# 245. Steroids and Sex Hormones

Part 262[1])

## The Radical Induced Stannane Reduction of Selenoesters and Selenocarbonates: A New Method for the Degradation of Carboxylic Acids to Nor-Alkanes and for Desoxygenation of Alcohols to Alkanes

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*Summary*

Esters of carboselenoic acids, formed from carboxylic acids by conventional methods, undergo reaction with tributyltin hydride in inert aromatic solvents, either by heating to give the corresponding aldehyde or the corresponding alkane depending on reaction temperature and the structure of the parent carboxylic acid, or by ultraviolet irradiation at ambient temperature when the aldehyde is formed predominantly in high yield. In the case of esters of $\alpha,\beta$-unsaturated carboselenoic acids the thermal reaction leads only to the corresponding aldehyde.

The above stannane reduction can also be applied to selenocarbonates of primary and secondary alcohols (prepared from the corresponding chloroformates), to give the alkane, the parent alcohol and the corresponding formate, in relative amounts depending on the reaction temperature.

These reactions thus constitute preparatively useful and high-yield degradation methods compatible with the presence of many other functional groups.

In connection with our work on the synthesis of quassinoid bitter principles [2] we have described in a previous publication [1] an example of what appeared to be a novel possible route for the degradation of a carboxylic acid to the corresponding nor-alkane *(Scheme 1)*. Carboxylic acid **1** was converted *via* its chloride **2** into the phenylcarboselenoate **3**. When this was heated with tributyltin hydride in benzene at 80° the 8$\beta$-methyl derivative **4** (product of reductive decarbonylation) and the alkenyl hemiacetal **5** (derived from the expected aldehyde, see **1**, X=H) were produced in about equal amounts.

In this paper we demonstrate that the radical-induced stannane reduction of phenyl carboselenoate **a** can lead to either aldehydes **b** or nor-alkanes **c** as main products, depending on temperature *(Scheme 2)*. In addition we shall describe the

[1]) Part 261, see [1].

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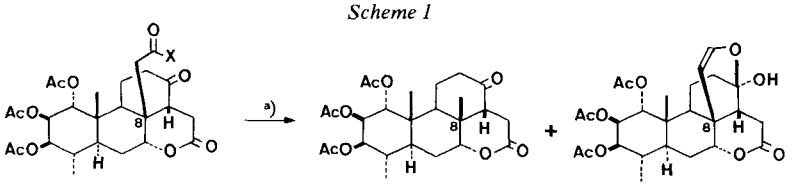
*Scheme 1*



**1** X = OH
**2** X = Cl
**3** X = $SeC_6H_5$

**4** **5**

a) $Bu_3SnH/AIBN/C_6H_6/80°$

extension of this reduction method to selenocarbonates **d** *(Scheme 3)*, which leads to formates **e**, alcohols **f** and/or desoxy products **g**, again depending on conditions.

Phenyl carboselenoates were obtained by reaction of phenylselenol with acyl chlorides in pyridine. Their reaction with tributyltin hydride was done by heating 0.2 mmol of the ester in the appropriate solvent (8 ml) under reflux, followed by addition of 1.5 mol-equiv. of the hydride and a trace of azo-bis-isobutyro-

*Scheme 2*

$$R^1COSeC_6H_5 + R^3SnH + \text{Initiator} \rightarrow R^1CHO \text{ and/or } R^1H$$

**a** **b** **c**

*Scheme 3*

$$R^1R^2CHOC(=O)SeC_6H_5 + R^3SnH + \text{Initiator} \rightarrow R^1R^2CHOC(=O)H \text{ and/or } R^1R^2CHOH \text{ and/or } R^1R^2CH_2$$

**d** **e** **f** **g**

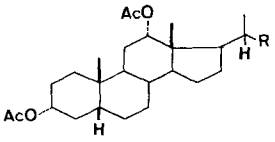
Table 1. *Reduction of selenoesters with tributyltin hydride*

| Selenoester | Solvent[a]) | Temp. | Products | | Remarks |
|---|---|---|---|---|---|
| | | | Nor-alkane | Aldehyde | |
| **6** | Bz | 80° | **7**: 8% | **8**: 92% | |
| | Xyl | 144° | **7**: 67% | **8**: 30% | |
| | TBM | 164° | **7**: 84% | **8**: 13% | |
| **9** | Bz | 80° | **10**: 17% | **11**: 82% | |
| | Xyl | 144° | **10**: 70% | **11**: 30% | |
| | TMB | 164° | **10**: 80% | **11**: 18% | |
| | Bz | RT., hν | **10**: 3% | **11**: 83% | |
| **12** | Bz | 80° | **13**: 98% | **14**: 1% | |
| | Bz | RT., hν | **13**: 79% | **14**: 18% | |
| **15** | Bz | 80° | **16**: 96% | **17**: – | 1:4-Mixture of |
| | Bz | RT., hν | **16**: 92% | **17**: – | C(1) epimers |
| **18** | Bz | 80° | **19**: 82% | **20**: – | (**18** is unstable) |
| **21** | Bz | 80° | | **22**: 69% | 5% starting |
| | TMB | 164° | | **22**: 51% | material recovered |

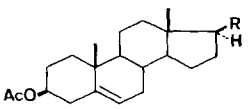
a) Bz = Benzene, Xyl = *o*-Xylene, TMB = 1,3,5-Trimethylbenzene (Mesitylene).

nitrile as initiator, heating being continued until the starting material was consumed. Alternatively the reaction mixture was irradiated with UV. light at room temperature, instead of being heated under reflux. The products were then separated by chromatography. *Table 1* and *Scheme 4* summarize results obtained with phenyl carboselenoate derived from a number of carboxylic acids ($\alpha$-mono, -di-, and -trisubstituted):

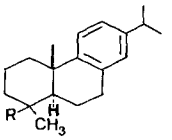
*Scheme 4*



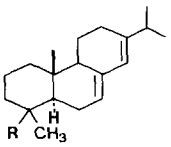
**6** R = $CH_2CH_2COSeC_6H_5$
**7** R = $CH_2CH_3$
**8** R = $CH_2CH_2CHO$
**12** R = $COSeC_6H_5$
**13** R = H
**14** R = CHO



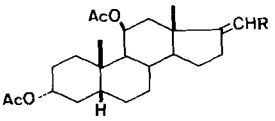
**9** R = $COSeC_6H_5$
**10** R = H
**11** R = CHO



**15** R = $\alpha$-$COSeC_6H_5$
**16** R = $\alpha$- and $\beta$-H, *ca.* 4:1
(**17** R = $\alpha$-CHO)



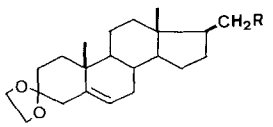
**18** R = $\alpha$-$COSeC_6H_5$
**19** R = $\alpha$- and $\beta$-H, *ca.* 1:1
(**20** R = $\alpha$-CHO)



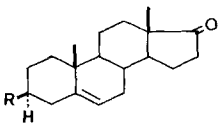
**21** R = $COSeC_6H_5$
**22** R = CHO

Phenyl selenocarbonates were obtained from alcohols by successive reaction with phosgene and then with phenylselenol. *Table 2* summarized results obtained by tributyltin hydride reduction of these (listed in *Scheme 5*) both under thermal and irradiation conditions:

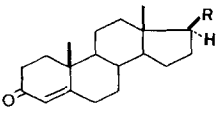
*Scheme 5*



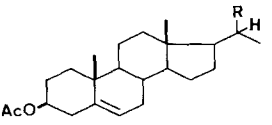
**23** R = $OCOSeC_6H_5$
**24** R = H
**25** R = OCHO
**26** R = OH



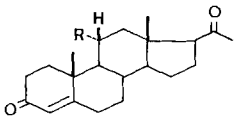
**27** R = $OCOSeC_6H_5$
**28** R = H
**29** R = OCHO
**30** R = OH



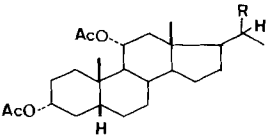
**31** R = $OCOSeC_6H_5$
**32** R = H
**33** R = OCHO
**34** R = OH



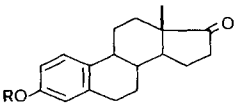
**35** R = $OCOSeC_6H_5$
**36** R = H
**37** R = OCHO
**38** R = OH



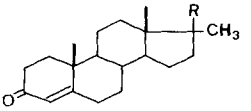
**39** R = $OCOSeC_6H_5$
**40** R = H
**41** R = OCHO
**42** R = OH



**43** R = $OCOSeC_6H_5$
**44** R = H
**45** R = OCHO
**46** R = OH



**47** R = $COSeC_6H_5$
**48** R = CHO
**49** R = H



**50** R = $OCOSeC_6H_5$
**51** R = $\alpha$-H
**52** R = $\beta$-OCHO

Table 2. *Reduction of selenocarbonates with tributyltin hydride*

| Seleno-carbonate | Solvent[a]) | Temp. | Products | | | Remarks |
|---|---|---|---|---|---|---|
| | | | Nor-alkane | Formate | Alcohol | |
| **23** | Bz | 80° | **24**: 18% | **25**: 62% | **26**: 20% | |
| | Tol | 110° | **24**: 38% | **25**: 25% | **26**: 30% | |
| | Xyl | 144° | **24**: 58% | **25**: 5% | **26**: 37% | |
| | TMB | 164° | **24**: 66% | **25**: 25% | **26**: 7% | |
| | Bz | RT., hν | – | **25**: 81% | **26**: 19% | |
| **27** | Bz | 80° | **28**: 5% | **29**: 76% | **30**: 9% | |
| | Tol | 110° | **28**: 39% | **29**: 42% | **30**: 14% | |
| | Xyl | 144° | **28**: 73% | **29**: 16% | **30**: 11% | |
| | TMB | 164° | **28**: 62% | **29**: 28% | **30**: 10% | |
| **31** | Bz | 80° | **32**: 7% | **33**: 59% | **34**: 29% | **31**: 4% |
| | Tol | 110° | **32**: 20% | **33**: 25% | **34**: 29% | **31**: 24% |
| | Xyl | 144° | **32**: 54% | **33**: 21% | **34**: 23% | |
| | TMB | 164° | **32**: 42% | **33**: 36% | **34**: 21% | |
| **35** | Bz | 80° | **36**: 51% | **37**: 43% | **38**: – | |
| | Tol | 110° | **36**: 75% | **37**: 16% | **38**: 6% | |
| | Xyl | 144° | **36**: 90% | **37**: 4% | **38**: 5% | |
| | Bz | RT., hν | **36**: 9% | **37**: 87% | **38**: 1% | |
| **39** | Xyl | 144° | **40**: 83% | **41**: 8% | **42**: 3% | |
| **43** | Xyl | 144° | **44**: 87% | **45**: 10% | **46**: 1% | |
| **47** | Xyl | 144° | – | **48**: 18% | **49**: 62% | **47**: 5% |
| **50**[b]) | Bz | 80° | **51**: 81% | **52**: 15% | – | |

*Reduction of formate* **25** *with tributyltin hydride*

| | | | |
|---|---|---|---|
| **25** | Xyl | 144°, 1½ hr. | **26**[c]) |

[a]) Bz = Benzene, Xyl = *o*-Xylene, Tol = Toluene, TMB = 1,3,5-Trimethylbenzene (Mesitylene).
[b]) 19 mg/run.
[c]) TLC. Analysis.

**Discussion.** – Inspection of the *Tables* shows that to a large extent selectivity of product formation can be controlled by varying the reaction temperature, while the steric environment of the corresponding carboxylic acid is another important factor in determining the nature of the products. Thus, at 80° or by irradiation at room temperature the primary ester **6** and secondary ester **9** give an optimal yield of the corresponding aldehydes **8** and **11** respectively, whereas reductive decarbonylation of such esters predominates only at a temperature of 164° (surprisingly, as we have found, the corresponding thiol esters are stable under these conditions). The secondary ester **12**, on the other hand, gives the nor-alkane **13**, both at 80° and following irradiation, as main product, while the tertiary selenoesters **15** and **18** are reductively decarbonylated exclusively under these conditions and the expected aldehydes **17** and **20** could not be detected at all.

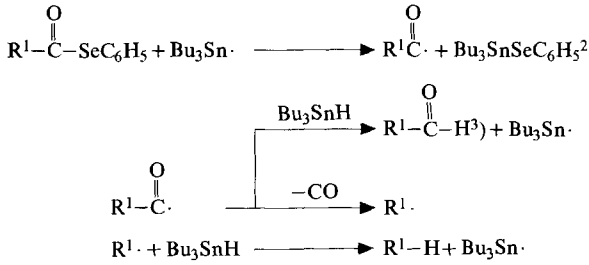
Somewhat analogous results were observed in the case of the selenocarbonates. Again some selectivity is possible by varying reaction temperature (although there is less specificity than with the selenoesters). Here the formation of the desoxy-

products is of greater preparative significance, and the optimal yield of these is at a reaction temperature of 144°. By-products are in this instance the corresponding alcohols and their esters with formic acid; and the fact that these can easily be reconverted into the selenocarbonates further underlines the preparative usefulness of this mild method for desoxygenation of alcohols. It does not, however, apply to tertiary alcohols in view of the difficulty of converting these into mixed carbonates.

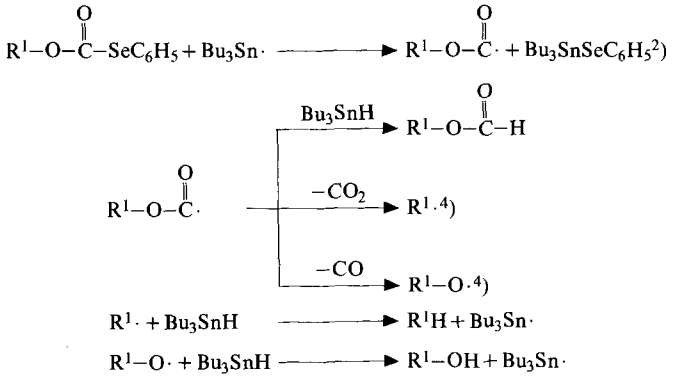
Another conclusion evident from our results is that by the route described it is not possible to convert either $\alpha,\beta$-unsaturated acids or phenols into the corresponding nor-hydrocarbons or desoxy product, resp.; instead the $\alpha,\beta$-unsaturated aldehyds or phenyl formates respectively are produced. On the other hand it is gratifying to note that ketone and ester groups and even the sensitive diene system present in abietic acid (see **18**) are unaffected under the reaction conditions used.

*Scheme 6*

a) *Selenoesters:*




b) *Selenocarbonates:*

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2) By careful chromatography on purified silica it was possible to separate the sensitive $Bu_3SnSeC_6H_5$ (see exper. Part).

3) This aldehyde-forming step is analogous to the conversion of acid chlorides into aldehydes by reduction with trialkylsilanes (with or without palladium as catalyst), first described by *Jenkins & Post* and later by *Citron* [3].

4) Presumably the alcohol is formed mainly *via* decarbonylation of the acyloxy radical, in competition with decarboxylation. The fact that the ester **25** is reduced by tributyltin hydride to the alcohol **26** within 30 minutes is not by itself of paramount significance, since *e.g.*, in the case of the reduction of the selenocarbonate **23** the final product composition (mixture of **24**, **25** and **26**) is evident by thin layer chromatography after only 2 minutes at 140°.

The reactions of seleno-esters and -carbonates with tributyltin hydride under radical-forming conditions can be rationalized by the series of chain processes suggested in *Scheme 6*.

The reduction of selenoesters to nor-alkanes which we have described appears to offer a number of advantages when compared with other known methods[5]): such as compatibility with other functional groups and experimental simplicity.

Another factor contributing to the value of our method is the recent finding by *Grieco* [8] that it is possible to convert carboxylic acids directly into selenoesters by reaction with phenyl selenocyanate in the presence of tributylphosphine.

Within the last few years a number of other methods have been reported which effect the conversion of alcohols and their derivatives into the corresponding hydrocarbons under mild and non-hydride useing conditions and in good yields[6]). The route which we have described here appears to constitute a useful complement to these methods.

*We are indebted to the Schweizerischer Nationalfonds zur Unterstützung der wissenschaftlichen Forschung,* and to *Ciba-Geigy AG,* Basel, for supporting this work.

## Experimental Part

For general remarks see [12]. Tributyltin hydride was prepared by $LiAlH_4$ reduction of the chloride and distilled, in a high vacuum (HV.).

*Preparation of selenoesters.* To a solution suspension of the carboxylic acid (1.7 mmol) in benzene (10 ml) was added oxalyl chloride (1 ml) at 0°, and the mixture was stirred at 0° for 1 h, after which the mixture was concentrated, finally i.HV. To the residue there were added THF (distilled from $LiAlH_4$, 6 ml), pyridine (0.2 ml) and a 0.35 M solution of selenophenol[7]) in benzene (6 ml). After stirring at RT. for 45 min the reaction mixture was worked up in the usual manner and the crude product purified by chromatography on silica. Yields were of the order of 80–90%.

*Preparation of selenocarbonates.* To a solution of the hydroxyl compound (1.9 mmol) in THF (10 ml) was added a solution of phosgene in toluene (20%, 3 ml) and the whole was stirred at RT. for 30 min (in the preparation of compounds **47** and **50** triethylamine (1.2 mol-equiv.) was also added). The mixture was then concentrated i.V. to half its volume, and then a solution of selenophenol in benzene (0.35 M, 7 ml) and pyridine (0.3 ml) were added. After stirring at RT. for 30 min the mixture was worked up in the usual manner and the crude product purified by chromatography on silica gel. The yields were of the order of 80–90% (in the case of product **50** the yield was 14%, 78% of starting material being recovered).

*Tributyltin hydride reduction of selenoesters and selenocarbonates.* – a) *Thermally.* A solution of the selenoester (0.2 mmol) in 8 ml solvent (benzene, toluene, *o*-xylene or mesitylene; see *Tables 1* and *2*) was heated under reflux after which tributyltin hydride (1.5 mol-equiv.) and a trace of azo-bis(isobutyronitrile) were added. Heating was continued until all starting material was consumed (TLC. control, 2–60 min). The mixture was then concentrated i.V. and the products separated by chromatography.

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[5]) Compare: (a) the reductive decarboxylation of carboxylic acids using lead tetraacetate as described by *Kochi et al.* [4]; (b) the halo-decarbonylation of acyl halides followed by a reduction step [5]; (c) the decomposition of acyl peroxides [6]; and (d) the decarbonylation of corresponding aldehydes catalyzed by transition metal complexes [7].

[6]) *E.g.,* the photochemical reduction of acetates in aqueous HMPTA described by *Pète et al.* [9]; the tributyltin hydride reduction of *O*-cycloalkyl thionebenzoates and *O*-cycloalkyl-*S*-methyl dithiocarbonates of secondary alcohols described by *Barton et al.* [10]; and the reduction of chlorocarbonates of primary and secondary alcohols using tripropyl silane described by *Jackson et al.* [11].

[7]) This was prepared by reduction of diphenyl diselenide with hypophosphorous acid [13].

b) *Photochemically.* A solution of the selenoester (0.2 mmol) in benzene (8 ml) and tributyltin hydride (1.5 mol-equiv.) was irradiated in a quartz vessel using a low pressure mercury lamp (type TNM K5/32, *Quarzlampen GmbH*, Hanau) until all starting material was consumed (TLC. control), after which it was worked up as described under (a).

*Phenyl 3α,12α-diacetoxy-5β-selenocholan-24-oate* (**6**). $[\alpha]_D = +68{,}4°$ ($c = 0.355$). – UV.: 221 (15700), 256 (4800). – IR.: 1720, 1580, 1250, 1022. – $^1$H-NMR.: 0.69 (*s*, $H_3C(18)$); 0.80 (*d*, $J = 5$, $H_3C(21)$); 0.88 (*s*, $H_3C(19)$); 1.98, 2.06 (2 *s*, 2 $CH_3COO$); 2.65 (*m*, $H_2C(23)$); 4.68 (br. *m*, H–C(3)); 5.06 (*m*, H–C(12)); 7.26–7.56 (*m*, $C_6H_5$). – MS. (175°): no $M^+$, 588 (2.2), 586 (1.2), 399 (17), 357 (98), *339* (100), 321 (25), 255 (27).

*3α,12α-Diacetoxy-20α-ethyl-5β-pregnane* (**7**). $[\alpha]_D = +99.8°$ ($c = 0.641$). – IR.: 1722, 1380, 1255, 1025. – $^1$H-NMR.: 0.70 (*s*, $H_3C(18)$); 0.88 (*s*, $H_3C(19)$); 1.99, 2.06 (2 *s*, 2 $CH_3COO$); 4.69 (br. *m*, H–C(3)); 5.07 (*m*, H–C(12)). – MS. (135°): 432 (0.1, $M^+$), 372 (3.8), *312* (100), 297 (12), 255 (54).

$C_{27}H_{44}O_4$ (432.62) Calc. C 74.95 H 10.25% Found C 74.90 H 10.30%

*3α,12α-Diacetoxy-5β-cholan-24-al* (**8**). $[\alpha]_D = +87.0°$ ($c = 0.310$). – IR.: 2720, 1720, 1377, 1250, 1023. – $^1$H-NMR.: 0.70 (*s*, $H_3C(18)$); 0.80 (*d*, $J = 5$, $H_3C(21)$); 0.88 (*s*, $H_3C(19)$); 1.99, 2.06 (2 *s*, 2 $CH_3COO$); 2.36 (*m*, $H_2C(23)$); 4.69 (br. *m*, H–C(3)); 5.06 (*m*, H–C(12)); 9.75 (*t*, $J = 1.5$, H–C(24)). – MS. (140°): 460 (0.2, $M^+$), 400 (10), *340* (100), 297 (19), 255 (78), 228 (24).

*Phenyl 3β-acetoxyandrost-5-ene-17β-carboselenoate* (**9**). Smp. 192°, $[\alpha]_D = +61.9°$ ($c = 1.03$). – UV. (Pentan): 224 (15500), 260 (4200). – IR.: 1717, 1677, 1250, 1030. – $^1$H-NMR.: 0.74 (*s*, $H_3C(18)$); 1.01 (*s*, $H_3C(19)$); 2.00 (*s*, $CH_3COO$); 2.73 (*m*, H–C(17)); 4.6 (br. *m*, H–C(3)); 5.36 (*m*, H–C(6)); 7.26–7.56 (*m*, $C_6H_5$). – MS. (110°): 343 (90), *255* (100).

$C_{28}H_{36}O_3Se$ (499.53) Calc. C 67.32 H 7.26% Found C 67.27 H 7.15%

*Androst-5-en-3β-ol acetate* (**10**) [14]. M.p. 99°, $[\alpha]_D = -76.9°$ ($c = 0.528$). – IR.: 1725, 1375, 1252, 1028. – $^1$H-NMR.: 0.70 (*s*, $H_3C(18)$); 1.01 (*s*, $H_3C(19)$); 1.99 (*s*, $CH_3COO$); 2.31 (*m*, $H_2C(4)$); 4.6 (br. *m*, H–C(3)); 5.37 (*m*, H–C(6)). – MS. (120°): *256* (100, $M^+ - 60$), 241 (42).

$C_{21}H_{32}O_2$ (316.47) Calc. C 79.70 H 10.19% Found C 79.76 H 10.17%

*3β-Acetoxyandrost-5-ene-17β-carboxaldehyde* (**11**) [15]. No m.p. (dec.), $[\alpha]_D = -16.4°$ ($c = 0.493$). – IR.: 2720, 1714, 1370, 1360, 1250, 1025. – $^1$H-NMR.: 0.75 (*s*, $H_3C(18)$); 1.01 (*s*, $H_3C(19)$); 1.99 (*s*, $CH_3COO$); 4.6 (br. *m*, H–C(3)); 5.37 (*m*, H–C(6)); 9.77 (*d*, $J = 1.5$, H–C(20)). – MS. (150°): *284* (100, $M^+ - 60$), 269 (28).

*Phenyl 3α,12α-diacetoxy-5β-pregnane-20-carboselenoate* (**12**). M.p. 116.5–117.5°, $[\alpha]_D = +60.1°$ ($c = 0.494$). – UV.: 233 (17100), 257 (4800). – IR.: 1720, 1579, 1376, 1362, 1250, 1022, 909. – $^1$H-NMR.: 0.74 (*s*, $H_3C(18)$); 0.89 (*s*, $H_3C(19)$); 1.13 (*d*, $J = 6$, $H_3C(21)$); 1.99, 2.09 (2 *s*, 2 $CH_3COO$); 2.69 (*m*, H–C(20)); 4.69 (br. *m*, H–C(3)); 5.02 (*m*, H–C(12)); 7.38 (*m*, $C_6H_5$). – MS. (155°): 589 (0.06, $M^+ + 2$), 587 (0.04, $M^+$), 529 (3.9), 527 (2.1), 389 (60), 343 (20), 329 (98), 311 (37), *283* (100), 255 (33).

$C_{32}H_{44}O_5Se$ (587.63) Calc. C 65.40 H 7.55% Found C 65.79 H 7.50%

*3α,12α-Diacetoxy-5β-pregnane* (**13**). M.p. 158–159°, $[\alpha]_D = +96.3°$ ($c = 0.508$). – IR.: 1720, 1252, 1023. – $^1$H-NMR.: 0.61 (*s*, $H_3C(18)$); 0.89 (*s*, $H_3C(19)$); 1.99, 2.05 (2 *s*, 2 $CH_3COO$); 4.7 (br. *m*, H–C(3)); 4.97 (*m*, H–C(12)). – MS. (135°): 344 (1.4, $M^+ - 60$), 302 (5), *284* (100), 269 (28), 255 (38).

$C_{25}H_{40}O_4$ (404.57) Calc. C 74.21 H 9.97% Found C 74.14 H 10.02%

*3α,12α-Diacetoxy-5β-pregnane-20-carboxaldehyde* (**14**). – IR.: 2820, 1720, 1250, 1024. – $^1$H-NMR.: 0.76 (*s*, $H_3C(18)$); 0.90 (*s*, $H_3C(19)$); 0.99 (*d*, $J = 7$, $H_3C(21)$); 2.00, 2.09 (2 *s*, 2 $CH_3COO$); 4.7 (br. *m*, H–C(3)); 5.04 (*m*, H–C(12)); 9.54 (*d*, $J = 3$, H–C(22)). – MS. (140°): 432 (0.3, $M^+$), 372 (5.9), 344 (14), 330 (15), 312 (79), *284* (100), 255 (75).

*Phenyl dehydroselenoabietate* (**15**). M.p. 86–87°, $[\alpha]_D = +31{,}3°$ ($c = 0.648$). – UV.: 221 (28000), 259 (4600), 275 (sh.). – IR.: 1708, 1610, 1580. – $^1$H-NMR.: 1.20 (*d*, $J = 6$, $(CH_3)_2CH$); 1.22 (*s*, $H_3C$–C(4a)); 1.35 (*s*, $H_3C$–C(1)); 6.8–7.5 (8, arom.). – MS. (145°): 441 (1.2, $M^+ + 2$), 439 (1, $M^+$), 283 (3.1), 255 (94), 239 (13), 185 (42), *173* (100).

$C_{26}H_{32}OSe$ (439.50) Calc. C 71.05 H 7.34% Found C 71.21 H 7.48%

*1,2,3,4,4a,9,10,10a-Octahydro-1ξ,4aβ-dimethyl-7-isopropyl-(10aα)-phenanthrene* (**16**). *Cf.* [16].

*Phenyl selenoabietate* (**18**). – IR.: 1702, 1580, 1438, 1383, 903. – $^1$H-NMR.: 0.83 (*s*, $H_3C$–C(4a)); 0.99 (*d*, $J$=6, $(H_3C)_2CH$); 1.34 (*s*, $H_3C$–C(1)); 5.34 (br. *s*, H–C(9)); 5.78 (*s*, H–C(8)); 7.25–7.50 (*m*, $C_6H_5$). – MS. (135°): 442 (1.2, $M^+$ + 1), 440 (0.7, $M^+$ – 1), *257* (100), 173 (26), 161 (20), 109 (25).

*1,2,3,4,4a,4b,5,6,10,10a-Decahydro-1ξ,4aβ-dimethyl-7-isopropyl-(10aα)-phenanthrene* (**19**). – IR.: 1600, 1458, 1380, 890. – $^1$H-NMR. (Mixture of C(1)-epimers *ca.* 1:1): 0.71, 0.77 (2 *s*, $H_3C$–C(4a) of both epimers); 0.82, 0.96 (2 *d*, $J$=6, resp. $J$=7, $H_3C$–C(1) of both epimers); 0.99 (*d*, $J$=6, $(H_3C)_2CH$); 5.40 (*m*, H–C(9)); 5.78 (br. *s*, H–C(8)). – MS. (200°): *258* (100, $M^+$), 243 (36), 215 (62).

*Phenyl 3α,11β-diacetoxy-5β-pregn-17(20)-en-20-carboselenoate* (**21**). – UV.: 241 (21600), 298 (6500). – IR.: 1726, 1700 (sh.), 1618, 1580, 1250, 1030, 1020. – $^1$H-NMR. (of *E*/*Z* mixture, *ca.* 6:1, signals of (*E*)-isomer only quoted): 0.93 (*s*, $H_3C$(18)); 1.02 (*s*, $H_3C$(19)); 1.98, 2.00 (2 *s*, 2 $CH_3COO$); 4.7 (br. *m*, H–C(3)); 5.28 (*m*, H–C(11)); 5.91 (*m*, H–C(20)); 7.26–7.56 (*m*, $C_6H_5$). – MS. (160°): 573 (0.1, $M^+$ + 2), 571 (0.1, $M^+$), 415 (56), 355 (12), 313 (22), *295* (100), 267 (27), 253 (18), 213 (19).

*3α,11β-Diacetoxy-5β-pregn-17(20)-en-21-al* (**22**). M.p. *ca.* 170° (dec.), $[\alpha]_D$ = +66.3° ($c$=0.484). – UV.: 243 (17600). – IR.: 1727, 1670, 1610, 1250, 1025. – $^1$H-NMR.: 0.96 (*s*, $H_3C$(18)); 1.03 (*s*, $H_3C$(19)); 1.97, 2.00 (2 *s*, 2 $CH_3COO$); 2.86 (*m*, $H_2C$(16)); 4.7 (br. *m*, H–C(3)); 5.29 (*m*, H–C(11)); 5.65 (*d*×*t*, $J_d$=8, $J_t$=2.5, H–C(20)); 9.81 (*d*, $J$=8, H–C(21)). – MS. (<155°): 417 (0.2, $M^+$ + 1), 356 (14), 341 (38), 296 (31), *281* (100), 267 (44), 212 (38).

$C_{25}H_{36}O_5$ (416.54) Calc. C 72.08 H 8.71% Found C 72.15 H 8.85%

*3,3-Ethylenedioxy-5-androsten-17β-yl-methyl Se-phenyl selenocarbonate* (**23**). M.p. 167.5–168.5°, $[\alpha]_D$ = –38.5° ($c$=0.698). – UV.: 255 (3200). – IR.: 1720, 1576, 1127. – $^1$H-NMR.: 0.64 (*s*, $H_3C$(18)); 1.01 (*s*, $H_3C$(19)); 3.90 (*s*, $OCH_2CH_2O$); 4.23 (*d*, $J$=7, $H_2C$–C(17)); 5.31 (*m*, H–C(6)); 7.29–7.65 (*m*, $C_6H_5$). – MS. (130°): 530 (13, $M^+$ + 1), 528 (7.3, $M^+$ – 1), 329 (22), 267 (12), 227 (12), *99* (100).

$C_{29}H_{38}O_4Se$ (529.55) Calc. C 65.77 H 7.23% Found C 65.75 H 7.28%

*3,3-Ethylenedioxy-17β-methylandrost-5-ene* (**24**). M.p. 158–161°, $[\alpha]_D$ = –48.3° ($c$=0.447). – IR.: 1374, 1360, 1093. – $^1$H-NMR.: 0.54 (*s*, $H_3C$(18)); 0.82 (*d*, $J$=6, $H_3C$–C(17)); 1.01 (*s*, $H_3C$(19)); 3.90 (*s*, $OCH_2CH_2O$); 5.33 (*m*, H–C(6)). – MS. (120°): 330 (8.2, $M^+$), *99* (100).

$C_{22}H_{34}O_2$ (330.49) Calc. C 79.95 H 10.37% Found C 79.81 H 10.39%

*3,3-Ethylenedioxyandrost-5-en-17-yl-methyl formate* (**25**). – IR.: 1717, 1171, 1097. – $^1$H-NMR.: 0.66 (*s*, $H_3C$(18)); 1.01 (*s*, $H_3C$(19)); 3.90 (*s*, $OCH_2CH_2O$); 4.14 (*d*, $J$=7, $H_2C$–C(17)); 5.32 (*m*, H–C(6)); 8.02 (*s*, OCHO). – MS. (<110°): 374 (8, $M^+$), *99* (100).

*17-Oxo-androst-5-en-3β-yl Se-phenyl selenocarbonate* (**27**). M.p. 150–150.5°, $[\alpha]_D$ = +4.3° ($c$=0.205). – UV.: 213 (sh.), 229 (sh.), 259 (5300), 302 (900). – IR.: 1727, 1576, 1129. – $^1$H-NMR.: 0.84 (*s*, $H_3C$(18)); 1.01 (*s*, $H_3C$(19)); 4.72 (br. *m*, H–C(3)); 5.38 (*m*, H–C(6)); 7.26–7.68 (*m*, $C_6H_5$). – MS. (100°): 428 (2.1), 426 (1.3), *271* (100), 253 (18).

$C_{26}H_{32}O_3Se$ (471.48) Calc. C 66.23 H 6.84% Found C 66.24 H 6.83%

*Androst-5-en-17-one* (**28**) [17]. M.p. 109–109.5°, $[\alpha]_D$ = –17.6° ($c$=0.763). – IR.: 1730, 1660, 1450, 1370. – $^1$H-NMR.: 0.85 (*s*, $H_3C$(18)); 1.00 (*s*, $H_3C$(19)); 5.27 (*m*, H–C(6)). – MS. (<100°): *272* (100, $M^+$), 257 (52), 239 (17), 215 (28), 203 (27).

$C_{19}H_{28}O$ (271.41) Calc. C 83.77 H 10.36% Found C 83.89 H 10.34%

*17-Oxo-androst-5-en-3-yl formate* (**29**). – IR.: 1720, 1173. – $^1$H-NMR.: 0.86 (*s*, $H_3C$(18)); 1.03 (*s*, $H_3C$(19)); 4.7 (br. *m*, H–C(3)); 5.41 (*m*, H–C(6)); 8.00 (*s*, OCHO). – MS. (100°): *270* (100), 255 (19), 121 (30).

*3-Oxo-androst-4-en-17β-yl Se-phenyl selenocarbonate* (**31**). M.p. 126.5–127°, $[\alpha]_D$ = +80.5° ($c$=0.504). – UV.: 219, 243. – IR.: 1720, 1660, 1610, 1577, 1125. – $^1$H-NMR.: 0.74 (*s*, $H_3C$(18)); 1.15 (*s*, $H_3C$(19)); 4.71 (*d*×*d*, $J$=7, $J'$=9, H–C(17)); 5.70 (br. *s*, H–C(4)); 7.28–7.70 (*m*, $C_6H_5$). – MS. (100°): 473 (1.2, $M^+$ + 2), 471 (0.7, $M^+$), 428 (6.7), 426 (3.5), *271* (100), 253 (53), 147 (49).

$C_{26}H_{32}O_3Se$ (471.48) Calc. C 66.23 H 6.84% Found C 66.24 H 6.89%

*Androst-4-en-3-one* (**32**) [18]. M.p. 105.5–106°, $[\alpha]_D = +102.9°$ ($c = 0.516$). – IR.: 1658, 1609. – $^1$H-NMR.: 0.73 (*s*, $H_3C(18)$); 1.15 (*s*, $H_3C(19)$); 5.70 (br. *s*, H–C(4)). – MS. (100°): 272 (81, $M^+$), 230 (96), 187 (49), 149 (73), *124* (100).

*3-Oxo-androst-4-en-17β-yl-methyl formate* (**33**). – IR.: 1718, 1660, 1611, 1178. – $^1$H-NMR.: 0.83 (*s*, $H_3C(18)$); 1.16 (*s*, $H_3C(19)$); 4.68 (*d*×*d*, $J = 7$, $J' = 9$, H–C(17)); 5.71 (br. *s*, H–C(4)); 8.04 (*s*, OCHO). – MS. (100°): 316 (97, $M^+$), *274* (100), 231 (34), 228 (31), 147 (58), 124 (94).

*3β-Acetoxy-20-benzeneselenocarbonyloxy-pregn-5-en-20-yl Se-phenyl selenocarbonate* (**35**). M.p. 163.4–164°, $[\alpha]_D = +7.5°$ ($c = 0.734$). – UV.: 255 (3100). – IR.: 1718, 1575, 1250, 1135. – $^1$H-NMR.: 0.66 (*s*, $H_3C(18)$); 1.00 (*s*, $H_3C(19)$); 1.24 (*d*, $J = 6$, $H_3C(21)$); 1.99 (*s*, $CH_3COO$); 2.30 (*m*, $H_2C(4)$); 4.60 (br. *m*, H–C(3)); 4.98 (br. *m*, H–C(20)); 5.35 (*m*, H–C(6)); 7.30–7.70 (*m*, $C_6H_5$). – MS. (< 110°): no $M^+$, 500 (4.1), 498 (2.1), *283* (100), 133 (41).

$C_{30}H_{40}O_4Se$ (543.58) Calc. C 66.28 H 7.42% Found C 66.36 H 7.34%

*3β-Acetoxy-pregn-5-ene* (**36**) [19]. M.p. 151.5–152°, $[\alpha]_D = -60.7°$ ($c = 0.394$). – IR.: 1722, 1371, 1361, 1250, 1027. – $^1$H-NMR.: 0.56 (*s*, $H_3C(18)$); 1.00 (*s*, $H_3C(19)$); 1.99 (*s*, $CH_3COO$); 2.30 (*m*, $H_2C(4)$); 4.60 (br. *m*, H–C(3)); 5.37 (*m*, H–C(6)). – MS. (< 105°): *284* (100, $M^+ - 60$), 269 (25), 176 (22), 163 (44).

$C_{23}H_{36}O_2$ (344.52) Calc. C 80.18 H 10.35% Found C 79.80 H 10.42%

*3β-Acetoxy-pregn-5-en-20-yl formate* (**37**). – IR.: 1715, 1374, 1361, 1250, 1028. – $^1$H-NMR.: 0.64 (*s*, $H_3C(18)$); 0.98 (*s*, $H_3C(19)$); 1.19 (*d*, $J = 6$, $H_3C(21)$); 1.98 (*s*, $CH_3COO$); 2.30 (*m*, $H_2C(4)$); 4.6 (br. *m*, H–C(3)); 4.96 (br. *m*, H–C(20)); 5.35 (*m*, H–C(6)); 8.01 (*s*, OCHO). – MS. (< 110°): no $M^+$, *328* (100), 313 (7), 282 (9), 267 (17), 253 (6), 161 (26), 121 (24).

*3,20-Dioxopregn-4-en-11α-yl Se-phenyl selenocarbonate* (**39**). M.p. 156.5–157.5°, $[\alpha]_D = +130.9°$ ($c = 0.724$). – UV.: *ca.* 215 (sh.), 241 (16900), 262 (sh.). – IR.: 1715 (sh.), 1700, 1660, 1610, 1576, 1116. – $^1$H-NMR.: 0.68 (*s*, $H_3C(18)$); 1.24 (*s*, $H_3C(19)$); 2.08 (*s*, $H_3C(21)$); 5.36 (br. *m*, H–C(11)); 5.74 (br. *s*, H–C(4)); 7.28–7.70 (*m*, $C_6H_5$). – MS. (165°): 515 (5.5, $M^+ + 2$), 513 (3.2, $M^+$), *313* (100), 297 (25), 295 (41), 227 (23).

*3,20-Dioxopregn-4-en-11α-yl formate* (**41**). – IR.: 1712, 1662, 1610, 1170. – $^1$H-NMR.: 0.75 (*s*, $H_3C(18)$); 1.26 (*s*, $H_3C(19)$); 2.08 (*s*, $H_3C(21)$); 5.4 (br. *m*, H–C(11)); 5.74 (br. *s*, H–C(4)); 8.02 (*s*, OCHO). – MS. (150°): 358 (6.5, $M^+$), *312* (100), 227 (39).

*3α,11α-Diacetoxy-5β-pregnan-20-yl Se-phenyl selenocarbonate* (**43**). M.p. 204.5–205.5°, $[\alpha]_D = +52.5°$ ($c = 0.610$). – UV.: 225 (sh.), 255 (3700). – IR.: 1718, 1244, 1135. – $^1$H-NMR.: 0.69 (*s*, $H_3C(18)$); 1.01 (*s*, $H_3C(19)$); 1.22 (*d*, $J = 6$, $H_3C(21)$); 1.93, 2.01 (2 *s*, 2 $CH_3COO$); 4.6–5.3 (H–C(3), H–C(11), H–C(20)); 7.3–7.7 (*m*, $C_6H_5$). – MS. (170°): 560 (1.0), 558 (0.6), 343 (13), *283* (100), 175 (20).

$C_{32}H_{44}O_6Se$ (603.63) Calc. C 63.67 H 7.35% Found C 63.52 H 7.39%

*3α,11α-Diacetoxy-5β-pregnane* (**44**). M.p. 111–112.5°, $[\alpha]_D = +5.6°$ ($c = 0.411$). – IR.: 1720, 1375, 1360, 1250, 1019. – $^1$H-NMR.: 0.60 (*s*, $H_3C(18)$); 1.01 (*s*, $H_3C(19)$); 1.90, 2.01 (2 *s*, 2 $CH_3COO$); 4.7 (br. *m*, H–C(3)); 5.08 (*d*×*t*, $J_d = 5$, $J_t = 10$, H–C(11)). – MS. (120°): 344 (1.0, $M^+ - 60$), *284* (100), 269 (26), 255 (14).

$C_{25}H_{40}O_4$ (404.57) Calc. C 74.21 H 9.97% Found C 74.39 H 9.98%

*3α,11α-Diacetoxy-5β-pregnan-20-yl formate* (**45**). – IR.: 1715, 1375, 1360, 1250, 1020. – $^1$H-NMR.: 0.66 (*s*, $H_3C(18)$); 1.00 (*s*, $H_3C(19)$); 1.18 (*d*, $J = 6$, $H_3C(21)$); 1.90, 2.00 (2 *s*, 2 $CH_3COO$); 4.5–5.2 (H–C(3), H–C(11), H–C(20)); 7.98 (*s*, OCHO). – MS. (155°): 342 (21), *328* (100), 282 (97), 267 (46).

*17-Oxo-estra-1,3,5(10)-trien-3-yl Se-phenyl selenocarbonate* (**47**). M.p. 134.5–135°, $[\alpha]_D = +97.3°$ ($c = 0.692$). – IR.: 1730, 1602, 1577, 1100, 1079, 1062. – $^1$H-NMR.: 0.87 (*s*, $H_3C(18)$); 6.88–7.70 (*m*, 8 H arom.). – MS. (145°): 454 (4.9, $M^+ + 1$), 452 (3.0, $M^+ - 1$), 426 (68), 424 (35), *269* (100), 251 (39), 227 (24).

$C_{25}H_{26}O_3Se$ (453.42) Calc. C 66.22 H 5.78% Found C 66.35 H 5.85%

*17α-Methyl-3-oxo-androst-4-en-17β-yl Se-phenyl selenocarbonate* (**50**). M.p. 153°, $[\alpha]_D = +85.4$ ($c = 0.497$). – UV.: 218, 235 (sh.), 242, 259 (sh.). – IR.: 1721, 1660, 1610, 1576, 1124, 1114. – $^1$H-NMR.: 0.82 (*s*, $H_3C(18)$); 1.16 (*s*, $H_3C(19)$); 1.46 (*s*, $H_3C$–C(17)); 5.70 (br. *s*, H–C(4)); 7.28–7.64 (*m*, $C_6H_5$). – MS. (105°): 284 (73), *269* (100), 266 (33), 161 (42), 158 (57).

$C_{27}H_{34}O_3Se$ (485.50) Calc. C 66.79 H 7.06% Found C 66.83 H 7.14%

*17β-Methyl-androst-4-en-3-one* (**51**) [20]. M.p. 106–108°. $[\alpha]_D = +102.9°$ ($c = 0.225$). – IR.: 1660, 1610. – $^1$H-NMR.: 0.58 (*s*, $H_3C(18)$); 0.83 (*d*, $J = 6$, $H_3C-C(17)$); 1.16 (*s*, $H_3C(18)$); 5.71 (br. *s*, H–C(4)). – MS. (120°): 286 (26, $M^+$), 244 (31), 201 (26), 163 (60), *124* (100).

*17α-Methyl-3-oxo-androst-4-en-17β-yl formate* (**52**). – IR.: 1710, 1660, 1610. – MS.: 330 (47, $M^+$), 284 (90), *269* (100), 161 (66).

*Tributyltin-phenylselenide.* – $^1$H-NMR.: 0.7–1.8 (*m*, H-aliph.); 7.0–7.6 (*m*, arom.). – MS. (200°): 446 (3.3, fragment containing $Se_1$, $Sn_1$), 389 (40, fragment containing $Se_1$, $Sn_1$), 275 (27, fragment containing $Se_1$, $Sn_1$), 120 (65), *105* (100), 77 (44).

$C_{18}H_{32}SeSn$ Calc. Sn 26.61 Se 17.70% Found Sn 25.94 Se 17.07%

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