Imidoylstannanes, Improved Preparation and Uses as Acylanion Equivalents

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An improved preparation of imidoylstannanes, by reaction of triorganostannyllithiums with imidoyl chlorides, is reported. This reaction is effective when phenyl or methyl groups are substituents on the tin atom, and when *N*-aryl *C*-alkyl or *C*-aryl imidoyl chlorides are used. After reaction with acyl chlorides, imidoylstannanes led to high yields of α-keto imines, which can be further hydrolysed into α-diketones. Transmetallation with organolithiums selectively gave the corresponding lithium reagents which showed a normal behaviour with alkyl halides, silicon halides, epoxides or chloroformates, leading to functional imines, hydrolysable to the corresponding ketones. This route forms a new entry to Walborski reagents.

Acyl anion equivalents are versatile intermediates in synthetic organic reactions.[1] They have been known for a long time as, for instance, acetylide anions that, after reaction and hydrolysis, can be converted into ketones,[2] or nitronate anions which after addition to carbonyl compounds can be transformed into a carbonyl group.[3] More recently, new acyl anion equivalents have been developed from the metallation of dithioacetals[4] and vinyl derivatives,[5] and studies in this field continued apace.[6] On the other hand, organotin compounds have proven to be important reagents in organic synthesis. The ease with which tin–carbon bonds are cleaved often allows the selective transfer of organic moieties from the metal to organic substrates.[7] This transfer can be performed after transmetallation with a lithium reagent from vinyl-,[8] allyl-,[9] benzyl[10] and α-hetero substituted[11] organostannanes, or under palladium catalysis.[12] The latter reaction broadened the scope of applications of organotins to carbon–carbon bond formation, since this mild method may be used in the presence of numerous functional groups.[12] Acylstannanes can be employed under catalysis, allowing an easy transfer of acyl groups to organic substrates such as acyl halides.[13] Imidoylstannanes, known for a long time,[14] and for which we recently proposed a new method of preparation,[15] have found only a limited number of applications.[16] However, recent findings on the access to (silyliminomethyl)stannanes by the palladium-catalysed reaction of isocyanides with organosilylstannanes,[17] and on their selective transmetallation with butyllithium,[18] showed the potential of this class of compounds. In the same field, Walborsky earlier demonstrated the stability and usefulness of iminoyllithiums, prepared by addition of lithium reagents to isocyanides.[19] Herein is reported an account of an improved synthesis of aryl imidoylstannanes by coupling triorganostannyllithiums with imidoyl chlorides, and of their reactivity towards acyl chlorides and organolithiums.

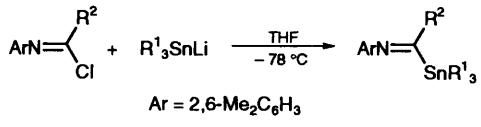
Results and Discussion

Imidoylstannanes were obtained in high yield by the coupling of imidoyl chlorides with triorganostannyllithiums. This route has previously been described to give imidoylstannanes in very low yield[14] and, with acyl chlorides, only impure acylstannanes[20] were obtained. With a careful control of the reaction temperature, however, and with the use of a bulky 2,6-xylyl group on nitrogen instead of a simple phenyl to improve stability towards oxygen, better results were obtained (Table 1). The stoichiometry of the reagents is also critical, since unchanged imidoyl chloride reacts with the imidoylstannane formed at room temperature, and thus lowers the yield of the reaction.

Table 1 Preparation of imidoyltriorganostannanes

R^1	R^2	Yield (%)
Me	Ph	86
Ph	Ph	79
Me	*p*-$MeOC_6H_4$	69
Me	*p*-ClC_6H_4	72
Me	Me	68
Bu	Me	16[a]
Me	Et	67
Me	Bu^t	69

[a] Estimated yield by ^{119}Sn NMR.



Ar = 2,6-$Me_2C_6H_3$

The reaction is general enough to tolerate alkyl (Me, Et, Bu^t) and aryl (Ph, *p*-$MeOC_6H_4$, *p*-ClC_6H_4) groups on the imidoyl carbon. On the tin atom, methyl and phenyl groups were successfully used. With tributylstannyllithium, the imidoylstannane was recovered in low yield, together with aldimine, which suggests a single electron-transfer process leading to reduction.[21] Imidoylstannanes are characterized by their ^{13}C NMR spectra having a signal for the imine carbon around 190 ppm with a $^1J(^{13}C\text{-}^{119}Sn)$ in the range 200–280 Hz. With methyl groups on the tin atom, the ^{119}Sn NMR resonance lies in the range −80 to −90 ppm; this is the same region as for acylstannanes.[20] NMR data indicate that only one isomer was formed during the reaction. Since imidoyl chlorides exist in the *Z* configuration[22] and, further, since the coupling of lithium reagents with vinylic species usually occurs stereospecifically,[23] it was reasonable to assign the *Z* configuration to the imidoylstannanes. A 2D NOESY experiment conducted on [4-chloro-α-(2,6-xylylimino)benzyl]trimethylstannane showed a clear correlation between the trimethylstannyl hydrogens and the methyl hydrogens of the xylyl group. No correlation was observed between *ortho* hydrogen of the 4-chlorobenzyl group and methyl hydrogens of the xylyl group. An independently reported NOE experiment on butyliminoethyl(tributyl)-

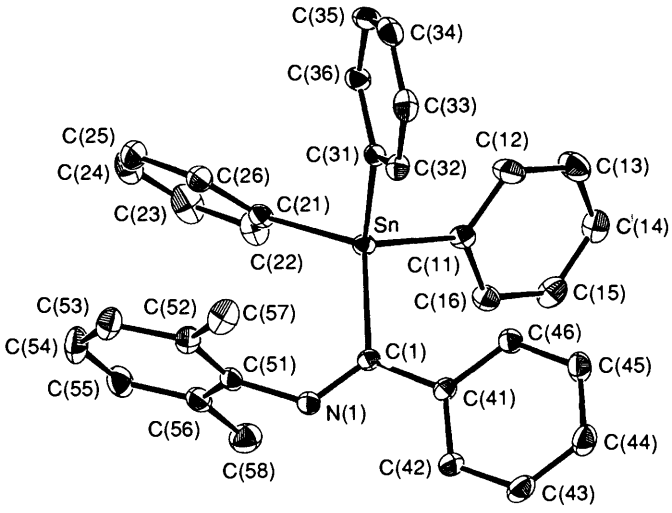


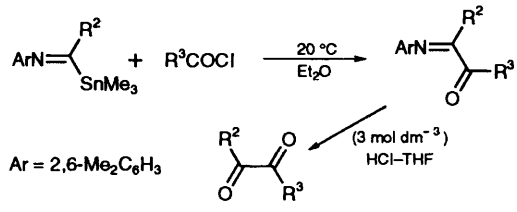
Fig. 1 ORTEP[38] view of 2,6-$Me_2C_6H_4NC(SnPh_3)Ph$ with thermal ellipsoids at the 20% probability level. Selected interatomic bond lengths (Å) and angles (°): Sn–C(1), 2.178(5); Sn–C(11), 2.121(6); Sn–C(21), 2.119(6); Sn–C(31), 2.122(6); C(1)–N(1), 1.272(7); C(1)–C(41), 1.484(8); N(1)–C(51), 1.414(8); C(1)–Sn–C(11), 107.7(2); C(1)–Sn–C(21), 117.7(2); C(1)–Sn–C(31), 110.3(2); C(11)–Sn–C(21), 108.8(2); C(11)–Sn–C(31), 107.5(2); C(21)–Sn–C(31), 104.5(2); Sn–C(1)–N(1), 122.8(4); Sn–C(1)–C(41), 119.4(4); N(1)–C(1)–C(41), 117.8(5); C(1)–N(1)–C(51), 123.4(5).

Table 2 Reaction of imidoylstannanes with acyl chlorides

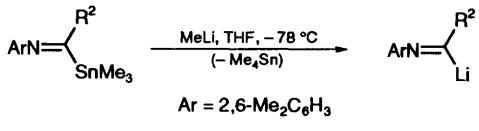
R^2	R^3	Keto imine yield (%)	α-Diketone yield (%)
Ph	Ph	80	76
Ph	*p*-$MeOC_6H_4$	79	73
Ph	*o*-$MeOC_6H_4$	78	69
Ph	*p*-ClC_6H_4	77	68
Ph	*p*-$NO_2C_6H_4$	46	40
Ph	α-Naphthyl	72	67
p-ClC_6H_4	*p*-$MeOC_6H_4$	74	68
Me	Ph	—	—
Ph	Me	—	—

stannane led to the same conclusion.[24] Nevertheless, a crystal structure determination was conducted on α-(2,6-xylylimino)benzyl(triphenyl)stannane (Fig. 1). It revealed a *Z* configuration which confirmed the NOESY studies. There were no significant intermolecular contacts; the closest non-hydrogen contact occurs between C(35) and C(35′) [3.41(1) Å]. In the molecule, the tin atom exists in a distorted tetrahedral geometry with the C–Sn-angles lying in the relatively narrow range of 104.5(2)–117.7(2)°; the greatest deviation from the ideal tetrahedral angle is found for C(1)–Sn–C(21). Reflecting the disparate organic groups, the Sn–C bond distances fall into two classes, *i.e.* the Sn–C(Ph) distances lie in the range 2.119(6)–2.122(6) Å, in contrast to the Sn–C(1) bond which is significantly longer at 2.178(5) Å, in the range of tin–vinyl bonds.[25] The C(1)–N(1) bond distance of 1.272(7) Å is consistent with significant double bond character and the angles subtended by the donor atoms at both the C(1) and N(1) are indicative of sp^2 centres. The Sn, N(1), C(1), C(41) and C(51) atoms lie 0.000(4), 0.035(6), 0.016(6), −0.024(6) and −0.046(7) Å, respectively, out of the least-squares plane through these atoms. The $PhC{=}NC_6H_3Me_2$ ligand is not planar, however, as shown in the torsion angles of 6.6(9) and −89.0(8)° for C(42)/C(41)/C(1)/N(1) and C(52)/C(51)/N(1)/C(1), respectively.

The imidoylstannanes were then treated with acyl chlorides under palladium catalysis, to give keto imines as previously described for acylstannanes.[13] In fact, they were much more reactive than acylstannanes, since a palladium catalyst, heating and long contact time were unnecessary to achieve the reaction. Indeed, the coupling occurred very rapidly at room temperature, leading to the desired products in good yield. These were purified by column chromatography on alumina, without hydrolysis of the imine moiety or by distillation. The reaction was very effective when aromatic imidoylstannanes and aromatic acyl chlorides were used (Table 2). With either aliphatic imidoylstannanes and aromatic acyl chlorides, or with aromatic imidoylstannanes and aliphatic acyl chlorides, the coupling failed, and only degradation products were recovered. Aliphatic acyl chlorides were also found unsuitable in the coupling with acylstannanes.[13] Keto imines, which can be considered as monoprotected 1,2-diketones,[26] cannot be obtained from unsymmetrical α-diketones since the monoimination of α-dicarbonylated compounds is only selective with well-differentiated groups around the carbonyls, such as in 1-phenylpropane-1,2-dione or phenylglyoxal.[27] After hydrolysis, 1,2-diketones can be recovered in high yield.



When treated with methyllithium, at −78 °C in THF, aromatic imidoylstannanes underwent clean transmetallation, leading to the corresponding iminoyllithiums. The reaction was very selective since no addition to the azomethine linkage was observed; this contrasts to what happens with acylstannanes. The imidoyllithium having R = Ph was characterized by treatment with deuterium oxide, which led to *N*-[^{2}H]benzylidene-2,6-xylylamine containing >95% deuterium incorporation. This method turns out to be a good way to prepare this class of lithium reagent, since addition of aryllithiums to isocyanides gives less good yields of the corresponding imidoyllithiums than aliphatic lithium compounds,[19] and since transmetallation of (silyliminomethyl)stannanes does not allow an access to aromatic imidoyllithiums.[18]



When the same transmetallation was attempted with 1-(2,6-xylylimino)ethyl(trimethyl)stannane and methyllithium, followed by alkylation with ethyl bromide, the coupling product was isolated in only 39% yield, together with 1-(2,6-xylylimino)butane (25%) and 3-(2,6-xylylimino)hexane (8%), indicating that lithiation occurred also on the methyl α to the azomethine.

The reactivity of the aromatic imidoyllithiums was then probed with alkyl halides, silicon halides, benzaldehyde and isobutyl chloroformate (Table 3). The corresponding products were isolated in high yield, indicating a normal behaviour of

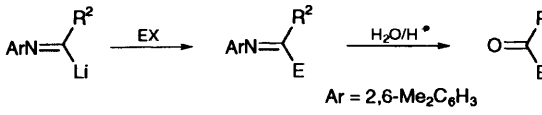


Table 3 Reactions of imidoyllithiums with selected electrophiles

R^2	EX	Imine 2,6-$Me_2C_6H_3N{=}CR^1R^2$ (% yield)	Aldehyde or ketone (% yield)
Ph	H_2O	R^1 = H, R^2 = Ph (98)	PhCHO (95)
Ph	D_2O	R^1 = D, R^2 = Ph (97)	PhCDO (95)
Ph	MeI	R^1 = Me, R^2 = Ph (85)	PhCOMe (81)
Ph	EtBr	R^1 = Et, R^2 = Ph (86)	PhCOEt (84)
p-ClC_6H_4	EtBr	R^1 = Et, R^2 = *p*-ClC_6H_4 (82)	*p*-ClC_6H_4COEt (78)
Ph	Me_3SiCl	R^1 = $SiMe_3$, R^2 = Ph (82)	
Ph	Bu^tMe_2SiCl	R^1 = $SiMe_2Bu^t$, R^2 = Ph (88)	$PhCOSi(Me_2)Bu^t$ (81)
Ph	PhCHO	R^1 = C(OH)Ph, R^2 = Ph (87)	PhCOCH(OH)Ph (82)
Ph	$ClCOOBu^i$	R^1 = CO_2Bu^i, R^2 = Ph (65)	$PhCOCO_2Bu^i$ (60)

Table 4 Crystallographic data for α-(2,6-xylylimino)benzyl(triphenyl)-stannane

Formula	$C_{33}H_{29}NSn$
Crystal size (mm)	0.23 × 0.23 × 0.40
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	16.510(2)
b/Å	9.036(3)
c/Å	18.896(2)
β/°	110.58(1)
V/Å^3	2638.9(7)
Z	4
ρ_c/g cm^{-3}	1.405
F(000)	1136
μ/cm^{-1}	9.89
Transmission coefficients	0.948–1.058
Data collected	$-h, +k, \pm l$
No. of data collected	6922
No. of unique data	6701
R_a	0.049
No. of unique data with $I \geqslant 3\sigma(I)$	4601
R	0.032
R_w	0.057
Residual density (e Å^{-3})	0.39

these lithium compounds. Alkylation was effective both with iodides (85%) and bromides (82%), when, in contrast, imidoyllithium prepared from [(butylimino)propyl]tributyl-stannane failed to give the expected coupling products with organic halides.[24] Trimethylchlorosilane and *tert*-butyl-(dimethyl)chlorosilane led into the corresponding iminoyl-silanes, which could be hydrolysed to acylsilanes. With benzaldehyde, the desired α-hydroxy imine was obtained (87%), and hydrolysed to give the corresponding α-hydroxy ketone (81%). It is noteworthy that the recently reported samarium-mediated coupling of organic halides, isocyanide and carbonyl compounds, very effective with alkyl halides, does not allow the preparation of aryl-substituted α-hydroxy imines.[28] Isobutyl chloroformate gave the desired α-imino ester (65%), which, in turn, led to the corresponding α-keto ester (60%), after hydrolysis.

Thus, the present procedure broadens the synthetic utilities of organostannanes. It provides a valuable access to imidoyl-stannanes and demonstrates their synthetic applications for carbon–carbon bond formation either by direct reaction with acyl chlorides, or after transmetallation with lithium reagents.

Experimental

All reactions were carried out under a nitrogen atmosphere. THF and diethyl ether were distilled from sodium benzophenone ketyl prior to use. Pentane and light petroleum were distilled from calcium hydride. Imidoyl chlorides were obtained from the reaction of the corresponding amides with phosphorus pentachloride.[30] Tributylstannyllithium[30] was prepared by deprotonation of tributylstannane. Lithium triphenyl- and trimethyl-stannates were prepared by cleavage of the corresponding hexaorganodistannane[31] by lithium in THF. The tin reagents were used immediately after preparation. ^1H and ^{13}C NMR spectra were recorded on a Bruker WH 250 (internal reference Me_4Si). ^{119}Sn NMR spectra were recorded on a Bruker AC 200 (internal reference Me_4Sn). *J* Values are given in Hz.

Crystallography.—Intensity data were measured (ω–2θ scan technique, room temperature) on a Rigaku AFC6R diffractometer using graphite-monochromatized Mo-Kα radiation, λ = 0.710 73 Å, up to a maximum Bragg angle of 27.5°. The data set was corrected for Lorentz and polarization effects[32] and an empirical absorption correction was applied.[33] The structure was solved by direct-methods[34] and refined by a full-matrix least-squares procedure based on F^1. Non-H atoms were refined with anisotropic thermal parameters and H atoms were included in the model at their calculated positions. Unit weights were employed in the refinement. The teXsan software package,[32] installed on an Iris Indigo workstation, was employed for data manipulation. For details of the crystal data see Table 4.

Tables of atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.*

Procedure for Preparation of Imidoylstannanes.—To a solution of imidoyl chloride (20 mmol) in THF (30 cm^3) at −78 °C were slowly added a triorganostannyllithium solution (20 mmol) *via* a cannula. The solution was stirred at −78 °C for 1 h and at ambient temperature for 1 h and was then evaporated. The residue was extracted with pentane (100 cm^3) and the extract then evaporated. The product was isolated by liquid chromatography on a deactivated (6% H_2O) alumina column using light petroleum as eluent. Alternatively, trimethylstannylated compounds can be distilled in a Kugelrohr apparatus. α-(2,6-Xylylimino)benzylidene(trimethyl)-stannane: 86%; m.p. 48 °C; δ_H(250 MHz; $CDCl_3$) 0.12 (9 H, s, $^2J_{Sn,H}$ 53), 2.25 (6 H, s) and 7.0–7.8 (8 H, m); δ_C(62.9 MHz; $CDCl_3$) −6.9 ($^1J_{Sn,C}$ 320), 18.3, 123.5, 127.1, 128.0, 128.5, 129.5, 143.9 ($^2J_{Sn,C}$ 107), 152.1 ($^3J_{Sn,C}$ 52); 162.5 and 190.9 ($^1J_{Sn,C}$ 317); δ_{Sn}(74.5 MHz; C_6D_6) −76.1; [Found (FABHRMS): 374.0904. Calc. for $C_{18}H_{25}NSn$: *m/z* 374.0931]. α-(2,6-Xylylimino)-benzylidene(triphenyl)stannane: 79%; m.p. 94 °C; δ_H(250 MHz; $CDCl_3$) 2.21 (6 H, s), 6.75 (3 H, m), 7.40 (18 H, m) and 8.15 (2 H, m); δ_C(62.9 MHz; $CDCl_3$) 18.7, 124.7, 125.7, 128.2, 128.6 ($^2J_{Sn,C}$ 51), 128.9, 130.5, 137.0 ($^3J_{Sn,C}$ 39), 139.4, 143.5, 151.8 and 186.3 ($^1J_{Sn,C}$ 297); δ_{Sn}(74.5 MHz; C_6D_6) −184.6 [Found

* For details of the scheme see 'Instructions for Authors (1994)', *J. Chem. Soc., Perkin Trans. 1*, 1994, Issue 1.

(FABHRMS): 560.1377. Calc. for $C_{33}H_{30}NSn$: *m/z* 560.1400]. 4-Methoxy-α-(2,6-xylylimino)benzylidene(trimethyl)stannane: 69%; b.p. 155 °C (10^{-4} Torr); δ_H(250 MHz; $CDCl_3$) 0.01 (9 H, s, $^2J_{Sn,H}$ 51), 2.08 (6 H, s), 3.49 (3 H, s), 6.9 (5 H, m) and 7.8 (2 H, m); δ_C(62.9 MHz; $CDCl_3$) −6.9 ($^1J_{Sn,C}$ 316), 18.4, 54.9; 114.1, 123.3, 128.1, 129.1, 130.1, 131.7, 136.5, 162 and 191.5 ($^1J_{Sn,C}$ 312); δ_{Sn}(74.5 MHz; C_6D_6) −79.6; [Found (FABHRMS): 404.1000. Calc. for $C_{19}H_{26}NOSn$: *m/z* 404.1036]. 4-Chloro-α-(2,6-xylylimino)benzylidene(trimethyl)stannane: 72%; m.p. 94 °C; b.p. 160 °C (10^{-4} Torr); δ_H(250 MHz; $CDCl_3$) −0.01 (9 H, s, $^2J_{Sn,H}$ 51), 2.08 (6 H, s) and 6.9–7.8 (7 H, m); δ_C(62.9 MHz; $CDCl_3$) −7.1 ($^1J_{Sn,C}$ 319), 18.4, 123.6, 128.2, 128.7, 128.8, 135.6, 142.1 ($^2J_{Sn,C}$ 112), 152.3 ($^3J_{Sn,C}$ 50); 160.9 and 188.0 ($^1J_{Sn,C}$ 308); δ_{Sn}(74.5 MHz; C_6D_6) −74.8 [Found (FABHRMS): 408.0539. Calc. for $C_{18}H_{23}ClNSn$: *m/z* 408.0541]. Trimethyl[1-(2,6-xylylimino)ethyl]stannane: 68%; b.p. 130 °C (10^{-4} Torr); δ_H(250 MHz; $CDCl_3$) −0.15 (9 H, s, $^2J_{Sn,H}$ 55), 1.94 (6 H, s), 2.35 (3 H, s, $^3J_{Sn,H}$ 28) and 6.7–6.9 (3 H, m); δ_C(62.9 MHz; $CDCl_3$) −8.7 ($^1J_{Sn,C}$ 316), 18.3, 31.8 ($^2J_{Sn,C}$ 137), 123.4, 128.1, 128.4, 152.4 ($^3J_{Sn,C}$ 60) and 191.6 ($^1J_{Sn,C}$ 313); δ_{Sn}(74.5 MHz; C_6D_6) −81.8 [Found: (HRMS): 311.0691. Calc. for $C_{13}H_{21}NSn$: *m/z* 311.0696]. Tributyl[1-(2,6-xylylimino)ethyl]stannane: 16%; b.p. 160 °C (10^{-4} Torr); δ_H(250 MHz; $CDCl_3$) 0.7–1.6 (27 H, m), 2.05 (6 H, s), 2.46 (3 H, s, $^3J_{Sn,H}$ 26) and 6.8–7.0 (3 H, m); δ_C(62.9 MHz; $CDCl_3$) 10.2 ($^1J_{Sn,C}$ 307), 13.6, 18.3, 27.3 ($^2J_{Sn,C}$ 60), 29.3, 32.7 ($^2J_{Sn,C}$ 112), 123.4, 127.8, 128.0, 152.4 ($^3J_{Sn,C}$ 50) and 192.8 ($^1J_{Sn,C}$ 312); δ_{Sn}(74.5 MHz; C_6D_6) −85.6; [Found (HRMS): 437.2197. Calc. for $C_{22}H_{39}NSn$; *m/z* 437.2104]. Trimethyl[1-(2,6-xylylimino)propyl]stannane: 67%; b.p. 135 °C (10^{-4} Torr); δ_H(250 MHz; $CDCl_3$) −0.13 (9 H, s, $^2J_{Sn,H}$ 55), 1.17 (3 H, t), 1.96 (6 H, s), 2.63 (2 H, q, $^3J_{Sn,H}$ 24) and 6.8–7.0 (3 H, m); δ_C(62.9 MHz; $CDCl_3$) −8.4 ($^1J_{Sn,C}$ 312), 10.8, 18.0, 38.0 ($^2J_{Sn,C}$ 123), 123.1, 126.0, 127.9, 151.9 ($^3J_{Sn,C}$ 49) and 195.0 ($^1J_{Sn,C}$ 302); δ_{Sn}(74.5 MHz; C_6D_6) −81.3; [Found (HRMS): 325.0858. Calc. for $C_{14}H_{23}NSn$: *m/z* 325.0852]. [2,2-Dimethyl-1-(2,6-xylylimino)ethyl]trimethylstannane: 69%; b.p. 140 °C (10^{-4} Torr); δ_H(250 MHz; $CDCl_3$) 0.03 (9 H, s, $^2J_{Sn,H}$ 56), 1.33 (9 H, s), 2.07 (6 H, s) and 6.8–7.0 (3 H, m); δ_C(62.9 MHz; $CDCl_3$) δ −5.1 ($^1J_{Sn,C}$ 304), 18.2, 28.1, 45.0 ($^2J_{Sn,C}$ 117), 123.0, 125.6, 128.0, 150.7 ($^3J_{Sn,C}$ 59) and 197.9 ($^1J_{Sn,C}$ 301); δ_{Sn}(74.5 MHz; C_6D_6) −89.0; [Found (HRMS): 353.1154. Calc. for $C_{16}H_{27}NSn$: *m/z* 353.1165].

Procedure for the Preparation of Keto Imines.—In a Schlenk tube containing a solution of imidoylstannane (10 mmol) in diethyl ether (10 cm^3) at room temperature, was added dropwise acyl chloride (10 mmol). After the mixture had been stirred for 15 min, it was evaporated and the residue chromatographed on silica gel (eluent light petroleum–diethyl ether 95:5). The crystalline keto imines were recrystallized from toluene–light petroleum (50:50). 1,2-Diphenyl(2,6-xylylimino)-ethanone: 80%; m.p. 108 °C (Found: C, 84.7; H, 5.7; N, 4.15. Calc. for $C_{22}H_{19}NO$: C, 84.32; H, 6.11; N, 4.47%); δ_H(250 MHz; $CDCl_3$) 2.12 (6 H, s) and 6.7–8.0 (12 H, m); δ_C(62.9 MHz; $CDCl_3$) 18.8, 124.1, 127.7, 128.1, 128.3, 128.5, 128.8, 129.0, 129.2, 131.9, 133.9, 135.2, 135.7, 167.3 and 197.1. 1-(4-Methoxyphenyl)-2-phenyl-2-(2,6-xylylimino)ethanone: 79%; m.p. 132 °C (Found: C, 80.2; H, 5.75; N, 3.8. Calc. for $C_{23}H_{21}NO_2$: C, 80.44; H, 6.16; N, 4.08%); δ_H(250 MHz; $CDCl_3$) 2.22 (6 H, s), 3.05 (3 H, s) and 6.3–8.1 (12 H, m); δ_C(62.9 MHz; $CDCl_3$) 18.9, 54.9, 114.0, 123.9, 126.6, 127.7, 128.0, 128.1, 128.3, 128.4, 128.8, 129.1, 131.8, 136.0, 167.4 and 194.9. 1-(3-Methoxyphenyl)-2-phenyl-2-(2,6-xylylimino)ethanone: 78% (Found: C, 80.05; H, 5.7; N, 3.8. Calc. for $C_{23}H_{21}NO_2$: C, 80.44; H, 6.16; N, 4.08%); δ_H(250 MHz; $CDCl_3$) 2.09 (6 H, s), 2.94 (3 H, s) and 6.8–7.9 (12 H, m); δ_C(62.9 MHz; $CDCl_3$) 18.8, 54.7, 112.1, 121.2, 122.6, 124.1, 127.7, 128.2, 128.3, 129.2, 129.6, 131.9, 135.8, 136.4, 147.8, 160.2, 167.2 and 196.9. 1-(4-Chlorophenyl)-2-phenyl-2-(2,6-xylylimino)ethanone: 77%; m.p. 98 °C (Found: C, 75.72; H, 4.94; N, 3.87. Calc. for $C_{22}H_{18}ClNO$: C, 75.97; H, 5.22; N, 4.03%); δ_H(250 MHz; $CDCl_3$) 2.05 (6 H, s) and 6.6–7.9 (12 H, m); δ_C(62.9 MHz; $CDCl_3$) 18.8, 124.3, 127.7, 128.0, 128.2, 128.3, 128.4, 129.0, 129.2, 130.4, 132.0, 133.3, 135.4, 166.7 and 195.9. 1-(4-Nitrophenyl)-2-phenyl-2-(2,6-xylylimino)ethanone: 46%; m.p. 118 °C (Found: C, 74.2; H, 5.3; N, 7.4. Calc. for $C_{22}H_{18}N_2O_3$: C, 73.73; H, 5.06; N, 7.82%); δ_H(250 MHz; $CDCl_3$) 2.08 (6 H, s) and 6.4–8.2 (12 H, m); δ_C(62.9 MHz; $CDCl_3$) 18.4, 118.0, 123.7, 124.3, 127.9, 128.0, 129.2, 129.3, 132.3, 134, 139.3, 146.6, 150.5, 165.9 and 196.3. 1-(1-Naphthyl)-2-phenyl-2-(2,6-xylylimino)ethanone: 72% (Found: C, 85.8; H, 6.0; N, 3.6. Calc. for $C_{26}H_{21}NO$: C, 85.92; H, 5.82; N, 3.85%); δ_H(250 MHz; $CDCl_3$) 2.13 (6 H, s) and 6.5–8.6 (15 H, m); δ_C(62.9 MHz; $CDCl_3$) 18.7, 123.7, 124.2, 125.9, 126.8, 128.1, 128.3, 128.5, 128.7, 129.2, 130.6, 131.7, 134.1, 135.9, 147.5, 167.8 and 199.4. 2-(4-Chlorophenyl)-1-(4-methoxyphenyl)-2-(2,6-xylylimino)ethanone: 74% (Found: C, 72.6; H, 4.95; N, 4.0. Calc. for $C_{23}H_{20}ClNO_2$: C, 73.11; H, 5.33; N, 3.71%); δ_H(250 MHz; $CDCl_3$) 2.25 (6 H, s), 3.13 (3 H, s) and 6.4–7.9 (11 H, m); δ_C(62.9 MHz; $CDCl_3$) 18.6, 54.7, 113.8, 123.9, 127.4, 127.8, 127.9, 128.2, 129.2, 129.4, 131.4, 134.1, 137.7, 147.5, 166.0 and 194.2.

Procedure for the Preparation of Diketones.—A solution of keto imine (5 mmol) in a mixture of THF (20 cm^3) and HCl (3 mol dm^{-3}; 10 cm^3) was stirred for 15 h at room temperature. The mixture was extracted with ether (2 × 30 cm^3), and the combined extracts were dried, filtered and evaporated. The product was then purified by column chromatography on silica (eluent: light petroleum–diethyl ether, 90:10). Benzil, 76%; m.p. 95 °C. 2-(4-Methoxyphenyl)-1-phenylethanedione: 73%; m.p. 53 °C (lit.,[35] 52 °C); δ_H(250 MHz; $CDCl_3$) 3.1 (3 H, s) and 7.0–7.9 (9 H, m); δ_C(62.9 MHz; $CDCl_3$) 54.6, 113.8, 126.5, 128.0, 128.4, 131.9, 136.7, 192.9 and 193.6. 2-(3-Methoxyphenyl)-1-phenylethanedione: 69%; m.p. 92 °C; δ_H(250 MHz; $CDCl_3$) 3.61 (3 H, s) and 7.0–7.8 (9 H, m); δ_C(62.9 MHz; $CDCl_3$) 55.4, 113.1, 121.7, 123.1, 129.1, 129.8, 130.1, 132.9, 134.2, 134.9, 160.1, 193.9 and 194.6 (Found: C, 74.4; H, 5.4. Calc. for $C_{15}H_{12}O_3$: C, 74.99; H, 5.03%). 2-(4-Chorophenyl)-1-phenylethanedione: 68%, m.p. 76 °C (lit.,[35] 75 °C); δ_H(250 MHz; $CDCl_3$) 7.1–7.9 (9 H, m); δ_C(62.9 MHz; $CDCl_3$) 129.1, 129.4, 129.9, 131.2, 131.3, 132.8, 135.1, 141.5, 193.0 and 193.8. 2-(4-Nitrophenyl)-1-phenylethanedione: 40%; m.p. 138 °C (lit.,[36] 139 °C); δ_H(250 MHz; $CDCl_3$) 7.0–8.2 (8 H, m); δ_C(62.9 MHz; $CDCl_3$) 118.2, 124.6, 129.0, 132.1, 134.2, 139.6, 146.1, 150.2, 192.8 and 193.3. 2-(1-Naphthyl)-1-phenylethanedione: 67%; m.p. 97 °C (lit.,[37] 97 °C); δ_H(250 MHz; $CDCl_3$) 6.8–8.0 (11 H, m) and 9.55 (1 H, d); δ_C(62.9 MHz; $CDCl_3$) 124.6, 127.2, 127.7, 128.1, 128.4, 129.0, 129.2, 129.6, 130.1, 134.5, 135.2, 135.8, 194.6 and 197.5. 1-(4-Chlorophenyl)-2-(4-methoxyphenyl)ethanedione: 68%; m.p. 127 °C (lit.,[36] 128 °C); δ_H(250 MHz; $CDCl_3$) 4.1 (3 H, s) and 6.9–8.0 (8 H, m); δ_C(62.9 MHz; $CDCl_3$) 61.0, 120.0, 130.2, 134.8, 136.4, 136.5, 137.4, 145.6, 170.2, 197.7 and 198.9.

Transmetallation of Imidoylstannanes.—To a solution of imidoylstannane (10 mmol) in THF (20 cm^3) at −78 °C, was added dropwise methyllithium in diethyl ether (1.6 mol dm^{-3}; 10 mmol). After 15 min, the electrophile (11 mmol) in THF (10 cm^3) was also added to the mixture and the whole was then stirred for 1 h at room temperature. After this it was hydrolysed and extracted with diethyl ether (2 × 50 cm^3). The solvents were evaporated and the products were purified by distillation (Kugelrohr apparatus). *N*-Benzylidene-2,6-xylylamine: 91%; b.p. 100 °C (0.05 Torr) (Found: C, 85.4; H, 7.6; N, 6.3. Calc. for $C_{15}H_{15}N$: C, 86.08; H, 7.22; N, 6.69%); δ_H(250 MHz; $CDCl_3$) 2.14 (6 H, s), 6.9–7.8 (8 H, m) and 8.15 (1 H, s); δ_C(62.9 MHz; $CDCl_3$) 18.3, 124.3, 127.6, 128.6, 129.0, 129.3, 132.0, 136.6, 151.7 and 162.6. *N*-([^{2}H]Benzylidene)-2,6-xylylamine: 93%; b.p.

100 °C (0.05 Torr); δ_H(250 MHz; $CDCl_3$) 2.14 (6 H, s) and 6.9–7.9 (8 H, m); δ_C(62.9 MHz; $CDCl_3$) 18.7, 124.1, 127.3, 128.5, 128.8, 129.1, 131.8, 136.4, 151.7 and 162.8 (t, $^1J_{C,D}$ 24). *N*-(1-Phenylethylidene)-2,6-xylylamine: 85%; b.p. 120 °C (0.05 Torr) (Found: C, 85.4; H, 8.1; N, 5.8. Calc. for $C_{16}H_{17}N$: C, 86.06; H, 7.67; N, 6.27%); δ_H(250 MHz; $CDCl_3$) 2.1 (6 H, s), 2.2 (3 H, s), 7.1–8.3 (8 H, m); δ_C(62.9 MHz; $CDCl_3$) 17.6, 18.2, 123.0, 125.8, 127.3, 128.1, 128.6, 129.0, 130.5, 139.3 and 162.7. *N*-(1-Phenylpropylidene)-2,6-xylylamine: 86%; b.p. 130 °C (0.05 Torr) (Found: C, 85.5; H, 7.8; N, 5.5. Calc. for $C_{17}H_{19}N$: C, 86.03; H, 8.07; N, 5.90%); δ_H(250 MHz; $CDCl_3$) 1.03 (3 H, t), 2.17 (6 H, s), 2.56 (2 H, q) and 7.0–8.1 (8 H, m); δ_C(62.9 MHz; $CDCl_3$) 11.7, 18.5, 24.1, 123.0, 125.8, 127.9, 128.2, 128.8, 130.6, 138.2, 149.1 and 170.5. *N*-[1-(4-Chlorophenyl)propylidene]-2,6-xylylamine: 82%; b.p. 140 °C (0.05) (Found: C, 75.7; H, 6.35; N, 4.8. Calc. for $C_{17}H_{18}ClN$: C, 75.17; H, 6.68; N, 5.15%); δ_H(250 MHz; $CDCl_3$) 1.08 (2 H, t), 2.21 (6 H, s), 2.59 (3 H, q) and 7.0–8.1 (7 H, m); δ_C(62.9 MHz; $CDCl_3$) 11.6, 18.4, 23.8, 123.1, 125.5, 128.2, 128.9, 129.2, 136.3, 136.6, 148.8 and 169.1. Trimethyl[(2,6-xylylimino)benzyl]silane: 82%; b.p. 130 °C (0.05 Torr) (Found: C, 76.2; H, 7.7; N, 5.2. Calc. for $C_{18}H_{23}NSi$: C, 76.81; H, 8.24; N, 4.98%); δ_H(250 MHz; $CDCl_3$) 0.40 (9 H, s), 2.03 (6 H, s), and 6.8–7.9 (8 H, m); δ_C(62.9 MHz; $CDCl_3$) −0.9, 18.6, 122.9, 125.7, 127.8, 128.3, 129.1, 129.9, 130.3 and 131.6. *tert*-Butyl(dimethyl)[α-(2,6-xylylimino)benzyl]silane: 88%; b.p. 145 °C (0.05 Torr) (Found: C, 78.4; H, 8.7; N, 4.8. Calc. for $C_{21}H_{29}NSi$: C, 77.96; H, 9.03; N, 4.33%); δ_H(250 MHz; $CDCl_3$) 0.44 (6 H, s), 1.20 (9 H, s), 2.17 (6 H, s) and 6.9–7.2 (8 H, m); δ_C(62.9 MHz; $CDCl_3$) −4.7, 19.0, 27.2, 122.2, 124.7, 125.6, 127.7, 127.9, 128.0, 141.8, 150.9 and 188.3. 1,2-Diphenyl-2-(2,6-xylylimino)ethanol: 87%; b.p. 180 °C (0.01 Torr) (Found: C, 83.5; H, 6.6; N, 4.75. Calc. for $C_{22}H_{21}NO$: C, 83.78; H, 6.71; N, 4.44%); δ_H(250 MHz; $CDCl_3$) 2.26 (6 H, s), 4.92 (1 H, s), 5.93 (1 H, s) and 6.8–7.9 (13 H, m); δ_C(62.9 MHz; $CDCl_3$) 19.4, 65.7, 122.1, 127.9, 128.1, 128.8, 128.9, 129.0, 129.1, 129.4, 133.6, 135.4, 138.6, 144.2 and 198.7. Isobutyl 2-phenyl-2-(2,6-xylylimino)acetate: 65%; b.p. 150 °C (0.05 Torr) (Found: C, 78.1; H, 7.0; N, 4.8. Calc. for $C_{20}H_{23}NO_2$: C, 77.64; H, 7.49; N, 4.53%); δ_H(250 MHz; $CDCl_3$) 0.97 (6 H, d), 2.00 (1 H, m), 2.12 (6 H, s), 4.15 (2 H, d) and 6.9–8.0 (8 H, m); δ_C(62.9 MHz; $CDCl_3$) 19.0, 27.7, 71.9, 124.3, 127.8, 128.6, 129.3, 128.9, 129.9, 132.5, 134.9, 164.1 and 170.0.

Hydrolysis of Imines.—A solution of imine (5 mmol) in a mixture of THF (20 cm^3) and HCl (10 cm^3; 3 mol dm^{-3}) was stirred for 15 h at room temperature and then extracted with ether (2 × 30 cm^3). The combined extracts were dried, filtered and evaporated. The product was then purified by column chromatography on silica (eluent: petroleum–diethyl ether, 90:10). Their characteristics were found identical with those of authentic materials.

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