

Paramagnetic intermediates in the photolysis of 2-methylpropanoyltripropylstannane studied by means of multinuclear CIDNP

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¹H, ¹³C and ¹¹⁹Sn CIDNP studies of 2-methylpropanoyltripropylstannane Pr₃SnC(O)Pr¹ 1 photolysis in benzene have shown that its photodecomposition occurs from the triplet excited state via Sn–C (tin–carbonyl) bond cleavage. Formation of Pr₃Sn[•], [•]COCHMe₂ and [•]CHMe₂ free radicals has been observed. Possibilities of their reactions with initial ketone and main reaction products have been discussed.

Introduction

Mechanisms of radical stages in photodecomposition reactions of carbonyl compounds with Group IV elements have been extensively studied for germanium- and silicon-containing species.^{1–5} An interesting feature of these processes as compared to photolytic decomposition of carbonyl compounds without organometallic substituents is the formation of rather stable (observed in EPR spectra) radical adducts resulting from interaction of R₃M[•] with the initial ketone molecule (attack to oxygen atom of carbonyl group).^{2–4}

There is a serious lack of data on ketones with tin-containing substituents in contrast to their germanium and silicon analogues. This may be a result of the low stability of R₃SnC(O)R[•] species.⁵

The present paper describes an attempt to apply ¹H, ¹³C and ¹¹⁹Sn CIDNP methods to define the reactive state multiplicity and to elucidate the structures of short-lived paramagnetic intermediates formed by 2-methylpropanoyltripropylstannane, Pr₃SnC(O)Pr¹ 1 photolysis in benzene.

Chemically induced dynamic nuclear polarization (CIDNP) is the only direct method of determination of the reactive state multiplicity.⁶ The technique has been successfully applied to investigations of the photolysis of a number of R₃MC(O)R[•] species. For example, the use of CIDNP has demonstrated that T₁ is a reactive state of Et₃GeC(O)Ph,⁷ whereas the S₁-state is characteristic of similar silicon-containing ketones.^{8,9}

Experimental

Compound 1 was synthesized according to Kosugi *et al.*⁵ Commercial [²H₆]benzene (V/O 'Izotop') was used without preliminary purification; benzyl chloride PhCH₂Cl ('Reanal') and (Me₂CH)₂CO 2 ('Reakhim') were doubly distilled prior to experiments. Solutions of 1 (10^{–2} M) in [²H₆]benzene in the presence (5 × 10^{–2} M) or in the absence of benzyl chloride were irradiated directly inside the probe of the NMR spectrometer. Concentration of the initial compound in [²H₆]benzene was higher (10^{–1} M) for ¹³C and ¹¹⁹Sn CIDNP measurements. Solutions were deaerated for 30 min by argon bubbling prior to irradiation. The light source was a high-pressure mercury lamp DRSh-500 (500 W) with a glass filter UG-5 (λ_{trans} = 300–450 nm). A thermal filter was also installed to prevent heating of the sample. CIDNP experiments were performed using a JNM FX-90Q (JEOL) NMR spectrometer with the resonance frequencies 89.6 MHz for ¹H, 22.5 MHz for ¹³C and 33.4 MHz for ¹¹⁹Sn. ¹H high-power gated decoupling was employed in ¹³C and

¹¹⁹Sn CIDNP experiments to suppress the interaction of these nuclei with protons.

Analysis of the photodecomposition products was performed using ¹H, ¹³C and ¹¹⁹Sn NMR spectra taken both during irradiation and after the reaction. Identification was carried out on the basis of literature data for chemical shifts of known compounds as well as by addition of reference compounds [(Me₂CH)₂CO, Me₂CHCHO, (PhCH₂)₂] to the reaction mixture.

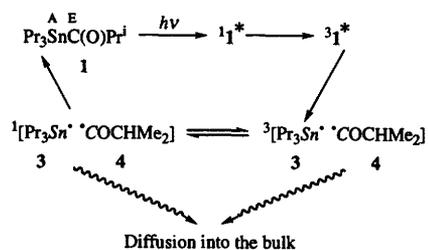
The reaction scheme proposed on the basis of CIDNP effects analysis and the set of reaction products was verified by comparing experimental ¹H CIDNP data with calculated data. To compare the contributions from different homogeneous radical pairs (RPs) to the net polarization of propene, we have generalized the well known kinetic expression for net polarization formed in a given F-pair⁶ (F^F) to the case of several RPs, precursors of the same product, eqn. (A), where *N* is

$$\frac{\partial F^F}{\partial t} \approx \sum_N K_N C^1 C^{2N} \Delta n_N^F \quad (\text{A})$$

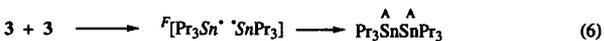
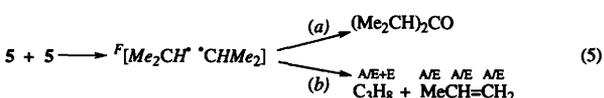
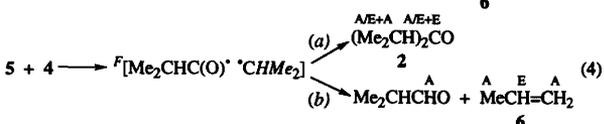
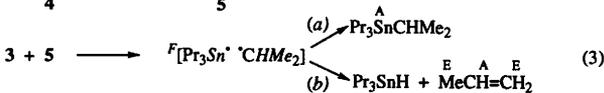
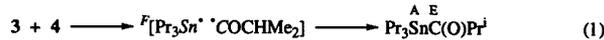
the number of the RPs, precursors of the product; *K_N* is a bimolecular reaction rate constant of the stage *N*; *C¹* are concentrations of the radicals, precursors of the product (in our case, isopropyl radical); *C^{2N}* are concentrations of the radical partners in the RP for the stage *N*. Δ*n_N^F* are values of non-equilibrium populations of the spin states (*i.e.* polarization) per one RP treated for stage *N*.

Non-equilibrium populations (Δ*n_N^F*) of propene resulting from RPs at stage (3) and (4) in Scheme 1 were calculated using known analytical expressions for CIDNP in the S–T₀ approximation.⁶ The following magnetic resonance parameters of the radicals studied were used for CIDNP analysis and in the calculations:¹⁰ Me₂CHCO[•]: *g* = 2.0007, 1 H: <0.1 mT; Me₂CH[•]: *g* = 2.0026, 6 H: 2.469 mT, 1 H: –2.195 mT; Pr₃Sn[•]: *g* = 2.0160, ¹¹⁹Sn: –0.16 T, 6 H: 0.3 mT.

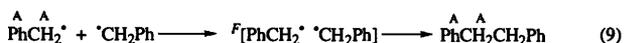
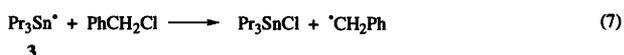
To define the origin of the decisive contribution to proton chemical polarization of propene, it is necessary to take into account the difference in concentrations of Me₂CHCO[•], Me₂CH[•] and tin-containing free radicals during the reaction. Under continuous UV-irradiation (*i.e.*, at constant rate of photo generation of the radicals) these are steady-state concentrations (d*Cⁱ*/d*t* = 0). In order to calculate the steady-state radical concentrations, we have found numerical solution of the system of non-linear kinetic equations (using the Newton method in MATLAB 4.0 for Windows) for paramagnetic species generated by the photolysis of 1 taking into account all



Reactions in the bulk:



Additionally, following bulk processes are observed in the presence of benzyl chloride:



Scheme 1 Note: nuclei responsible for CIDNP formation in RPs are italicized. Abbreviations of CIDNP effects observed: E is emission, A is absorption. Multiplet polarizations within the chemical shifts range between 2.5 and 2.8 ppm (Fig. 2) could be assigned to methyne and methylene protons of $\text{PhCH}_2\text{CHMe}_2$ formed at the stage (10).

stages from Scheme 1. The following values of reaction rate constants have been used (index of each constant corresponds to the stage number in Scheme 1): $K_1 = 2 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $K_2 = 1 \times 10^7 \text{ s}^{-1}$ (ref. 11), $K_3 = 2 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $K_4 = 3 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (ref. 11), $K_5 = 3 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (ref. 12), $K_6 = 1 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (ref. 12), $K = 3.5 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (for recombination of $\text{Me}_2\text{CHCO} \cdot$ radicals, ref. 12), for photolysis in the presence of benzyl chloride, the following reaction rate constants were used additionally: $K_7 = 1.1 \times 10^6 \text{ s}^{-1}$ (ref. 2), $K_8 = 2.5 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $K_9 = 2 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (ref. 12), $K_{10} = 2.5 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. For recombination of $\text{PhCH}_2 \cdot$ with $\cdot\text{SnPr}_3$: $K = 1.5 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The rate of photogeneration of the radicals was $10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Cross-recombination rate constants K_{AB} were estimated using known values from: $(K_{AA} + K_{BB})/2$.

Analysis of ^1H and ^{13}C CIDNP effects has been performed in accordance with Kaptein rules.¹³

The vicinal spin-spin interaction constant for the double bond protons in propene, J_{HH} , is positive.¹⁴

Our calculations on the basis of the diffusion model¹⁵ have shown that to analyse ^{119}Sn CIDNP net effects formed in the RP with one tin-centred radical, one may employ Kaptein rules, provided that the ΔgH_0 term and HFI constant in this pair have comparable magnitudes.

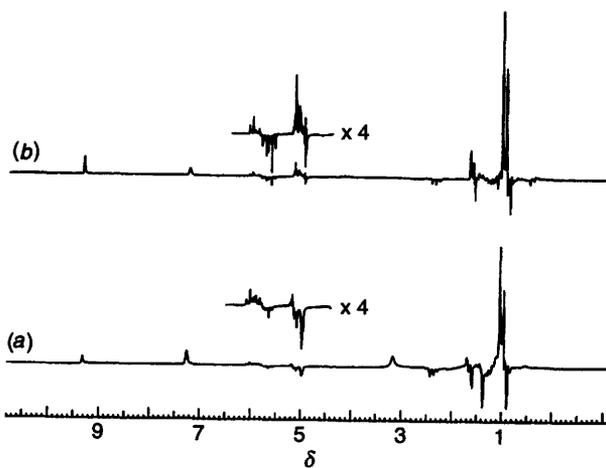


Fig. 1 ^1H CIDNP effects observed in the photolysis of 2-methylpropanoyltripropylstannane and diisopropyl ketone in $[\text{}^2\text{H}_6]$ benzene (only the spectra under irradiation are shown): (a) $\text{Pr}_3\text{SnC}(\text{O})\text{Pr}^i$; (b) $(\text{Me}_2\text{CH})_2\text{CO}$

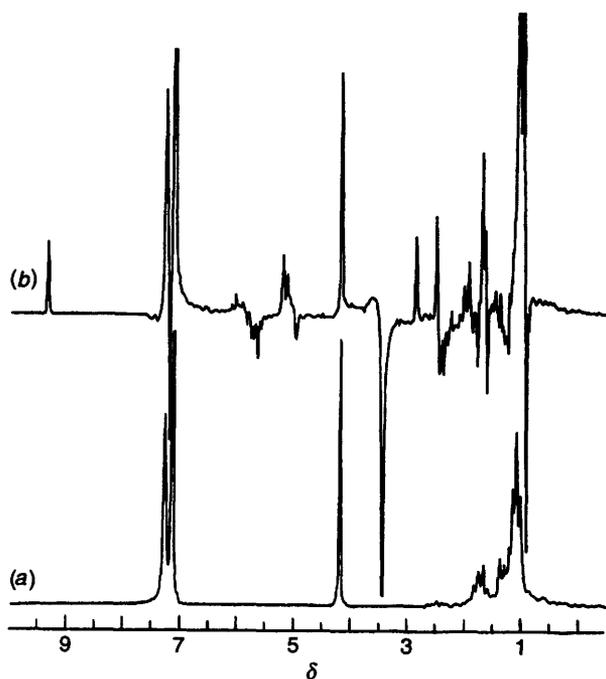


Fig. 2 ^1H CIDNP effects observed in the photolysis of $\text{Pr}_3\text{SnC}(\text{O})\text{Pr}^i$ in $[\text{}^2\text{H}_6]$ benzene in the presence of PhCH_2Cl : (a) initial; (b) under UV irradiation

Results and discussion

Photolysis of **1** has been carried out in $[\text{}^2\text{H}_6]$ benzene in the presence and in the absence of the trap of metal-centred radicals, benzyl chloride [$K_t = 1.1 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (ref. 2)]. ^1H , ^{13}C and ^{119}Sn CIDNP effects detected in these reactions are shown in Figs. 1(a), 2–4. Chemical shifts of the species under study as well as the assignment of the observed nuclear polarization effects are listed in Tables 1–3.

The appearance of ^{13}C CIDNP effects for the carbonyl group of **1** (emission (E), $\delta_{\text{C}} 249.8$ [C, s, $\text{-C}(\text{O})\text{-}$], Fig. 3) is evidence of the formation of acyl radicals $\cdot\text{C}(\text{O})\text{R}$. In principle, this means the realization of Norrish Type 1 cleavage $\text{Sn}-\text{C}(\text{O})$ or $\text{C}-\text{C}(\text{O})$ bond breaking leading to the following radical pairs (RPs):



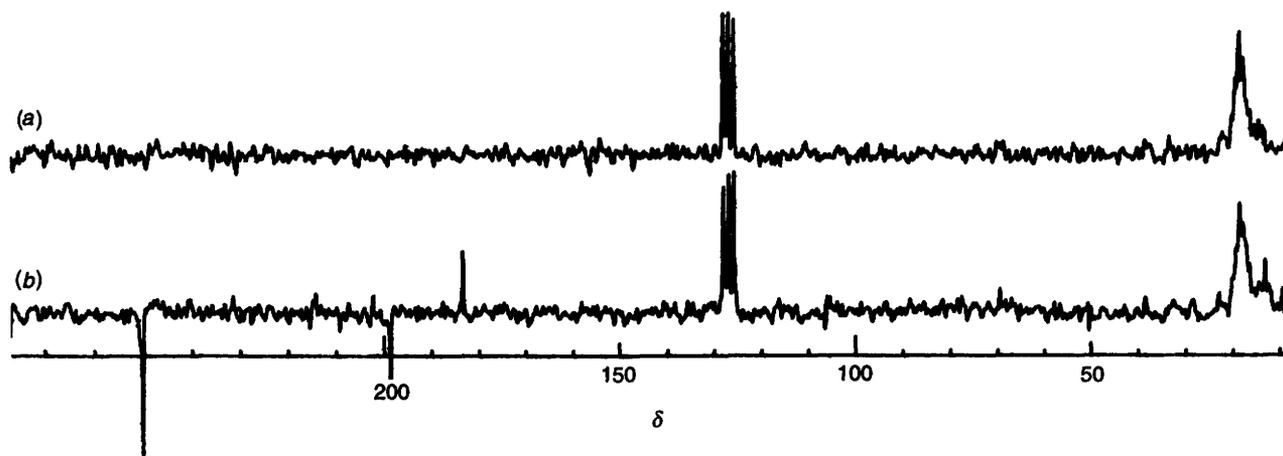


Fig. 3 ^{13}C CIDNP effects in the photolysis of $\text{Pr}_3\text{SnC}(\text{O})\text{Pr}^{\text{I}}$ in $[\text{}^2\text{H}_6]\text{benzene}$ (100 scans): (a) under UV irradiation; (b) dark spectrum after photolysis

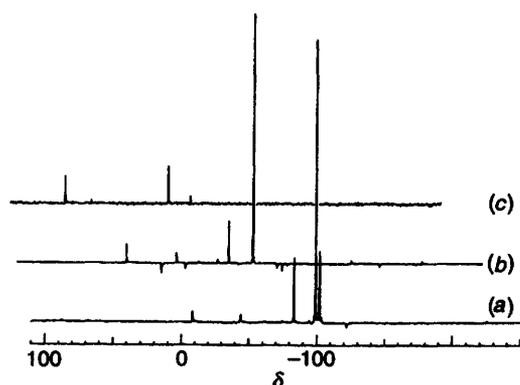


Fig. 4 ^{119}Sn CIDNP effects detected in the photolysis of $\text{Pr}_3\text{SnC}(\text{O})\text{Pr}^{\text{I}}$ in $[\text{}^2\text{H}_6]\text{benzene}$. Under UV irradiation, each scan taken after 5 s of irradiation: (a) 60 scans, (b) 60 scans more. (c) Dark spectrum after photolysis, 2000 scans.

Table 1 ^1H CIDNP effects observed in the photolysis of $\text{Pr}_3\text{SnC}(\text{O})\text{Pr}^{\text{I}}$ in $[\text{}^2\text{H}_6]\text{benzene}$ (A: absorption, E: emission)

Compound	Group of nuclei	Shift δ_{H} , ppm (multiplicity)	CIDNP sign
$\text{MeCH}=\text{CH}_2$	<i>Me</i> -	1.65 (dd)	A/E + E
	- <i>CH</i> =	5.90 (m)	A/E + A
	<i>CH</i> ₂ =	5.10 (m)	A/E + E
$\text{Me}_2\text{CHC}(\text{O})\text{H}$	<i>Me</i> ₂ -	1.12 (d)	—
	- <i>CH</i> -	2.38 (sp)	—
	- <i>C(O)H</i>	9.33 (d)	A
$(\text{Me}_2\text{CH})_2\text{CO}$	<i>Me</i> ₂ -	1.02 (d)	A/E + A
	- <i>CH</i> -	2.44 (sp)	A/E + E
MeCH_2Me	<i>CH</i> ₃ -	0.93 (t)	A/E + E
$\text{Pr}_3\text{SnC}(\text{O})\text{CHMe}_2$	<i>CH</i> ₃ - <i>CH</i> ₂ - <i>CH</i> ₂ -	0.90-1.25	<i>a</i>
	<i>CH</i> ₃ - <i>CH</i> ₂ - <i>CH</i> ₂ -	1.67 (sp)	<i>a</i>
	<i>CH</i> ₃ - <i>CH</i> ₂ - <i>CH</i> ₂ -	0.90-1.25	<i>a</i>
	<i>Me</i> ₂ <i>CH</i> -	2.45 (sp)	<i>a</i>
	<i>Me</i> ₂ <i>CH</i> -	1.35 (d)	<i>a</i>

^a Due to overlap of signals of the initial $\text{Pr}_3\text{SnC}(\text{O})\text{Pr}^{\text{I}}$ with the products of its photolysis we are unable to perform the analysis of CIDNP effects.

Observation of ^{119}Sn CIDNP effects for **1** (Fig. 4, Table 3) speaks in favour of the latter RP, *i.e.* is consistent with Sn-C(O) bond breaking, similar to the case of $\text{Et}_3\text{GeC}(\text{O})\text{Ph}$ photolysis.^{4,7} According to the existing rules of CIDNP analysis, ^{13}C emission of the carbonyl group of the initial compound implies that this polarization is formed in the primary triplet RP. The opposite sign of the ^{13}C CIDNP effect of carbon monoxide [enhanced absorption (A), δ_{C} 183 (C, s, CO), Fig. 3] allows us to assume that disproportionation of **4** with CO liberation occurs mainly in the bulk [K_{CO} ca. 10^7 s^{-1}

Table 2 ^1H CIDNP effects observed in addition to those listed in Table 1 when the photolysis of $\text{Pr}_3\text{SnC}(\text{O})\text{Pr}^{\text{I}}$ performed in $[\text{}^2\text{H}_6]\text{benzene}$ in the presence of PhCH_2Cl (A-absorption, E-emission)^a

Compound	Group of nuclei	Shift δ_{H} , ppm (multiplicity)	CIDNP sign
$\text{MeCH}=\text{CH}_2$	<i>Me</i> -	1.65 (dd)	A/E + A
	- <i>CH</i> =	5.90 (m)	A/E + E
	<i>CH</i> ₂ =	5.10 (m)	A/E + A
$(\text{PhCH}_2)_2$	- <i>CH</i> ₂ -	2.77 (s)	A
	- <i>CH</i> ₂ -	3.47 (s)	E
$\text{PhCH}_2\text{C}(\text{O})\text{CHMe}_2$	- <i>CH</i> ₂ -	3.47 (s)	E
	<i>H-ortho</i>	7.20 (s)	E

^a Due to the same reasons (Table 1) we were also unable to perform the analysis of CIDNP effects of the starting compound $\text{Pr}_3\text{SnC}(\text{O})\text{Pr}^{\text{I}}$.

Table 3 ^{119}Sn CIDNP effects observed during the photolysis of $\text{Pr}_3\text{SnC}(\text{O})\text{Pr}^{\text{I}}$ in $[\text{}^2\text{H}_6]\text{benzene}$ (A-absorption, E-emission)^{a,b}

Compound	Group of nuclei	Shift δ_{Sn} , ppm	CIDNP sign
$\text{Pr}_3\text{SnC}(\text{O})\text{Pr}^{\text{I}}$	- <i>Sn</i> -	-98.0	A
$\text{Pr}_3\text{Sn}(\text{Pr}^{\text{I}})$	- <i>Sn</i> -	-8.0	A
$\text{Pr}_3\text{SnSnPr}_3$	- <i>Sn</i> -	-82.0	A
		-44.0 ^c	A ^c
		-121.0 ^c	E ^c
$\text{Pr}_3\text{SnSn}(\text{Pr}_2)\text{SnPr}$	Pr_3Sn -	-75.0 ^d	A ^d
	- <i>Sn</i> (Pr_2)-	-225.0 ^d	A ^d

^a Chemical shifts are given relative to Me_4Sn . ^b In the presence of PhCH_2Cl the polarization signs are the same, though the formation of polarized tristannanes is not detected. ^c $J(^{119}\text{Sn}-^{117}\text{Sn})$ satellites. ^d Observed only after prolonged irradiation.

(ref. 11)]. The same conclusion about the multiplicity of the starting radical pair is made on the basis of the analysis of ^{119}Sn CIDNP effects of the initial ketone (absorption).

Absorption of ^{119}Sn in $\text{Pr}_3\text{Sn}(\text{Pr}^{\text{I}})$ points to its formation in the triplet RP, too. However, in view of the fact that the above-mentioned decarbonylation of $\cdot\text{COCHMe}_2$ free radical occurs in the bulk, one should conclude that $\text{Pr}_3\text{Sn}(\text{Pr}^{\text{I}})$ is a product of homogeneous recombination of $\text{Pr}_3\text{Sn}^{\cdot}$ and $\cdot\text{CHMe}_2$ radicals (F-pair).

We have also observed positively polarized products of the recombination of two $\text{Pr}_3\text{Sn}^{\cdot}$ radicals, hexapropyl-distannane $\text{Pr}_3\text{SnSnPr}_3$. Assignment of this compound in ^{119}Sn spectra presents no special problems, because of the appearance of satellites from $^{119}\text{Sn}-^{117}\text{Sn}$ spin-spin interaction with typical constant $J(^{119}\text{Sn}-^{117}\text{Sn})$ 2574 Hz.

To understand the influence of the tripropyltin group upon the reaction mechanism, CIDNP effects in the photolysis of **1**

Table 4 Calculated values of non-equilibrium populations Δn^F for protons of CH_2 group of propene $\text{MeCH}=\text{CH}_2$,^a steady-state concentrations of radicals and contributions to net CIDNP from different RPs

RP, stage (Scheme 1)	$\Delta n^F(\text{CH}_2)$	Without radical traps		In the presence of PhCH_2Cl	
		Steady-state conc./M ^b	Contribution to CIDNP/arb. units ^d	Steady-state conc./M ^c	Contribution to CIDNP/arb. units ^d
3	-7.0×10^{-3}	[3] = 10^{-12}	1	[3] = 10^{-12}	1
4	$+4.2 \times 10^{-3}$	[4] = 6×10^{-8}	-3.9×10^4	[4] = 1.7×10^{-12}	-0.18

^a Calculations of CIDNP for (3) take into account the natural abundance of ^{119}Sn and ^{117}Sn isotopes. ^b [5] = 3.3×10^{-8} M. ^c [5] = 3.2×10^{-8} M. ^d For the identical rates of disproportionation in (3) and (4) (Scheme 1), i.e. $K_{3b} = K_{4b}$. To obtain real contributions these values should be multiplied by $K_{\text{disp}}/(K_{\text{disp}} + K_{\text{rec}})$.

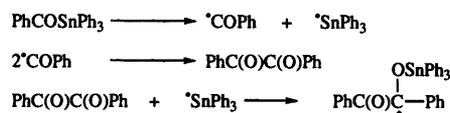
were compared with those observed in photodecomposition of diisopropylketone 2. ^1H CIDNP effects formed in the photolysis of 2 in [$^2\text{H}_6$]benzene are shown in Fig. 1(b). Special attention should be paid to the similarity of ^1H CIDNP effects observed in the photolyses of 1 [Fig. 1(a)], 2 [Fig. 1(b)], and 1 in the presence of benzyl chloride (Fig. 2) in [$^2\text{H}_6$]benzene. Since there is no doubt that benzyl chloride reacts as a trap of tripropyltin $\text{Pr}_3\text{Sn}^\bullet$ radicals 3, the above mentioned similarity of CIDNP means that in the photolysis of 1 the polarization effects are formed in the RPs deprived of $\text{Pr}_3\text{Sn}^\bullet$ radicals. Comparison of the set of products in the photolyses of 1 and 2 shows that all compounds observed in the case of 2 are also present among the products of photodecomposition of 1. Thus, all the above data on ^1H , ^{13}C and ^{119}Sn CIDNP allow us to suggest the mechanism of radical stages in the photolysis of 1 (Scheme 1). Stages (1)–(3) in Scheme 1 are proposed on the basis of ^{13}C and ^{119}Sn CIDNP data, because of the strong overlap between the signals of 1 and its phototransformation products in ^1H spectra [Figs. 1(a), 2]. According to Scheme 1, and similar to the photolysis of 2,^{11,16,17} net polarizations of aldehyde Me_2CHCHO and propene $\text{CH}_2=\text{CHMe}$ 6 originate in the RP involving 2-methylpropanoyl 4 and isopropyl 5 free radicals (4b, Scheme 1). Multiplet CIDNP effects (A/E) of methylene and methyne protons of propane and propene [Figs. 1(a) and 2, Tables 1 and 2] are formed in the homogeneous RP of two isopropyl radicals 5 (5, Scheme 1). Analysis of net and multiplet nuclear polarization effects according to the conventional rules¹³ confirms the assumption of the origin of the observed effects.

The sole difference in ^1H CIDNP effects detected in the photolyses of 1 and 2 is the sign of net polarizations of propene, its multiplet polarizations being identical in both cases [cf. Fig. 1(a) and (b)]. Note that analysis of the observed net polarization effects of propene formed by the photolysis of 1 in the absence of a radical trap shows that $\text{MeCH}=\text{CH}_2$ results from the RP involving a radical-partner with a *g*-factor greater than that of the isopropyl radical. It is quite reasonable to assume that, in the case of 1, the above mentioned difference arises due to participation of the tin-centred radical. Indeed, net CIDNP effects of propene coincide with those observed in photodecomposition of 2 when 1 is photolysed in the presence of the trap of tin-centred radicals, benzyl chloride PhCH_2Cl , which prevents $\text{Pr}_3\text{Sn}^\bullet$ radicals from entering the reactions in the bulk (cf. Figs. 2 and 1). The radical pair responsible for the observed net polarization of propene in the absence of PhCH_2Cl is shown in Scheme 1, stage (3). If both recombination and disproportionation (resulting in tripropyltin hydride Pr_3SnH and $\text{MeCH}=\text{CH}_2$) occur at stage (3), it is possible to explain the observed CIDNP sign of propene having regard to competition of (3b) between (4b) (Scheme 1). It is quite difficult to estimate the probability of disproportionation process proposed in (3b), since the reaction rate constant of hydrogen-atom abstraction from $\text{Me}_2\text{CH}^\bullet$ by $\text{Pr}_3\text{Sn}^\bullet$ radical is unknown. It is also necessary to note that the process of Pr_3SnH formation is not favourable due to the low dissociation energy of Sn–H bond (ca. 230 kJ mol⁻¹). Compounds with Sn–H bonds

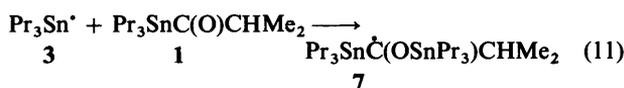
are also widely known as extremely effective donors of hydrogen atoms. Therefore, one might expect that if tripropyltin hydride is formed, it will be rapidly consumed in the reactions with 4 and 5 free radicals leading to Me_2CHCHO and propane.

To check the possibility of competition between various RPs participating in the process of CIDNP formation we have performed model calculations of net polarization effects of propene. Contributions from the RPs (3) and (4) to net polarizations of propene have been estimated using the procedure described in the Experimental section, and the results are shown in Table 4. It is seen from Table 4 that the contribution of step (3) to CIDNP changes dramatically in the presence of benzyl chloride, whilst in the absence of PhCH_2Cl the contribution of polarization formed in step (3) exceeds that from step (4) by more than four orders of magnitudes. The lack of polarized Pr_3SnH in ^{119}Sn CIDNP spectra (with simultaneous observation of polarized $\text{Pr}_3\text{SnCHMe}_2$) shows that disproportionation is not the main pathway of RP degradation at stage (3). However, it follows from the data in Table 4, that even with the rate of disproportionation in step (3) two or three orders of magnitude lower than that of recombination, stage (3) could be still responsible for net CIDNP effects of propene.

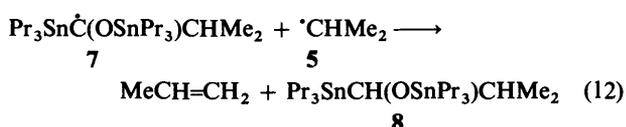
On the other hand, when considering the participation of tin-containing paramagnetic intermediates in the reaction under study, one should not exclude the possibility of formation of so-called radical adducts. Radical adducts were also observed previously^{2,3} during photolytic decomposition of $\text{Et}_3\text{GeC(O)Ph}$.⁴ Tin-containing radical adducts are also described in the literature.^{2,3} These species result from addition of tin-centred free radicals to aryltriaryltin $\text{Ph}_3\text{SnC(O)Ar}$ and/or its decomposition products.³



In the case of the of 1 it is necessary to compare the possibilities of formation of two types of adducts resulting from addition of $\text{Pr}_3\text{Sn}^\bullet$ radical to 1 or to the transformation products of $\text{Me}_2\text{CHCO}^\bullet$ radicals. To draw the analogy with the above listed reactions of PhCOSnPh_3 , let us compare the lifetimes of PhCO^\bullet and $\text{Me}_2\text{CHCO}^\bullet$ free radicals. As has already been mentioned, $\text{Me}_2\text{CHCO}^\bullet$ radical undergoes rather fast decarbonylation [stage (2), Scheme 1, K_{CO} ca. 10^7 s⁻¹ (ref. 11)]. At the same time, aryl free radicals are not involved in the reactions of such type (see, e.g. the photolysis of benzophenone or acetophenone). Therefore, we assume the formation of the radical adduct resulting from the addition of the $\text{Pr}_3\text{Sn}^\bullet$ radical to 1 [eqn. (11)] to be the most probable.



Disproportionation, eqn. (12), of homogeneous RP (F-pair)

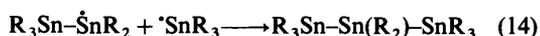
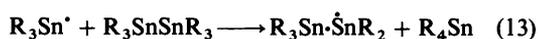


comprised of the radical adduct 7 (with *g*-factor greater than 2.003) and $\text{Me}_2\text{CH}\cdot$ radical may produce propene with net polarization signs identical to those observed experimentally (emission of $\text{CH}_2\cdot$ and absorption of CH-protons).

Unfortunately, the formation of 8 has not been proved experimentally. We have seen an unidentified positively polarized ^{119}Sn signal [A, $\delta_{\text{Sn}} - 102.0$ (Sn, s, ?), Fig. 4(a)] in the ^{119}Sn CIDNP spectrum. However, it is detected only during the first 300 s of photolysis and, later, does not result in any stable product with the above mentioned δ_{Sn} value in the final 'dark' spectrum after photolysis [Fig. 4(c)]. In the absence of experimental evidences for eqn. (12), one could only postulate that if $\text{Pr}_3\text{Sn}\cdot$ radicals do react with the initial ketone 1, then this reaction is slower than that with benzyl chloride. Different signs of net CIDNP of propene observed in the presence and in the absence of PhCH_2Cl (see Scheme 1) also corroborate this conclusion. Considering the concentrations of reactants used in the present study (see Experimental section), rate constant of the reaction of $\text{Pr}_3\text{Sn}\cdot$ with initial ketone 1 should be less than $5 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

Thus, the consideration of stationary concentrations and calculated intensities of CIDNP effects formed in different RPs shows that contribution of the process (3b) to ^1H CIDNP of propene (Table 4) is prevalent when 1 is photolysed in the absence of PhCH_2Cl . For this case, the observed polarization of propene arises from a disproportionation reaction in the RP of $\text{Pr}_3\text{Sn}\cdot$ and $\cdot\text{CHMe}_2$ radicals leading to propene and Pr_3SnH . Involvement of the radical adduct could be proposed as an alternative. However, this should only be considered as a hypothesis, since we have failed to obtain conclusive evidence for the formation of 7.

Additional evidence for the involvement of tin-containing paramagnetic species different from $\text{Pr}_3\text{Sn}\cdot$ radicals is provided by the data obtained at higher conversions of initial ketone 1. Prolonged photolysis leads to the appearance of a number of positively and negatively polarized signals in ^{119}Sn NMR spectra, their intensities being 30–100 times lower compared with those of the initial ketone 1 [Fig. 4(b)]. Concentrations of these unknown species are insignificant, since they appear only in CIDNP spectra and do not appear after irradiation even at long-run acquisition [Fig. 4(c)]. The logical conclusion could be that these are the products of $\text{Pr}_3\text{Sn}\cdot$ radical reactions in the bulk. Note that the reactions of various trialkyltin radicals with hexaalkylditins were previously studied by means of ^{119}Sn CIDNP.¹⁸ The processes shown in eqns. (13) and (14) have been reported.¹⁸



We have also observed polarized tristannanes in ^{119}Sn spectra (Table 3). However, there are other polarized signals, too [cf. Table 3 and Fig. 4(c)]. Here, the formation of the above mentioned radical adducts [reactions (11) and (12)] appears to be the most probable explanation. The addition of the $\text{Pr}_3\text{Sn}\cdot$ radical to C–C and C–O double bonds of the products of

photolysis of 1 (propene and aldehyde) must not be ruled out either.

Conclusions

Like benzoyltriethylgermane $^4 \text{Et}_3\text{GeC}(\text{O})\text{Ph}$, the photolysis of 2-methylpropanoyltriethylstannane $\text{Pr}_3\text{SnC}(\text{O})\text{Pr}^1$ in non-polar solvents proceeds *via* a Norrish Type I Sn–C(O) bond cleavage leading to a triplet radical pair of $\text{Pr}_3\text{Sn}\cdot$ and $\cdot\text{COCHMe}_2$ radicals. Dimerization is a major decay pathway for $\text{Pr}_3\text{Sn}\cdot$ radicals. There is also experimental evidence in favour of possible $\text{Pr}_3\text{Sn}\cdot$ radical addition to hexapropylidistannane as well as to the oxygen atom of C–O bond in the initial ketone molecule 1. $\cdot\text{COCHMe}_2$ radical formed in the primary act of photodecomposition of the triplet-excited 1, reacts similarly to the same species when formed in the photolysis of di-isopropyl ketone.

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