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O- AND *C*-STANNYLATION OF NITROALKANES

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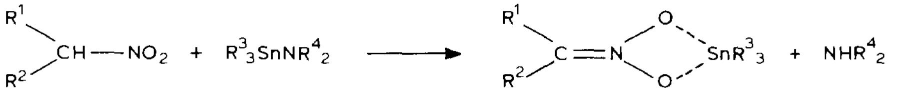
Summary

Stannylation of nitroalkanes by tributylstannyl amides and bis(tributylstannyl) or bis(triphenylstannyl) oxides has been found to give mainly tin nitronates. Some *C*-stannylated species have been also characterized.

Introduction

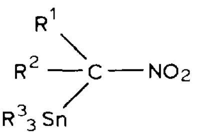
The preparation of trialkyltin nitronates **B** by reaction of aminostannanes **A** with nitroalkanes was described several years ago [1–3] eq. 1.



(1)

A B

We were interested in the use of *C*-stannylated products **C** for synthetic purposes, and this led us to investigate the preparation of compounds **B** and the eventual isolation of compounds **C**.



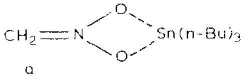
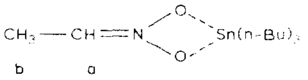
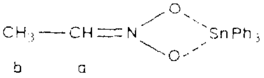
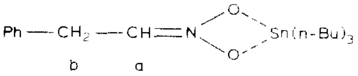
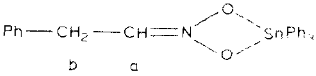
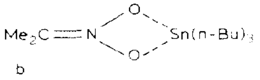
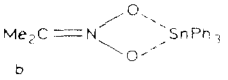
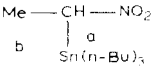
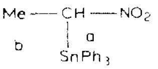
C

Results and discussion

As expected [2], reactions between nitroalkanes CH_3NO_2, $CH_3CH_2NO_2$, $PhCH_2CH_2NO_2$, Me_2CHNO_2 and tributylstannyl dimethylamide (1 mol per mol)

TABLE 1

NMR DATA FOR TRIALKYL- AND TRIARYLTIN NITRONATES AND FOR α-STANNYLATED NITROALKANES

		^1H NMR [a]			^{119}Sn NMR [b]
		δ(a) (ppm)	δ(b) (ppm)	J(HCCH) (Hz)	δ(ppm)
1		5.77 (s) (C_6D_6)		–	35.6 (C_6D_6)
2		5.95 (q)	1.55 (d) (C_6D_6)	6.0	31.5 (C_6D_6)
3		5.76 (q) 6.18 (q)	1.40 (d) (C_6D_6) 1.83 (d) ($CDCl_3$)	6.0	−183.4 ($CDCl_3$)
4		6.15 (t)	3.45 (d) (C_6D_6)	6.5	–
5		5.90 (t) 6.36 (t)	3.25 (d) (C_6D_6) 3.64 (d) ($CDCl_3$)	6.5	–
6			1.98 (s) (C_6D_6)	–	30 ($CDCl_3$)
7			1.48 (s) (C_6D_6) 1.95 (s) ($CDCl_3$)	–	199.9 ($CDCl_3$)
8	 $\underset{b}{Me}-\underset{\underset{Sn(n\text{-}Bu)_3}{\vert}}{\overset{a}{C}H}-NO_2$	3.40 (q) (C_6D_6)		7.5	–
9	 $\underset{b}{Me}-\underset{\underset{SnPh_3}{\vert}}{\overset{a}{C}H}-NO_2$	3.33(q)	1.17(d) ($CDCl_3$)	7.5	

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[a] Reference: TMS. [b] Reference: Me_4Sn.

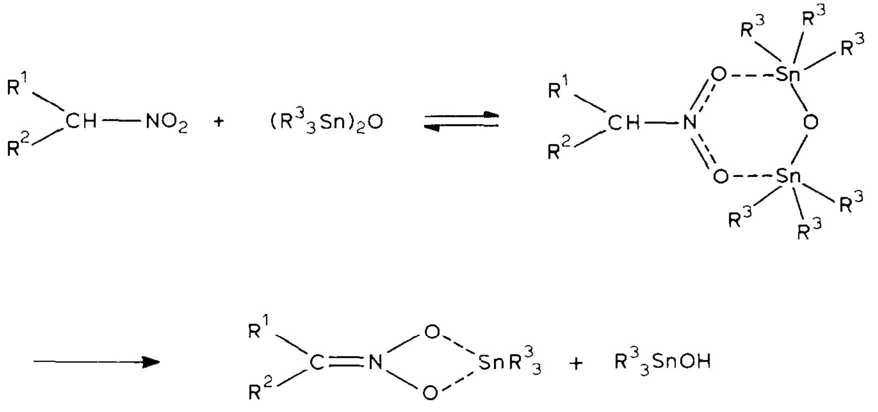
TABLE 2

SHIELDING OF ^1H NMR SIGNALS WHEN STARTING MATERIALS WERE MIXED

Starting materials	$\Delta\delta$ (ppm)		Solvent
	a	b	
$CH_3NO_2 + (Ph_3Sn)_2O$ a	0.80		Toluene-d_8
$CH_3CH_2NO_2 + (Ph_3Sn)_2O$ b a	0.48	0.32	C_6D_6
$CH_3CH_2NO_2 + (n\text{-}Bu_3Sn)_2O$ b a	0.38		C_6D_6
$CH_3CH_2NO_2 + (Ph_3Sn)_2O$ b a	0.15	0.04	$CDCl_3$

in benzene at room temperature gave the corresponding nitronates **1**, **2**, **4** and **6** quickly (< 10 min) (Table 1). The least stable of these compounds, **1**, decomposed rapidly at room temperature to give several unidentified products. The most stable compound, **7**, was purified by distillation.

We also tried to obtain tin nitronates from bis(tributylstannyl) and bis(triphenylstannyl) oxides, which are commercially available. When an excess of oxide was mixed with nitroalkanes (1.2 mol of oxide per mol) at room temperature in benzene a shielding of the ^1H NMR signals of the starting nitroalkanes was immediately observed (Table 2). This shielding can be accounted for in terms of the formation of a pentacoordinated tin complex (eq. 2), such complexes are well known [4].



(2)

(3)

$$2R^3_3SnOH \rightleftharpoons (R^3_3Sn)_2O + H_2O \qquad (4)$$

Refluxing of these solutions with continuous azeotropic removal of the water generated, led to the slow formation of tin nitronates. The reactions were monitored by ^1H NMR spectroscopy and typically required 20 to 70 h for completion (Table 3). The amount of water recovered from the reaction mixture corresponded to that expected for dehydration of Ph_3SnOH (which is rather easy [5,6]) or of $n\text{-}Bu_3SnOH$ (which is even easier [6] (eq. 4). Several nitronates were obtained in this way (Table 3), but the tin nitronate derived from nitromethane was too unstable to be isolated.

TABLE 3

FORMATION OF TRIALKYL- AND TRIARYLTIN NITRONATES IN THE REACTION BETWEEN R^1NO_2 AND $(R^2_3Sn)_2O$ IN REFLUXING BENZENE

R^1	R^2	Time (h)
Et	n-Bu	20
Et	Ph	20
$PhCH_2CH_2$	n-Bu	50
$PhCH_2CH_2$	Ph	50
i-Pr	Ph	70

The ^{119}Sn NMR spectra of several nitronates were recorded (Table 1). When n-butyl groups were replaced by phenyl groups a strong shielding effect was observed, as is the case for enolates [7].

In most cases the nitronates were the main products of a procedure in which $n-Bu_3SnNMe_2$ was used instead of $(n-Bu_3Sn)_2O$ or $(Ph_3Sn)_2O$. However the formation of *C*-stannylated products was sometimes also observed. Thus, the nitronate **2** was obtained quickly from the reaction between $n-Bu_3SnNMe_2$ and $C_2H_5NO_2$, but after 4 h in solution at room temperature the *C*-stannylated species **8** was dominant, and after 48 h a stable **8**:**2** ratio of 85 : 15 was finally obtained. The *C*-stannylated product could not be isolated but was characterized by its ^1H NMR spectrum (Table 1) and by mass spectrometry. Analysis by GC/MS (electron impact) of the mixture showed a strongly dominant product, presumably **8**, whose mass spectrum was characterized by the presence of two main fragments corresponding to the loss of n-butyl groups (m/e 308, M − n-Bu with ^{120}Sn (100); 194, M − 3n-Bu (33)). The mass spectrum by fast atom bombardment ionization (xenon) with *m*-nitrobenzyl alcohol as matrix allowed observation of the quasi molecular ion MH^+ (m/e 366 with ^{120}Sn) as well as the $(M - NO_2 + H)^+$ ion (m/e 320). Moreover the experimental isotopic distribution of the MH^+ ion was found to be in excellent agreement with that calculated. In contrast, mass spectrometry by chemical ionization (NH_3) of the nitronate **2** also gave a quasi molecular ion MH^+ (m/e 366 (7.5)) but no fragment corresponding to the loss of the nitro group. GC/MS analysis of **2** was not possible owing to its thermal unstability. The nitronate **6** also gave the MH^+ ion (m/e 380 (18)) when analysed by chemical ionization (NH_3) mass spectrometry.

The reaction between $CH_3CH_2NO_2$ and $(Ph_3Sn)_2O$ gave mainly the nitronate **3** and a very low proportion of the *C*-stannylated product **9**. However, the nitronate **3** could be partially removed by fractional recrystallization (pentane-ether) and a mixture containing about 30% of the *C*-stannylated isomer was thus obtained; **9** was identified from its ^1H NMR data.

Thus two *C*-stannylated products **8** and **9** were characterized; in other cases such *C*-stannylated species were not detected.

Experimental

^1H NMR spectra were recorded with a Perkin–Elmer R32 (90 MHz) instrument. ^{119}Sn NMR spectra were recorded with a Bruker AM 250 instrument. Electron impact and chemical ionization mass spectra were obtained with a Girdel–Nermag R10-10 mass spectrometer and fast atom bombardment, (xenon) mass spectra were obtained with a double focussing VG 70-250 instrument.

Tributylstannyl dimethylamide was prepared by reaction between tributylchlorostannane and lithium dimethylamide (obtained from n-butyllithium and dimethylamine) [8].

Reactions of nitroalkanes and tributylstannyl dimethylamide

The nitroalkane (1 mmol) was added to a solution of tributylstannyl dimethylamide (334 mg, 1 mmol) in benzene-d_6 (1.5 ml) at room temperature under nitrogen. ^{1}H NMR spectroscopy revealed the formation of nitronates $R^1(R^2)$-$C{=}NO_2Sn(n\text{-}Bu)_3$ **1** (R^1 = H, R^2 = H), **2** (R^1 = H, R^2 = Me), **4** (R^1 = H, R^2 = $PhCH_2$) or **6** (R^1 = R^2 = Me) within a few minutes (Table 1). Compound **1** decomposed rapidly to give unidentified products, **4** was stable for several hours in solution, and **7** was purified by distillation (bulb to bulb, 0.7 mmHg, 150–160°C; lit. [3], 0.1 mmHg, 90–93°C). Compound **2** was not stable under these conditions, and the formation of the corresponding *C*-stannylated product **8** was detected by ^{1}H NMR spectroscopy; a stable **8** : **2** ratio of 85 : 15 was obtained after 48 h. However, **8** could not be isolated pure.

Reactions of nitroalkanes and bis(tributylstannyl) or bis(triphenylstannyl) oxides

In a typical procedure a mixture of nitroethane (150 mg, 2 mmol) and bis(triphenylstannyl) oxide (1.718 g, 2.4 mmol) in benzene (20 ml) was refluxed for 20 h in a Dean and Stark apparatus and water was continuously removed. The mixture was subsequently cooled and the benzene was evaporated off under vacuum. Benzene-d_6 or $CDCl_3$ (3 ml) was added to the residue and the ^{1}H NMR spectra of the solutions recorded; these showed the presence of the corresponding nitronate **3** as the main product and of a low proportion of the *C*-stannylated product **9**. The solvent was again evaporated, and fractional recrystallization (pentane-ether) partially removed the less soluble species (**3** and the starting oxide), which was filtered off. Evaporation of the solution left a residue which was dissolved in $CDCl_3$ (0.5 ml). The ^{1}H NMR spectrum of the solution showed that the mixture contained about 30% of the *C*-stannylated isomer.

Reactions of bis(triphenylstannyl)oxide with $PhCH_2CH_2NO_2$ and $i\text{-}PrNO_2$ and of bis(tributylstannyl)oxide with $EtNO_2$ and $PhCH_2CH_2NO_2$ were carried out by the same procedure, and required 50, 70, 20 and 50 h, respectively, for completion. Under these conditions only the *O*-stannylated species were characterized.

Acknowledgements

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