Dehydrogenation of Steroidal and Triterpenoid Ketones using Benzeneseleninic Anhydride

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Steroid and triterpenoid ketones can be smoothly dehydrogenated in high yield with benzeneseleninic anhydride in chlorobenzene at 95—120 °C. With an excess of benzeneseleninic anhydride and longer reaction times 4,4-dimethyl ketones give ring-A-contracted diketones in moderate yield.

THE dehydrogenation of steroidal ketones to give biologically important enones has been an active area of research for many years. However the methods commonly employed, dicyanodichloroquinone (DDQ),[1] selenium dioxide,[2] and dehydrohalogenation,[3] all have synthetic limitations, and new methodology is still required. Here we discuss in detail [4] the use of benzeneseleninic anhydride (1) as a new dehydrogenating reagent.

RESULTS AND DISCUSSION

In typical reactions we find that 3-oxo-steroids can be dehydrogenated in chlorobenzene using the anhydride (1) to give high yields of products (Table). The major by-product of the reaction is diphenyl diselenide which is recovered and re-oxidised to the anhydride with nitric acid.[5] The dehydrogenated products were usually isolated by preparative layer chromatography.

Of special interest in the examples chosen in the Table is cholestanone which reacts with 2 equiv. of the anhydride to smoothly afford the 1,4-dienone (2). However on treatment with 3 equiv. we were unable to obtain the 1,4,6-trienone (3) although it could be obtained by oxidation of cholesta-4,6-dienone with (1). As the stability of the trienone was limited it was normally isolated as the 1α,2α-epoxide (4), as this was required for further synthetic transformation.[6] The reaction was easily carried out on a synthetically useful scale (*i.e.* 10 g). Other desirable features of the dehydrogenation procedure are that ketones such as α- and β-amyrone, lupeone, and 4,4-dimethylcholest-5-en-3-one contain remote double bonds which are not affected by the anhydride under normal reaction conditions, a reaction which is in direct contrast to the corresponding oxidations using SeO_2. That one is not restricted to ring-A-dehydrogenation is indicated by the excellent oxidation of hecogenin acetate to the 9(11)-enone (5).

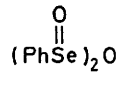
Reactions of the anhydride with 3-oxo-steroids under more vigorous conditions, *i.e.* with more anhydride and longer reaction times, led to the formation of other products (Table). For example both α- and β-amyrone with two equivalents of the anhydride after 17 h, apart from the normal dehydrogenated product, gave significant quantities of ring-A-nor-compounds (6) and (7), respectively, and in a similar manner 4,4-dimethylcholest-5-en-3-one gave (8).† Lanostanone, however, gives (9) as one of the reaction products, even at 95 °C over a relatively short period of time (45 min). The other minor product that was also formed in the reaction was shown to be the 2-phenylseleno-derivative (10) by

Reaction of steroidal ketones with benzeneseleninic anhydride (BSA)

	Reaction conditions			Products (%)		
Ketone	Temperature(°C)	BSA(equiv.)	Time	Enone	A-Nor-2,3-dione	2-Phenylseleno ketone
Lanostanone	95	1	45 min	1-enone (67)	(13)	(4)
	100	2	18 h	(38)	(41)	
	100	1 *	150 min	(64)	(10)	
Cholest-4-en-3-one	132	1	40 min	1,4-dienone (92)		
4,4-Dimethylcholest-5-en-3-one	95—100	1	25 min	1,5-dienone (58)	(29)	
	95—100	2	19 h	(23)	(33)	
α-Amyrone	95—100	1	25 min	1-enone (74)		
	95—100	2	17 h	(32)	(42)	
β-Amyrone	95—100	1	15 min	1-enone (54)	(8)	
	95—100	2	18 h	(27)	(46)	
Hecogenin acetate	132	2	50 min	9,(11)-enone (91)		
	100	2 *	160 min	(81)		
Lupeone	95—100	1	15 min	1-enone (58)		
Cholestan-3-one	132	2	3 h	1,4-dienone (83)		
Cholest-1-en-3-one	95	1	45 min	1,4-dienone (76)		
Cholesta-4,6-dien-3-one	95	1	1 h	1,4,6-trienone (>50)		

* Benzenseleninic acid.

† In our preliminary communication [4] these substances were incorrectly represented as A-nor-monoketones.



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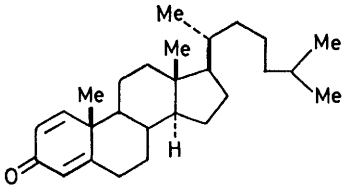

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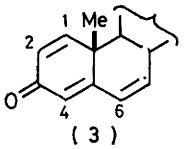

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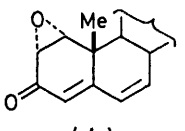

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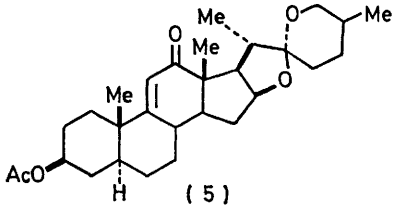
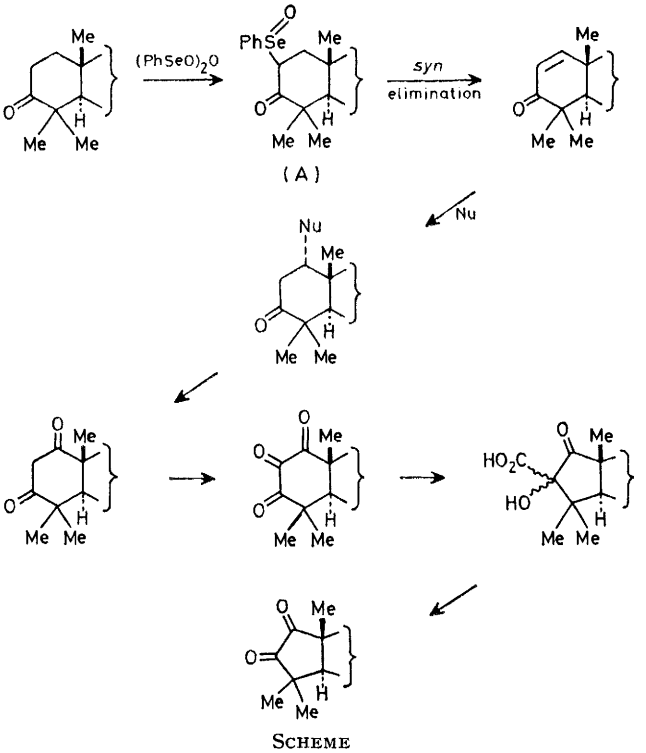


(5)

comparison with an authentic sample prepared by treatment of the enolate of lanostanone with benzeneselenenyl chloride.

At 120 °C one would certainly expect that benzeneseleninic acid would dehydrate rapidly in solution and therefore be equivalent in properties to the anhydride. In the two examples we have studied both lanostanone and hecogenin acetate gave the corresponding enones in high yield on reaction with benzeneseleninic acid (Table).

In order to rationalise the formation of the various products of oxidation of oxo-steroids with benzeneseleninic anhydride we propose that the ketone, *via* its enolic form, reacts to give an intermediate seleneno-ester (A) (Scheme). This ester would spontaneously eliminate benzeneseleninic acid to give the enone, a reaction which has ample literature precedence.[7] The formation of the A-nor-steroid diketone is in part undoubtedly derived by a benzylic acid type of reaction.[8] That the product is a cyclopentane-dione rather than the normal



(A)

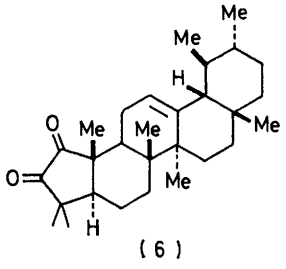
SCHEME

keto-hydroxyacid is accounted for by the observation that benzilic acid itself is converted to benzophenone in 95% yield by the anhydride.

As the A-nor-diketone is formed at the expense of the enone under more vigorous conditions lanost-1-en-3-one was treated with the anhydride in a separate experiment and gave a 48% yield of (9) on work-up.

The phenylselenated by-products presumably arise by reaction of the initial ketone with a phenylselenating agent which is most likely a partially reduced form of the initial anhydride and could be either PhSeOSePh or PhSeOSe(O)Ph.

In an effort to develop a catalytic dehydrogenation procedure we have found that lanostan-3-one can be dehydrogenated in 69% yield by the *in situ* formation of the anhydride from only 0.25 equiv. of diphenyl



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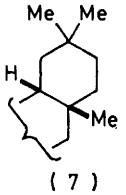

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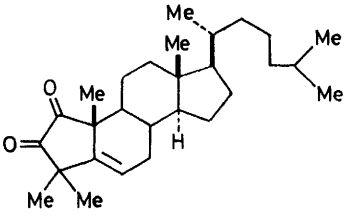

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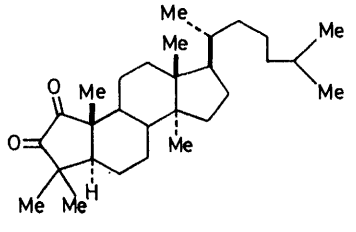

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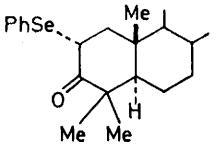

(10)

diselenide and a 5-fold molar excess of t-butyl hydroperoxide.

The reactions described above constitute a new method for dehydrogenation of steroidal ketones showing in many cases an improvement over existing literature procedures.

In a recent communication Yamakawa *et al.*[9] have shown that certain ketones adjacent to, and enolisable towards, a tertiary centre are oxidised smoothly by benzeneseleninic anhydride to α-hydroxyketones. It would seem reasonable that attack by the anhydride on the enol should occur at carbon when this position is unhindered but at oxygen when this position is hindered. The latter would give,[9] after rearrangement, α-oxygenation. Alternatively one could argue that, in the anhydride, attack at selenium is more liable to steric retardation than attack at oxygen.

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. ^{1}H N.m.r. spectra were obtained for solutions in $CDCl_3$ ($SiMe_4$ as internal standard) at 60 MHz. Thin-layer (t.l.c.) and preparative-layer chromatography (p.l.c.) were carried out on silica gel (Merk GF_{254} Type 60). Light petroleum refers to the fraction of b.p. 60—80 °C. Solutions were dried over sodium sulphate and solvents dried by standard techniques. Benzeneseleninic anhydride was prepared by the literature method.[5] U.v. spectra were taken in EtOH, i.r. spectra as Nujol mulls, and $[\alpha]_D$ in $CHCl_3$.

General Procedure for Dehydrogenation.—To a solution of ketone (100 mg) in dry chlorobenzene (0.7 ml) was added in one portion finely ground benzeneseleninic anhydride (1 equiv.). The mixture was heated to 95 °C with stirring until t.l.c. indicated complete reaction. P.l.c. afforded the dehydrogenated ketone and diphenyl diselenide, which was isolated and re-oxidised to benzeneseleninic anhydride.[5]

Dehydrogenation of Cholestan-3-one.—Cholestan-3-one (100 mg, 0.26 mmol) with the anhydride (188 mg, 0.52 mmol) gave cholesta-1,4-dien-3-one (83.3 mg, 83%), m.p. 110—112 °C (from methanol); $\lambda_{max.}$ 242 nm (ε 14 500), [lit.,[10] $\lambda_{max.}$ 242 nm (ε 15 000)]; $\nu_{max.}$ 1 660, 1 620, 1 600, 1 290, 1 240, 885, and 810 cm^{-1}; $[\alpha]_D^{22}$ +28° (lit.,[9] +28°); *m/e* 382 (M^+, 100%), 269, 261, and 247.

Dehydrogenation of Cholest-4-en-3-one.—Cholest-4-en-3-one (100 mg, 0.26 mmol) with the anhydride (94 mg, 0.26 mmol) gave cholesta-1,4-dien-3-one (92 mg, 92%), m.p. 110—112 °C (from methanol) (lit.,[10] 111.5—112.5 °C) identical with the previous sample.

Dehydrogenation of 4,4-Dimethylcholest-5-en-3-one.—Dimethylcholest-5-en-3-one (100 mg, 0.24 mmol) with the anhydride (87 mg, 0.24 mmol) gave (*a*) diphenyl diselenide (47.7 mg, 63%), m.p. 61—63 °C (lit.,[11] 63 °C); (*b*) A-nor-4,4-dimethylcholest-5-ene-1,2-dione (29.0 mg, 29%), m.p. 147—149 °C (from CH_2Cl_2–pentane) (lit.,[8] 149 °C); and (*c*) 4,4-dimethylcholest-1,5-dien-3-one (58.1 mg, 58%), m.p. 75—76 °C (from ethanol–water) (lit.,[12] 77—78 °C); $\nu_{max.}$ 1 685 cm^{-1}; $\lambda_{max.}$ 230 nm (ε 7 200) [lit.,[12] $\lambda_{max.}$ 227 nm (ε 9 350)]; δ 6.5 (1 H, d), 5.9 (1 H, d), and 5.6 (1 H, m); $[\alpha]_D^{22}$ +54.9° (*c* 1.00) {lit.,[8] $[\alpha]_D$ +53° (*c* 1.00)}; *m/e* 410.

Reaction of 4,4-Dimethylcholest-5-en-3-one with Excess of Benzeneseleninic Anhydride.—4,4-Dimethylcholest-5-en-3-one (100 mg, 0.24 mmol) with the anhydride (174 mg, 0.48 mmol) gave (*a*) diphenyl diselenide (139.2 mg), m.p. 61—63 °C; (*b*) A-nor-4,4-dimethylcholest-5-en-1,2-dione (33.2 mg, 33%), m.p. 146—148 °C (from CH_2Cl_2–pentane) (lit.,[8] 149 °C); $\nu_{max.}$ 1 765, 1 745, and 1 685 cm^{-1} (lit.,[8] $\nu_{max.}$ 1 770, 1 750, and 1 690 cm^{-1}); $\lambda_{max.}$ ($CHCl_3$) 510 nm (ε 90), [lit.,[8] $\lambda_{max.}$ ($CHCl_3$) 510 nm (ε 97)]; $[\alpha]_D^{22}$ +418 °C (*c* 1.10) (lit.,[8] $[\alpha]_D$ +435°); and (*c*) 4,4-dimethylcholest-1,5-dien-3-one (23.1 mg, 23%), m.p. 75—77 °C (from ethanol), identical to previous samples.

Dehydrogenation of Lanostan-3-one.—Lanostanone (100 mg, 0.23 mmol) with the anhydride (85 mg, 0.24 mmol) gave (*a*) 2-phenylselenolanostan-3-one (4.0 mg, 3%) identical with an authentic sample; (*b*) A-*nor-lanostan-1,2-dione* (12.3 mg, 13%), m.p. 169—171 °C; $\nu_{max.}$ 1 760, 1 750, and 1 740 cm^{-1}; $\lambda_{max.}$ 488 nm (ε 67); $[\alpha]_D$ +410° (*c* 0.3); *m/e* 428 (Found: C, 80.5; H, 11.05. $C_{29}H_{48}O_2$ requires C, 81.25; H, 11.3%); and (*c*) lanost-1-en-3-one (67 mg, 67%), m.p. 119—120 °C (from ethanol) (lit.,[13] 118—120 °C); $\nu_{max.}$ 1 670 cm^{-1}; $\lambda_{max.}$ 232 nm (ε 9 200) [lit.,[13] $\lambda_{max.}$ 229 nm (ε 9 000)]; $[\alpha]_D^{22}$ +48.4° (*c* 1.00) {lit.,[13] $[\alpha]_D$ +47° (*c* 0.53)}; *m/e* 426.

Reaction of Lanostan-3-one with Excess of Benzeneseleninic Anhydride.—Lanostan-3-one (100 mg, 0.23 mmol) with the anhydride (170 mg, 0.48 mmol) gave lanost-1-en-3-one (37.8, 38%), m.p. 119—120 °C (from ethanol–water) (lit.,[13] 118—120 °C) and A-nor-lanostan-1,2-dione (41.2 mg, 41%), m.p. 169—171 °C, identical to previous samples.

Preparation of 2-Phenylselenolanostan-3-one.—To a solution of dry di-isopropylamine (47 mg, 0.47 mmol) in dry THF (2 ml) at −78 °C was added n-butyl-lithium (1.66M, 0.76 ml) with stirring under nitrogen. After stirring for a further 5 min at −78 °C, a solution of lanostan-3-one (200 mg, 0.47 mmol) in THF (2 ml) was added and stirring continued at −78 °C for 10 min. A solution of benzeneselenenyl chloride (87.5 mg, 0.46 mmol) in dry THF (2 ml) was added dropwise to the solution with stirring at −78 °C and then the mixture was allowed to attain room temperature over a period of 15 min. The complete reaction mixture was poured into dilute sulphuric acid (1M, 10 ml) and extracted with methylene chloride (2 × 5 ml). Drying, evaporation of the solvent, and recrystallisation from ethanol–water gave *2-phenylselenolanostan-3-one* (170 mg, 62%), m.p. 150—152 °C; $\nu_{max.}$ 1 705, 1 580, 745, and 700 cm^{-1}; *m/e* 584 (Found: C, 73.9; H, 9.65. $C_{36}H_{56}OSe$ requires C, 73.95; H, 9.6%).

Dehydrogenation of α-Amyr-3-one.—α-Amyrone (100 mg, 0.23 mmol) with the anhydride (85 mg, 0.24 mmol) gave (*a*) diphenyl diselenide (54.9 mg, 75%), m.p. 61—63°, and (*b*) *α-amyr-1-en-3-one* (74.0 mg, 74%), m.p. 156—158 °C; $\nu_{max.}$ 1 665 cm^{-1}; $\lambda_{max.}$ 229 nm (ε 8 800); $[\alpha]_D^{22}$ +136.4° (*c* 1.00); *m/e* 422 (Found: C, 85.1; H, 11.0. $C_{30}H_{44}O$ requires C, 85.25; H, 11.0%).

Dehydrogenation of α-Amyr-3-one with Excess of Benzeneseleninic Anhydride.—α-Amyrone (100 mg, 0.23 mmol) with the anhydride (170 mg, 0.47 mmol) gave (*a*) diphenyl diselenide (104 mg), m.p. 61—63 °C; (*b*) α-amyr-1-en-3-one (32.3 mg, 32%), m.p. 156—158 °C; and (*c*) A-*nor-α-amyr-1,2-dione* (42.4 mg, 42%) m.p. 194—196° (from pentane); $\nu_{max.}$ 1 765, 1 745, and 1 740 cm^{-1} (Found: C, 81.9; H, 10.55. $C_{29}H_{44}O_2$ requires C, 82.0; H, 10.45%).

Dehydrogenation of β-Amyr-3-one.—β-Amyrone (100 mg, 0.23 mmol) with the anhydride (85 mg, 0.24 mmol) gave (*a*) diphenyl diselenide (56.3 mg, 76%), m.p. 61—63 °C; (*b*) A-*nor-β-amyr-1,2-dione* (7.3 mg, 8%), m.p. 174—176 °C;

$\nu_{max.}$ 1 760, 1 750, and 1 740 cm^{-1}; $\lambda_{max.}$ 480 nm (ε 51); $[\alpha]_D^{21}$ +446° (*c* 1.00); *m/e* 424 (Found: C, 81.7; H, 10.65. $C_{29}H_{24}O_2$ requires C, 82.0; H, 10.45%); and (*c*) β-amyr-1-en-3-one (54.0 mg, 54%), m.p. 174—175 °C (from ethanol) (lit.,[14] 174—175 °C); $[\alpha]_D^{22}$ +140° (*c* 0.50) {lit.,[14] $[\alpha]_D^{22}$ +141° (*c* 1.5)}; *m/e* 422.

Reaction of β-Amyr-3-one with Excess of Benzeneseleninic Anhydride.—β-Amyrone (100 mg, 0.23 mmol) with the anhydride (170 mg, 0.47 mmol) gave (*a*) diphenyl diselenide (134.3 mg), m.p. 61—63 °C; (*b*) β-amyr-1-en-3-one (26.7 mg, 27%), m.p. 174—175 °C (from ethanol); and (*c*) A-nor-β-amyr-1,2-dione (45.0 mg, 46%), m.p. 174—176 °C, identical to previous samples.

Dehydrogenation of Hecogenin Acetate.—Hecogenin acetate (100 mg, 0.21 mmol) with the anhydride (152 mg, 0.42 mmol) gave 9(11)-dehydrohecogenin acetate (90.3 mg, 91%), m.p. 217—220 °C (from methanol) (lit.,[15] 218—220 °C); $\nu_{max.}$ 1 730 and 1 670 cm^{-1}; $\lambda_{max.}$ 237 nm (ε 19 000) [lit.,[15] $\lambda_{max.}$ 238 nm (ε 15 000)]; $[\alpha]_D^{22}$ −7.6° (*c* 1.00) (lit.,[15] $[\alpha]_D^{22}$ −8.7°).

Dehydrogenation of Lupeone.—Lupeone (100 mg, 0.24 mmol) with the anhydride (85 mg, 0.24 mmol) gave (*a*) diphenyl diselenide (53.1 mg, 70%), m.p. 61—63 °C; and (*b*) lup-1,20(30)-dien-3-one (57.6 mg, 58%), m.p. 163—165 °C (lit.,[17] 164—165°); $\nu_{max.}$ 1 660 cm^{-1} (lit.,[16] $\nu_{max.}$ 1 660 cm^{-1}); $\lambda_{max.}$ 227 nm (ε 11 000) [lit.,[16] $\lambda_{max.}$ 228 nm (ε 10 000)].

Preparation of 1α,2α-Epoxycholesta-1,4,6-trien-3-one from Cholesta-4,6-dien-3-one.—To a solution of cholesta-4,6-dien-3-one (10.0 g, 0.028 mol) in dry chlorobenzene (80 ml) heated to 95 °C with stirring in the dark, was added benzeneseleninic anhydride (10.0 g, 0.027 mol) in portions over a period of 1 h. The solution was allowed to crystallise at 0 °C and the benzeneseleninic acid (4.6 g) filtered off and washed with a little cold chlorobenzene. The filtrate was distilled under reduced pressure to yield a yellow oil. The oil was dissolved in methanol (250 ml) at room temperature and treated with methanolic sodium hydroxide (10%, 2.6 ml) and hydrogen peroxide (30%, 18 ml) and allowed to stand at room temperature overnight. Cooling to −30 °C afforded crude 1α,2α-epoxycholesta-1,4,6-trien-3-one (6.0 g, 54%), m.p. 96—98 °C (from methanol) (5.5 g, 50%). Further recrystallisation from methanol–acetone afforded pure 1α,2α-epoxycholesta-1,4,6 trien-3-one, m.p. 104—106 °C (lit.,[17] 106—108 °C); $\lambda_{max.}$ 291 nm (ε 18 500) [lit.,[17] $\lambda_{max.}$ 292 nm (ε 19 000)]; $[\alpha]_D^{22}$ +192° (*c* 1.00) (lit.,[12] $[\alpha]_D$ +220°).

Reaction of Benzilic Acid with Benzeneseleninic Anhydride.—To a solution of benzilic acid (114 mg, 0.5 mmol) in chlorobenzene (0.6 ml) was added benzeneseleninic anhydride (180 mg, 0.5 mmol), and the suspension heated to reflux with stirring for 20 h. P.l.c. afforded benzophenone (86.5 mg, 95%), m.p. 57—58 °C (from ethanol) (lit.,[18] 57—58 °C).

Reaction of Lanostan-3-one with Benzeneseleninic Acid.—Lanostan-3-one (100 mg, 0.23 mmol) with benzeneseleninic acid (85 mg, 0.45 mmol) at 100 °C afforded lanost-1-en-3-one (63.5 mg, 64%), m.p. 119—120 °C (from methanol) (lit.,[13] m.p. 118—120 °C), identical to previous samples, and A-nor-lanostan-1,2-dione (9.4 mg, 10%), m.p. 169—171 °C, identical with previous samples.

Reaction of Hecogenin Acetate with Benzeneseleninic Acid.—Hecogenin acetate (100 mg, 0.21 mmol) with benzeneseleninic acid (77 mg, 0.41 mmol) at 100 °C afforded 9(11)-dehydrohecogenin acetate (80.8 mg, 81%), m.p. 217—220 °C (from methanol) (lit.,[15] 218—220 °C), identical with previous samples.

Catalytic Dehydrogenation of Lanostan-3-one using t-Butyl Hydroperoxide and Diphenyl Diselenide.—To a solution of lanostan-3-one (100 mg, 0.23 mmol) in chlorobenzene (1 ml) was added diphenyl diseleninde (15 mg, 0.048 mmol) and t-butyl hydroperoxide (110 mg, 1.22 mmol) and the solution heated to 100 °C with stirring under nitrogen for 25 min. P.l.c. afforded lanost-1-en-3-one (68.5 mg, 69%), m.p. 107—113 °C (from methanol) (lit.,[13] m.p. 118—120 °C); $\nu_{max.}$ 1 710 cm^{-1} (contaminant) and 1 670 cm^{-1}; $\lambda_{max.}$ 232 nm (ε 6 400) (lit.,[13] $\lambda_{max.}$ 229 nm (ε 9 000)).

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