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Some Addition Reactions of *N*-Tributylstannyldiphenylmethyleneamine

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N-Tributylstannyldiphenylmethyleneamine reacts with the multiply bonded reagents isocyanates, isothiocyanates, aldehydes, ketones, acrylonitrile, di-α-naphthylcarbodi-imide, *N*-phenylsulphinylamine, sulphur dioxide, trichloroacetonitrile, carbon disulphide, and carbonyl sulphide to form 11 new classes of organotinamino-derivatives. Many of the adducts are readily hydrolysed to the hitherto unreported protic compounds, which have also been synthesised from reaction between diphenylmethyleneamine and the acceptor reagent. The addition of chloral to the aldehyde adducts results in the elimination of aldehyde and the formation of the chloral adduct; except in the case of the bromal adduct, where further addition takes place. Addition also appears to take place with iso(thio)-cyanates; equilibria being established in some cases.

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REACTIONS involving the addition of a metal– or metalloid–nitrogen bond, M–N, across the multiple bond of an unsaturated substrate, A=B, have been characterised for a wide range of amino-derivatives.[1] No similar reactions involving *N*-metallo-imines have been investigated. Ketimine (azomethine = methyleneamine) derivatives of lithium,[2,3] magnesium,[4] boron,[2] aluminium,[5] silicon,[2,3] germanium,[3] and tin [3] have been prepared but few reactions are known. *N*-Lithio,[2,3] -magnesyl,[4] and -silyl [2] derivatives have been used as ketimino-transfer reagents; and ketimine–enamine tautomerism has been demonstrated for silicon derivatives which possess the Si–N=C–C–H grouping.[3] Here we report some addition reactions of *N*-tributylstannyldiphenylmethyleneamine (I) and the parent diphenylmethyleneamine.

DISCUSSION

N-Tributylstannyldiphenylmethyleneamine (I) reacted rapidly and exothermically with alkyl and aryl isocyanates to give *N*-tributylstannyl-*N*-alkyl(aryl)-*N*′-diphenylmethyleneaminoureas (II) as viscous, golden yellow oils. Rapid hydrolysis of these yields the hitherto unreported amino-ureas (IIa) as white solids with sharp melting points. Identical products are obtained from the direct reaction of the diphenylmethylene and the same isocyanate.

$$\begin{array}{l} Bu_3Sn{\cdot}N{:}CPh_2 + RN{:}C{:}O \longrightarrow Bu_3Sn{\cdot}NR{\cdot}CO{\cdot}N{:}CPh_2 \\ \quad (I) \qquad\qquad\qquad\qquad\qquad \downarrow H_2O \quad (II) \\ HN{:}CPh_2 + RN{:}C{:}O \longrightarrow RNH{\cdot}CO{\cdot}N{:}CPh_2 \\ \qquad\qquad\qquad\qquad\qquad\quad (IIa) \end{array} \qquad (1)$$

Methyl and phenyl isothiocyanate also reacted rapidly and exothermically to give orange-yellow oils. The

$$\begin{array}{l} Bu_3Sn{\cdot}N{:}CPh + RN{:}C{:}S \longrightarrow \\ Bu_3Sn{\cdot}NR{\cdot}CS{\cdot}NCPh_2 \xleftarrow{(R=Ph)} \tfrac{1}{2}(Bu_3Sn)_2O + NHPh{\cdot}CS{\cdot}N{:}CPh_2 \\ \quad (III) \\ \quad or \\ Bu_3Sn{\cdot}S{\cdot}C(:NR){\cdot}N{:}CPh_2 \\ \quad (IIIa) \qquad\qquad\qquad\qquad\qquad (2) \\ \quad \downarrow H_2O \text{ (for R = Me)} \\ NHR{\cdot}CS{\cdot}N{:}CPh_2 \longleftarrow RN{:}C{:}S + HN{:}CPh_2 \\ \quad (IIIb) \end{array}$$

N-phenyl derivative, which is stable to atmospheric moisture, may also be prepared from bistributyltin oxide and *N*-phenyl-*N*′-diphenylmethyleneaminothiourea in boiling benzene. An analogous reaction for *N*-methyl compound fails to occur, the *N*-tributylstannyl derivative of which is readily hydrolysed to the parent compound. Two intense ν(C=N) stretching frequencies at 1595 and 1620 cm^{-1} and the lack of bands which are readily assignable to ν(C=S) in the i.r. spectrum of both adducts suggest the Sn⁻S bonded structure.

With aldehydes and activated ketones, compound (I) reacts exothermically to give *O*-tributylstannyl acetals (IV; $R^2 = H$) and *O*-tributylstannyl acetals (IV; $R^1 = R^2 = CCl_3$; $R^1 = CCl_2F$, $R^2 = CClF_2$) as almost

$$Bu_3Sn{\cdot}N{:}CPh_2 + R^1R^2CO \longrightarrow \underset{(IV)}{Bu_3Sn{\cdot}O{\cdot}CR^1R^2{\cdot}N{:}CPh_2} \qquad (3)$$

colourless viscous oils. When $R^2 = H$ and $R^1 = CCl_3$, CBr_3, Ph, Me, Et, Pr^i reaction proceeds to completion; $R = Pr^n$, an equilibrium is established.

Details of the reaction of compound (I) with other acceptor molecules is given in Table 1. All the compounds (V)—(XI) were coloured oils, which were [except (X)] easily hydrolysed by atmospheric moisture.

Because the aldehydic, C*H*=O, and acetal (C*H*–O) protons fall in clear regions, it was possible to undertake a brief examination of the relative acceptor strengths and reactivities of the various multiply bonded acceptor molecules.

Addition of 1 mol of an acceptor molecule, A=B, to the adduct of (I) and an aldehyde, RCH=O, can result in either displacement or further addition, six- and four-centre, respectively, transition states being easily accessible.[6] One might expect the acetal proton of

$$\begin{array}{l} Bu_3Sn{\cdot}A{\cdot}B{\cdot}O{\cdot}CHR{\cdot}N{:}CPh_2 \xleftarrow[A=B]{(b)} Bu_3Sn{\cdot}O{\cdot}CHR{\cdot}N{:}CPh_2 \xrightarrow[A=B]{(a)} \\ \quad (XII) \qquad\qquad\qquad\quad (XIII) \\ Bu_3Sn{\cdot}A{-}B{\cdot}N{:}CPh_2 + RCH{=}O \qquad (4) \end{array}$$

(XII) to be more deshielded than that in (XIII) and hence moved to slightly lower field. The results are given in Table 2.

With the sole exception of the bromal adduct, with

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TABLE 1

Products of the reaction of $Bu_3Sn{\cdot}N{=}CPh_2$ with weaker acceptors

	A=B	Conditions	Structure of adduct	Colour	Sn Analysis Found	Sn Analysis Reqd.	ν(C=N) (cm⁻¹)
(V)	$CH_2{=}CH{-}C{\equiv}N$	10 min. at room temp.	$Bu_3Sn{\cdot}CH(CN){\cdot}CH_2{\cdot}N{=}CPh_2$ [a]	Pale yellow	22·2	22·7	1620m
(VI)	α-Np·N=C=N·α-Np	Immediate	$Bu_3Sn{\cdot}N(\alpha\text{-Np}){\cdot}C(N{\cdot}\alpha\text{-Np}){\cdot}N{=}CPh_2$ [b]	Orange-red			1630s
(VII)	PhN=S=O	Exothermic	$Bu_3Sn{\cdot}NPh{\cdot}S(:O){\cdot}N{=}CPh_2$	Orange-red			1590m
(VIII)	O=S=O	Exothermic	$Bu_3Sn{\cdot}O{\cdot}S(:O){\cdot}N{=}CPh_2$ [c]	Yellow	21·6	22·2	1595m
(IX)	$CCl_3{\cdot}C{\equiv}N$	0·5 hr at room temp.	$Bu_3Sn{\cdot}N{=}C(CCl_3){\cdot}N{=}CPh_2$ [d]	Yellow	20·2	20·6	1650m, 1620s
(X)	S=C=S	5 min. at room temp.	$Bu_3Sn{\cdot}S{\cdot}C(:S){\cdot}N{=}CPh_2$ [e]	Deep red	19·0	19·4	1625s
(XI)	O=C=S	5 min. at room temp.	$Bu_3Sn{\cdot}O{\cdot}C(:S){\cdot}N{=}CPh_2$ [f]	Pale yellow	19·5	20·0	1640s, 1625s

[a] $\nu_{C\equiv N}$ 2210w cm⁻¹; n.m.r. triplet τ 7·94(1H), doublet τ 6·49 (2H), J(H–H) = 6·6 Hz, J(Sn–H) = 39·6 Hz. [b] Hydrolysis yields *N*-α-naphthyl-*N'*-diphenylmethyleneamino-*N'*-α-naphthylguanidine, m.p. 210° (decomp.) (Found: C, 86·9; H, 5·2; N, 8·0%. $C_{34}H_{25}N_3$ requires C, 85·9; H, 5·3; N, 8·8%). [c] $\nu_{S=O}$ 1000vs cm⁻¹ broad. [d] ν_{C-Cl} 790vs cm⁻¹. [e] $\nu_{C=S}$ 1120vs cm⁻¹. [f] $\nu_{C=S}$ 1190s; ν_{C-O}: 1080s, and 1055s cm⁻¹.

TABLE 2

Products of the reaction of $Bu_3Sn{\cdot}O{\cdot}CHR{\cdot}N{=}CPh_2$ and A=B [a]

R	A=B	Conditions (°C)	Products
Aldehydes:			
CCl_3	$CCl_3{\cdot}CHO$	2 days (33·5)	No reaction
CBr_3	$CCl_3{\cdot}CHO$	Exothermic	$Bu_3Sn{\cdot}O{\cdot}CH(CCl_3){\cdot}O{\cdot}CH(CBr_3){\cdot}N{=}CPh_2$ τ 4·80; τ 5·06
Me	$CCl_3{\cdot}CHO$	Immediate	$Bu_3Sn{\cdot}O{\cdot}CH(CCl_3){\cdot}N{=}CPh_2$ + MeCHO τ 4·81 quartet τ 0·32, J(H–H) = 2·8 Hz
Pr^i	$CCl_3{\cdot}CHO$	Immediate	$Bu_3Sn{\cdot}O{\cdot}CH(CCl_3){\cdot}N{=}CPh_2$ + Pr^iCHO τ 4·80 doublet τ 0·43, J(H–H) = 1·6 Hz
Et	$CCl_3{\cdot}CHO$	Mildly exothermic	$Bu_3Sn{\cdot}O{\cdot}CH(CCl_3){\cdot}N{=}CPh_2$ + EtCHO τ 4·81 triplet τ 0·27, J(H–H) = 1·3 Hz
Ph	$CCl_3{\cdot}CHO$	Immediate	$Bu_3Sn{\cdot}O{\cdot}CH(CH_3){\cdot}N{=}CPh_2$ + PhCHO τ 4·82 0·03
Ketones:			
CBr_3	$(CCl_3)_2CO$	5 days (33·5)	[$(CCl_3)_2CO$ adduct] + $CBr_3{\cdot}CHO$ (10%) [b] τ 1·30
CBr_3	$CCl_2F{\cdot}CO{\cdot}CF_2Cl$	17 hr (RT) [c]	[$CCl_2F{\cdot}CO{\cdot}CClF_2$ adduct] + $CBr_3{\cdot}CHO$ (60%) [b] τ 1·32
Ph	$CCl_2F{\cdot}CO{\cdot}CF_2Cl$	Immediate	[$CCl_2F{\cdot}CO{\cdot}CClF_2$ adduct] + PhCHO τ 0·05
Me	$(CCl_3)_2CO$	44 hr (RT) [c]	[$(CCl_3)_2CO$ adduct] + MeCHO (5%) quartet τ 0·30, J(H–H) = 2·5 Hz
Isocyanates:			
Me	MeN=C=O	Exothermic	$Bu_3Sn{\cdot}NMe{\cdot}CO{\cdot}O{\cdot}CH(Me){\cdot}N{=}CPh_2$ quartet τ 4·40, J = 6 Hz [d]
Me	EtN=C=O	1 hr (RT) [c]	$Bu_3Sn{\cdot}NEt{\cdot}CO{\cdot}O{\cdot}CH(Me){\cdot}N{=}CPh_2$ quartet τ 4·18, J = 6 Hz [e]
Me	PhN=C=O	Exothermic	$Bu_3Sn{\cdot}NPh{\cdot}CO{\cdot}O{\cdot}CH(Me)N{=}CPh_2$ quartet τ 4·14, J = 6 Hz
CBr_3	MeN=C=O	17 hr (33·5)	$Bu_3Sn{\cdot}NMe{\cdot}CO{\cdot}O{\cdot}CH(CBr_3)N{=}CPh_3$ (75%) [b] τ 3·78 [f]
CBr_3	EtN=C=O	17 hr (33·5)	$Bu_3Sn{\cdot}NEt{\cdot}CO{\cdot}O{\cdot}CH(CBr_3)N{=}CPh_2$ (50%) τ 3·80 [g]
CBr_3	PhN=C=O	17 hr (33·5)	$Bu_3Sn{\cdot}NPh{\cdot}CO{\cdot}O{\cdot}CH(CBr_3)N{=}CPh_2$ (80%) τ 3·71
Ph	EtN=C=O	1 hr (RT) [c]	$Bu_3Sn{\cdot}NEt{\cdot}CO{\cdot}O{\cdot}CHPh{\cdot}N{=}CPh_2$ τ 3·48 [h]
Ph	PhN=C=O	Exothermic	$Bu_3Sn{\cdot}NPh{\cdot}CO{\cdot}O{\cdot}CHPh{\cdot}N{=}CPh_2$ τ 3·39
Isothiocyanates:			
Me	PhN=C=S	44 hr (RT) [c]	$Bu_3Sn{\cdot}S{\cdot}N(=CPh){\cdot}O{\cdot}CH(CH_3){\cdot}N{=}CPh_2$ (50%) quartet τ 4·11, J = 6 Hz

[a] In CCl_4 solution. τ Values refer to acetal or aldehydic protons. All reactions went to completion unless otherwise stated. [b] RT = room temperature (*ca.* 20°). [c] By integration. [d] τ 7·30 (N–CH_3). [e] Unresolved quartet τ 6·90 (N–CH_2). [f] τ 7·22 (N–CH_3). [g] Unresolved quartet τ 6·70 (N–CH_2). [h] Unresolved quartet τ 6·90 (N–CH_2).

which chloral appeared to form a double adduct similar to those observed with tributyltin methoxide and bistributyltin oxide and 2 mol of chloral,[6] the addition of 1 mol of chloral to the aldehyde adducts resulted in complete displacement of the aldehyde and the formation of the chloral adduct. No reaction between chloral and the chloral adduct could be detected even after two days at 33·5°. The hexahalogeno-ketones are much weaker acceptors, and mixtures of the ketones and the aldehyde adducts resulted in equilibria between free

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aldehyde, free ketone, and their two respective adducts. Isocyanates and isothiocyanates behaved differently; inserting into the Sn–O bond of the aldehyde adducts, like the well characterised reactions of organotin oxides and alkoxides.[7,8] No elimination of aldehyde could be detected, although, in many cases, equilibria were set up, consistent with the deactivated nature of the alkoxides.

EXPERIMENTAL

All manipulations were performed under an atmosphere of dry nitrogen.

TABLE 3

Products of the reaction of $Bu_3Sn{\cdot}N{=}CPh_2$ with isocyanates and isothiocyanates

	R	ν(C=N) (cm^{-1})	N.m.r. (τ)	Sn Analysis Found	Sn Analysis Reqd.
(II;	Me)	1630vs, 1600vs	7·40 (N–CH_3)	22·0	22·5
(II;	Et)	1630vs, 1595vs	7·05 (N–CH_2) [a]	21·9	22·3
(II;	Bu)	1630vs, 1595vs	7·12 (N–CH_2) [b]	20·5	21·3
(II;	Ph)	1625vs, 1585vs		20·4	20·1
(III;	Me)	1620vs, 1595vs	7·27 (N–CH_3)	21·2	21·8
(III;	Ph)	1620s, 1595s			

[a] Quartet J(H–H) = 7·2 Hz. [b] Unresolved multiplet.

N-Tributylstannyldiphenylmethyleneamine was prepared by the method of Chan and Rochow [3] as a yellow oil, b.p. 180°/0·3 mm, $\nu_{C=N}$: 1620vs cm^{-1}. Diphenylmethyleneamine was prepared according to Pickard and Tolbert [4] as a colourless oil, b.p. 103°/0·35 mm, $\nu_{C=N}$: 1605s, ν_{N-H}: 3250w; τ 0·31 (N–H).

Further Reactions of the Aldehyde Adducts.—These reactions were carried out on an n.m.r. scale in *ca.* 10% CCl_4 solution. Typically, the aldehyde adduct was prepared as described above, then an equimolecular quantity of the appropriate reagent was added, and the course of the reaction was followed by observing the acetal–aldehyde proton in the n.m.r. Details are given in Table 2.

TABLE 4

Products of the reaction $Bu_3Sn{\cdot}N{=}CPh_2 + R^1R^2C{=}O \longrightarrow Bu_3Sn{\cdot}O{\cdot}CR^1R^2{\cdot}N{:}CPh_2$

R^1	R^2	% Reaction	τ (CH)	J(H–H) (Hz)	J(Sn–H) (Hz)
CCl_3 [a]	H	100	4·81		38·4
CBr_3 [k]	H	100	5·26		36·0
Me [b]	H	100	4·88 [c]	5·6	
Et	H	100	5·19 [e]	6·0	
Pr^i	H	100	5·48 [f]	6·6	
Pr^n	H	85 [d]	5·07 [e]	8·4	
Ph [g]	H	100	4·09		51·0
CCl_3	CCl_3 [h]	100			
CCl_2F	$CClF_2$ [i]	100			

[a] $\nu_{C=N}$: 1620s cm^{-1} (Found: Sn, 18·7%. Required: Sn, 19·2%). [b] $\nu_{C=N}$: 1650s cm^{-1} (Found: Sn, 22·5%. Required: Sn, 23·1%). [c] Centre of quartet. Also doublet τ 7·95. [d] By integration. [e] Centre of triplet. [f] Centre of doublet. [g] $\nu_{C=N}$: 1640s cm^{-1} (Found: Sn, 20·1%. Required: Sn, 20·6%). [h] $\nu_{C=N}$: 1640s; ν_{C-O}: 1180s; ν_{C-Cl}: 875s, 840vs cm^{-1} (Found: Sn, 15·5%. Required: Sn, 16·2%). [i] $\nu_{C=N}$: 1650s; ν_{C-O}: 1195s, 1155vs; ν_{C-F}: 1040s; ν_{C-Cl}: 880s cm^{-1} (Found: Sn, 17·0%. Required: Sn, 17·3%). [k] $\nu_{C=N}$: 1630s cm^{-1} (Found: Sn, 15·6%. Required: Sn, 15·8%).

Reactions of Diphenylmethyleneamine with Acceptor Molecules.—Typically the reagents were mixed in light petroleum ether, when an exothermic reaction was accompanied by crystallisation of the product. Physical data is given in Table 5.

TABLE 5

Derivatives of diphenylmethyleneamine

A=B	Product	M.p.	Colour	ν_{N-H} (cm^{-1})	$\nu_{C=N}$ (cm^{-1})	Analysis (%) Calc. C	Calc. H	Calc. N	Found C	Found H	Found N
MeN=C=O	$Ph_2C{=}N{\cdot}CO{\cdot}NMeH$ [a]	179—180°	White	3250s	1645vs	75·6	5·9	11·8	76·0	6·2	11·7
EtN=C=O	$Ph_2C{=}N{\cdot}CO{\cdot}NEtH$ [a]	155—156	White	3240s	1645vs, 1620s	76·2	6·4	11·1	76·2	6·7	11·1
BuN=C=O	$Ph_2C{=}N{\cdot}CO{\cdot}NBuH$ [a]	93—95	White	3250s	1625vs, br	77·1	7·1	10·0	76·6	7·4	9·9
PhN=C=O	$Ph_2C{=}N{\cdot}CO{\cdot}NPhH$ [a]	152·5—154	White	3270s	1650vs	79·9	5·3	9·3	79·6	5·7	9·3
MeN=C=S	$Ph_2C{=}N{\cdot}CS{\cdot}NMeH$ [a]	162—164	Pale yellow	3160s	1615m	71·0	5·5	11·0	69·9	5·5	10·7
PhN=C=S	$Ph_2C{=}N{\cdot}CS{\cdot}NPhH$ [a]	136—137	Yellow	3190s	1645vs	76·0	5·1	8·9	76·0	5·5	8·6
$CCl_3{\cdot}CHO$	$Ph_2C{=}N{\cdot}CH(CCl_3){\cdot}OH$ [b]	105—107	White	3160s	1615vs	54·9	3·7	4·3	54·6	3·5	3·8
$CBr_3{\cdot}CHO$	$Ph_2C{=}N{\cdot}CH(CBr_3){\cdot}OH$ [c]	97—100	White	3200s	1615vs	39·0	2·6	3·0	40·8	2·9	3·0
α-Np·N=C=N·α-Np	$Ph_2C{=}N{\cdot}C(:N{\cdot}\alpha\text{-Np}){\cdot}N{\cdot}\alpha\text{-Np}$	210 (decomp.)	Yellow	3210m	1640s	85·9	5·3	8·8	85·3	6·0	8·2

[a] Too insol. for n.m.r. [b] N.m.r. ($CDCl_3$ soln.): τ 5·19 (C–H), 5·51 (broad) (–C–OH). [c] N.m.r. ($CDCl_3$ soln.): τ 5·30 (–C–H), 3·95 (broad) –(C–OH).

I.r. spectra were recorded using a Unicam SP 200 instrument as Nujol mulls or liquid films. N.m.r. spectra were recorded at 33·5° using a Perkin-Elmer R10 instrument in *ca.* 10% CCl_4 solution with Me_4Si as an internal standard. Tin was determined gravimetrically as stannic oxide.

The Addition of N-Tributylstannyldiphenylmethyleneamine to Acceptor Molecules.—Details of the addition of compound (I) to acceptor molecules are given in Tables 1,3, and 4.

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