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Electron-Impact-Induced Fragmentation of *N*-(Triarylmethyl)- and *N*-(Triarylsilyl)triarylphosphinimines

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Mass spectra of *N*-(triarylmethyl)- and *N*-(triarylsilyl)triarylphosphinimines are presented. The cleavage products of *N*-(triarylmethyl)triarylphosphinimines are analogous to those of *N*-phenyltriphenylphosphinimine and derivatives previously reported. The relative intensities are considerably different.

In view of the recent interest in mass spectrometric behavior of *N*-phenyltriphenylphosphinimines (*N*-phenyliminotriphenylphosphoranes) (*1*) (I–IV, Table I), it was thought worthwhile to examine the mass spectra of the structurally related *N*-(triarylmethyl)triarylphosphinimines (V–VIII, Table I) and of *N*-(triarylsilyl)triarylphosphinimines (XIII–XVIII, Table III) (*3*). The most interesting fragment ions, *m/e* greater than 100, are summarized in Tables I–III.

Discussion

An interesting anomaly is observed in the spectra of compounds XI and XII (Table II). No molecular ions are observed. The peaks at *m/e* 461, which correspond to the molecular ions of compounds IX and X, suggest that isomers XI and XII lose

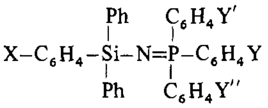
Table I. Main Fragment Ions of *N*-Aryltriphenylphosphinimines (I -IV) and *N*-(Triarylmethyl)triphenylphosphinimines (V-VIII) [*m/e* and Their Relative Intensities (%)]

Compound	X	$[M]^+$	$[M-Ph]^+$	$[PPh_3]^+$	$[PPh_2]^+$	$[PPh_2-2H]^+$	$[Ph_2-2H]^+$	$[PPh]^+$
				$XC_6H_4N{=}P(Ph)_3$				
I	H	353 (100)	276 (9)	262 (15)	185 (14)	183 (52)	152 (12)	108 (13)
II	p-OCH$_3$	383 (100)	306 (2)	262 (8)	185 (7)	183 (18)	152 (3)	108 (13)
III	p-F	371 (100)	294 (8.3)	262 (94)	185 (27)	183 (94)	152 (14)	108 (29)
IV	m-F	371 (100)	294 (6.2)	262 (62)	185 (18)	183 (75)	152 (8)	108 (12)
				$XC_6H_4C(Ph)_2N{=}P(Ph)_3$				
V	H	519 (2)	442 (32)	262 (100)	185 (32)	183 (6)	152 (11)	108 (32)
VI	p-OCH$_3$	549 (1)	472 (22)	262 (100)		183 (50)	152 (10)	108 (25)
VII	p-F	537 (1)	460 (48)	262 (100)		183 (53)	152 (13)	108 (53)
VIII	m-F	537 (3)	460 (40)	262 (100)	185 (13)	183 (80)	152 (3)	108 (50)

Table II. Main Fragment Ions of *N*-Aryl- and *N*-(Triarylmethyl)tris(*p*-methoxyphenyl)phosphinimines [*m/e* as Their Relative Intensities (%)]

Compound	X	$[M]^+$	$[M-C(Ph)_2]^+$	$[M-C_6H_4F]^+$	$HN{=}P(C_6H_4\text{-}OCH_3)_3$	$P(C_6H_4\text{-}OCH_3)_3$	$P(C_6H_4\text{-}OCH_3)_2$	$P(C_6H_4\text{-}OCH_3)$	$C_6H_4OCH_3$
				$XC_6H_4N{=}P(C_6H_4\text{-}p\text{-}OCH_3)_3$					
IX	m-F	461 (100)		366 (61)		352 (85)	245 (61)	138 (61)	107 (2)
X	p-F	461 (80)		366 (100)		352 (60)	245 (100)	138 (40)	107 (10)
				$XC_6H_4C(Ph)_2N{=}P(C_6H_4\text{-}p\text{-}OCH_3)_3$					
XI	m-F		461 (8)		367 (40)	352 (12)	245 (40)	138 (100)	107 (60)
XII	p-F		461 (16)		367 (100)	352 (42)	245 (72)	138 (8)	107 (2)

Table III. Main Fragment Ions of *N*-(Triphenylsilyl)triphenylphosphinimine and Its Derivatives [*m*/*e* and Their Relative Intensities (%)][a]



$$\mathrm{X{-}C_6H_4{-}\underset{Ph}{\overset{Ph}{Si}}{-}N{=}\underset{C_6H_4Y''}{\overset{C_6H_4Y'}{P}}{-}C_6H_4Y}$$

Compound	XYY'Y''	$[M]^+$	$[M-H]^+$	$[M-Ph]^+$	$[M-C_6H_4F]^+$	$\left[M\begin{matrix}-Ph\\-C_6H_4F\end{matrix}\right]^+$	$C_{12}H_8P^+$	$C_{12}H_9Si^+$	Other significant ions
XIII	HHHH	535 (39)	534 (32)	458 (100)		381 (18.8) $[M-2Ph]^+$	183 (10.9)	181 (14.1)	257 (15.6) $C_{18}H_{13}Si^+$
XIV	H*p*-FHH	553 (42.9)	552 (33.3)	476 (100)	458 (28.6)	381 (16.7)	183 (10)	181 (14.3)	280 (9.5) $C_{18}H_{14}FP^+$ 257 (21 4) $C_{18}H_{13}Si^+$
XV	*p*-FHHH	553 (62.2)		476 (100)	458 (32.4)	381 (10.8)	183 (56.8)	181 (10.3)	277 (16.2) $C_{18}H_{14}FSi^+$ 262 (70.3) $C_{18}H_{15}P^+$
XVI	*p*-F*p*-FHH	571 (53.3)	570 (40)	494 (100)	476 (33.3)	399 (10)	183 (10)	181 (10)	277 (11.1) $C_{18}H_{14}FSi^+$
XVII	*p*-F(*p*-OCH_3)$_3$	643 (75.0)	642 (87.5)	566 (100)	548 (37.5)				260 (25) $C_{18}H_{13}P^+$
XVIII	*p*-F(*p*-CH_3)$_3$	595 (65)	594 (75)	518 (100)	500 (40)				258 (25) $C_{18}H_{11}P^+$

[a] The $[M + 1]^+$ and other isotopic peaks are omitted.

diphenylcarbene on electron impact, giving compounds IX and X. This appears to be substantiated by the fragmentation patterns of isomers XI and XII which, after the separation of the $[M - (Ph)_2C]^+$ fragment, show a striking resemblance to the patterns of compounds IX and X.

An $[M - H]^+$ ion is found in most of the spectra of *N*-(triarylsilyl)triarylphosphinimines. This loss of a hydrogen is most probably associated with formation of a C–C bond between two phenyl groups of the $P(Ph)_3$ radical and rearrangement of a second hydrogen from one of these phenyl groups to the nitrogen (*2*).

Experimental Section

Mass spectra were obtained on a Consolidated Electrodynamics Corp. mass spectrometer, Model 21-110. All samples were introduced into the spectrometer through the direct insertion probe. Source temperature was 200 °C. Probe temperature was between 100 and 200 °C. Resolution was at about 5000. The ionizing voltage was maintained at 70 eV. The preparation of *N*-aryl-, *N*-(aryldiphenylmethyl)-, and *N*-(aryldiphenylsilyl)-triarylphosphinimines has been reported earlier (*3*).

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Synthesis and Spectral Characterization of Cinchoninic Acids

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Eight cinchoninic acids were synthesized by the Pfitzinger method from 5,7-dichloroisatin and a series of ketones. UV, IR, and NMR data for the cinchoninic acids are presented.

Eight cinchoninic acids were synthesized by the Pfitzinger method (*1*–*3*) for use in biological activity studies, through the condensation of 5,7-dichloroisatin with the following ketones: acetone, cyclopentanone, cyclohexanone, cycloheptanone, cyclooctanone, and α-, β-, and γ-acetylpyridines. The structure and physical properties of the synthesized cinchoninic acids are given in Table I. UV, IR, and NMR data for these acids are given in Tables II–IV.

Experimental Section

Melting points were taken using a Kofler hot bench and are uncorrected. Elemental analyses were performed by Alfred

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