Journal of Organometallic Chemistry, *443* (1993) C1–C2 C1

JOM 23112PC

Preliminary Communication

Preparation of new *C*-alkyl-*C*-stannylimines

Bernard Jousseaume, Michel Pereyre, Nathalie Petit and Jean-Baptiste Verlhac

Laboratoire de Chimie Organique et Organométallique, URA 35, Université Bordeaux I, 351, cours de la Libération, 33405-Talence (France)

Alfredo Ricci

Dipartimento di Chimica Organica "A. Mangini", Università di Bologna, 40136 Bologna (Italy)

(Received July 29, 1992)

Abstract

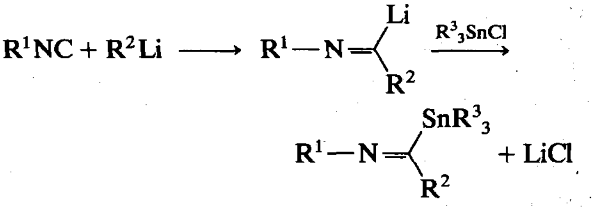
Treatment of (1,1,3,3-tetramethyl)butyl isocyanide with one equivalent of alkyllithium reagent followed by one equivalent of chlorotrialkylstannane afforded 1,1,3,3-tetramethyl-*N*-[1-(trialkylstannyl)alkylidene]butanamines in good yields. Similarly, the reaction of 2,6-dimethylphenyl isocyanide with one equivalent of diethylzinc then with one equivalent of chlorotrimethylstannane gave 2,6-dimethyl-*N*-[1-(trimethylstannyl)-propylidene]benzenamine.

Organotin compounds are valuable intermediates in organic synthesis, either as reagents for selective transformations or as intermediates for the creation of carbon–carbon bonds. In the latter case, the high selectivity of tin–carbon bond cleavage involved in direct reactions, transmetallations, or transition-metal catalyzed couplings is very useful [1]. The recently developed chemistry of acyltins [2] suggests interesting alternatives to the use of classical acyl anions [3]. Despite this potential, only few examples of preparations and reactions of *C*-stannylimines have been so far reported. These compounds were first synthesized by coupling imidoyl chlorides with stannyllithium reagents [4] and then reacted with organic halides in the presence of potassium fluoride to give ketimines [5]. The kinetics of their methanolysis to aldimines have been determined [6]. Trimethylsilyltributylstannane adds to isocyanides in the presence of tetrakis(triphenylphosphine)palladium as catalyst. In this way, *C*-stannyl-*C*-silylimines have been obtained and their reactivity, especially transmetallation with organolithium reagents has been studied [7]. However, neither method of preparation is able to give *C*-alkyl-*C*-stannylimines. The first method has only been described for *C*-aryl-*C*-stannylimines and the second one for *C*-silyl-*C*-stannylimines. Here we report the preparation of new *C*-alkyl-*C*-stannylimines.

The addition of lithium reagents to isocyanides produces lithium aldimines, which have been used as precursors for many organic compounds [8]. These intermediates were prepared and the coupling with trialkylchlorostannanes attempted. This reaction (see eqn. (1)) proceeded easily giving the expected *C*-alkyl-*C*-stannylimines in good yield.

The *C*-stannylimines are thermally stable enough to be purified by distillation under high vacuum. They are air-sensitive and have to be handled under dinitrogen to avoid decomposition. This preparation is also suitable for *C*-trimethylstannylimines and for *C*-tributylstannylimines.

In a typical procedure, to 6.96 g (50 mmol) of 1,1,3,3-tetramethylbutyl isocyanide in 30 ml of dry THF at −5°C were added 20 ml of a solution of n-butyllithium (50 mmol, 2.5 N). After 45 min at −5°C, the mixture was cooled to −75°C, and 16.3 g (50 mmol) of tributyltin chloride in 10 ml of THF were added slowly. After 1 h at −75°C, the solvents were evaporated and the residue extracted with pentane. After filtration and evaporation of pentane, the product was distilled



$$R^1NC + R^2Li \longrightarrow R^1{-}N{=}\!\Big\langle\begin{matrix}Li\\R^2\end{matrix} \xrightarrow{R^3_3SnCl} R^1{-}N{=}\!\Big\langle\begin{matrix}SnR^3_3\\R^2\end{matrix} + LiCl \qquad (1)$$

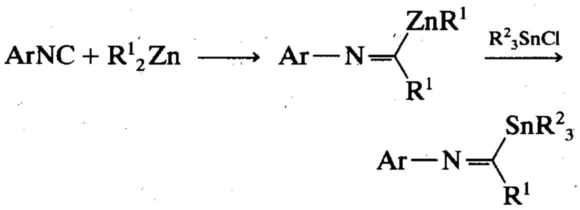
R^1	R^2	R^3	Yield (%)
$(CH_3)_3CCH_2C(CH_3)_2$	Bu	Me	80
$(CH_3)_3CCH_2C(CH_3)_2$	Bu	Bu	76
$(CH_3)_3CCH_2C(CH_3)_2$	2-MeC_3H_6	Me	79
$(CH_3)_3CCH_2C(CH_3)_2$	2-MeC_3H_6	Bu	73
$(CH_3)_3CCH_2C(CH_3)_2$	2,2-$Me_2C_2H_3$	Me	82
$(CH_3)_3CCH_2C(CH_3)_2$	2,2-$Me_2C_2H_3$	Bu	72
$(CH_3)_3C$	2,2-$Me_2C_2H_3$	Me	69

Correspondence to: Dr. B. Jousseaume.

0022-328X/93/$6.00

(Kugelrohr apparatus). B.p.$_{0.00015}$ = 140°C. Yield = 76%. ^{119}Sn NMR: δ (ppm, $C_6'D_6$) − 88.7. ^{13}C NMR: δ (ppm, $CDCl_3$) 177.6 (^1J(Sn–C) = 210 Hz), 60.4, 57.0, 47.6 (^2J(Sn–C) = 139 Hz) 32.1, 32.0, 29.9, 29.4, 28.9, 27.5, 22.7, 14.1, 13.6, 13.2. ^{1}H NMR: δ (ppm, $CDCl_3$) 2.31 (m, 2H), 1.6–1.0 (m, 18H) 1.0–0.8 (m, 33H).

Only tertiary alkyl '*N*-imine' can be obtained by this way, as aryl isocyanides tend to oligomerize in the presence of lithium reagents. To get *N*-aryl-*C*-stannylimine, another intermediate, a zinc aldimine [9], has been used. This organometallic reagent, prepared by addition of diethylzinc to 2,6-dimethylphenylisocyanide, reacted smoothly with trimethyltin chloride to give the desired *N*-aryl-*C*-stannylimine.



$$\mathrm{ArNC} + \mathrm{R^1_2Zn} \longrightarrow \mathrm{Ar{-}N{=}C(ZnR^1)(R^1)} \xrightarrow{\mathrm{R^2_3SnCl}} \mathrm{Ar{-}N{=}C(SnR^2_3)(R^1)} \quad (2)$$

(R^1 = Et, R^2 = Me, yield = 69%)

A mixture of 1.31 g (10 mmol) of 2,6-dimethylphenylisocyanide and 10 ml of a solution of diethylzinc in toluene (11 mmol, 1.1 N) was heated for 5 h. Then a solution of 4.95 g (25 mmol) of trimethyltin chloride in 2 ml of dry DMF was added and, after stirring at room temperature for 15 h, the mixture was treated as in the previous preparation. After a forerun of unreacted isocyanide, the *N*-aryl-*C*-stannylimine was isolated. B.p.$_{0.00015}$ = 135°C. Yield (based upon 60% of consumed isocyanide) = 69%. ^{119}Sn NMR: δ (ppm, C_6D_6) −81.3. ^{13}C NMR: δ (ppm, $CDCl_3$) 195.0, 151.9, 127.8, 126.0, 123.1, 38.9, 18.0, 10.8, −8.3. ^{1}H NMR δ (ppm, $CDCl_3$) 6.9–6.7 (m, 3H), 2.64 (q, 2H), 1.95 (s, 6H), 1.17 (t, 3H), −0.13 (s, 9H).

Although these synthetic methods are complementary in terms of the substituents attached to the sp^2 carbon atom, they are limited to aliphatic derivatives, as aryllithiums are not nucleophilic enough to add easily to isocyanides. Further work is in progress to achieve access to *C*-aryl-*C*-stannylimines and to test their reactivity towards electrophiles.

Acknowledgments

We are indebted to Schering–France for a generous gift of chemicals.

References

1 M. Pereyre, J.-P. Quintard and A. Rahm; *Tin in Organic Synthesis*, Butterworths, London, 1987.

2 G. J. D. Peddle, *J. Organomet. Chem.*, *14* (1968) 139; E. Lindner and U. Kunze, *J. Organomet. Chem.*, *21* (1970) 19; A. Chabeaud, *Thesis*, Bordeaux, 1972; M. Kosugi, H. Naka, H. Sano and T. Migita, *Bull. Chem. Soc. Jpn.*, *60* (1987) 3462; J.-B. Verlhac, E. Chanson, B. Jousseaume and J.-P. Quintard, *Tetrahedron Lett.*, *26* (1985) 6075; J.-B. Verlhac, M. Pereyre and H. Shin, *Organometallics*, *10* (1991) 3007; J.-B. Verlhac, H. Kwon and M. Pereyre, *J. Organomet. Chem.*, 437 (1992) C13; J. A. Marshall and W. Y. Gung, *Tetrahedron*, *45* (1989) 1043; J. A. Marshall and G. P. Luke, *J. Org. Chem.*, *56* (1991) 483; A. Capperucci, A. Degl'Innocenti, C. Faggi, G. Reginato and A. Ricci, *J. Org. Chem.*, *54* (1989) 2966.

3 J.-P. Collman, *Acc. Chem. Res.*, *8* (1975) 342; D. Seyferth and R. M. Weinstein, *J. Am. Chem. Soc.*, *104* (1982) 5534; S. Murai, I. Ryn, J. Iriguchi and N. Sonoda, *J. Am. Chem. Soc.*, *106* (1984) 2440; G. E. Niznik and H. M. Walborsky, *J. Org. Chem.*, *37* (1972) 187; D. Seebach and E. J. Corey, *J. Org. Chem.*, *40* (1975) 231; J. E. Baldwin, G. Hofle and O. W. Lever, *J. Chem. Soc., Chem. Commun.*, (1975) 519; V. Rautenstrauch and M. Joyeux, *Angew. Chem., Int. Ed. Engl.*, *18* (1979) 83; R. Burstinghaus and D. Seebach, *Chem. Ber.*, *110* (1977) 841; J. A. Soderquist and G. J.-H. Hsu, *Organometallics*, *1* (1980) 830; M. Murakami, H. Ito, W. Bakar, A. Baba and Y. Ito, *Chem. Lett.*, (1989) 1603; A. R. Katritzky, Z. Yang and J. N. Lam, *J. Org. Chem.*, 56 (1991) 6917; J. Hartmann, M. Stähle and M. Schlosser, *Synthesis*, (1974) 888; K. Oshima, K. Shimoji, H. Takahashi, M. Yamamoto and H. Nozaki, *J. Am. Chem. Soc.*, *95* (1973) 2694; S. Sengupta and V. Snieckus, *J. Org. Chem.*, *55* (1990) 5680.

4 J. Jappy and P. N. Preston, *Inorg. Nucl. Chem. Lett.*, *7* (1971) 181.

5 A. Degl'Innocenti, S. Pike, D. R. M. Walton, G. Seconi, A. Ricci and M. Fiorenza, *J. Chem. Soc., Chem. Commun.*, (1980) 1201.

6 G. Seconi, G. Pirazzini, A. Ricci, M. Fiorenza and C. Eaborn, *J. Chem. Soc., Perkin II*, (1981) 1043.

7 Y. Ito, T. Bando, T. Matsuura and M. Ishihawa, *J. Chem. Soc., Chem. Commun.*, (1986) 981; Y. Ito, T. Matsuura and M. Murakami, *J. Am. Chem. Soc.*, *109* (1987) 7888; Y. Ito and M. Murakami, *Synlett.*, *1* (1990) 245.

8 G. E. Niznik, W. H. Morrison III and H. M. Walborsky, *J. Org. Chem.*, *39* (1974) 600.

9 M. Murakami, M. Ito and Y. Ito, *J. Org. Chem.*, *53* (1988) 4158.