Radical-initiated Reduction of Chloroformates to Alkanes by Tri-n-propylsilane: Removal of Unwanted Hydroxy Groups from Organic Molecules

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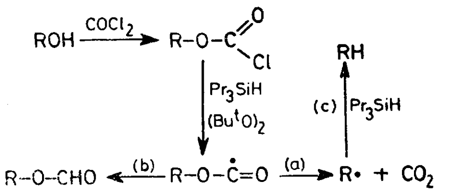
Summary Chloroformates of primary and secondary alcohols, produced by the reaction of the alcohol with phosgene, are reduced to the corresponding alkane in excellent yields by reaction with tri-n-propylsilane in the presence of t-butyl peroxide at 140 °C.

THERE has been considerable recent interest (see *e.g.* refs. 1—4) in methods for replacement of hydroxy groups by hydride in organic molecules. The use of established methods often gives rise to difficulties especially when other reducible groups such as C=O are present. Our method, outlined in the Scheme, gives good yields for reduction of primary and secondary alcohols to the corresponding alkanes.† The dehydroxylation has been carried out in the presence of a ketone.



SCHEME

The alkyl chloroformate, prepared from the corresponding alcohol by reaction with phosgene,[5] is heated in a sealed ampoule with tri-n-propylsilane and t-butyl peroxide either alone or in the presence of an alkane solvent. Optimum conditions were found to include the use of *ca.* 2—5 mol of tripropylsilane and 0·5—1 mol of peroxide per mol of the chloroformate, at 140 °C. The presence or absence of a hydrocarbon solvent (dodecane) had little effect on the yield. Under these conditions, excellent yields of alkanes were obtained from chloroformates derived from primary and secondary alcohols (see Table).

Organosilicon and organotin radicals are known to abstract halogen atoms readily from organic molecules. A high temperature should favour the fragmentation reaction (a); we chose to use an organosilane for the reduction because organotin hydrides more readily undergo reactions of type (b)[6] which would reduce the yield of the desired alkane. The low yield obtained from phenyl chloroformate is probably due to the greater strength of the Ph–O bond, and that from the benzyl compound may be caused by the relative difficulty of reaction (c) for the stabilized benzyl radical.

Most of the data in the Table were obtained by gas chromatography. However, the octyl chloroformate reduction gave 85% of pure octane by direct fractionation of the reaction mixture, and 3β-cholestanol gave cholestane in 69% yield (based on the alcohol) after chromatography on alumina and crystallization from acetone–methanol.

The synthetic scope of the reaction is being investigated further, particularly with regard to the influence of other functional groups. Initial results are encouraging: we obtain a 69% yield of pentan-2-one from $MeCO[CH_2]_3$-OCOCl, which indicates that by our method a hydroxy group can be removed from a molecule whilst leaving a ketone group untouched. The need for the high concentration of t-butyl peroxide, unusual in free-radical reactions, is also being investigated.

TABLE. Reaction of chloroformates ROCOCl with Pr_3SiH at 140 °C.

R	Reagents (mol per mol of ROCOCl)			Time/h	% Yield of RH[a]
	Pr_3SiH	$(Bu^tO)_2$	$C_{12}H_{26}$		
n-C_8H_{17}	4·6	0·5	8	4	92
n-C_8H_{17}	1·8	0·5	0	24	85[b]
Cyclohexyl	3·2	0·9	13	4	91
$C_{27}H_{47}$[d]	3·4	1·1	49[e]	24	69[b,c]
$PhCH_2$	1·9	0·9	0	8	11
Ph	1·9	0·6	12	4	Trace

[a] Yields by g.l.c. unless indicated. [b] Isolated. [c] Yield based on original alcohol. [d] 3β-cholestanyl. [e] Hexane used as solvent.

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† Tertiary alcohols are excluded for the present; Et_3COH suffers dehydration on treatment with phosgene.

Recently, free radical reduction methods based on carboxylic esters[3,4] and thio-esters[2] have been suggested. Each has a somewhat different scope; our method appears particularly promising for the reduction of primary and secondary alcohols.

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[1] S. Masamune, G. S. Bates, and P. E. Georghiou, *J. Amer. Chem. Soc.*, 1974, **96**, 3686.

[2] D. H. R. Barton and S. W. McCombie, *J.C.S. Perkin I*, 1975, 1574; D. H. R. Barton and R. Subramanian, *J.C.S. Chem. Comm.*, 1976, 867.

[3] L. E. Khoo and H. H. Lee, *Tetrahedron Letters*, 1968, 4351.

[4] H. Deshayes, J. P. Pète, and C. Portella, *Tetrahedron Letters*, 1976, 2019.

[5] M. S. Kharasch, Yu Cheng Liu, and W. Nudenberg, *J. Org. Chem.*, 1954, **19**, 1150.

[6] H. G. Kuivila and E. J. Walsh, Jr., *J. Amer. Chem. Soc.*, 1966, **88**, 571; P. Beak and S. W. Mojé, *J. Org. Chem.*, 1974, **39**, 1320.