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Chemically Induced Dynamic Nuclear Polarization in the Dehalogenation of *gem*-Dihalocyclopropanes under the Action of *i*-Bu_2AlH in the Presence of $Zr(acac)_4$

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Abstract—The integral and multiplet effects associated with the chemically induced dynamic nuclear polarization in the catalytic dehalogenation of alkyl- and aryl-*gem*-dibromocyclopropanes under the action of diisobutylaluminum hydride in the presence of $Zr(acac)_4$ have been discovered and investigated. The main products of the reaction are monobromocyclopropanes and cyclopropanes. The other reaction products are isobutane, isobutylene, and isobutyl bromide. Integral polarization is observed for the isobutylene protons; multiplet polarization, for the isobutyl bromide protons. Integral polarization arises in a geminal singlet radical pair between an isobutyl radical and a Zr(III) paramagnetic ion that have resulted from the homolysis of an *i*-Bu–Zr bond.

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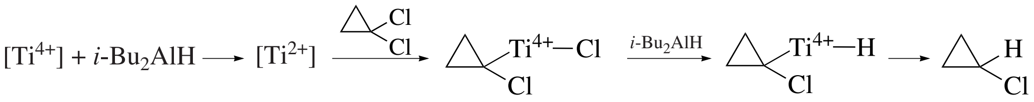
The reductive dehalogenation of *gem*-dihalocyclopropanes (GDHCPs) to monohalocyclopropanes and cyclopropanes can be carried out using *i*-Bu_2AlH in the presence of catalytic amounts of Ti or Zr [1]. It was postulated that this reaction includes the following sequence of steps [1, 2]:



Scheme 1.

Initially, the Ti or Zr compound is reduced under the action of *i*-Bu_2AlH to yield a coordinatively unsaturated complex. The oxidative addition of GDHCP to the central atom of the catalyst, with C–halogen bond cleavage, yields a catalytically active complex having a cyclopropyl–M–halogen bond (M = Ti, Zr). In the presence of excess *i*-Bu_2AlH, this complex turns into a cyclopropyl–M–H complex. Subsequent intramolecular elimination yields a monohalocyclopropane. We believe that only the Al–H bond of *i*-Bu_2AlH is involved in the reaction, while the isobutyl groups are not. Similar reaction schemes lead from monohalocyclopropanes to cyclopropanes.

Since these conversions, catalyzed by metal complexes, often proceed via the formation of free-radical intermediates [3, 4], we posed the problem of investigating the chemically induced dynamic nuclear polarization (CIDNP) in $Zr(acac)_4$-catalyzed GDHCP reduction with *i*-Bu_2AlH in order to reveal homolytic processes in this reaction. The reductions of substituted 1,1-dibromocyclopropanes, namely, benzyl-, phenyl-, and 2,2-dimethyl-1,1-dibromocyclopropanes were chosen to be the model reactions.

EXPERIMENTAL

The reducing agent was a 1 M solution of commercial *i*-Bu_2AlH. NMR measurements were carried out in dioxane-d_8 dried by boiling over sodium followed by distillation. *gem*-Dihalocyclopropanes were synthesized by the Makosha method [5, 6]. The catalysts $Zr(acac)_4$, Cp_2ZrCl_2, and $(BuO)_4Ti$ were prepared in advance.

In order to observe the CIDNP effects, the reactions were carried out just in the sensor of a Tesla BS-467 NMR spectrometer (60 MHz, CW). GDHCP (0.10–0.15 ml) was syringed into an *i*-Bu_2AlH solution (1 M, 0.4 ml) with $Zr(acac)_4$ (3 mg) in a 5-mm NMR tube placed in the NMR sensor at 80°C. After 5–10 s, we began recording the ^1H NMR spectrum. Under the above conditions, multiplet and integrated polarization effects were observed for ~2 min. This time was sufficiently long to record the spectrum in the CW mode

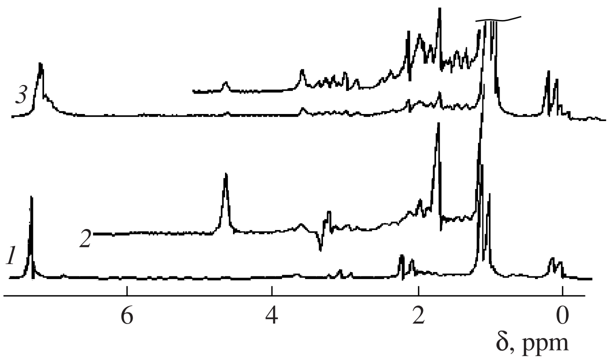


Fig. 1. ^{1}H NMR spectra recorded during the reduction of dibromocyclopropane **Ia**: (*1*) initial i-Bu$_2$AlH solution in dioxane-d$_8$ in the presence of Zr(acac)$_4$, (*2*) reaction mixture in the course of the reaction after addition of 1,1-dibromo-2-phenylcyclopropane at 80°C, and (*3*) reaction products.

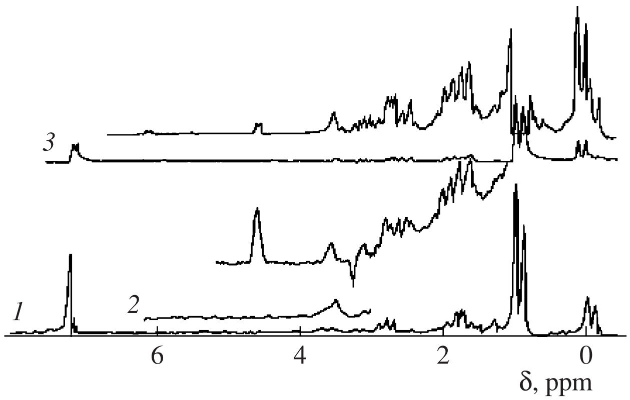


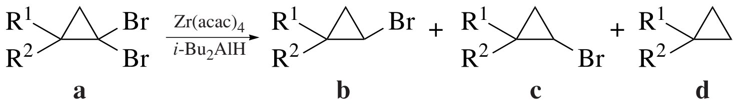
Fig. 2. ^{1}H NMR spectra recorded during the reduction of dibromocyclopropane **IIa**: (*1*) initial i-Bu$_2$AlH solution in dioxane-d$_8$ in the presence of Zr(acac)$_4$, (*2*) reaction mixture in the course of the reaction after addition of 1,1-dibromo-2-benzylcyclopropane at 80°C, and (*3*) reaction products.

several times. In order to rule out signal distortion at a high sweep rate, the frequency was swept in both the forward and backward directions and each experiment was replicated at different recording speeds.

In order to identify the reaction products, the reaction was carried out in a glass flask under conditions described in [2]. The gaseous products were collected in a gasometer and were analyzed on an Agat gas chromatograph (6.8 m × 4 mm column packed with 25% *n*-hexadecane on Celite C-22 (40–60 mesh), ~20°C, thermal-conductivity detector, hydrogen as the carrier gas). The reference was *n*-butane. The reaction between 5 mmol (1.38 g) of 1,1-dibromo-2-phenylcyclopropane and 10 mmol (2.4 ml) of i-Bu$_2$AlH in 10 ml of dioxane in the presence of 0.08 mmol (39 mg) of Zr(acac)$_4$ yielded 77 ml of a gas consisting of isobutane (97%) and isobutylene (3%); that is, the reaction yielded an equimolar amount of gases with respect to the haloalkane reacted for a haloalkane conversion of 73%.

RESULTS AND DISCUSSION

Earlier [1, 2], we found that the reaction of the above 1,1-dibromocyclopropanes with i-Bu$_2$AlH yields a mixture of substituted (**b**) *cis*- and (**c**) *trans*-monohalocyclopropanes and (**d**) cyclopropanes ([**b**] : [**c**] : [**d**] = 4 : 3 : 2).



I: R^1 = H, R^2 = PhCH$_2$; **II**: R^1 = H, R^2 = Ph; **III**: R^1 = CH$_3$, R^2 = CH$_3$

Scheme 2.

The structures of the resulting cyclopropanes **b**–**d** (**I**–**III**) were determined by spectroscopic methods and by comparison with known samples.

At 20°C, the dibromocyclopropanes are reduced slowly and the reaction is complete in 6 h, while, for the detection of the polarization effects, it is necessary that the reaction be complete in a few minutes. After raising the temperature of the reaction mixture (0.5 ml of 1 M i-Bu$_2$AlH in dioxane-d$_8$, 0.1 ml of GDHCP, and 2–3 mg of Zr(acac)$_4$) to 80°C, the reduction rate is much higher and is sufficient for the CIDNP effect to be recorded.

The ^{1}H NMR spectra indicating the CIDNP effects for compounds **Ia**, **IIa**, and **IIIa** are shown in Figs. 1–3.

It is noteworthy that all the spectra show both the integral polarization (IP) and multiplet polarization (MP) of protons.[1] The integrally polarized signals at 4.63 and 1.75 ppm, with a positive phase, are due to the protons of isobutylene that has resulted from the reaction and has dissolved in the reaction mixture. Indeed, the gaseous products contain ~2% isobutylene apart from isobutane. Obviously, polarized isobutylene forms from the isobutyl radical, which accumulates

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[1] The integral polarization of nuclei in NMR spectra is observed as a substantial strengthening of the absorption signal (positive phase, absorption, A) from the polarized nucleus or as a negative electromagnetic emission signal (negative phase, emission, E). Multiplet polarization with phase EA is the negative polarization of the left-hand (low-field) side of the signal from the polarized nucleus and the positive polarization of the right-hand (high-field) side of the signal. Phase AE corresponds to opposite polarization.

polarization in the radical pair (RP1) with a heteroradical (X) characterized by a *g*-factor of $g(X) \neq g(i\text{-Bu})$ [7]. Since no other signal with IP was observed, it was impossible to identify the heteroradical from these spectra.

For all of the three reactions examined, we observed MP with phase EA for the signal at 3.27 ppm. This polarized doublet is due to the methylene protons of isobutyl bromide. The two other signals from *i*-BuBr must also be polarized, but they cannot be observed because they are masked by stronger lines from the reaction mixture. MP is known to appear in pairs of radicals with similar or equivalent *g*-factors. Therefore, the MP of the methylene protons of *i*-BuBr appears in the radical pair of two isobutyl radicals (RP2). RP2 can result from a random encounter of isobutyl radicals diffusing in the solution:[2]

$$\underset{\text{RP2}}{\overline{(CH_3)_2CH\dot{C}H_2\ \ \dot{C}H_2CH(CH_3)_2}^{\,F}}$$

$$\xrightarrow{\text{dissociation}} (CH_3)_2CH\overset{\bullet EA}{C}H_2 \xrightarrow{\text{SBr}} (CH_3)_2CH\overset{EA}{C}H_2Br.$$

The dissociation of RP2 yields two polarized isobutyl radicals. Abstracting a bromine atom from 1,1-dibromocyclopropane, these radicals form *i*-BuBr with MP. The phase of MP predicted by applying Kaptein's rule [7] to this scheme is in agreement with the experiment.

The disproportionation of RP2 yields isobutylene and isobutane, and its recombination yields isooctane:

$$\text{RP2} \xrightarrow{\text{disproporcionation}} (CH_3)C{=}CH_2 + (CH_3)_2CHCH_3,$$

$$\text{RP2} \xrightarrow{\text{recombination}} (CH_3)CHCH_2CH_2CH(CH_3)_2.$$

These hydrocarbons must also show MP, but it cannot be observed in their spectra. The MP of isobutylene is masked by more intense IP, and the signals of isobutane and isooctane are overlapped with the strong signals from other components of the reaction mixture. Further evidence of the formation of a diffusion pair of isobutyl radicals is the formation of considerable amounts of isooctane, which was identified in the reaction mixture by GC-MS.

Note that, in all cases, the negatively polarized, left-hand line of the doublet from the Ch_2-group protons in *i*-BuBr has a significantly larger amplitude than the positively polarized, right-hand line. In the case of pure MP, the amplitudes of the negatively and positively polarized lines are generally equal. Therefore, the superposition of MP with phase EA and IP with phase E takes place in *i*-BuBr. It is likely that the isobutyl radical resulting from RP1 dissociation acquires negative IP. In solution, it forms a diffusion RP2 in which it has MP. Since the negative polarization of the isobutyl radical results from RP1 dissociation, it can be assumed that the opposite (positive) polarization of isobutylene results from the intracellular interaction (RP1 disproportionation) of the isobutyl radical with another, unidentified heteroradical:

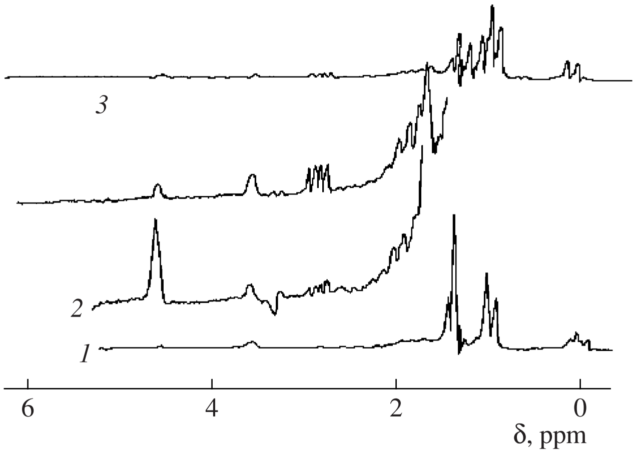

Fig. 3. ^{1}H NMR spectra recorded during the reduction of dibromocyclopropane **IIIa**: (*1*) initial *i*-Bu_2AlH solution in dioxane-d_8 in the presence of $Zr(acac)_4$, (*2*) reaction mixture in the course of the reaction after addition of 1,1-dibromo-2,2-dimethylcyclopropane at 80°C, and (*3*) reaction products.

$$\underset{\text{RP1}}{\overline{(CH_3)_2CH\overset{\bullet\bullet}{C}H_2X}^{\,S}}$$

$$\xrightarrow{\text{disproportionation}} (\overset{A}{C}H_3)_2C{=}\overset{A}{C}H_2 + \overset{E}{X}H.$$

Positively polarized signals from isobutylene hydrogen atoms are observed in the experiment. The dissociation of this RP1 yields the isobutyl radical whose methylene protons are negatively polarized:

$$\text{RP1} \xrightarrow{\text{dissociation}} (CH_3)_2CH\overset{\bullet E}{C}H_2 + \dot{X}.$$

It can be assumed with good reason that this RP1 is geminal; that is, the resulting radicals are in one cell at the instant they appear. Therefore, the RP1 must be singlet. Based on this assumption and the experimentally determined polarization signs, we can estimate the *g*-factor of the heteroradical using Kaptein's rule. For the protons of the CH_2 group of isobutylene [7],

$$\Gamma_{\text{int}} = \mu\varepsilon\Delta g a_i > 0.$$

In this relationship, $\mu = +1$ if the precursor of the molecule is a triplet pair and $\mu = -1$ if the precursor is a singlet pair; $\mu = +1$ for the recombination or disproportionation product and $\varepsilon = -1$ for the conversion product of the radicals that have left the pair; Δg determines the sign of the difference between the *g*-factors of the radicals in the pair; a_i determines the signs of the hyperfine coupling constants for the radicals. $\Gamma > 0$ corresponds to positive polarization (A); $\Gamma < 0$, to negative polarization (E).

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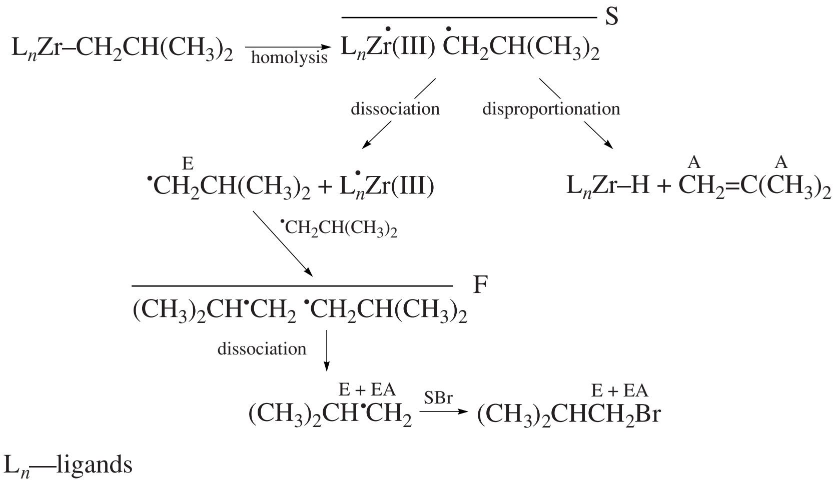
[2] $\overline{\dot{R}_1\dot{R}_2}^{\,F}$ will designate a diffusion RP; $\overline{\dot{R}_1\dot{R}_2}^{\,S}$, a singlet RP.

In our case, $\mu < 0$ since we assume that RP1 is singlet, $\varepsilon > 0$ since isobutylene is an intracellular product, and $a_i < 0$ since the hyperfine coupling constant for the nuclear spins of the CH_2 hydrogen atoms of the isobutyl radical, with an unpaired electron, is negative [8]. As a result, we obtain

$$\Gamma_{\text{int}} = (-)(+)\Delta g(-) > 0.$$

For Γ_{int} to be positive, Δg must also be positive. In other words, the above suggests that the g-factor of the heteroradical is smaller in magnitude than the g-factor of the isobutyl radical. The g-factors of most heteroradicals, including the organic radicals considered, in which the unpaired electron is localized on an oxygen atom or on a carbon atom bonded to an oxygen or a bromine atom, are much larger than the g-factor of the isobutyl radical (g = 2.0026). According to the literature [9], one of the paramagnetic centers in the system examined can be a Zr(III) complex with g = 1.96. This led us to conclude that the other paramagnetic center in RP1, which is responsible for IP in isobutylene, is likely an intermediate, catalytically active Zr(III) complex. In this case, RP1 obviously results from the homolysis of the C–Zr bond. The CIDNP effect can then be explained by the following scheme:



Scheme 3.

Note that CIDNP in a radical pair involving a paramagnetic ion of ^{119}Sn was observed in the reactions of the *tert*-butylstannyl anion with n-BuBr and n-BuI [10].

Nuclear polarization in the reaction examined is observed for hydrogen atoms of the isobutylene and i-BuBr molecules and is not detected in the dehalogenation products **b–d** (**I–III**). Therefore, under our experimental conditions, these products are not directly involved in free-radical processes.

From the CIDNP data, we infer that the reaction yields labile zirconium compounds containing isobutyl groups that initially belonged to the starting i-Bu_2AlH. Since some authors [7, 8] hold that the isobutyl groups do not participate in the reaction, we examined its gaseous products.

It was found that, for all GDHCPs, the amount of gaseous products resulting from dehalogenation is 1 mol per mole of GDHCP reacted. Isobutane and isobutylene were identified among the gaseous products. The complex $Zr(acac)_4$ or Cp_2ZrCl_2 can be used in place of $Zr(acac)_4$ without loss in efficiency [1, 2]. The equally large amount of gaseous products of the same composition forms in the presence of these catalysts. However, no CIDNP was observed in these cases. This can be explained by the fact that, for a CIDNP effect to take place, the lifetime and the relaxation times of the spin of the unpaired electron of the paramagnetic centers constituting the RP must not be shorter than 10^{-9} s [7]. These conditions are likely satisfied only by the paramagnetic complexes $L_nZr(III)$ that result from $Zr(acac)_4$, since it is known that these zirconium(III) complexes are characterized by well-resolved EPR spectra consisting of narrow lines [11].

Thus, the above data suggest that the isobutyl groups of the initial i-Bu_2AlH are directly involved in the catalytic process, forming an unstable i-Bu–Zr bond. The earlier postulated scheme 1 does not imply the participation of the isobutyl group in the reaction. Therefore, further studies are necessary to determine the structure of the zirconium complex and to elucidate its role in the catalysis of the main process of GDHCP dehalogenation.

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