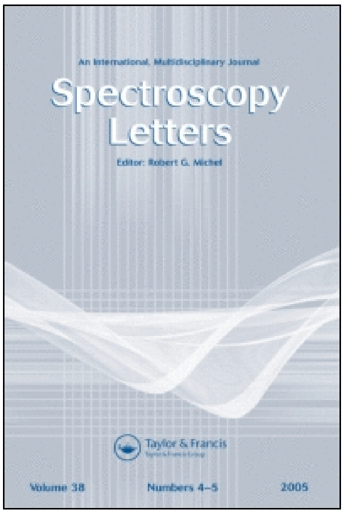

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The Mass Spectra of Substituted Diaryl α-Iminonitriles

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THE MASS SPECTRA OF SUBSTITUTED DIARYL α-IMINONITRILES

Key Words: mass spectrometry, imidoyl cyanides, α-iminonitriles

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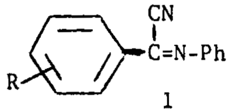
Abstract

The mass spectra of a series of substituted diaryl α-iminonitriles are reported. The most significant fragmentations arise from the following processes: (1) cleavage of the C-CN bond, (2) elimination of the R group from the substituted aryl ring, (3) formation of a phenyl cation ($C_6H_5^+$), and (4) loss of a hydrogen atom from the parent ion. Anomolous behaviour was shown by the p-(t-butyl) derivative and reasons for this are discussed.

Introduction

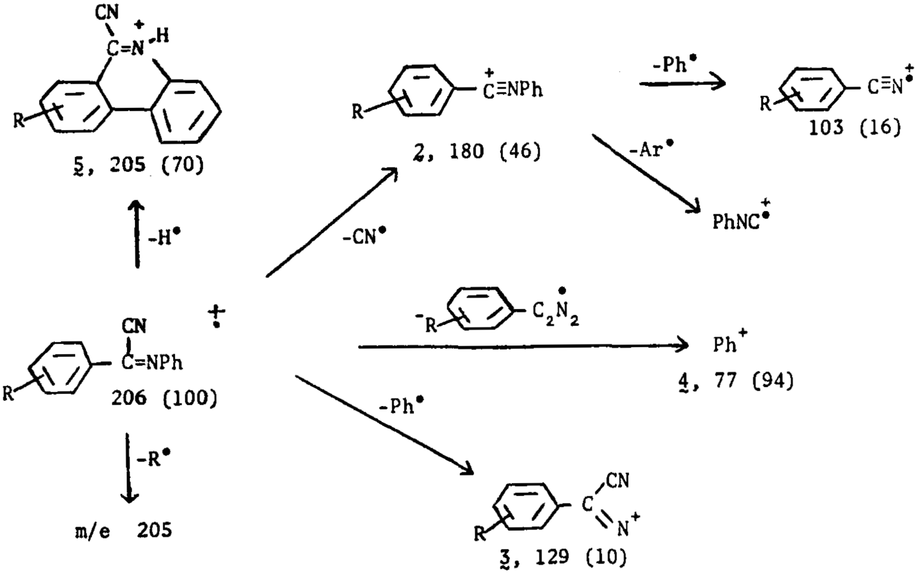
The preparation of diaryl imidoyl chlorides is a standard laboratory procedure[1] but only recently have the corresponding diaryl α-iminonitriles been prepared.[2,3] We have synthesized a series of such compounds, 1, and report here their mass spectra.



1

R = H, p-Me, m-Me, p-MeO, p-t-Bu, p-Cl, o-Cl, m-Br

All α-iminonitriles examined gave strong molecular ions and frequently this ion was the base peak. Fragmentation of the molecular ion can occur by cleavage of any one of the three bonds attached to the central C=N. In fact, cleavage of the Ar-C bond proved to be of minor importance. However, loss of cyanide radical from the molecular ion to give 2 (Scheme 1) was significant



The m/e (rel. intensities) shown are for R=H

SCHEME I. Fragmentation of Diaryl Imidoyl Cyanides in all cases (except 1, R=p-t-Bu) and metastable ions were observed for this fragmentation. Cleavage of the Ph-N bond was important and occurred in two ways; fragmentation to give 4 (m/e=77) and loss of phenyl to give ion 3. The former was by far the more favored mode of decomposition but ion 3 was detected in all cases.

Two other fragmentations of the molecular ion were observed, loss of a hydrogen and a loss of the substituent group R. The M^{+}-1 peak 5 was quite intense (except for 1, R=p-t-Bu) and, by analogy with the M^{+}-1 peak formed in the case of benzophenone anil[4], the phenanthridine structure 5 shown in Scheme 1 is suggested. Loss of the substituent group from the molecular ion gave the ion (m/e=205) in each case. Again the intensity of this ion was small in the case of 1 (R=t-bu) relative to the intensities observed in all other cases. Table 1 contains a comparison of these fragmentations of the molecular ion.

Further fragmentation of ion 2 can occur by loss of one or the other of the two aryl groups attached to the C-N triple bond. Both modes of fragmentation were observed although the intensities of the fragment ions were low. Substituents had little effect on the partitioning between these two fragmentation pathways except in the case of the *ortho*-Cl substituent where loss of the unsubstituted phenyl was clearly facilitated. Table 2 compares the intensities of the two product ions.

A careful examination of the mass spectra of 1 (R=p-t-Bu) shows the fragmentation pattern characteristic of the other imidoyl cyanides. However, the intensity of these ions is quite

Table I

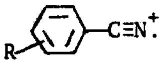
Fragmentation of the Molecular Ion of Imidoyl Cyanides, **1**

Compound **1**, R=	fragment, m/e (rel. intensity)*				
	M^+	M^+-1	M^+-CN	M^+-R	M^+-Ph
H	206 (100)	205 (70)	180 (46)	205 (70)	129 (10)
p-Me	220 (100)	219 (46)	194 (46)	205 (36)	143 (15)
m-Me	220 (100)	219 (45)	194 (37)	205 (26)	143 (11)
p-MeO	236 (100)	235 (42)	210 (48)	205 (10)	159 (13)
p-t-Bu	262 (100)	261 (1)	236 (1)	205 (2)	185 (1)
p-Cl	240 (100)	239 (45)	214 (41)	205 (30)	163 (8)
	242 (33)	241 (30)	216 (14)		165 (3)
o-Cl	240 (100)	239 (31)	214 (62)	205 (95)	163 (6)
	242 (38)	241 (28)	216 (24)		165 (2)
m-Br	284 (100)	283 (29)	258 (28)	205 (38)	207 (5)
	286 (97)	285 (46)	260 (26)		209 (5)

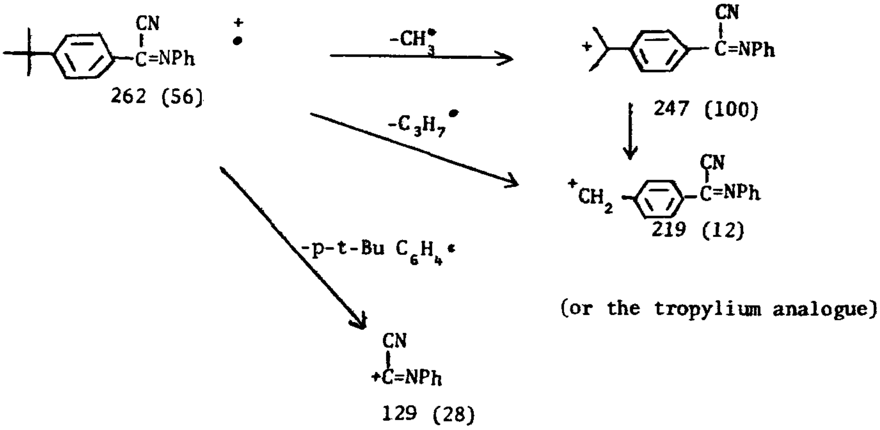
• compared to M^+ as 100.

Table 2

Fragmentation of ion **2**

Compound **1**, R=	Product Ion, m/e (rel. intensity)	
		$PhC\equiv N^{+\cdot}$
H	-	103 (16)
p-Me	117 (10)	103 (16)
m-Me	117 (7)	103 (7)
p-MeO	133 (8)	103 (7)
p-t-Bu	159 (0.5)	103 (0.5)
p-Cl	137 (5)	103 (7)
	139 (2)	
o-Cl	137 (13)	103 (8)
	139 (10)	
m-Br	181 (3)	103 (10)
	183 (3)	

low in comparison to the principal peaks which derive from the fragmentation shown in Scheme 2. Thus the base peak is M^+-CH_3



SCHEME II. Fragmentation of 1 (R=p-t-Bu)

(m/e=247) and ions M^+ -C_3H_7 (m/e=219) and M^+-p-t-Bu C_6H_4 (m/e=129) are readily observed as well as a metastable ion at 194.3 (247→219). It would appear that the facile loss of a methyl group from the parent ion diverts the decomposition of the molecular ion into a path not available to the other imidoyl cyanides examined.

Experimental

Mass spectra were obtained on a Varian Mat CH7 Mass Spectrometer, using an accelerating potential 4kV, 70 eV electrons and a trap of 300 μA. The temperature of the source was held constant at 200° C. The mass spectral data is summarized in Table 3.

The compounds used in this study were prepared as described previously[3]. The p-t-butyl derivate (**1**,R-p-*t*-Bu) was prepared in 80% yield, melting point 80°C. Found: C,82.14; H,6.96; N,10.63. $C_{18}H_{18}N_2$ requires C,82.40; H,6.91; N,10.68%).
^{1}H-N.M.R. ($CDCl_3$): δ=8.2-7.0(m, 9M), δ=1.3 (s,9H).

Table 3 . Mass Spectra of Diaryl Imidoyl Cyanides, **1**.

			1, R=				
H m/e (RI)	p-Me m/e (RI)	m-Me m/e (RI)	p-MeO m/e (RI)	p-t-Bu m/e (RI)	p-Cl m/e (RI)	o-Cl m/e (RI)	m-Br m/e (RI)
207 (15)	221 (17)	221 (17)	237 (17)	263 (11)	242 (22)	242 (15)	287 (11)
206 (100)	220 (86)	220 (100)	236 (100)	262 (56)	241 (20)	241 (11)	286 (66)
205 (70)	219 (40)	219 (45)	235 (42)	248 (19)	240 (66)	240 (39)	285 (31)
180 (46)	205 (31)	205 (26)	210 (48)	247 (100)	239 (30)	239 (12)	284 (68)
129 (10)	194 (40)	194 (37)	205 (10)	219 (12)	216 (9)	216 (9)	283 (20)
104 (10)	143 (13)	143 (11)	192 (13)	129 (28)	214 (28)	214 (24)	260 (18)
103 (16)	136 (16)	91 (18)	167 (10)	116 (23)	205 (20)	205 (37)	258 (19)
78 (17)	117 (10)	78 (21)	159 (13)	77 (86)	114 (12)	139 (10)	205 (26)
77 (94)	116 (13)	77 (89)	78 (16)		102 (12)	137 (13)	114 (10)
	103 (13)		77 (93)		78 (19)	78 (16)	103 (10)
m* 157.3	91 (22)				77 (100)	77 (100)	102 (12)
	89 (16)		m* 187	m* 233,	m* 190		78 (11)
	85 (49)	m* 171		154.3		m* 190	77 (100)
	83 (70)						
	78 (26)						m* 235,234
	77 (100)						
	m* 171						

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