Thiols as Polarity Reversal Catalysts for Hydrogen-atom Transfer from Organosilanes to Alkyl Radicals: Reduction of Alkyl Halides by Triethylsilane

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Triethylsilane reduces alkyl halides to alkanes under mild conditions in the presence of thiols, which act as polarity reversal catalysts for hydrogen-atom transfer from the silane to an alkyl radical.

Organotin hydrides react with many types of organic compounds by radical chain mechanisms and play an important role in synthesis.[1,2] However, organotin compounds are toxic and are often difficult to remove from the desired reaction product. Organosilicon hydrides would be preferable for many applications, but the greater strength of the Si–H bond compared with the Sn–H bond has proved to be an obstacle to their general use. For example, tributylstannane readily reduces alkyl halides to alkanes at moderate temperatures by the radical chain mechanism shown in equations (1) and (2).

$$\mathrm{Bu_3Sn^{\bullet} + RHal \xrightarrow{fast} Bu_3SnHal + R^{\bullet}} \qquad (1)$$

$$\mathrm{R^{\bullet} + Bu_3SnH \xrightarrow{fast} RH + Bu_3Sn^{\bullet}} \qquad (2)$$

By contrast, triethylsilane is ineffective under similar conditions, because reaction (4) of the corresponding propagation cycle is too slow to maintain the chain.[3]

$$\mathrm{Et_3Si^{\bullet} + RHal \xrightarrow{fast} Et_3SiHal + R^{\bullet}} \qquad (3)$$

$$\mathrm{R^{\bullet} + Et_3SiH \xrightarrow{slow} RH + Et_3Si^{\bullet}} \qquad (4)$$

Recently, it has been shown that tris(trimethylsilyl)silane is an efficient reducing agent for alkyl halides,[4,5] because the Si–H bond in $\mathrm{(Me_3Si)_3SiH}$ is appreciably weaker than that in $\mathrm{Et_3SiH}$ (331 kJ mol^{-1} compared with 377 kJ mol^{-1}).[6] However, reaction (4) is still exothermic even if R$^{\bullet}$ is a tertiary alkyl radical [bond dissociation energy, $DH^{\circ}(\mathrm{Me_3C{-}H}) = 392$ kJ mol^{-1}][7] and we reasoned that unfavourable polar factors might be responsible for its general sluggishness, since a nucleophilic alkyl radical is abstracting an electron rich hydrogen atom from silicon. If this is so, reaction (4) should be subject to polarity reversal catalysis (PRC)[8] and the strength of the S–H bond (384 kJ mol^{-1} in MeSH)[7] suggested that thiols might be suitable 'acceptor' catalysts.[8] Thiyl radicals are electrophilic and, in the presence of a thiol, reaction (4) would be replaced by the catalytic cycle of reactions (5) and (6), both of which will benefit from favourable polar effects. We report here our preliminary findings which show that thiols do indeed effectively catalyse the reduction of alkyl halides by triethylsilane.

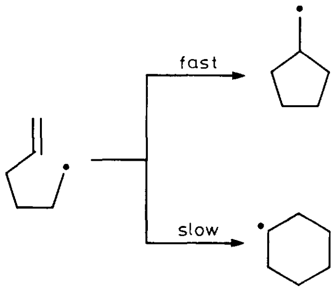
$$\mathrm{R^{\bullet} + XSH \xrightarrow{fast} RH + XS^{\bullet}} \qquad (5)$$

$$\mathrm{XS^{\bullet} + Et_3SiH \xrightarrow{fast} XSH + Et_3Si^{\bullet}} \qquad (6)$$

Table 1. Reduction of alkyl halides and dioctyl sulphide by triethylsilane[a]

Entry	RHal or R_2S	Yield RH (%)
1[b]	1-Bromo-octane	10
2		99[c]
3[d]		0
4	1-Chloro-octane	96
5	1-Iodo-octane	91
6	2-Bromo-octane	96
7	1-Bromo-adamantane	99
8[e]	1-Bromo-1-methylcyclohexane	95
9[f]	1-Bromo-octane	98
10[g]		98
11[h]		93
12[i]	Dioctyl sulphide	73

[a] Unless otherwise noted, reaction mixtures consisted of Et_3SiH (10.0 mmol), alkyl halide or sulphide (5.0 mmol), t-dodecanethiol (0.1 mmol), TBHN (0.25 mmol), and internal standard (usually decane, 3.5 mmol) in hexane (15 cm^3). The mixture was refluxed under argon for 1 h, allowed to cool, washed with water (15 cm^3), then with saturated aqueous sodium hydrogen carbonate (15 cm^3), and dried ($MgSO_4$) before being analysed by g.l.c. [b] No thiol present; *ca.* 90% of the bromo-octane remained unreacted. Much of the octane is probably formed by a non-chain pathway. [c] The same yield was obtained after refluxing for 0.5 h. [d] No TBHN present. [e] Et_3SiH (20.0 mmol) and t-dodecanethiol (0.2 mmol); lower yields were obtained with lower concentrations of these reagents. [f] 1-Adamantanethiol (0.1 mmol) present in place of t-dodecanethiol. [g] Refluxing cyclohexane solvent; dilauroyl peroxide (0.1 mmol) present as initiator in place of TBHN. [h] Ph_3SiH (10.0 mmol) used in place of Et_3SiH. [i] Hexane (7.5 cm^3) solvent.



(7)

As shown in Table 1 (entry 1), only a small amount of octane was produced when 1-bromo-octane (5.0 mmol), triethylsilane (10.0 mmol), and di-t-butyl hyponitrite[9] (TBHN) (0.25 mmol) were refluxed together in hexane (15 cm^3) under argon for 1 h. However, in the presence of t-dodecanethiol† (0.1 mmol) under otherwise identical conditions, quantitative reduction of the bromide to octane was achieved (entry 2). In the presence of thiol but without TBHN, no octane was produced, providing support for the proposed radical chain mechanism.

1-Chloro-, 1-iodo-, and 2-bromo-octane were also reduced to octane in high yield by the thiol–silane couple. The tertiary alkyl bromides 1-bromo-1-methylcyclohexane and 1-bromoadamantane were similarly reduced to the corresponding hydrocarbons. The readily synthesised 1-adamantanethiol[10] was equally efficient as a polarity reversal catalyst (entry 9); a tertiary thiol may be preferable because steric effects should militate against reactions of $XS^{\bullet}$ other than hydrogen atom transfer (*e.g.* addition to C=C bonds). Alkyl halide reduction could also be brought about by the thiol–silane couple in refluxing cyclohexane using dilauroyl peroxide as initiator (entry 10). Triphenylsilane is also an effective reducing agent for 1-bromo-octane in the presence of thiol (entry 11).

We have shown previously[11] that trialkylsilyl radicals readily displace alkyl radicals from sulphur in dialkyl sulphides and, in accord with this result, dioctyl sulphide was reduced to octane in reasonable yield by the thiol–silane couple in refluxing hexane (entry 12). Analogous reductions should proceed more efficiently for selenides and tellurides.[12]

Cyclisation of the hex-5-enyl radical to give mainly the cyclopentylmethyl radical is one of the best-known homolytic rearrangements [equation (7)].[13] Reduction of 6-bromohex-1-ene by Et_3SiH in decane at 70 °C in the presence of 1-adamantanethiol (0.013 M)‡ gave methylcyclopentane, cyclohexane, and hex-1-ene in the ratio of 14.8:0.30:1, respectively. When the thiol concentration was increased to 0.13 M, the relative yields obtained were 1.5:0.04:1, under otherwise identical conditions.§ Apart from confirming the homolytic character of the reduction, these results serve to demonstrate how the nature and concentration of the thiol catalyst could be used to control the relative rates of chain transfer and rearrangement when such processes compete (*cf.* ref. 5).

Polarity reversal catalysis of hydrogen-atom transfer from readily available organosilanes to carbon-centred radicals should be applicable to a variety of chain reactions which are of importance in organic synthesis. In addition to hydrosilylation of alkenes, these might include reactions of carbonyl- and thiocarbonyl-containing compounds[14] and reductive alkylation of electron-poor alkenes with organic halides or chalconides,[2] all of which could be mediated by simple silanes rather than by stannanes or germanes.[1]

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References

1 W. P. Neumann, *Synthesis*, 1987, 665.
2 B. Giese, 'Radicals in Organic Synthesis: Formation of Carbon–Carbon Bonds,' Pergamon Press, Oxford, 1986.
3 J. Lusztyk, B. Maillard, and K. U. Ingold, *J. Org. Chem.*, 1986, **51**, 2457.
4 C. Chatgilialoglu, D. Griller, and M. Lesage, *J. Org. Chem.*, 1988, **53**, 3641; 1989, **54**, 2492.
5 B. Giese, B. Kopping, and C. Chatgilialoglu, *Tetrahedron Lett.*, 1989, **30**, 681.
6 J. M. Kanabus-Kaminska, J. A. Hawari, D. Griller, and C. Chatgilialoglu, *J. Am. Chem. Soc.*, 1987, **109**, 5267.
7 D. Griller, J. M. Kanabus-Kaminska, and A. Maccoll, *J. Mol. Struct. (Theochem)*, 1988, **163**, 125.
8 V. Paul and B. P. Roberts, *J. Chem. Soc., Chem. Commun.*, 1987, 1322; *J. Chem. Soc., Perkin Trans. 2*, 1988, 1183; V. Paul, B. P. Roberts, and C. A. S. Robinson, *J. Chem. Res. (S)*, 1988, 264; V. Paul, B. P. Roberts, and C. R. Willis, *J. Chem. Soc., Perkin Trans. 2*, in the press.
9 H. Kiefer and T. G. Traylor, *Tetrahedron Lett.*, 1966, 6163.
10 K. K. Khullar and L. Bauer, *J. Org. Chem.*, 1971, **36**, 3038; J. M. Kokosa, L. Bauer, and R. S. Egan, *ibid.*, 1975, **40**, 3196.
11 W. B. Gara and B. P. Roberts, *J. Organomet. Chem.*, 1977, **135**, C20.
12 J. C. Scaiano, P. Schmid, and K. U. Ingold, *J. Organomet. Chem.*, 1976, **121**, C4.
13 C. Chatgilialoglu, K. U. Ingold, and J. C. Scaiano, *J. Am. Chem. Soc.*, 1981, **103**, 7739; A. L. J. Beckwith, C. J. Easton, T. Lawrence, and A. K. Serelis, *Aust. J. Chem.*, 1983, **36**, 545.
14 W. Hartig, *Tetrahedron*, 1983, **39**, 2609.

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† This is the mixture of isomers $C_{12}H_{25}SH$ as obtained from the Aldrich Chemical Company.

‡ The reaction was carried out in a sealed glass tube with octane as internal standard; otherwise the conditions were as specified in the first footnote of Table 1.

§ The quantitative dependence on initial thiol concentration of the ratio of cyclised to uncyclised products was not very reproducible. This is probably because of the variable extent to which the thiol is consumed by addition to the double bond and by reaction with triethylbromosilane produced in the reduction.