Organometallics **1999,** *18,* 2941−2943

Mechanism of the Reaction of Tri-*n*-butylstannyl Anion with *n*-Butyl Bromide and Iodide As Studied by the ^{119}Sn CIDNP Technique

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Received February 12, 1999

Summary: The mechanism of the reaction of the tri-n-butylstannyl anion with n-butyl bromide and iodide in THF was studied by the chemically induced dynamic nuclear polarization (CIDNP) technique. Strong ^{119}Sn CIDNP spectra were observed for the first time. The emissive CIDNP phase of the tetra-n-butylstannane proves that radical intermediates are involved in the present reactions.

The mechanism of the reactions of organostannyl anions with alkyl halides has received considerable attention over the past half-century.[1−4]

$$R_3SnM + R'X \rightarrow R_3SnR' + MX \qquad (1)$$
$$M = Li, Na, K; X = Cl, Br, I$$

Because this reaction often has shown unexpected behavior with respect to yields and stereochemistry,[5,6] extensive studies have been carried out on the stereochemical course of such reactions and on quantitative analyses of product distributions.[1−6] Three basic mechanistic pathways have been proposed: (1) classical S_N2 substitution, (2) a radical pathway (initial electron-transfer process from the anion to the halide, leading to radical intermediates), and (3) an ionic pathway (initial halogen−metal exchange, leading to carbanion intermediates).[1−4] For reactions of the tri-*n*-butylstannyl anion with *n*-butyl bromide and iodide, it was reported that both the classical S_N2 substitution and a radical pathway are involved.[2,7]

An important approach to the question of the mechanism of such reactions is that of direct observation of a reaction intermediate. However, there have been few reports concerning intermediates in such reactions. Recently, we carried out stopped-flow measurements of the reaction of tri-*n*-butylstannyl anion with *s*- and *tert*-butyl bromides and iodides and succeeded in the direct observation of the tri-*n*-butylstannyl radical for the first time.[8] However, in the case of the reactions with *n*-butyl halides, the formation of a stannyl radical could not be observed. Thus, to this day, a reaction intermediate of the title reactions has not been observed directly, and so the reaction mechanism is still unclear.

Chemically induced dynamic nuclear polarization (CIDNP) is the most powerful technique for studying radical reactions.[9−16] The appearance of enhanced absorption or emission in the NMR spectra of products generated through a radical pathway gives vital details concerning the reaction mechanism. Therefore, extensive ^{1}H and ^{13}C CIDNP studies have been carried out for many types of photochemical reactions.[15,17] However, such CIDNP techniques are inappropriate for fast thermal reactions.[18] This is so because it is necessary to use a sample flow system, in which the reactants are mixed in an NMR tube placed in an NMR spectrometer, and to remove the reaction products continuously from the NMR tube during signal accumulation. Since, in such a flow system, the NMR tube cannot be rotated, the resolution and sensitivity of the ^{1}H and ^{13}C NMR spectra are much lower than usual.[19] We chose to apply the ^{119}Sn CIDNP technique[20] and found strong CIDNP spectra of the reaction products. Especially, the emissive ^{119}Sn CIDNP phase of the main product, tetra-*n*-

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[18] In the case of slow thermal reactions, ^{1}H and ^{13}C CIDNP spectra have been easily observed.[9,10]

[19] In the present reactions, moreover, an insoluble salt (KX) was generated in the NMR tube. Thus the resolution and sensitivity of the ^{1}H and ^{13}C NMR spectra were very low, and the ^{1}H and ^{13}C CIDNP spectra could not be observed.

[20] The chemical shift (~600 ppm) and relative sensitivity (2.23 times larger than that of ^{13}C) of ^{119}Sn NMR are much larger than those of ^{1}H and ^{13}C NMR.

10.1021/om990094p CCC: $18.00

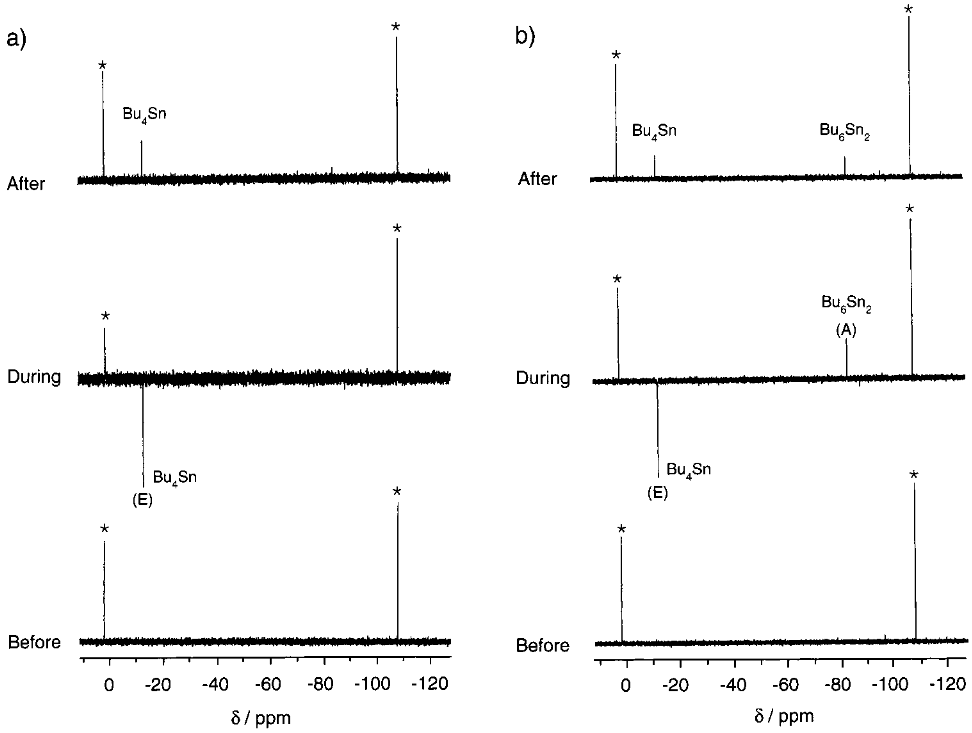

Figure 1. NMR spectra observed for the reaction of the tri-*n*-butylstannyl anion with (a) n-BuBr and (b) n-BuI in THF. The signals denoted by * are Et_4Sn (+2.2 ppm) and Me_6Sn_2 (−109 ppm).

butylstannane, proves that radical intermediates are involved in the present reactions.

Tri-*n*-butylstannylpotassium, the stannyl anion reagent used, was prepared by reaction of hexa-*n*-butyldistannane ($Bu_3SnSnBu_3$, Aldrich Chemical Co.) with potassium in dry THF under an argon atmosphere at 0 °C.[21]

$$Bu_3SnSnBu_3 + 2K \rightarrow 2Bu_3Sn^- K^+ \qquad (2)$$

The CIDNP spectra measurements were carried out with a 500 MHz FT-NMR instrument (JEOL α-500).[22] THF-d_8 was used as a lock substance. Tetraethylstannane (Et_4Sn; δ +2.2 ppm) and hexamethyldistannane (Me_6Sn_2; δ −109 ppm) were used as internal standards for the chemical shifts[23] and the signal phase. THF-d_8, Et_4Sn, and Me_6Sn_2 were placed in a capillary (1 mm), which was fixed in the NMR tube (5 mm). The THF solutions of the stannyl anion and the alkyl halide were separately charged into the NMR tube and mixed in the NMR spectrometer.[24] The concentrations of tri-*n*-butylstannyl anion and alkyl halide in the employed THF solutions were (2.5−2.9) × 10^{-1} and 5.4 × 10^{-1} mol dm^{-3}, respectively.

The ^{119}Sn NMR spectra of the reaction of the stannyl anion with *n*-butyl halides in THF were measured at room temperature. Although the *J*-coupling between tin and proton would give the polarization by the multiplet effects, to observe a simple ^{119}Sn CIDNP spectrum, ^1H decoupling was employed. The ^{119}Sn NMR spectra obtained before, during, and after reactions of the stannyl anion with n-BuBr and n-BuI are shown in Figure 1. Several new signals were observed in the spectra obtained during and after the reactions. On the basis of NMR data reported in the literature,[25] the signals observed at −12 and −83 ppm can safely be assigned to the ^{119}Sn resonances of tetra-*n*-butylstannane (Bu_4Sn) and hexa-*n*-butyldistannane (Bu_6Sn_2), respectively. The main signal due to Bu_4Sn shows strong emission (*E*). In addition, the signal due to Bu_6Sn_2, observed in the reaction with n-BuI, shows enhanced absorption (*A*).[26]

Although the S_N2 pathway cannot be wholly excluded, these polarized signals prove that the formation mechanisms of Bu_4Sn and Bu_6Sn_2 involve radical pathways. Therefore, the mechanism of the n-Bu_3SnK/n-BuX reaction can be rationalized as shown in Scheme 1. In the primary process, the stannyl radical and the alkyl halide anion radical are generated. Since electron transfer to *n*-butyl bromide and iodide is dissociative,[4] the *n*-butyl radical and halide anion are generated immediately. In the cage, the tri-*n*-butylstannyl and *n*-butyl radicals couple to form Bu_4Sn. However, the stannyl radicals can partially escape from the cage. Those that escape may couple with each other, resulting in formation of n-Bu_6Sn_2.

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(21) Tri-*n*-butylstannylpotassium was prepared similarly to the preparation of trimethylstannylsodium as described in ref 5. In a typical reaction, 5.30 g (136 mmol) of finely cut potassium was added to 300 mL of dry THF. Hexa-*n*-butyldistannane, 25.0 g (43.1 mmol), was added, and the mixture was stirred at 0 °C for 3−4 h. All procedures were carried out under an argon atmosphere.

(22) ^{119}Sn spectra were taken with an observed frequency of 186.4 MHz, a scan range of 26109.66 Hz, and an acquisition time of 1.255 s. The total interval of one scan including the signal acquisition was 5.055 s. The pulse width was 5.6 μs (as a 90° pulse). Typically, the signal was accumulated 64 times. Thus, the total time required to record a spectrum was about 5.4 min. The peak width of Bu_4Sn was 6.6 Hz.

(23) The chemical shifts are given as δ values with tetramethylstannane as standard.

(24) THF solutions of the stannyl anion and alkyl halide flowed through an NMR tube with a flow rate of 0.5−1.0 mL/s.

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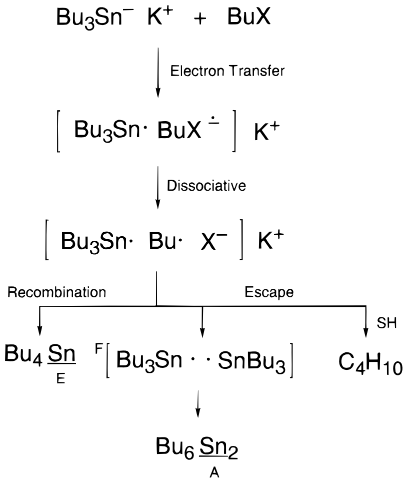
(26) In the case of the reaction with n-BuBr, we could not observe a clear CIDNP spectrum of n-Bu_6Sn_2. This may be due to the low yield of n-Bu_6Sn_2.

Scheme 1



The polarization observed in the present reaction cannot be explained by Kaptein's CIDNP phase rule with the high-field approximation, in which only $S-T_0$ transition is considered.[27] This is so because the ^{119}Sn hyperfine coupling (hfc) constant in the trialkylstannyl radicals ($a(^{119}\text{Sn}) = -0.161$ T)[28] is not small compared to the electronic interaction in the radical pairs ($\Delta gB = (g(\text{Bu}_3\text{Sn}^\bullet)^{29} - g(\text{Bu}^\bullet)^{30}) \times B = (2.016-2.0027) \times 11.74$ T $= 0.156$ T), and the high-field approximation breaks down in the rule. For a quantitative analysis of the ^{119}Sn CIDNP spectra, one should use the stochastic Liouville equation including $S-T_{-1}$ and $S-T_{+1}$ transitions and all necessary interactions,[15,31] but this is beyond the scope of the present paper. However, from the experimental and theoretical results reported previously,[32] the qualitative features of the ^{119}Sn CIDNP spectra for the reactions of trialkylstannyl radicals ($\Delta g > 0$, $a < 0$) can be summarized as follows: (1) in-cage and out-of-cage products show the same polarization, (2) the products generated from a triplet radical pair or a free pair show enhanced absorption, and (3) the distannane generated from a free pair shows enhanced absorption. In the present reactions, if the geminate radical pair of the stannyl and *n*-butyl radicals is a triplet one, the in-cage product of n-Bu_4Sn is expected to show enhanced absorption. As shown in Figure 1, n-Bu_4Sn, however, shows emission. Therefore, the geminate radical pair is considered to be a singlet radical pair. On the other hand, n-Bu_6Sn_2 is considered to be formed from a free pair of two stannyl radicals.

According to the CIDNP technique, a small amount of polarized species can give a strong CIDNP spectrum. To avoid such over interpretation of ^{119}Sn CIDNP, quantitative analyses of products also were carried out. The reactions of the tri-*n*-butylstannyl anion with *n*-butyl bromide and iodide gave n-Bu_4Sn (94% (with n-BuBr) and 69% (with n-BuI)), n-Bu_6Sn_2 (2% (with n-BuBr) and 30% (with n-BuI)), and butane.[33] The formation of n-Bu_6Sn_2[34] and butane is consistent with the intermediacy of the tri-*n*-butylstannyl and *n*-butyl radicals. In the presence of dicyclohexylphosphine (2.4 M), which is a well-known radical trap,[2,7] the yields of n-Bu_4Sn dropped to 74% (with n-BuBr) and 55% (with n-BuI).[35] From these results, the yield of n-Bu_4Sn generated through the radical pathway is at least 20%, but it is considered to be much larger.[36]

Finally, the coupling rate constant of the geminate radical pair is considered. From the experiments with a cyclizable radical probe, in which both cyclic and unrearranged products were generated, Ashby and coworkers reported that the reaction of alkyl halide with trimethylstannyl anion proceeded by an electron-transfer process involving radical intermediates.[7] This means that the rate of the coupling reaction of the geminate radical pair is comparable to that of cyclization of the radical probe. San Filippo and Silbermann, however, suggested that the rate of cyclization (10^5 s^{-1}) is 10^{4-5} times smaller than that of the diffusion-controlled coupling reaction (10^{9-10} s^{-1}).[6] Furthermore, Newcomb and Curran reported that the observation of rearranged products in a cyclizable radical probe experiment does not provide conclusive evidence for an electron-transfer process involving radical intermediates, because its intermediates may not always be on the direct pathway between reactants and products.[3] Thus, the geminate coupling process is considered to be much faster than that reported by Ashby and coworkers. In the present study, the rate constant of the coupling reaction was considered to be as fast as 10^{9-10} s^{-1}, because it is necessary for the appearance of the CIDNP that the rate constant of the coupling reaction of the radical pair is comparable to that of the singlet−triplet spin conversion due to the hyperfine coupling mechanism (10^{9-10} s^{-1}).[15] It is noteworthy that the CIDNP technique is much more powerful for determination of the radical pathway than the cyclizable radical probe.

In the present study, we found the strong emissive CIDNP signal of the main product of n-Bu_4Sn. This result proves that the reactions of the tri-*n*-butylstannyl anion with *n*-butyl bromide and iodide involve a radical pathway. It is expected that the ^{119}Sn CIDNP technique can systematically clarify the mechanisms of reactions of organostannyl anions with many other halides.

Acknowledgment. We thank Prof. Hisaharu Hayashi (The Institute of Physical and Chemical Research) for his encouragement. M.W. thanks a partial support from the President's Special Research Grant of The Institute of Physical and Chemical Research.

OM990094P

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(33) Not quantified.

(34) Although product analyses have been made extensively in previous studies, the formation of hexaalkyldistannane was not reported. In the present study, an aliquot was treated with excess water and unreacted hexa-*n*-butyldistannane was found to be present in only trace yield (<1%) by GLC using a Rtx-1 capillary column (Restek Co., 15 m × 0.25 mm). Thus, it is clear that hexa-*n*-butyldistannane is the product derived from coupling of the stannyl radicals.

(35) Similar decreases in the yields of substituted products were already reported in refs 2 and 7.

(36) Since the coupling of the geminate radical pair is very fast (10^{9-10} s^{-1}), DCPH could not trap all *n*-butyl radicals in the pair. If the coupling and trapping rate constants are 1×10^{10} s^{-1}and 1×10^9 s^{-1} M^{-1}, respectively, four-fifths of the radical pairs cannot be trapped by DCPH (2.4 M).

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