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# Reduction of Alkyl Halides by Organotin Hydrides[1,2]

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Alkyl halides are reduced by organotin hydrides in the order RI > RBr > RCl > RF. Butyl- and phenyltin hydrides follow the reactivity sequence $(C_6H_6)_2SnH_2 \cong n\text{-}C_4H_9SnH_3 > (C_6H_5)_3SnH \cong (n\text{-}C_4H_9)_2SnH_2 > (n\text{-}C_4H_9)_3SnH$. Geminal polyhalides undergo stepwise reduction. Vicinal dibromides undergo elimination. Halo ketones can be dehalogenated in high yields. The use of organotin groups as hydrogen transfer agents has been realized.

In the course of their exploration of the addition of organotin hydrides to olefins van der Kerk, *et al.*, observed that triphenyltin hydride and allyl bromide underwent reaction to form propene and triphenyltin bromide.[4-6] They and others observed also that alkyl,[2,5-9] cycloalkyl,[2,9] acyl,[5,10] and aryl[6,11] halides can be reduced by organotin hydrides. Our interest in the reactions of organotin hydrides, particularly from the mechanistic standpoint, led us into an investigation of the reductions of alkyl and acyl halides. When this work was initiated only the publications of van der Kerk and his colleagues had appeared, so it seemed most appropriate to begin with an examination of the scope of the reduction of alkyl halides. Results of this study are reported herein.

A general survey of the scope of the reduction reaction, results of which are summarized in Table I, embraced more than twenty different halides and three organotin hydrides. Several characteristics of the reaction can be inferred from the results. The reactivity sequence for halides is RI > RBr > RCl > RF. *n*-Heptyl iodide (item 20) is reduced more easily than *n*-octyl bromide (item 4). Benzyl bromide (item 1) is reduced more readily than benzyl chloride (item 13) and the same order is observed with the phenacyl derivatives (items 9 and 15). Benzotrichloride undergoes exothermic reduction by tri-*n*-butyltin hydride in the absence of a solvent whereas benzotrifluoride is largely unaffected by the hydride after several hours at 80°. Simple alkyl chlorides are reduced with extreme difficulty, compared with the bromides. In addition to those included in Table I isoamyl chloride and propylene chlorohydrin were examined and found to be substantially unaffected by tri-*n*-butyltin hydride at 100° in twenty-four hours. When 1.5 mole per cent of azobisisobutyronitrile[2] was used as a catalyst, however, neophyl chloride was reduced readily at 80° in toluene. Only *t*-butylbenzene was formed, indicating that the neophyl radical reacts more rapidly with the organotin hydride than it rearranges to the 2-methyl-1-phenyl-2-propyl radical.

The efficacy of the azonitrile as a catalyst for the reduction of both alkyl and aryl halides is further revealed by the data in Table II. Cyclohexyl chloride is reduced by tri-*n*-butyltin hydride more than seventy times as fast in the presence of 1.5 mole per cent of azonitrile than in its absence at 80°. Even chlorobenzene, which cannot be reduced effectively with the more reactive triphenyltin hydride (see Table II) at 150°, can be reduced in fair yield, although massive amounts of the azonitrile are required. The radical catalysis obviously broadens the scope of, and makes more convenient, the reduction of organic halides by organotin hydrides.

One of the more striking characteristics of the reaction lies in its utility for the stepwise reduction of geminal polyhalides. Benzotrichloride is cleanly reduced to benzal chloride, which can be reduced in turn to benzyl chloride in high yield. Similar stepwise reductions have been reported recently by other in-

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[2] For a preliminary report on a portion of this work see H. G. Kuivila, L. W. Menapace, and C. R. Warner, *J. Am. Chem. Soc.*, **84**, 3584 (1962).

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TABLE I

REDUCTION OF ORGANIC HALIDES BY ORGANOTIN HYDRIDES

| Item | Tin hydride | Halide | Conditions[a] | % Yield[b] Reduction product | % Yield[b] Organotin halide |
|---|---|---|---|---|---|
| 1 | $(n\text{-}C_4H_9)_3SnH$ | $C_6H_5CH_2Br$ | 4 *M* in ether ex., 12 hr. | 68 | 91 |
| 2 | $(n\text{-}C_4H_9)_3SnH$ | $C_6H_5CH_2CH_2Br$ | 100°, 4 hr. | 85 | 87 |
| 3 | $(n\text{-}C_4H_9)_3SnH$ | Cyclo-$C_6H_{11}Br$ | Ex., 1 hr. | 71 | 94 |
| 4 | $(n\text{-}C_4H_9)_3SnH$ | $n\text{-}C_8H_{17}Br$ | Ex., 1 hr. | 80 | 90 |
| 5 | $(n\text{-}C_4H_9)_3SnH$ | $C_6H_{13}CHBrCH_3$ | Ex., 1 hr. | 78 | 92 |
| 6 | $(n\text{-}C_4H_9)_2SnH$ | *meso*-$(C_6H_5CHBr)_2$ | 100°, 15 hr. | 85[c] | [d] |
| 7 | $(n\text{-}C_4H_9)SnH$ | $CH_3CHBrCH_2Br$ | 4 *M* in pentane, ambient temp., 3 hr. | 81 | 90 |
| 8 | $(n\text{-}C_4H_9)_3SnH$ | $C_6H_5CH{=}CHBr$ | 100°, 4.5 hr. | 35 | 71 |
| 9 | $(n\text{-}C_4H_9)_3SnH$ | $C_6H_5COCH_2Br$ | 4 *M* in $C_6H_6$, ambient temp., 12 hr. | 84[e] | 96 |
| 10 | $(n\text{-}C_4H_9)_3SnH$ | 3-Bromocamphor | 4 *M* in ether, ex., 2 hr. | 61[e] | [d] |
| 11 | $(n\text{-}C_4H_9)_3SnH$ | $(C_6H_5)_3CCl$ | 2 *M* in benzene, ex., 2.5 hr. | 75 | 81 |
| 12 | $(n\text{-}C_4H_9)_3SnH$ | $C_6H_5CHClCH_3$ | 100°, 17 hr. | 77 | 90 |
| 13 | $(n\text{-}C_4H_9)_3SnH$ | $C_6H_5CH_2Cl$ | 150°, 20 min. | 78 | 80 |
| 14 | $(n\text{-}C_4H_9)_3SnH$ | Cyclo-$C_6H_{11}Cl$ | 120°, 40 min. inc. reaction | 36 | [d] |
| 15 | $(n\text{-}C_4H_9)_3SnH$ | $C_6H_5COCH_2Cl$ | 150°, 45 min. | 71[e] | 82 |
| 16 | $(n\text{-}C_4H_9)_3SnH$ | $C_6H_5CHCl_2$ | 180 hr. | 76 | [d] |
| 17 | $(n\text{-}C_4H_9)_3SnH$ | $C_6H_5CCl_3$ | 1.5 *M* in ether, ambient temp., 9 days | 88[f] | [d] |
| 18 | $(n\text{-}C_4H_9)_3SnH$ | $C_6H_5COCH_2Cl$ | 0.8 *M* in benzene, 80°[g] | 99 | [d] |
| 19 | $(n\text{-}C_4H_9)_3SnH$ | $(CH_2)_2C(C_6H_5)CH_2Cl$ | 0.8 *M* in toluene, 80°[h,g] | 95 | [d] |
| 20 | $(n\text{-}C_4H_9)_3SnH$ | $n\text{-}C_7H_{15}\text{-}I$ | 1.5 *M* in bromobenzene, ambient temp., 60 hr. | 95[f] | [d] |
| 21 | $(C_6H_5)_3SnH$ | $C_6H_5CHClCH_3$ | Ex., 19 hr. | 89 | 96 |
| 22 | $(C_6H_5)_3SnH$ | $C_6H_5COCH_2Cl$ | 100°, 1 hr. | 86 | 88 |
| 23 | $(n\text{-}C_4H_9)_2SnH_2$ | $C_6H_5CH_2Cl$ | Ex., 12 hr. | 83 | 96 |
| 24 | $(n\text{-}C_4H_9)_2SnH_2$ | $n\text{-}C_8H_{17}Br$ | Ex.,[h] | 84 | 87 |
| 25 | $(n\text{-}C_4H_9)_2SnH_2$ | $n\text{-}C_6H_{13}CHBrCH_3$ | Ex.,[h] | 99 | 90 |
| 26 | $(n\text{-}C_4H_9)_2SnH_2$ | Cyclo-$C_6H_{11}Br$ | Ex.,[h] | 82 | 87 |
| 27 | $(n\text{-}C_4H_9)_2SnH_2$ | $C_6H_5CH_2Br$ | Ex.,[h] | 60 | 97 |
| 28 | $(n\text{-}C_4H_9)_2SnH_2$ | 3-Bromocamphor | Ambient temp., 60 hr. | 78 | [d] |
| 29 | $(n\text{-}C_4H_9)_2SnH_2$ | $C_6H_5CCl_3$ | Ambient temp., 16.5 hr. | 88 | [d] |
| 30 | $(n\text{-}C_4H_9)_2SnH_2$ | $C_6H_5CH_2Cl$ | Ex.,[h] | 82 | 96 |
| 31 | $(n\text{-}C_4H_9)_2SnH_2$ | $C_6H_5COCH_2Cl$ | 2 *M* in ether | 95[i] | [d] |

[a] Ex.—reactants mixed at room temperature, exothermic reaction; temp. allowed to rise no higher than 50°; no solvent used except where specified. [b] Isolated products, infrared spectra compared with those of authentic samples. [c] *trans*-Stilbene; 92% of theoretical $H_2$ collected. [d] Not isolated. [e] Product unhalogenated ketone only, no alcohol. [f] Yield determined by gas chromatography. [g] 1.5 Mole % azobisisobutyronitrile used as initiator. [h] Reaction mixture allowed to stand a day or more before work-up, reaction probably complete in a few hours at most. [i] Product contained about 3% 1-phenylethanol.

vestigators,[7,8] and it has been pointed out that this is probably the best method available.

The two vicinal dibromides, 1,2-dibromopropane and *meso* stilbene dibromide, which were used in this survey, underwent elimination according to equation 1.[12] Only *trans*-stilbene resulted from *meso* stilbene dibromide.

$$RCHBrCHBrR' + 2\,(n\text{-}C_4H_9)_3SnH \longrightarrow RCH{=}CHR' + H_2 + 2\,(n\text{-}C_4H_9)_3SnBr \quad (1)$$

Rothman and Becker[11] showed that temperatures of 100° or higher are required for reduction of aryl halides in a few hours. Similar low reactivity is indicated for β-bromostyrene (item 8) which yielded 35% of styrene after four hours at 100°. All of the tri-*n*-butyltin hydride was consumed, but 24% of unchanged starting material was isolated suggesting that some of the hydride added to styrene to form β-phenylethyltri-*n*-butyltin.

All of the α-halo ketones were dehalogenated in high yields. The only case in which any alcohol was observed was in the reduction of phenacyl chloride by di-*n*-butyltin dihydride in which case about 3% of 1-phenylethanol was observed. Dehalogenation was the only process observed with γ-chlorobutyrophenone.

TABLE II

AZOBISISOBUTYRONITRILE-CATALYZED REDUCTION OF HALIDE REDUCTIONS BY TRI-*n*-BUTYLTIN HYDRIDE AT 80°

| Halide | Solvent | Time (min.) | % Reduction Uncatalyzed | % Reduction Catalyzed |
|---|---|---|---|---|
| $C_6H_5CH_2Cl$ | $C_6H_5Cl$ | 30 | 26 | 100[a] |
| Cyclo-$C_6H_{11}Cl$ | $C_6H_5CH_3$ | 35 | 1 | 70[a] |
| $C_6H_5Br$ | $C_6H_5CH_3$ | 30 | 4.7 | 41[a] |
| $C_6H_5Cl$ | None | 1290 | None | 64[b] |

[a] Azobisisobutyronitrile, 1.5 mole %. [b] Azobisisobutyronitrile, 16 mole %.

The reactivities of the halides implied by the data in Table I suggested that at least some of the reductions would occur more rapidly with organotin hydrides than with lithium aluminum hydride. Yet it is obvious from the method used in the preparation of the organotin hydrides that reduction of organotin halides by lithium aluminum hydride occurs very rapidly. This suggested that organotin halides might be used as hydrogen carriers as shown in the following equations.

$$\begin{tikzcd}[column sep=small]
LiAlH_4 + & 4R_3SnX \arrow[dr, dashed, leftrightarrow] & \longrightarrow LiAlX_4 + 4R_3SnH & (2) \\
R_3SnH + R'X \longrightarrow R'H + & & R_3SnX & (3)
\end{tikzcd}$$

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[12] More recent work by K. Aso in these laboratories shows that the two bromohydrins derived from propylene are reduced to the corresponding propanols in high yields. Thus, any analogy to zinc dust dehalogenation and dehydroxyhalogenation is a limited one.

The reduction of bromocyclohexane was chosen as a means of testing this hypothesis. To a solution of the halide in refluxing ethyl ether was added an excess of lithium aluminum hydride and 2.5 mole per cent of organotin chloride. The course of reduction with five organotin chlorides is shown in Table III. Stannic chloride and phenyltin trichloride also were used, but no reduction occurred because the corresponding hydrides decomposed too rapidly under the conditions of the experiments. Examination of the results in the table suggests a reactivity sequence for the hydrides as follows: $(C_6H_5)_2SnH_2 \cong n\text{-}C_4H_9SnH_3 > (C_6H_5)_3SnH \cong (n\text{-}C_4H_9)_2SnH_2 > (n\text{-}C_4H_9)_3SnH$. Although this sequence has practical value, its precise significance is doubtful because it is not known what the actual reducing agents are in the case of the di- and trihalides; the role of mixed hydride halides is unknown. This procedure should be a convenient one for the reduction of halides which have no functional groups which are readily reduced by lithium aluminum hydride. An alternative procedure which has not been used would be to reduce the organotin halide first with exactly one equivalent of lithium aluminum hydride and then add the halide to be reduced. Each procedure circumvents the isolation of organotin hydride.

TABLE III

HYDROGEN CARRIER EXPERIMENTS WITH BROMOCYCLOHEXANE AND LITHIUM ALUMINUM HYDRIDE[a]

| Organotin halide | Reaction time, min. | % Reduction |
|---|---|---|
| None | 2645 | 1.4 |
| $(C_6H_5)_3SnCl$ | 30 | 18 |
| | 150 | 80 |
| $(n\text{-}C_4H_9)_3SnCl$ | 45 | 1.0 |
| | 1610 | 47 |
| $(C_6H_5)_2SnCl_2$ | 30 | 22 |
| | 110 | 89 |
| $(n\text{-}C_4H_9)_2SnCl_2$ | 40 | 7.0 |
| | 780 | 80 |
| $C_4H_9SnCl_2$ | 35 | 22 |
| | 90 | 99 |

[a] In refluxing ethyl ether, 1.2 *M* bromocyclohexane, 0.8 *M* $LiAlH_4$, 2.5 mole % organotin halide.

A cautionary note regarding the relative reactivities reported should be made. Occasionally the reactions showed induction periods, and apparent periods necessary for complete reaction varied at times by a factor of two. The reaction must, therefore, be subject to catalysis or inhibition by adventitious impurities. A brief examination of the role of oxygen was made, providing the results shown in Table IV. These were obtained by evacuating flasks containing 0.2 *M* tri-*n*-butyltin hydride and *n*-butyl bromide in chlorobenzene and introducing an atmosphere of known composition. After an alloted time at 45° the reaction mixtures were examined by gas chromatography. It is evident that the reaction proceeds more slowly in a nitrogen atmosphere than in one containing 5% oxygen, and still more slowly if the atmosphere contains 30% oxygen. For these reasons accurate relative reactivities are better determined by competitive experiments. Such studies now are being made and the results will be reported in due course in connection with those of a detailed study of the reaction mechanism.

TABLE IV

| Reaction | % Oxygen in atmosphere[a] | Time, hr. | % Reaction | Additional time, hr. | % Reaction |
|---|---|---|---|---|---|
| 1 | 0 | 22 | 21 | 18[b] | 55 |
| 2 | 4.3 | 15 | 42 | 35[c] | 71 |
| 3 | 10.1 | 15 | 55 | 35[c] | 64 |
| 4 | 20.5 | 15 | 0.8 | 35[c] | 44 |
| 5 | 31.0 | 15 | 1.9 | 35[c] | 51 |

[a] Balance of atmosphere was nitrogen. [b] Flask exposed to air for a minute, stoppered, and kept at 45° for 18 hr. [c] Flask evacuated and an atmosphere of 4% oxygen and 96% nitrogen introduced, and kept at 45° for 35 hr.

## Experimental

All reactions involving organotin hydrides were conducted in ordinary laboratory apparatus under an atmosphere of prepurified nitrogen (Matheson).

**Materials.**—The halides used were the best grades available commercially and were redistilled if discolored or if the gas chromatograms showed more than 5% impurity. Organotin hydrides were prepared by methods described in the literature.[13,14]

**General Reduction Procedure.**—Five milliliters (5.5 g., 18.9 mmoles) of tri-*n*-butyltin hydride, neat or in solution, was added to 18.0 mmoles of the halide. If the reaction was exothermic, the mixture was cooled if necessary to maintain the temperature below about 50°. If the reaction was not exothermic, the mixture was heated to the temperature indicated until no gas evolution was observed upon addition of a few drops to a solution of sulfuric acid in ethyl ether. The mixture was then distilled if the product was a liquid, and the product characterized by comparison of its infrared spectrum with that of authentic material. Exceptions were neophyl chloride where the *t*-butylbenzene was characterized by its nuclear magnetic resonance spectrum; and the products of reduction of phenacyl chloride by di-*n*-butyltin hydride and tri-*n*-butyltin hydride, and of benzal chloride, benzotrichloride, and iodoheptane by tri-*n*-butyltin hydride which were characterized by their retention times in gas chromatograms.

**Hydrogen Carrier Experiments.**—Into a 250-ml. three-neck flask were placed 25 ml. of an ether solution 1.2 *M* in bromocyclohexane and 0.03 *M* in organotin chloride. After addition of 9 ml. of 0.80 *M* lithium aluminum hydride the solution was heated to reflux. At appropriate times aliquots were removed, treated with water, and the ether layer analyzed by gas chromatography using a 2-ft. column of 20% silicone rubber on 60–80-mesh Chromosorb P (firebrick).

**Catalysis by Azobisisobutyronitrile.**—Two solutions 0.95 *M* in tri-*n*-butyltin hydride and substrate were prepared and azonitrile added to one. Aliquots were sealed in ampoules and placed in a constant temperature bath at 80°, removed after appropriate time intervals, and analyzed by gas chromatography using the silicone rubber on Chromosorb column.

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