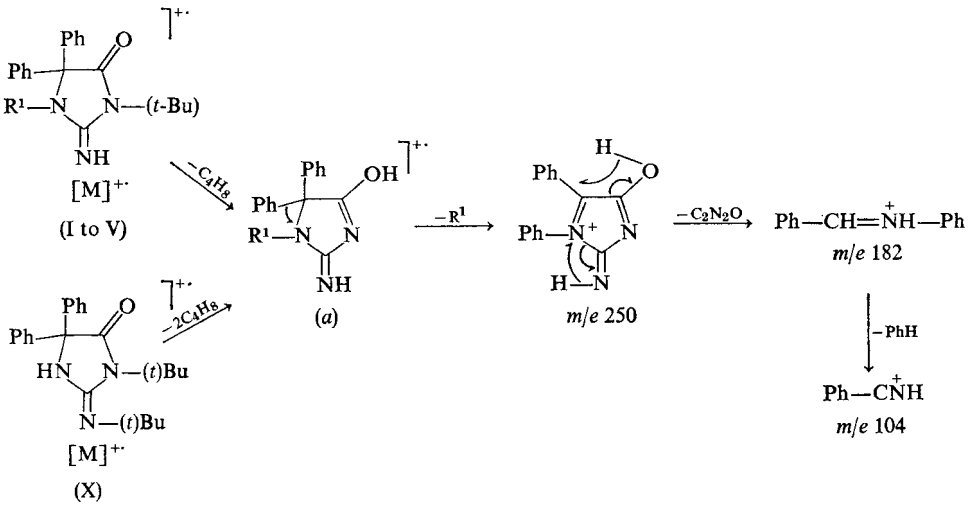
m/e	(I)	(II)	(III)	(IV)	(V)	(VI)	(VII)	(VIII)	(IX)	(X)	(XI)	(XII)	(XIII)
265		*100*						5,8			3,2	3,2	16
264	16				15			4,1					
252	10								32	11			1,7
251	*100*						1,1		22	*100*	5,5	3,6	21
250	18	61	*100*	*100*	*100*	*100*	0,8	4,1	19	37			
237							2,4					0,5	
236		4,9						3,3				0,4	1,4
235			1,8						13				
210			15										
208	28		16	0,6	16	7,0	*100*	*100*	*100*	36	*100*	*100*	*100*
207		2,6		1,1		6,1			2,7	71			
197													5,5
196		51											
194		7,6	5,1	13				0,5			0,3		
193							1,5	2,1	4,5	2,8			
182	89	15	16	10	17	26		5,6	18	5,7			
180	17				5,9	16	8,0				6,7	6,4	3,1
166	12	11	5,9	9,1	8,5	17	2,7	2,8	3,0	3,0	2,5	2,4	2,1
165	30	26	16	13	15	31	13	14	17	19	9,0	9,5	6,8
118		36											
105	17		5,1			11					2,9	3,1	6,8
104	41	15	34	11	31	53	8,7	10	19	63	6,8	5,0	3,0
91				27				52				21	
77	25	25	16	7,1	14	34	27	26	31	41	19	18	13
57	18	9,6	6,1	3,1	16	22	12	15	27	31	11	16	16

RESULTS AND DISCUSSION

The 70 eV mass spectral data of the compounds investigated are presented in Table 2. To study the decomposition processes, first and second field free metastable ions were used and when necessary, the exact mass of ions was measured.

The molecular ions appear in the mass spectra of all compounds studied and their characteristic main primary fragmentation processes include the rupture of an N—(*t*-Bu) bond, either homolytically or with a H rearrangement.

The main characteristic fragmentation of 3-(*t*-Bu)-glycocyamidines is shown in Scheme 1. Here fragmentation starts with the elimination of the 3-(*t*-Bu) group with

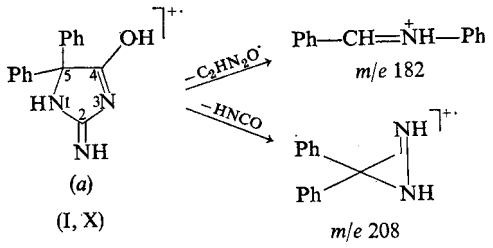


SCHEME 1

a hydrogen transfer (McLafferty rearrangement) which yields the ions *a*. This is followed by the loss of the R^1 group (giving the *m/e* 250 ions). The importance of the latter process largely increases in the I → V direction, i.e. with increasing steric size of the R^1 group and increasing stability of the R^1 radical formed. Therefore, the elimination of R^1 can be assisted by participation of the phenyl groups in position 5 and the formation of the ion at *m/e* 250, as indicated by its high stability, is accompanied by the migration of a phenyl group.

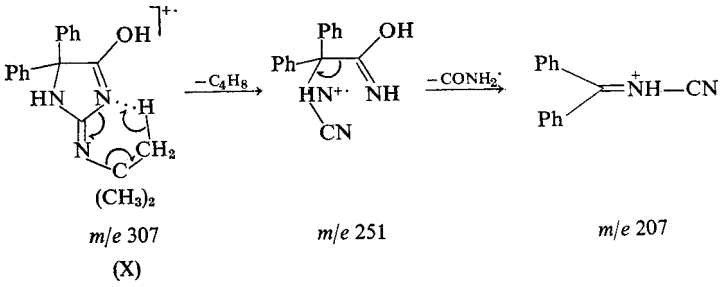
Decomposition of the *m/e* 250 ion yields the *m/e* 182 ion. This process involves the migration of two hydrogen atoms via 4-membered cyclic transitions in both cases. The *m/e* 182 ion, gives rise to a protonated benzonitrile and/or protonated phenylisocyanide ion (*m/e* 104) by elimination of constituents of benzene.

For both energetic and steric considerations, the driving force for the loss of R^1 = H from ion *a* of I (transition 251 → 250) is small and hence the further decomposition pathway in this case is mainly the 251 → 182 process. Additionally, cleavages of the 2–3 and 4–5 bonds of the hetero-ring are also observed. This process leads to the *m/e* 208 ion (Scheme 2).



SCHEME 2

In the case of X, both *t*-Bu groups are eliminated via H rearrangement. One product of these reactions is the type *a* ion. In this case, the *t*-Bu group attached to the imino group leaves behind one of its H atoms on the imino group. The H atom can also migrate to the N atom in position 3, however, if this process is preceded by the loss of the 3-(*t*-Bu) group. Then an open structure *m/e* 251 ion will be formed (Scheme 3), which decomposes to an abundant *m/e* 207 ion that is not so intense in the spectra of the other compounds examined.



SCHEME 3

In the case of VI (R^2 = H), the main primary decomposition process is the loss of the R^1(= *t*-Bu) group, presumably also with a phenyl group migration, leading to the *m/e* 250 ion. Further decomposition of the product ion also yields the *m/e* 182 ion in the cases of compounds I to V.

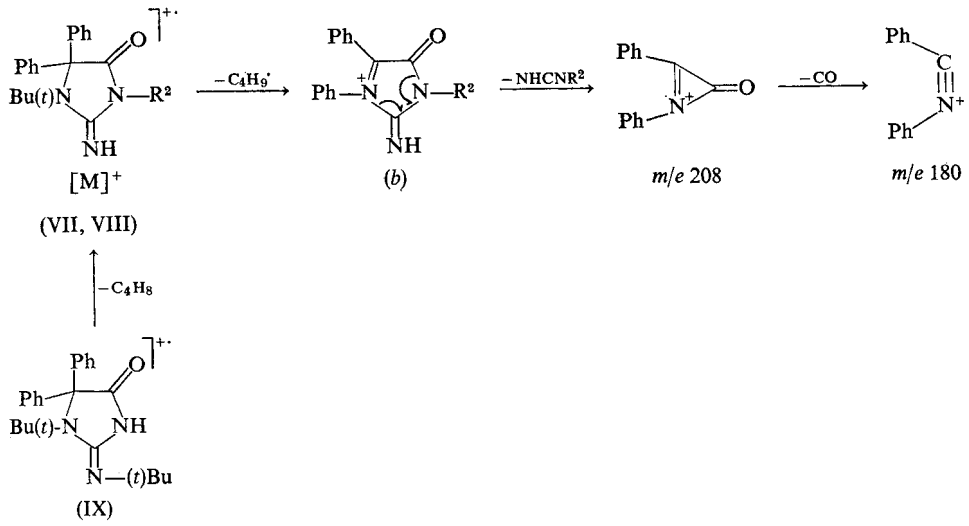
Similarly to VI, the primary fragmentation process of VII and VIII containing the 1-(*t*-Bu) group is loss of R^1 (Scheme 4).

In the case of IX, the loss of R^1 is preceded by the loss of the substituent attached to the imino group as C_4H_8.

In contrast to type *a* ions, the ions *b* decompose mainly to give the ion at *m/e* 208 which is the base peak in the spectra of VII to IX. The elemental composition and the structure of this ion differ from those of the ion at *m/e* 208 ion obtained from I. They are capable of losing CO to a slight extent, thereby producing *m/e* 180 ions (Scheme 4).

In the case of VII and VIII, loss of a methyl group from the molecular ion is also observable. Furthermore, the spectrum of VIII exhibits a $[C_7H_7]^+$ ion. The former process can be interpreted as the cleavage of a C—C bond β to N which is well known with N-alkyl substituted hydantoins (R > CH_3).[2]

The fragmentation of the hydantoin derivatives examined (XI to XIII) is generally similar to that of the analogous glycocyamidines. As in the case of compounds VI



SCHEME 4

to IX, the main fragmentation route leads to the formation of *m/e* 208 ions by expulsion of the R^1 group. However, with hydantoin derivatives, loss of the R^1 = *t*-Bu group involving H migration is also observable, suggesting that R^1 elimination via a McLafferty rearrangement is more favourable in the presence of 2-carbonyl group as compared with that of the imino group. Cleavage of the C—C bond β to N in the N-substituents also usually takes place giving the $[M - 15]^+$ ions. This process is particularly important for the 3-ethyl derivatives (XI).

EXPERIMENTAL

Compounds I to V and XII were prepared as described earlier.[4] For the preparation of compound VI see Ref. 5. Compounds VII to X were obtained by allowing N-(*t*-Bu)-α-chloro-α,α-diphenylacetamide to react with the appropriate potassium N-cyanoamide in anhydrous DMSO.[6] Deimination of VII, VIII and V furnished compounds XI to XIII, respectively.

The mass spectra were obtained using an AEI MS-902 double focusing mass spectrometer operating at an ionising energy of 70 eV and an ion chamber temperature of 160 to 180 °C. The samples were introduced into the source via a direct inlet system. When necessary, the elemental composition of the ions was determined by high resolution mass measurements (±3 ppm).

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