Registry No. 1-Bromopentane, 110-53-2; 1-chloropentane, 543-59-9; 1-iodopentane, 628-17-1; 1-bromooctane, 111-83-1; 1-chlorooctane, 111-85-3; benzyl chloride, 100-44-7; 1-bromo-3-methylbutane, 107-82-4; 1-bromo-3,3-dimethylbutane, 1647-23-0; 1,4-dibromobutane, 110-52-1; 2-bromopentane, 107-81-3; 3-bromopentane, 1809-10-5; ethyl bromoacetate, 105-36-2; hexanenitrile, 628-73-9; nonanenitrile, 2243-27-8; phenylacetonitrile, 140-29-4; 4-methylpentanenitrile, 542-54-1; 4,4-dimethylpentanenitrile, 15673-05-9; hexanedinitrile, 628-73-9; 2-methylpentanenitrile, 6339-13-5; pentyl phenyl sulfide, 1129-70-0; dipentyl sulfide, 872-10-6; pentyl thiocyanate, 32446-40-5; dibenzyl sulfide, 538-74-9; benzyl thiocyanate, 3012-37-1; 1-iodooctane, 629-27-6; 2-iodooctane, 557-36-8; 1-iodo-3-methylbutane, 541-28-6; 1-iodo-3,3-dimethylbutane, 15672-88-5; 1,4-diiodobutane, 628-21-7; benzyl iodide, 620-05-3; 1-azidopentane, 26330-06-3; 2-azidopentane, 73746-39-1; benzyl azide, 622-79-7; dibromomethane, 74-95-3; pentyl phenyl ether, 2050-04-6; 3-methylbutyl phenyl ether, 1129-64-2; catechol diphenyl ether, 3379-37-1; 1-pentoxy-2-isopropylbenzene, 73746-40-4; 1,3-benzodioxole, 274-09-9; pentyl acetate, 628-63-7; benzyl acetate, 140-11-4; polystyrene, 9003-53-6; diethyl sodiomalonate, 996-82-7.

Communications

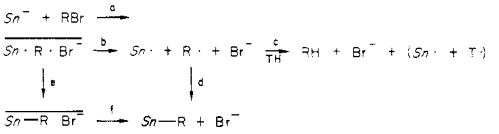
Estimation of Electron-Transfer Contributions in Reactions of Alkyl Bromides with (Trimethyltin)sodium

Summary: Estimates of the minimum degrees of electron-transfer contributions to the mechanisms of reaction of primary, secondary, and tertiary alkyl bromides with (trimethyltin)sodium have been obtained by the use of dicyclohexylphosphine as a free-radical trap.

Sir: Several mechanisms have been proposed[1] for the reactions of organic halides with organotinalkalis. These proposals have been based on stereochemical observations,[2-4] anion trapping,[5,8] kinetics,[6] and the formation of rearranged products.[4b,7] Because ionic or radical[5] intermediates are indicated in certain cases, we have sought to apply simple trapping techniques for their identification.

In the case of free radicals, successful trapping would have an advantage over CIDNP and ESR in providing a measure of the extent of their involvement, which would be quantitative if the trapping occurred with unit efficiency. A simple electron-transfer mechanism is shown in Scheme I, where *Sn* = Me_3Sn, the cation is omitted, and the electron transfer is assumed to be dissociative.

Scheme I



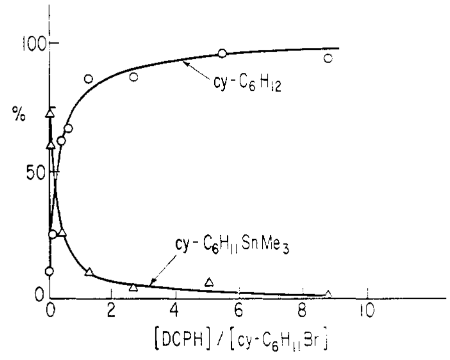


Figure 1. Effect of dicyclohexylphosphine on the yields of cyclohexane and cyclohexyltrimethyltin: THF solvent at 0 °C, cyclohexyl bromide, 0.54 M for first four points, 0.20 M for last two.

Previous stereochemical studies on substituted bromocyclohexanes suggest predominant or exclusive reaction by an electron-transfer mechanism.[5] We now have observed that cyclohexane (10%), cyclohexene (9%), dicyclohexyl (trace), and trimethylcyclohexyltin (73%) were the products from reaction of bromocyclohexane and (trimethyltin)sodium in THF at 0 °C. These results also support an electron-transfer mechanism. Because Sn^- is a good base,[9] a powerful nucleophile,[10] and good reducing agent,[11] the choice of a suitable radical trap is severely restricted. However, the commercially available dicyclohexylphosphine (DCPH) was selected because the P–H bond dissociation energy in PH_3 is about 77 kcal/mol, so hydrogen abstraction from the phosphine by R· should be exothermic and rapid. In Figure 1 are shown the results obtained with bromocyclohexane from a series of reactions in which the DCPH concentration was varied. It is seen that the cyclohexane yield increases and the cyclohexyltrimethyltin yield decreases as the DCPH concentration is increased.

Concomitantly the yields of cyclohexene and dicyclohexyl fall to undetectable values. At the highest [DCPH]/[Sn^-]$_0$ value (8.81), the only product observed is cyclohexane, indicating negligible geminate or direct displacement reaction under these conditions. The results

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of a similar series of experiments with 2-bromobutane gave a plot similar to Figure 1, with the difference that at the highest $[\mathrm{DCPH}/Sn^-]_0$ value 17% 2-butyltrimethyltin was formed, suggesting some residual direct displacement (although any geminate reaction would also be included in this value).

1-Bromoadamantane reacts with (trimethyltin)sodium in THF to yield 95% trimethyladamantyltin. The same yield is obtained in liquid ammonia as solvent. Bromobenzene, which has been shown to react by way of phenyl anion intermediates, yields 95% benzene in liquid ammonia. Thus an anion mechanism is unlikely for bromoadamantane. Its reaction with (trimethyltin)sodium in THF in the presence of varying concentrations of DCPH resulted in a decrease in yield of the substitution product to ca. 2% and an increase in the yield of adamantane to 98% in the presence of a threefold or greater excess of DCPH over $(\mathrm{Me_3Sn})\mathrm{Na}$ initial concentration. Consequently a possible multicenter mechanism can be excluded in favor of one involving free admantyl radicals, as in Scheme I. The simple tertiary triethylcarbinyl bromide yielded less unambiguous results. In the absence of trap the products were 46% 3-ethyl-2-pentene and 53% 3-ethylpentane. In the presence of excess (4.6-fold) DCPH the yields changed to 32% alkene and 67% alkane. The nearly equal product distribution in the first example suggested disporportionation of triethylcarbinyl radicals. However, only 14% of these were diverted to alkane by the DCPH as indicated by the increase in yield from 53% to 67%. It may be that adamantyl radicals, which should be more reactive, are less hindered from the front side because they are pyramidal, and do not undergo disporportionation, are efficiently trapped. The triethylcarbinyl radicals, being more stable, probably planar, and somewhat sterically hindered, react by disproportionation in effective competition with being trapped. The relatively high concentrations of radicals which might form in this fast reaction, and the low value of 60 kcal/mol[12] for the bond dissociation energy of the β-C–H bond in carbon radicals may be crucial in this case.

When we examined primary bromides under the reaction conditions used, only substitution was observed with simple cases such as *n*-butyl and isobutyl, both in the presence and absence of DCPH. These are presumably S_N2 reactions. When sufficient steric hindrance was introduced to slow down this mechanism sufficiently, as in the case of neopentyl bromide, the results changed. In the absence of trap, 99% substitution product and about 1% neopentane were formed. With a 4.1-fold excess of DCPH, 58% substitution product and 40% neopentane were observed as products. When *tert*-butylamine was present in 9-fold excess, 8% neopentane was formed.[13] As the amine did not function as a trap in the experiments cited above, this suggests that 8% of this reaction proceeded by an anion intermediate mechanism, 32% proceeded by the radical mechanism of Scheme I, and the remainder by S_N2 and geminate reactions.

Bock and Whitesides observed about 80% inversion in the reaction of (trimethyltin)lithium in THF at 0 °C with 1-bromo-3,3-dimethylbutane-*1,2*-d_2.[2e] The less than quantitative inversion may be due to the incursion of an electron-transfer mechanism due to the steric hindrance to the S_N2 mechanism introduced by the presence of the *tert*-butyl group.

Several control experiments were conducted to test the validity of the results reported above.[13] DCPH did not react with the halides under the reaction conditions. 1-Bromoadamantane was observed to react at a slightly slower rate in the presence of DCPH than in its absence. This implies that it functions as a trap only after the rate-determining step. Because the retardation in rate is relatively small, a free radical chain mechanism of the SR_N1 type is not involved. Also, in experiments in which either DCPH or 1-bromoadamantane was initially present in a concentration higher than that of $\mathrm{Me_3SnNa}$, the amount of bromide which reacted did not exceed that of tin anion used.

In conclusion, we have shown that DCPH can function as an efficient free-radical trap and thus provide information on the minimum degree of participation of a free-radical mechanism in the reaction of halides with a trimethyltin anionoid. By extension it should be applicable to other nucleophiles whose conjugate acids have pK_a's less than that of DCPH (about 38) and to substrates other than halides.

Acknowledgment. We are grateful to the National Science Foundation for support of this work.

Registry No. Cyclohexane, 110-82-7; cyclohexene, 110-83-8; (trimethylcyclohexyl)tin, 3531-48-4; bromocyclohexane, 108-85-0; (trimethyltin)sodium, 16643-09-7; dicyclohexylphosphine, 829-84-5; 1-bromoadamantane, 768-90-1; (trimethyladamantyl)tin, 51533-74-5; bromobenzene, 108-86-1; benzene, 71-43-2; 2-bromobutane, 78-76-2; (2-butyltrimethyl)tin, 15095-79-1; adamantane, 281-23-2; triethylcarbinyl bromide, 73908-04-0; 3-ethyl-2-pentene, 816-79-5; 3-ethylpentane, 617-78-7; butyl bromide, 109-65-9; *iso*-butyl bromide, 78-77-3; neopentyl bromide, 630-17-1; (trimethyl neopentyl)tin, 55204-72-3; neopentane, 463-82-1.

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[13] In the reaction of (trimethyltin)sodium with bromobenzene, *tert*-butylamine was shown to be as effective as *tert*-butyl alcohol[8] in trapping phenyl anions. Only 3% loss of (trimethyltin)sodium (p*Ka* ~25)[9] occurred in the presence of dicyclohexylphosphine in 24 h. The very fast reaction of the anion with 1-bromobutane to form 1-butyltrimethyltin quantitatively was used for analysis.

N-Nitrosoenamines, Versatile New Synthesis Intermediates[1]

Summary: *N*-Nitrosoenamines are reactive toward nucleophilic reagents such as dialkylcopper lithium and enolate ions, as well as being active in electrophilic reactions such as acid-catalyzed additions.

Sir: We have recently reported[2] several convenient preparations of *N*-nitrosoenamines (α,β-unsaturated nitrosamines). These novel substances have proven to be very useful intermediates for the synthesis of a number of interesting substances and hold the promise of much wider exploitation. We present here some representative reactions which will serve to illustrate the versatility of these reagents. It should be remembered that the nitroso

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