Spin chemistry of organometallic compounds
Part 1. Interaction of *N*-bromohexamethyldisilazane with allyltriethylstannane

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Abstract

It has been shown, on the basis of the analysis of CIDNP effects, that allene and $(Me_3Si)_2NH$ — major products of the photoinduced reaction of $Et_3SnCH_2CH=CH_2$ and $(Me_3Si)_2NBr$ — result from a radical pair comprised of $^\bullet CH_2CHBrCH_2SnEt_3$ and $^\bullet N(SiMe_3)_2$ free radicals. Allene is formed through the β-cleavage of the short-lived homolytic substitution product $Et_3SnCH_2CBr=CH_2$. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Photoinduced reactions of the homolytic addition of various reagents to multiple bonds of unsaturated organic derivatives of Group 14 elements, particularly to corresponding tin derivatives, are of great importance as synthetic routes to a number of rather complex alycyclic and heterocyclic compounds [1]. The analysis of the basic peculiarities of these processes allows to conclude that otherwise almost inaccessible unusual products could also be formed in the reactions of homolytic substitution of hydrogen atom in the organic substituent of organotin species; in particular, if the hydrogen atom is substituted by halogen. A major challenge is to select a proper reagent capable of having regiospecific interaction with the substrate which would proceed solely via free-radical mechanism, since the ionic reactions usually lead to the elimination of an organic substituent. The present study considers one of

the examples of these unusual transformations, the photoinitiated reaction of allyltriethylstannane, $Et_3SnCH_2CH=CH_2$, with *N*-bromohexamethyldisilazane, $(Me_3Si)_2NBr$, leading to the high yield of allene $CH_2=C=CH_2$ (ca. 92%). The bromination reagent $(Me_3Si)_2NBr$ has been selected on the basis of reference data [2] demonstrating that its interaction with olefins results in the products of allylic bromination. It has been suggested [2] that the reaction proceeds via free-radical mechanism, and this forms the grounds to assume that the reaction of $(Me_3Si)_2NBr$ with $Et_3SnCH_2CH=CH_2$ will also follow the allylic bromination mechanism.

If the process under study indeed follows a free-radical pathway, i.e. involves spin selective reaction stages, it would be possible to elucidate the mechanism of allene formation by means of the CIDNP method. This is the main goal of the present paper.

It has been shown earlier [3] that the application of spin chemistry methods to the investigations of photoinduced reactions of organometallic compounds allows to derive important data on the elementary mechanisms of these processes.

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2. Experimental

Standard techniques were used to synthesize allyltriethylstannane, $Et_3SnCH_2CH=CH_2$ [4], and N-bromohexamethyldisilazane, $(Me_3Si)_2NBr$ [5]. Their physical constants matched with the reference data, and the purity grade was not lower than 99.5% (determined by GLC).

2.1. Reaction of Et₃SnCH₂CH=CH₂ with (Me₃Si)₂NBr

A mixture of 13 g (0.052 M) of $Et_3SnCH_2CH=CH_2$ and 12.6 g (0.052 M) of $(Me_3Si)_2NBr$ was subjected to UV irradiation (UV lamp DRT-375) during 10 h in a sealed vacuum tube. The tube was opened and the allene collected (2 g, ca. 92%).

IR data (KBr) of the gaseous product (cm^{-1}): 1870, 1910 $(\nu_{C=C=C})$; 950 $(\delta_{=CH_2})$; 1440 $(\gamma_{=CH_2})$; 3000, 3090, 3120 $(\nu_{=CH_2})$. The observed frequencies correspond to the reference spectrum of allene [6].

GLC analysis of the liquid fraction using reference substances has shown that its basic components include hexamethyldisilazane, $(Me_3Si)_2NH$, and bromotriethylstannane, Et_3SnBr, in nearly equimolar proportion. The products were separated by fractional distillation; their physical constants matched with the reference data.

After the photolysis of $Et_3SnCH_2CH=CH_2$ the composition of the products was analyzed using a GLC 'Tsvet-500' (heat conductivity detector, He, stainless steel column, 4 mm × 3 m, 10% PMS-1000 on a Chromaton N-AW-HMDS, 0.2–0.25 mm grain).

[1]H-CIDNP spectra were detected by means of a JEOL JNM FX90Q high-resolution NMR spectrometer (operating at 90 MHz frequency) equipped with a special in-house device for the irradiation of the samples directly in the probe of the spectrometer. The irradiation was carried out in standard Pyrex 5 mm NMR tubes using the full light of a DRSH-1000 high-pressure mercury lamp (1 kW). A thermal filter was used to prevent the heating of the sample.

2.2. Reaction of Et₃GeCH₂CH=CH₂ with (Me₃Si)₂NBr

A mixture of 20 g (0.099 M) of allyltriethylgermane and 23.9 g (0.099 M) of $(Me_3Si)_2NBr$ was subjected to UV irradiation (UV lamp DRT-375) during 10 h in a sealed vacuum tube. The tube was then opened; however, the analysis of the reaction mixture revealed no traces of allene.

2.3. Reaction of Et₃SiCH₂CH=CH₂ with (Me₃Si)₂NBr

A mixture of 10 g (0.038 M) of allyltriethylsilane and 16 g (0.066 M) of $(Me_3Si)_2NBr$ was subjected to UV irradiation (UV lamp DRT-375) during 10 h in a sealed vacuum tube. The tube was then opened; however, the

analysis of the reaction mixture revealed no traces of allene.

3. Results and discussion

The photolysis of the reaction mixture of $Et_3SnCH_2CH=CH_2$ and $(Me_3Si)_2NBr$ directly in the probe of the NMR spectrometer has allowed the detection of [1]H-CIDNP effects (Fig. 1) of the methyl protons of $(Me_3Si)_2NBr$ and $(Me_3Si)_2NH$, and the methylene protons of allene. The spectrum also demonstrates the polarization effects in the region of olefin protons of the initial $Et_3SnCH_2CH=CH_2$.

Thus, the following equation describes the brutto-reaction of $Et_3SnCH_2CH=CH_2$ with $(Me_3Si)_2NBr$:

$$Et_3SnCH_2CH=CH_2 + BrN(SiMe_3)_2 \xrightarrow{h\nu} Et_3SnBr$$

$$+ HN(SiMe_3)_2 + H_2C=C=CH_2$$
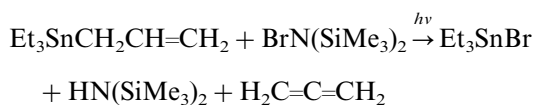
According to the data published earlier [2], the primary act of the process is the homolytic decomposition of $(Me_3Si)_2NBr$ (generation stages, Scheme 1). Note that $Et_3SnCH_2CH=CH_2$ is stable under UV irradiation and does not form the photocleavage products in the absence of initiators, in this case, $(Me_3Si)_2NBr$. Further reaction stages include the interactions of $Et_3SnCH_2-CH=CH_2$ with the $(Me_3Si)_2N^\bullet$ radical and bromine atom. Previous CIDNP studies [3] of the photoinduced interaction of $Et_3SnCH_2CH=CH_2$ with $BrCCl_3$ have shown that bromine adds to the least hydrogenated carbon atom of $Et_3SnCH_2CH=CH_2$. It has been shown in Ref. [3] that the brominated product with the bromine atom in β-position to triethyltin substituent undergoes fast β-cleavage — only polarized signals of this product were detected and no traces could be seen in the NMR spectrum after photolysis. In the present case, CIDNP effects of the allene protons suggest that similar to the main product of the photolysis of $Et_3SnCH_2CH=CH_2$ with $BrCCl_3$ (trichlorobutene $CH_2=CHCH_2CCl_3$ [3]), $CH_2=C=CH_2$ results from the β-cleavage of the brominated product $Et_3SnCH_2C-Br=CH_2$ (**I**, Scheme 1). Compound **I** originates from the disproportionation of the radical pair of $^\bullet CH_2CHBr-CH_2SnEt_3$ and $(Me_3Si)_2N^\bullet$ radicals; another product of this pair is polarized $(Me_3Si)_2NH$, since according to Ref. [2] the $(Me_3Si)_2N^\bullet$ radical readily abstracts hydrogen from the hydrocarbon radical and does not enter the recombination reaction.

The analysis of the observed CIDNP effects, which form the basis of Scheme 1, has been carried out assuming that the g-factor of the $(Me_3Si)_2N^\bullet$ radical is greater than that of its carbon-centered partner in the radical pair, and the HFI constants of Me protons in $(Me_3Si)_2N^\bullet$ radical are positive. The bromosubstituted $^\bullet CH_2CHBrCH_2SnEt_3$ radical has the following HFI

constants: $A(\alpha\text{-}CH_2) < 0$, $A(CHBr) > 0$, $A(CH_2Sn-) < 0$ [7].

The results of the analysis of CIDNP effects are in agreement with the above assumption on the reaction mechanism. On the other hand, it has been demonstrated in Ref. [8] that compounds with bromine atom in β-position to Alk_3Si and Alk_3Ge groups (in contrast to their tin analogs) are quite stable in solution, and the reaction of β-cleavage is observed only during the attempt to separate them. If the above assumptions on the mechanism of $CH_2{=}C{=}CH_2$ formation are correct (Scheme 1), the high yield of allene should not be observed in the photoreactions of allyltriethylsilane and -germane with *N*-bromohexamethyldisilazane. Our experiments have shown that the mixture after the reaction does not contain $CH_2{=}C{=}CH_2$ at all (see Section 2). Instead, the resulting mixture contains a complex set of products, whose analysis is not a part of the present study.

Another polarized product, initial *N*-bromohexamethyldisilazane, could result in the reaction of chemical exchange between the polarized $(Me_3Si)_2N^\bullet$ radical with the initial $(Me_3Si)_2NBr$ (chemical exchange, Scheme 1).

Earlier research [2] of the photolysis of $(Me_3Si)_2NBr$ in the presence of olefins also suggested that in the presence of readily abstractable allylic hydrogen, the $(Me_3Si)_2N^\bullet$ radical is capable of producing the allylic type radicals; in the present case, this will correspond to the formation of the $Et_3Sn\dot{C}HCH{=}CH_2$ radical. Indeed,

there are several unassigned CIDNP signals in the region of the protons of the initial compound $Et_3SnCH_2CH{=}CH_2$ (Fig. 1), which could be attributed to the transformations of this radical. However, both NMR and chromatographic analysis of the reaction mixture have not identified any products that could be associated with the above allylic radical. Therefore, it would be quite reasonable to refrain from speculations concerning the pathways of generation and decay of $Et_3Sn\dot{C}HCH{=}CH_2$.

Let us again emphasize the unusual character of the observed results. It is a common belief that radicals usually attack the terminal γ-carbon atom of the allylic substituent. Indeed, CIDNP effects detected in the photolysis of $Et_3SnCH_2CH{=}CH_2$ in the presence of $BrCCl_3$ [3] unambiguously point to the formation of the radical-adduct $Et_3SnCH_2\dot{C}HCH_2CCl_3$, resulting from the addition of the $^\bullet CCl_3$ radical to the terminal γ-carbon. In the case under study, we do not observe the products that could stem from the analogous addition of the $(Me_3Si)_2N^\bullet$ radical to the allylic γ-carbon or CIDNP effects that could be ascribed to certain unstable para- or diamagnetic intermediates formed through the said addition. Instead, the bromine $^\bullet Br$ attacks the least hydrogenated β-carbon atom of allylstannane and the resulting $Et_3SnCH_2CHBr\dot{C}H_2$ radical becomes the precursor of the unusual products of the reaction of homolytic substitution.
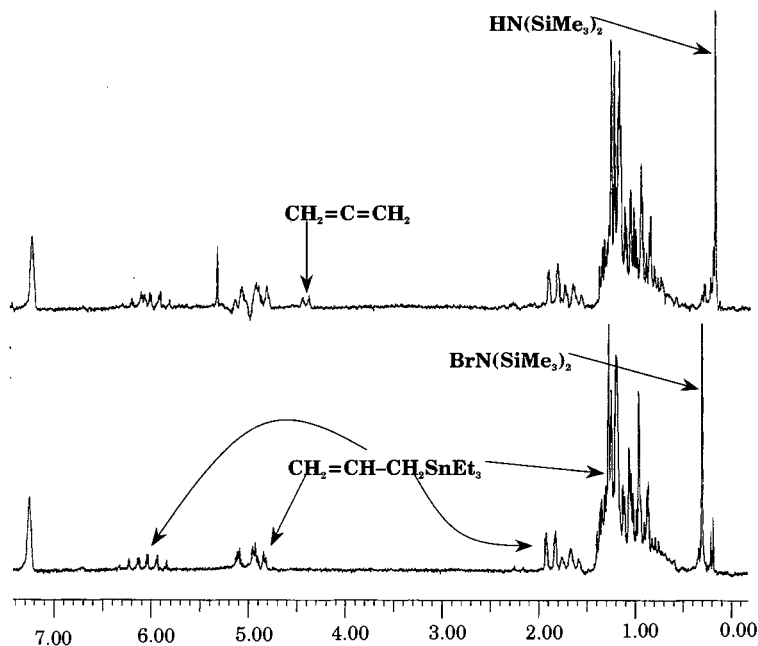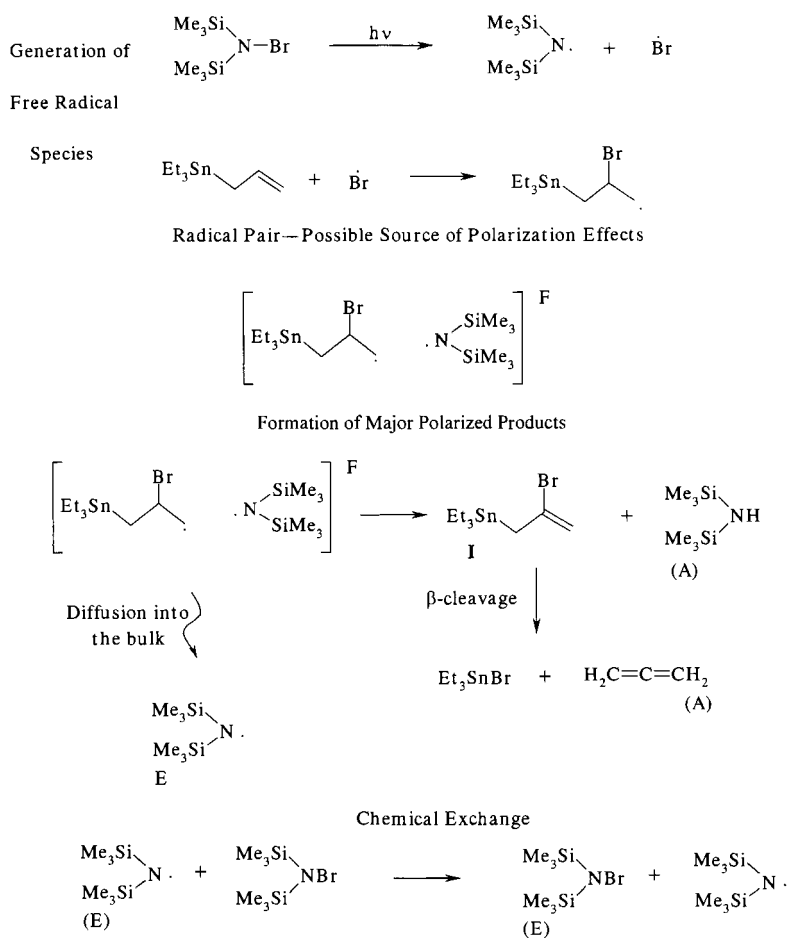

Fig. 1. 90 MHz ^{1}H-NMR spectra of the reaction mixture of $Et_3SnCH_2CH{=}CH_2$ with $(Me_3Si)_2NBr$ in deuterobenzene. Bottom spectrum, the initial reaction mixture; upper spectrum, CIDNP effects detected 20 s after the UV irradiation. Spectra show polarized signals corresponding to main reaction products.

Scheme 1. Radical stages of the photolysis of allyltriethylstannane, Et$_3$SnCH$_2$CH=CH$_2$, with *N*-bromohexamethyldisilazane, (Me$_3$Si)$_2$NBr (A, absorption; E, emission; F, free uncorrelated radical pair).

4. Conclusions

Thus, the analysis of CIDNP effects observed during the photolysis of Et$_3$SnCH$_2$CH=CH$_2$ in the presence of (Me$_3$Si)$_2$NBr as well as the quantitative yield of one of the main products of this process, allene CH$_2$=C=CH$_2$, shows that the β-cleavage pathway of the bromosubstituted allylic tin derivative Et$_3$SnCH$_2$CBr=CH$_2$ with bromine in β-position with respect to tin atom (Scheme 1) is prevalent. In contrast to the earlier studied photoinitiated reaction of Et$_3$SnCH$_2$CH=CH$_2$ with bromotrichloromethane BrCCl$_3$ [3] the present case does not demonstrate the formation of a radical-adduct which could be expected to result from the addition of (Me$_3$Si)$_2$N$^•$ radical to Et$_3$SnCH$_2$CH=CH$_2$.

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[7] According to reference data from: H. Fischer, K.-H. Hellwege (Eds.), Landolt–Boernstein New Series. Numerical Data and Functional Relationship in Science and Technology, Springer, Berlin, 1979, Parts B–D. The g-factor of $R_2N^\bullet$ radicals amounts to 2.0040, and the presence of the attached Me_3Si groups will slightly increase this value. The g-factor of $^\bullet CH_2CHBrCH_2SnEt_3$ is ≤ 2.003, analogous species could be found in the reference book.

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