Journal of Organometallic Chemistry, 322 (1987) 49–56
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

THE PHOTOLYSIS OF BENZYLTIN COMPOUNDS INVESTIGATED BY ^{1}H CIDNP

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(Received September 30th, 1986)

Summary

The photochemical decomposition of $(PhCH_2)_3SnMe$ and $(PhCH_2)_3SnCl$ has been investigated by steady-state and time-resolved chemically induced nuclear polarization (CIDNP) ^{1}H spectroscopy of the methylene protons using 308 nm pulses of an excimer laser and a 250 MHz NMR spectrometer. From the sign of the polarization it is concluded that $(PhCH_2)_3SnMe$ reacts like other comparable tin compounds via triplet radical pairs; the CIDNP effects are not influenced by the solvent. In contrast the CIDNP effects of $(PhCH_2)_3SnCl$ are solvent dependent: in C_6D_6 the polarization is accounted for by a singlet radical pair precursor, while in $CDCl_3$ both singlet and triplet radical pairs are formed. The formation of singlet radical pairs during the reaction of $(PhCH_2)_3SnCl$ in C_6D_6 may be interpreted as evidence for stannylene formation.

Introduction

Chemically induced nuclear polarization detected by NMR-techniques, i.e. CIDNP spectroscopy, can give valuable information about reaction mechanism [1]. In particular it has been used to establish the radical mechanism of photolysis of many organic tin compounds [2–6]. On the other hand, the presence of stannylenes or stannylenoids, which have been shown to be intermediates [7–9] has as yet not been confirmed by CIDNP studies although this has been possible in the case of germylenes [10]. This paper describes a study of the mechanism of the photochemical decomposition of $(PhCH_2)_3SnMe$ and $(PhCH_2)_3SnCl$ in various solvents by steady-state and time-resolved ^{1}H CIDNP spectroscopy.

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0022-328X/87/$03.50

Experimental

$(PhCh_2)_3SnCl$ was prepared by a published method [11] and $(PhCh_2)_3SnMe$ by a Grignard reaction from $(PhCh_2)_3SnCl$ and methyl iodide. Solvents for NMR studies were dried over molecular sieves before use.

Concentrations of the samples investigated varied between 0.01 and 0.1 mol/l, corresponding to an effective optical density in 5 mm tubes of 0.15 to 0.6 at 308 nm. All samples were deaerated by purging with nitrogen. The samples were irradiated in the modified probe head of a 250 MHz superconducting FT NMR spectrometer (WM 250, Bruker) with the light from an excimer laser (308 nm, 20–70 mJ per pulse of 10 ns duration, EMG 500, Lambda Physik).

Each CIDNP spectrum was recorded by one of three techniques, viz.: (i) as a pseudo-steady-state spectrum with a laser repetition rate of 5–10 Hz, (ii) as a pure polarization spectrum by presaturation of the background signals, and (iii) as a time resolved pure polarization spectrum with a delay between the laser and NMR observation pulses of 0.5–1000 μs. Full details are given in earlier publications [12,13].

Since benzylstannanes absorb only weakly at 308 nm rather high concentrations of the starting material had to be used. Thus it was not always possible to attain complete saturation of the equilibrium magnetization, and no reliable determination of the sign of the polarization of the starting material was possible. In all cases the full ^1H NMR spectra were recorded but in the context of this work only the polarizations of the methylene resonances are considered.

To minimize photoreactions of products which absorb at 308 nm the total conversion was kept below 5%. In time-resolved experiments samples were removed from the magnet and shaken after 100–150 laser pulses.

Results and discussion

A. Photoreaction of $(PhCH_2)_3SnMe$

Figure 1 shows part of the ^1H NMR spectrum in the methylene region before, during, and after the irradiation of $(PhCH_2)_3SnMe$ in C_6D_6 (A) and $CDCl_3$ (B). The main products of the reaction in C_6D_6 are bibenzyl, which shows emission, and coloured polystannanes. These were not detected in the NMR spectra, but were identified by the NMR spectra of the species produced from them by treatment with iodine. During the reaction in $CDCl_3$ bibenzyl emission also appears, while the formation of the polystannanes is suppressed and $(PhCH_2)_2MeSnCl$ and $PhCH_2CDCl_2$ are formed instead. The former was not polarized while the latter exhibited enhanced absorption.

Figure 2A shows the time-resolved CIDNP spectra in the methylene region for the photolysis of $(PhCH_2)_3SnMe$ in $CDCl_3$. Simultaneous growth of the bibenzyl and $PhCH_2CDCl_2$ signals is observed within 50 μs.

The polarization of the starting material could not be determined by techniques (ii) or (iii) but its sign was assumed on the basis of analogy with the results obtained in the photolysis of tetraallylstannane. During the photolysis of $(CH_2{=}CHCH_2)_4Sn$ in C_6D_6 Benn [14] found enhanced absorption for the methylene protons of the starting material and emission for the product $(CH_2{=}CHCH_2)_2$ and we confirmed these results. Additionally we photolysed $(CH_2{=}CHCH_2)_4Sn$ in $CDCl_3$. In this

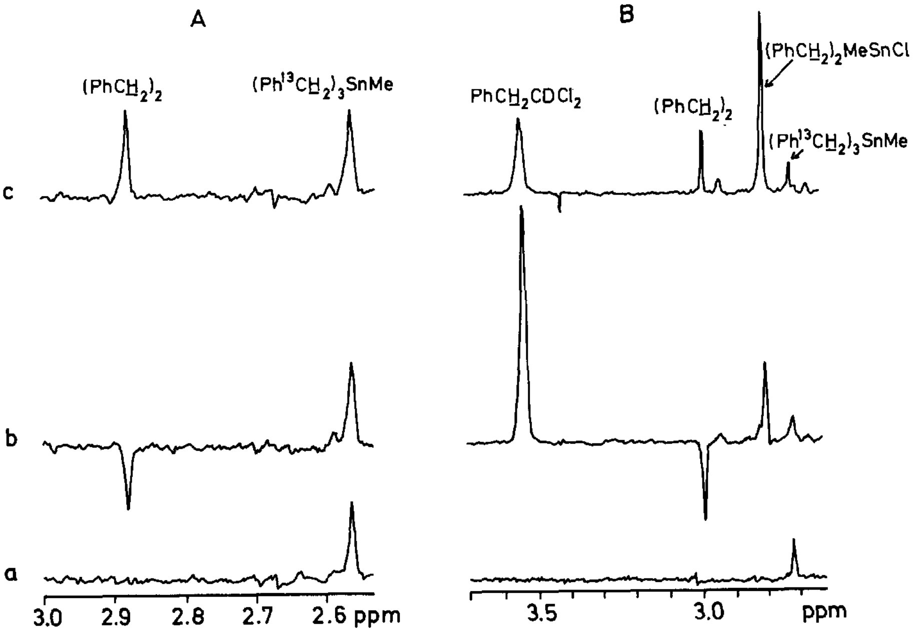

Fig. 1. Section of the ^{1}H NMR spectra in the region of methylene resonances of products before (a), during (b), and after irradiation (c) of (PhCH$_2$)SnMe in C$_6$D$_6$ (A) and CDCl$_3$ (B).

case the starting material and (CH$_2$=CHCH$_2$)$_2$ exhibit the same sign of methylene polarization as in C$_6$D$_6$, while the methylene resonances of the product CH$_2$=CHCH$_2$CDCl$_2$ exhibit enhanced absorption. Thus the mechanism of photoly-

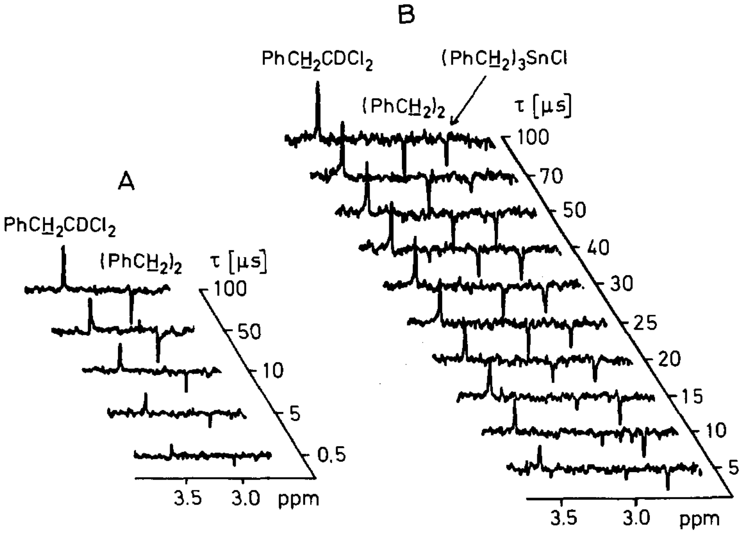

Fig. 2. Part of the time-resolved ^{1}H CIDNP spectra produced by laser photolysis of (PhCH$_2$)$_3$SnMe (A) and (PhCH$_2$)$_3$SnCl (B) in CDCl$_3$.

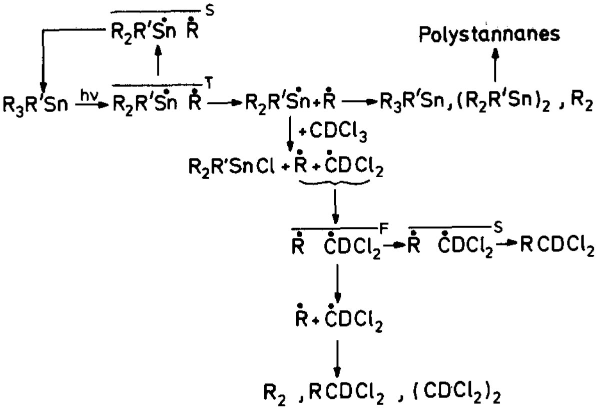

Fig. 3. Reaction scheme for the photochemical decomposition of $R_3R'Sn$ ($R = CH_2Ph$, $R' = Me$).

sis of $(PhCH_2)_3SnMe$ is analogous to that of $(CH_2{=}CHCH_2)_4Sn$, and we conclude that the methylene resonance in $(PhCH_2)_3SnMe$ will exhibit enhanced absorption.

The CIDNP effects can be interpreted in terms of the spin dependent reaction rates in the radical pair, as depicted in the reaction scheme given in Fig. 3. To enable application of Kaptein's first rule for the net effect, the data on magnetic properties of the intermediate radicals are listed in Table 1. The magnetic properties of the $(PhCH_2)_2MeSn$ radical are unknown, and are taken to be approximately equal to those of the Me_3Sn radical, which are known.

The CIDNP effects observed will be discussed with the aid of Table 2. The

TABLE 1

MAGNETIC PROPERTIES OF RADICALS USED IN TABLES 2 AND 3

Radical	g-factor	HF-constant a (mT)
$Ph\dot{C}H_2$	2.00263 [14]	$a(^1H) = -1.65$ [2]
$\dot{C}HCl_2$	2.0080 [15]	
$(CH_3)_3\dot{S}n$	2.0170 [14]	

TABLE 2

APPLICATION OF KAPTEIN'S FIRST RULE TO THE POLARIZATION OF METHYLENE PROTONS IN THE PHOTOLYSIS OF $(PhCH_2)_3SnMe$

Precursor	$\Gamma_{ne} = \mu \cdot \epsilon \cdot \Delta g \cdot a$		Solvent
	Cage product	Escape product	
$\overline{(PhCH_2)_2MeS\dot{n}\ \dot{C}H_2Ph}^{T}$	$(PhCH_2)_2MeSnCH_2Ph$ [A = + = + + − −]	$(PhCH_2)_2$ E = − = + − − −	C_6D_6
$\overline{(PhCH_2)_2MeS\dot{n}\ \dot{C}H_2Ph}^{T}$	$(PhCH_2)_2MeSnCH_2Ph$ [A = + = + + − −]	$(PhCH_2)_2$ E = − = + − − −	$CDCl_3$
$\overline{Ph\dot{C}H_2\ \dot{C}DCl_2}^{F}$	$PhCH_2CDCl_2$ A = + = + + − −	$(PhCH_2)_2$ E = − = + − − −	$CDCl_3$

polarization of the starting material is built up in the triplet radical pair $\overline{Ph\dot{C}H_2\ \dot{S}nMe(PhCH_2)_2}^{T}$. Since the escape product, bibenzyl, shows emission and the cage products have the opposite polarization, the starting material $(PhCH_2)_3SnMe$ probably appears in enhanced absorption. Additionally, photolysis of $(PhCH)_2)_3SnMe$ in $CDCl_3$ yields bibenzyl as an escape product of the F-pair $\overline{Ph\dot{C}H_2\ \dot{C}DCl_2}^{F}$, which according to Table 2 also gives an emission signal. The corresponding cage product, $PhCH_2CDCl_2$, shows enhanced absorption as expected. Thus the mechanism of photolysis of $(PhCH_2)_3SnMe$ is analogous to that of di- and tri-stannanes as described by Lehnig [4,5]. It is obvious from Fig. 2 that the reactions of the free radicals under these experimental conditions take place in a time of the order of 10 μs. Precise determination of rate parameters was not attempted.

B. Photoreaction of $(PhCH_2)_3SnCl$

The CIDNP effects caused by the photoreaction of $(PhCH_2)_3SnCl$ are qualitatively different from those of $(PhCH_2)_3SnMe$. Figure 4 shows the methylene part of the NMR spectra (a–c) before, during, and after irradiation in C_6D_6 and $CDCl_3$, and also (d), the pure polarization obtained with the presaturation technique (ii). In both solvents the methylene resonances of the starting material show emission while that of bibenzyl varies with the solvent: it exhibits enhanced absorption in C_6D_6 and emission in $CDCl_3$. The methylene resonances of $PhCH_2CDCl_3$ formed in

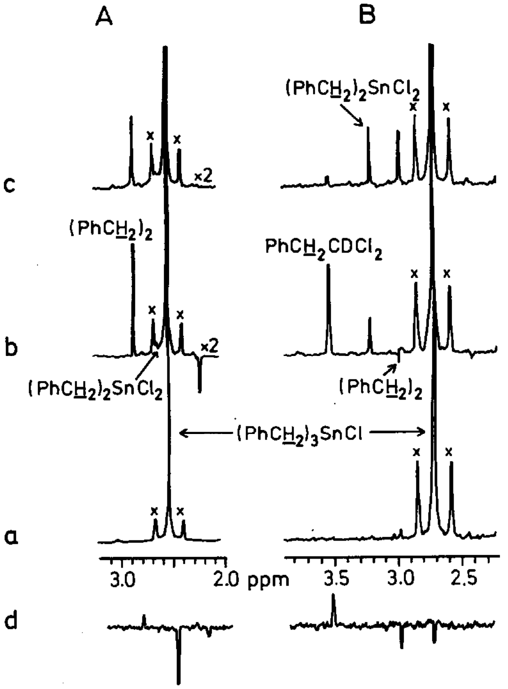

Fig. 4. Section of the ^1H NMR spectra before (a), during (b), after (c), and the pure polarization during irradiation (d) of $(PhCH_2)_3SnCl$ in C_6D_6 (A) and $CDCl_3$ (B). × denotes ^{117}Sn and ^{119}Sn satellites.

TABLE 3

POLARIZATION OF THE METHYLENE PROTONS OF CAGE AND ESCAPE PRODUCTS IN THE PHOTOLYSIS OF $(\mathrm{PhCH_2})_3\mathrm{SnCl}$

Precursor	$\Gamma_{\mathrm{ne}} = \mu \cdot \epsilon \cdot \Delta g \cdot a$	
	Cage product	Escape product
RP-1:	$(\mathrm{PhCH_2})_2\mathrm{ClSnC}\mathit{H}_2\mathrm{Ph}$	$(\mathrm{PhC}\mathit{H}_2)_2$
$\overline{(\mathrm{PhCH_2})_2\mathrm{ClS\dot{n}}\ \mathrm{\dot{C}H_2Ph}}^{\mathrm{S}}$	E = − = − + − −	A = + = − − − −
RP-2:	$(\mathrm{PhCH_2})_2\mathrm{ClSnC}\mathit{H}_2\mathrm{Ph}$	$(\mathrm{PhC}\mathit{H}_2)_2$
$\overline{(\mathrm{PhCH_2})_2\mathrm{ClS\dot{n}}\ \mathrm{\dot{C}H_2Ph}}^{\mathrm{T}}$	A = + = + + − −	E = − = + − − −
RP-3:	$\mathrm{PhC}\mathit{H}_2\mathrm{CDCl_2}$	$(\mathrm{PhC}\mathit{H}_2)_2$
$\overline{\mathrm{Ph\dot{C}H_2}\ \mathrm{\dot{C}DCl_2}}^{\mathrm{F}}$	A = + = + + − −	E = − = + − − −

$\mathrm{CDCl_3}$ show enhanced absorption. The emission signal at 2.20 ppm in $\mathrm{C_6D_6}$ and at 2.40 in $\mathrm{CDCl_3}$ could not be identified. In both solvents $(\mathrm{PhCH_2})_2\mathrm{SnCl_2}$ is formed, but shows no polarization. In $\mathrm{C_6D_6}$ the yield of $(\mathrm{PhCH_2})_2\mathrm{SnCl_2}$ is small and that of polystannanes is high. In $\mathrm{CDCl_3}$ on the other hand the formation of polystannanes is suppressed and more $(\mathrm{PhCH_2})_2\mathrm{SnCl_2}$ is produced (see Fig. 4; note the large difference of chemical shifts in two the solvents).

A special feature of the time resolved CIDNP spectra caused by the reaction of $(\mathrm{PhCH_2})_3\mathrm{SnCl}$ in $\mathrm{CDCl_3}$ (Fig. 2B) is that the polarization of the $(\mathrm{PhCH_2})_2$ and the $\mathrm{PhCH_2CDCl_2}$ signals do not develop synchronously. The polarization of $\mathrm{PhCH_2}$-$\mathrm{CDCl_2}$ appears early on and that of $(\mathrm{PhCH_2})_2$ later. The polarization of the starting material is established within less than 5 μs, and thus could not be resolved in time.

On the basis of the reaction scheme in Fig. 3 for the photolysis of $(\mathrm{PhCH_2})_3\mathrm{SnMe}$, the polarizations to be expected for $(\mathrm{PhCH_2})_3\mathrm{SnCl}$ can be predicted as follows. If triplet radical pairs are formed by photolysis in $\mathrm{C_6D_6}$, Kaptein's first rule would result in a signal of enhanced absorption for the cage polarization of $(\mathrm{PhCH_2})_3\mathrm{SnCl}$, and an emission signal for the escape polarization of $(\mathrm{PhCH_2})_2$ (see Table 3; radical pair 2 = RP-2). The polarizations observed are, in fact, opposite. It is highly unlikely that this is due to the magnetic properties of the $(\mathrm{PhCH_2})_2\mathrm{SnCl}$ radical; the relevant data are not available, but the sign of the HF constant, *a*, and the magnitude of the *g*-factor should not differ from that of the $(\mathrm{PhCH_2})_3\mathrm{Sn}$ radical. We thus conclude that in the photoreaction of $(\mathrm{PhCH_2})_3\mathrm{SnCl}$ in $\mathrm{C_6D_6}$ the singlet radical pair $\overline{(\mathrm{PhCH_2})_2\mathrm{S\dot{n}Cl}\ \mathrm{\dot{C}H_2Ph}}^{\mathrm{S}}$ is formed as precursor (RP-1).

The retarded growth of the bibenzyl polarization in the time resolved CIDNP spectra during the reaction of $(\mathrm{PhCH_2})_3\mathrm{SnCl}$ in $\mathrm{CDCl_3}$ can be accounted for in terms of the simultaneous generation of both singlet and triplet pairs: $(\mathrm{PhCH_2})_2$ is formed as an escape-product from RP-1, and RP-2, and also from RP-3. Kaptein's first rule indicates enhanced absorption for RP-1 and emission for RP-2 and RP-3. The onset of the $(\mathrm{PhCH_2})_2$ polarization from RP-1 and RP-2 is earlier than that from RP-3, since RP-3 is formed from freely diffusing radicals. RP-1 and RP-2 give rise to polarizations of opposite sign which compensate one another, and subsequently the emission signal, due to RP-3, develops. For the polarization of the starting material an overall emission signal results, because recombination is more probable for a singlet than for a triplet radical pair.

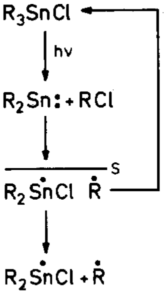

Fig. 5. Stannylene mechanism of $(PhCH_2)_3SnCl$ photolysis ($R = CH_2Ph$).

Recently the question of whether stannylenes or stannylenoids are present as intermediates in reactions of organotin compounds has been discussed [7,8]. The fact that a singlet radical pair is formed in the photoreaction of $(PhCH_2)_3SnCl$ in C_6D_6 could be interpreted in terms of stannylene formation, as suggested in the scheme in Fig. 5. The starting material is photolysed to benzyl chloride and dibenzylstannylene, which abstracts a Cl atom from $PhCH_2Cl$ to form a singlet radical pair owing to the singlet character of the stannylene [18]. These radicals will then react to give the usual termination products as shown in the scheme in Fig. 3 with R′ = Cl. Stannylene formation may become possible by "self-complexation" of $(PhCH_2)_3SnCl$ such as was postulated by Neumann for the thermolysis of 1,2-disubstituted distannanes [7]. This idea is supported by the fact that in C_6D_6 as solvent $(PhCH_2)_2SnCl_2$ is also formed. As shown above, our experimental data reveal a preference for singlet radical precursors, presumably formed via stannylenes in benzene and triplet radical precursors in chloroform. We suggest that solvents like chloroform reduce the self complexation which is regarded as an essential for stannylene formation [7].

Acknowledgements

This work was financially supported by the Fonds der Chemie and by Forschungsmittel des Landes Niedersachsen.

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