Tetrahedron Letters No. 37, pp 3323 - 3326, 1974. Pergamon Press. Printed in Great Britain.

PHOTO-CLEAVAGE OF THE Sn-N BOND IN TRIMETHYLSTANNYL-DIETHYLAMINE AS STUDIED BY CIDNP

Manfred Lehnig

Lehrstuhl für Organische Chemie, Universität Dortmund, 46 Dortmund, BRD

(Received in UK 8 July 1974; accepted for publication 25 July 1974)

CIDNP has been applied in photochemistry to determine precursor spin multiplicities, reaction mechanisms, and the nature of free radical and diamagnetic reaction intermediates, mainly in the reactions of peroxides, ketones, aldehydes, and azo compounds$^{1)}$.

In the present paper, the mechanism of the photochemical decomposition of trimethylstannyl-diethylamine has been studied using CIDNP. The unfiltered light of a 1000 W Hg-Xe compact arc lamp (HANOVIA 977B-1) was focussed with two quartz lenses onto a quartz rod which guided the light to the sensitive region of the NMR spectrometer (BRUKER HFX 90). In order to obtain an improved signal-to-noise ratio, the Fourier transform technique was applied; this gives qualitatively the same results as the CW technique.

From PMR spectra recorded after complete decomposition of the stannylamine in benzene-d_6, the overall reaction is as follows:

$$(1) \quad 2\ Me_3Sn\text{-}NEt_2 \longrightarrow Me_3Sn\text{-}SnMe_3 + Et_2NH + Me\text{-}CH{=}NEt$$

Fig.1 shows a PMR spectrum taken during a 16 scan irradiation (ca. 1 min) of a 0.5 m solution of trimethylstannyl-diethylamine in benzene-d_6. The chemical shift is given in δ values (ppm from tetramethylsilane). The assignment of the different line groups and the observed CIDNP effects (E = emission, A = enhanced absorption, N = no effect) are presented in Table I. No CIDNP effects could be observed in the other parts of the PMR spectrum.

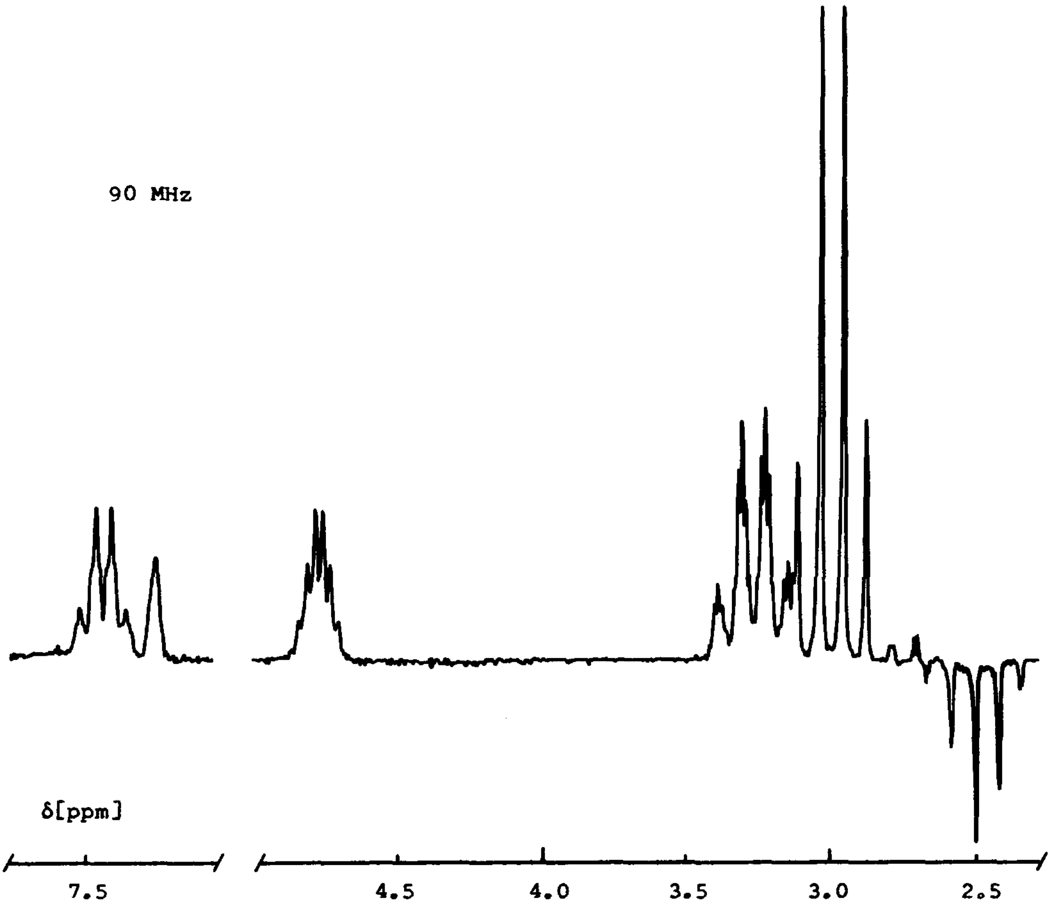

Fig.1: CIDNP during photolysis of 0.5 m $Me_3Sn{-}NEt_2$ in C_6D_6

The following reaction scheme is given

$$\text{(2)}\quad Me_3Sn{-}NEt_2 \longrightarrow \overline{Me_3Sn\cdot\,\cdot NEt_2}^{\,S} \longrightarrow \left\{\begin{array}{l} \rightarrow Me_3SnH + Me{-}CH{=}NEt \\ \rightarrow Me_3Sn\cdot + Et_2N\cdot \end{array}\right.$$

$$\text{(3)}\quad Me_3SnH + Me_3Sn{-}NEt_2 \longrightarrow Me_3Sn{-}SnMe_3 + Et_2NH$$ 2)

$$\text{(4a)}\quad 2\ Me_3Sn\cdot \longrightarrow Me_3Sn{-}SnMe_3$$

$$\text{(4b)}\quad 2\ Et_2N\cdot \longrightarrow Me{-}CH{=}NEt + Et_2NH$$ 3)

$$\text{(4c)}\quad Me_3Sn\cdot + Et_2N\cdot \longrightarrow Me_3SnH + Me{-}CH{=}NEt$$

Table I: CIDNP during photolysis of $Me_3Sn{-}NEt_2$ in C_6D_6

$CH_3{-}\underline{CH}{=}N{-}CH_2{-}CH_3$	$\delta = 7.4$	quartet	A
$CH_3{-}CH{=}N{-}\underline{CH_2}{-}CH_3$	$\delta = 3.3$	quartet	A
$Me_3Sn\underline{H}$	$\delta = 4.8$	decet	A
$(CH_3{-}\underline{CH_2}{-})_2NH$	$\delta = 2.5$	quintet	E
$Me_3Sn{-}N({-}\underline{CH_2}{-}CH_3)$	$\delta = 3.0$	quartet with Sn satellites	N
solvent	$\delta = 7.2$		N

The nuclear polarisations can be explained, if they are built up in radical pairs $\overline{Me_3Sn\cdot\cdot NEt_2}^{S}$ formed by a homolytic Sn-N cleavage from singlet states of $Me_3Sn{-}NEt_2$. With the further assumptions $g(Et_2N\cdot) < g(Me_3Sn\cdot)$ and $0 < a_H^{CH_2}(Et_2N\cdot)$ (see Table II), Kaptein's rule gives A for the CH and CH_2 protons of $Me{-}CH{=}NEt$ and the hydride proton from reaction (2), and E for the CH_2 protons of Et_2NH from (4b); these effects were in fact observed (see Table I). Multiplet type polarisations from (2) are not expected because of the large g factor difference of $Me_3Sn\cdot$ and $Et_2N\cdot$[5].

If this interpretation is correct, radical pairs $\overline{Me_3Sn\cdot\cdot NEt_2}^{F}$ formed by free radical encounter (4c) should give the same CIDNP pattern as $\overline{Me_3Sn\cdot\cdot NEt_2}^{S}$, but less intensive and of opposite sign[6]. Consequently, the magnitude of the CIDNP patterns should be increased by addition of a scavenger to remove the stannyl

Table II: Magnetic properties of $Me_3Sn\cdot$ and $Et_2N\cdot$

$Me_3Sn\cdot$	$g = 2.017$ [7]	$a_H = 0.275$ mT[7]	
$Et_2N\cdot$	$g \approx 2.004$ *)	$a_H^{CH_2} = +3.69$ mT[8,**)]	$a_H^{CH_3}$ not resolved [8,***)]

*) The g factor of $Et_2N\cdot$ is not known, but it can be assumed that its value is very similar to that of $Me_2N\cdot$ ($g = 2.0044$[9]).

**) In [8] a hyperconjugative mechanism is assumed for explaining the CH_2 splitting which gives a positive sign for $a_H^{CH_2}$.

***) It can be seen from the ESR spectrum of $Et_2N\cdot$ given in [8] that the value of $a_H^{CH_3}$ is less than 0.1 mT.

radicals. t-Butyl chloride is known to cause the following reactions$^{10)}$

(5) $Me_3Sn\cdot + t\text{-}BuCl \longrightarrow Me_3SnCl + t\text{-}Bu\cdot$

(6) $t\text{-}Bu\cdot + Me_3SnH \longrightarrow t\text{-}BuH + Me_3Sn\cdot$

It is found that the formation of $Me_3Sn\text{-}SnMe_3$ is greatly suppressed during irradiation of $Me_3Sn\text{-}NEt_2$ with an excess of t-butyl chloride, the yield being less than 10 per cent. Instead of $Me_3Sn\text{-}SnMe_3$, Me_3SnCl is formed. While the rates of disappearance of $Me_3Sn\text{-}NEt_2$ and formation of Et_2NH and Me-CH=NEt are not changed significantly, the magnitude of the CIDNP patterns of Et_2NH and Me-CH=NEt is increased by a factor of ca. 2, as expected. Furthermore, the hydride polarisation is not observed because of reaction (6).

As the t-butyl radicals cause additional CIDNP effects, a more detailed analysis of the system $Me_3Sn\text{-}NEt_2$/t-butyl chloride will not be given here.

Acknowledgement. The author thanks Prof.W.P.Neumann for his stimulating interest in this work and Dr.T.N.Mitchell for helpful discussions.

REFERENCES

1) For a review, see: H.D.Roth, Mol.Photochem. 5 (1973) 91
2) W.P.Neumann, B.Schneider und R.Sommer, Liebigs Ann.Chem. 692 (1966) 1
3) W.P.Neumann und H.Hillgärtner, Chem.Ber. 000 (0000) 000
4) R.Kaptein, Chem.Comm. 1971, 732
5) M.Lehnig und H.Fischer, Z.Naturforsch. 27a (1972) 1300
6) H.Fischer, Z.Naturforsch. 25a (1970) 1951
7) G.B.Watts and K.U.Ingold, J.Amer.Chem.Soc. 94 (1972) 1300
8) W.C.Danen, J.Amer.Chem.Soc. 92 (1970) 5235
9) W.C.Danen and T.T.Kensler, Tetrahedron Lett. 1971, 2247
10) D.J.Carlsson and K.U.Ingold, J.Amer.Chem.Soc. 90 (1968) 7047