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AN INVESTIGATION OF THE MECHANISM OF THE REACTION OF ALLYLTRIETHYLSTANNANE WITH BROMOTRICHLOROMETHANE BY RADIOFREQUENCY PROBING AND CHEMICALLY INDUCED DYNAMIC NUCLEAR POLARIZATION (CIDNP)

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Summary

The methods of radiofrequency probing (RFP) and chemically induced dynamic nuclear polarization (CIDNP) have been used to study the mechanism of the reaction of allyltriethylstannane with bromotrichloromethane. The CIDNP effects which have been detected prove the presence of radical stages in this reaction. An assumption has been made about a possible radical pathway for the β-decomposition of elementorganic compounds.

Introduction

Recently it has been shown that the compounds I–V are produced in the homolytic reaction of trialkylallylstannanes with polyhalomethanes [1] and alkanthiols [2]. A comprehensive scheme for the homolytic addition reaction of the general reagent (XY) to unsaturated derivatives of Group IVB elements has previously been proposed [3] (see Scheme 1).

$$X{-}Y \xrightarrow{h\nu} \dot{X} + \dot{Y}$$

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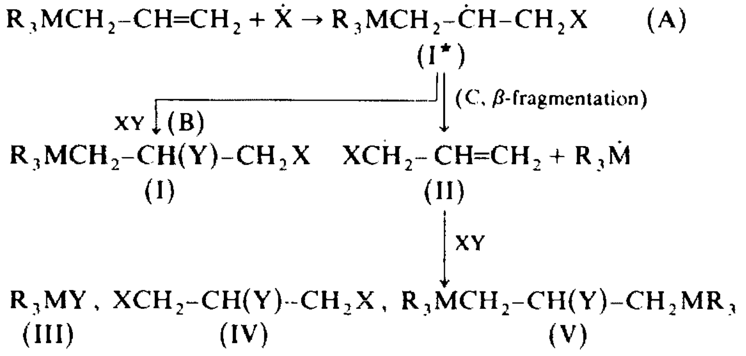

(R = Alk; M = Si, Ge, Sn)

SCHEME 1

The aim of the present work is to verify the above scheme by the methods of radiofrequency probing and CIDNP, as applied to the reaction of allyltriethylstannane with bromotrichloromethane [1] (eq. 1).

$$\underset{}{Et_3SnCH_2-CH=CH_2 + BrCCl_3} \xrightarrow{h\nu} \underset{(III)}{Et_3SnBr} + \underset{(II)}{CH_2=CH-CH_2CCl_3} \qquad (1)$$

The method of radiofrequency probing (RFP) consists of the action of an additional radiofrequency field upon certain atoms or groups of atoms in the studied substance according to the NMR spectra detected during the reaction. As a result, the NMR signal intensity of the reaction product can be either reduced (saturation of the signal in the case of homonuclear decoupling) or increased (due to the nuclear Overhauser effect in the case of heteronuclear decoupling). Under certain conditions [4] the RFP of molecules allows one to trace the fate of "labelled" atoms during the reaction and to determine the reaction mechanism using the NMR spectra.

Experimental

The starting compounds were obtained as previously described [10,11]. According to GLC data, their purity was not less than 99.9%.

The reactions were performed in 5 mm "Pyrex" tubes placed directly into the probes of the NMR spectrometers, "XL-200" (Varian, 200 MHz) and "BS 487C" (Tesla, 80 MHz), under full illumination of a high pressure mercury DRSh-1000 lamp. The light was directed to the probe through a system of focus lens and a quartz light guide, the IR-region being "cut-out" by a thermal filter. The reaction mixtures were: 0.02–0.1 *M* allyltriethylstannane and 0.2–0.4 *M* $BrCCl_3$ solutions in cyclohexane-d_{12} for the "XL-200" spectrometer, and 0.1–0.5 *M* and 1–2 *M* solutions, respectively, for the "BS 487C". Chemical shifts for ^1H were measured relative to hexamethyldisiloxane (HMDSO) as the internal standard, on the δ scale.

Results and discussion

Figure 1 shows the PMR spectra of the reaction mixture of allyltriethylstannane with bromotrichloromethane in cyclo-C_6D_{12} under successive selective saturation at

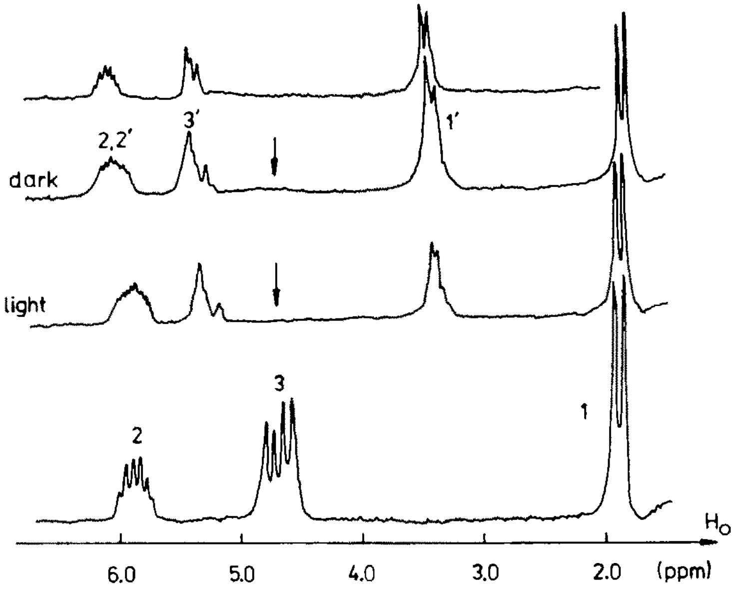

Fig. 1. PMR spectra of the $Et_3Sn\overset{1}{C}H_2-\overset{2}{C}H=\overset{3}{C}H_2/BrCCl_3$ mixture in cyclo-C_6D_{12} and the product $Cl_3\overset{1'}{C}-\overset{2'}{C}H=\overset{3'}{C}H_2$ taken by a "XL-200" spectrometer with successive saturation (shown by an arrow) of certain proton groups. The lower and upper lines are the PMR spectra of the initial compound and the product 1,1,1-trichlorobutene, respectively (the part of the spectra associated with the ethyl groups is omitted).

homonuclear decoupling [4] of various proton groups of the allyl fragment in $Et_3Sn\overset{1}{C}H_2-\overset{2}{C}H=\overset{3}{C}H_2$ molecules, under ultraviolet irradiation and in the dark. The spectra demonstrate that the saturation of the signal in the 3 position of allyltriethylstannane reduces the signal intensity of protons in the 1′ position in the $CCl_3\overset{1}{C}H_2-\overset{2}{C}H=\overset{3}{C}H_2$ product molecules (II) by 30–40%.

The saturation of the protons 1 of allyltriethylstannane reduces the signal intensity of the 3′ protons of compound II. In this case the saturation of the protons 2 of the initial compound conveys no information, since the chemical shifts of the 2 and 2′ protons are nearly equal.

The results obtained (1 → 3′ and 3 → 1′ transitions of a "saturation label") show that the initial stage in the reaction is the addition of the trichloromethyl radical to the terminal carbon atom of the allyltriethylstannane double bond, thereupon the Sn–C bond breaks, in full accord with the above scheme. Possible alternative mechanisms (recombination of trichloromethyl and allyl radicals, or the "concerted" reaction with simultaneous breaking of C–Br and Sn–C bonds) do not fit the experimental data obtained.

The radical stages of the reaction were studied by the ^1H CIDNP technique. CIDNP effects arise during photolysis of the allyltriethylstannane/bromotrichloromethane mixture in deuterocyclohexane or deuterobenzene in the probe of the NMR spectrometer at a magnetic field strength of 1.88 T. No CIDNP effect originated in a 4.7 T field, wherein the RFP effect was realized.

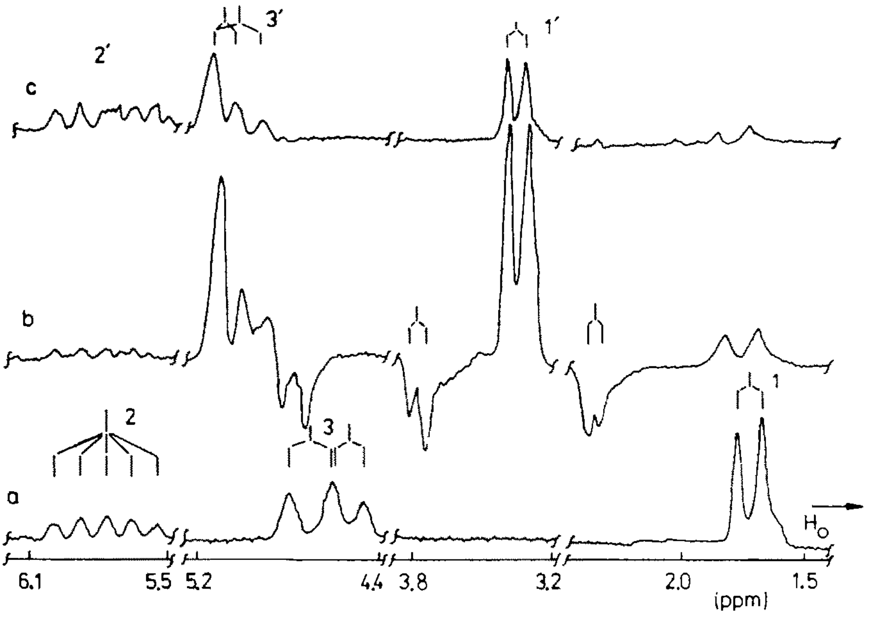

Fig. 2. General picture of the ^1H CIDNP detected in the reaction of $Et_3SnCH_2-CH=CH_2$ with $BrCCl_3$ in cyclo-C_6D_{12}(b); Also shown are the spectra before (a) and after (c) the reaction. (The numbering of protons corresponds to Fig. 1, and the part of the spectra associated with the ethyl groups is omitted.)

Since the chemical polarization detected is mainly of an integral character (Fig. 2), one may expect that the radical pairs (RP) showing these polarizations have noticeably different *g*-factor values [5]. In analysing the CIDNP effects, one can reasonably postulate [5] * that the newly generated free radicals already contain the trichloromethyl group (RFP data, stage A in the scheme).

From the above reasoning it follows that the integral CIDNP of protons 1' and 3' of 1,1,1-trichlorobutene (II) results from the encounter of I^* and $\dot{C}Cl_3$ free radicals in solution (F-pairs):

$$\overline{Et_3SnCH_2\text{-}\dot{C}H\text{-}CH_2CCl_3 \qquad \dot{C}Cl_3}^{\,F} \qquad (RP\text{-}1)$$

In this case, 1,1,1-trichlorobutene is generated by the disproportionation (β-fragmentation, [8]) of the radical-adduct I^* with separation from RP-1 (stage C in the scheme).

CIDNP effects are also observed in the region of the methine protons of II (Fig. 2b), their analysis, however, is hampered by the overlap with the allyltriethylstannane spectrum (cf. Fig. 1).

Moreover, the PMR spectrum taken during the reaction (Fig. 2b) showed two negatively polarized signals at δ 2.4 ppm and δ 3.8 ppm which are not observed in the equilibrium spectrum (Fig. 2c). The splitting pattern (doublets, *J* 6–7 Hz) and

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* The analysis employed the following characteristics of free radicals: $g(I^*) = 2.0060$, $g(\dot{C}Cl_3) = 2.0090$ [6]; for I^* $a(CH) < 0$, $a(CH_2) > 0$ [7], where *a* represents the hyperfine interaction constants.

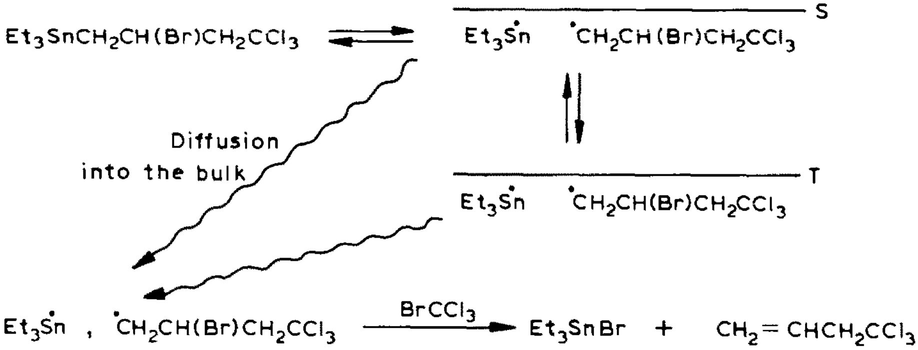
the position in the spectrum make it possible to assign them to methylene protons 1 and 3 of the "normal" addition product: 1-triethyltin-2-bromo-4,4,4-trichlorobutane ($Et_3Sn\overset{1}{C}H_2-\overset{2}{C}H(Br)-\overset{3}{C}H_2-CCl_3$) *.

As previously reported [8], elementorganic compounds of Group IVB, containing the halogen atom in the β-position with respect to the element, are not stable and decompose by the (β-decomposition) scheme:

$R_3MCH_2CH(Hal)CH_2R' \rightarrow R_3MHal + R'CH_2CH{=}CH_2$

($M = Si$, Ge, Sn; Hal = halogen; R, R' = alkyl, or $R' = CCl_3$, etc.).

The analysis shows that the CIDNP effects of compound I cannot originate in RP-1. Hence, it is possible to assume that they arise through the β-decomposition of I:



In this case, protons of I are polarized due to the partial back recombination. CIDNP analysis does not provide evidence against the assumption that the CIDNP effects of 1,1,1-trichlorobutene also arise in RP-2. Thus, CIDNP analysis indicates two possible ways of generating the basic reaction product 1,1,1-trichlorobutene (II): β-decomposition of I and δ-fragmentation of radical-adduct I* escaping from RP-1 (see the scheme).

However, there are reasons why the assumption that the β-decomposition of I is the main route for 1,1,1-trichlorobutene formation is not correct. Recently it has been shown [2], that in the homolytic addition of various reagents to allyltriethylstannane, the yield of "normal" addition product I is determined by the rate of the reaction of the radical-adduct I* with the reagent (stage B in the scheme). For instance, in the case of reactions with Et_3SeH, Et_3SH and Et_3SD, the yield of I decreases from 100% for the ethylselenol to 33% for the deuterothiol, along with the change in their activity in the chain prolongation reaction. Bromotrichloromethane is a much less reactive agent than thiols [2] and, hence any substantial yield of I in the reaction under study would not be expected.

Experiments with radiofrequency pumping in the resonance region of the protons of compound I provide additional support for the statement that I is not the main

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* The analogous product in the reactions of the allyl derivatives of silicon and germanium have nearly equal chemical shifts: $\delta(1)$ 2.0, $\delta(2)$ 4.5, $\delta(3)$ 3.2 ppm (for Si); $\delta(1)$ 2.5, $\delta(2)$ 4.5, $\delta(3)$ 3.3 ppm (for Ge).

precursor of 1,1,1-trichlorobutene (II). Under conditions of complete saturation * of the signals of I the saturation at $\delta = 2.3-4.5$ and 3.6–3.8 ppm does not reduce the intensity of the corresponding protons of 1,1,1-trichlorobutene (II) in the PMR spectra taken during the reaction.

Thus, II seems to result mainly from β-fragmentation of radical-adduct I*, as was mentioned above.

The detection of CIDNP effects in $Et_3SnCH_2CHBrCH_2CCl_3$ (I), which is generated in small amounts as an intermediate, is of fundamental importance. It is possible that the β-decomposition of elementorganic compounds with electron-acceptor substituents at the β-carbon atom occurs by a radical mechanism and this assumption will be the subject of further investigations.

Thus, NMR (RFP and ^1H CIDNP) studies of the reaction of allyltriethylstannane with bromotrichloromethane have confirmed the reaction scheme proposed previously.

Conclusions

(1) The detected CIDNP effects definitively prove the presence of radical stages in the reaction of allyltriethylstannane with bromotrichloromethane.

(2) An assumption has been made of a possible radical pathway for β-decomposition of elementorganic compounds with electron-acceptor substituents at the β-carbon atoms.

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* The condition of complete saturation: $\gamma^2 H_2^2 T_2 T_1 \gg 1$ [9], where H_2 is the saturating radiofrequency field energy (in our experiment, 35 Hz) and T_1 and T_2 are the spin-lattice and spin-spin relaxation times. From our estimations of linewidth and decay rate of the compound I polarized signals: $T_1 = 6-7$ sec, $T_2 = 0.25$ sec.