Journal of Organometallic Chemistry, 299 (1986) 271–277
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

PHOTOINITIATED REACTIONS OF ALLYLTRIORGANO-SILANES AND -GERMANES WITH POLYHALOIDALKANES. STUDY OF THE MECHANISMS OF THE REACTIONS BY MEANS OF THE ^{1}H CIDNP METHOD

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(Received June 5th, 1985)

Summary

The radical stages in the photolysis reactions of various allyltriorgano-silanes and -germanes ($R_3MCH_2CH{=}CH_2$; $M = Si$, Ge) with polyhaloidalkanes have been studied using the ^{1}H CIDNP method. It has been shown that the mechanism of the photochemical reaction for $M = Si$, Ge is different from the case when $M = Sn$. Some rather stable $R_3MCH_2CH(Hal)CH_2R'$ ($M = Si$, Ge) derivatives were isolated and characterized.

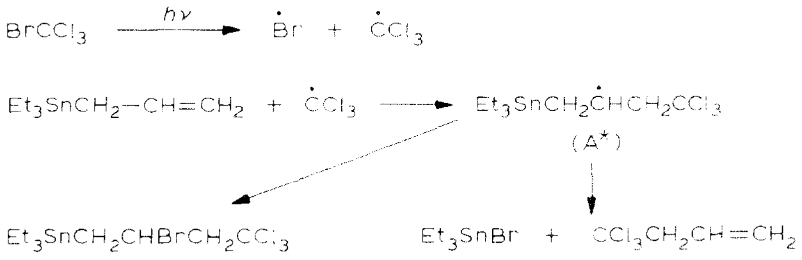
Introduction

We have previously reported the reactions of polyhaloidalkanes with $R_3MCH_2CH{=}CH_2$ ($M = Si$, Ge, Sn) under UV irradiation. These reactions follow the scheme [1,2]:

$$R_3MCH_2CH{=}CH_2 + R'X \xrightarrow{h\nu} R_3MX + CH_2{=}CHCH_2R',$$

(where $M = Si$, Ge, Sn; $R_3 = Et_3$, Me_3, $ClMe_2$, Cl_2Me, Cl_3; $R' = C_3F_7$, CCl_3;
$X = Br$, I).

The existence of free radical stages in the photoinitiated reaction of allyltriethylstannane with bromotrichloromethane is confirmed by the chemically induced dynamic nuclear polarization on the protons (^{1}H CIDNP method). In this case, the main path of the formation of bromotriethylstannane and 4,4,4-trichlorobut-1-ene is the disproportionation of the radical-adduct ($A^\star$) in solution [3] (Scheme 1):



SCHEME 1

The present paper reports a detailed study of the interaction pathways between polyhaloidalkanes and some allyltriorgano-silanes and -germanes ($R_3MCH_2CH=CH_2$; M = Si, Ge; R_3 = Et_3, Me_3, $ClMe_2$, Cl_2Me, Cl_3). The mechanisms of these reactions were studied by the ^{1}H CIDNP method.

Experimental

A mixture of the corresponding allyltriorgano-silane (or -germane) with bromotrichloromethane or perfluoropropyl iodide was UV irradiated in a sealed ampoule at 25–30°C for 6 h. The composition of the mixture was analysed by GLC (Tsvet-212 apparatus: thermal conductivity detector, carrier gas: helium, 3 m × 4 mm stainless-steel column packed with 10% PMS-1000 on Chromaton N-AW-HMDS with granulation of 0.20–0.25 mm), GC/MS (Varian spectrometer MAT-212; direct injection system, J_{ion} 70 eV) and ^{1}H NMR spectroscopy (Tesla BS 487C and Varian XL-200 spectrometers). The products of the reaction were separated by vacuum distillation and were studied by elemental analysis and ^{1}H NMR spectroscopy.

The study of the reaction mechanism by the ^{1}H CIDNP method was carried out under UV irradiation of the mixture of the corresponding allyltriorgano-silane (or -germane) (0.2 *M* solution in cyclo-C_6D_{12} or C_6D_6) with bromotrichloromethane (taken in a 1/3 ratio) in 5 mm glass NMR tubes directly in the probe of a Tesla BS 487C NMR spectrometer (80 MHz operating frequency). The photochemical device for the UV irradiation has been described previously [3]. The full light of a super high-pressure DRSh-1000 mercury lamp (1 kW power) was used for UV irradiation.

Results and discussion

As follows from the ^{1}H NMR spectral data, the reaction of allyltriorgano-silanes and -germanes with polyhaloidalkanes, proceeds more slowly than the previously studied reaction of isostructural compounds with M = Sn. The main products of the reaction are the usual adducts $R_3MCH_2CHXCH_2R'$. The formation of noticeable amounts of the decomposition product is not observed, and only a trace quantity of 4,4,4-trichlorobut-1-ene is found. The addition products are stable in solution and do not undergo noticeable decomposition upon heating up to 120°C in the probe of the NMR spectrometer. However, an attempt to separate them by vacuum distillation at 1 mmHg led to their intensive decomposition to R_3MX and 4,4,4-trichlorobut-1-ene. In addition, the decomposition rate depends on the electronic structure of the R_3M group. The passage from M = Ge to M = Si and also sequential replace-

TABLE 1

PHYSICOCHEMICAL CHARACTERISTICS OF THE SYNTHESIZED COMPOUNDS

No.	Compound	Yield (%)	B.p. (°C/mmHg)	n^{20}
I	$ClMe_2SiCH_2CHBrCH_2CCl_3$	79	122/6	1.5050
II	$Cl_2MeSiCH_2CHBrCH_2CCl_3$	86	94–95/1	1.5164
III	$Cl_3SiCH_2CHBrCH_2CCl_3$	90	97–98/1	1.5196
IV	$Cl_2EtGeCH_2CHBrCH_2CCl_3$	57	120/2	1.5403
V	$ClMe_2SiCH_2CHICH_2C_3F_7$	88	52/2	1.4260
VI	$Cl_2MeSiCH_2CHICH_2C_3F_7$	81	69–70/3	1.4310
VII	$Cl_3SiCH_2CHICH_2C_3F_7$	95	60/1	1.4344

ment of the alkyl groups at the atom of the element by more electron-accepting chlorine atoms lead to significant stabilization of the $R_3MCH_2CHXCH_2R'$ adducts. For instance, it is possible to isolate from the reaction mixture the products of the addition of bromotrichloromethane to allyltrichlorosilane in a 90% yield. They are stable upon heating up to 250°C.

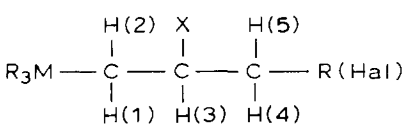
Table 1 lists the physicochemical properties of the products of the addition of bromotrichloromethane and perfluoropropyl iodide to allyltriorgano-silanes and -germanes. Table 2 gives the parameters of their ^1H NMR spectra. It was impossible to analyse the resulting adducts by GLC and mass spectroscopy because in all cases only the signals of the corresponding decomposition products were detected.

During the photoinitiated reaction of allyltriorgano-silanes and -germanes with bromotrichloromethane, ^1H CIDNP effects were observed in the molecules of the adducts (A), on the protons of the initial compounds, and in the 4,4,4-trichlorobut-1-ene molecules (Figs. 1 and 2). As mentioned above, only the polarized signals of the latter compound were detected. Table 3 shows the CIDNP effects observed and their analysis using Kaptein's rules [4]. It should be noted that no ^1H CIDNP effects were found in the reactions of allyltriorgano-silanes and -germanes with perfluoropropyl iodide.

(Continued on p. 276)

TABLE 2

PARAMETERS OF THE ^1H NMR SPECTRA OF THE COMPOUNDS [a]



$$R_3M-\overset{H(2)}{\underset{H(1)}{C}}-\overset{X}{\underset{H(3)}{C}}-\overset{H(5)}{\underset{H(4)}{C}}-R(Hal)$$

No.	R_3M	X	R(Hal)	Chemical shifts δ(ppm)		
				H(1); H(2)	H(3)	H(4); H(5)
II	Cl_2MeSi	Br	CCl_3	1.77; 2.11	4.45	3.03; 3.34
III	Cl_3Si	Br	CCl_3	2.08; 2.31	4.24	3.02; 3.34
IV	Cl_2EtGe	Br	CCl_3	2.40; 2.60	4.50	3.20; 3.40
V	$ClMe_2Si$	I	C_3F_7	1.88; 2.11	5.53	2.87
VI	Cl_2MeSi	I	C_3F_7	2.08; 2.35	5.53	2.88
VII	Cl_3Si	I	C_3F_7	2.05; 2.36	4.33	2.70; 3.00

[a] The proton spin–spin coupling constants in the above compounds are (Hz): J(H(1)–H(2)) 15.5, J(H(4)–H(5)) 15.5, J(H(1)–H(3)) and/or J(H(2)–H(3)) 9.0 and/or 4.5, J(H(3)–H(4)) and/or J(H(3)–H(5)) 5.8 and/or 6.3.

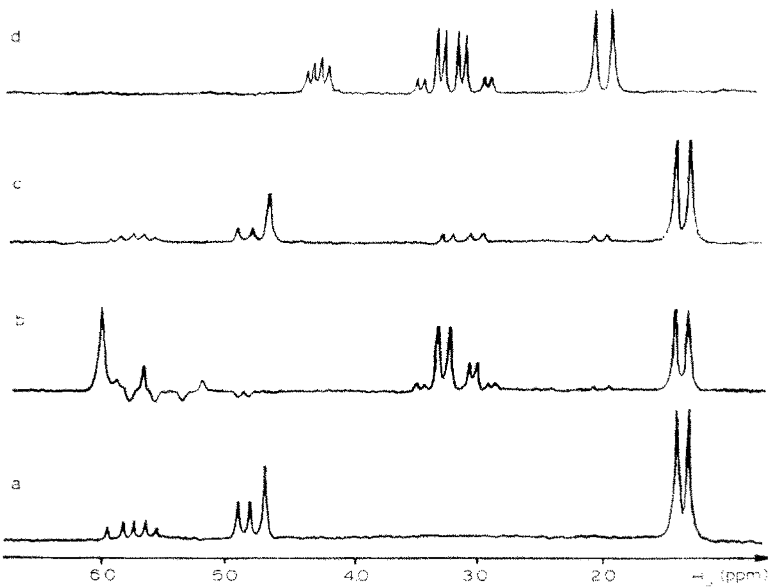


Fig. 1. General picture of the ^{1}H NMR spectra of the mixture of $Me_3SiCH_2CH{=}CH_2$ with $BrCCl_3$ in cyclo-C_6D_{12}. (a) Before the reaction; (b) during the photochemical reaction; (c, d) after the reaction. The part of the spectrum associated with the methyl protons has been omitted. Line assignments are given in Tables 2 and 3.

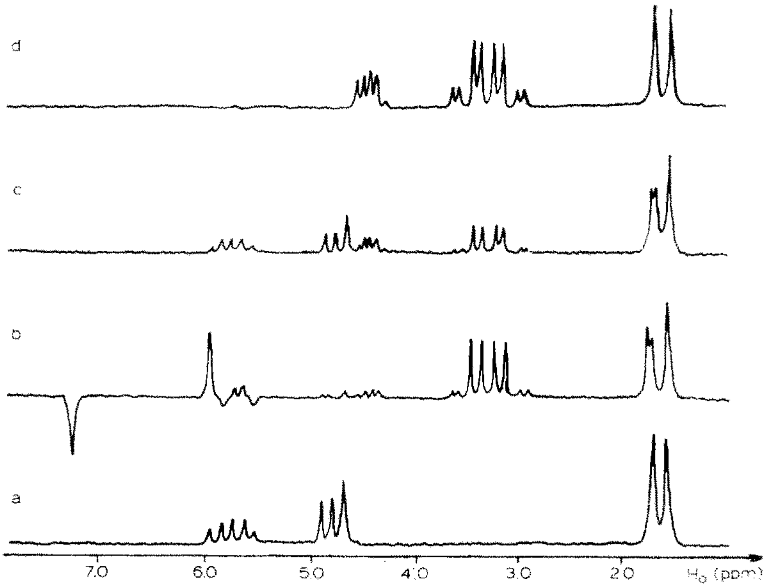


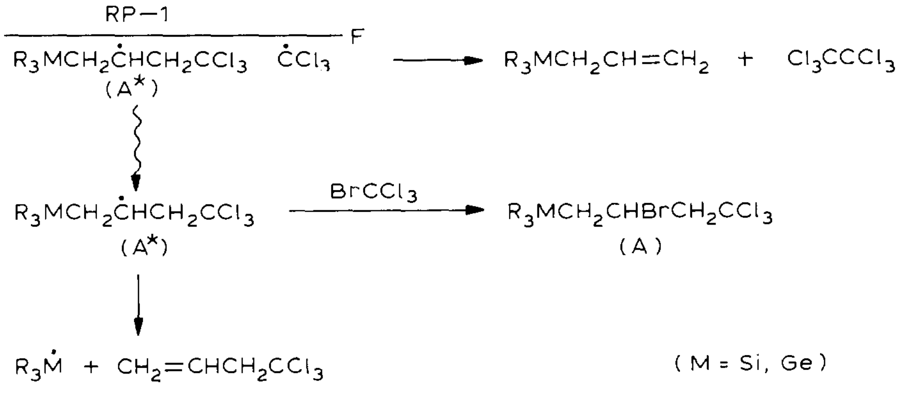
Fig. 2. General picture of the ^{1}H NMR spectra of the mixture of $Et_3GeCH_2CH{=}CH_2$ with $BrCCl_3$ in cyclo-C_6D_{12}. (a) Before the reaction; (b) during the photochemical reaction; (c, d) after the reaction. Part of the spectrum associated with the ethyl protons has been omitted. Line assignments are given in Tables 2 and 3.

TABLE 3

CIDNP EFFECTS OBSERVED IN THE REACTIONS OF $R_3MCH_2CH{=}CH_2$ WITH $BrCCl_3$ IN C_6D_6 AND cyclo-C_6D_{12} (A absorption, E emission) [a]

Polarized compounds	Radical pair	^1H CIDNP effects in different positions [b]		
		1	2	3
1 2 3 $R_3MCH_2CH{=}CH_2$ (M = Si, Ge)	1	[c] (1.3, M = Si) (1.8, M = Ge)	A + A/E (5.8)	E (4.8)
1 2 3 $CCl_3CH_2CH{=}CH_2$	1	A (3.3)	-	A (5.4)
1 2 3 $R_3MCH_2CHBrCH_2$ | CCl_3 (M = Si, Ge)	1	[c] (2.0, M = Si) (1.9, M = Ge)	E (4.5, M = Si) (4.8, M = Ge)	A (3.3, M = Si) (3.3, M = Ge)
1 2 3 $R_3SnCH_2CHBrCH_2$ | CCl_3	2	E (2.1)	-	E (3.7)
1 $CHCl_3$	1	E (7.3)		

[a] To analyse the CIDNP effects, the following characteristics of the free radicals were used: for the radical-adduct: g 2.0060; $A(CH) < 0$, $A(CH_2) > 0$; $g(\dot{C}Cl_3)$ 2.0090 [5]; for $\dot{C}H_2CHBrCH_2CCl_3$: g 2.0027; $A(CH_2) < 0$, $A(CH) > 0$, $A(\gamma\text{-}CH'_2) > 0$, $A(\gamma\text{-}CH''_2) < 0$ (γ-protons in different conformations of the radical); $g(Et_3\dot{S}n)$ 2.015 [5,6]. [b] The values of the chemical shifts, δ(ppm), of the polarized signals are given in parentheses. [c] The absence of CIDNP effects on the protons in position 1 may be associated with the shortening of their spin-lattice relaxation time down to 7 s due to the nearness of element atom M, compared to 10–13 s characteristic of the protons in positions 2 and 3.



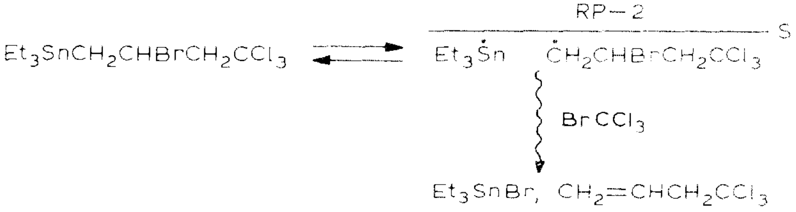
SCHEME 2

Analysis of the CIDNP effects shows that, similarly to the reactions of allyltriethylstannane, chemical polarizations arise in the radical pair (RP) of the radical-adduct (A$^\bullet$) and $\dot{C}Cl_3$ free radical [3] (see Scheme 2).
The initial compounds are polarized as "in-cage" products, and 4,4,4-trichlorobut-1-ene and adduct (A) are polarized as escape products of RP-1.

The formation of small amounts of polarized $CHCl_3$ was detected during the photochemical reaction of allyltriethylgermane with bromotrichloromethane. The sign of the polarization in the chloroform molecules allows one to assume that $CHCl_3$ is also the product of the "in-cage" disproportionation of RP-1. The other product of the disproportionation of this pair is possibly $Et_3GeCH_2CH{=}CHCCl_3$, which is generated in trace amounts. Its NMR signals are registered only during accumulation of the spectra.

$$\overline{Et_3GeCH_2\dot{C}HCH_2CCl_3\ \dot{C}Cl_3}^{F} \rightarrow Et_3GeCH_2CH{=}CHCCl_3 + CHCl_3$$

An assumption has been made previously [3] that the CIDNP effects observed on the protons of (A) molecules during the reaction of allyltriethylstannane with bromotrichloromethane arise directly in the course of the breaking up of (A), β-decomposition (Scheme 3):



SCHEME 3

Indeed, the amount of 1-triethyltin-2-bromo-4,4,4-trichlorobutane did not rise during the reaction: only its polarized ^1H NMR signals were seen [3] (Fig. 3).

Thus, analysis of the CIDNP effects indicates that compounds A in the cases of M = Si, Ge and M = Sn are polarized in the different RPs (RP-1 and RP-2, respectively). To verify this conclusion we studied the temperature dependence of the CIDNP effects in the reactions of allyltriethyl-stannane, -germane and -silane with bromotrichloromethane in toluene-d_8 within the temperature range -50 to $+20$°C. It was found that there is no noticeable dependence * of the CIDNP effects in the initial compounds and 4,4,4-trichlorobut-1-ene on the temperature in all the reactions studied. The polarized protons of compound A demonstrate the same behaviour (in the case of M = Si, Ge).

Polarization in the 1-triethyltin-2-bromo-4,4,4-trichlorobutane molecules completely disappears at -5°C, and no increase of the concentration of this product occurs (Fig. 3). This observation confirms the conclusion made on the basis of the CIDNP effects that, in the case of M = Sn, the polarizations of the main product of reaction 4,4,4-trichlorobut-1-ene and of compound (A) arise in the different RPs. Moreover, the existence of a temperature dependence means that the β-decomposi-

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* Only broadening of the lines and a small decrease in the observed enhancement coefficients were detected.

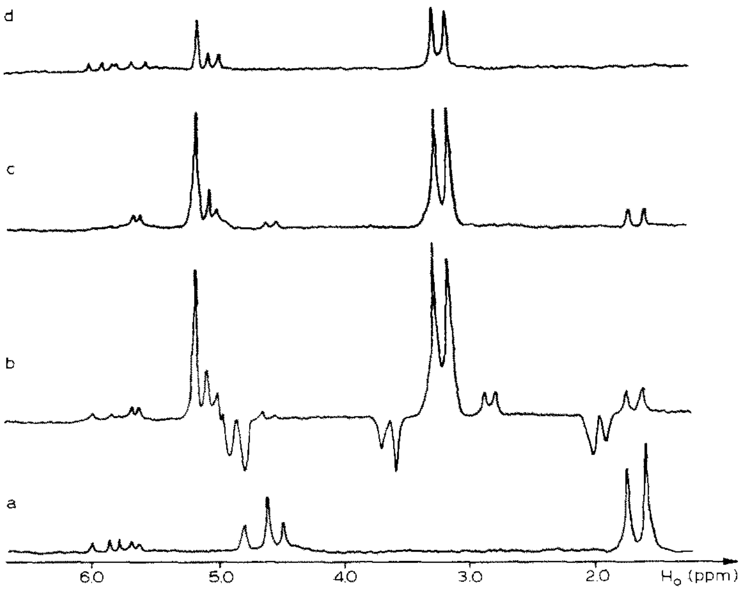

Fig. 3. ^{1}H NMR spectra taken for the reaction mixture of $Et_3SnCH_2CH{=}CH_2$ with $BrCCl_3$ in toluene-d_8 (internal standard hexamethyldisiloxane). (a) Spectrum before the reaction ;(b) spectrum taken during UV irradiation at +20°C; (c) the same as (b) at −30°C; (d) spectrum after the reaction (−30°C). The part of the spectrum associated with ethyl protons has been omitted. For line assignment, see Tables 2, 3 and ref. 1.

tion reaction of 1-triethyltin-2-bromo-4,4,4-trichlorobutane occurs without any UV irradiation (in the dark).

Conclusions

Thus the investigations carried out show that the reaction of bromotrichloromethane with allyl derivatives of the Group IVB elements, $R_3MCH_2CH{=}CH_2$, proceeds by different mechanisms in the cases of M = Sn and M = Si, Ge. This behaviour may originate from either the nature of the M atom or the differences in the electron donating properties of the R_3M. Clarification of these points will be the subject of further investigations.

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