The Invention of New Radical Chain Reactions. Part 11.† A New Method for the Generation of Tertiary Radicals from Tertiary Alcohols

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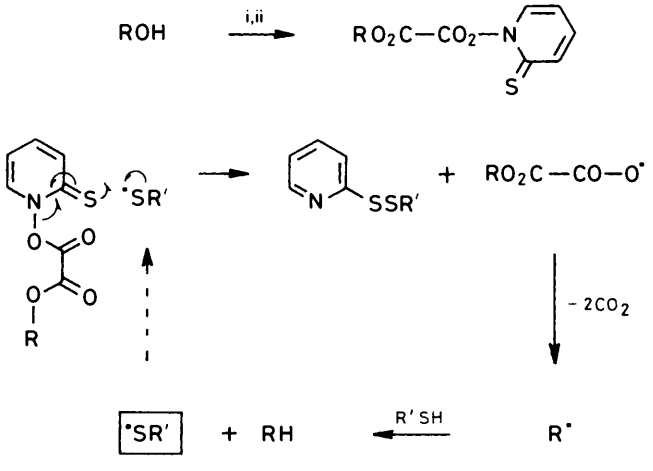
A convenient procedure for the radical deoxygenation of tertiary alcohols has been invented using the double half esters of oxalic acid with the t-alcohol and *N*-hydroxypyridine-2-thione. Decomposition of this type of ester in the presence of 1,1-dimethylethane- or (better) 1,1-diethylpropane-thiol gave the corresponding hydrocarbons in good yield. It has been shown that the oxalate fragmentation is not concerted, but involves a stepwise loss of carbon dioxide. Tertiary alcohols are also a convenient source of radicals for addition to suitable alkenes with formation of quaternary centres.

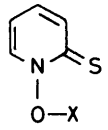
The free radical deoxygenation of secondary alcohols by the action of tributylstannane on derived thiocarbonyl esters is a proven synthetic method.[1,2] Primary alcohols can be similarly deoxygenated by the use of higher temperatures[3] and we considered that such a method for the reductive deoxygenation of tertiary alcohols, not interfering with any adjacent chiral centre, would be useful in the manipulation of complex natural products. Tertiary alcohol thiocarbonyl esters of the kind used in secondary alcohol deoxygenations are unstable and undergo facile Chugaev type elimination. They are, therefore, unsuitable. Tertiary alcohol thioxoformates, however, are stable in benzene at reflux and have been used in clean deoxygenation reactions.[4] A slightly different approach involves the treatment of tertiary alcohol selenocarbonates with tributylstannane.[5]

We wish to report in detail[6] here a new approach to the deoxygenation of tertiary alcohols which makes use of the free radical chemistry of *O*-esters of thiohydroxamic acids (mixed anhydrides) recently developed in our laboratory.[7] We conceived that the treatment of the chlorides of tertiary alcohol half-esters with oxalic acid with reagent (**1**) in the presence of a suitable thiol would lead *via* a free radical chain mechanism to the nor-hydrocarbon (Scheme 1).



Scheme 1. *Reagents:* i, $(COCl)_2$; ii, reagent (**1**)

Thus treatment of the model tertiary alcohol (**3**) with excess of oxalyl chloride led to the formation of its half-ester chloride after removal of the excess reagent. Subsequent addition of this crude chloride to a suspension of the reagent (**1**) and 1,1-dimethylethanethiol (**11**) in benzene, at reflux, under nitrogen furnished the hydrocarbon (**4**) in 63% yield after 1 h (Table 1, entry 1). The expected disulphide (**16**) and the mixed oxalate (**7**) were formed in 62 and 25% yields respectively in this reaction. It was evident from the formation of compound (**7**) that 1,1-dimethylethanethiol



$Me(CH_2)_{16}CMe_2X$

(**1**) X = Na^+
(**2**) X = H
(**3**) X = OH
(**4**) X = H
(**5**) X = $OSiMe_3$
(**6**) X = $OSnBu_3$
(**7**) X = OCOCOSCMe$_3$
(**8**) X = OCOCOS—$C_6H_2Me_3$ - 2,4,6
(**9**) X = OCHO
(**10**) X = 2 - Pyridylthio

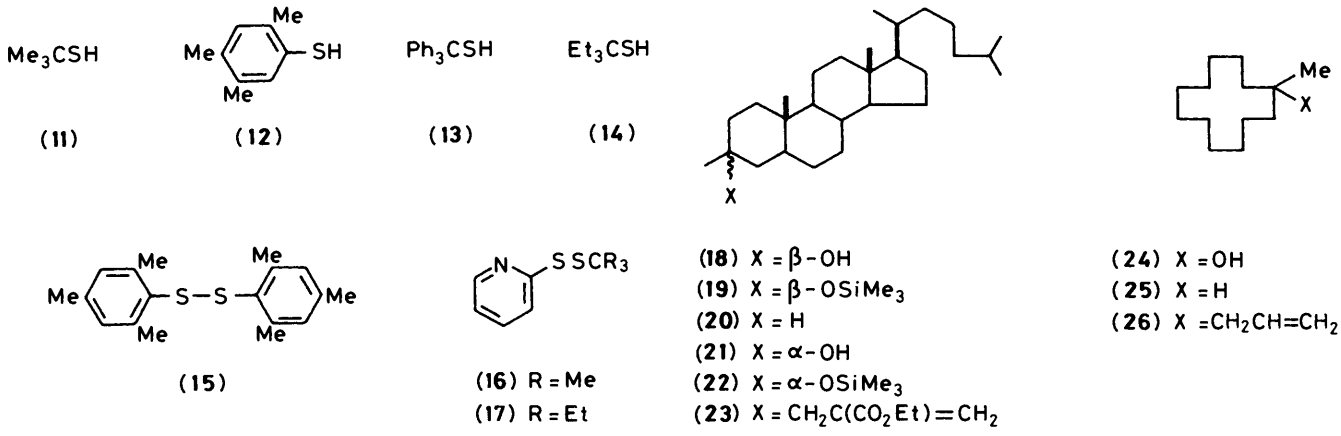
was competing with compound (**1**) for nucleophilic attack on the highly reactive oxalyl monochloride and that in order to increase the overall yield of the reaction it would be necessary either to increase the nucleophilicity of compound (**1**) or to employ a less nucleophilic thiol. The use of mesitylenethiol[8] (**12**) resulted in a similar yield of compound (**4**) but also in the formation of the mixed oxalate ester (**8**) in 31% yield (Table 1, entry 2). Triphenylmethanethiol (**13**) led to a lower yield of hydrocarbon which probably reflects a lower chain propagating ability of the triphenylmethylthio radical (Table 1, entry 3). In an attempt to increase the nucleophilicity of the thiohydroxamic acid we substituted the insoluble reagent (**1**) for the soluble mixture of the free acid (**2**) and pyridine and were indeed able to increase the yield of compound (**4**) to 69% although the formation of the ester (**7**) was not totally suppressed (Table 1, entry 4). Finally we synthesised the highly sterically hindered thiol 1,1-diethylpropanethiol (**14**) by the action of hydrogen sulphide and conc. sulphuric acid on 1,1-diethylpropanol. This compound (**14**) had previously been prepared by treatment of carbon disulphide with triethylaluminium.[9] The use of compound (**14**) in the deoxygenation of compound (**3**) under standard conditions yielded (**4**) in 81% yield together with the disulphide (**17**) in 72% yield (Table 1, entry 5).

† Part 10, D. H. R. Barton, H. Togo, and S. Z. Zard, *Tetrahedron*, 1985, **41**, 5507.

Table 1. Alcohol deoxygenation

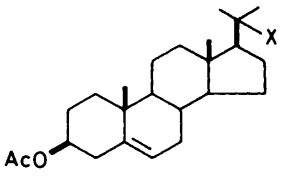
Entry	Substrate	Esterification time (h)	Temp. (°C)	Thiol (mmol)	Time (h)	Products (% yield)
1	(3)	18	80	(11) (4)	1	(4) (63) + (7) (25) + (16) (62)
2	(3)	18	80	(12) (2)	1.5	(4) (63) + (15) (52) + (8) (31)
3	(3)	18	80	(13) (2)	1	(4) (50)
4	(3)[a]	18	80	(11) (4)	1	(4) (69) + (7) (6) + (16) (75)
5	(3)	18	80	(14) (2)	0.5	(4) (81) + (17) (72)
6	(3)	18	80	(14) (10)	1	(4) (83) + (9) (5)
7	(3)[a,g]	18	r.t.	(14) (2)	1	(4) (65) + (9) (12)
8	(3)[a,g]	18	r.t.	(14) (10)	1	(4) (38) + (9) (26)
9	(5)	3	80	(14) (2)	1	(4) (76) + (17) (82)
10	(6)	1	80	(14) (1.2)	1	(4) (65)
11	(19)	18	80	(14) (2)	1	(20) (80) + (17) (82)
12	(22)	20	80	(14) (2)	0.75	(20) (79) + (17) (86)
13	(24)	18	80	(11) (4)	1.5	(25) (55)
14	(24)	18	80	(14) (2)	1	(25) (70) + (17) (67)
15	(27)	18	80	(11) (4)	1	(28) (90)
16	(29)	18	80	(11) (15)	1	(36) (67)
17	(31)[b]	2	80	(14) (2)	0.5	(32) (77)
18	(33)	2	80	(11) (4)	2	(35) (74)
19	(33)	2	132[c]	(11) (4)	2	(34) (31) + (35) (46)
20	(37)	2	132[c]	(14) (2)	2	(38) (43) + (39) (15) + (17) (51)
21	(37)	2	152[d]	(14) (2)	2	(38) (53) + (39) (37) + (17) (34)
22	(37)	2	178[e]	(14) (2)	2	(38) (40) + (39) (40)
23	(40)	2	110[f]	(14) (2)	1	(41) (36) + (42) (29)
24	(40)	2	110[f]	(14) (10)	1	(41) (17) + (42) (50)
25	(40)	2	110[f]		1.5	(43) (33) + (44) (27)
26	(3)[a,g]	18	r.t.		1.5	(10) (79)
27	(46)	4	80		1	(47) (48)

[a] Esterification with compound (2) and pyridine. [b] Catalysis with $Bu_4N^+F^-$. [c] Chlorobenzene. [d] Cumene. [e] *o*-Dichlorobenzene. [f] Toluene. [g] Deoxygenation carried out at room temperature in normal laboratory light.

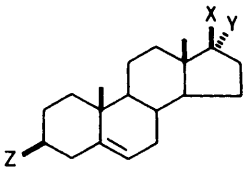


Application of the general method to other tertiary alcohols gave good yields of reduction products (Table 1, entries 13, 14, and 15) however, the alcohol (**29**) provided the rearranged 13(14)-unsaturated steroid (**36**) in 67% yield (Table 1, entry 16). Compound (**36**) was considered to be the product of the action of hydrogen chloride on compound (**29**) during its reaction with oxalyl chloride, rather than of a new radical rearrangement. Bearing this in mind the trimethylsilyl ether (**5**) of the alcohol (**3**) was prepared, which on reaction with oxalyl chloride should lead to the desired acyl chloride and chlorotrimethylsilane thus maintaining the neutrality of the reaction mixture. The use of compound (**5**) as a substrate in the deoxygenation procedure gave the expected hydrocarbon (**4**) in 76% yield (Table 1, entry 9). For similar reasons and also in order to increase the nucleophilicity–reactivity of highly hindered alcohols we prepared the tributylstannyl ether (**6**) of the alcohol (**3**) according to the method of Davies *et al.*[10] Application of the general procedure to (**6**) gave the hydrocarbon (**4**) in 65% yield (Table 1, entry 10). Trimethylsilylation of the monoacetate (**30**) of the diol (**29**) gave the ether (**31**) in excellent yield. The reaction sequence for deoxygenation of (**31**) provided the expected product (**32**) in 77% yield with no trace of (**36**) (Table 1, entry 17). The silylation–deoxygenation procedure was also applied to the two epimeric steroidal alcohols (**18**) and (**21**). Thus the trimethylsilyl ethers (**19**) and (**22**) both provided 3β-methylcholestane (**20**) in high yield (Table 1, entries 11 and 12). We were unable to detect any 3α-methylcholestane by highfield ^1H n.m.r. spectroscopy in either of these two latter reactions. We have, therefore, an interesting illustration of stereoselectivity induced by quenching of the radical from the less hindered side.

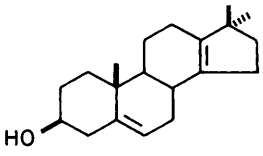
This deoxygenation procedure might well find application in the macrolide series, for example the deoxygenation of a suitable erythromycin A derivative[11] would be important.



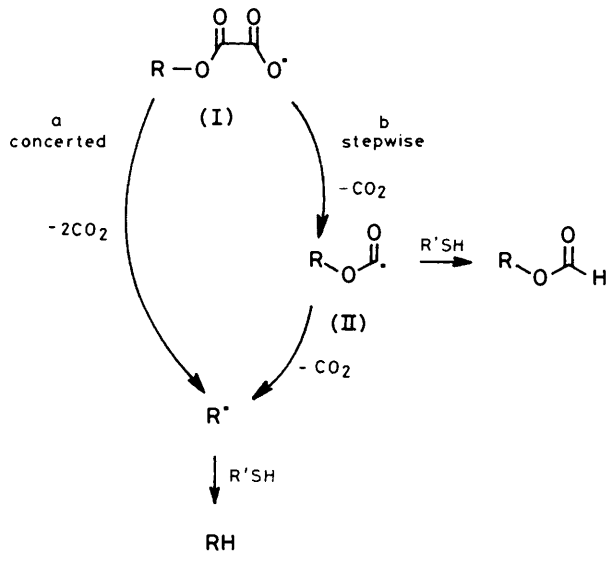
(27) X = OH
(28) X = H



(29) X = Z = OH, Y = Me
(30) X = OH, Z = OAc, Y = Me
(31) X = $OSiMe_3$, Z = OAc, Y = Me
(32) X = Me, Z = OAc, Y = H
(33) X, Y = O, Z = OH
(34) X, Y = O, Z = H
(35) X, Y = O, Z = OCOCOSCMe$_3$



(36)



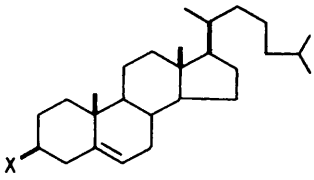
Scheme 2.

Having thus established a method for free radical deoxygenation of tertiary alcohols we turned our attention to secondary alcohols. The tin hydride–dithiocarbonate procedure[1] is an expedient method for the deoxygenation of secondary and primary alcohols but we considered that a method which did not require the use of an organotin hydride would find use in natural product chemistry. We first of all applied the general tertiary alcohol method to 17-oxoandrost-5-en-3β-ol (**33**) using benzene as the solvent. Not surprisingly, we only isolated one major product, the mixed oxalyl ester (**35**) in 74% yield (Table 1, entry 18) from this reaction. Obviously the use of the highly hindered thiol (**14**) is just as necessary with secondary alcohols as with tertiary ones. However, on performing the same reaction in chlorobenzene at reflux we were able to isolate the deoxygenation product (**34**) in 31% yield (Table 1, entry 19).

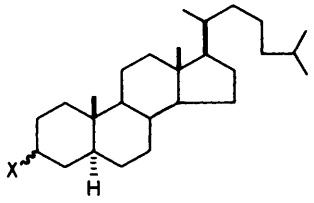
It is well known that alkoxycarbonyl radicals derived from secondary alcohols, unlike those derived from tertiary alcohols, undergo decarboxylation with reluctance in toluene at reflux. Thus Graf and collaborators, on treatment of various secondary alcohol phenylselenocarbonates with tributylstannane, found[5] little deoxygenation at 80 °C in benzene, the major product being the formate. At 110 °C in toluene the yields of nor-alkane were *ca.* 40%, whilst in xylene at reflux (144 °C) yields of 50—90% could be obtained. Similarly Jackson *et al.* in their procedure using chloroformates and tri-isopropylsilane had recourse to temperatures of 140 °C in order to obtain high yields of deoxygenation product.[12] We were intrigued by the idea that alkoxycarbonyl acyloxyl radicals (I) might possibly lose two molecules of carbon dioxide in a concerted manner (Scheme 2, path a) rather than *via* a stepwise procedure involving the alkoxycarbonyl radical (II) (Scheme 2, path b). If this were the case we might expect higher yields of deoxygenation product from secondary alcohols than if the radical II had a definite existence in the reaction.

In order to test this hypothesis we studied the deoxygenation of cholesterol in PhCl at 132 °C, using the thiol (**14**) and found 43% of the deoxygenation product cholestene (**38**) and some formate (Table 1, entry 20). This is very comparable with the yield of 39% deoxygenation found by Graf[5] when his procedure was applied to a 3β-hydroxy-Δ^5-steroid in toluene at reflux. In cumene at reflux we found 53% deoxygenation and 37% of the formate (**39**) (Table 1, entry 21) whilst in *o*-dichlorobenzene at reflux the yield of deoxygenation product was only 40% (Table 1, entry 22). The formation of significant quantities of the formate (**39**) in each of these reactions points to a stepwise mechanism (Scheme 2, path b) but it may still be inferred that some or all of the deoxygenation product (**38**) was formed *via* a concerted mechanism (Scheme 2, path a). In order to differentiate unambiguously between the two mechanistic possibilities we decided to carry out a series of experiments with the saturated cholestanol series under essentially identical conditions varying only the concentration of thiol present in the reaction mixture. An increase in the ratio of formate:deoxygenation product with thiol concentration would be strongly indicative of a stepwise mechanism. In the event, the ratio of (**42**):(**41**) (formate:deoxygenated product) was 1:1.04 when cholestanol (**40**) was subjected to the general procedure in toluene and in the presence of 2 equivalents of the thiol (**14**) (Table 1, entry 23) and 2.9:1 when 10 equivalents of thiol were used. Evidently then, at least in the case of secondary alcohols radicals of the type I (Scheme 2) fragment in a stepwise manner. It is interesting to note that Jensen and Moder[13] obtained cyclohexyl chloride in 48% yield on thermolysis of *O*-cyclohexyl *OO*-t-butyl monoperoxyoxalate ($C_6H_{11}OCO–CO–OOCMe_3$) in tetrachloromethane at reflux (77 °C). Obviously tetrachloromethane is a less efficient trap for alkoxycarbonyl radicals than thiols are. We attempted the deoxygenation of cholestanol (**40**) in the absence of any extraneous radical trap in toluene at 110 °C and only two products were isolated from this reaction, the sulphide (**43**) and the thiocarbonate (**44**) in 33 and 27% yields respectively (Table 1, entry 25). Both products are presumably formed *via* free chain mechanisms analogous to the rearrangement of *O*-esters of thiohydroxamic acids,[7] although we cannot rule out the possibility that (**44**) is formed by an intramolecular rearrangement of the 'highly favoured' 6-*exo*-*trig* type.[14]

Having adequately demonstrated the stepwise mechanism (Scheme 2, path b) for secondary alcohols we attempted to do likewise for tertiary alcohols. When the standard deoxygenation of alcohol (**3**) was carried out in benzene at reflux but using 10 equivalents of the thiol (**14**), deoxygenation was still the major pathway and only 5% of the formate was formed (Table 1, entry 6). At room temperature the difference was more significant,

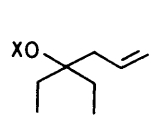


(37) X = OH
(38) X = H
(39) X = OCHO

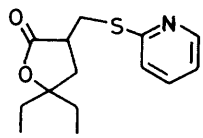


(40) X = β-OH
(41) X = H
(42) X = β-OCHO
(43) X = α-(2-pyridylthio)
(44) X = β-OCO-(2-pyridylthio)

thus when 2 equivalents of compound (**14**) were employed the ratio of formate:hydrocarbon was 1:5.4 (Table 1, entry 7) whilst with 10 equivalents it was 1:1.5 (Table 1, entry 8). When no thiol was used the expected sulphide (**10**) was formed in 79% yield even at room temperature (Table 1, entry 26). Evidently the fragmentation of tertiary alkoxycarbonyl radicals at 80 °C in benzene is too rapid to allow intermolecular trapping whilst the same radical is sufficiently persistent at room temperature for it to be quenched by hydrogen transfer from a thiol. We were, however, successful in trapping a tertiary alkoxycarbonyl radical at 80 °C in an intramolecular fashion. Thus when the tributylstannyl ether (**46**) derived from the homoallylic alcohol (**45**) was treated first with oxalyl chloride and then with the reagent (**1**) in benzene at reflux the lactone (**47**) was isolated in 48% yield, thus demonstrating both the intermediacy of the alkoxycarbonyl radical and also the efficiency of the *5-exo-trig*



(45) X = H
(46) X = $SnBu_3$



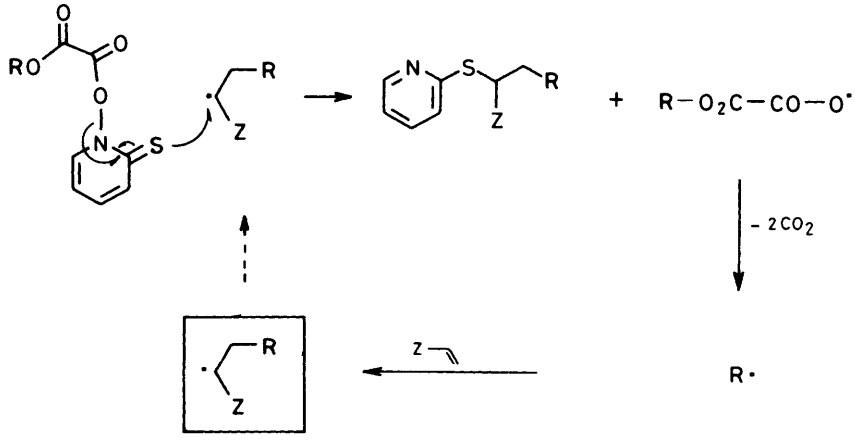
(47)

(48) X = OH
(49) X = CH(CN)CH(CN)-(2-pyridylthio)
(50) X = $CH_2C(=CH_2)CO_2Et$

type radical ring closure reaction. We conclude therefore that the fragmentation of radicals of the type I (Scheme 2) proceeds *via* a two step mechanism involving the alkoxycarbonyl radical II. Bartlett and collaborators[15] previously reached a similar conclusion having isolated di-t-butyl carbonate from the decomposition of di-t-butyl monoperoxalate (Me_3COO_2C–CO_2CMe_3) at 25 °C.

Having established a facile method for the reductive deoxygenation of tertiary alcohols we next attempted to construct a free radical system for the formation of quaternary carbon centres from tertiary alcohols. Two systems exist in the literature for the formation of new carbon–carbon bonds from secondary alcohols.[16,17] Both systems are based upon the attack of stannyl radicals on the thiocarbonyl sulphur of a derived thiocarbonyl ester[18] as used in our original deoxygenation procedure,[1] and are thus not applicable to tertiary alcohols as outlined above. Quaternary carbon centres have been formed by free radical routes in both the aliphatic[19] and aromatic[20] $S_{RN}1$ reactions, by our own decarboxylation procedures[21,22] and also from tertiary nitro compounds.[23] Tertiary alcohols themselves have been quaternised with both trimethylaluminium[24] and titanium(IV) reagents,[25] but to the best of our knowledge their quaternisation by free radical methods is a hitherto unknown reaction.[26]

We first of all envisaged the addition of radicals derived from the deoxygenation of tertiary alcohols to electron-deficient alkenes by a free radical chain mechanism (Scheme 3).



Z = electron-withdrawing group.

Scheme 3.

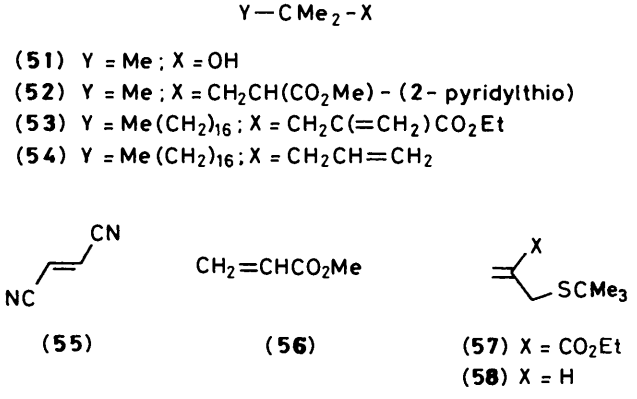
Table 2. Formation of quaternary carbon centres

Entry	Substrate	Alkene (mmol)	Temp. (°C)	Products (% yield)
1	(**48**)	(**55**) (1.1)	80[a]	(**49**) (32)
2	(**51**)	(**56**) (2.2)	80[a]	(**52**) (32)
3	(**48**)	(**57**) (1.5)	132[b]	(**50**) (53) + (**16**) (55)
4	(**48**)	(**57**) (2)	80[a]	(**50**) (50)
5	(**19**)	(**57**) (1.2)	132[b]	(**23**) (52)
6	(**3**)	(**57**) (2)	80[a]	(**53**) (46)
7	(**24**)	(**58**) (30)	132[b]	(**26**) (49) + (**16**) (51)
8	(**3**)	(**58**) (15)	132[b]	(**54**) (54)

[a] Benzene. [b] Chlorobenzene.

Indeed when adamantan-1-ol was subjected to the general deoxygenation procedure and the thiol replaced by fumarodinitrile we were able to isolate the expected adduct (**49**) in 32% yield (Table 2, entry 1). Similarly deoxygenation of t-butyl alcohol in the presence of methyl acrylate led to the adduct (**52**) also in 32% yield (Table 2, entry 2). These results are comparable to those obtained previously by the decarboxylation of carboxylic acids in the presence of Michael acceptors.[21]

Ethoxycarbonylallylation[22] was a cleaner and more efficient reaction. Thus deoxygenation in the presence of the non-polymerisable alkene (**57**) in chlorobenzene at reflux led to



moderate yields of adducts (Table 2, entries 3 and 5) according to a free-radical chain mechanism (Scheme 4, X = CO_2Et). Our original ethoxycarbonyl results[22,6] were obtained in chlorobenzene at reflux, but we now find that equally good yields can be obtained in benzene at reflux (Table 2, entries 4 and 6).

Finally we note that free-radical allylation (Scheme 4; X = H) using allyl t-butyl sulphide was a much less efficient process. However, using a large excess of allyl t-butyl sulphide we were able to obtain moderate yields of the compounds (**26**) and (**54**) by quaternisation of the alcohols (**24**) and (**3**) (Table 2, entries 7 and 8).

Experimental

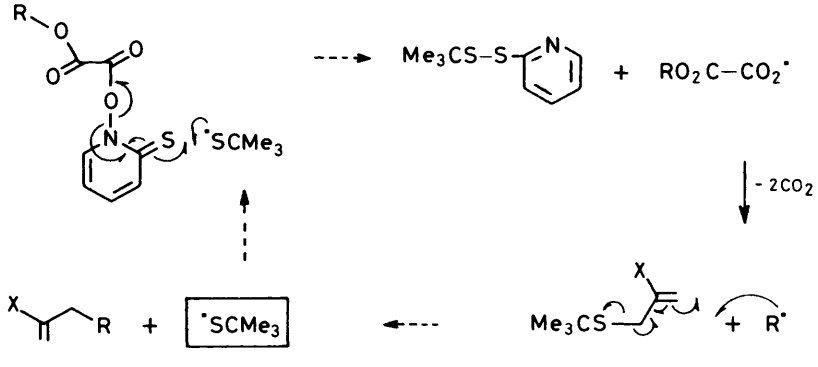
Unless otherwise stated n.m.r. spectra were recorded at 60 MHz with a Varian EM 360L spectrometer and as solutions in deuteriochloroform. Chemical shifts are in p.p.m. downfield from tetramethylsilane as the internal standard. 200 MHz n.m.r. spectra were measured with a Bruker WM 200 spectrometer. I.r. spectra were obtained with either a Perkin-Elmer 257 or 297 spectrophotometer. 70 ev E.i. mass spectra were recorded on either an AEI MS-9 or AEI MS-50 apparatus. Melting points were taken on a Reichert hot stage apparatus and are uncorrected. Optical rotations were measured with a Perkin-Elmer 151 polarimeter for solutions in chloroform and u.v. spectra with a Jobin Yvon Duospec 203 spectrophotometer. All solvents were dried and distilled according to standard procedures.

General Method for the Preparation of Tertiary Alcohol Trimethylsilyl Ethers.—A mixture of trimethylsilyl chloride, trimethylsilylimidazole and bis(trimethylsilyl)acetamide (2:3:3; 1 ml) was added at room temperature under nitrogen to a stirred solution of the alcohol (2 mmol) in dichloromethane (10 ml). When the reaction was complete (t.l.c. control) the mixture was poured into water (20 ml), and after decantation the organic phase was washed with water (20 ml), dried (Na_2SO_4), filtered, and evaporated to dryness giving the crude product which was purified by distillation or recrystallisation as appropriate.

2-Methyl-2-trimethylsilyloxynonadecane (**5**). The alcohol (**3**) (596 mg) yielded the *silyl ether* (**5**) (621 mg, 84%) as a colourless oil after Kugelrohr distillation (b.p. 150 °C/5 mmHg); δ 0.01 (9 H, s), 0.90 (3 H, t), and 1.3 (38 H, br m); *m/z* 369 ($M^+ - 1$); 355 ($M^+ - 15$); $\nu_{max.}$(film) 1 455, 1 250, 1 040, and 840 cm^{-1} (Found: C, 74.45; H, 13.4. $C_{23}H_{50}OSi$ requires C, 74.51; H, 13.59%).

3α-Methyl-3β-trimethylsilyloxy-5αH-cholestane (**19**). 3α-Methylcholestan-3β-ol (**18**)[27] (500 mg, 1.2 mmol) gave the *trimethylsilyl ether* (**19**) (460 mg, 80%) after crystallisation from acetone, m.p. 133—135 °C; $[\alpha]_D^{20}$ +27° (*c*, 1); δ −0.01 (9 H, s), 0.50 (3 H, s), 0.65 (3 H, s), and 0.80 (3 H, s); *m/z* 474 (M^+); 459 ($M^+ - 15$); $\nu_{max.}$(Nujol) 1 450, 1 370, 1 240, and 830 cm^{-1} (Found: C, 78.3; H, 12.1. $C_{31}H_{58}OSi$ requires C, 78.41; H, 12.31%).

3β-Methyl-3α-trimethylsilyloxy-5αH-cholestane (**22**). Silylation of the alcohol (**21**)[27] gave the *title compound* (**22**) in 78% yield after recrystallisation from acetone, m.p. 82—82.5 °C; $[\alpha]_D^{20}$ +20° (*c*, 1.7); δ −0.01 (9 H, s), 0.5 (3 H, s), 0.6 (3 H, s), and 0.8 (3 H, s); *m/z* 474 (M^+) and 459 ($M^+ - 15$);



Scheme 4.

$\nu_{max.}$($CHCl_3$) 1 440, 1 360, 1 020, and 830 cm^{-1} (Found: C, 78.45; H, 12.2. $C_{31}H_{58}OSi$ requires C, 78.41; H, 12.31%).

3β-*Acetoxy*-17α-*methyl*-17β-*trimethylsilyloxyandrost*-5-*ene* (**31**). The alcohol (**30**)[28] gave the *silyl ether* (**31**) in 75% yield on recrystallisation from acetone, m.p. 144—145 °C; $[\alpha]_D^{20}$ −85° (*c*, 1.6); δ −0.01 (9 H, s), 0.65 (3 H, s), 0.95 (3 H, s), 1.85 (3 H, s), 4.30 (1 H, m), and 5.25 (1 H, m); *m/z* 403 (M^+ − 15); 359 (M^+ − AcO); $\nu_{max.}$(CH_2Cl_2) 1 720, 1 010, and 820 cm^{-1} (Found: C, 71.7; H, 9.9. $C_{25}H_{42}O_3Si$ requires C, 71.71; H, 10.12%).

2-*Methyl*-2-*tributylstannyloxynonadecane* (**6**).—Tributylstannyl ethyl ether[10] (1.002 g, 3 mmol) was added to a stirred solution of the alcohol (**3**) (900 mg, 3 mmol) under nitrogen in toluene (10 ml) at reflux. After 4 h at reflux with azeotropic distillation, the solvent was removed under reduced pressure and the residue subjected to vacuum distillation to give the *title stannyl ether* (**6**) (1.48 g, 84%) as a colourless oil, b.p. 250 °C/0.1 mm; $\nu_{max.}$(film) 1 450 and 965 cm^{-1} (Found: C, 64.85; H, 11.65. $C_{32}H_{68}OSn$ requires C, 65.41; H, 11.67%).

1,1-*Diethylpropanethiol* (**14**).—Concentrated sulphuric acid (3 ml) was added dropwise over 10 min to a solution of 1,1-diethylpropanol (4 g) in dichloromethane (10 ml) through which hydrogen sulphide was being continually passed *via* a sintered frit. The flow of hydrogen sulphide was maintained for a further 30 min and the reaction then allowed to stand at room temperature for 1 h before being poured into water (50 ml). After decantation the aqueous phase was extracted with dichloromethane (2 × 20 ml) and the combined organic phases dried (Na_2SO_4), filtered and evaporated to dryness. Vacuum distillation of the crude product gave the *title thiol* (**14**) as a colourless oil (1.8 g, 40%), b.p. 72 °C/36 mmHg (lit.,[9] 92—95 °C/95 mmHg); δ 0.90 (9 H, t, *J* 8 Hz), 1.20 (1 H, s), and 1.55 (6 H, q, *J* 8 Hz).

General Method for Alcohol Deoxygenation.—The substrate (1 mmol) in benzene (1 ml) was added at room temperature, under nitrogen to a stirred solution of oxalyl chloride (0.5 ml) in benzene (5 ml). After the reaction had been stirred for the appropriate time (see the Table) the solvent and excess oxalyl chloride were removed under reduced pressure. The residue was taken up in the appropriate solvent (5 ml) (see Table 1) and added over 10 min to a stirred suspension of compound (**1**) (180 mg, 1.2 mmol), DMAP (12 mg, 0.1 mmol) and a thiol (see Table 1) at reflux under nitrogen, in the appropriate solvent (5 ml) (see Table 1). After completion (t.l.c. control) the cooled reaction mixture was filtered on Celite and evaporated to dryness. Chromatography on silica gel gave the pure reaction products.

2-*Methylnonadecane* (**4**). This colourless oil was eluted with pentane and was identical to an authentic sample. It had δ 0.9 (9 H, m) and 1.40 (33 H, m); *m/z* 282 (M^+).

Methylcyclododecane (**25**). 1-Methylcyclododecanol (**24**) afforded methylcyclododecane (**25**) after chromatography (eluant: pentane) as a colourless oil with δ 1.1 (3 H, d) and 1.5 (23 H, m); *m/z* 182 (M^+).

1,1-*Dimethyloctadecyl* S-t-*Butyl Thio-oxalate* (**7**).—The deoxygenation of compound (**3**) using 1,1-dimethylethanethiol, gave the *title compound* (**7**) which was eluted with dichloromethane. It had δ 0.9 (3 H, t), 1.3 (32 H, m), and 1.5 (15 H, s); *m/z* 280 (M^+ − OCOCOSCMe$_3$); $\nu_{max.}$(film) 1 730, 1 680, 1 450, and 1 000 cm^{-1}; $\lambda_{max.}$(EtOH) 267 nm (ε 6 700) (Found: C, 70.45; H, 11.4; S, 6.75. $C_{26}H_{50}O_3S$ requires C, 70.53; H, 11.38; S, 7.24%).

1,1-*Dimethyloctadecyl* S-*mesityl thio-oxalate* (**8**). Deoxygenation of compound (**3**) in the presence of mesitylenethiol[8] gave the *title compound* (**8**) as a by-product which showed δ 0.9 (3 H, t), 1.3 (32 H, m), 1.5 (6 H, s), 2.3 (9 H, s), and 6.8 (2 H, s); $\nu_{max.}$(film) 1 720, 1 690, 1 595, and 1 460 cm^{-1}; $\lambda_{max.}$ 236 (ε 17 400) and 276 nm (ε 3 800) (Found: C, 73.95; H, 10.45; S, 6.1. $C_{31}H_{52}O_3S$ requires C, 73.76; H, 10.36; S, 6.35%).

1,1-*Dimethyloctadecyl formate* (**9**). This *oil* was obtained as a by-product from the reduction of the alcohol (**3**). It had b.p. 200 °C/0.5 mmHg (Kugelrohr), δ 0.9 (3 H, m), 1.3 (32 H, m), 1.4 (6 H, s), and 8.1 (1 H, s); $\nu_{max.}$(film) 2 930, 2 850, 1 735, 1 195, and 910 cm^{-1} (Found: C, 77.05; H, 13.05. $C_{21}H_{42}O_2$ requires C, 77.24; H, 12.96%).

t-Butyl 2-*pyridyl disulphide* (**16**). In the deoxygenation experiments using 1,1-dimethylethanethiol, the disulphide (**16**) was obtained which, after elution over silica gel with dichloromethane, was found to be identical to an authentic sample.

2-*Pyridyl* 1,1-*diethylpropyl disulphide* (**17**). Deoxygenation using 1,1-diethylpropanethiol (**14**) led to the formation of the *mixed disulphide* (**17**) as a colourless oil with b.p. 180 °C/0.2 mmHg (Kugelrohr), δ 0.85 (9 H, t, *J* 8 Hz), 1.6 (6 H, t, *J* 8 Hz), 7.08 (1 H, m), 7.75 (2 H, m), and 8.25 (1 H, d, *J* 5 Hz); *m/z* 241 (M^+); $\nu_{max.}$(CH_2Cl_2) 2 875, 1 575, 1 560, 1 110, and 900 cm^{-1} (Found: C, 60.0; H, 7.8; N, 5.65; S, 26.4. $C_{12}H_{19}NS_2$ requires C, 59.70; H, 7.93; N, 5.80; S, 26.56%).

Dimesityl disulphide (**15**). This disulphide was formed during the reduction with mesitylenethiol (**11**). It was eluted with pentane and had m.p. 123—124 °C (EtOH) (lit.,[29] 123—124 °C).

3β-*Acetoxy*-20-*methylpregn*-5-*ene* (**28**). The tertiary alcohol (**27**)[30] gave the steroid (**28**) in 90% yield after chromatography (eluant: dichloromethane), m.p. 122—124 °C (MeOH–water) (lit.,[31] 121—121.5 °C); $[\alpha]_D^{16}$ −62° (*c*, 0.6) (lit.,[31] $[\alpha]_D^{16}$ −69°).

17,17-*Dimethyl*-18-*norandrosta*-5,13-*dien*-3-*ol* (**36**). Application of the general method to diol (**29**)[32] gave the Wagner-Meerwein product (**36**) which was purified by chromatography on silica (eluant: dichloromethane) and had m.p. 133—135 °C (MeOH–water) (lit.,[33] 133—133.5 °C).

3β-*Acetoxy*-17β-*methylandrost*-5-*ene* (**32**). This compound was obtained by deoxygenation of the silyl ether (**31**). It was eluted from silica gel with dichloromethane and had m.p. 125—127 °C (acetone) (lit.,[34] 124—126 °C); $[\alpha]_D^{20}$ −69° (*c*, 1) (lit.,[34] $[\alpha]_D$ −65°).

3β-*Methyl*-5αH-*cholestane* (**20**). This compound which was a single diastereoisomer at position 3, was obtained from either compounds (**19**) or (**22**). It had m.p. 95—96 °C (acetone) [lit., 96—97 °C (acetone),[35] 97—98 °C,[36] 105—106 °C ($CHCl_3$–MeOH),[27] $[\alpha]_D^{20}$ +27° (*c*, 1) (lit., $[\alpha]_D$ +23°,[27] +11°[36]).

Cholest-5-*ene* (**38**) *and* 3β-*formyloxycholest*-5-*ene* (**39**). These two compounds were obtained from the deoxygenation of cholesterol and have the following characteristics: (**38**) m.p. 90—92 °C (acetone) (lit.,[1] 90—92 °C); (**39**) m.p. 96 °C (acetone) (lit.,[37] 96 °C).

Androst-5-*en*-17-*one* (**34**). Deoxygenation of 17-oxoandrost-5-en-3β-ol (**33**) gave the title compound which had m.p. 106—108 °C (EtOH) (lit.,[38] 105—107 °C).

17-*Oxoandrost*-5-*en*-3β-*yl* S-*t-butyl oxalate* (**35**). Deoxygenation of 17-oxoandrost-5-en-3β-ol (**33**) in the presence of 1,1-dimethylethanethiol gave the *title ester* (**35**) as a crystalline solid after filtration on silica gel (eluant: dichloromethane), m.p. 187—188 °C (EtOH); $[\alpha]_D^{20}$ +16° (*c*, 0.9); δ (80 MHz) 0.85 (3 H, s, 19-H_3), 1.01 (3 H, s, 18-H_3), 1.45 (9 H, s), 4.70 (1 H, m, 3α-H), and 5.4 (1 H, m, 6-H); *m/z* 270 (M^+ − $Me_3CSCOCOOH$); $\nu_{max.}$(Nujol) 1 725, 1 670, 1 250, and 980 cm^{-1}; $\lambda_{max.}$(EtOH) 270 nm (ε 4 200) (Found: C, 69.55; H, 8.35. $C_{25}H_{36}O_4S$ requires C, 69.41; H, 8.38%).

5αH-*Cholestane* (**41**) *and* 3β-*formyloxy*-5αH-*cholestane* (**42**). Deoxygenation of cholestan-3β-ol (**40**) led to 5αH-cholestane (**41**), m.p. 80 °C (acetone) (lit.,[37] 80—80.5 °C) and cholestan-3β-yl formate (**42**), m.p. 82—84 °C (EtOH) (lit.,[39] m.p. 82—84 °C).

3α-(2-*Pyridylthio*)-5αH-*cholestane* (**43**) *and* O-*cholestan*-3β-*yl* S-(2-*pyridyl*)*thiocarbonate* (**44**).—Cholestan-3β-ol (194 mg, 0.5 mmol) in benzene (5 ml) was treated with oxalyl chloride (1 ml) at room temperature for 2 h. After evaporation, the crude oxalyl monochloride was taken up in toluene (1 ml) and added rapidly to compound (**1**) (85 mg, 0.6 mmol) in toluene (5 ml), at reflux, under nitrogen. After 0.5 h at reflux the cooled reaction mixture was filtered and the filtrate evaporated to dryness. Chromatography on silica gel of the crude reaction product gave firstly the *sulphide* (**43**) (80.2 mg, 33%) which contained 10—15% of the 3β-isomer (eluant: dichloromethane). Recrystallisation from ether–acetone gave the pure compound (**43**) which had m.p. 124.5 °C; $[\alpha]_D^{20}$ +28.6° (*c*, 1); δ (200 MHz), δ 0.66 (3 H, s, 18-H_3), 0.84 (3 H, s, 19-H_3), 0.87 (6 H, d, *J* Hz), 0.91 (3 H, d, *J* 7 Hz, 21-H_3), 4.4 (1 H, 3β-H*), 7.0 (1 H, dd, J_1 6 Hz, J_2 8 Hz), 7.2 (1 H, d, *J* 8 Hz), 8.5 (1 H, dd, $J_1 \simeq J_2$ 8 Hz), 8.46 (1 H, d, *J* 8 Hz); *m/z* 483 (M^+) and 450 (M^+ − HS); $\nu_{max.}$(Nujol) 1 580, 1 415, and 1 125 cm^{-1} (Found: C, 79.85; H, 10.55; N, 3.05; S, 6.4. $C_{32}H_{51}NS$ requires C, 79.77; H, 10.67; N, 2.91; S, 6.65%). Further elution with dichoromethane gave the *thiocarbonate* (**44**) (70 mg, 27%), m.p. 118—120 °C (acetone); $[\alpha]_D^{20}$ +8.4° (*c*, 0.8); δ 0.66 (3 H, s), 4.9 (1 H, m, 3α-H); 7.45 (2 H, m), 7.9 (1 H, d, *J* 6 Hz), and 8.7 (1 H, d, *J* 6 Hz); *m/z* 525 (M^+); $\nu_{max.}$(Nujol) 1 725, 1 160, 1 150, and 1 115 cm^{-1} (Found: C, 75.25; H, 9.7; N, 2.55; S, 5.95. $C_{33}H_{51}NO_2S$ requires C, 75.38; H, 9.78; N, 2.66; S, 6.10%).

2-*Methyl*-2-(2-*pyridylthio*)*nonadecane* (**10**).—Oxalyl chloride (2 ml) was added to a stirred solution of compound (**3**) (1.49 g, 5 mmol) in benzene (20 ml) at room temperature. After the reaction had been stirred at room temperature for 18 h the mixture was evaporated to dryness and the residue taken up in dry ether (10 ml) and added to a stirred solution of compound (**2**) (698 mg, 5.5 mmol) and pyridine (435 mg, 5.5 mmol) in dry ether (20 ml), under nitrogen at room temperature. The resulting bright yellow solution (precipitate of PyH^+Cl^-) was stirred in the light for 2 h at room temperature, then filtered and the filtrate evaporated to dryness. Filtration on silica gel [eluant: dichloromethane–hexane (1:1)] gave the pure *sulphide* (**10**) (1.55 g, 79%) as a pale yellow oil, b.p. 220 °C/1 mmHg (Kugelrohr), δ 0.9 (3 H, m), 1.2 (32 H, m), 1.45 (6 H, s), 7.1 (1 H, m), 7.35 (2 H, m), 8.5 (1 H, d, *J* 5 Hz); $\nu_{max.}$(film) 2 930, 2 860, 1 585, 1 560, 1 460, 1 420, and 1 125 cm^{-1} (Found: C, 76.8; H, 11.6; N, 3.75; S, 8.05. $C_{25}H_{45}NS$ requires C, 76.66; H, 11.58; N, 3.58; S, 8.32%).

4-*Ethylhex*-1-*en*-4-*ol* (**45**).—Allyl chloride (7.6 g, 0.1 mol) was dissolved in dry ether (200 ml) and a portion of the resulting solution (20 ml) was added to magnesium turnings (5 g, 0.2 mol) under nitrogen in a 500-ml flask. When the reaction had commenced, the remaining solution was added dropwise over 30 min with stirring such that the reaction refluxed gently. After a further 1h at reflux the reaction mixture was cooled to room temperature and a solution of pentan-2-one (4.3 g, 0.05 mol) in ether (50 ml) was added over 15 min. The reaction was then heated to reflux for 1 h. The cooled reaction mixture was then decanted from the excess of magnesium and quenched with ice-cold aqueous 2M-ammonium hydroxide (200 ml). The ether phase was washed with water (2 × 200 ml), dried ($MgSO_4$), filtered, and the filtrate evaporated to dryness. The residue was distilled to yield pure 4-ethylhex-1-en-4-ol (5.5 g, 86% based on the ketone), b.p. 45 °C/15 mmHg (lit.,[40] b.p. 49 °C/20 mmHg); δ 0.80 (6 H, t, *J* 7 Hz), 1.4 (1 H, s), 1.45 (4 H, q, *J* 7 Hz), 2.2 (2 H, d, *J* 7 Hz), 5.0 (1 H, m), 5.3 (1 H, m), and 5.5—6.3 (1 H, m); $\nu_{max.}$(film) 3 400br, 2 980, 2 970, 1 640, 1 460, and 910 cm^{-1}.

* [Note that the 3β-isomer of compound (**43**) has its 3α-H resonance at δ 3.73].

4-*Ethyl*-4-(*tributylstannyl*)*oxyhex*-1-*ene* (**46**).—The alcohol (**45**) (640 mg, 5 mmol) and tributyltin ethoxide[10] (1.67 g, 5 mmol) were heated to reflux under nitrogen, in toluene (10 ml) with continuous azeotropic distillation for 6 h. After distillation of the solvent, the residue was rapidly Kugelrohr distilled (170 °C/0.5 mmHg) to give the title stannyl ether (**46**) (1.9 g, 91%) as a colourless oil with δ 0.7—2.6 (37 H, m), 2.1 (2 H, d, *J* 8 Hz), 5.0 (1 H, m), 5.2 (1 H, m), and 5.5—6.3 (1 H, m); $\nu_{max.}$(film) 2 980, 2 960, 1 460, and 1 380 cm^{-1}; *m/z* 417 (M^+).

3(-2-*Pyridylthiomethyl*)-5,5-*diethyl*-2,3,4,5-*tetrahydrofuran*-2-*one* (**47**).—The stannyl ether (**46**) (626 mg, 1.5 mmol) in benzene (10 ml) was treated with oxalyl chloride (1 ml) with stirring at room temperature under nitrogen for 4 h. After the removal of the volatiles, the residue was taken up in benzene (20 ml) and added to a stirred suspension of the reagent (**1**) (240 mg, 1.6 mmol) in benzene (10 ml) at reflux, under nitrogen. After 1 h at reflux, the cooled reaction mixture was filtered and evaporated to dryness. Chromatography of the residue on silica gel (eluant: dichloromethane) gave the *lactone* (**47**) (48%) which was an oil, b.p. 150 °C/0.5 mmHg (Kugelrohr), δ (200 MHz) 0.8 (6 H, t, *J* 7 Hz), 1.55 (4 H, m), 1.83 (1 H, m, ring CH_2), 2.17 (1 H, m, ring CH_2), 3.17 (2 H, m, 1 × SCH_2 + ring CH), 3.83 (1 H, m, SC*H*H), 6.95 (1 H, m), 7.15 (1 H, d, *J* 8 Hz), 7.45 (1 H, m), and 8.43 (1 H, m); *m/z* 265 (M^+), 236 (M^+ − Et), 111 (pyridine-2-thione); $\nu_{max.}$(film), 2 960, 1 740, 1 560, 1 460, 1 420, and 1 130 cm^{-1} (Found: C, 63.5; H, 7.25; N, 5.15; S, 11.95. $C_{14}H_{19}NO_2S$ requires C, 63.36; H, 7.22; N, 5.28; S, 12.08%).

3-(*Adamantan*-1-yl)-3-*cyano*-2-(2-*pyridylthio*)*propanonitrile* (**49**).—Oxalyl chloride (0.25 ml) was added to a stirred solution of adamantan-1-ol (**48**) (152 mg, 1 mmol) in benzene (5 ml) at room temperature. After the reaction had been stirred for 18 h at room temperature and evaporated to dryness, the residue was taken up in benzene (5 ml) and added under nitrogen to a stirred suspension of the reagent (**1**) (180 mg, 1.2 mmol) and fumarodinitrile (**55**) (78 mg, 1.1 mmol) at reflux in benzene (5 ml). After 1 h at reflux the cooled reaction mixture was filtered and evaporated to dryness. Filtration on silica gel (eluant: dichloromethane) gave the title compound (103 mg, 32%) as a mixture of diastereoisomers with m.p. 140—143 °C (ether–hexane), δ 1.80 (6 H, m), 1.95 (3 H, m), 2.30 (6 H, m), 2.80 (1 H, d, *J* 3 Hz, 5.30 (1 H, d, *J* 3 Hz), 6.8—7.8 (3 H, m), and 8.40 (1 H, d, *J* 5 Hz); *m/z* 323 ($M^{+\bullet}$), 290 (M^+ − HS), and 188 (M^+ − $C_{10}H_{15}$); $\nu_{max.}$(CH_2Cl_2) 2 230, 1 580, and 1 560 cm^{-1} (Found: C, 70.3; H, 6.45; N, 12.9; S, 9.8. Calc. for $C_{19}H_{21}N_3S$: C, 70.55; H, 6.54; N, 12.99; S, 9.91%).

Methyl 4,4-*Dimethyl*-2-(2-*pyridylthio*)*pentanoate* (**52**).—t-Butyl alcohol (80 mg, 1.1 mmol) was stirred in benzene (5 ml) with oxalyl chloride (0.25 ml) for 18 h at room temperature. The reaction was then evaporated to dryness and the residue taken up in benzene (2 ml) and added rapidly to a stirred suspension of compound (**1**) (180 mg, 1.2 mmol), methyl acrylate (190 mg, 2.2 mmol), and 4-dimethylaminopyridine (12 mg, 0.1 mmol) in benzene (5 ml) at reflux under nitrogen. After 45 min at reflux the reaction mixture was cooled to room temperature, filtered, and the filtrate evaporated to dryness. Chromatography on silica gel (eluant: dichloromethane) gave the *title compound* (**52**) (82 mg, 32%) as a colourless oil with b.p. 110 °C/2 mmHg (Kugelrohr); δ 1.10 (9 H, s), 2.0 (2 H, m), 4.70 (1 H, dd, J_1 10 Hz, J_2 4 Hz), 6.8—7.8 (3 H, m), and 8.5 (1 H, d, *J* 5 Hz); *m/z* 253 (M^+) and 196 (M^+ − C_4H_9); $\nu_{max.}$(film) 1 730, 1 580, 1 555, 1 450, 1 410, 960, and 920 cm^{-1} (Found: C, 61.4; H, 7.6; N, 5.5; S, 12.65. $C_{13}H_{19}NO_2S$ requires C, 61.63; H, 7.56; N, 5.53; S, 12.66%).

Ethyl 3-(*Adamantan*-1-*yl*)-2-*methylenepropanoate* (**50**).—Adamantan-1-ol (**48**) (152 mg, 1 mmol) was treated with oxalyl chloride (0.25 ml) in benzene (5 ml) at room temperature for 16 h. After the reaction had been evaporated to dryness the residue was taken up in chlorobenzene (5 ml) and added dropwise over 5 min to a stirred suspension of the reagent (**1**) (180 mg, 1.2 mmol) and alkene (**57**) (300 mg, 1.5 mmol) in chlorobenzene, at reflux, under nitrogen. After 1 h at reflux, the cooled reaction mixture was filtered, the filtrate evaporated to dryness, and the residue filtered on silica gel [eluant: dichloromethane–pentane (1:1)] to give the *ester* (**50**) (132 mg, 53%) as a colourless oil, b.p. 150 °C/3 mmHg (Kugelrohr), δ 1.33 (3 H, t, *J* 8 Hz), 1.60 (6 H, m), 1.75 (6 H, m), 2.00 (3 H, m), 2.25 (2 H, s), 4.30 (2 H, q, *J* 8 Hz), 5.55 (1 H, s), and 6.35 (1 H, s); *m/z* 248 (M^+; $\nu_{max.}$(film) 1 710, 1 620, and 1 180 cm^{-1} (Found: C, 77.75; H, 9.9. $C_{16}H_{24}O_2$ requires C, 77.38; H, 9.74%). Further elution with dichloromethane gave the disulphide (**16**) (105 mg, 55%).

Ethyl 2-*Methylene*-3-(3-αβ-*methylcholestan*-3βα-*yl*)*propanoate* (**23**).—Oxalyl chloride (0.25 ml) and tetrabutylammonium fluoride (5 mg) were added to a stirred solution of the silyl ether (**19**) (100 mg, 0.21 mmol) in benzene (5 ml) and the mixture stirred for 2 h at room temperature before it was evaporated to dryness. The residue was taken up in chlorobenzene (1 ml) and added over 5 min to a stirred suspension of the reagent (**1**) (35 mg) and the alkene (**57**) (50 mg) at reflux under nitrogen in chlorobenzene (5 ml). After 45 min at reflux, the reaction was cooled to room temperature and filtered. The filtrate was evaporated and the residue filtered through silica gel [eluant: dichloromethane–pentane (1:1)] to give compound (**23**) (55 mg, 52%) as a mixture of diastereoisomers in the form of a viscous oil: *major isomer* δ (200 MHz) 0.63 (3 H, s), 0.74 (3 H, s), 1.28 (3 H, t, *J* 9 Hz), 2.4 (2 H, s), 4.17 (2 H, q, *J* 9 Hz), 6.16 (1 H, d, *J* 2 Hz), and 5.37 (1 H, d, *J* 2 Hz); *minor isomer* δ (200 MHz) 0.69 (3 H, s), 0.75 (3 H, s), 1.28 (3 H, t, *J* 9 Hz), 2.23 (2 H, s), 4.17 (2 H, q, *J* 9 Hz), 5.43 (1 H, d, *J* 2 Hz), and 6.10 (1 H, d, *J* 2 Hz); *m/z* 498 (M^+), 483 (M^+ − Me), and 384 (M^+ − $MeC(=CH_2)CO_2Et$); $\nu_{max.}(CH_2Cl_2)$ 1 715 cm^{-1} (Found: C, 82.05; H, 11.9. Calc. for $C_{34}H_{58}O_2$: C, 81.87; H, 11.72%).

Ethyl 4,4-*Dimethyl*-2-*methylenehenicosanoate* (**53**).—The alcohol (**3**) (298 mg, 1 mmol) and oxalyl chloride (0.25 ml) were stirred in benzene (5 ml) at room temperature for 18 h. After the reaction had been evaporated to dryness, the residue was taken up in benzene (2 ml) and added to a stirred refluxing suspension of the reagent (**1**) (180 mg, 1.2 mmol) and the alkene (**57**) (404 mg, 2 mmol) in benzene (5 ml) under nitrogen. After 2 h at reflux the cooled reaction mixture was filtered and the filtrate evaporated to dryness before filtration of the residue through silica gel (eluant: dichloromethane–hexane (1:1) yielding the αβ-*unsaturated ester* (**53**) (180 mg, 46%) as a viscous colourless oil with b.p. 220 °C/1 mmHg (Kugelrohr), δ 0.8 (12 H, m), 1.2 (34 H, m), 2.3 (2 H, s), 4.30 (2 H, q, *J* 8 Hz), 5.5 (1 H, s), and 6.4 (1 H, s); $\nu_{max.}$(film) 2 920, 2 850, 1 735, and 1 630 cm^{-1} (Found: C, 79.35; H, 12.85. $C_{26}H_{50}O_2$ requires C, 79.12; H, 12.77%).

1-*Allyl*-1-*methylcyclododecane* (**26**).—1-Methylcyclododecanol (**24**) (198 mg, 1 mmol) was treated with oxalyl chloride (0.25 ml) in benzene (5 ml) for 18 h. After evaporation to dryness the residue was taken up in chlorobenzene (2 ml) and added over 5 min to a stirred suspension of the reagent (**1**) (180 mg, 1.2 mmol) and allyl t-butyl sulphide[41] (4 ml) in chlorobenzene at reflux, under nitrogen. After 1 h at reflux the cooled reaction mixture was filtered, the filtrate evaporated to dryness and the residue purified by filtration through silica gel (eluant: pentane) to yield the *title compound* (109 mg, 49%) as a colourless oil with b.p. 150 °C/1 mmHg (Kugelrohr), δ 0.9 (3 H, m), 1.3 (22 H, m), 2.0 (2 H, m), 5.0 (2 H, m), and 5.9 (1 H, m); *m/z* (c.i.; isobutene), 279 ($M^+ + C_4H_9$), 223 (MH^+), 221 (M^+ − H), and 181 ($MH^+ - C_3H_5$) (Found: C, 86.45; H, 13.6. $C_{16}H_{30}$ requires C, 86.40; H, 13.60%). Further elution with dichloromethane afforded the disulphide (**16**) (111 mg, 55%).

4,4-*Dimethylhenicos*-1-*ene* (**54**).—The *title compound*, a colourless oil, was prepared from the alcohol (**3**) in a manner exactly analogous to that used for the preparation of compound (**26**). It had δ 0.9 (9 H, m), 1.3 (32 H, m), 2.0 (2 H, m), 5.0 (2 H, m), and 5.9 (1 H, m); *m/z* 282 ($MH^+ - C_3H_5$) (Found: C, 85.6; H, 14.5. $C_{23}H_{46}$ requires C, 85.63; H, 14.37%).

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