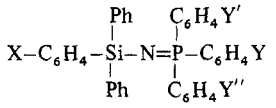
Table III. Main Fragment Ions of *N*-(Triphenylsilyl)triphenylphosphinimine and Its Derivatives [*m/e* and Their Relative Intensities (%)][a]



Compound	XYY'Y''	$[M]^+$	$[M-H]^+$	$[M-Ph]^+$	$[M-C_6H_4F]^+$	$\left[M-Ph-C_6H_4F\right]^+$	$C_{12}H_8P^+$	$C_{12}H_9Si^+$	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*).

Acknowledgment

We wish to thank Drs. Noel Einolf and Burnaby Munson for running the mass spectra.

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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.

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Experimental Section

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

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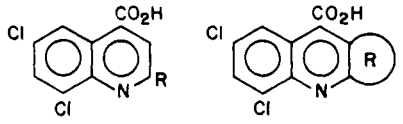
Table I. Physical Properties of Cinchoninic Acids



1 2

No.	Molecular formula	R	Mp, °C (dec)	Yield, %
1a	$C_{11}H_7Cl_2NO_2$	CH_3	236-237	62
1b	$C_{15}H_8Cl_2N_2O_2$	α-Pyridyl	330-332	65
1c	$C_{15}H_8Cl_2N_2O_2$	β-Pyridyl	314-315	60
1d	$C_{15}H_8Cl_2N_2O_2$	γ-Pyridyl	325-326	70
2a	$C_{13}H_9Cl_2NO_2$	Cyclopentane	268-269	55
2b	$C_{14}H_{11}Cl_2NO_2$	Cyclohexane	330-332	75
2c	$C_{15}H_{13}Cl_2NO_2$	Cycloheptane	263-264	70
2d	$C_{16}H_{15}Cl_2NO_2$	Cyclooctane	249-250	62

recorded on a Varian A60A spectrometer in deuterated dimethyl sulfoxide (Me_2SO-d_6) and trifluoroacetic acid (TFA), with tetramethylsilane as the internal reference.

Materials. 5,7-Dichloroisatin and α-acetyl-, β-acetyl-, and γ-acetylpyridines were Aldridge Chemical Co. products. Other Chemicals were Fluka Products. They were all used without further purification.

General Procedure for the Preparation of Cinchoninic Acids. The isatin (0.03 mol) was dissolved in a warm ethanolic solution of potassium hydroxide (100 mL, 33%). The ketone (0.034 mol) in ethanol (20 mL) was then added gradually. The mixture was kept under continuous stirring and heating for 72 h. The contents of the flask were allowed to cool to room temperature, extracted twice with ether to remove excess ketone, and neutralized (pH 6-7) with dilute hydrochloric acid (10%). Recrystallization of the product from ethanol gave the pure cinchoninic acid.

Table II. Infrared Absorption Data (cm^{-1}) for Cinchoninic Acids

No.	ν(OH)	ν(C=NH⁺)	ν(CO_2^-, C=O)	ν(=C-H, C=C, C=N)	δ(C-H) in-plane def	δ(C-H) out-of-plane def
1a	3390 w, 2500 w	2323 w	1315 m, 1720 s	3010 w, 1600 s	1200 s, 1100 w, 1058 m	867 s, 800 m, 760 m, 690 s
1b	3385 w, 2380 w	2380 w	1473 s, 1334 s, 1695 s	3030 w, 1587 s	1282 s, 1177 s, 1093 m, 1042 s, 1010 m	925 m, 893 m, 870 s, 791 w, 778 s 764 s, 743 m, 717 m
1c	3510 s	2225 m	1400 s, 1323 m, 1699 s	1615 s, 1588 s	1227 m, 1072 w	882 m, 866 m, 803 w, 787 w, 770 w, 741 w, 703 w
1d	3500 w, 2380 m	2380 m	1482 m, 1352 s, 1735 s	3110 w, 1625 s, 1600 s	1250 m, 1185 m, 1040 s, 1025 s	807 s, 833 s, 787 m, 766 m, 714 w
2a	3385 w, 2820 w	2440 m	1481 m, 1325 m, 1710 s	3063 w, 1588 w	1198 s, 1132 w, 1089 w	862 s, 816 w, 763 s, 685 s
2b	3450 w, 2860 w, 2440 w	2390 m	1430 s, 1335 s, 1720 s	3130 w, 1598 s	1198 m, 1135 m, 1091 m	862 s, 861 w, 760 m, 685 m
2c	3470 w, 2820 m, 2500 m	2500 m	1478 s, 1335 s, 1720 s	3130 w, 1598 s	1190 s, 1135 m, 1098 m, 1032 m, 110 w	950 s, 910 s, 882 m, 867 s, 817 s, 797 m, 758 s, 730 m, 697 s
2d	3400 w, 2700 w, 2410 m	2410	1438 m, 1283 m, 1915 s	3075 w, 1588 m	1235 s, 1183 s, 1048 m	862 s, 820 w, 763 m, 713 s, 700 s

Table III. Nuclear Magnetic Resonance Data for Cinchoninic Acids[a]

No.	Solvent	Aliphatic H	Aromatic H	NH
1a	Me_2SO	2.85 CH_3	7.97 d, 8.88 d, 8.06 d	7.6 b shifted upfield on dilution
1b	TFA		8.4 m, 9.1 b, s, 9.5 m	
1c	TFA		10.2 d, 9.74 dd, 9.16 dd, 9.02 s, 9.0 d, 8.6 dd, 8.1 d	10.8 b
1d	TFA		8.08 d, 9.01 d, 9.28 s, 9.18 s	
2a	TFA	2.70 m, 3. 9 m	8.36 d, 8.84 d, 3.9 m	
2b	TFA	2.22 bs, 3.33 bs, 3.67 bs	8.5 d, 8.65 d	
2c	Me_2SO	1.87 d, 3.0 m, 3.33 m	7.81 d, 8.0 d	9.5 b
2d	Me_2SO	1.43 m, 1.86 m	8.3 d, 9.4 d	

[a] Key: s = singlet, b = broad, m = multiplet, d = doublet, dd = double doublet; TFA = trifluoroacetic acid, Me_2SO = dimethyl-d_6 sulfoxide. Chemical shifts are expressed in parts per million (ppm) $J_{5,7}$ = 2.5 Hz.

Table IV. Ultraviolet Absorption Data (nm) for Cinchoninic Acids

	Ethanal	Dioxane	0.1 N NaOH	Water
No.	λ_{max} (log e)	λ_{max} (log e)	λ_{max} (log e)	λ_{max}
1a	203 (3.75)	252 (3.79)	225 (5.31)	222
	237 (4.32)	295 (3.13)	238 (5.32)	241
	295 (3.53)	337 (3.31)	330 (4.54)	330
1b	212 (3.57)	242 (4.114)	218 (4.57)	210
	252 (3.80)	363 (4.24)	253 (4.72)	253
	278 (3.72)	282 (4.22)	277 (4.61)	277
	345 (3.34)	350 (3.78)	345 (4.16)	245
1c	214 (3.90)	267 (3.39)	219 (4.09)	203
	263 (4.19)	352 (3.85)	261 (4.25)	214
	347 (3.37)		345 (3.52)	260
1d	211 (4.58)	235 (3.15)	222 (4.20)	204
	277 (4.60)	270 (3.54)	261 (4.53)	222
	350 (4.18)	350 (3.03)	340 (3.84)	261
2a	223 (4.50)	250 (4.27)	222 (3.40)	339
	241 (4.32)	335 (3.69)	241 (3.43)	220
	330 (2.50)		331 (2.63)	241

Bernhardt Laboratories, Ruhr, Germany. Ultraviolet spectra were obtained by a Unicam Sp 800 ultraviolet spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer Model 137 infracord spectrophotometer as KBr wafers. NMR spectra were

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