The Reaction of Trichlorosilyl Radicals with Cyclohexyl Octyl Ether. An S_H2 Reaction at an Ether Oxygen Atom

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Summary Trichlorosilane reacts with cyclohexyl octyl ether to give cyclohexane, octane, and (after methylation of the reaction product) octyloxytrimethylsilane; the results are interpreted as involving S_H2 attack by the trichlorosilyl radical at the ether oxygen atom.

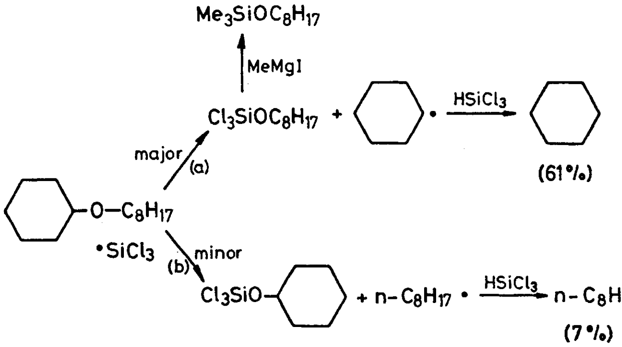
S_H2 REACTIONS at saturated centres of first-row elements to the right of boron are difficult because of the energy involved in expansion of the octet. Reported S_H2 reactions at saturated oxygen centres have mainly involved peroxides where the O–O bond to be broken is weak.[1] Recently, Avar and Neumann obtained evidence for S_H2 attack at the oxygen atom of phosphinite esters,[2] but there appears to be no authentic case of attack at the oxygen atom of a saturated ether.

We reasoned that the very strong covalent bond formed between silicon and oxygen might form the driving force for such a reaction, and accordingly investigated the reactions of trichlorosilyl or tripropylsilyl radicals with a number of ethers. The ether R_2O (1 mol) was heated with the silicon hydride (Cl_3SiH or Pr_3SiH, 1—2 mol) and t-butyl peroxide (0·1—1·0 mol) in a sealed tube at 140 or 170 °C for up to 17 h. Significant yields of the alkane RH (determined by g.l.c.) were obtained from dioctyl ether [maximum 52% for $R_2O:Cl_3SiH:(Bu^tO)_2 = 1:1:1$ at 140 °C for 16 h] and dibenzyl ether [maximum 20% for $R_2O:Cl_3SiH:(Bu^tO)_2 = 1:2{\cdot}1:0{\cdot}1$ at 140 °C for 17 h] when trichlorosilane was used, with somewhat lower yields if tripropylsilane was used as the reducing agent. Variation of the temperature between 140 and 170 °C made no substantial difference to the yields. Diphenyl ether with tripropylsilane and t-butyl peroxide gave no benzene. These results indicate that silicon-centred radicals attack the saturated oxygen atom in aliphatic ethers by an S_H2 process [reaction (1)], displacing an alkyl radical which abstracts hydrogen from the silicon hydride to give the alkane. However, it is conceivable that hydrogen abstraction is taking place by reaction (2) in which initial hydrogen abstraction takes place α to the ether oxygen atom, followed by fragmentation and hydrogen transfer to give the alkane.

$$(RCH_2)_2O + {\cdot}SiCl_3 \xrightarrow{S_H2} RCH_2OSiCl_3 + RCH_2{\cdot} \xrightarrow{HSiCl_3} RCH_3 \qquad (1)$$

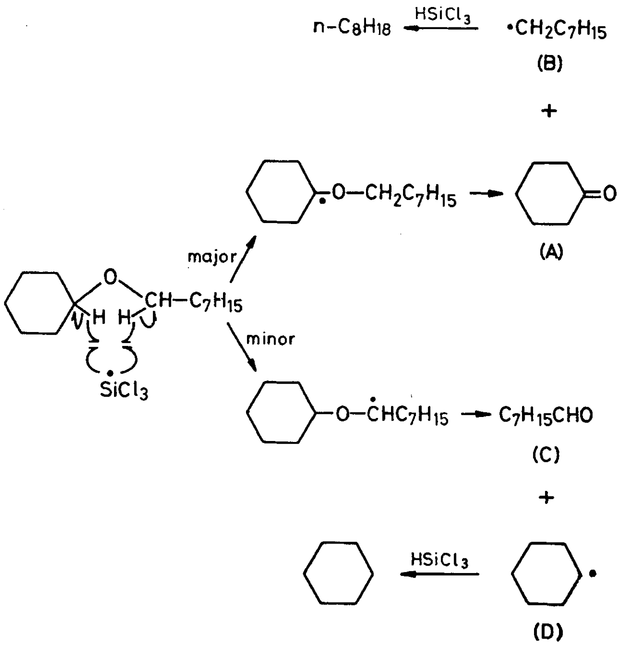
$$(RCH_2)_2O + {\cdot}SiCl_3 \rightarrow HSiCl_3 + R\dot{C}HOCH_2R \rightarrow RCHO + {\cdot}CH_2R \xrightarrow{HSiCl_3} RCH_3 \qquad (2)$$

To provide a possible distinction between these routes, an equimolar mixture of cyclohexyl octyl ether, trichlorosilane, and t-butyl peroxide was heated at 140 °C for 17 h. Cyclohexane (61%) and octane (7%) were the hydrocarbon products, a result which favours the S_H2 mechanism (Scheme 1). If the $\cdot SiCl_3$ radical attacks the ether oxygen by an S_H2 process, it would be expected that the more stable free radical (cyclohexyl rather than n-octyl) would be formed so that route (a) will be favoured over route (b), as is observed. In a similar experiment (but with more $HSiCl_3$ present), the reaction product was treated with methylmagnesium iodide, giving about 30% of octyloxytrimethylsilane, thus providing additional support for this route.



Scheme 1

An alternative route to the hydrocarbon products involves initial abstraction of a hydrogen α to the ether oxygen (Scheme 2). Such a reaction would involve abstraction of hydrogen by trichlorosilyl radicals from C–H bonds, which in view of the relative weakness of the Si–H bond is not expected to be a particularly favourable process. However, even if reaction does take place at the α-hydrogen atoms, abstraction should take place preferentially at the cyclohexane ring to give the more stable substituted cyclohexyl radical, leading to a preponderance of octane over cyclohexane, contrary to our observation. If the original hydrogen abstraction is reversible, the route to octane should be favoured on thermodynamic grounds, since products A + B can be estimated to be approximately 2 kcal mol^{-1}† more stable than C + D (related to the greater stability of a ketone compared with the isomeric aldehyde). The absence of cyclohexanone or octanal from the reaction products provides additional, though weaker evidence against Scheme 2 since trichlorosilyl radicals would be expected to add readily to the carbonyl oxygen atom. Thus, we conclude that the reaction proceeds by Scheme 1, involving S_H2 attack at the oxygen atom of a saturated unstrained ether. As far as we are aware, this is the first example of such a reaction.



Scheme 2

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† 1 cal = 4·184 J.

[1] K. U. Ingold and B. P. Roberts, 'Free Radical Substitution Reactions,' Wiley-Interscience, New York, 1971.
[2] G. Avar and W. P. Neumann, *J. Organomet. Chem.*, 1977, **131**, 207.