Organic Synthesis with Carbon Monoxide: The Synthesis of Carbamoylstannanes and Aromatic Carbamoylation

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The lithium salts of secondary amines were carbonylated and the carbamoyl-lithium species (**1**) produced quenched with ketones, alkyl halides and trialkyltin chlorides. The latter gave tributyl-, triphenyl- and trimethyl-carbamoylstannanes (**2**) in good yield. These were found to undergo palladium-catalysed cross coupling with aryl, alkenyl, and hetaryl halides (I, Br) to give the amides (**4**), (**5**), and (**6**) respectively, in fair to excellent yield, the trimethyl series being the reagents of choice.

Carbon monoxide is used extensively on both the laboratory and industrial scale in the transition metal-catalysed synthesis of a wide range of organic intermediates,[1] and is therefore of considerable economic importance. In contrast, its use in non-transition metal mediated organic synthesis is very limited and reports of its reaction with organic reagents are few in number.[2] The most studied reactions to date are the carbonylations of lithium carbanions[3] and nitrogen anions.[4] These reactions are rapid at ambient pressures but the products, acyl-lithiums and carbamoyl-lithiums respectively, are unstable, highly reactive, and difficult to use with any efficiency and for this reason have made little impact in synthetic methodology even though they are highly desirable synthetic intermediates. Indeed the array of acyl anion equivalents now available[2] is a consequence of the intransigence of these species.

Nevertheless, carbon monoxide is potentially an excellent vehicle for the 'no carrier added' synthesis[5] of ^{11}C-labelled molecules for biological and clinical studies because the low ambient concentration of the species minimises inadvertent isotopic dilution. We have therefore undertaken a study of the carbonylation of the lithiated secondary amines and the reactions of the carbamoyl-lithium products and now report the results of the initial experiments. An important constraint of these studies to the application to ^{11}C labelled compounds is that for technical reasons, carbon monoxide must be used at atmospheric pressure.

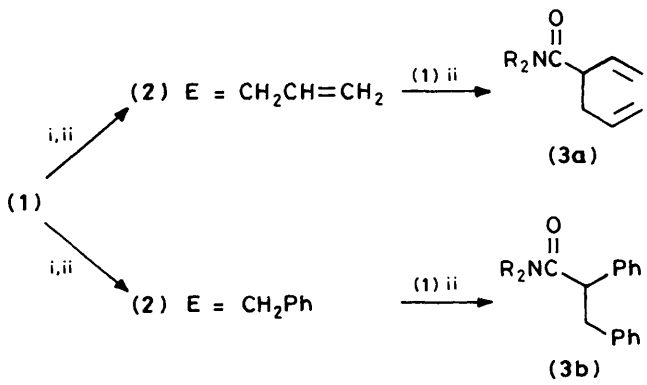
The lithiated secondary amines (**1**) rapidly absorbed carbon monoxide at atmospheric pressure at −78 °C in THF or THF–DME (1:1) solution to give stable orange-yellow solutions of the carbamoyl-lithiums. Quenching these with carbon electrophiles (Scheme 1) was carried out as previously reported (see Experimental section).

$$R_2NH \xrightarrow{i} \underset{(1)}{R_2N\text{–}Li} \xrightarrow{ii,\ iii} \underset{(2)}{R_2N\text{–}\overset{\overset{O}{\|}}{C}\text{–}E}$$

Scheme 1. *Reagents and conditions:* i, BuLi–DME–THF, −20 °C; ii, CO, −78 °C; iii, E^+

As expected, the reactions with carbonyl compounds worked well because the anionic products (**2**; E = $(Alkyl)_2CO$) were intrinsically protected against further attack, but alkylation was uncontrollable. Thus except for epoxides, with which the anions did not react, the alkylating agents gave neutral products (**2**; E = alkyl) which were too susceptible to attack by the highly reactive carbamoyl-lithium (**1**) even under conditions of slow inverse addition.

In the cases of allylation and benzylation the lability of the protons α- to the carbamoyl groups in (**2**; E = allyl or benzyl) caused secondary alkylation to occur (Scheme 2) to give bis-alkylation products (**3**) (91 and 89% respectively). We therefore



Scheme 2. *Reagents and conditions:* i, CO–DME–THF, −78 °C; ii, E = CH_2=$CHCH_2Br$ (a)

sought to control the reactivity of the system by transmetallation to a new carbamoyl metal which could be purified and further reacted.

Acylsilanes are well established synthetic intermediates[6] and initially we attempted to generate the corresponding carbamoyl silanes (**2**; E = SiR_3) by the above route but despite many attempts, even with highly hindered silyl chlorides (*e.g.*, Pr^i_3SiCl) no carbamoylsilane could be detected. The usual technique of having the silyl chloride quench present throughout the carbonylation procedure[2] could not be used as the lithium amides were rapidly silylated and the silylamine products did not carbonylate.

We turned therefore to the stannylated species (**2**; E = SnR_3). In one previous report,[7] Schroder had shown that t-butyl-carbamoyl-lithium reacts with Me_3SnCl to give the carbamoyl-stannane (**2**; R_2 = Bu^t, H; E = $SnMe_3$; 55%).

In our hands, reaction of a secondary amine with butyl-lithium followed by carbonylation at −78 °C and at atmospheric pressure and quenching with a triorganotin chloride gave the carbamoyl stannanes (**2**; E = SnR'_3) in 40—87% yield (Table 1). The compounds (**2**; E = SnR'_3) are oils or waxy solids, the latter showing good long term stability under normal conditions.

Stille had previously reported that acid chlorides could be successfully coupled with organotin reagents in excellent yield to give unsymmetrical ketones.[8,9] During the course of our studies, Stille also reported that palladium catalysed cross-coupling of allyl halides with aryl and vinyl tin reagents in the presence of carbon monoxide (1—3 atm) gives high yields of the unsymmetrical allyl vinyl or allyl aryl ketones.[9]

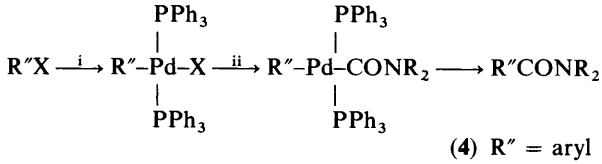
Consequently we considered that one application of the carbamoyl tin reagents should be the palladium-catalysed

Table 1. Synthesis of carbamoylstannanes (**2**; E = SnR'_3)

$R_2NH \longrightarrow R_2NCOSnR'_3$

Run No.	Amine (R_2NH) R_2	Carbonylation time (min)	R'_3SnCl R′	$R_2NCOSnR'_3$ Yield (%)
1	$(CH_2)_5$	30	Bu	87
2	$(CH_2)_4$	30	Bu	90
3	Pr^i_2	20	Bu	78
4	$(CH_2)_5$	30	Me	61
5	$(CH_2)_4$	30	Me	58
6	Pr^i_2	20	Me	40
7	$(CH_2)_5$	30	Ph	53
8	$(CH_2)_4$	30	Ph	57

coupling with aryl, vinyl and hetaryl halides under mild conditions (carbon monoxide at 1 atmosphere pressure, short reaction time) to produce amides or alkene amides and this was our first topic for study.



(**4**) R″ = aryl
(**5**) R″ = alkenyl
(**6**) R″ = hetaryl

Scheme 3. *Reagents and conditions:* i, 2 mol % $Pd(PPh_3)_4$–PhMe or THF; ii, (**2**; E = $SnBu_3$), heat.

Initially the tributyl tin reagents were employed using tetrakis(triphenylphosphine)palladium(0) as the catalyst in THF (Scheme 3). The results are shown in Table 2.

At room temperature little or no reaction occurred between the tin reagent [**2**; $R_2 = (CH_2)_5$, E = $SnBu_3$] and iodobenzene except that some homocoupling of the aryl halide was observed (Run 1). However, at higher temperatures (65 °C) reasonable yields of cross coupling were found after long periods of heating (Runs 2—4). Vinyl iodides and bromides also enter into the cross-coupling reaction to give good to moderate yields of the alkene amides (Runs 11—14, 18, 19). As observed in other cases[8] the *E*-geometry of the double bond in the vinyl iodide is maintained in the coupled product. Attempts at using the analogous chlorides were unsuccessful.

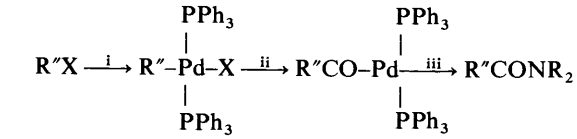
We considered that the slowness of reaction could be due to steric hindrance of the tributyltin groups in the ligand exchange (metathesis) stage (see Scheme 3, step 2).[10] To overcome this problem there were three options: i, higher temperature; ii, smaller cone angle of the ligands attached to palladium; iii, smaller R groups on the tin residue.

The first option was employed by using toluene as the reaction solvent (Runs 15—19). Gentle reflux at 111 °C did result in shorter reaction times (down to 2 h) and higher yields (up to 68%), but at these elevated temperatures the carbamoyltin reagent slowly decomposed. In an attempt to avoid this, the triphenyltin compounds were studied (Table 3). However, although yields were comparable or improved (*cf.* Table 2, Runs 8, 11, 18 with Table 3, Runs 3, 2, 5 respectively), the products were always accompanied by phenylated analogues. The migratory aptitude of the groups R′ on tin is in reverse order to the bond dissociation energies of the tin carbon bond but can be correlated with the Sn–C bond polarity[8] (Ph ≥ vinyl > Bu > Me).

The combination of options 1 and 3 using trimethyltin reagents for the cross coupling reactions achieved higher yields (49—83%) and shorter reaction times (40—80 min) (see Table 4) and these proved to be the reagents of choice. The reaction requires 3—5 mol% of palladium(0) catalyst and takes place under neutral conditions.

As with the tributyltin reagents, the trimethyltin series gave exclusive transfer of the amide group. In practical terms, the trimethyltin series is favoured by the fact that the byproduct (Me_3SnI) can be removed easily by a water wash whereas the tributyltin iodide can only be removed properly after exhaustive washing with KF solution.

Verlhac recently reported a synthesis of unsymmetrical and symmetrical α-diketones *via* the cross-coupling of acyltins with acyl halides using $PdCl_2(PPh_3)_2$ in toluene.[11] These reactions also showed some decarbonylation and butyl group transfer. Neither of these processes were observed in our experiments. The acylstannane coupling reactions, although involving a different reaction sequence, thus proves to be comparable to the palladium-catalysed carbonylative coupling procedure developed by Heck[12,13,14] (Scheme 4). In our hands, the overall



Scheme 4. *Reagents and conditions:* i, 2 mol % $Pd(PPh_3)_4$–THF, r.t.; ii, CO, 1 atm.; iii, R_2NH

yields of the two sequences are similar and their application to carbon-11 labelling has yet to be evaluated. When considering this application to micro-scale labelling, the reaction times would be decreased further by using a stoicheiometric amount of Pd(0). We are exploring this modification for the synthesis of radiopharmaceuticals.

In summary we have shown that carbamoyltin reagents will react with aryl, vinyl, and hetaryl halides under mild conditions to produce good yields of aroyl, alkenoyl and hetaroyl amides and that they hold promise in the growing search for new synthetic methods to prepare complex organic molecules labelled with carbon-11 from ^{11}C carbon monoxide.*

Experimental

Column chromatography was carried out on silica gel (Merck Kieselgel 60). Commercial reagents and solvents were purified by standard methods.[15] ^1H N.m.r. spectra were recorded at 60 MHz (Varian EM-360); 90 MHz (Perkin-Elmer R32); or 250 MHz (Brucker WH 250 Spectrometer). I.r. spectra were run on a Perkin-Elmer 298 spectrometer and mass spectra on a VG 7070B spectrometer. Tetrakis(triphenylphosphine)palladium(0) was prepared according to the method of Coulson[16] in 94% yield. The product was thoroughly washed with ethanol and diethyl ether and dried *in vacuo* to m.p. 113—115 °C (dec) [lit.,[16] m.p. 116 °C (dec)] and stored under nitrogen at −15 °C. The aryl and vinyl halides not commercially available were prepared according to literature procedures: (*E*)-ω-iodostyrene,[17] 1-iodocyclohexene,[18] (*E*)-1-iodoheptene,[17] 2-iodofuran[19] and 2-iodothiophene.[19] Ether refers to diethyl ether.

General Procedure for the Preparation of Carbamoylstannanes.—Under a nitrogen atmosphere a 100-ml round bottom flask containing a magnetic stirring bar was charged with freshly distilled tetrahydrofuran (THF) (20 ml), amine (0.01 mol), and butyl-lithium (0.01 mol) whilst the temperature was maintained at −10 °C. The resulting solution was stirred for 5 min then cooled to −78 °C, whereupon a slow stream of carbon

* Preliminary results using lithiated secondary amides show that ^{11}CO is rapidly absorbed to give the formamides (after protonation) in radioactive yields of 40—50%.

Table 2. Synthesis of carbamoyl-arenes (**4**), and -alkenes (**5**): tributyltin Series

$$Bu_3SnCONR_2 + R''X + Pd(PPh_3)_4 \longrightarrow R''CONR_2$$

Run No.	$Bu_3SnCONR_2$ R_2	R″X	Temp. (°C)	Time (h)	Solvent	R″CONR₂ Yield (%)
1	$(CH_2)_5$	PhI	18	18	THF	(10)[a]
2	$(CH_2)_5$	PhI	65	4	THF	43
3	$(CH_2)_5$	PhBr	65	5	THF	33
4	$(CH_2)_4$	PhI	65	6	THF	58
5	Pr^i_2	PhI	65	7	THF	42
6	$(CH_2)_5$	4-$MeOC_6H_4I$	18	20	THF	17
7	$(CH_2)_5$	4-$MeOC_6H_4I$	65	6	THF	49
8	$(CH_2)_5$	4-$MeOC_6H_4I$	65	12	THF	54
9	$(CH_2)_4$	4-$MeOC_6H_4I$	65	6	THF	53
10	Pr^i_2	4-$MeOC_6H_4I$	65	9	THF	50
11	$(CH_2)_5$	*E*-$C_5H_{11}CH{=}CHI$	65	6	THF	43
12	$(CH_2)_4$	*E*-$C_5H_{11}CH{=}CHI$	65	1	THF	40
13	$(CH_2)_5$	1-Iodocyclohexene	65	6	THF	42
14	$(CH_2)_4$	1-Iodocyclohexene	65	6	THF	48
15	$(CH_2)_5$	PhI	111	2	PhMe	62
16	$(CH_2)_4$	4-$MeOC_6H_4I$	111	2	PhMe	62
17	Pr^i_2	4-$MeOC_6H_4I$	111	3	PhMe	68
18	$(CH_2)_4$	*E*-$C_5H_{11}CH{=}CHI$	111	1.5	PhMe	67
19	$(CH_2)_5$	1-Iodocyclohexene	111	2	PhMe	63

[a] The product was biphenyl derived from homocoupling of the iodobenzene.

Table 3. Synthesis of carbamoyl-arenes (**4**) and -alkenes (**5**): triphenyltin series

$$Ph_3SnCONR_2 + R''X + Pd(PPh_3)_4 \longrightarrow R''CONR_2$$

Run No.	$Ph_3SnCONR_2$ R_2	R″X	Products[a] R″Ph (%)	Products[a] R″CONR₂ (%)
1	$(CH_2)_5$	*E*-PhCH=CHI	17	71
2	$(CH_2)_5$	*E*-$C_5H_{11}CH{=}CHI$	19	52
3	$(CH_2)_5$	4-$MeOC_6H_4I$	—	62
4	$(CH_2)_4$	*E*-n-$C_5H_{11}CH{=}CHI$	24	46
5	$(CH_2)_4$	4-$MeOC_6H_4I$	23	62
6	$(CH_2)_4$	1-Iodocyclohexene	—	53

[a] Reaction conditions: toluene solvent, reflux, 1—2.5 h.

Table 4. Synthesis of carbamoyl-arenes (**4**), -alkenes (**5**) and -heteroarenes (**6**): trimethyltin series

$$Me_3SnCOR_2 + R''X + Pd(PPh_3)_4 \longrightarrow R''CONR_2$$

Run No.	$Me_3SnCONR_2$ R_2	R″X	R″CONR₂ Yield (%)[a]
1	$(CH_2)_5$	PhI	72
2	$(CH_2)_5$	*E*-PhCH=CHBr	49
3	$(CH_2)_5$	*E*-PhCH=CHI	77
4	$(CH_2)_5$	1-Iodocyclohexene	58
5	$(CH_2)_5$	4-$MeOC_6H_4I$	72
6	$(CH_2)_5$	*E*-$C_5H_{11}CH{=}CHI$	64
7	$(CH_2)_4$	1-Iodocyclohexene	62
8	$(CH_2)_4$	4-$MeOC_6H_4I$	80
9	$(CH_2)_4$	*E*-$C_5H_{11}CH{=}CHI$	79
10	$(CH_2)_4$	*E*-PhCH=CHI	82
11	Pr^i_2	*E*-$C_5H_{11}CH{=}CHI$	71
12	Pr^i_2	4-$MeOC_6H_4I$	83
13	Pr^i_2	PHI	78
14	$(CH_2)_5$	2-Iodofuran	84
15	$(CH_2)_5$	2-Iodothiophene	24[b]
16	$(CH_2)_5$	2-Bromothiophene	57
17	$(CH_2)_5$	3-Bromopyridine	63

[a] Reaction conditions: toluene solvent, reflux 40—80 min. [b] Also formed was 2-piperidinocarbonyl-5-(2-thienyl)thiophene (32%).

monoxide (10 ml min^{-1}) was bubbled through the solution at atmospheric pressure for a period of 30 min. The resulting yellow solution was quenched[21] with trialkyltin chloride (0.01 mol) either as a neat liquid or as a solution in THF (10 ml), and stirred for a further 2 h. The reaction solution was allowed to warm to room temperature and added to diethyl ether (40 ml). The organic layer was washed with aqueous KF (3 × 20 ml) and distilled water (5 × 30 ml). The ether layer was dried ($MgSO_4$) and concentrated to an oil. Purification of the carbamoylstannane was achieved by flash column chromatography and by recrystallisation when appropriate. The following compounds were prepared (see Table 1) by this method:

Tributylpiperidinocarbonylstannane [**2**; $R_2 = (CH_2)_5$, E = $SnBu_3$]. Flash chromatography [eluant: 40—60 °C light petroleum–ether (1:1)] gave a colourless oil (87%); $\nu_{max.}$ (liq.) 2 940, 2 880, and 1 580 cm^{-1}; δ (90 MHz, $CDCl_3$) 0.7—1.9 (33 H, m), 3.3 (2 H, m), and 3.5 (2 H, m); *m/z* 401 (M^+, 2%), 345 (51%), 287 (100%), 230 (38%), 177 (54%), and 112 (26%). (Found: C, 53.6; H, 9.5; N, 3.5. $C_{18}H_{37}NOSn$ requires C, 53.75; H, 9.27; N, 3.48%).

Tributylpyrrolidinylcarbonylstannane [**2**; $R_2 = (CH_2)_4$, E = $SnBu_3$]. Flash chromatography (eluant: ether) gave the product as a colourless oil (77%); $\nu_{max.}$ (liq.) 2 900 and 1 570 cm^{-1}; δ (90 MHz, $CDCl_3$) 0.7—2.0 (31 H, m), and 3.5 (4 H, m); *m/z* 389 (M^+, 2%), 332 (11%), 304 (11%), 276 (27%), 219 (100%), 179 (52%), and 172 (54%). (Found: C, 52.75; H, 9.15; N, 3.65. $C_{17}H_{35}NOSn$ requires C, 52.60; H, 9.09; N, 3.61%).

Tributyl-N,N-di-isopropylcarbamoylstannane [**2**; R = Me_2-CH, E = $SnBu_3$]. Flash chromatography (eluant: ether) gave a colourless oil (71%); $\nu_{max.}$ (liq) 2 950, 2 890, and 1 580 cm^{-1}; δ (90 MHz, $CDCl_3$) 0.7—1.8 (39 H, m), 3.3 (1 H, hept), and 3.75 (1 H, hept); *m/z* 418 (M^+, 1%), 362 (20%), 306 (38%), 304 (30%), 291 (25%), 250 (100%), 248 (87%), 233 (38%), 177 (33%), 175 (27%), 128 (10%), and 100 (5%). (Found: C, 54.7; H, 10.05; N, 3.25. $C_{19}H_{41}NOSn$ requires C, 54.56; H, 9.88; N, 3.34%).

Trimethylpiperidinocarbonylstannane [**2**; $R_2 = (CH_2)_5$, E = $SnMe_3$]. Flash chromatography [eluant: 40—60 °C light petroleum–ether (1:1)] gave a waxy solid (51%); $\nu_{max.}$ (Nujol) 2 940, 2 860, and 1 575 cm^{-1}; δ (90 MHz, $CDCl_3$) 0.6 (9 H, s), 1.7

(6 H, m), and 3.6 (4 H, m); *m/z* 277 (M^+, 10%) 262 (18%), 247 (12%), 232 (15%), 165 (34%), 112 (73%), and 84 (100%). (Found: C, 39.25; H, 7.05; N, 5.0. $C_9H_{19}NOSn$ requires C, 39.17; H, 6.94; N, 5.01%).

Trimethylpyrrolidinylcarbonylstannane [**2**; $R_2 = (CH_2)_4$, E = $SnMe_3$]. Flash chromatography (eluant:ether) gave a waxy material (48%); $\nu_{max.}$(Nujol) 2 980, 1 670, and 1 570 cm^{-1}; δ (90 MHz, $CDCl_3$) 0.7 (9 H s), 2.3 (4 H, m), and 3.9 (4 H, m); *m/z* 263 (M^+, 16%), 247 (28%), 232 (17%), 217 (18%), 164 (100%), and 134 (30%). (Found: C, 36.95; H, 6.3; N, 5.6. $C_8H_{17}NOSn$ requires C, 36.68; H, 6.54; N, 5.35%).

Trimethyl-N,N-di-isopropylcarbamoylstannane (**2**; R = Me_2-CH, E = $SnMe_3$). Flash chromatography (eluant:ether) yielded a waxy material (47%); $\nu_{max.}$(Nujol) 2 980, 2 870, and 1 580 cm^{-1}; δ (90 MHz, $CDCl_3$) 0.3 (9 H, s), 1.2 (6 H, d, *J* 7 Hz), 1.40 (6 H, d, *J* 7 Hz), 3.35 (1 H, hept, *J* 7 Hz), and 3.85 (1 H, hept, *J* 7 Hz); *m/z* 293 (M^+, 7%), 278 (4%), 250 (14%), 165 (65%), 163 (49%), 134 (12%), 128 (51%), and 86 (100%). (Found: M^+, 291.9876. $C_{10}H_{23}NOSn$ requires *M*, 291.9878).

Triphenylpiperidinocarbonylstannane [**2**; $R_2 = (CH_2)_5$, E = $SnPh_3$]. Flash chromatography [eluant: 40—60 °C light petroleum–ether (1:1)] yielded a white waxy solid (53%); $\nu_{max.}$(Nujol) 2 940, 2 880, 1 590, and 1 575 cm^{-1}; δ (90 MHz, $CDCl_3$) 1.5 (6 H, m), 3.45 (2 H, m), 3.65 (2 H, m), 7.35 (9 H, m), and 7.6 (6 H, m); *m/z* 462 (M^+, 7%), 386 (12%), 384 (100%), 308 (33%), 306 (24%), 272 (10%), 195 (31%), and 112 (50%). (Found: C, 62.25; H, 5.35; 2.9; $C_{24}H_{25}NOSn$ requires: C, 62.37; H, 5.45; N, 3.03%).

Triphenylpyrrolidinylcarbonylstannane [**2**; $R_2 = (CH_2)_4$, E = $SnPh_3$]. Flash chromatography (eluant: 40—60 °C light petroleum–ether) yielded a white waxy solid (49%); $\nu_{max.}$(Nujol) 2 940, 2 860, and 1 560 cm^{-1}; δ (90 MHz, $CDCl_3$) 1.8 (2 H, m), 3.5 (4 H, m), 7.3 (9 H, m), and 7.6 (6 H, m); *m/z* 448 (M^+, 14%), 371 (96%), 294 (24%), and 197 (100%). (Found: C, 61.3; H, 5.0; N, 2.85. $C_{23}H_{23}NOSn$ requires: C, 61.64; H, 5.17; N, 3.12%).

General Procedure for Palladium-catalysed Cross Coupling Reactions of Amidostannanes and Aryl or Vinyl Halides.—A dry 100 ml round bottom flask containing a magnetic stirrer bar was purged with nitrogen and charged with either a vinyl halide (1.0 mmol) or an aryl halide (1 mmol), freshly distilled THF or toluene (20 ml) and tetrakis(triphenylphosphine)palladium(0) (5 mol%). In a separate flask a solution of the stannane (1.0 mmol) in dried THF or toluene (20 ml) was prepared under a nitrogen atmosphere. This was added slowly, under nitrogen at room temperature, to the former solution and set to gentle reflux and the reaction followed by t.l.c. until complete. The coupled products were isolated by two different methods depending on whether THF or toluene had been used as solvent.

Method (*a*) (THF solvent). The reaction was diluted with ether (40 ml), washed with 30% aqueous potassium fluoride (to remove most of the tin residues) and distilled water (5 × 20 ml), and dried ($MgSO_4$). The drying agent was filtered off and the organic layer concentrated under reduced pressure to leave the crude products generally as oils. These were further purified by flash chromatography on silica (Kieselgel 60) (eluant: 40—60 °C light petroleum–ether) to give the pure amides.

Method (*b*) (toluene solvent). The toluene was removed under reduced pressure and the crude product was taken up in ether (40 ml), filtered and then worked up as in Method (*a*).

The results are given in Tables 2, 3 and 4. The products (**4**), (**5**) or (**6**) were characterised spectroscopically and by microanalysis and were compared with the reported data for these compounds where known. Products not previously reported were: (E)-1-*Piperidino-oct-2-enone* [**5**; $R_2 = (CH_2)_5$, R″ = $C_5H_{11}CH$=CH]. Colourless liquid, $\nu_{max.}$(liq) 3 060, 2 940, 2 860, 1 660, and 1 615 cm^{-1}; δ (250 MHz, $CDCl_3$) 0.9 (3 H, t, *J* 6.7 Hz), 1.31 (2 H, m), 1.43 (2 H, m), 1.58 (8 H, m), 2.2 (2 H, m), 3.5 (4 H, m), 6.24 (1 H, dd, *J* 15 and 1.5 Hz), and 6.83 (1 H, dd, *J* 15 and 7 Hz); *m/z* 209 (M^+, 23%), 188 (35%), 166 (22%), 138 (100%), 112 (5%), and 105 (36%). (Found: C, 74.7; H, 10.85; N, 6.85. $C_{13}H_{23}NO$ requires C, 74.59; H, 11.07; N, 6.69%).

(E)-1-*Pyrrolidinyloct-2-enone* [**5**; $R_2 = (CH_2)_4$, R″ = C_5H_{11}-CH=CH]. Colourless oil, $\nu_{max.}$(liq) 2 960, 2 940, 2 800, 1 660, and 1 620 cm^{-1}; δ (90 MHz, $CDCl_3$) 0.9 (3 H, t, *J* 7 Hz), 1.2 (2 H, m), 1.4 (6 H, m), 1.9 (2 H, m), 2.25 (2 H, m), 3.6 (4 H, m), 6.1 (1 H, dd, *J* 15 and 1.5 Hz), and 6.9 (1 H, dd, *J* 15 and 7 Hz); *m/z* 195 (M^+, 57%), 180 (4%), 166 (15%), 152 (100%), 121 (37%), and 113 (11%). (Found: C, 73.75; H, 10.9; N, 7.04. $C_{12}H_{21}NO$ requires C, 73.79; H, 10.88; N, 7.17%).

(E)-N,N-*Di-isopropyloct-2-enamide* (**5**; R = Pr^i, R″ = C_5-$H_{11}CH$=CH). Colourless oil, $\nu_{max.}$(liq) 3 060, 3 003, 2 970, 2 930, 1 710, and 1 610 cm^{-1}; δ (90 MHz, $CDCl_3$) 0.9 (3-H, t, *J* 7 Hz), 1.2 (2 H, m), 1.4 (14 H, m), 1.9 (2 H, m), 2.27 (2 H, m), 3.5 (2 H, m), 4.2 (2 H, m), 6.36 (1 H, dd, *J* 15 and 1.6 Hz), and 6.84 (1 H, dd, *J* 15 and 6 Hz); *m/z* 225 (M^+, 42%), 210 (5%), 182 (100%), 166 (17%), 128 (4%), and 125 (16%). (Found: C, 74.6; H, 12.05; N, 6.25; $C_{14}H_{27}NO$ requires; C, 74.59; H, 12.08; N, 6.22%).

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