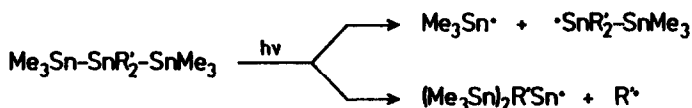


ALKYL AND STANNYL RADICAL GENERATION BY C-Sn AND Sn-Sn BOND DISSOCIATION IN PHOTOLYTICALLY EXCITED PERALKYLATED TRISTANNANES AS STUDIED BY ESR AND ^{119}Sn -CIDNP

Christian Grugel, Manfred Lehnig, Wilhelm P. Neumann*, and Josef Sauer
 Lehrstuhl für Organische Chemie I der Universität, D 4600 Dortmund 50

Summary: Tristannanes used as photochemical precursors for the synthesis of organic compounds react via triplet states followed by homolytic C-Sn and Sn-Sn bond scission.

Tristannanes $\text{R}_3\text{Sn-SnR}'_2\text{-SnR}_3$ ($\text{R}, \text{R}' = \text{alkyl}$) have been used for photochemical stannyleneid reactions, e.g. the formation of 2-stanna-1,3-dioxolanes from aldehydes². Triplet states of the tristannanes and free radicals $\text{R}_3\text{Sn}^\cdot$ have been proposed as intermediates. Since the photochemical behaviour of tristannanes has not yet been described, it will be investigated here using ESR spectroscopy and ^{119}Sn -CIDNP³⁻⁵ for two tristannanes ($\text{R} = \text{Me}$, $\text{R}' = \text{Me}$, Et). During UV irradiation ethyl radicals are observed with $\text{R}' = \text{Et}$ indicating a C-Sn bond scission besides the Sn-Sn bond cleavage giving $\text{Me}_3\text{Sn}^\cdot$ radicals (ESR, n-pentane, 193 K)



Before and after 5 min. irradiation only the normal ^{119}Sn NMR signals of the starting materials are recorded at room temperature as indicated in Fig.1 by the bars. During the reaction, however, ^{119}Sn -CIDNP appears (see Table I and Fig.1.). All evidence points to the following reaction scheme (tin atoms showing CIDNP are underlined).

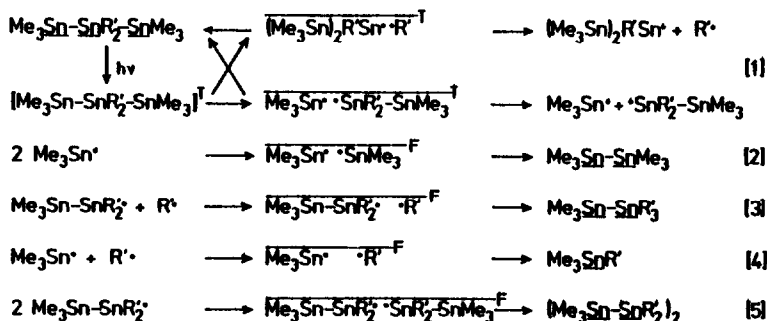


Table I. ^{119}Sn -CIDNP during irradiation of tristannanes $\text{Me}_3\text{Sn-SnR}'_2\text{-SnMe}_3$ ($\text{R}' = \text{Me, Et}$) in benzene- d_6 (0.2 mol/l) without and with EtBr (1 mol/l) Chemical shifts with Me_4Sn as standard.

Assignment	Chemical shift (ppm)		Polarisation	
	$\text{R}' = \text{Me}$	$\text{R}' = \text{Et}$	without EtBr	with EtBr
$\text{Me}_3\text{Sn-SnR}'_2\text{-SnMe}_3$	- 98.3	- 99.1	A	A
$\text{Me}_3\text{Sn-SnR}'_2\text{-SnMe}_3$	- 259.9	- 199.1	A	A
$\text{Me}_3\text{SnR}'$	00	+ 4.7	A	-
$\text{Me}_3\text{Sn-SnMe}_3$	- 109.0	- 109.3	A	-
$\text{Me}_3\text{Sn-SnR}'_3$	- 109.0	- 108.3	A	-
$\text{Me}_3\text{Sn-SnR}'_3$	- 109.0	- 62.6	A	-
$(\text{Me}_3\text{Sn-SnR}'_2)_2$	- 96.8	-	A	-
$(\text{Me}_3\text{Sn-SnR}'_2)_2$	- 248.6	- 188.8	A	-
$\text{Me}_3\text{Sn-SnR}'_2\text{Br}$ (?)	- 65.6	- 69.0	-	E
Me_3SnEt	+ 5.3	-	-	A
$\text{Me}_3\text{Sn-SnR}'_2\text{Et}$	- 107.8	- 108.3	-	A
$\text{Me}_3\text{Sn-SnR}'_2\text{Et}$	- 92.1	- 62.6	-	A

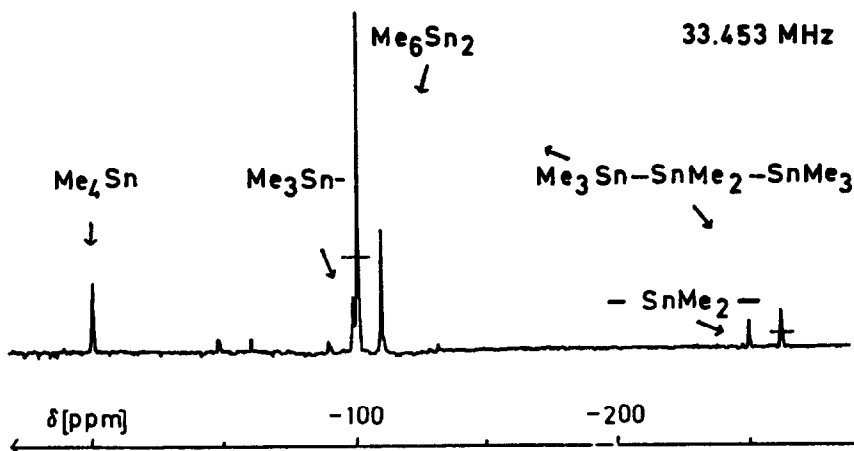
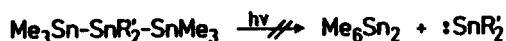
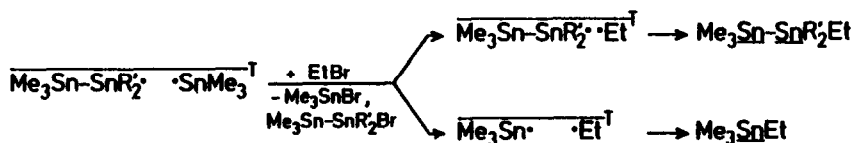


Fig. 1. ^{119}Sn -CIDNP during irradiation of Me_6Sn_2 in benzene- d_6 . Scan time: 5 m. The signals at $\delta = -46.0$, -57.4 , and -88.0 are $^{117,119}\text{Sn}$ satellites.

These CIDNP effects are built up in radical pairs formed by splitting of the tristannanes from triplet states (T) or by encounters of independently generated free radicals (F). It has to be assumed that a (^{119}Sn , α) and a (^{119}Sn , β) both are negative³. To establish the T mode decomposition of the tristannanes, in additional experiments EtBr was added to the solutions which is known as an efficient scavenger for stannyl radicals (see Table I and Fig.2). The CIDNP effects built up by diffusing radicals, reactions 2 - 5, are suppressed, while the tristannanes' polarisations still appear thus proving their triplet state origin, reaction 1. Also, the formation of Me_6Sn_2 is completely suppressed (GC) excluding the alternative formation of free stannylenes which had to be discussed previously



The A effects additionally observed are caused by cage substitution reactions



The emission signals at $\delta = -65.6$ and -69.0 presumably are due to bromotin compounds.

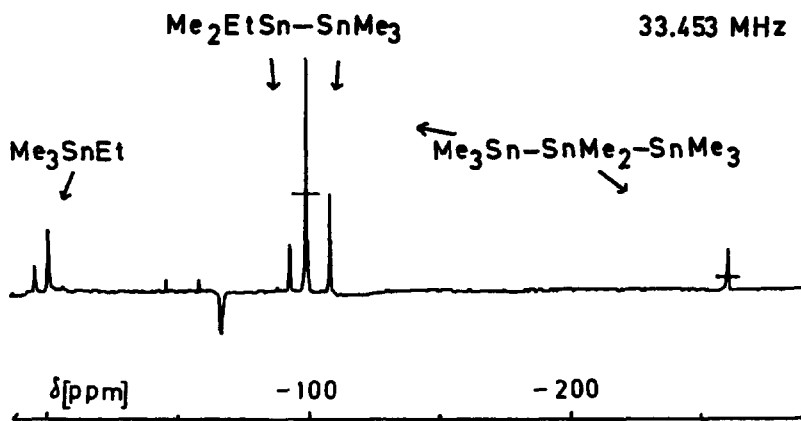


Fig. 2 ^{119}Sn -CIDNP during irradiation of Me_6Sn_3 in benzene- d_6 with EtBr. Scan time 5 m. For reference, Me_4Sn was added.

The enhancement factor of the ^{119}Sn signal at $\delta = -98.3$ in Me_8Sn_3 is found to be 5 900 ($T_1 = 1.5$ s, no nuclear Overhauser effect). Kaptein's treatment combined with den Hollander's "perturbed S- T_0 evolution"⁷ gives a value of 7 100 for the radical pair $\overline{\text{Me}_3^{119}\text{Sn}}\cdot\cdot\text{R}^{\cdot}$ (R without magnetic nuclei, $a(^{119}\text{Sn}) = -161.1$ mT)⁸) showing that triplet state Me_8Sn_3 is at least the predominant ^{119}Sn -CIDNP precursor. The dissociation from excited singlet states, however, cannot be excluded as a minor pathway by CIDNP experiments.

During irradiation of the tristannanes with aldehydes, the H-CIDNP effects usually observed during photoreactions of aldehydes are suppressed. In contrast to this, the ^{119}Sn -CIDNP effects can still be observed in the tristannanes. It is concluded that the reaction of aldehydes with tristannanes² occurs via excited states of the tristannanes.

Acknowledgement. We are grateful to the Deutsche Forschungsgemeinschaft, Bonn-Bad Godesberg, for support, to the Schering AG for organotin starting materials, and to the Fonds der Chemischen Industrie for valuable substances.

REFERENCES

1. Presented at the 4th EUCHEM Conference "Organic Free Radicals", Cirencester (England), Sep. 10.-14.1979, and based in part on the Dissertation of Ch. Grugel, Univ. Dortmund, 1977.
2. Ch. Grugel, W.P. Neumann, J. Sauer, and P. Seifert, *Tetrahedron Lett.* 1978, 2847.
3. M. Lehnig, *Chem. Phys.* 8, 419 (1975).
4. M. Lehnig, W.P. Neumann, and P. Seifert, *J. Organomet. Chem.* 162, 145 (1978).
5. M. Lehnig, *Chem. Phys. Lett.*, in press.
6. R. Kaptein, *J. Amer. Chem. Soc.* 94, 6251 (1972).
7. J.A. den Hollander, *Chem. Phys.* 15, 397 (1976).
8. J.E. Bennett and J.A. Howard, *Chem. Phys. Lett.* 15, 322 (1972).

(Received in Germany 9 November 1979)