Deoxygenation of tertiary and secondary alcohols ROH by thiol-catalysed radical-chain redox decomposition of derivatives $ROCH_2X$ to give RH and XCHO

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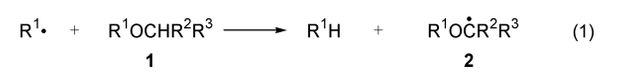
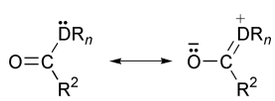
Compounds of the type $ROCH_2X$, in which the substituent X is an electron-donating alkoxy, aryl or amido group, undergo thiol-catalysed radical-chain decomposition to give RH and XCHO. This reaction has been applied for the deoxygenation of representative tertiary and secondary alcohols ROH under metal-free conditions that require no stoichiometric co-reactant. Of the derivatives investigated, methoxymethyl (MOM) ethers and 1-alkoxymethylpyrrolidin-2-ones (PYRM ethers) proved to be the most generally successful and typical conditions for the redox decomposition to give RH involve heating under reflux in octane solvent in the presence of a peroxide initiator and tri-*tert*-butoxysilanethiol [$(Bu^tO)_3SiSH$] as a protic polarity-reversal catalyst. Conversions to RH were negligible in the absence of thiol. Several different types of tertiary alcohol, including steroidal and carbohydrate examples, were deoxygenated as their MOM and PYRM ethers to give very good isolated yields of RH. Although the MOM and PYRM ethers derived from many types of secondary alcohol also afforded good yields of RH, the MOM ether of diacetone D-glucose gave the 3-deoxy sugar in poor yield and the yield from the corresponding PYRM ether was still only moderate.

Introduction

The functional group transformation ROH ⟶ RH is of key importance in organic synthesis and new methods to accomplish this deoxygenation reaction are always in demand, particularly when the use of toxic or costly metal-containing reagents can be avoided. The application of free-radical chemistry to bring about this type of transformation can offer a number of advantages over conventional heterolytic methodology, including neutral reaction conditions, less sensitivity to steric retardation if the group R is bulky and the avoidance of unwanted ionic rearrangement processes. Several radical-based procedures are available for the deoxygenation of alcohols, especially secondary alcohols, and methods that involve chain reactions of thiocarbonyl derivatives ROC(=S)X with tributyltin hydride have enjoyed widespread application in organic synthesis.[1] However, because of the toxicity of organotin compounds and the difficulty of eliminating all traces of tin residues from the end product, considerable efforts have been made to devise more acceptable replacements for the tin hydride. Amongst these, we have reported[2,3] that triphenylsilane functions as an effective substitute for tributyltin hydride in the classic Barton–McCombie procedure[4] for the deoxygenation of alcohols *via* their *S*-methyl xanthate (dithiocarbonate) derivatives ROC(=S)SMe. It appears[3] that a thiol is formed *in situ* in the silane-mediated reaction and that this thiol serves as a protic polarity-reversal catalyst[5] to promote the indirect transfer of hydrogen from the silane to the alkyl radical R$^\bullet$, a reaction that would be relatively slow in the absence of a catalyst.

It would be very convenient if a simple alcohol derivative of the type **1** could be induced to undergo a redox decomposition by the radical-chain mechanism shown in eqns. (1) and (2), since here no stoichiometric co-reactant is required. However, the difficulty with reaction (1) is that the α-alkoxyalkyl radical **2** will be nucleophilic, a property that is usually shared by the radical $R^{1\bullet}$, so that the transition state for hydrogen-atom transfer will not benefit from charge-transfer stabilisation. Such adverse polar effects might be overcome in the presence of a suitable protic polarity-reversal catalyst El–H,[5] that affords an electrophilic radical El$^\bullet$, when the direct hydrogen-atom abstraction reaction (1) is replaced by the cycle of reactions (3) and (4), both of which benefit from favourable polar effects. Furthermore, if the leading atom of the group R^3 is a π-electron donor (*e.g.* D = O, N or S), this should promote the β-scission process (2) by stabilising the carbonyl-containing product (see structures **3a** and **3b**), while hopefully not providing significant extra stabilisation to the radical **2** over that afforded by the single π-donor group R^1O.[6] The presence of the group DR_n should also facilitate the preparation of the derivative **4** from R^1OH, because of the high reactivity of compounds such as **5** (LG = electronegative leaving group) as *O*-alkylating agents. In fact, formation of the derivative **4** could also serve to protect the hydroxy function during heterolytic transformations, offering the possibility of deoxygenation without the need to first deprotect the OH group.





3a **3b**

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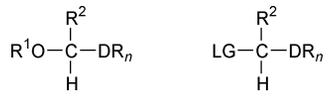
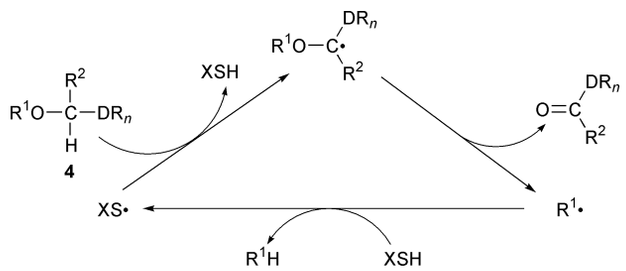


4 **5**

In the present paper we describe the use of compounds of the type **4** for the deoxygenation of alcohols, in the presence of thiols as protic polarity-reversal catalysts, according to the general mechanism shown in Scheme 1. Some of our preliminary results in this area have been communicated previously.[7]



Scheme 1

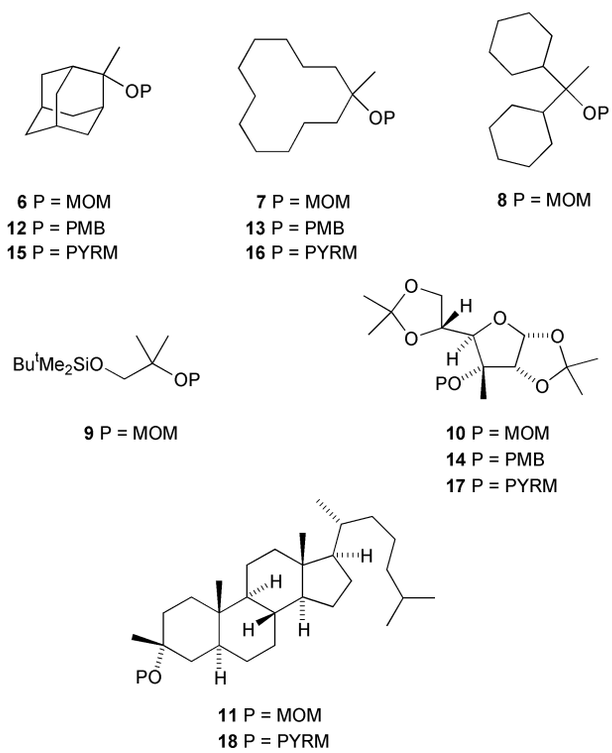
Results and discussion

The group DR_n in the alcohol derivative **4** must be chosen with care if the proposed deoxygenation reaction is to be successful and there are a number of considerations that must be borne in mind when making this choice. The *O*-alkylating agent **5** must be sufficiently stable to be handled easily and it should react with the alcohol to form **4** under mild conditions. The group DR_n should not contain very readily abstractable hydrogen atoms or possess other sites of high reactivity towards radicals. The lone pair of electrons on the donor atom D should be readily available to stabilise positive charge on the attached carbon atom in the transition state for abstraction of hydrogen from **4** by the electrophilic thiyl radical, as well as to stabilise the carbonyl-containing product as described above (**3a** ↔ **3b**). The ultimate goal is to design the derivative **4** such that hydrogen is abstracted rapidly and selectively by thiyl radicals from the R^1OCH group, with minimal irreversible reaction elsewhere in the molecule, to give an α-alkoxyalkyl radical that undergoes rapid β-scission to give $R^{1\bullet}$. The group R^2 also needs to be chosen with care. For example, although an alkyl or aryl group could offer further stabilisation to the radical formed by abstraction of hydrogen from **4**, it could also hinder this abstraction both sterically and stereoelectronically, the latter by forcing the C–H bond to lie close to orthogonal to the low-energy lone pairs on the π-donor R^1O and DR_n groups in the most stable conformation of **4**.[8] However, in a derivative of the type $R^1OCH_2DR_n$ there will always be a C–H bond that is stereoelectronically well placed for abstraction. Furthermore, the thermal stability of the alkylating agent **5** and its reactivity towards R^1OH could well be compromised when R^1 = alkyl or aryl, compared with the choice of R^2 = H, and derivatives of the type $R^1OCH_2DR_n$ have indeed proved most generally successful in our investigations to date.

Deoxygenation of tertiary alcohols

Although the Barton–McCombie methodology can be applied for the deoxygenation of tertiary alcohols *via* the corresponding xanthates,[9] the relative instability of the latter can lead to difficulties and alternative methods for deoxygenation of tertiary alcohols would be particularly useful. In one approach designed to circumvent this problem, Barton and Crich[10] utilised the mixed anhydrides (PTOC oxalates) produced by sequential treatment of oxalyl chloride with one equivalent of the tertiary alcohol ROH, followed by one equivalent of *N*-hydroxypyridine-2-thione. These derivatives undergo a radical-chain double decarboxylation reaction with a stoichiometric amount of thiol (in particular Et_3CSH) to give the deoxy compound RH.[10]

In the present work, a number of derivatives RO–P of representative tertiary alcohols ROH were examined as potential precursors of RH; the group P was methoxymethyl (MOM), *p*-methoxybenzyl (PMB) or the amidomethyl group PYRM, introduced by *O*-alkylation with methoxymethyl chloride, *p*-methoxybenzyl chloride or 1-chloromethylpyrrolidin-2-one, respectively. The structures of these derivatives are presented in Scheme 2 and the deoxygenated products are shown in Scheme 3.



6 P = MOM
12 P = PMB
15 P = PYRM

7 P = MOM
13 P = PMB
16 P = PYRM

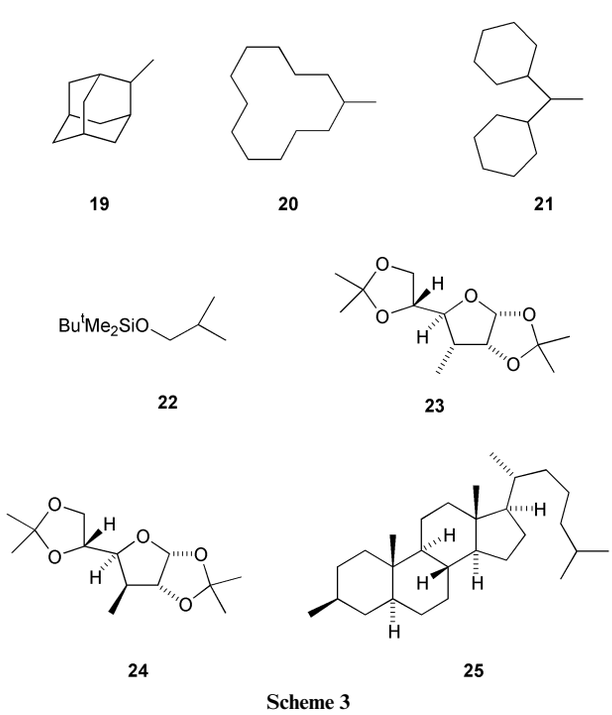
8 P = MOM

9 P = MOM

10 P = MOM
14 P = PMB
17 P = PYRM

11 P = MOM
18 P = PYRM

Scheme 2



19 **20** **21**

22 **23**

24 **25**

Scheme 3

Table 1 TBST-catalysed radical-chain decomposition of methoxymethyl ethers in refluxing octane[a]

Entry	Ether RO–MOM	Conversion to RH (%)	Isolated yield of RH (%)
1	**6**	95	87
2	**7**	98	82
3	**8**	96	88
4	**9**[b]	88	78
5	**10**[b,c]	95	90[d]
6	**11**[c]	87[e]	82
7	**28**[c]	85	74
8	**28**[f]	92	83
9	**29**[c]	15	—
10	**30**	78	72

[a] The thiol (3 mol%) and DBPB initiator (3 mol%) were added initially and again after 40 min unless stated otherwise; the total reaction time was 2 h 40 min. [b] Collidine (10 mol%) was also present. [c] TBST (3 mol%) and DBPB (3 mol%) were added initially, again after 20 min and again after 40 min; the total reaction time was 3 h. [d] Mixture of **23** and **24** (91 : 9). [e] Only 3β-methylcholestane **25** was formed and none of the 3α-epimer was detected in the crude reaction product. [f] TBST (5 mol%) and DBPB (5 mol%) were added initially, again after 20 min and again after 40 min; the total reaction time was 3 h.

Methoxymethyl ethers. Bearing in mind the considerations set out above, it appeared that if the π-donor atom D is oxygen, methoxymethyl ethers $ROCH_2OMe$ would probably be the best choice for the derivative RO–P. MOM ethers are readily prepared from alcohols and the latter are routinely protected as this class of derivative.[11] The radical-chain decomposition of a MOM ether according to the mechanism generalised in Scheme 1 will lead to the deoxygenated compound RH and methyl formate, as shown in eqn. (5).

$$ROCH_2OMe \longrightarrow RH + MeOCHO \qquad (5)$$

When the MOM ether **6** derived from 2-methyladamantan-2-ol was heated for a total of 2 h 40 min in refluxing octane, in the presence of 2,2-bis(*tert*-butylperoxy)butane (DBPB, two additions of 3 mol%) as a thermal source of initiating alkoxyl radicals, no 2-methyladamantane **19** was detected in the reaction mixture and most of the MOM ether was recovered unchanged. However, when this reaction was repeated in the presence of tri-*tert*-butoxysilanethiol [$(Bu^tO)_3SiSH$, TBST, two additions of 3 mol%], the reaction proceeded smoothly as shown in eqn. (5) and 2-methyladamantane was isolated in 87% yield. As predicted, the thiol here acts as a protic polarity-reversal catalyst to mediate the abstraction of hydrogen from the MOM ether by the nucleophilic 2-methyladamant-2-yl radical.

The MOM ethers **7**–**9** underwent similar redox decomposition to give the corresponding deoxygenated products **20**–**22** in good isolated yields, as summarised in Table 1. Only traces of the deoxy compounds were formed in the absence of thiol catalyst, under otherwise identical conditions, and the majority of the starting MOM ether could be then recovered unchanged.

To investigate the applicability of the methodology to the deoxygenation of more complex alcohols, the two MOM ethers **10** and **11** were examined. Somewhat more forcing conditions than those used for **6**–**9** were required for the reductive removal of the protecting group from the carbohydrate derivative **10**, but treatment of the latter with TBST (3 × 3 mol%) and DBPB (3 × 3 mol%) in refluxing octane for a total of 3 h, in the additional presence of 2,4,6-trimethylpyridine (collidine, 10 mol%), afforded a 91 : 9 mixture of the deoxy compounds **23** and **24** in a total isolated yield of 90% (entry 5). Yields of deoxy compounds from the thiol-catalysed decomposition of MOM ethers were often improved in the presence of collidine, the function of which is probably to act as a scavenger of acid resulting from reactions of the initiator with the thiol.[12] The predominance of **23** over its C(3) epimer **24** is presumably a consequence of preferred attack by the thiol at the more accessible *exo*-face of the intermediate C(3)-centred radical.

Reductive removal of the protecting group from the MOM ether **11** was similarly successful and afforded 3β-methylcholestane **25** in 82% isolated yield, under the conditions used for **10**, but in the absence of collidine (entry 6). None of the 3α-methyl isomer was detected in the crude reaction product and, again, the epimeric composition of the product is evidently determined by steric control during approach of the thiol to the intermediate C(3)-centred radical, this time favouring quenching from the α-face of the steroidal radical. The same result has been observed by Barton and Crich for quenching of this radical by thiols.[10] At this stage, not all the reaction conditions have been individually optimised to give maximum conversion of RO–P to RH and, to aid comparisons between the various classes of derivative, the conditions were kept generally similar. Thus, a reported conversion of <100% does not necessarily imply that the reaction cannot be pushed to completion by further additions of initiator and longer reaction times. For a particular application in synthesis, the best procedure is clearly to monitor the progress of the reaction in order to maximise the conversion of RO–P to RH.

***p*-Methoxybenzyl ethers.** *p*-Methoxybenzyl ethers were investigated next, on the basis that the ethereal CH_2 group is rendered benzylic while retaining the activating polar effect of the methoxy group (now conducted through the benzene ring) on the hydrogen abstraction step. The desired decomposition process for a PMB ether is shown in eqn. (6). Potential disadvantages, recognised at the outset, are that the CHO group of the *p*-methoxybenzaldehyde produced will be extremely reactive towards abstraction of hydrogen by electrophilic radicals, including thiyl radicals, and the *p*-methoxyphenyl group is very easily oxidised. Nevertheless, screening was considered worthwhile and the PMB ethers of 2-methyladamantan-2-ol (**12**) and 1-methylcyclododecanol (**13**) were used to explore the scope of the reaction. The results are summarised in Table 2.

$$ROCH_2C_6H_4OMe\text{-}p \longrightarrow RH + p\text{-}MeOC_6H_4CHO \qquad (6)$$

With TBST as catalyst and DBPB as initiator, in refluxing octane, the ether **12** afforded 2-methyladamantane **19** in only 58% yield, but using pentafluorothiophenol (PFTP) as catalyst conversion was essentially complete and the isolated yield was 90% (entry 2). An arenethiol can be used as a catalyst for the decomposition of the PMB ethers because the resonance-stabilised arenethiyl radical is capable of abstracting the weakly bound benzylic hydrogen atom; the thiyl radical is also particularly electrophilic in this case.[13,14] Encouraged by the results using PFTP as catalyst, we attempted to use lower reaction temperatures, in refluxing toluene with 1,1-bis(*tert*-butylperoxy)-cyclohexane (DBPC) as initiator (entry 3) and in refluxing

Table 2 Thiol-catalysed radical-chain decomposition of *p*-methoxybenzyl ethers and benzyl ethers in refluxing solvent[a]

Entry	Ether RO–PMB or RO–Bn	Thiol catalyst[a]	Initiator[a]	Solvent	Conversion to RH (%)[b]
1	**12**	TBST	DBPB	Octane	62 (58)
2	**12**	PFTP	DBPB	Octane	95 (90)
3	**12**	PFTP	DBPC	Toluene	55
4	**12**	PFTP	DLP	Benzene	47
5	**13**	TBST	DBPB	Octane	94 (90)
6	**13**	PFTP	DBPB	Octane	90 (85)
7	**13**	PFTP	DBPC	Toluene	58
8	**13**	TBST	DBPC	Toluene	24
9	**14**	TBST	DBPB	Octane	12
10	**31**	TBST	DBPB	Octane	15
11	**32**	TBST	DBPB	Octane	8
12	**33**	TBST	DBPB	Octane	7

[a] The thiol and initiator (3 mol% of each) were added at the start of the reaction, again after 20 min and again after 40 min; the total reaction time was 3 h. [b] Approximate values obtained by ^{1}H NMR spectroscopic analysis of the crude reaction product and based on the ratio of RH to unreacted $ROCH_2X$. The isolated yields are given in parentheses.

Table 3 TBST-Catalysed radical-chain decomposition of PYRM or OXAM ethers in refluxing solvent[a]

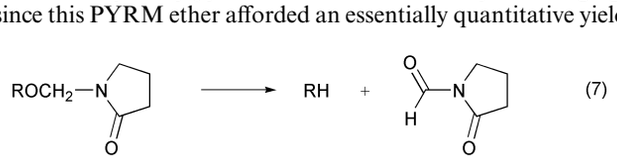
Entry	Ether RO–PYRM or RO–OXAM	Initiator	Solvent	Conversion to RH (%)[b]
1	**15**	DBPB	Octane	≥98 (90)
2	**15**	DBPC	Toluene	95 (86)
3	**15**	DLP	Benzene	25
4	**15**	TBHN	Benzene[c]	45
5	**16**	DBPB	Octane	≥98 (92)
6	**16**	DBPC	Toluene	25
7	**16**	TBHN	Benzene[c]	50
8	**17**	DBPB	Octane	88 (78)[d]
9	**18**	DBPB	Octane	≥98 (94)[e]
10	**34**	DBPB	Octane	≥98 (93)
11	**34**	DBPC	Toluene	10
12	**35**	DBPB	Octane	40
13	**36**	DBPB	Octane	65
14	**36**[f]	DBPB	Octane	≥98 (91)
15	**37**	DBPB	Octane	≥98 (90)
16	**38**	DBPB	Octane	45

[a] The thiol and initiator (3 mol% of each) were added at the start of the reaction, again after 20 min and again after and 40 min; the total reaction time was 3 h. [b] Approximate values obtained by ^{1}H NMR spectroscopic analysis of the crude reaction product and based on the ratio of RH to unreacted $ROCH_2X$. The isolated yields are given in parentheses. [c] Bath temperature 60 °C. [d] The epimeric ratio **23** : **24** was 90 : 10. [e] 3β-Methylcholestane. [f] The thiol and initiator (3 mol% of each) were added at the start of the reaction and again after 20 and after 40 min. After heating for a further 30 min, more DBPB (3 × 3 mol%) was added at 30 min intervals; the total reaction time was 4 h.

benzene with dilauroyl peroxide (DLP) as initiator (entry 4), but these conditions proved less successful. Deoxygenation of 1-methylcyclododecanol *via* its PMB ether **13** proceeded smoothly in refluxing octane, using either TBST or PFTP as catalyst (entries 5 and 6), but again the results in refluxing toluene were less good (entries 7 and 8).

In contrast, only very poor yields of the 3-deoxysugars **23** and **24** were obtained from the PMB ether **14** under all conditions investigated (*e.g.* entry 9) and deoxygenation *via* the corresponding MOM ether was much more successful (see above).

***N*-Alkoxymethylpyrrolidin-2-ones (PYRM ethers).** With the aim of extending the range of electron-donating groups DR_n in the alcohol derivative **4**, we turned our attention to the *N*-alkoxymethylpyrrolidin-2-ones (PYRM ethers), which were expected to undergo thiol-catalysed radical-chain decomposition to give the deoxy compound and 1-formylpyrrolidin-2-one **26**, as shown in eqn. (7). Preliminary experiments with 1-*tert*-butoxymethylpyrrolidin-2-one **27** were very encouraging, since this PYRM ether afforded an essentially quantitative yield



(7)

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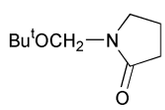
of **26** after treatment with TBST and DBPC in refluxing toluene (the gaseous isobutane produced would be lost). A representative selection of PYRM ethers of tertiary alcohols were then prepared and subjected to thiol-catalysed radical-chain decomposition under a variety of conditions; the results are summarised in Table 3.



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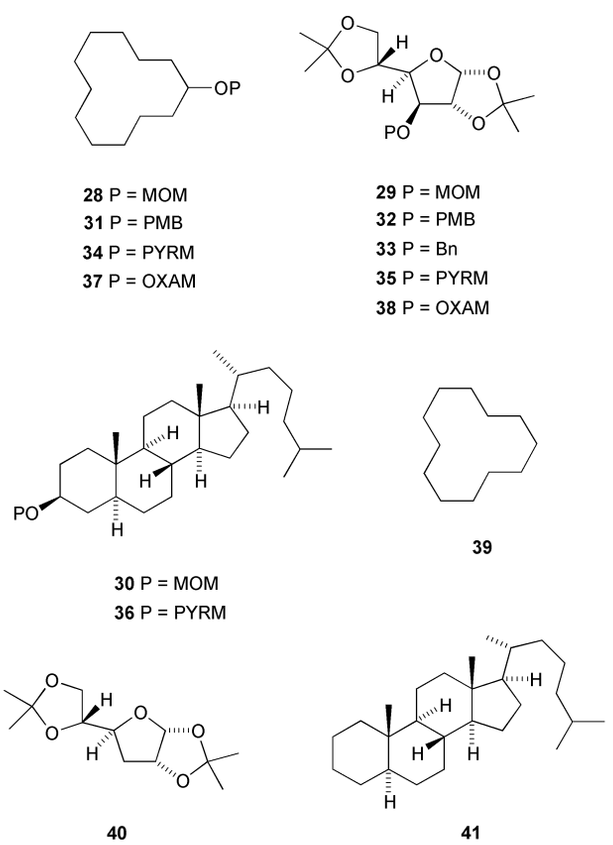
Deoxygenations of 2-methyladamantan-2-ol and 1-methylcyclododecanol as their PYRM ethers **15** and **16**, respectively, were quantitative in refluxing octane, using TBST as catalyst and DBPB as initiator (entries 1 and 5). Other conditions were less reliable or less effective. In particular, the use of refluxing benzene as solvent, in conjunction with di-*tert*-butyl hyponitrite (TBHN) as initiator (entries 4 and 7), led to conversions of only *ca.* 50% after the same number of additions of thiol and initiator as resulted in complete conversion in refluxing octane. When the PYRM ethers **15** and **16** were heated in refluxing octane under the conditions of entries 1 and 5, except that no thiol was present, most of the ether was unchanged and the conversions to 2-methyladamantane and methylcyclododecane were only 6 and 8%, respectively.

Redox decomposition of the PYRM ethers **17** and **18** also proceeded successfully in refluxing octane, in the presence of TBST and DPPB, to give an epimeric mixture of the deoxy sugars **23** and **24** (90 : 10) and 3β-methylcholestanol **25**, respectively (entries 8 and 9). However, as was found for the other alcohol derivatives investigated, the conversion to RH under the same conditions was lower (88%) for the carbohydrate ether **17** than for the steroidal ether **18**, which affords an *unfunctionalised* hydrocarbon as the deoxygenated product. The reason for these differences in behaviour is not clear at present, but it may be related to the presence of several electron-withdrawing oxygen atoms in the carbohydrate residue, which is likely to slow down both the abstraction of hydrogen from the ether by the electrophilic thiyl radical and the β-scission of the resulting alkoxyalkyl radical.

Deoxygenation of secondary alcohols

The secondary alcohol derivatives RO–P investigated and their deoxygenation products RH are shown in Scheme 4; the results



28 P = MOM
31 P = PMB
34 P = PYRM
37 P = OXAM

29 P = MOM
32 P = PMB
33 P = Bn
35 P = PYRM
38 P = OXAM

30 P = MOM
36 P = PYRM

39

40

41

Scheme 4

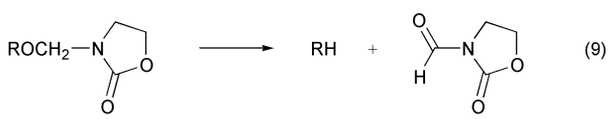
are presented in Tables 1–3. Under the standard conditions in refluxing octane, the MOM ether **28** derived from cyclododecanol afforded cyclododecane **39** in 74% isolated yield (Table 1, entry 7). Using more initiator and thiol (entry 8) resulted in 92% conversion of the ether to cyclododecane, which was isolated in 83% yield. However, conversion of the MOM ether **29** derived from diacetone D-glucose to the 3-deoxy sugar **40** was very low and isolation of the product was not attempted (entry 9). In contrast, the MOM ether **30** from 3β-cholestanol underwent smooth redox decomposition under standard conditions to give cholestane **41** in 72% isolated yield (entry 10).

The PMB ethers **31** and **32** derived from cyclododecanol and diacetone D-glucose, respectively, proved unsuitable for deoxygenation of these secondary alcohols and conversions were very low under the standard conditions using either TBST or PFTP as catalyst (Table 2, entries 10 and 11). Bearing in mind that the high reactivity of *p*-methoxybenzaldehyde towards electrophilic radicals might be causing a problem here, the benzyl ether **33** of diacetone D-glucose was investigated [eqn. (8)], but conversion to the 3-deoxy sugar was similarly very low (entry 12).

$$ROCH_2Ph \longrightarrow RH + PhCHO \qquad (8)$$

In welcome contrast, the PYRM ether **34** from cyclododecanol gave an excellent yield of cyclododecane when subjected to the standard conditions in refluxing octane solvent (Table 3, entry 10), although the conversion was much lower in refluxing toluene (entry 11). Conversion of the PYRM ether **35** from diacetone D-glucose to the 3-deoxy sugar was much greater than that obtained with the corresponding MOM, PMB or benzyl ethers, but the yield was still only moderate (entry 12). Under the standard conditions, conversion of the PYRM ether **36** from 3β-cholestanol to cholestane was 65% (entry 13), but this was readily optimised to essentially quantitative (91% isolated yield) by adding more initiator (entry 14).

N-Alkoxymethyloxazolidin-2-ones **42** (OXAM ethers) were examined next, on the basis that the nitrogen lone pair could be more available to the exocyclic substituent than in the PYRM ethers, because the π-accepting capacity of the carbonyl group would be partly satisfied by the adjacent oxygen atom. The OXAM ethers were prepared in a similar way to the PYRM ethers, by treatment of 3-chloromethyloxazolidin-2-one with the appropriate sodium alkoxide. However, while conversion of the OXAM ether **37** to cyclododecane was essentially quantitative in refluxing octane [eqn. (9)], conversion of the OXAM ether **38** derived from diacetone D-glucose was only slightly greater than for the corresponding PYRM ether (Table 3, entries 15 and 16).

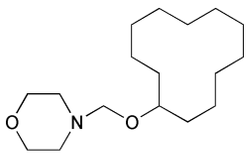


(9)

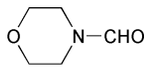
42

Thus, it appears that inductive electron withdrawal by the ring-oxygen atom present in the OXAM ethers counterbalances its π-electron donating capacity towards the carbonyl group, to render the nitrogen lone pair similarly available to the exocyclic *N*-substituent in both PYRM and OXAM ethers.

Our initial choice of nitrogen donor substituent DR_n in the alcohol derivatives of the general type **4** was restricted to amido groups, because it was anticipated that aminol ethers would be too sensitive to acid-catalysed hydrolysis for these derivatives to be of practical use for deoxygenation. However, since from the standpoint of the desired chain reaction shown in Scheme 1, $DR_n = NR_2$ would appear to be an ideal choice, the representative aminol ether **43** was examined. This compound was prepared by the base-catalysed reaction of cyclododecanol with morpholine and formaldehyde, using a modification of a procedure in the literature,[15] and indeed proved to be very susceptible to acid-catalysed hydrolysis. It was not stable to chromatography on silica gel (with or without Et_3N in the eluent) or on Florisil®, although it was stable at 150 °C during distillation under reduced pressure. When the redox decomposition of **43** was carried out under the usual conditions in refluxing octane that had been freshly further dried by distillation from calcium hydride, taking all reasonable precautions to exclude moisture, none of the aminol ether remained. However, although cyclododecane and 4-formylmorpholine **44** were formed in equal yields of 40%, a large amount of cyclododecanol (60%) was also produced. The extent of deprotection *versus* deoxygenation was not increased significantly when



43



44

the reaction was repeated in the presence of collidine (10 mol%) or finely-powdered $CaCO_3$ (20 mol%). We conclude, therefore, that aminol ethers are unlikely to be practically useful derivatives for the deoxygenation of alcohols.

Conclusion

We have shown that alcohol derivatives of the type $ROCH_2DR_n$, in which the substituent DR_n is an electron-donating alkoxy, aryl or amido group, undergo thiol-catalysed radical-chain decomposition to give RH and R_nDCHO. We have further shown that this reaction can be used with advantage for the catalytic radical-chain deoxygenation of tertiary and secondary alcohols, without the need for tin- or other metal-containing reagents and, indeed, requires no stoichiometric co-reactant. MOM and PYRM ethers have proved to be the most successful derivatives for redox decomposition, in the presence of tri-*tert*-butoxysilanethiol as a protic polarity-reversal catalyst. Yields of deoxy-alcohol RH were generally very good, except from the secondary carbohydrate alcohol diacetone D-glucose.

Experimental

NMR spectra were recorded using a Bruker ADVANCE 500 instrument (500 MHz for ^{1}H, 125.7 MHz for ^{13}C). Unless stated otherwise, the solvent was $CDCl_3$ and chemical shifts are reported relative to Me_4Si; *J* values are quoted in Hz and the use of [multiplet] indicates an apparent multiplet associated with an averaged coupling constant. Column chromatography and TLC were carried out using Merck Kieselgel 60 (230–400 mesh) and Kieselgel $60F_{254}$ aluminium-backed pre-coated plates, respectively. Optical rotations were measured on an AA Series Polaar 2000 polarimeter (Optical Activity Ltd.) using a 1 dm cell and are given in units of 10^{-1} deg cm^2 g^{-1}.

All manipulations and reactions of air-sensitive compounds were carried out under an atmosphere of dry argon or nitrogen and all extracts were dried over anhydrous $MgSO_4$. Light petroleum refers to the fraction of bp 40–60 °C.

Materials

Anhydrous octane, nonane and 1,4-dioxane (Aldrich) were used as received unless stated otherwise. 2,2-Bis(*tert*-butylperoxy)-butane (50% w/w in mineral oil) and 1,1-bis(*tert*-butylperoxy)cyclohexane (50% w/w in mineral oil) were obtained commercially (Laporte Organics or Aldrich) and were used as received.

Tri-*tert*-butoxysilanethiol (TBST) was prepared according to a modification of the method described in the literature.[13,16,17] All other thiols were obtained commercially (Aldrich) and were used as received.

2-Methyladamantan-2-ol was obtained commercially (Aldrich). 1,1-Dicyclohexylethanol[18] and 1,2:5,6-diisopropylidene-3-*C*-methyl-α-D-allofuranose[19] were prepared according to literature methods from the appropriate ketones and methylmagnesium iodide. 1-Methylcyclododecanol[20] was prepared in a similar way from cyclododecanone and showed mp 91–92 °C (lit.,[20] 91–92.5 °C); δ_H 1.17 (3 H, s, Me), 1.22 (1 H, br s, OH), 1.25–1.56 (22 H, m, CH_2); δ_C 19.9, 22.0, 22.5, 26.0, 26.4, 29.0, 36.1, 73.7.

3β-Methylcholestan-3α-ol[21] was obtained as a mixture with the 3α-epimer from the reaction of methylmagnesium iodide with cholestan-3-one.[22] The 3β-epimer was isolated in a pure state by column chromatography (eluent: light petroleum–diethyl ether, 5 : 1 then 3 : 1).

1-(*tert*-Butyldimethylsiloxy)-2-methylpropan-2-ol

1-(*tert*-Butyldimethylsiloxy)-2-methylpropan-2-one[23] (9.40 g, 50.0 mmol) in dry diethyl ether (20 cm^3) was added dropwise to a solution of methylmagnesium iodide, prepared from iodomethane (8.98 g, 63.3 mmol) and magnesium (1.70 g, 70.8 mmol) in ether (100 cm^3), cooled in an ice–water bath. The reaction mixture was stirred at room temperature for 16 h, and then treated with saturated aqueous NH_4Cl solution (80 cm^3) at 0 °C. The organic phase was separated and the aqueous phase was extracted with diethyl ether (3 × 25 cm^3). The combined organic phase was washed with saturated brine (30 cm^3) and dried. The solvent was removed by evaporation and the residue was distilled to give the product as an oil (8.34 g, 82%), bp 35 °C/0.05 mmHg; δ_H 0.07 (6 H, s, Me_2Si), 0.91 (9 H, s, Bu^t), 1.16 (6 H, s, Me), 2.42 (1 H, br s, OH), 3.38 (2 H, s, OCH_2); δ_C −5.5, 18.3, 25.5, 25.9, 70.5, 71.4 (Found: C, 58.6; H, 11.9. $C_{10}H_{24}O_2Si$ requires C, 58.8; H, 11.8%).

1-(Chloromethyl)pyrrolidin-2-one[24]

This was prepared by the reaction of thionyl chloride with 1-(hydroxymethyl)pyrrolidin-2-one, following the published procedure,[24] bp 78–80 °C/0.05 mmHg (lit.,[24] 102–103 °C/2.0 mmHg); δ_H 2.09 (2 H, m, CH_2), 2.42 (2 H, t, *J* 7.9, CH_2), 3.55 (2 H, t, *J* 7.0, CH_2), 5.23 (2 H, s, CH_2Cl); δ_C 17.5, 30.6, 45.6, 53.5, 175.6.

1-Chloromethyloxazolidin-2-one[25]

This was prepared in a similar way[25] from 1-(hydroxymethyl)-oxazolidin-2-one,[26] and was used without purification; δ_H 3.74 (2 H, m, CH_2), 4.41 (2 H, m, CH_2), 5.27 (2 H, s, CH_2Cl); δ_C 42.6, 56.0, 62.1, 157.0.

Preparation of alcohol derivatives. General method

Unless recorded otherwise, the same general method was used to prepare all the derivatives RO–P, *viz.* by alkylation of the corresponding sodium alkoxide with methoxymethyl chloride, 4-methoxybenzyl chloride, benzyl chloride, 1-chloromethylpyrrolidin-2-one or 1-chloromethyloxazolidin-2-one; the method is illustrated for a MOM ether. The alcohol (20.0 mmol) in dry *N*,*N*′-dimethylformamide (DMF, 10 cm^3) was added at 0 °C under argon to a stirred suspension of sodium hydride (60% w/w in mineral oil, 1.00 g, 25.0 mmol) in DMF (20 cm^3) and benzene (10 cm^3). The mixture was stirred at room temperature for 2 h and then chloromethyl methyl ether (1.61 g, 20.0 mmol) was added dropwise at 0 °C. The reaction mixture was stirred at room temperature for 16 h and then quenched with cold water (50 cm^3). The organic phase was separated and the aqueous phase was extracted with diethyl ether (4 × 20 cm^3). The combined organic phase was washed with saturated brine (25 cm^3) and dried. The solvent was removed by evaporation and the residual oil was purified chromatographically using light petroleum followed by light petroleum–diethyl ether (10 : 1) as eluent, to give the MOM ethers with the characteristics given below.

2-Methoxymethoxy-2-methyladamantane 6

Oil (yield 86%); δ_H 1.35 (3 H, s, Me), 1.48 (2 H, br d, *J* 12.0, CH), 1.65–1.95 (10 H, m, CH_2), 2.20 (2 H, br d, *J* 12.0, CH), 3.40 (3 H, s, OMe), 4.72 (2H, s, OCH_2O); δ_C 22.8, 27.1, 27.6, 32.8, 34.7, 36.8, 38.5, 55.6, 79.1, 90.1 (Found: C, 74.5; H, 10.3. $C_{13}H_{22}O_2$ requires C, 74.2; H, 10.5%).

1-Methoxymethoxy-1-methylcyclododecane 7

Oil (yield 89%); δ_H 1.18 (3 H, s, Me), 1.25–1.70 (22 H, m, CH_2), 3.36 (3 H, s, OMe), 4.71 (2H, s, OCH_2O); δ_C 19.7, 22.1, 22.6,

25.1, 26.1, 26.5, 34.1, 55.1, 79.3, 90.6 (Found: C, 74.5; H, 12.3. $C_{15}H_{30}O_2$ requires C, 74.3; H, 12.5%).

1,1-Dicyclohexylethyl methoxymethyl ether 8

Oil (yield 73%); δ_H 1.11 (3 H, s, Me), 0.90–1.25 (10 H, m, CH_2), 1.48 (2 H, m, CH), 1.60–1.85 (10 H, m, CH_2), 3.34 (3 H, s, OMe), 3.40 (3 H, s, OMe), 4.67 (2H, s, OCH_2O); δ_C 26.8, 26.9, 27.0(5), 27.0(8), 45.1, 55.5, 82.6, 92.0 (Found: C, 74.3; H, 11.7. $C_{16}H_{30}O_2$ requires C, 75.5; H, 11.9%).

2-*tert*-Butyldimethylsiloxy-1,1-dimethylethyl methoxymethyl ether 9

This was prepared according to the literature procedure.[27] A mixture of powdered sodium iodide (9.10 g, 60.7 mmol) and chloromethyl methyl ether (5.23 g, 65.0 mmol) in dry 1,2-dimethoxyethane (DME, 50 cm^3) was stirred at room temperature for 30 min. A solution of 1-(*tert*-butyldimethylsiloxy)-2-methylpropan-2-ol (4.1 g, 20.3 mmol) and diisopropylethylamine (9.11 g, 70.5 mmol) in DME (50 cm^3) was added dropwise over 5 min and the mixture was stirred at room temperature for 1 h, and then at 50 °C for 16 h, before being quenched with 20% w/v aqueous Na_2CO_3 (200 cm^3). Solid material was removed by filtration and washed with diethyl ether. The organic phase was separated from the filtrate and the aqueous phase was extracted with diethyl ether (3 × 30 cm^3). The combined organic phase was washed with saturated brine (80 cm^3) and dried. The solvent was removed under reduced pressure and the residue was distilled to give the MOM ether **9** as an oil (65%), bp 45–47 °C/0.05 mmHg; δ_H 0.05 (6 H, s, Me_2Si), 0.90 (9 H, s, Bu^t), 1.21 (6 H, s, Me), 3.36 (3 H, s, OMe), 3.46 (2 H, s, CH_2OSi), 4.76 (2 H, s, OCH_2O); δ_C −5.5, 18.3, 23.5, 25.9, 55.0, 70.4, 79.1, 91.4 (Found: C, 59.3; H, 9.3. $C_{12}H_{28}O_3Si$ requires C, 59.5; H, 9.2%).

1,2:5,6-Di-*O*-isopropylidene-3-*C*-methyl-3-*O*-methoxymethyl-α-D-allofuranose 10

Viscous oil (yield 65%), $[\alpha]_D^{20}$ +52.5 (*c* 2.63, $CHCl_3$); δ_H 1.30 (3 H, s, Me-3), 1.33 (3 H, s, Me), 1.34 (3 H, s, Me), 1.42 (3 H, s, Me), 1.57 (3 H, s, Me), 3.43 (3 H, s, OMe), 3.93 (1 H, dd, *J* 8.4 and 5.7, H-4), 4.05 (3 H, m, H-5 and -6), 4.25 (1 H, d, *J* 3.5, H-2), 4.79 (1 H, d, *J* 7.4, OCH^AH^BO), 4.91 (1 H, d, *J* 7.4, OCH^AH^BO), 5.65 (1 H, d, *J* 3.5, H-1); δ_C 17.0, 25.4, 26.5, 26.6, 27.0, 55.8, 67.4, 73.7, 81.1, 81.8, 84.5, 92.7, 103.6, 109.2, 112.8 (Found: C, 56.5; H, 8.3. $C_{15}H_{26}O_7$ requires C, 56.6; H, 8.2%).

3β-Methyl-3α-(methoxymethoxy)-5α-cholestane 11

Viscous oil (yield 62%), $[\alpha]_D^{20}$ +24.4 (*c* 1.22, $CHCl_3$); δ_H 0.64 (3 H, s, Me-11), 0.75 (3 H, s, Me-19), 0.85 (3 H, d, *J* 6.6, Me-26 or -27), 0.90 (3 H, d, *J* 6.6, Me-21), 0.90–2.00 (31 H, complex), 3.39 (3 H, s, OMe), 4.68 and 4.70 (2 H, ABq, *J* 7.2, OCH_2O); δ_C 11.6, 12.0, 18.7, 21.0, 22.6, 22.8, 23.8, 24.2, 27.5, 28.0, 28.2, 28.4, 32.1, 32.5, 34.0, 35.3, 35.6, 35.8, 36.2, 39.5, 40.1, 40.3, 40.6, 42.6, 54.4, 55.4, 56.3, 56.6, 75.1, 90.8 (Found: C, 80.5; H, 12.3. $C_{30}H_{54}O_2$ requires C, 80.7; H, 12.2%).

2-(4-Methoxybenzyloxy)-2-methyladamantane 12

Viscous oil (yield 84%); δ_H 1.38 (3 H, s, Me), 1.59 (2 H, m, CH_2), 1.65–1.95 (10 H, m, CH_2 + CH), 2.27 (2 H, m, CH_2), 3.80 (3 H, s, OMe), 4.37 (2H, s, OCH_2), 6.88 (2 H, d, *J* 8.7, Ph), 7.31 (2 H, d, *J* 8.7, Ph); δ_C 21.4, 27.1, 27.8, 32.8, 34.8, 36.2, 38.4, 55.3, 61.2, 77.7. 113.7, 128.6, 132.2, 158.7. (Found: C, 79.6; H, 9.3. $C_{19}H_{26}O_2$ requires C, 79.7; H, 9.2%).

1-(4-Methoxybenzyloxy)-1-methylcyclododecane 13

Recrystallised from light petroleum (yield 88%); mp 42 °C; δ_H 1.19 (3 H, s, Me), 1.28–1.50 (20 H, m, CH_2), 1.70 (2 H, m, CH_2), 3.79 (3 H, s, OMe), 4.37 (2H, s, OCH_2), 6.86 (2 H, d, *J* 8.6, Ph), 7.26 (2 H, d, *J* 8.6, Ph); δ_C 19.8, 22.2, 22.6, 23.7, 26.2, 26.6, 33.5, 55.3, 62.7, 78.0, 113.7. 128.7, 132.1, 158.7 (Found: C, 79.0; H, 10.8. $C_{21}H_{34}O_2$ requires C, 79.2; H, 10.8%).

1,2:5,6-Di-*O*-isopropylidene-3-*C*-methyl-3-*O*-(4-methoxybenzyl)-α-D-allofuranose 14

Viscous oil (yield 66%); $[\alpha]_D^{20}$ +31.4 (*c* 2.31, $CHCl_3$); δ_H 1.27 (3 H, s, Me), 1.34 (3 H, s, Me), 1.35 (3 H, s, Me), 1.41 (3 H, s, Me), 1.60 (3 H, s, Me), 3.80 (3 H, s, OMe), 3.99 (1 H, dd, *J* 8.4 and 5.7, H-4), 4.04 (1 H, dd, *J* 10.7 and 5.3, H^A-6), 4.16 (2 H, m, H-5 and H^B-6), 4.32 (1 H, d, *J* 3.7, H-2), 4.58 and 4.61 (2 H, ABq, *J* 7.5, OCH_2Ph), 5.72 (1 H, d, *J* 3.7, H-1), 6.86 (2 H, d, *J* 8.6, Ph), 7.32 (2 H, d, *J* 8.6 Ph); δ_C 17.0, 25.4, 26.6, 26.7, 27.0, 55.3, 66.0, 66.7, 73.8, 80.9, 82.2, 83.8, 103.9, 109.1, 112.9, 113.5, 128.7, 131.2, 158.8 (Found: C, 63.6; H, 7.9. $C_{21}H_{30}O_7$ requires C, 63.9; H, 7.7%).

1-(2-Methyladamantan-2-yloxymethyl)pyrrolidin-2-one 15

Viscous oil (yield 76%) that solidified on standing at room temperature, mp 52–53 °C; δ_H 1.32 (3 H, s, Me), 1.47 (2 H, br d, *J* 12.2, CH), 1.65–1.85 (10 H, m, CH_2), 2.01 (2 H, m, CH_2 pyr), 2.38 (2 H, t, *J* 8.3, CH_2 pyr), 3.53 (2 H, t, *J* 7.1, CH_2N), 4.74 (2 H, s, OCH_2N); δ_C 17.8, 21.9, 26.9, 27.5, 31.3, 32.8, 34.6, 36.2, 38.3, 46.1, 65.1, 78.7, 174.9 (Found: C, 72.8; H, 9.6; N, 5.2. $C_{16}H_{25}NO_2$ requires C, 73.0; H, 9.6, N, 5.3%).

1-(1-Methylcyclododecyloxymethyl)pyrrolidin-2-one 16

Recrystallised from dichloromethane–light petroleum, mp 45–46 °C; δ_H 1.14 (3 H, s, Me), 1.36 (20 H, m, CH_2), 1.63 (2 H, m, CH_2), 2.01 (2 H, m, CH_2 pyr), 2.37 (2 H, t, *J* 7.9, CH_2 pyr), 3.49 (2 H, t, *J* 7.0, CH_2N), 4.73 (2 H, s, OCH_2N); δ_C 17.8, 19.7, 22.1, 22.6, 24.0, 26.1, 26.5, 31.4, 33.5, 45.9, 66.1, 78.9, 174.7 (Found: C, 73.4; H, 11.6; N, 4.5. $C_{18}H_{33}NO_2$ requires C, 73.2; H, 11.3, N, 4.7%).

1,2:5,6-Di-*O*-isopropylidene-3-*C*-methyl-3-*O*-(2-oxopyrrolidin-1-ylmethyl)-α-D-allofuranose 17

Recrystallised from dichloromethane–light petroleum (70%), mp 101–103 °C; $[\alpha]_D^{20}$ +21.9 (*c* 2.01, $CHCl_3$); δ_H 1.27 (3 H, s, Me), 1.28 (3 H, s, Me), 1.32 (3 H, s, Me), 1.40 (3 H, s, Me), 1.53 (3 H, s, Me), 1.98 (2 H, m, CH_2 pyr), 2.33 (2 H, m, CH_2 pyr), 3.45 (1 H, m, CH^AH^BN), 3.70 (1 H, m, CH^AH^BN), 3.93 (1 H, dd, *J* 8.3 and 6.0, H^A-6), 4.00 (1 H, d, *J* 5.9, H-4), 4.01 (1 H, dd, *J* 8.3 and 6.1, H^B-6), 4.09 (1 H, [t], *J* 6.1, H-5), 4.21 (1 H, d, *J* 3.6, H-2), 4.67 (1 H, d, *J* 11.2, O CH^AH^BN), 5.09 (1 H, d, *J* 11.2, O CH^AH^BN), 5.62 (1 H, d, *J* 3.6, H-1); δ_C 16.1, 17.7, 25.4, 26.5(4), 26.6(0), 27.0, 31.4, 46.0, 67.0, 67.7, 73.7, 81.0, 81.5, 83.7, 104.0, 109.1, 112.5, 175.5 (Found: C, 58.4; H, 8.1; N, 3.6. $C_{18}H_{29}O_7$ requires C, 58.2; H, 7.9; N, 3.8%).

1-(3β-Methylcholestan-3α-yloxymethyl)pyrrolidin-2-one 18

Viscous oil (yield 41%), $[\alpha]_D^{20}$ +22.7 (*c* 2.02, $CHCl_3$); δ_H 0.64 (3 H, s, Me-11), 0.74 (3 H, s, Me-19), 0.85(5) (3 H, d, *J* 6.6, Me-26 or -27), 0.86(0) (3 H, d, *J* 6.6, Me-27 or -26), 0.90 (3 H, d, *J* 6.6, Me-21), 0.90–2.00 (31 H, complex), 1.14 (3 H, s, Me-3), 2.03 (2 H, m, CH_2 pyr), 2.37 (2 H, m, CH_2 pyr), 3.49 (2 H, m, CH_2N), 4.63 (1 H, d, *J* 10.1, NCH^AH^B), 4.76 (1 H, d, *J* 10.1, NCH^AH^B); δ_C 11.6, 12.1, 17.9, 18.7, 21.0, 22.6, 22.8, 23.8, 24.2, 26.6, 28.0, 28.2, 28.3, 31.4, 32.1, 32.2, 34.0, 35.3, 35.5, 35.8, 36.2, 39.2, 39.5, 40.0, 40.8, 42.6, 46.0, 54.5, 56.3, 56.5, 66.1, 75.0, 174.6 (Found: C, 70.5; H, 11.3; N, 2.6. $C_{33}H_{57}NO_2$ requires C, 79.3; H, 11.5; N, 2.8%).

1-(*tert*-Butoxymethyl)pyrrolidin-2-one[24] 27

Viscous oil [yield 91%, using 2 molar equivalents of 1-(chloromethyl)pyrrolidin-2-one]; δ_H 1.21, (9 H, s, Bu^t), 2.00 (2 H, m, CH_2 pyr), 2.35 (2 H, t, *J* 8.0, CH_2 pyr), 3.47 (2 H, t, *J* 8.0,

CH_2N), 4.73 (2H, s, NCH_2O); δ_C 17.6, 27.8, 31.4, 45.7, 66.7, 74.0, 174.9.

Methoxymethylcyclododecane[28] 28

Oil (yield 92%); δ_H 1.20–1.80 (22 H, m, CH_2), 3.37 (3 H, s, OMe), 3.57 (1 H, m, OCH), 4.64 (2H, s, OCH_2O); δ_C 20.9, 23.2, 23.3, 24.5, 29.5, 55.3, 74.5, 94.7.

1,2:5,6-Di-*O*-isopropylidene-3-*O*-methoxymethyl-α-D-glucofuranose[29] 29

Syrup (65%), $[\alpha]_D^{20}$ −20.5 (*c* 1.80, $CHCl_3$) {lit.[29] $[\alpha]_D^{20}$ −17.9 (*c* 2.2, $CHCl_3$)}; δ_H 1.32 (3 H, s, Me), 1.34 (3 H, s, Me), 1.42 (3 H, s, Me), 1.50 (3 H, s, Me), 3.41 (3 H, s, OMe), 3.99 (1 H, dd, *J* 8.6 and 5.5, H^A-6), 4.10 (1 H, dd, *J* 8.6 and 6.0, H^B-6), 4.11(1 H, dd, *J* 8.6 and 3.0, H-4), 4.21 (1 H, d, *J* 3.0, H-3), 4.28 (1 H, d[t], *J* 8.5 and 5.9, H-5), 4.57 (1 H, d, *J* 3.6, H-2), 4.71 and 4.74 (2 H, ABq, *J* 6.7, OCH_2OMe), 5.88 (1 H, d, *J* 3.6, H-1); δ_C 25.4, 26.3, 26.8 (2C), 55.8, 67.5, 72.3, 79.1, 81.1, 83.3, 96.1, 105.2, 109.1, 111.9.

3β-(Methoxymethoxy)cholestane[30] 30

Recrystallised from light petroleum (88%), mp 64–65 °C (lit.[30b] 64–64 °C); $[\alpha]_D^{22}$ +18.4 (*c* 1.51, $CHCl_3$) {lit.[30b] $[\alpha]_D^{22}$ +18.5 ($CHCl_3$)}; δ_H 0.64 (3 H, s, Me-11), 0.80 (3 H, s, Me-19), 0.85 (3 H, d, *J* 6.5, Me-26 or -27), 0.86 (3 H, d, *J* 6.5, Me-27 or -26), 0.89 (3 H, d, *J* 6.5, Me-21), 0.90–2.00 (31 H, complex), 3.36 (3 H, s, OMe), 3.49 (1 H, m, H-3), 4.67 and 4.68 (2 H, ABq, *J* 7.0, OCH_2O); δ_C 12.0, 12.2, 18.6, 21.2, 22.5, 22.8, 23.8, 24.2, 28.0, 28.2, 28.7, 28.8, 32.1, 35.2, 35.5, 35.6, 35.8, 36.1, 37.0, 39.5, 40.0, 42.6, 44.8, 54.3, 55.1, 56.2, 56.4, 76.3, 94.5.

(4-Methoxybenzyloxy)cyclododecane 31

Viscous oil (yield 89%); δ_H 1.30 (18 H, m, CH_2), 1.52 (2 H, m, CH_2), 1.64 (2 H, m, CH_2), 3.51 (1 H, m, OCH), 3.80 (3 H, s, OMe), 4.44 (2 H, s, OCH_2Ph), 6.87 (2 H, d, *J* 8.4, Ph), 7.27 (2 H, d, *J* 8.4, Ph); δ_C 20.8 (2 C), 23.1 (2 C), 23.3 (2 C), 24.1, 24.6 (2 C), 28.9 (2 C), 55.3, 69.9, 75.9, 113.7 (2 C), 129.2 (2 C), 131.4, 159.0 (Found: C, 78.7; H, 10.8. $C_{20}H_{32}O_2$ requires C, 78.9; H, 10.6%).

1,2:5,6-Di-*O*-isopropylidene-3-*O*-(4-methoxybenzyl)-α-D-glucofuranose 32

Viscous oil (yield 71%); $[\alpha]_D^{20}$ −22.2 (*c* 2.34, $CHCl_3$); δ_H 1.31 (3 H, s, Me), 1.38 (3 H, s, Me), 1.43 (3 H, s, Me), 1.49 (3 H, s, Me), 3.81 (3 H, s, OMe), 3.99 (1 H, dd, *J* 8.3 and 6.3, H^A-6), 4.00 (1 H, d, *J* 3.1, H-3), 4.10 (1 H, dd, *J* 8.3 and 6.3, H^B-6), 4.13 (1 H, dd, *J* 7.6 and 3.1, H-4), 4.34 (1 H, ddd, *J* 7.6, 6.3 and 5.7, H-5), 4.56 (1 H, d, *J* 3.7, H-2), 4.58 (2 H, ABq, *J* 11.4, OCH_2Ph), 5.88 (1 H, d, *J* 3.7, H-1), 6.87 (2 H, d, *J* 8.7, Ph), 7.27 (2 H, d, *J* 8.7, Ph); δ_C 25.5, 26.3, 26.7(7), 26.8(4), 55.3, 67.4, 72.1, 73.0, 81.3(1), 81.3(3), 82.7, 105.3, 108.9, 111.8, 113.8, 129.3, 129.7, 159.4 (Found: C, 63.3; H, 7.2. $C_{20}H_{28}O_7$ requires C, 63.1; H, 7.4%).

1,2:5,6-Di-*O*-isopropylidene-3-*O*-benzyl-α-D-glucofuranose[31] 33

Viscous oil (yield 71%); bp 130–132 °C/0.02 mmHg (lit.,[31] 150–155 °C/0.5 mmHg); $[\alpha]_D^{20}$ −25.2, (*c* 2.87, $CHCl_3$)], $[\alpha]_D^{20}$ −28.6 (*c* 2.22, EtOH) {lit.,[31] $[\alpha]_D^{20}$ −25 (*c* 2, EtOH)}; δ_H 1.31 (3 H, s, Me), 1.38 (3 H, s, Me), 1.43 (3 H, s, Me), 1.49 (3 H, s, Me), 4.00 (1 H, dd, *J* 8.7 and 5.7, H^A-6), 4.02 (1 H, d, *J* 3.1, H-3), 4.11 (1 H, dd, *J* 8.7 and 6.2, H^B-6), 4.15 (1 H, dd, *J* 7.7 and 3.1, H-4), 4.37 (1 H, ddd, *J* 7.7, 6.2 and 5.7, H-5), 4.58 (1 H, d, *J* 3.7, H-2), 4.64 and 4.67 (2 H, ABq, *J* 7.4, OCH_2Ph), 5.90 (1 H, d, *J* 3.7, H-1), 7.28–7.36 (5 H, m, Ph); δ_C 25.4, 26.2, 26.7(8), 26.8(4), 67.4, 72.4, 72.5, 81.3, 81.7, 82.7, 105.3, 109.0, 111.8, 127.6, 127.8, 128.4, 137.7.

1-Cyclododecyloxymethylpyrrolidin-2-one 34

Recrystallised from dichloromethane–light petroleum (yield 85%), mp 50–52 °C; δ_H 1.35 (18 H, m, CH_2), 1.43 (2 H, m, CH_2), 1.61 (2 H, m, CH_2), 2.04 (2 H, m, CH_2 pyr), 2.41 (2 H, t, *J* 8.3, CH_2 pyr), 3.50 (2 H, t, *J* 8.3 CH_2 pyr), 3.56 (1 H, m, OCH), 4.73 (2 H, s, OCH_2N); δ_C 17.9, 20.9 (2 C), 23.2 (2 C), 23.4 (2 C), 24.1, 24.1 (2 C), 29.2 (2 C), 31.2, 45.9, 70.4, 74.3, 175.6 (Found: C, 72.5; H, 11.2, N, 4.7. $C_{17}H_{31}NO_2$ requires C, 72.5; H, 11.1; N, 5.0%).

1,2:5,6-Di-*O*-isopropylidene-3-*O*-(2-oxopyrrolidin-1-ylmethyl)-α-D-glucofuranose 35

Syrup (yield 76%), $[\alpha]_D^{20}$ −25.2 (*c* 1.59, $CHCl_3$); δ_H 1.30 (3 H, s, Me), 1.33 (3 H, s, Me), 1.40 (3 H, s, Me), 1.47 (3 H, s, Me), 2.03 (2 H, m, CH_2 pyr), 2.42 (2 H, m, CH_2 pyr), 3.40 (1 H, m, CH^AH^BN), 3.66 (1 H, m, CH^AH^BN), 3.98 (1 H, dd, *J* 8.6 and 5.2, H^A-6), 4.04 (1 H, dd, *J* 8.7 and 3.0, H-4), 4.05 (1H, d, *J* 3.0, H-3), 4.09 (1 H, dd, *J* 8.6 and 6.1, H^B-6), 4.25 (1 H, ddd, *J* 8.7, 6.1 and 5.2, H-5), 4.57 (1 H, d, *J* 3.6, H-2), 4.61 (1 H, d, *J* 10.5, OCH^AH^BN), 5.02 (1 H, d, *J* 10.5, OCH^AH^BN), 5.85 (1 H, d, *J* 3.6, H-1); δ_C 18.0, 25.4, 26.2, 26.8, 26.9, 31.1, 45.9, 53.4, 67.7, 71.5, 72.2, 79.1, 80.9, 82.8, 105.3, 109.1, 112.0, 176.2 (Found: C, 57.2; H, 7.8; N, 3.8. $C_{17}H_{27}NO_7$ requires C, 57.1; H, 7.6; N, 3.9%).

1-(Cholestan-3β-yloxymethyl)pyrrolidin-2-one 36

Recrystallised from light petroleum (yield 81%), mp 108–109 °C, $[\alpha]_D^{20}$ +10.6 (*c* 1.06, $CHCl_3$); δ_H 0.63 (3 H, s, Me-11), 0.78 (3 H, s, Me-19), 0.85 (3 H, d, *J* 6.6, Me-26 or -27), 0.86 (3 H, d, *J* 6.6, Me-27 or -26), 0.89 (3 H, d, *J* 6.6, Me-21), 0.90–2.00 (31 H, complex), 2.05 (2 H, m, CH_2 pyr), 2.41 (2 H, t, *J* 7.9, CH_2 pyr), 3.31 (1 H, m, H-3), 3.48 (2 H, t, *J* 7.1, CH_2N), 4.75 and 4.79 (2 H, ABq, *J* 7.9, OCH_2N); δ_C 11.9, 12.2, 17.9, 18.6, 21.1, 22.5, 22.8, 23.7, 24.1, 27.9, 28.2, 28.3, 28.7, 31.2, 31.9, 34.8, 35.4, 35.5, 35.7, 36.1, 36.8, 39.4, 39.9, 42.5, 44.6, 45.7, 54.2, 56.1, 56.4, 70.3, 76.3, 175.5 (Found: C, 79.2; H, 11.3; N, 3.0. $C_{32}H_{55}NO_2$ requires C, 79.1; H, 11.4; N, 2.9%).

3-Cyclododecyloxymethyloxazolidin-2-one 37

Recrystallised from light petroleum (yield 89%), mp 72–74 °C; δ_H 1.30–1.60 (22 H, complex), 1.45 (2 H, m, CH_2), 1.63 (2 H, m, CH_2), 3.62 (1 H, m, OCH), 3.72 (2 H, m, CH_2 oxa), 4.35 (2 H, m, CH_2 oxa), 4.75 (2 H, s, OCH_2N); δ_C 20.8 (2 C), 23.1 (2 C), 23.3 (2 C), 23.9, 24.5 (2 C), 29.1 (2 C), 43.1, 62.0, 72.6, 74.8, 158.1 (Found: C, 67.6; H, 10.4, N, 4.9. $C_{16}H_{29}NO_3$ requires C, 67.8; H, 10.3; N, 4.9%).

1,2:5,6-Di-*O*-isopropylidene-3-*O*-(2-oxooxazolidin-3-ylmethyl)-α-D-glucofuranose 38

Syrup (yield 64%), $[\alpha]_D^{20}$ −29.3 (*c* 2.48, $CHCl_3$); δ_H 1.31 (3 H, s, Me), 1.33 (3 H, s, Me), 1.42 (3 H, s, Me), 1.48 (3 H, s, Me), 3.63 (1 H, m, CH^AH^BCO), 3.88 (1, H, m CH^AH^BCO), 4.01 (1 H, dd, *J* 8.8 and 4.6, H^A-6), 4.05 (1 H, dd, *J* 8.9 and 3.0, H-4), 4.10 (1 H, dd, *J* 8.8 and 6.2, H^B-6), 4.17 (1H, d, *J* 3.0, H-3), 4.25 (1 H, ddd, *J* 8.9, 6.2 and 4.6, H-5), 4.36 [2 H, m, $CH_2OC(=O)$], 4.56 (1 H, d, *J* 3.7, H-2), 4.71 (1 H, d, *J* 11.0, OCH^AH^BN), 4.98 (1 H, d, *J* 11.0, O CH^AH^BN), 5.86 (1 H, d, *J* 3.7, H-1); δ_C 25.4, 26.2, 26.8, 27.0, 43.0, 62.2, 67.7, 72.3, 73.8, 80.0, 80.9, 82.9, 105.3, 109.2, 112.1, 158.3 (Found: C, 53.8; H, 7.0; N, 3.6. $C_{16}H_{25}NO_8$ requires C, 53.5; H, 7.0; N, 3.9%).

4-Cyclododecyloxymethylmorpholine 43

This was obtained by a modification of a literature method for the preparation of aminol ethers.[15] A mixture of morpholine (4.40 g, 50.0 mmol), cyclododecanol (9.20 g, 50.0 mmol) and anhydrous potassium carbonate (6.90 g, 50.0 mmol) in

dichloromethane (200 cm^3) was stirred at 0 °C for 15 min under nitrogen. Paraformaldehyde (1.50 g, 50.0 mmol) was added in one portion and the mixture was stirred at room temperature for 30 min. The reaction mixture was then heated and dichloromethane–water azeotrope was slowly removed by distillation (*ca.* 1 cm^3 min^{-1}) until about 50 cm^3 of liquid remained. Solid material was then removed by filtration, the solvent was removed from the filtrate by evaporation and the residue was distilled under reduced pressure to give the aminol ether **43** as an oil (8.15 g, 58%), bp 148–151 °C/0.2 mmHg; δ_H 1.30–1.60 (22 H, m, CH_2), 2.66 (4 H, m, CH_2N), 3.55 (1 H, m, OCH), 3.71 (4 H, m, CH_2O), 4.04 (2 H, s, OCH_2N); δ_C 20.8 (2 C), 23.1 (2 C), 23.2, 23.3 (2 C), 24.5 (2 C), 29.2 (2 C), 49.9 (2 C), 67.0 (2 C), 74.9, 86.7 (Found: C, 71.8; H, 11.6; N, 5.0. $C_{17}H_{33}NO_2$ requires C, 72.0; H, 11.7; N, 4.9%).

Conditions for redox decomposition

Deoxygenation reactions were carried out in various solvents at the temperature of reflux. The initiator was 2,2-bis(*tert*-butylperoxy)butane (DBPB) in octane, 1,1-bis(*tert*-butylperoxy)-cyclohexane (DBPC) in toluene, or dilauroyl peroxide (DLP) in benzene. Di-*tert*-butyl hyponitrite[32] (TBHN) was also used as initiator in benzene solvent at a bath temperature of 60 °C.

Representative general procedure

A solution containing the alcohol derivative (1.0 mmol), TBST (9 mg, 3 mol%) and DBPB (18 μl of a 50% w/w solution in mineral oil, 3 mol%) in dry octane (1.2 cm^3) was stirred and heated under gentle reflux (bath temperature 140–145° C, preheated) under an atmosphere of argon. After 40 min, more initiator and thiol (3 mol% of each) were added and heating was continued for a further 2 h. The solvent was removed by evaporation under reduced pressure and the residue was subjected to flash chromatography on silica gel (generally light petroleum eluent) to give the deoxygenated alcohols with the following characteristics.

2-Methyladamantane[33] 19

Crystalline solid, mp 146–147 °C (lit.,[33] mp 146–148 °C); δ_H 1.03 (3 H, d, *J* 7.2, Me), 1.40–2.00 (15 H, m, CH_2 and CH); δ_C 18.9, 28.0, 28.3, 31.2, 33.7, 38.5, 39.3, 39.6.

Methylcyclododecane[10] 20

Oil; δ_H 0.86 (3 H, d, *J* 6.6, Me), 1.10 (2 H, m, CH_2), 1.35 (20 H, m, CH_2), 1.56 (1 H, m, CH); δ_C 21.3, 22.2, 23.6(1), 23.6(4), 24.2, 28.1, 31.8.

1,1-Dicyclohexylethane[34] 21

Oil; δ_H 0.65 (3 H, d, *J* 7.0, Me), 0.70–1.25 (13 H, m), 1.45–1.67 (10 H, m); δ_C 12.2, 26.8, 26.9, 28.9, 32.0, 39.6.

1-(*tert*-Butyldimethylsiloxy)-2-methylpropane[35] 22

Oil; δ_H 0.04 (6 H, s, Me_2Si), 0.88 (6 H, d, *J* 6.5, Me), 0.90 (9 H, s, Bu^t), 1.72 (1 H, nonet, *J* 6.5, CH), 3.35 (2 H, d, *J* 6.5, OCH_2); δ_C −5.3, 18.4, 19.0, 26.0, 30.9, 69.9.

1,2:5,6-Di-*O*-isopropylidene-3-*C*-methyl-3-deoxy-α-D-allofuranose[36a] 23

Oil, containing 9% of the C-3 epimer **24**; δ_H 5.79 (*J* 3.5 for H-1); δ_H 1.19 (3 H, d, *J* 6.9, Me-3) 1.32 (3 H, s, Me), 1.35 (3 H, s, Me), 1.42 (3 H, s, Me), 1.51 (3 H, s, Me), 1.94 (1 H, m, H-3), 3.73 (1 H, dd, *J* 9.8 and 6.2, H-4), 3.92 (1 H, dd, *J* 7.5 and 4.8, H^A-6), 4.06 (2 H, m, H-5 and H^B-6), 4.52 (1 H, dd, *J* 4.2 and 3.5, H-2), 5.75 (1 H, d, *J* 3.5, H-1); δ_C 10.1, 25.3, 26.4, 26.6, 26.8, 42.5, 67.3, 77.7, 82.8, 83.6, 104.9, 109.5, 111.6.

1,2:5,6-Di-*O*-isopropylidene-3-*C*-methyl-3-deoxy-α-D-glucofuranose[36b] 24

A chromatographically enriched sample (**23** : **24** = 70 : 30) showed δ_H 1.08 (3 H, d, *J* 6.9, Me-3), 1.32 (3 H, s, Me), 1.37 (3 H, s, Me), 1.40 (3 H, s, Me), 1.49 (3 H, s, Me), 2.11 (1 H, m, H-3), 3.75 (1 H, dd, *J* 13.8 and 3.4, H-4), 3.93 (1 H, m, H^A-6), 4.05 (2 H, m, H-5 and H^B-6), 4.54 (1 H, m, H-2), 5.79 (1 H, d, *J* 3.5, H-1).

3β-Methyl-5α-cholestane[37] 25

Recrystallised from acetone, mp 94–96 °C (lit.,[37] mp 90.5–92 °C); δ_H 0.64 (3 H, s, Me-11), 0.75 (3 H, s, Me-19), 0.86 (3 H, d, *J* 6.6, Me-26 or -27), 0.87 (6 H, d, *J* 6.6, Me-3 and Me-27 or -26), 0.90 (3 H, d, *J* 6.6, Me-21), 0.90–2.00 (32 H, complex); δ_C 12.0, 12.3, 18.7, 21.0, 22.6, 22.7, 22.8, 23.9, 24.2, 28.0, 28.3, 29.0, 31.0, 32.2, 33.2, 35.6, 35.7(5), 35.8(2), 36.2, 37.9, 38.7, 39.5, 40.1, 42.6, 46.8, 54.7, 56.3, 56.6.

Cyclododecane 39

Mp 60–61 °C; δ_H 1.34 (s); δ_C 23.7; identical with a commercial sample.

3-Deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-*ribo*-hexofuranose 40[4]

Oil, $[\alpha]_D^{20}$ −7.8 (*c* 1.87, $CHCl_3$) {lit.,[4] $[\alpha]_D^{20}$ −7.5 (*c* 10, EtOH)}; δ_H 1.32 (3 H, s, Me), 1.36 (3 H, s, Me), 1.42 (3 H, s, Me), 1.51 (3 H, s, Me), 1.77 (1 H, ddd, *J* 13.7, 8.8 and 5.0, H^A-3), 2.18 (1 H, dd, *J* 13.7 and 4.1, H^B-3), 3.82 (1 H, dd, *J* 7.9 and 5.0, H-4), 4.13 (3 H, m, H-5 and -6), 4.75 (1 H, [t], *J* 4.0, H-2), 5.81 (1 H, d, *J* 3.7, H-1); δ_C 25.1, 26.1, 26.4, 26.8, 35.2, 67.2, 76.7, 78.6, 80.4, 105.6, 109.6, 111.3.

5α-Cholestane[38] 41

Recrystallised from acetone, mp 77–78 °C (lit.,[38] mp 79–80 °C); δ_H 0.64 (3 H, s, Me-11), 0.77 (3 H, s, Me-19), 0.85 (3 H, d, *J* 6.6, Me-26 or -27), 0.86 (3 H, d, *J* 6.6, Me-27 or -26), 0.89 (3 H, d, *J* 6.6, Me-21), 0.90–2.00 (33 H, complex); δ_C 12.0, 12.2, 18.6, 20.7, 22.1, 22.5, 22.8, 23.8, 24.1, 26.8, 28.0, 28.2, 29.0, 29.1, 31.4, 32.1, 35.5, 35.8, 36.1, 36.2, 38.6, 39.5, 40.1, 42.5, 47.0, 54.7, 56.6.

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