Synthesis and Reactions of t-Butyltellurocarbonyloxyalkanes

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Summary Reaction of t-butyl(chloromethylene)dimethylammonium chloride with alcohols and sodium hydrogen telluride gave t-butyltellurocarbonyloxyalkanes; 3β-t-butyltellurocarbonyloxy-5α-cholestane [Bu^{t}C(=Te)OR]

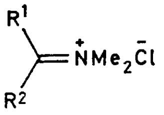
with diphenylseleninic anhydride and sodium hydrogen telluride gave, respectively, esters (Bu^tCO_2R) and ethers (Bu^tCH_2OR) and [$(Bu^tCHOR)_2$].

THE reaction of substituted alkoxymethylenedimethylammonium chlorides (**1a**) with hydrogen sulphide–pyridine or with sodium hydrogen selenide provides a general route to thio- (**2a**) and seleno-esters (**2b**).[1] We now report that alkyltellurocarbonyloxyalkanes (**2c**) (hereinafter 'telluroesters'), hitherto an unknown class of compounds, exist and are reasonably stable at room temperature. Previously, we reported[1] that the reduction of cholest-5-en-3β-yloxyphenylmethylenedimethylammonium chloride (**3a**) with sodium hydrogen telluride gave 3β-benzyloxycholest-5-ene (**3b**) probably *via* the telluroester (**3c**) and hydrogen atom transfer. An alkyl telluroester should be more stable on account of less ready H• transfer. In order to suppress possible enolisation, polymerisation, *etc.*, the sterically hindered t-butyltellurocarbonyloxyalkanes were chosen for study.

TABLE

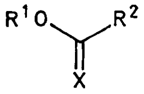
Telluroester[a]	% Yield	M.p. (T/°C)	δ (^{1}H; $CDCl_3$)
(**4b**)[b]	89	116—120 (decomp.)	5·55 (3α-H), 1·28 (Bu^t)
(**5**)[c]	28	160—165 (decomp.)	5·65 (3α-H), 5·32 (11-H), 4·65—4·15 (16α-H), 3·4 (26-H_2)
(**6**)[d]	63	Oil	4·2 (OCH_2), 1·37 (Bu^tCTe), 1·1 (Bu^t)
(**7**)[e]	91	<25	4·12 (OCH_2), 1·35 (Bu^t)
(**8**)	6	Oil	6·0—5·3 (OCH), 1·27 (Bu^t)

[a] Microanalyses were consistent with the formulations (**4b**) and (**5**)—(**8**). (**6**)—(**8**) gave molecular ion measurements (^{130}Te) in good agreement with theory. [b] [α] (578 nm; $CHCl_3$) $-43·8°$. [c] [α] (578 nm; $CHCl_3$) $-104°$. [d] δ (^{13}C; $CDCl_3$) 229·38 (s, C=Te), 94·61 (t, OCH_2), 58·43 (s, *C*–C=Te), 32·05 (s, *C*–CH_2–O), 29·84 (q, *Me*$_3$C–C=Te), and 26·68 (*Me*$_3$C–CH_2O) p.p.m. [e] 229·20 s, C=Te), 94·96 (OCH_2), 58·61 (s, *C*–C=Te), and 29·94 (*Me*$_3$C) p.p.m.



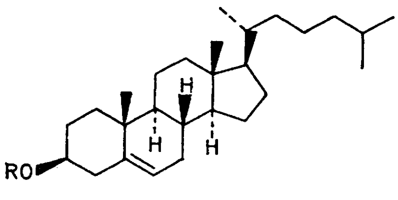
(1)

a; R^1 = alkoxy
b; R^1 = Bu^t, R^2 = Cl



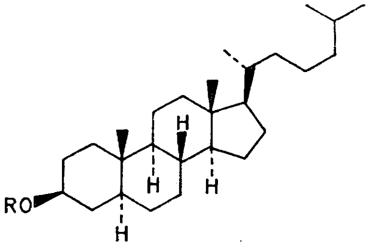
(2)

a; X = S
b; X = Se
c; X = Te



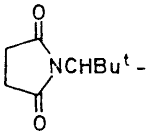
(3)

a; R = $Cl^- Me_2\overset{+}{N}{=}C(Ph)-$
b; R = $PhCH_2-$
c; R = $PhC({=}Te)-$



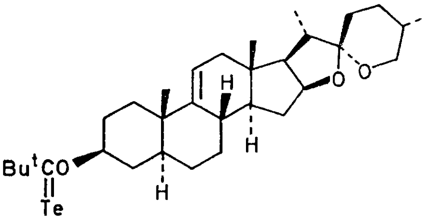
(4)

a; R = H
b; R = $Bu^tC({=}Te)-$
c; R = $Bu^tC({=}O)-$
d; R = Bu^tCH_2-
e; R = $-Bu^tCH-Bu^tCH-$
f; R = Bu^tCH•
g; R = $-Bu^tCHTe_n-CHBu^t-$ (n = 1-4)
h; R =

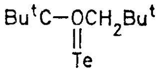


Typically, 5α-cholestan-3β-ol (**4a**) (2·5 mmol) in dichloromethane was added to the phosgene-free chloride (**1b**) in dichloromethane at 0 °C. After 0·5—1·5 h sodium hydrogen telluride [from tellurium (2·0 mmol) and sodium borohydride (4·0 mmol)[1] buffered with acetic acid (4·0 mmol) at -20 °C] in ethanol (-78 °C) was also added. After 10—20 min, quenching with aqueous sodium hydrogen carbonate, diethyl ether–water partition, and rapid chromatography on alumina gave the telluroester (**4b**) (89%). All manipulations must be carried out under nitrogen in subdued lighting. Both microanalysis† and the mass spectrum (*m/e* 586, 584, 582, 581, and 580) support assignment as the telluroester (**4b**). By analogous procedures the telluroesters (**5**)—(**8**) were prepared (Table). The telluroester (**4b**) shows u.v. maxima at 243 (ϵ 4290), 266 sh (830), 346 (7600), and 592 nm (320) and (**5**)—(**8**) show maxima at similar positions. The tellurocarbonyl resonance appears at δ *ca.* 229 p.p.m. in the ^{13}C n.m.r. spectra of (**6**) and (**7**).

Although the telluroester (**4b**), when pure, was stable to air in the dark or on photolysis (>500 nm) with exclusion

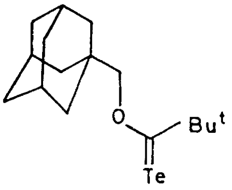


(5)

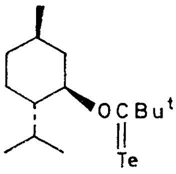


$$Bu^tC(=Te)-OCH_2Bu^t$$

(6)



(7)



(8)

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† All new compounds have excellent microanalytical results unless stated to the contrary.

of oxygen all subsequent reactions were conducted in the dark under nitrogen. Oxidation with diphenyl seleninic anhydride[2] in tetrahydrofuran gave the pivaloate (**4c**) (96%), m.p. 164—166 °C, $[\alpha]_D^{21}$ + 14·3° ($CHCl_3$, *c* 0·5) ν_{max} (Nujol) 1725 cm^{-1}. Reduction of the telluroester (**4b**) with buffered sodium hydrogen telluride in dichloromethane–ethanol gave initially (3 h) a tellurium-containing species and finally (4 days) a crystalline homogeneous (t.l.c.) ether (57%), m.p. 120—126 °C. This was tentatively identified as a mixture of the neopentyl ether (**4d**) and the pinacol diether (**4e**). All spectral data (M^+ *m/e* 458) and microanalysis were in agreement with formulation as the ether (**4d**). However, the n.m.r. spectrum [δ 4·06 (s), 3·78 (m, 3α-H), and 3·42 (m)] showed the presence of both products. Plausibly, the radical (**4f**) was a common intermediate. The tellurium-containing species was most reasonably‡ the oligotelluride mixture (**4g**), δ ($CDCl_3$) 5·72—5·4 (Bu^{t}C*H*O), 3·81—3·1 (3α-H), and 1·08 (Bu^t). Reaction of this mixture with *N*-bromosuccinimide gave the pure imide (**4h**) (68%), m.p. 138—140 °C with resolidification, second m.p. 160—165 °C, $[\alpha]_D^{23}$ + 13° (*c* 0·4, $CHCl_3$), ν_{max} (Nujol) 1785 and 1705 cm^{-1}, δ ($CDCl_3$) 5·05 (Bu^{t}C*H*), 3·05 (3α-H), 2·65 ($COCH_2CH_2CO$), and 0·97 (Bu^t).

Clearly, Vilsmeier methodology provides telluroacylating species as yet unavailable by other means.

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‡ Found: C, 63·05; H, 9·55. $C_{64}H_{114}O_2Te_n$ requires C, 73·65, 65·65, 59·2, 53·9; H, 11·0, 9·8, 8·85, 8·05% for *n* = 1, 2, 3, 4, respectively.

[1] D. H. R. Barton and S. W. McCombie, *J.C.S. Perkin I*, 1975, 1574; D. H. R. Barton, P-E. Hansen, and K. Picker, *ibid.*, 1977, 1723.
[2] D. H. R. Barton, N. J. Cussans, and S. V. Ley, *J.C.S. Chem. Comm.*, 1978, 393.