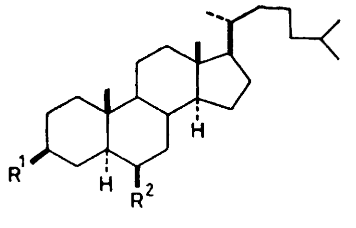
Novel Method for the Deoxygenation of Alcohols

By ANTHONY G. M. BARRETT* and PANAYIOTIS A. PROKOPIOU
(*Department of Chemistry, Imperial College, London* SW7 2AY)
and DEREK H. R. BARTON
(*Institut de Chimie des Substances Naturelles, C.N.R.S., Gif-sur-Yvette, France*)

Summary Primary and secondary alcohols have been deoxygenated in high yield by the reduction of derived thiocarbamates in t-butylamine with potassium solubilised by 18-crown-6.

RECENTLY we reported the selective deoxygenation of hindered alcohols by the lithium and ethylamine reduction of the derived carboxylic esters.[1] For example 3β,6β-diacetoxy-5α-cholestane (**1a**) gave 5α-cholestan-3β-ol (**1b**) (60%) and 5α-cholestane-3β,6β-diol (**1c**) (29%). Since carboxylic esters are readily available from alcohols the deoxygenation provides a useful synthetic method. Herein we report that non-hindered secondary and primary alcohols can be readily converted into alkanes by the reduction of their dialkylaminothiocarbonyl derivatives with potassium and 18-crown-6. This complements the selective ester reduction.



(1)

a; $R^1=R^2=AcO$
b; $R^1=HO, R^2=H$

c; $R^1=R^2=HO$
d; $R^1=R^2=MeS{\cdot}CS{\cdot}O$
e; $R^1=R^2=EtNH{\cdot}CS{\cdot}O$

f; $R^1=R^2=\overline{CH_2-[CH_2]_3-N}{\cdot}CS{\cdot}O$

g; $R^1=H, R^2=HO$
h; $R^1=R^2=H$

i; $R^1=\overline{CH_2-[CH_2]_4-N}{\cdot}CS{\cdot}O, R^2=H$
j; $R^1=Et_2N{\cdot}CS{\cdot}O, R^2=H$

k; $R^1=Me_2NCH_2CH_2N(Me){\cdot}CS{\cdot}O, R^2=H$

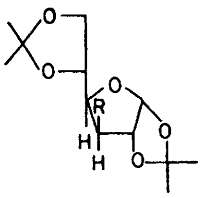
TABLE. Potassium 18-crown-6 reduction of dithiocarbonates and thiocarbamates[a]

	Starting material	Product(s) (% yield)
1	(**1d**)	(**1h**) (38), (**1b**) (19), (**1c**) (8), (**1g**) (2)
2	(**1e**)	(**1c**) (45), (**1b**) (18)
3	(**1f**)	(**1h**) (62), (**1g**) (15), (**1b**) (12), (**1c**) (5)
4	(**1i**)	(**1h**) (74), (**1b**) (14)
5	(**1j**)	(**1h**) (86), (**1b**) (8)
6	(**1j**)	(**1h**) (58), (**1b**) (40)
7	(**1k**)	(**1h**) (83), (**1b**) (12)
8	$Me[CH_2]_{17}O{\cdot}CS{\cdot}NEt_2$	$Me[CH_2]_{16}Me$ (87), $Me[CH]_2]_{17}$-OH (12)
9	(**2a**)	(**2b**) (55), (**2c**) (14)

[a] All reductions were carried out in t-butylamine (entries 1—3, 5—9) or 1,2-dimethoxyethane (entry 4) at room temperature except entry 7 (−30 °C). New compounds were characterised by spectral data and microanalyses. All yields refer to pure isolated materials.

Reductions of the dithiocarbonate (**1d**) and thiocarbamates (**1e**, **f**, **i**—**k** and **2a**) by potassium in t-butylamine solubilised by 18-crown-6 are in the Table. Typically the thiocarbonyl derivative (1 mmol) in tetrahydrofuran (THF) was added dropwise at room temperature to potassium (12 mg atom) and 18-crown-6 (3 mmol) in t-butylamine or 1,2-dimethoxyethane (20 ml). The reduction was complete when the blue colour of the solution was restored. Clearly both primary and secondary alcohols can be thus conveniently deoxygenated. The thiocarbamates are readily available from the alcohol *via* the methylthiothiocarbonyl derivative and dialkylamine.[2]

The deoxygenation herein described is more convenient than many existing methods. Carbohydrate thiocarbamates have been converted into alkanes *via* photolytic homolysis.[3,4]



(2)

a; $R=Et_2N{\cdot}CS{\cdot}O$
b; $R=HO$
c; $R=H$

We consider that the mechanism of reduction of these thiocarbonyl derivatives is comparable to that presented in the preceding communication for ordinary esters.[5] That is, that a transfer of an electron to give a radical anion is followed by the collapse of the latter to thiocarboxylate anion (specially stabilised) and carbon radical. It was consideration of this mechanism that led us to the method presented above.

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[1] R. B. Boar, L. Joukhadar, J. F. McGhie, S. C. Misra, A. G. M. Barrett, D. H. R. Barton, and P. A. Prokopiou, *J.C.S. Chem. Comm.*, 1978, 68; see also H. Deshayes and J.-P. Pete, *ibid.*, p. 567.

[2] D. H. R. Barton, R. V. Stick, and R. Subramanian, *J.C.S. Perkin I*, 1976, 2112.

[3] R. H. Bell, D. Horton, and D. M. Williams, *Chem. Comm.*, 1968, **323**; R. H. Bell, D. Horton, D. M. Williams, E. Winter-Mihaly, *Carbohydrate Res.*, 1977, **58**, 109.

[4] See also T. Tsuchiya, I. Watanabe, M. Yoshida, F. Nakamura, T. Usui, M. Kitamura, and S. Umezawa, *Tetrahedron Letters*, 1978, 3365; T. Tsuchiya, F. Nakamura, and S. Umezawa, *ibid.*, 1979, 2805; W. Tochtermann and R. G. H. Kirrstetter, *Chem. Ber.*, 1978, **111**, 1228; R. G. H. Kirrstetter, *ibid.*, 1979, **112**, 2804.

[5] A. G. M. Barrett, P. A. Prokopiou, D. H. R. Barton, R. B. Boar, and J. F. McGhie, *J.C.S. Chem. Comm.*, preceding communication.