12,13-Epoxy-*C*-nor-*D*-homosteroids. VIII.[1] Transformation of 12α,13α-Epoxyetiojerv-5-ene-3,17-dione 3,3-Ethylene Acetal into Testosterone[2]

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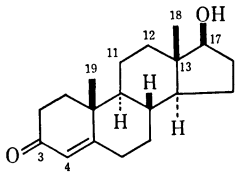
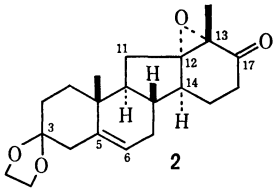
Transformation of the title epoxy ketone (**2**) into testosterone (**1**), which implies synthesis of the hormone **1** from jervine, is described. Irradiation of **2** by a low-pressure lamp in dioxane afforded an androstane-12,17-dione derivative, which was reduced regioselectively with lithium tri-*t*-butoxyaluminium hydride to give 12β-hydroxy ketone (**5**). The compound **5** was transformed *via* a four-step process into androstan-4-ene-3,17-dione, which was converted into **1** by a known procedure. The overall yield amounted to 1.8% from jervine.

In a recent preliminary communication[3] we reported the synthesis of testosterone (**1**) from jervine *via* the title epoxy ketone (**2**) as a result of continuing studies on the preparation of biologically active steroid hormones from jervine, one of the most readily available veratrum alkaloids. In the present paper we describe the details of the transformation from **2** into **1**, since the preparation of **2** had already been reported.



1



2

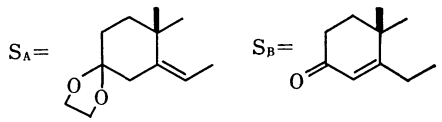
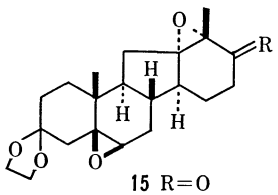


Photo-transformation of α,β-epoxy ketones has been investigated extensively and demonstrated to give a variety of products including rearranged 1,3-diketones.[5] With the expectation that the title 12α,13α-epoxy 17-ketone (**2**) would be transformed into an androstane-12,17-dione derivative, we examined the photolysis of **2** under various conditions (Experimental, Table 1). It was found that irradiation of **2** by a low pressure lamp in dioxane produced two isomeric 1,3-diketones (**3**), mp 253—254 °C, and (**4**), mp 181—183 °C, in 14 and 10% yields, respectively, a considerable amount (67%) of the starting material (**2**) being recovered unchanged. In accordance with the assigned structures, the respective compounds (**3** and **4**) had the same molecular formula $C_{21}H_{28}O_4$ as **2** and exhibited two absorption maxima at the carbonyl region and two three-proton singlets at high field in the IR and NMR spectra: **3**, ν_{max} 1756 and 1707 cm^{-1}; δ 1.13 and 1.23 (19- and 18-H): **4**, ν_{max} 1745 and 1708 cm^{-1}; δ 0.97 and 1.23. The calculated δ-values (1.167 and 1.293) for 19- and 18-methyl protons[6] and mechanistic considerations[5] indicated that a normal steroid skeleton could be assigned to the former (**3**), while a bicyclo[3.3.1]nonane-2,9-dione partial structure to the latter (**4**). The former was then obtained in 40% yield by the repeated photo-transformations.

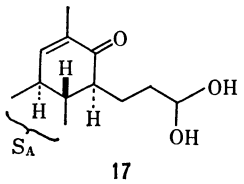
Table 1. Photolysis of **2**[a]

Solvent	Time	Products (yield/%)						
		2	**3**	**4**	**15**	**17**	**18**	**19**
Dioxane	1 d	67	14	10	—	—	—	—
Ether	1 d	76	5	5	—	—	—	—
DME[b]	1 d	67	10	6	—	—	—	—
Cyclohexane	1 d	75	4	3	—	—	—	—
THF	1 d	70	7	4	—	—	—	—
CH_3CN	10 h	35	6	5	18[d]	—	—	—
CCl_4[c]	3.5 h	84	—	—	4[d]	—	—	—
CCl_4+O_2[e]	20 h	27	—	—	38	—	—	—
Benzene[d]	10 h	24	—	—	—	19	8	22

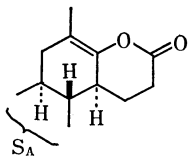
a) Carried out by a 15-W low pressure mercury lamp at room temperature. b) DME, 1,2-dimethoxyethane. c) By a 100-W high pressure lamp. d) Formation of **15** would be attributed to the presence of oxygen gas contaminated in the solvents. e) Carried out in stream of oxygen.



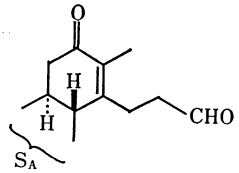
15 R=O
16 R=⋯OH, —H



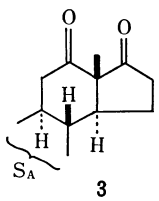
17



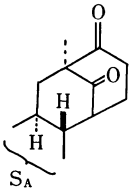
18



19

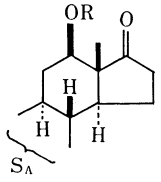


3

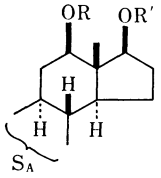


4

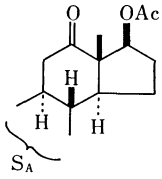
Transformation of the 12,17-diketone (**3**) into **1** was carried out by two usual routes. Reduction of **3** with lithium tri-*t*-butoxyaluminium hydride in tetrahydrofuran (THF) proceeded regioselectively to give 12β-hydroxy 17-ketone (**5**), mp 195—197 °C [ν_{max} 1736 cm^{-1}; δ 3.81 (1H, do d, J=10 and 5 Hz, 12-H)], in 96% yield, which was converted readily into the corresponding 12β-mesylate (**6**), mp 156—158 °C. Attempted reductive elimination of the mesyl group by treatment with lithium aluminium hydride resulted in the S–O bond cleavage of the group to give only 12β,17β-diol (**7**), mp 186—188 °C [δ 3.52 (1H, do d, J=10 and 5 Hz, 12-H) and 3.88 (1H, t, J=8 Hz, 17-H)]. The diol (**7**) was also obtained by direct reduction of **3** with the hydride reagent in 94% yield.[7] Partial acetylation of **7**, however, led to formation of a 3:2 mixture of the 17β- and 12β-monoacetates (**8a** and **8b**), which without further purification was oxidized with chromium(VI) oxide (CrO_3) in pyridine to yield a 1:1 mixture of the corresponding 17-oxo 12-acetate (**9a**) and 12-oxo 17-acetate (**9b**). The mixture was then submitted to the Wolff-Kishner reduction followed by purification by preparative TLC to give 17β-hydroxyandrost-5-en-3-one 3,3-ethylene acetal[8] (**10**) in low (12%) yield from **3**. This compound (**10**) underwent deacetalization by a known procedure[8] to yield testosterone (**1**).



5 R=H
6 R=CH_3SO_2
9a R=Ac
10 RO=H

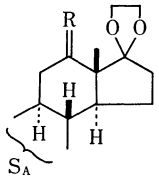


7 R=R'=H
8a R=H, R'=Ac
8b R=Ac, R'=H

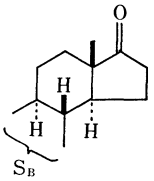


9b

An alternate and improved transformation of **3** into **1** was commenced by acetalization of 12β-hydroxy 17-ketone (**5**) with ethylene glycol and acid (*p*-TsOH). The resulting acetal (**11**), mp 219—220 °C, was oxidized by the usual procedure (CrO_3 in Py) to 12,17-diketone 17-acetal (**12**), mp 215—216 °C, in 66% yield from **5**. The Wolff-Kishner reduction of **12** produced 3,17-diacetal (**13**), mp 175—176 °C, which on deacetalization with the acid in aqueous acetone gave androst-4-ene-3,17-dione[8] (**14**), mp 175—176 °C, in 85% yield from **12**. This diketone (**14**) was transformed by a known procedure[8] into testosterone (**1**). The overall yield amounted to 35% from the photolysis product (**3**) and 1.8% from jervine.



11 R=—OH, ···H
12 R=O
13 R=H_2



14

Experimental

All the melting points were uncorrected. The homogeneity of each compound was always checked by TLC on silica gel (Wakogel B-5) with various solvent systems, and the spots were developed with cerium(IV) in dil sulfuric acid and/or iodine. Column chromatography was carried out over silica gel (Merck, Kieselgel 60, 70—230 mesh) and preparative TLC over silica gel (Wakogel B-5F, 20×20 cm^2). The optical rotations, UV, IR, and NMR (100 MHz) spectra were measured in chloroform, ethanol, Nujol, and chloroform-*d*, respectively, unless otherwise stated. The abbreviations "s, d, t, m, br, and do" in the NMR spectra denote "singlet, doublet, triplet, multiplet, broad, and double," respectively.

Photolysis of 12α,13α-Epoxyetiojerv-5-ene-3,17-dione 3,3-Ethylene Acetal (2). The photolysis was examined under various conditions and the results were summarized in Table 1. A few representative examples were described below. i) Compound **2** (1.12 g) in dioxane (200 ml) was irradiated by a 15-W low-pressure mercury lamp at room temperature for 2 d under nitrogen. The reaction mixture was evaporated to leave resinous material (1.10 g), which was separated by chromatography over silica gel (35 g) with benzene-ether mixtures. Elution with benzene-ether (5:1) led to recovery of **2** (750 mg). Early fractions eluted with benzene-ether (2:1) afforded semi-crystalline substance, which was purified by preparative TLC (6 plates) over silica gel with benzene–ether (3:2) to give a bicyclo [3.3.1]nonane-2,9-dione derivative (**4**, 120 mg), mp 181—183 °C (from ether) and $[\alpha]_D$ −24.2°; MS, *m/e* 344 (M^+); IR, ν_{max} 1745, 1708, 1275, and 1095 cm^{-1}; NMR, δ 0.97 and 1.23 (19- and angular CH$_3$), 3.94 (4H, s, OC_2H_4O), and 5.42 (1H, br, W_H=10 Hz, 6-H). Found: C, 73.19; H, 7.98%. Calcd for $C_{21}H_{28}O_4$: C, 73.22; H, 8.19%. Later fractions eluted with benzene-ether (1:1) gave a crystalline substance, which was also purified by preparative TLC (8 plates) under the same conditions as mentioned above to give androst-5-ene-3,12,17-trione 3,3-ethylene acetal (**3**, 157 mg), mp 242—243 °C and 253—254 °C (from acetone) and $[\alpha]_D$ +68.4°; MS, *m/e* 344 (M^+) and 149; IR, ν_{max} 1756, 1707, 1291, and 1095 cm^{-1}; NMR, δ 1.13 and 1.23 (each 3H, s, 19- and 18-H), 3.94 (4H, s, OC_2H_4O), and 5.41 (1H, br, W_H=10 Hz, 6-H). Found: C, 73.00; H, 8.38%. Calcd for $C_{21}H_{28}O_4$: C, 73.22; H, 8.19%.

ii) An acetonitrile solution (20 ml) of **2** (200 mg) was irradiated for 10 h under the same conditions. The mixture

was worked up as usual to leave amorphous residue (190 mg), which was submitted to chromatography over silica gel (15 g) to give **2** (70 mg), **4** (10 mg), a new compound (**15**, 35 mg), and **3** (12 mg) as benzene–ether eluates (5:1, 10:3, 10:4, and 1:1), respectively. The new compound (**15**), 5β,6β:12α,13α-diepoxyetiojervane-3,17-dione 3,3-ethylene acetal, mp 129—130 °C (from diisopropyl ether) and $[\alpha]_D$ −37°; MS, *m/e* 360 (M^+); IR, ν_{max} 1720, 1125, 1104, 1075, and 1015 cm^{-1}; NMR, δ 0.98 and 1.30 (each 3H, s, 19- and 18-H), 3.14 (1H, d, J=2 Hz, 6-H), and 3.92 (4H, s, $OC_2\underline{H}_4O$). This diepoxide was obtained by oxidation of a known compound, 5β,6β:12α,13α-diepoxy-17α-hydroxyetiojervan-3-one 3,3-ethylene acetal[4] (**16**) as follows. To a suspended mixture of CrO_3 (1.0 g) in pyridine (10 ml) was added **16** (100 mg) in pyridine (1 ml) under stirring. The mixture was stirred at room temperature for 4 h. After addition of ether (20 ml), the mixture was worked up as usual to leave amorphous residue, which was purified by passing through a silica gel column (6 g) to give **15** (70 mg), mp 129—130 °C. This was identical with one of the photolysis products in acetonitrile (MS, IR, NMR, and TLC).

iii) Compound **2** (170 mg) was irradiated in benzene (thiophene-free, 30 ml) under the afore-mentioned conditions for 10 h. The mixture, after being worked up as usual, left a complex mixture (205 mg), which was separated by chromatography over silica gel (7.0 g) with benzene–ether mixtures. While eluates with benzene–ether (20:1) gave **2** (40 mg), those with benzene–ether (10:1, 5:1, and 5:2) were further purified by preparative TLC (each 2, plates) over silica gel with a 3:2 mixture of benzene–ether, respectively, to yield three new compounds (**17**, 34 mg), (**18**, 16 mg), and (**19**, 37 mg), respectively. These compounds were tentatively assigned the respective formulas on the basis of the following spectral data: **17**, amorphous; MS, *m/e* 344 (M^+−18), 316, 301, 288, and 256; UV, λ_{max} 237 nm (ε 6500); IR, ν_{max} (neat) 3440, 1673, 1115, 1095, and 1020 cm^{-1}; NMR, δ 1.06 and 1.76 (19-H and $C\underline{H}_3$), 3.92 (4H, s, $OC_2\underline{H}_4O$), 5.36 (1H, br, W_H=9 Hz, 6-H), and 6.43 (1H, br, W_H=10 Hz, $C\underline{H}(OH)_2$]; **18**, amorphous, MS, *m/e* 344 (M^+); IR, ν_{max} ($CHCl_3$) 1749, 1714, 1265, 1162, and 1110 cm^{-1}; NMR, δ 1.00 and 1.70 (each 3H, s, 19-H and $C\underline{H}_3$), 3.95 (4H, s, $OC_2\underline{H}_4O$), and 5.34 (1H, br, W_H=10 Hz, 6-H): **19**, amorphous, MS, *m/e* 344 (M^+), 316, 300, and 272; UV, λ_{max} 244 nm (ε 10000); IR, ν_{max} ($CHCl_3$), 2725, 1731, 1663, 1615, and 1097 cm^{-1}; NMR, δ 1.07 and 1.84 (each 3H, s, 19-H and $C\underline{H}_3$), 3.97 (4H, s, $OC_2\underline{H}_4O$), 5.46 (1H, br, W_H=10 Hz, 6-H), and 9.78 (1H, s, $C\underline{H}O$).

12β-Hydroxyandrost-5-ene-3,17-dione 3,3-Ethylene Acetal (5). A THF solution (12 ml) of **3** (100 mg) was stirred with lithium tri-*t*-butoxyaluminium hydride (160 mg) at room temperature for 8 h. The reaction was ceased by addition of aq ammonium sulfate, and the mixture was filtered. The filtrate was concentrated, mixed with water, and extracted with chloroform (3×30 ml). The chloroform solution was washed with water, dried over anhydrous sodium sulfate and evaporated to leave a crystalline substance, which was recrystallized from acetone to yield **5** (97 mg), mp 195—197 °C and $[\alpha]_D$ +2.8°; MS, *m/e* 346 (M^+), IR, ν_{max} 3500, 1736, 1133, 1119, and 1100 cm^{-1}; NMR, δ 0.98 and 1.07 (each 3H, s, 18- and 19-H), 3.81 (1H, do d, J=10 and 5 Hz, 12-H), 3.95 (4H, s, $OC_2\underline{H}_4O$), and 5.37 (1H, br, W_H=10 Hz, 6-H). Found: C, 72.61; H, 8.77%. Calcd for $C_{21}H_{30}O_4$: C, 72.80; H, 8.73%.

12β,17β-Dihydroxyandrost-5-en-3-one 3,3-Ethylene Acetal (7). i) To a dichloromethane solution (4 ml) of **5** (60 mg) cooled at −8 °C (ice-water-NaCl) was added dropwise triethylamine (0.07 ml) and then methanesulfonyl chloride (0.02 ml) under stirring. The mixture was stirred at the temperature for 2 h and then diluted with dichloromethane (20 ml). The solution was washed with water (20 ml), 2 M hydrochloric acid (HCl, 20 ml), 5% aq sodium hydrogencarbonate ($NaHCO_3$, 2×20 ml), and water (3×20 ml), dried and evaporated to leave a crystalline substance (50 mg), which was purified by passing through a silica gel column (3 g) to give the 12β-mesylate (**6**, 32 mg) of **5**, mp 156—158 °C (from ether): NMR, δ 1.04 and 1.07 (each 3H, s, 18- and 19-H), 3.22 (3H, s, $C\underline{H}_3SO_2$), 3.95 (4H, s, $OC_2\underline{H}_4O$), 4.40 (1H, do d, J=10 and 5 Hz, 12-H), and 5.38 (1H, br, W_H=10 Hz, 6-H).

To a suspended mixture of lithium aluminium hydride (LAH, 26 mg) in THF (10 ml) cooled with ice-water was added **6** (30 mg) in THF (10 ml) under stirring, and the mixture was refluxed for 3 h under nitrogen and then cooled. After dropwise addition of water (4 ml) and 4 M aq sodium hydroxide (1 ml) under cooling with ice-water, the mixture was filtered. The filtrate was concentrated, mixed with water and extracted with chloroform (4×50 ml). The extracts were worked up as usual to leave a crystalline substance, which was purified by passing through a silica gel column (2.0 g) to yield **7** (23 mg), mp 186—188 °C (from diisopropyl ether) and $[\alpha]_D$ −31.9°; MS, *m/e* 348 (M^+); IR, ν_{max} 3400, 1140, 1102, 1062, and 1025 cm^{-1}; NMR, δ 0.82 and 1.06 (each 3H, s, 18- and 19-H), 3.52 (1H, do d, J=10 and 5 Hz, 12-H), 3.88 (1H, t, J=8 Hz, 17-H), 3.95 (4H, s, $OC_2\underline{H}_4O$), and 5.32 (1H, br, W_H=10 Hz, 6-H). Found: C, 70.33; H, 9.11%. Calcd for $C_{21}H_{32}O_4 \cdot 1/2H_2O$: C, 70.55, H, 9.31%.

ii) To a mixture of LAH (40 mg) in THF (8 ml) cooled with ice-water was added **3** (50 mg) in THF (30 ml) under stirring, and the whole mixture was refluxed for 3 h. The reaction mixture was worked up and purified as described above to give **7** (45 mg), mp 186—188 °C, which was identical with a sample of the afore-mentioned diol (**7**) (IR, NMR, and TLC).

17β-Hydroxyandrost-5-en-3-one 3,3-Ethylene Acetal (10). A benzene solution (3 ml) of **7** (55 mg) was treated with acetic anhydride (0.1 ml) and pyridine (0.1 ml) at room temperature for 31 h. The solution was diluted with ether (100 ml) and worked up as usual to give a mixture of the 12β- and 17β-monoacetates (**8a** and **8b**, total 34 mg) of **7**; amorphous; NMR, δ 0.80 and 0.86 (total 3H, 3:2, each s, 18-H), 1.06 (3H, s, 19-H), 2.09 and 2.07 (total 3H, 3:2, each s, $OCOC\underline{H}_3$), 3.58 (2/3H, do d, J=10 and 5 Hz, 12-H), 3.96 (≈4H, s, $OC_2\underline{H}_4O$ and 17-H), 4.75 (1H, br m, W_H=24 Hz, 12- and 17-H), and 5.36 (1H, br, W_H=10 Hz, 6-H).

The mixture (**8a** and **8b**, 34 mg) in pyridine (2 ml) was treated with CrO_3 (340 mg) in pyridine (3.4 ml) at room temperature for 1.5 h under stirring. The reaction mixture was worked up as usual to give a 1:1 mixture of 17- and 12-ketones (**9a** and **9b**), amorphous: **9a**, 0.97 and 1.06 (each 1.5H, s, 18- and 19-H), 2.09 (1.5H, $OCOC\underline{H}_3$), and 4.96 (0.5H, br, W_H=16 Hz, 12-H); **9b**, 1.14 and 1.19 (each 1.5H, s, 19- and 18-H), 2.04 (1.5H, s, $OCOC\underline{H}_3$), and 5.06 (0.5H, br, W_H=20 Hz, 17-H); **9a** and **9b**, 3.94 (3H, s, $OC_2\underline{H}_4O$) and 5.37 (1H, br, W_H=10 Hz, 6-H).

To a solution of the mixture (**9a** and **9b**, 24 mg) in ethylene glycol (6 ml) was added 85% aq hydrazine hydrate (0.18 ml) and powdered potassium hydroxide (KOH, 0.32 g). The solution was heated at 100—110 °C for 1.5 h and then refluxed at 180—190 °C for 18.5 h. The reaction mixture was cooled, poured into ice-water, and extracted with chloroform (3×40 ml). The chloroform solution was washed with 2 M HCl (2×50 ml) and water (4×80 ml), dried and evaporated

under reduced pressure to leave amorphous residue (23 mg), which was separated by preparative TLC (2 plates) over silica gel with benzene–ether (2:1). A fraction with the highest R_f value gave a crystalline substance, which was recrystallized from acetone to yield **10** (7.1 mg), mp 188—189 °C and $[\alpha]_D$ −45.6°; MS, *m/e* 332 (M^+); IR, ν_{max} 3260, 1136, 1097, 1055, and 1025 cm^{-1}; NMR, δ 0.76 and 1.05 (each 3H, s, 18- and 19-H), 3.65 (1H, t, J=8 Hz, 17-H), 3.96 (4H, s, OC_2H_4O), and 5.34 (1H, br, W_H=10 Hz, 6-H). This sample was identical with an authentic specimen[8] obtained by acetalization of **1**.

*12β-Hydroxyandrost-5-ene-3,17-dione 3,3-Ethylene Acetal (**11**).* Compound **5** (42 mg) was dissolved in benzene (20 ml) and ethylene glycol (2 ml) containing *p*-toluenesulfonic acid (*p*-TsOH, 3 mg), and the solution was refluxed (oil-bath temperature, 100±5 °C) for 16 h under stirring, water being removed under a Dean-Stark apparatus. The mixture was washed with 5% aq $NaHCO_3$ (3×50 ml) and water (3×40 ml), dried and evaporated to leave a crystalline substance, which was purified by passing through a silica gel column (1.8 g) to give **11** (31 mg), mp 219—220 °C (from ether) and $[\alpha]_D$ −70.8°; MS, *m/e* 390 (M^+) and 372; IR, ν_{max} 3540, 1105, 1028, 995, and 945 cm^{-1}; NMR, δ 0.93 and 1.05 (each 3H, s, 18- and 19-H), 3.96 (8H, br, s, $2OC_2H_4O$), and 5.35 (1H, br, W_H=10 Hz, 6-H). Found: C, 70.56; H, 8.75%. Calcd for $C_{23}H_{34}O_5$: C, 70.74; H, 8.78%.

*Androst-5-ene-3,12,17-trione 3,3:17,17-Bis(ethylene acetal) (**12**).* To a suspended mixture of CrO_3 (300 mg) in pyridine (3 ml) was added **11** (30 mg) in pyridine (2 ml) under stirring. The mixture was stirred at room temperature for 1.5 h, cooled and then filtered. The filtrate and precipitates were washed with ethyl acetate (4×50 ml and 50 ml), respectively. All the ethyl acetate solutions were worked up as described above to leave a crystalline substance, which was purified by passing through a silica gel column (1.5 g) to give **12** (21 mg), mp 215—216 °C (from ether) and $[\alpha]_D$ +10.5°; MS, *m/e* 388 (M^+); IR, ν_{max} 1715, 1100, 1025, and 990 cm^{-1}; NMR, δ 1.08 and 1.11 (each 3H, s, 18- and 19-H), 3.94 (4H, s, 3-OC_2H_4O), 4.02 (4H, m, 17-OC_2H_4O), and 5.39 (1H, br, W_H=10 Hz, 6-H). Found: C, 71.06; H, 8.32%. Calcd for $C_{23}H_{32}O_5$: C, 71.10; H, 8.30%.

*Androst-5-ene-3,17-dione 3,3:17,17-Bis(ethylene acetal) (**13**) and Androst-5-ene-3,17-dione 3,3-Ethylene Acetal (**14**).* i) An ethylene glycol solution (3 ml) of **12** (9 mg) was heated with 85% aq hydrazine hydrate (0.08 ml) and KOH (0.08 g) at 100—110 °C (bath temp) for 1 h and then refluxed (bath temp, 180—200 °C) for 20 h. After being cooled, the mixture was poured into ice–water (20 ml) and then extracted with chloroform (4×40 ml). The chloroform extracts were worked up as mentioned above to yield amorphous residue (9 mg), which was purified by passing through a silica gel column (0.5 g) and crystallized on trituration with ether. Recrystallization from ethanol–ether afforded **13** (7.4 mg), mp 174—176 °C and $[\alpha]_D$ −64.0°; MS, *m/e* 374 (M^+); IR, ν_{max} 1100, 1037, 1025, and 990 cm^{-1}; NMR, δ 0.86 and 1.04 (each 3H, s, 18- and 19-H), 3.89 and 3.94 (each 4H, s, 17- and 3-OC_2H_4O). Found: C, 73.62; H, 9.17%. Calcd for $C_{23}H_{34}O_4$: C, 73.76; H, 9.15%.

Compound **13** (45 mg) was heated with *p*-TsOH (15 mg) in acetone (15 ml) and water (3 ml) under reflux for 17 h. After being cooled, the mixture was evaporated, mixed with water and then extracted with chloroform (4×20 ml). The chloroform extracts were worked up as mentioned above to leave amorphous residue (59 mg), which was purified by passing through a silica gel column (3 g) and crystallized on trituration with ether. This was recrystallized from ether to give **14** (29 mg), mp 175—176 °C and $[\alpha]_D$ +198.8°; MS, *m/e* 286 (M^+) and 244; UV, λ_{max} 239 nm (ε 12000); IR, ν_{max} 1740, 1662, and 1613 cm^{-1}; NMR δ 0.93 and 1.23 (each 3H, s, 18- and 19-H), and 5.74 (1H, s, 4-H). Found: C, 79.49; H, 9.28%. Calcd for $C_{19}H_{26}O_2$: C, 79.68; H, 9.15%. This compound (**14**) was identical with an authentic sample obtained by oxidation of **1** (MS, UV, IR, NMR, TLC, and mixed mp), and was converted into **1** by a known procedure.[8]

References

1) Part VII, A. Murai, H. Sasamori, and T. Masamune, *Bull. Chem. Soc. Jpn.*, **53**, 254 (1980).

2) Part XXXV of "*C*-Nor-*D*-homosteroids and Related Alkaloids;" Part XXXIV, Ref. 1.

3) A. Murai, N. Iwasa, and T. Masamune, *Chem. Lett.*, **1977**, 235.

4) A. Murai, N. Iwasa, M. Takeda, H. Sasamori, and T. Masamune, *Bull. Chem. Soc. Jpn.*, **50**, 429 (1977).

5) a) A. Padwa, "Organic Photochemistry," ed by O. L. Chapman, Marcel Dekker, Inc., New York, N. Y. (1967), Vol. 1, p. 91; b) M. Debono, R. M. Molloy, D. Bauer, T. Iizuka, K. Schaffner, and O. Jeger, *J. Am. Chem. Soc.*, **92**, 420 (1970); H. Wehrli, C. Lehmann, T. Iizuka, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **50**, 2403 (1967); H. Wehrli, C. Lehmann, P. Keller, J. J. Bonet, K. Schaffner, and O. Jeger, *ibid.*, **49**, 2218 (1966); H. Wehrli, C. Lehmann, K. Schaffner, and O. Jeger, *ibid.*, **47**, 1336 (1964); c) H. Hart, Cheng-tai Peng, and Eng-mu Shih, *Tetrahedron Lett.*, **1977**, 1641; H. Hart, Cheng-tai Peng, and Eng-mu Shih, *J. Org. Chem.*, **42**, 3635 (1977); J. Muzart and J. P. Pete, *Tetrahedron Lett.*, **1977**, 303, 307; D. J. Dewar and R. G. Sutherland, *J. Chem. Soc., Perkin Trans. 2*, **1977**, 1522; *cf.*, R. K. Murray, Jr., T. K. Morgan, Jr., J. A. S. Polley, C. A. Andruskiewicz, Jr., and D. L. Goff, *J. Am. Chem. Soc.*, **97**, 940 (1975).

6) N. S. Bhacca and D. H. Williams, "Application of NMR Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, California (1964), p. 19.

7) *Cf.*, J. K. Norymberski and G. F. Woods, *J. Chem. Soc.*, **1955**, 3426.

8) H. L. Herzog, M. A. Jevnik, M. E. Tully, and E. B. Hershberg, *J. Am. Chem. Soc.*, **75**, 4425 (1953); H. J. Dauben, Jr., B. Löken, and H. J. Ringold, *ibid.*, **76**, 1359 (1954); W. S. Johnson, B. Bannister, R. Pappo, and J. E. Pike, *ibid.*, **78**, 6354 (1956).