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The role of hydrogen atoms in CIDNP effects in the reaction of diisobutylaluminum hydride with CCl_4

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Integral polarization of chloroform, methylene dichloride, and pentachloroethane was observed in the ^1H NMR spectra during the exothermal reaction of a 1 *M* solution of $Bu^i{}_2AlH$ in 1,4-dioxane with CCl_4. CIDNP was shown to appear in the diffusion radical pair of the hydrogen atom and trichloromethyl radical.

Key words: CIDNP, hydrogen atom, trichloromethyl radical, radical reaction, diisobutylaluminum hydride, carbon tetrachloride.

We have shown previously[1] that during the reactions of trialkylalkanes with CCl_4, chemically induced dynamic nuclear polarization (CIDNP) appears in the radical pair (RP) of alkyl and trichloromethyl radicals. When R_3Al is replaced by R_2AlH, the formation of RP consisting of the H atom and $^{\cdot}CCl_3$ should be expected, because the Al—H bond is the most active. Examples of CIDNP involving H atoms are known in radiation chemistry.[2]

Results and Discussion

During the fast exothermal reaction of an 1 *M* solution of $Bu^i{}_2AlH$ in dioxane-d_8 with an equivalent or higher quantity of CCl_4, the detector of an ^1H NMR spectrometer shows negatively polarized signals of chloroform and methylene dichloride with chemical shifts at 7.53 and 5.3 ppm, respectively, in the spectrum of the reaction mixture (Fig. 1). In addition, a positively po-

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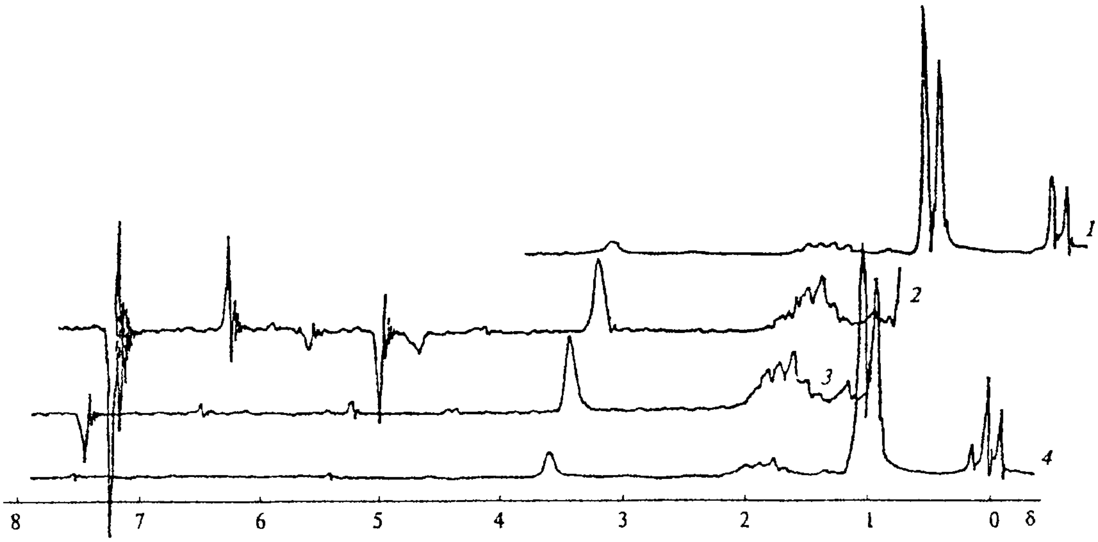

Fig. 1. ^{1}H NMR spectra of the reaction mixture of diisobutylaluminum hydride (1 mol L^{-1}) with CCl_4 (2 mol L^{-1}) in dioxane-d_8: *1*, starting diisobutylaluminum hydride; *2* and *3*, 1 and 3 min, respectively, after the addition of CCl_4; and *4*, reaction products 1 h after.

larized singlet at 6.55 ppm, which is presumably assigned to $CHCl_2CCl_3$, and nonidentified negatively polarized signals (5.80 D) and (5.00 S), which disappear when the reaction is ceased, are detected. The yield of these products is very low, since their signals are observed in the polarized form only. It can be assumed that the polarized chloroform molecule appears due to recombination of a diffusion RP-1, which is formed as a result of the one-electron transfer from Bu^i_2AlH to CCl_4 and consists of the H atom and $^\cdot CCl_3$ radical.

$$\mathrm{Bu^i_2AlH + CCl_4 \longrightarrow [Bu^i_2AlH^{\cdot +}CCl_4^{\cdot -}] \longrightarrow Bu^i_2AlCl + H^\cdot + {}^\cdot CCl_3}$$

$$\mathrm{H^\cdot + {}^\cdot CCl_3 \longrightarrow \underset{RP\text{-}1}{\overline{H^\cdot\ {}^\cdot CCl_3}^{\,F}} \longrightarrow \overset{E}{CHCl_3}}$$

Let us consider the correspondence of our assumptions to the experimentally observed emission of a proton of $CHCl_3$. The g-factors of paramagnetic species in RP-1 are not equivalent (g(H) = 2.00225,[3] $g(CCl_3)$ = 2.0091,[4] $\Delta g = -0.0068$); therefore, integral polarization is observed in the products of transformation of RP-1. To predict the sign of polarization of $CHCl_3$, let us use the Kaptein rule[5] for integral polarization:

$$\Gamma = \mu\varepsilon\Delta g a_k.$$

In this correlation, $\mu = +1$ for triplet (diffusion) or $\mu = -1$ for singlet (geminal) RP; $\varepsilon = +1$ for the cage recombination product or $\varepsilon = -1$ for the product of the reaction of radicals leaving RP; Δg is the difference between the g-factors of the radical to which the kth magnetic nucleus belongs and the radical-partner; and a_k is the constant of isotropic HFC with the nucleus, whose integral polarization was not considered. For chloroform formed in the recombination of RP-1, we have $\mu = +1$, $\varepsilon = +1$, $\Delta g < 0$, and a_k(H) = +50.69 mT > 0.[6] As a result, $\Gamma < 0$, *i.e.*, emission occurs.

Methylene dichloride is formed in the reaction of $CHCl_3$ with Bu^i_2AlH. This is confirmed in a particular experiment when $CHCl_3$ is mixed with a solution of Bu^i_2AlH; however, no polarization of CH_2Cl_2 and no other products were observed in this reaction. The emission of CH_2Cl_2 in the reaction studied can probably be explained by the fact that $CHCl_3$ in the polarized form reacts with Bu^i_2AlH and transfers its polarization to a molecule of the product formed. This is indirectly confirmed by the fact that when the starting CCl_4 is taken in deficiency, methylene dichloride is formed in a greater amount than $CHCl_3$, *i.e.*, under these conditions, a great portion of $CHCl_3$ reacts with excess Bu^i_2AlH to be transformed into CH_2Cl_2. The yield of CH_2Cl_2 increases until the amounts of CCl_4 and Bu^i_2AlH become equal. When the amount of the starting CCl_4 further increases, the yield of CH_2Cl_2 remains unchanged, and that of $CHCl_3$ continues to increase.

The positively polarized compound $CHCl_2CCl_3$ is most likely formed during recombination of a diffusion RP-2.

$$\mathrm{{}^\cdot CHCl_2 + {}^\cdot CCl_3 \longrightarrow \underset{RP\text{-}2}{\overline{{}^\cdot CHCl_2\ {}^\cdot CCl_3}^{\,F}}}.$$

Here $g(CHCl_2)$ = 2.008,[7] $\Delta g = -0.0011$, and $a_k(CHCl_2) = -1.7$ mT < 0;[8] therefore, an enhanced absorption (A) occurs, according to the Kaptein rule, in the product of intracage recombination of $CHCl_2CCl_3$. The $^\cdot CHCl_2$ radical can appear due to the reaction of

$CHCl_3$ with $Bu^i{}_2AlH$ or dichlorocarbene CCl_2, whose formation has been assumed previously.[9] In order to check experimentally the existence of CCl_2, the reaction was carried out in the presence of the traditional carbene trap, cyclohexene. The product of the reaction of cyclohexene with CCl_2 (dichloronorcarane) was observed by CL-MS along with the main products of addition of the $^{\cdot}CCl_3$ radical to cyclohexene, but its quantity was insignificant.

When the reaction was carried out in the presence of styrene, the yields of $CHCl_3$ and CH_2Cl_2 were substantially lower. This indicates that these products are mainly formed *via* the radical route.

Experimental

A 1 *M* solution of $Bu^i{}_2AlH$ pre-purified from a triisobutylaluminum admixture by vacuum distillation was used. Entirely deuterated 1,4-dioxane dried by boiling over sodium followed by distillation was used for NMR measurements. CCl_4 was dried with $CaCl_2$ and then distilled. Styrene-d_8 was used in experiments with the radical trap. Cyclohexene dried over $MgSO_4$ was used as the dichlorocarbene trap. The reaction products in the presence of cyclohexene were identified on a Finnigan LC-MS mass spectrometer.

Dichloronorcarane used as the standard in GLC and MS analyses was synthesized by the known procedure.[10]

In the study of CIDNP, the reactions were carried out directly in the probe of a Tesla BS-467 NMR spectrometer (60 MHz, CW) at room temperature. Carbon tetrachloride was added by a syringe to a solution of $Bu^i{}_2AlH$ in a 5-mm ampule under an argon atmosphere in the detector.

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Synthesis of *O,O*-diethyl *Se*-alkyl selenophosphates by the reactions of diethyl phosphite with alkaneselenenyl halides*

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The reactions of diethyl phosphite with alkaneselenenyl halides in chloroform at 20 °C afforded the corresponding *O,O*-diethyl *Se*-alkyl selenophosphates.

Key words: diethyl phosphite, alkaneselenenyl chlorides, alkaneselenenyl bromides, *O,O*-diethyl *Se*-alkyl selenophosphates.

Several procedures are known for the synthesis of *O,O*-dialkyl *Se*-aryl selenophosphates, most of which have been reported previously.[1] However, only a few examples of the synthesis of compounds $(AlkO)_2P(O)SeAlk$ are available in the literature. Thus, it was reported that ether $(EtO)_2P(O)SeMe$ was obtained by the reaction with halosilanes.[2] *O,O*-Diethyl *Se*-butyl selenophosphate was prepared from *O,O,O*-triethyl selenophosphate and bromobutane.[3] The reac-

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* Dedicated to the memory of Academician M. I. Kabachnik on his 90th birthday.

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