

## Some Addition Reactions of *N*-Tributylstannyldiphenylmethyleamine

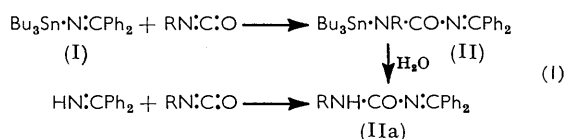
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*N*-Tributylstannyldiphenylmethyleamine reacts with the multiply bonded reagents isocyanates, isothiocyanates, aldehydes, ketones, acrylonitrile, di- $\alpha$ -naphthylcarbodi-imide, *N*-phenylsulphonylamine, sulphur dioxide, trichloroacetonitrile, 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 diphenylmethyleamine 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.

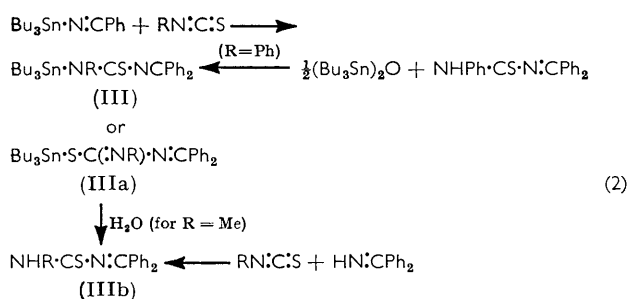
REACTIONS involving the addition of a metal- or metalloid-nitrogen bond, M-N, across the multiple bond of an unsaturated substrate, A=B, have been characterised for a wide range of amino-derivatives.<sup>1</sup> No similar reactions involving *N*-metallo-imines have been investigated. Ketimine (azomethine = methyleneamine) derivatives of lithium,<sup>2,3</sup> magnesium,<sup>4</sup> boron,<sup>2</sup> aluminium,<sup>5</sup> silicon,<sup>2,3</sup> germanium,<sup>3</sup> and tin<sup>3</sup> have been prepared but few reactions are known. *N*-Lithio,<sup>2,3</sup> -magnesiyl,<sup>4</sup> and -silyl<sup>2</sup> 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.<sup>3</sup> Here we report some addition reactions of *N*-tributylstannyldiphenylmethyleamine (I) and the parent diphenylmethyleamine.

### DISCUSSION

*N*-Tributylstannyldiphenylmethyleamine (I) reacted rapidly and exothermically with alkyl and aryl isocyanates to give *N*-tributylstannyl-*N*-alkyl(aryl)-*N'*-diphenylmethyleaminoureas (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 diphenylmethyleamine and the same isocyanate.

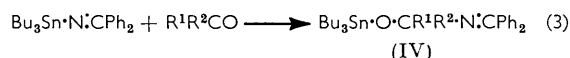


Methyl and phenyl isothiocyanate also reacted rapidly and exothermically to give orange-yellow oils. The



*N*-phenyl derivative, which is stable to atmospheric moisture, may also be prepared from dibutyltin oxide and *N*-phenyl-*N'*-diphenylmethyleaminothiourea 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  $\nu(\text{C}=\text{N})$  stretching frequencies at 1595 and 1620  $\text{cm}^{-1}$  and the lack of bands which are readily assignable to  $\nu(\text{C}=\text{S})$  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;  $\text{R}^2 = \text{H}$ ) and *O*-tributylstannyl acetals (IV;  $\text{R}^1 = \text{R}^2 = \text{CCl}_3$ ;  $\text{R}^1 = \text{CCl}_2\text{F}$ ,  $\text{R}^2 = \text{CClF}_2$ ) as almost

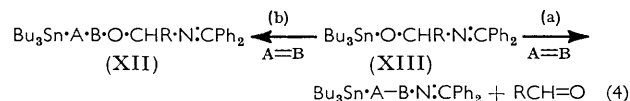


colourless viscous oils. When  $\text{R}^2 = \text{H}$  and  $\text{R}^1 = \text{CCl}_3$ ,  $\text{CBr}_3$ , Ph, Me, Et, Pr<sup>i</sup> reaction proceeds to completion;  $\text{R} = \text{Pr}^n$ , an equilibrium is established.

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,  $\text{CH}=\text{O}$ , and acetal ( $\text{CH}-\text{O}$ ) 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,  $\text{RCH}=\text{O}$ , can result in either displacement or further addition, six- and four-centre, respectively, transition states being easily accessible.<sup>6</sup> One might expect the acetal proton of



(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

<sup>1</sup> L.-H. Chan and E. G. Rochow, *J. Organometallic Chem.*, 1967, **9**, 231.

<sup>2</sup> P. L. Pickard and J. Tolbert, *J. Org. Chem.*, 1961, **26**, 4886; and references contained therein.

<sup>3</sup> K. Wade and B. K. Wyatt, *J. Chem. Soc. (A)*, 1969, 1121.

<sup>4</sup> A. G. Davies and W. R. Symes, *J. Chem. Soc. (C)*, 1967, 1009.

<sup>1</sup> M. F. Lappert and B. Prokai, *Adv. Organometallic Chem.*, 1967, **5**, 225.

<sup>2</sup> C. Summerford and K. Wade, *J. Chem. Soc. (A)*, 1969, 1487.

TABLE 1  
Products of the reaction of  $\text{Bu}_3\text{Sn}\cdot\text{N}=\text{CPh}_2$  with weaker acceptors

A=B	Conditions	Structure of adduct	Colour	Sn Analysis		$\nu(\text{C}=\text{N})$ ( $\text{cm}^{-1}$ )
				Found	Reqd.	
(V) $\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$	10 min. at room temp.	$\text{Bu}_3\text{Sn}\cdot\text{CH}(\text{CN})\cdot\text{CH}_2\cdot\text{N}=\text{CPh}_2^a$	Pale yellow	22.2	22.7	1620m
(VI) $\alpha\text{-Np}\cdot\text{N}=\text{C}=\text{N}\cdot\alpha\text{-Np}$	Immediate	$\text{Bu}_3\text{Sn}\cdot\text{N}(\alpha\text{-Np})\cdot\text{C}(\text{N}\cdot\alpha\text{-Np})\cdot\text{N}=\text{CPh}_2^b$	Orange-red			1630s
(VII) $\text{PhN}=\text{S}=\text{O}$	Exothermic	$\text{Bu}_3\text{Sn}\cdot\text{NPh}\cdot\text{S}(\text{O})\cdot\text{N}=\text{CPh}_2$	Orange-red			1590m
(VIII) $\text{O}=\text{S}=\text{O}$	Exothermic	$\text{Bu}_3\text{Sn}\cdot\text{O}\cdot\text{S}(\text{O})\cdot\text{N}=\text{CPh}_2^c$	Yellow	21.6	22.2	1595m
(IX) $\text{CCl}_3\cdot\text{C}\equiv\text{N}$	0.5 hr at room temp.	$\text{Bu}_3\text{Sn}\cdot\text{N}=\text{C}(\text{CCl}_3)\cdot\text{N}=\text{CPh}_2^d$	Yellow	20.2	20.6	1650m, 1620s
(X) $\text{S}=\text{C}=\text{S}$	5 min. at room temp.	$\text{Bu}_3\text{Sn}\cdot\text{S}\cdot\text{C}(\text{S})\cdot\text{N}=\text{CPh}_2^e$	Deep red	19.0	19.4	1625s
(XI) $\text{O}=\text{C}=\text{S}$	5 min. at room temp.	$\text{Bu}_3\text{Sn}\cdot\text{O}\cdot\text{C}(\text{S})\cdot\text{N}=\text{CPh}_2^f$	Pale yellow	19.5	20.0	1640s, 1625s

<sup>a</sup>  $\nu_{\text{C}=\text{N}}$  2210w  $\text{cm}^{-1}$ ; n.m.r. triplet  $\tau$  7.94(1H), doublet  $\tau$  6.49 (2H),  $J(\text{H}-\text{H}) = 6.6$  Hz,  $J(\text{Sn}-\text{H}) = 39.6$  Hz. <sup>b</sup> Hydrolysis yields *N*- $\alpha$ -naphthyl-*N'*-diphenylmethyleamino-*N''*- $\alpha$ -naphthylguanidine, m.p. 210° (decomp.) (Found: C, 86.9; H, 5.2; N, 8.0%.  $\text{C}_{34}\text{H}_{25}\text{N}_3$  requires C, 85.9; H, 5.3; N, 8.8%). <sup>c</sup>  $\nu_{\text{S}=\text{O}}$  1000vs  $\text{cm}^{-1}$  broad. <sup>d</sup>  $\nu_{\text{C}-\text{Cl}}$  790vs  $\text{cm}^{-1}$ . <sup>e</sup>  $\nu_{\text{C}=\text{S}}$  1120vs  $\text{cm}^{-1}$ . <sup>f</sup>  $\nu_{\text{C}=\text{S}}$  1190s;  $\nu_{\text{C}-\text{O}}$ : 1080s, and 1055s  $\text{cm}^{-1}$ .

TABLE 2

Products of the reaction of  $\text{Bu}_3\text{Sn}\cdot\text{O}\cdot\text{CHR}\cdot\text{N}=\text{CPh}_2$  and A=B <sup>a</sup>

R	A=B	Conditions ( $^{\circ}\text{C}$ )	Products
Aldehydes:			
$\text{CCl}_3$	$\text{CCl}_3\cdot\text{CHO}$	2 days (33.5)	No reaction
$\text{CBr}_3$	$\text{CCl}_3\cdot\text{CHO}$	Exothermic	$\text{Bu}_3\text{Sn}\cdot\text{O}\cdot\text{CH}(\text{CCl}_3)\cdot\text{O}\cdot\text{CH}(\text{CBr}_3)\cdot\text{N}=\text{CPh}_2$ $\tau$ 4.80; $\tau$ 5.06
Me	$\text{CCl}_3\cdot\text{CHO}$	Immediate	$\text{Bu}_3\text{Sn}\cdot\text{O}\cdot\text{CH}(\text{CCl}_3)\cdot\text{N}=\text{CPh}_2 + \text{MeCHO}$ $\tau$ 4.81 quartet $\tau$ 0.32, $J(\text{H}-\text{H}) = 2.8$ Hz
Pr <sup>i</sup>	$\text{CCl}_3\cdot\text{CHO}$	Immediate	$\text{Bu}_3\text{Sn}\cdot\text{O}\cdot\text{CH}(\text{CCl}_3)\cdot\text{N}=\text{CPh}_2 + \text{Pr}^i\text{CHO}$ $\tau$ 4.80 doublet $\tau$ 0.43, $J(\text{H}-\text{H}) = 1.6$ Hz
Et	$\text{CCl}_3\cdot\text{CHO}$	Mildly exothermic	$\text{Bu}_3\text{Sn}\cdot\text{O}\cdot\text{CH}(\text{CCl}_3)\cdot\text{N}=\text{CPh}_2 + \text{EtCHO}$ $\tau$ 4.81 triplet $\tau$ 0.27, $J(\text{H}-\text{H}) = 1.3$ Hz
Ph	$\text{CCl}_3\cdot\text{CHO}$	Immediate	$\text{Bu}_3\text{Sn}\cdot\text{O}\cdot\text{CH}(\text{CH}_3)\cdot\text{N}=\text{CPh}_2 + \text{PhCHO}$ $\tau$ 4.82 0.03
Ketones:			
$\text{CBr}_3$	$(\text{CCl}_3)_2\text{CO}$	5 days (33.5)	[( $\text{CCl}_3$ ) <sub>2</sub> CO adduct] + $\text{CBr}_3\cdot\text{CHO}$ (10%) <sup>e</sup> $\tau$ 1.30
$\text{CBr}_3$	$\text{CCl}_2\text{F}\cdot\text{CO}\cdot\text{CF}_2\text{Cl}$	17 hr (RT) <sup>b</sup>	[( $\text{CCl}_2\text{F}\cdot\text{CO}\cdot\text{CClF}_2$ ) adduct] + $\text{CBr}_3\cdot\text{CHO}$ (60%) <sup>e</sup> $\tau$ 1.32
Ph	$\text{CCl}_2\text{F}\cdot\text{CO}\cdot\text{CF}_2\text{Cl}$	Immediate	[( $\text{CCl}_2\text{F}\cdot\text{CO}\cdot\text{CClF}_2$ ) adduct] + PhCHO $\tau$ 0.05
Me	$(\text{CCl}_3)_2\text{CO}$	44 hr (RT) <sup>b</sup>	[( $\text{CCl}_3$ ) <sub>2</sub> CO adduct] + MeCHO (5%) quartet $\tau$ 0.30, $J(\text{H}-\text{H}) = 2.5$ Hz
Isocyanates:			
Me	$\text{MeN}=\text{C}=\text{O}$	Exothermic	$\text{Bu}_3\text{Sn}\cdot\text{NMe}\cdot\text{CO}\cdot\text{O}\cdot\text{CH}(\text{Me})\cdot\text{N}=\text{CPh}_2$ quartet $\tau$ 4.40, $J = 6$ Hz <sup>d</sup>
Me	$\text{EtN}=\text{C}=\text{O}$	1 hr (RT) <sup>b</sup>	$\text{Bu}_3\text{Sn}\cdot\text{NEt}\cdot\text{CO}\cdot\text{O}\cdot\text{CH}(\text{Me})\cdot\text{N}=\text{CPh}_2$ quartet $\tau$ 4.18, $J = 6$ Hz <sup>e</sup>
Me	$\text{PhN}=\text{C}=\text{O}$	Exothermic	$\text{Bu}_3\text{Sn}\cdot\text{NPh}\cdot\text{CO}\cdot\text{O}\cdot\text{CH}(\text{Me})\cdot\text{N}=\text{CPh}_2$ quartet $\tau$ 4.14, $J = 6$ Hz
$\text{CBr}_3$	$\text{MeN}=\text{C}=\text{O}$	17 hr (33.5)	$\text{Bu}_3\text{Sn}\cdot\text{NMe}\cdot\text{CO}\cdot\text{O}\cdot\text{CH}(\text{CBr}_3)\cdot\text{N}=\text{CPh}_2$ (75%) <sup>e</sup> $\tau$ 3.78 <sup>f</sup>
$\text{CBr}_3$	$\text{EtN}=\text{C}=\text{O}$	17 hr (33.5)	$\text{Bu}_3\text{Sn}\cdot\text{NEt}\cdot\text{CO}\cdot\text{O}\cdot\text{CH}(\text{CBr}_3)\cdot\text{N}=\text{CPh}_2$ (50%) $\tau$ 3.80 <sup>g</sup>
$\text{CBr}_3$	$\text{PhN}=\text{C}=\text{O}$	17 hr (33.5)	$\text{Bu}_3\text{Sn}\cdot\text{NPh}\cdot\text{CO}\cdot\text{O}\cdot\text{CH}(\text{CBr}_3)\cdot\text{N}=\text{CPh}_2$ (80%) $\tau$ 3.71
Ph	$\text{EtN}=\text{C}=\text{O}$	1 hr (RT) <sup>b</sup>	$\text{Bu}_3\text{Sn}\cdot\text{NEt}\cdot\text{CO}\cdot\text{O}\cdot\text{CHPh}\cdot\text{N}=\text{CPh}_2$ $\tau$ 3.48 <sup>h</sup>
Ph	$\text{PhN}=\text{C}=\text{O}$	Exothermic	$\text{Bu}_3\text{Sn}\cdot\text{NPh}\cdot\text{CO}\cdot\text{O}\cdot\text{CHPh}\cdot\text{N}=\text{CPh}_2$ $\tau$ 3.39
Isothiocyanates:			
Me	$\text{PhN}=\text{C}=\text{S}$	44 hr (RT) <sup>b</sup>	$\text{Bu}_3\text{Sn}\cdot\text{S}\cdot\text{N}(\text{CPh})\cdot\text{O}\cdot\text{CH}(\text{CH}_3)\cdot\text{N}=\text{CPh}_2$ (50%) quartet $\tau$ 4.11, $J = 6$ Hz

<sup>a</sup> In  $\text{CCl}_4$  solution.  $\tau$  Values refer to acetal or aldehydic protons. All reactions went to completion unless otherwise stated. <sup>b</sup> RT = room temperature (ca. 20°). <sup>c</sup> By integration. <sup>d</sup>  $\tau$  7.30 (N-CH<sub>3</sub>). <sup>e</sup> Unresolved quartet  $\tau$  6.90 (N-CH<sub>2</sub>). <sup>f</sup>  $\tau$  7.22 (N-CH<sub>3</sub>). <sup>g</sup> Unresolved quartet  $\tau$  6.70 (N-CH<sub>2</sub>). <sup>h</sup> Unresolved quartet  $\tau$  6.90 (N-CH<sub>2</sub>).

which chloral appeared to form a double adduct similar to those observed with tributyltin methoxide and bis-tributyltin oxide and 2 mol of chloral,<sup>6</sup> the addition of 1 mol of chloral to the aldehyde adducts resulted in complete displacement of the aldehyde and the form-

ation 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

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.<sup>7,8</sup> 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  $\text{Bu}_3\text{Sn}\cdot\text{N}=\text{CPh}_2$  with isocyanates and isothiocyanates

R	$\nu(\text{C}=\text{N})$ ( $\text{cm}^{-1}$ )	N.m.r. ( $\tau$ )	Sn Analysis	
			Found	Reqd.
(II; Me)	1630vs, 1600vs	7.40 (N-CH <sub>3</sub> )	22.0	22.5
(II; Et)	1630vs, 1595vs	7.05 (N-CH <sub>2</sub> ) <sup>a</sup>	21.9	22.3
(II; Bu)	1630vs, 1595vs	7.12 (N-CH <sub>2</sub> ) <sup>b</sup>	20.5	21.3
(II; Ph)	1625vs, 1585vs		20.4	20.1
(III; Me)	1620vs, 1595vs	7.27 (N-CH <sub>3</sub> )	21.2	21.8
(III; Ph)	1620s, 1595s			

<sup>a</sup> Quartet  $J(\text{H}-\text{H}) = 7.2$  Hz. <sup>b</sup> Unresolved multiplet.

N-Tributylstannylidiphenylmethylenamine was prepared by the method of Chan and Rochow<sup>3</sup> as a yellow oil, b.p.  $180^\circ/0.3$  mm,  $\nu_{\text{C}=\text{N}}$ :  $1620\text{vs cm}^{-1}$ . Diphenylmethylenamine was prepared according to Pickard and Tolbert<sup>4</sup> as a colourless oil, b.p.  $103^\circ/0.35$  mm,  $\nu_{\text{C}=\text{N}}$ :  $1605\text{s}$ ,  $\nu_{\text{N}-\text{H}}$ :  $3250\text{w}$ ;  $\tau$  0.31 (N-H).

*Further Reactions of the Aldehyde Adducts.*—These reactions were carried out on an n.m.r. scale in ca. 10%  $\text{CCl}_4$  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

TABLE 4

Products of the reaction  $\text{Bu}_3\text{Sn}\cdot\text{N}=\text{CPh}_2 + \text{R}^1\text{R}^2\text{C}=\text{O} \longrightarrow \text{Bu}_3\text{Sn}\cdot\text{O}\cdot\text{CR}^1\text{R}^2\cdot\text{N}:\text{CPh}_2$

R <sup>1</sup>	R <sup>2</sup>	% Reaction	$\tau$ (CH)	$J(\text{H}-\text{H})$ (Hz)	$J(\text{Sn}-\text{H})$ (Hz)
$\text{CCl}_3^a$	H	100	4.81		38.4
$\text{CBr}_3^k$	H	100	5.26		36.0
Me <sup>b</sup>	H	100	4.88 <sup>c</sup>	5.6	
Et	H	100	5.19 <sup>e</sup>	6.0	
Pr <sup>l</sup>	H	100	5.48 <sup>f</sup>	6.6	
Pr <sup>n</sup>	H	85 <sup>d</sup>	5.07 <sup>e</sup>	8.4	
Ph <sup>g</sup>	H	100	4.09		51.0
$\text{CCl}_3$	$\text{CCl}_3^h$	100			
$\text{CCl}_2\text{F}$	$\text{CCl}_2\text{F}^i$	100			

<sup>a</sup>  $\nu_{\text{C}=\text{N}}$ :  $1620\text{s cm}^{-1}$  (Found: Sn, 18.7%. Required: Sn, 19.2%). <sup>b</sup>  $\nu_{\text{C}=\text{N}}$ :  $1650\text{s cm}^{-1}$  (Found: Sn, 22.5%. Required: Sn, 23.1%). <sup>c</sup> Centre of quartet. Also doublet  $\tau$  7.95. <sup>d</sup> By integration. <sup>e</sup> Centre of triplet. <sup>f</sup> Centre of doublet. <sup>g</sup>  $\nu_{\text{C}=\text{N}}$ :  $1640\text{s cm}^{-1}$  (Found: Sn, 20.1%. Required: Sn, 20.6%). <sup>h</sup>  $\nu_{\text{C}=\text{N}}$ :  $1640\text{s}$ ;  $\nu_{\text{C}-\text{O}}$ :  $1180\text{s}$ ;  $\nu_{\text{C}-\text{Cl}}$ :  $875\text{s}$ ,  $840\text{vs cm}^{-1}$  (Found: Sn, 15.5%. Required: Sn, 16.2%). <sup>i</sup>  $\nu_{\text{C}=\text{N}}$ :  $1650\text{s}$ ;  $\nu_{\text{C}-\text{O}}$ :  $1195\text{s}$ ,  $1155\text{vs}$ ;  $\nu_{\text{C}-\text{F}}$ :  $1040\text{s}$ ;  $\nu_{\text{C}-\text{Cl}}$ :  $880\text{s cm}^{-1}$  (Found: Sn, 17.0%. Required: Sn, 17.3%). <sup>k</sup>  $\nu_{\text{C}=\text{N}}$ :  $1630\text{s cm}^{-1}$  (Found: Sn, 15.6%. Required: Sn, 15.8%).

reaction was followed by observing the acetal-aldehyde proton in the n.m.r. Details are given in Table 2.

*Reactions of Diphenylmethylenamine with Acceptor Molecules.*—Typically the reagents were mixed in light petroleum

TABLE 5

Derivatives of diphenylmethylenamine

A=B	Product	M.p.	Colour	$\nu_{\text{N}-\text{H}}$ ( $\text{cm}^{-1}$ )	$\nu_{\text{C}=\text{N}}$ ( $\text{cm}^{-1}$ )	Analysis (%)					
						Calc.			Found		
						C	H	N	C	H	N
$\text{MeN}=\text{C}=\text{O}$	$\text{Ph}_2\text{C}=\text{N}\cdot\text{CO}\cdot\text{NMeH}^a$	179—180°	White	3250s	1645vs	75.6	5.9	11.8	76.0	6.2	11.7
$\text{EtN}=\text{C}=\text{O}$	$\text{Ph}_2\text{C}=\text{N}\cdot\text{CO}\cdot\text{NEtH}^a$	155—156	White	3240s	1645vs, 1620s	76.2	6.4	11.1	76.2	6.7	11.1
$\text{BuN}=\text{C}=\text{O}$	$\text{Ph}_2\text{C}=\text{N}\cdot\text{CO}\cdot\text{NBuH}^a$	93—95	White	3250s	1625vs, br	77.1	7.1	10.0	76.6	7.4	9.9
$\text{PhN}=\text{C}=\text{O}$	$\text{Ph}_2\text{C}=\text{N}\cdot\text{CO}\cdot\text{NPhH}^a$	152.5—154	White	3270s	1650vs	79.9	5.3	9.3	79.6	5.7	9.3
$\text{MeN}=\text{C}=\text{S}$	$\text{Ph}_2\text{C}=\text{N}\cdot\text{CS}\cdot\text{NMeH}^a$	162—164	Pale yellow	3160s	1615m	71.0	5.5	11.0	69.9	5.5	10.7
$\text{PhN}=\text{C}=\text{S}$	$\text{Ph}_2\text{C}=\text{N}\cdot\text{CS}\cdot\text{NPhH}^a$	136—137	Yellow	3190s	1645vs	76.0	5.1	8.9	76.0	5.5	8.6
$\text{CCl}_3\cdot\text{CHO}$	$\text{Ph}_2\text{C}=\text{N}\cdot\text{CH}(\text{CCl}_3)\cdot\text{OH}^b$	105—107	White	3160s	1615vs	54.9	3.7	4.3	54.6	3.5	3.8
$\text{CBr}_3\cdot\text{CHO}$	$\text{Ph}_2\text{C}=\text{N}\cdot\text{CH}(\text{CBr}_3)\cdot\text{OH}^c$	97—100	White	3200s	1615vs	39.0	2.6	3.0	40.8	2.9	3.0
$\alpha\text{-Np}\cdot\text{N}=\text{C}=\text{N}\cdot\alpha\text{-Np}$	$\text{Ph}_2\text{C}=\text{N}\cdot\text{C}(\cdot\text{N}\cdot\alpha\text{-Np})\cdot\text{N}\cdot\alpha\text{-Np}$ (decomp.)	210	Yellow	3210m	1640s	85.9	5.3	8.8	85.3	6.0	8.2

<sup>a</sup> Too insol. for n.m.r. <sup>b</sup> N.m.r. ( $\text{CDCl}_3$  soln.):  $\tau$  5.19 (C-H), 5.51 (broad) (-C-OH). <sup>c</sup> N.m.r. ( $\text{CDCl}_3$  soln.):  $\tau$  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  $33\cdot5^\circ$  using a Perkin-Elmer R10 instrument in ca. 10%  $\text{CCl}_4$  solution with  $\text{Me}_4\text{Si}$  as an internal standard. Tin was determined gravimetrically as stannic oxide.

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

<sup>7</sup> A. G. Davies and P. G. Harrison, *J. Chem. Soc. (C)*, 1967, 1313.

ether, when an exothermic reaction was accompanied by crystallisation of the product. Physical data is given in Table 5.

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<sup>8</sup> P. G. Harrison and J. J. Zuckerman, *Inorg. Chem.*, 1970, 9, 175.