SYNTHESIS AND PHOTOCHEMICAL TRASFORMATIONS OF 19-PHENYLSULFONYL PROVITAMIN D ANALOGUE

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Dedicated to Dr Jan Fajkos on the occasion of his 75th birthday.

The synthesis of provitamin D analogue 19-(phenylsulfonyl)androsta-5,7-diene-3β,17β-diyl 3-acetate 17-pivalate (**20**) has been accomplished from 19-hydroxyandrost-5-ene-3β,17β-diyl 3-acetate 17-pivalate. 19-(Phenylsulfonyl)androst-5-ene-3β,17β-diyl 3-acetate 17-pivalate (**10**), a precursor of **20**, was first obtained in low yield in the nucleophilic displacement reactions of 19-halogenated-5-ene steroids with sodium benzenesulfinate. Then a more efficient method has been used, which involves protection of the double bond as an epoxide. Introduction of the C(7)–C(8) double bond into olefin **10** has been also achieved in two ways. The first involved bromination–dehydrobromination and the other consisted of an allylic oxidation of olefin **10** leading to enone and the Bamford–Stevens reaction of its tosylhydrazone. UV irradiation of 5,7-diene **20** resulted in formation of a complex mixture of products. The structures of five isolated compounds were established on the basis of their ^{1}H NMR spectra and mechanistic rationale.

Key words: 5,7-Androstadienes; Steroids; Photochemistry; Sulfones; Provitamin D; Vitamines.

The main photoisomerization path in the vitamin D series was established by Velluz[1] in 1955. It has been deduced that the main photochemical processes consist of the conrotatory electrocyclic ring B opening in the steroidal 5,7-diene (provitamin D) to form the 9,10-seco-5(10),6,8-triene (previtamin D) which can be subsequently isomerized to its 6*E*-form (tachysterol). Previtamin D also undergoes a thermally induced [1,7]-sigmatropic rearrangement to the 5,7,10(19)-triene system characteristic of vitamin D compounds. The intramolecular nature of this antarafacial migration of hydrogen was

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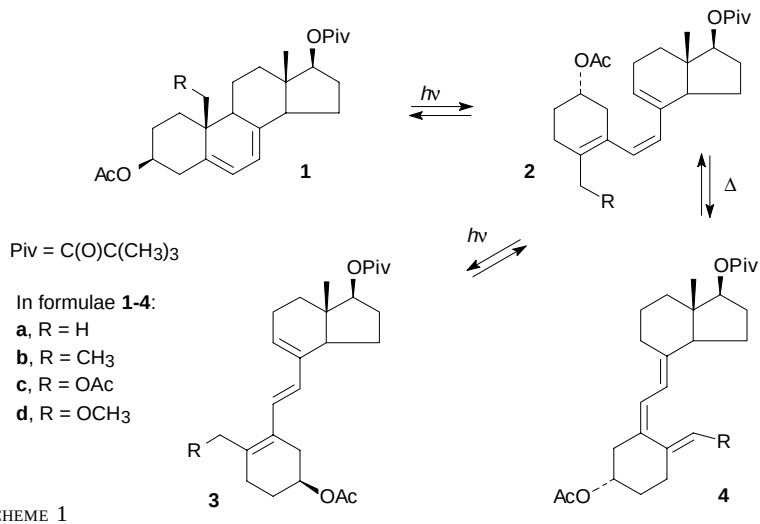
determined by Havinga[2] in 1964. Thermodynamics and kinetics of photochemical and thermal interconversions of pro- and previtamin D compounds have been intensively studied during the last four decades[3–6]. However, very few studies have been reported examining electronic effects of the C-19 substituents on these processes[7–9]. Considering the fact that 19-methyl group in provitamin D is attached directly to a C(9)–C(10) bond which undergoes photolytic opening and that rehybridization at C-19 occurs during previtamin–vitamin rearrangement, we initiated studies on 19-functionalized provitamin D analogues. In our previous papers[10,11], we reported the synthesis of provitamin D in androstane series (**1a**), and its analogues substituted at C-19: homologue **1b**, acetate **1c** and methyl ether **1d** (Scheme 1). It turned out that ultraviolet irradiation of dienes **1a**–**1d** produces a similar distribution of photoproducts, previtamins **2a**–**2d** and tachysterol analogues[11,12] **3a**–**3d**. It has also been found that in the case of thermal previtamin–vitamin conversion, the equilibrium mixture of 19-unsubstituted analogue consisted of **2a** and **4a** in a 1 : 3 ratio whereas for all 19-functionalized compounds, the equilibrium of thermal reaction lies far towards the side of the vitamin D forms **4b**–**4d**.

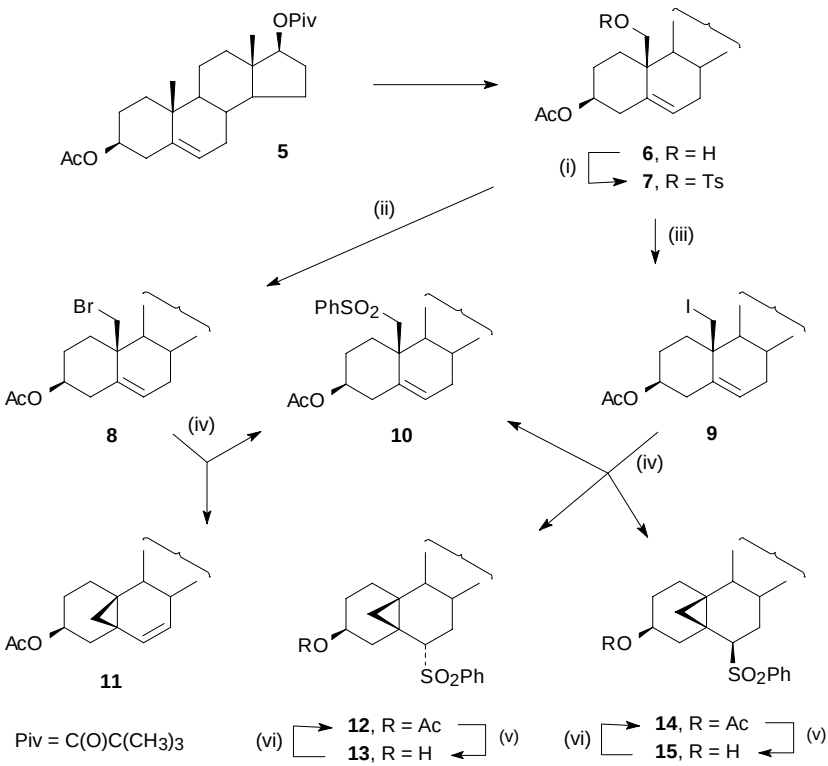


SCHEME 1

We explained this phenomenon by postulating that all of the 19-substituents studied (methyl, acetoxy and methoxy), which exert positive mesomeric effect, stabilize the vitamin D triene system. It was therefore of interest to perform further studies on photochemical and thermal isomerizations of the analogues substituted at position 19 with a group that can withdraw electrons by both inductive and mesomeric effects. The present paper deals with the synthesis and photochemistry of a compound which fulfils this condition, *i.e.*, androsta-5,7-diene bearing 19-phenylsulfonyl substituent.

In our earlier work[13], we described the transformation of androst-5-ene-3β,17β-diyl 3-acetate 17-pivalate (**5**) into 19-alcohol **6** (Scheme 2). Its tosyl derivative[14] **7** was used

now to obtain the corresponding 19-bromo and 19-iodo compounds **8** and **9** by the modified Counsell procedure[15]. As expected, no significant homoallylic rearrangement was observed and both 19-halogeno compounds were formed in high yields. Then a direct nucleophilic displacement of the halogen atom in **8** and **9** by $PhSO_2^-$ was attempted. It could be anticipated[16] that this reactive nucleophile might also form product with unrearranged carbon skeleton, *i.e.*, 19-phenylsulfonyl derivative **10**. However, the desired compound **10** was only a minor product (10% yield) of the iodo derivative **9**



(i) TsCl/pyridine; (ii) LiBr/propan-2-ol, reflux; (iii) NaI/propan-2-ol, reflux; (iv) $PhSO_2Na$/DMF, 65 °C; (v) K_2CO_3/MeOH, H_2O, 40 °C; (vi) Ac_2O/pyridine

SCHEME 2

reaction with sodium phenylsulfinate. The polar fraction of the reaction consisted of the isomeric 5β,19-cyclo compounds, **12** and **14** (1 : 1.4, 38% yield) substituted at C-6 with phenylsulfonyl group. These compounds could be separated chromatographically only after their hydrolysis to the respective 3β-alcohols **13** and **15** which were then reacetylated for further identification. The analysis of ^{13}C and ^1H NMR spectra of both products **12** and **14**, showing no olefinic protons, the presence of high-field signals of the

cyclopropyl protons at C-19 and the presence of the methine proton signals at *ca* 3.4 ppm clearly demonstrated their rearranged structure. Analysis of the coupling constants of the latter signals allowed one to establish the configuration of C-6 substituents. In order to determine the preferred conformation of compounds **12** and **14**, molecular mechanics calculations were employed*. The torsional angles between the C-6 proton and the vicinal 7α- and 7β-protons in the energy-minimized structures (173.0° and 52.9° for **12**; 42.1° and –73.9° for **14**) were used to calculate the expected ^1H–^1H coupling constants. The respective vicinal couplings for compounds **12** and **14** were calculated on the basis of Altona's modified Karplus relationship[17]. The experimental coupling constants for the C-6 methine proton (brd, J = 8.3 Hz) in the major isomer were in agreement with the values calculated for 6β-phenylsulfonyl compound **14** (J(6α,7α) = 6 Hz, J(6α,7β) = 1 Hz), whereas the observed couplings of H-6 in the minor isomer (dd, J = 10.3, 5.4 Hz) provided a better match with those calculated** for epimeric 6α-substituted compound **12** (J(6β,7α) = 12 Hz, J(6β,7β) = 4 Hz). It should be added that blank experiments performed with compounds **12** and **14** revealed that these isomers were unchanged during a prolonged treatment with $PhSO_2Na$ in DMF or with K_2CO_3 in methanol. Thus, the possibility of their interconversion due to epimerization process at C-6, occurring during the displacement reaction or hydrolysis, has been excluded. Reaction of 19-bromo-5-ene **8** with the sodium phenylsulfinate proceeded similarly as in the case of the iodo compound **9** but the yield of the desired product **10** was lower. It was established that a major product of the reaction was 5β,19-cyclo-6-ene compound **11**; this rearranged olefin was also formed by the elimination of a 4-methylbenzene sulfonic acid from the tosylate **7**. The predominant formation of the 5β,19-cyclo compounds in these processes confirmed that the displacement of 19-halogenated steroidal 5-enes with $PhSO_2^-$ occurs mainly with the concomitant homoallylic rearrangement.

Low yields of the 19-phenylsulfonyl olefin **10** formed in the displacement reactions examined, encouraged us to seek for an alternative method of its preparation. In order to prevent the participation of the homoallylic double bond in the nucleophilic substitution at C-19, we decided to epoxidize the double bond in the B ring. Thus, 19-bromo

* Molecular modelling was performed using the MM^+ algorith (an enhanced version of MM2) included in the HyperChem™ (release 4.0) software package (*Autodesk, Inc*. 1994) The least energy conformers were further subjected to rotations (30°) of angles: H–C(6)–S–O, C(6)–S–C′(1)–C′(2) and C(5)–C(6)–C(7)–C(8) using the conformational search option of ChemPlus™ (release 1.5) software package.

**Some of the discrepancies between the calculated and observed couplings may stem from the electronegativity of the C-6 substituent. Since the electronegativity of the phenylsulfonyl group, to our knowledge, has not been described in literature, we used in our calculations a value of 2.60 corresponding to the electronegativity of a sulfur atom.

olefin **8** was treated with 3-chloroperoxybenzoic acid in dichloromethane and the resulting mixture of 5α- and 5β-epoxides **16** and **18** (4.9 : 1) was separated by crystallization and column chromatography (Scheme 3). Both epoxides were next subjected to the reaction with $PhSO_2Na$. It was found that only α-epoxide **16** underwent the substitution to yield the 19-phenylsulfonyl derivative **17** as the sole product, whereas the isomeric compound **18** was remained unchanged. Therefore, it was also possible to use a mixture of epoxides **16** and **18** for the substitution reaction with subsequent easy separation of the product **17**. The remarkable difference in reactivity between the isomeric 19-bromo-5,6-epoxides was rationalized in terms of molecular mechanics calculations of the preferred conformations of an angular C(10)–CH_2Br arrangement in both compounds **16** and **18**. The rotation of this bulky group is restricted by the axial substituents of the A, B and C rings, situated on the β-face of the molecules. Energy minimization of structures **16** and **18** was first done using the MM+ force field. Then, three conformers of each epoxide were generated by 120° increment rotation around the C(10)–C(19) bond and energy was minimized for all of the conformers involved. Finally, the geometry optimization of the resulting structures was performed using the semi-empirical AM1 method. Comparison of the structures and energies of all six conformers (Fig. 1) indicates that the orientations of the CH_2Br group in the least-energy conformers (**a** and **b**) of the α-epoxide **16** favour an S_N2 displacement reaction, whereas in the case of the third conformer (**c**), access of the nucleophile would be hindered severely by an angular methyl group at C-13 and the axial hydrogens at C-8

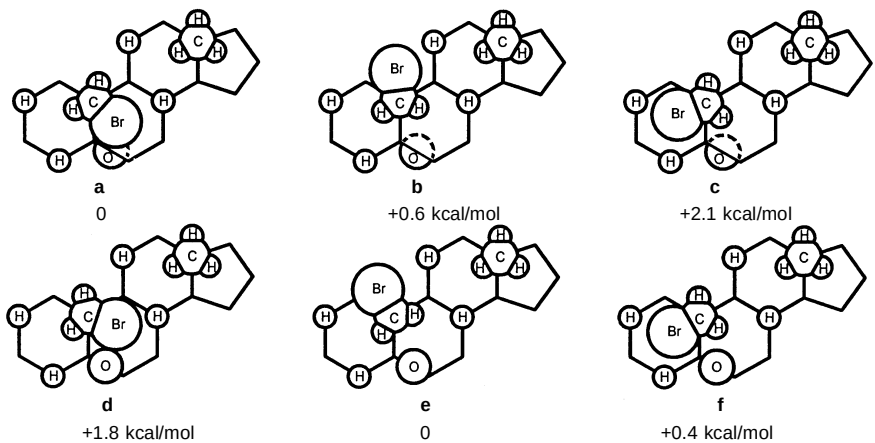
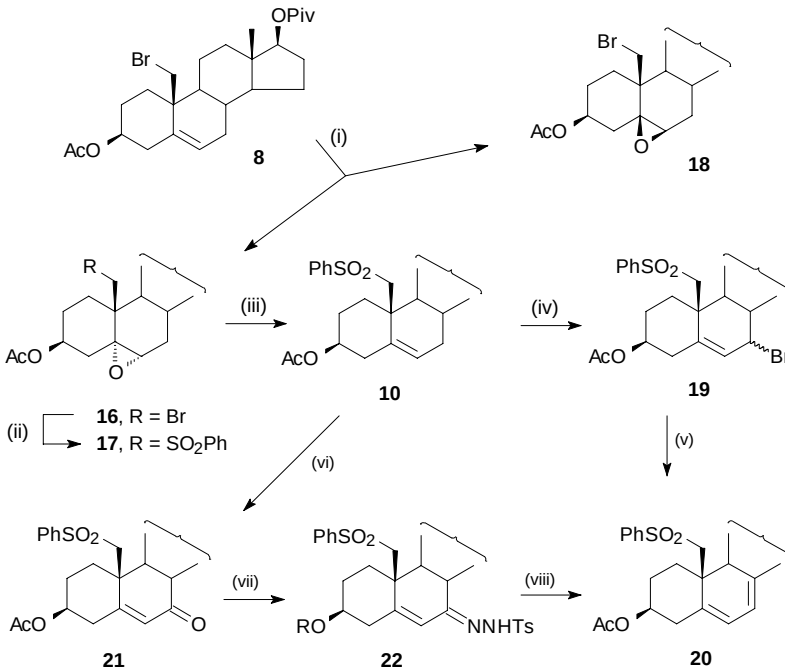


FIG. 1

Schematic top view of the energy-minimized conformers of the 19-bromo-5α,6-epoxide **16** (**a**, **b**, **c**) and its 5β,6-isomer **18** (**d**, **e**, **f**) resulting from rotation of bromomethyl group around the C(10)–C(19) bond. The steric energy differences between the preferred conformers and the corresponding rotamers are given

and C-11. On the contrary, an attack of the nucleophile on the CH_2Br group in β-epoxide **18** could take place only for the conformer of the highest energy (**d**).



Piv = $C(O)C(CH_3)_3$

(i) 3-chloroperoxybenzoic acid/CH_2Cl_2; (ii) $PhSO_2Na$/DMF, 65 °C; (iii) AlI_3/benzene, MeCN; (iv) 1,3-dibromo-5,5-dimethylhydantoin, $NaHCO_3$/benzene, hexane, reflux; (v) tetrabutylammonium fluoride, 2,4,6-trimethylpyridine/THF; (vi) CrO_3-(pyridine)$_2$ complex/CH_2Cl_2; (vii) $TSNHNH_2$/MeOH, 65 °C; (viii) LiH/toluene, reflux

SCHEME 3

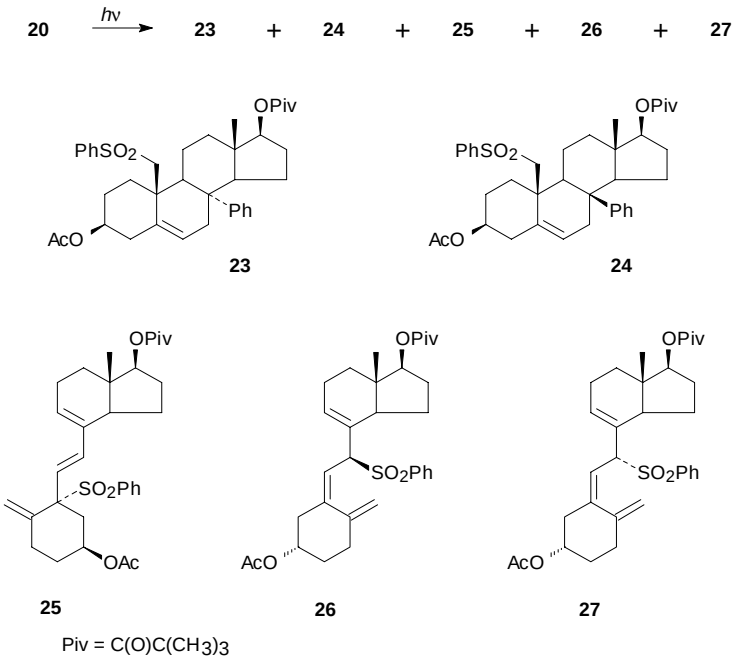
Reduction of epoxide **17** with aluminium triiodide[18] regenerated the C(5)=C(6) double bond providing the expected product **10** in 50% yield. The next synthetic step involved the introduction of an additional C(7)=C(8) double bond into olefin **10**. This goal was achieved by two methods. First, the well-known procedure of allylic bromination–dehydrobromination[19] was examined. Compound **10** was treated with 1,3-dibromo-5,5-dimethylhydantoin in refluxing benzene–hexane and the resulted allylic bromides **19** were subjected to the fluoride-promoted dehydrobromination[20]. However, the overall yield of the desired 5,7-diene **20** was not acceptable (9% based on **10**). An alternative method of the synthesis of diene **20** consisted of allylic oxidation of **10** with chromium(VI) oxide–(pyridine)$_2$ complex in dichloromethane providing 7-oxo compound **21** in 61% yield. This was converted quantitatively to tosylhydrazone **22** which,

in turn, was subjected to a modified Bamford–Stevens reduction (lithium hydride in refluxing toluene) to give diene **20** in 67% yield.

Ultraviolet irradiation of diene **20** was carried out in benzene–ether (1 : 4) solution at 0 °C and the resulting complex mixture of products (Scheme 4) was separated by repeated column chromatography on silica. The following compounds were isolated (in the elution order): isomeric 8α- and 8β-phenyl-5-enes **23** and **24** (4.5 : 1), 5α-phenylsulfonyl-9,10-seco-6,8,10(19)-triene **25** and isomeric 7*S*- and 7*R*-phenylsulfonyl-9,10-seco-5,8,10(19)-trienes **26** and **27** (1.9 : 1). The structural assignments were based on spectral data and mechanistic rationale. The presence of only one olefin proton signal in the ^{1}H NMR spectrum of **23** practically excluded the possibility of the 9,10-seco structure and suggested that this product might have a normal steroidal tetracyclic skeleton. Comparison of the ^{1}H NMR spectra of the product **23** and olefin **10** indicated that the compounds might contain the same structural moiety consisting of A ring, 19-phenylsulfonyl group and a double bond C(5)=C(6). The signals of aromatic protons at 7.13, 7.19 and 7.28 ppm indicated the presence of an additional phenyl ring attached to an alkyl fragment. Taking into account that **23** was the main reaction product formed from diene **20**, it was reasonable to place the phenyl ring at 8α-position. An alternative position at C-7 was excluded because of lack, in the ^{1}H NMR spectrum of **23**, of the deshielded signal of H-7 coupled with olefinic H-6. The minor isomer **24**, with the protons at C-18 and C-19 considerably more shielded owing to the presence of the 8β-phenyl substituent, would result from the attack of the phenyl radical at C-8 of the 5,7-diene system in **20**, occurring from the more shielded β-face of the molecule. The phenyl radical attack at C-8 gives an allylic radical that can abstract hydrogen from benzene. This begins the free radical relay. The stronger secondary C-H bond at C-7 (rather than the weaker tertiary bond at C-5) is preferentially formed without allylic rearrangement. The process of the formation of **23** and **24** could be initiated by photolytic decomposition of the phenylsulfonyl substituent leading to phenyl radical, SO_2 and alkyl radical[21]. The next photoproduct was very unstable undergoing decomposition soon after its isolation. Therefore, structure **25** can be proposed on the basis of the ^{1}H NMR spectrum only. The presence of the signals of five olefinic protons indicated strongly the 9,10-seco system, whereas the characteristic coupling constant (J = 16.3 Hz) between the protons resonating at 5.47 and 6.08 ppm suggested a tachysterol-like structure. The third olefinic proton, resonating as a multiplet at 5.71 ppm was therefore ascribed to H-9. Its chemical shift as well as the chemical shift of methyl group at C-13 closely resembled those observed for the tachysterol compounds prepared by us previously[11] (*e.g.*, **3c**). Since the two remaining olefinic protons, resonating at 5.33 and 5.79 ppm as singlets, come from the exomethylene group at C-10, the phenylsulfonyl substituent the most likely is attached to C-5. Thus, analysis of the olefinic protons pattern seems to be sufficient for elucidation of the structure **25**. Such a product is probably derived from the intermediate tachysterol analogue. Its 19-phenylsulfonyl group,

being in allylic position to the triene system, underwent 1,3-migration occurring at the less hindered α-face of the ring A. It is very likely that analogous 1,5-migration of 19-phenylsulfonyl substituent in previtamin and/or tachysterol intermediates was also responsible for the formation of the remaining photoproducts **26** and **27**. Both compounds show very similar ^{1}H NMR spectra, indicating the presence of four olefinic protons. The signals of protons at 4.75, 4.97 and 5.69 ppm are very similar to the corresponding signals of some 9,10-seco-5,10(19)-diene steroids[22,23]. The latter signal derives from the olefinic proton at C-6 which is coupled with a methine proton at C-7 (δ 4.34, d, J = 10.7 Hz), bearing the phenylsulfonyl substituent. The chemical shift of the proton resonating at δ 5.86 is similar to the shifts of the corresponding olefinic protons at C-9 in closely related systems[24]. Analysis of the ^{1}H NMR spectra did not allow to establish the configuration at C-7 in both isomers **26** and **27**. However, analysis of the Dreiding models of the previtamin and tachysterol analogues derived from diene **20** reveals that among the conformers suitable for 1,5-migration of the phenylsulfonyl group, those leading to the 7*S*-substituted compound are less crowded. Therefore, 7*S*-configuration of the phenylsulfonyl substituent has been tentatively ascribed to the predominant isomer **26**.

From the present study it is evident that ultraviolet light irradiation of 19-phenylsulfonyl substituted provitamin D analogue **20** caused the ring B opening, resulting in formation of the corresponding 19-substituted previtamin and tachysterol analogues.



SCHEME 4

These photoproducts, however, underwent further transformations, consisting mainly in 1,3- and 1,5-migration of the 19-phenylsulfonyl group, being in the allylic position in respect to the triene systems. The studies on the photochemistry of other 19-substituted provitamin D analogues are in progress.

EXPERIMENTAL

Melting points were measured on a Kofler type (Boetius) hot-stage apparatus and are given without corrections. Optical rotations were measured in chloroform using a Perkin–Elmer 241 automatic polarimeter at 22 °C, $[\alpha]_D$ values are given in 10^{-1} deg cm^2 g^{-1}. Ultraviolet spectra (λ_{max}, nm; ε) were measured on a Beckman Acta M VI apparatus in hexane solutions. Infrared spectra (wavenumbers in cm^{-1}) were recorded on a Zeiss UR-20 spectrometer in KBr pellets unless stated otherwise. ^{1}H and ^{13}C NMR spectra were recorded at 500 and 125 MHz with a Bruker AM-500 spectrometer using $CDCl_3$ as a solvent and tetramethylsilane as an internal standard. Chemical shifts are given in ppm (δ scale), coupling constants (*J*) and half-width of multiplets (*W*) in Hz. For ^{13}C NMR spectra, the number of directly bonded hydrogen atoms was determined from the proton-decoupled "attached proton test". Mass spectra were determined with an AMD-604 instrument at 70 eV. High-resolution data were obtained by peak matching.

Thin-layer chromatography (TLC) was carried out on precoated aluminium silica sheets from Merck, column chromatography on silica gel Macherey–Nagel (100–200 mesh) and flash chromatography on silica gel 60 (230–400 mesh, Merck No. 9385).

Androst-5-ene-3β,17β,19-triyl 3-Acetate 17-Pivalate 19-Tosylate[11] (**7**)

A solution of 19-alcohol **6** (21.63 g, 0.05 mol) and tosyl chloride (19.07 g, 0.1 mol) in anhydrous pyridine (70 ml) was allowed to react for 4 days at room temperature. The mixture was poured into ice/water and extracted with benzene. The organic phase was washed with water, saturated $CuSO_4$, again water, dried (Na_2SO_4) and evaporated. The crystalline residue was washed twice with cold methanol and the solvent was decanted. The colourless residue was filtered and air dried to give 22.1 g (76%) of 19-tosylate **7**, m.p. 136.5–140.5 °C, $[\alpha]_D$ –71 (*c* 1.3), which was sufficiently pure to be used in the following synthetic steps without further purification.

19-Bromoandrost-5-ene-3β,17β-diyl 3-Acetate 17-Pivalate (**8**)

A solution of tosylate **7** (11.74 g, 0.02 mol) and LiBr (8.68 g, 0.1 mol) in propan-2-ol (525 ml) was gently refluxed for 4 h. The solution was concentrated to a small volume *in vacuo*, poured into water and extracted with dichloromethane. The extract was washed with water and dried (Na_2SO_4). The solvent was evaporated to give a colourless solid residue which was crystallized from acetone to obtain 6.44 g (65%) of pure 19-bromo steroid **8**. The mother liquor was chromatographed on silica gel column. Elution with dichloromethane–hexane (80 : 20 →95 : 5) gave additional 1.39 g of crystalline **8** (total yield 7.83 g; 79%), 160–162 °C; $[\alpha]_D$ –71 (*c* 1.3). IR spectrum: 1 735, 1 483, 1 373, 1 292, 1 252, 1 170, 1 034. ^{1}H NMR spectrum: 0.90 s, 3 H (3 × H-18); 1.20 s, 9 H ($(CH_3)_3CCOO$); 2.04 s, 3 H (CH_3COO); 3.50 d, 1 H, *J* = 11.1 (H-19); 3.78 d, 1 H, *J* = 11.1 (H-19); 4.64 brm, 2 H (H-3α and H-17α); 5.69 m, 1 H (H-6). For $C_{26}H_{39}BrO_4$ (495.5) calculated: 63.03% C, 7.93% H; found: 63.19% C, 8.00% H.

19-Iodoandrost-5-ene-3β,17β-diyl 3-Acetate 17-Pivalate (**9**)

The title compound **9** was prepared in 90% yield from tosylate **7** and NaI by a method analogous to that described above for compound **8**. Crystallization from hexane–acetone afforded the pure product **9,** m.p. 144–148 °C, $[\alpha]_D$ –84 (*c* 1.0). IR spectrum: 1 732, 1 482, 1 293, 1 254, 1 175, 1 036. ^{1}H NMR spectrum: 0.92 s, 3 H (3 × H-18); 1.20 s, 9 H ($(CH_3)_3CCOO$); 2.03 s, 3 H (CH_3COO); 3.30 d, 1 H, *J* = 11.0 (H-19); 3.59 d, 1 H, *J* = 11.0 (H-19); 4.58 brm, 2 H (H-3α and H-17α); 5.66 m, 1 H (H-6). For $C_{26}H_{39}IO_4$ (542.5) calculated: 57.57% C, 7.25% H; found: 57.49% C, 7.15% H.

Reaction of 19-Bromo and 19-Iodo Olefins **8** and **9** with Sodium Phenylsulfinate

Olefin **9** (995 mg, 1.83 mmol) and $PhSO_2Na$ (398 mg, 2.43 mmol) in anhydrous DMF (5 ml) were heated at 65 °C for 24 h. The reaction mixture was poured into water and extracted three times with dichloromethane. The combined extracts were washed with saturated $NaHCO_3$ and water, dried and evaporated to give a dark yellow oily residue which was subjected to column chromatography on silica. Elution with benzene and benzene–ether (99 : 1) gave a mixture (212 mg) of starting material and some elimination products. Further elution with benzene–ether (99 : 1) yielded slightly impure fractions (120 mg) of 19-phenylsulfonyl olefin **10** which after rechromatography in the same solvent system yielded pure and crystalline product **10** (103 mg, 10%). Elution with benzene–ether (99 : 1 and 98 : 2) afforded a mixture of polar 5β,19-cyclo compounds **12** and **14** (391 mg, 38%) in a 1 : 1.4 ratio.

19-(Phenylsulfonyl)androst-5-ene-3β,17β-diyl 3-acetate 17-pivalate (**10**): m.p. 175–177 °C (hexane–acetone), $[\alpha]_D$ –99.1 (*c* 1.0). IR spectrum (CCl_4): 1 730, 1 480, 1 447, 1 369, 1 326, 1 308, 1 285, 1 241, 1 164, 1 155, 1 033. ^{1}H NMR spectrum: 1.04 s, 3 H (3 × H-18); 1.21 s, 9 H ($(CH_3)_3CCOO$); 2.03 s, 3 H (CH_3COO); 3.13 d, 1 H, *J* = 14.8 (H-19); 3.49 d, 1 H, *J* = 14.8 (H-19); 4.62 brm, 2 H (H-3α and H-17α); 5.63 d, 1 H, *J* = 5.5 (H-6); 7.57 m, 2 H (2 × H_m-Ar); 7.65 m, 1 H (H_p-Ar); 7.93 m, 2 H (2 × H_o-Ar). ^{13}C NMR spectrum: 12.3 (q), 21.3 (q), 22.2 (t), 23.4 (t), 27.3 (q), 27.6 (t), 27.7 (t), 30.8 (t), 31.5 (d), 37.4 (t), 38.5 (t), 38.6 (t), 38.9 (s), 41.5 (s), 43.0 (s), 51.0 (d), 52.6 (d), 57.7 (t), 73.2 (d), 82.2 (d), 126.6 (d), 127.5 (d), 129.3 (d), 133.4 (d), 133.8 (s), 142.0 (s), 170.4 (s), 178.7 (s). Mass spectrum, *m/z* (%): 496 (21, M – AcOH), 354 (37, 496 – $PhSO_2H$), 341 (38), 239 (87), 57 (100). For $C_{32}H_{44}O_6S$ (556.8) calculated: 69.03% C, 7.97% H; found: 69.09% C, 7.87% H.

An analogously performed reaction of 19-bromo compound **8** (551 mg, 1.11 mmol) with sodium benzenesulfinate (251 mg, 1.53 mmol) in DMF (2.5 ml), followed by standard work-up and column chromatography, afforded unreacted substrate, some nonpolar products (290 mg) consisting mainly of 5β,19-cyclo olefin **11**, and 19-phenylsulfonyl olefin **10** (32 mg, 5%).

5β,19-Cycloandrost-6-ene-3β,17β-diyl 3-Acetate 17-Pivalate (**11**)

A solution of tosylate **7** (500 mg, 0.85 mmol) in anhydrous pyridine (10 ml) was refluxed for 18 h. The mixture was poured into water and extracted with benzene. The extract was washed with water, 5% HCl, again water and saturated $NaHCO_3$, dried (Na_2SO_4) and evaporated. The residue was crystallized from a small volume of hexane to yield 187 mg of pure 5β,19-cyclo olefin **11**. The mother liquor was chromatographed on silica. Elution with benzene gave additional 109 mg of crystalline **11** (total yield 296 mg, 84%), m.p. 145–147 °C (hexane), $[\alpha]_D$ +1.3 (*c* 1.2). IR spectrum (KBr): 1 727, 1 482, 1 370, 1 286, 1 251, 1 167, 1 032. ^{1}H NMR spectrum: 0.55 d, 1 H, *J* = 4.7 (H-19); 0.81 s, 3 H (3 × H-18); 1.15 d, 1 H, *J* = 4.7 (H-19); 1.20 s, 9 H ($(CH_3)_3CCOO$); 2.01 s, 3 H (CH_3COO); 4.60 dd, 1 H, *J* = 9.1, *J′* = 7.7 (H-17α); 4.63 brm, 1 H (H-3α); 5.22 dd, 1 H, *J* = 9.8, *J′* = 1.6 (H-6); 5.72 dd, 1 H, *J* = 9.8, *J′* = 3.0 (H-7). For $C_{26}H_{38}O_4$ (414.6) calculated: 75.33% C, 9.24% H; found: 75.23% C, 9.07% H.

Hydrolysis of 3β-Acetoxy Group in 5β,19-Cyclo Compounds **12** and **14**

A mixture of polar 5β,19-cyclo compounds **12** and **14** (390 mg), obtained in the experiment described above (reaction of **9** with $PhSO_2Na$), was dissolved in warm (40 °C) methanol (35 ml) and a solution of K_2CO_3 (1 g) in water (3.5 ml) was added. After 30 min of stirring at 40 °C, the reaction mixture was poured into water and extracted three times with dichloromethane. The combined extracts were washed with water, dried (Na_2SO_4) and evaporated to give a crystalline residue which was subjected to column chromatography on silica. Elution with benzene–ether (90 : 10) gave crystalline 3β-alcohol **13** (128 mg). Subsequent elution with benzene–ether (80 : 20) afforded the isomeric compound **15** (182 mg) as colourless crystals. Both products were recrystallized from hexane–acetone.

3β-Hydroxy-6α-(phenylsulfonyl)-5β,19-cycloandrostan-17β-yl pivalate (**13**): m.p. 124–127 °C (hexane–acetone), $[\alpha]_D^{22}$ +26.7 (*c* 1.0). IR spectrum (KBr): 1 725, 1 444, 1 304, 1 292, 1 173, 1 154, 1 137, 1 084, 1 042. ^{1}H NMR spectrum: 0.69 d, 1 H, *J* = 5.6 (H-19); 0.70 d, 1 H, *J* = 5.6 (H-19); 0.72 s, 3 H (3 × H-18); 1.17 s, 9 H ($(CH_3)_3CCOO$); 3.06 dd, 1 H, *J* = 14.0, *J*′ = 5.8 (H-4α); 3.41 dd, 1 H, *J* = 8.6, *J*′ = 6.8 (H-6β); 3.92 brm, 1 H (H-3α); 4.54 dd, 1 H, *J* = 9.0, *J*′ = 7.9 (H-17α); 7.56 m, 2 H (2 × H_m-Ar); 7.64 m, 1 H (H_p-Ar); 7.88 m, 2 H (2 × H_o-Ar). ^{13}C NMR spectrum: 12.2 (q), 20.9 (s), 22.9 (t), 23.3 (t), 24.7 (t), 27.0 (s), 27.2 (q), 27.3 (t), 28.0 (t), 28.1 (t), 29.1 (t), 33.9 (d), 36.7 (t), 38.5 (t), 43.4 (s), 46.7 (d), 49.0 (d), 51.1 (s), 67.3 (d), 68.6 (d), 81.9 (d), 128.2 (d), 129.1 (d), 133.4 (d), 140.4 (s), 178.4 (s). For $C_{30}H_{42}O_5S$ (514.7) calculated: 70.01% C, 8.22% H; found: 70.09% C, 8.11% H.

3β-Hydroxy-6β-(phenylsulfonyl)-5β,19-cycloandrostan-17β-yl pivalate (**15**): m.p. 191–194 °C (hexane–acetone), $[\alpha]_D^{22}$ +49.4 (*c* 1.0). IR spectrum (KBr): 1 732, 1 479, 1 444, 1 290, 1 167, 1 142, 1 083, 1 042. ^{1}H NMR spectrum: 0.49 d, 1 H, *J* = 5.6 (H-19); 0.82 s, 3 H (3 × H-18); 1.19 s, 9 H ($(CH_3)_3CCOO$); 1.63 d, 1 H, *J* = 5.6 (H-19); 3.47 d, 1 H, *J* = 8.3 (H-6α); *ca* 3.48 brm, 1 H (H-3α); 4.57 dd, 1 H, *J* = 9.1, *J*′ = 7.6 (H-17α); 7.57 m, 2 H (2 × H_m-Ar); 7.66 m, 1 H (H_p-Ar); 7.94 m, 2 H (2 × H_o-Ar). ^{13}C NMR spectrum: 12.3 (q), 18.0 (t), 18.8 (s), 23.1 (t), 24.5 (t), 26.4 (s), 27.1 (t), 27.2 (q), 27.4 (t), 28.9 (t), 29.5 (t), 30.7 (d), 36.7 (t), 38.9 (s), 43.2 (s), 46.8 (t), 48.4 (d), 49.2 (d), 67.7 (d), 68.4 (d), 82.1 (d), 129.08 (d), 129.14 (d), 133.7 (d), 139.4 (s), 178.6 (s). For $C_{30}H_{42}O_5S$ (514.7) calculated: 70.01% C, 8.22% H; found: 69.95% C, 8.14% H.

Acetylation of 3β-Hydroxy Compounds **13** and **15**

Samples of alcohols **13** and **15** (50 mg) were acetylated in the mixture pyridine–acetic anhydride (2 : 1, 1 ml) at room temperature overnight. After standard isolation procedure, the crude acetylation products (single spots on TLC) were crystallized from hexane–acetone.

6α-(Phenylsulfonyl)-5β,19-cycloandrostane-3β,17β-diyl 3-acetate 17-pivalate (**12**): m.p. 167–168 °C (hexane–acetone), $[\alpha]_D^{22}$ +15.1 (*c* 0.7). IR spectrum (KBr): 1 732, 1 479, 1 445, 1 363, 1 303, 1 287, 1 247, 1 167, 1 140, 1 084, 1 025. ^{1}H NMR spectrum: 0.65 d, 1 H, *J* = 5.3 (H-19); 0.73 s, 3 H (3 × H-18); 0.77 d, 1 H, *J* = 5.3 (H-19); 1.17 s, 9 H ($(CH_3)_3CCOO$); 2.00 s, 3 H (CH_3COO); 2.95 dd, 1 H, *J* = 14.6, *J*′ = 6.1 (H-4α); 3.34 dd, 1 H, *J* = 10.3, *J*′ = 5.4 (H-6β); 4.54 dd, 1 H, *J* = 9.0, *J*′ = 7.8 (H-17α); 4.99 brm, 1 H (H-3α); 7.56 m, 2 H (2 × H_m-Ar); 7.63 m, 1 H (H_p-Ar); 7.90 m, 2 H (2 × H_o-Ar). ^{13}C NMR spectrum: 12.2 (q), 20.6 (s), 21.4 (q), 22.8 (t), 22.9 (t), 24.6 (t), 25.8 (t), 26.8 (s), 27.2 (q), 27.2 (t), 27.3 (t), 28.3 (t), 33.4 (t), 34.1 (d), 36.7 (t), 38.8 (s), 43.5 (s), 46.9 (d), 48.9 (d), 68.6 (d), 69.8 (d), 81.9 (d), 128.3 (d), 129.1 (d), 133.4 (d), 140.3 (s), 170.2 (s), 178.4 (s). For $C_{32}H_{44}O_6S$ (556.8) calculated: 69.03% C, 7.97% H; found: 69.15% C, 7.90% H.

6β-(Phenylsulfonyl)-5β,19-cycloandrostane-3β,17β-diyl 3-acetate 17-pivalate (**14**): m.p. 156–157 °C (hexane–acetone), $[\alpha]_D^{22}$ +11.7 (*c* 1.0). IR spectrum (KBr): 1 729, 1 479, 1 444, 1 361, 1 297, 1 283, 1 245, 1 167, 1 137, 1 082, 1 031. ^{1}H NMR spectrum: 0.58 d, 1 H, *J* = 5.7 (H-19); 0.82 s, 3 H (3 × H-18); 1.19 s, 9 H ($(CH_3)_3CCOO$); 1.66 d, 1 H, *J* = 5.7 (H-19); 1.97 s, 3 H (CH_3COO); 3.46 d, 1 H, *J* = 8.3

(H-6α); 4.56 dd, 1 H, J = 9.1, J' = 7.7 (H-17α); 4.60 brm, 1 H (H-3α); 7.57 m, 2 H (2 × H_m-Ar); 7.65 m, 1 H (H_p-Ar); 7.91 m, 2 H (2 × H_o-Ar). ^{13}C NMR spectrum: 12.3 (q), 17.9 (t), 18.3 (s), 21.3 (q), 23.1 (t), 24.5 (t), 25.8 (t), 26.1 (s), 27.2 (q), 27.4 (t), 28.3 (t), 29.7 (t), 30.4 (d), 36.7 (t), 38.9 (s), 42.4 (t), 43.2 (s), 48.0 (d), 49.0 (d), 67.8 (d), 70.0 (d), 82.0 (d), 128.9 (d), 129.1 (d), 133.6 (d), 139.2 (s), 170.6 (s), 178.6 (s). For $C_{32}H_{44}O_6S$ (556.8) calculated: 69.03% C, 7.97% H; found: 68.85% C, 7.89% H.

19-Bromo-5α,6-epoxy-5α-androstane-3β,17β-diyl 3-Acetate 17-Pivalate (**16**) and
19-Bromo-5β,6-epoxy-5β-androstane-3β,17β-diyl 3-Acetate 17-Pivalate (**18**)

A solution of 19-bromo olefin **8** (2.0 g, 4.0 mmol) in dichloromethane (50 ml) was treated with 3-chloroperoxybenzoic acid (80–85%, 2.3 g) added in portions. The temperature of the reaction mixture was maintained below 25 °C. After addition of all reagent, the mixture was allowed to stand at room temperature for 24 h with occasional shaking. The aromatic acids were removed by extraction with 5% NaOH, and the organic layer was washed with water and dried. The solvent was evaporated to give a colourless solid residue (2.1 g) consisting of 5α,6- and 5β,6-epoxides **16** and **18** in 4.9 : 1 ratio (established from ^{1}H NMR spectrum). The epoxide mixture was repeatedly crystallized from hexane–acetone to obtain 1.06 g of pure compound **16**. The mother liquor was chromatographed on silica gel column. Elution with benzene–ether (99 : 1) gave an additional 0.3 g of crystalline **16** (total yield 1.36 g, 66%). Further elution afforded a mixture of the epoxides (0.4 g) and pure isomeric 5β,6-oxide **18**, which was crystallized from acetone–hexane (yield 0.25 g, 12%).

19-Bromo-5α,6-epoxide **16**: m.p. 190–192 °C, $[\alpha]_D^{22}$ –74.1 (*c* 1.0). IR spectrum (KBr): 1 732, 1 483, 1 448, 1 369, 1 298, 1 288, 1 249, 1 168, 1 037. ^{1}H NMR spectrum: 0.81 s, 3 H (3 × H-18); 1.18 s, 9 H ($(CH_3)_3CCOO$); 2.02 s, 3 H (CH_3COO); 3.07 d, 1 H, J = 3.4 (H-6β); 3.71 s, 2 H (2 × H-19); 4.53 dd, 1 H, J = 9.3, J' = 7.3 (H-17α); 4.96 brm, 1 H (H-3α). For $C_{26}H_{39}BrO_5$ (511.5) calculated: 61.05% C, 7.69% H; found: 61.18% C, 7.79% H.

19-Bromo-5β,6-epoxide **18**: m.p. 154–156 °C, $[\alpha]_D^{22}$ –31.9 (*c* 0.9). IR spectrum (KBr): 1 735, 1 485, 1 460, 1 369, 1 288, 1 253, 1 171, 1 036. ^{1}H NMR spectrum: 0.83 s, 3 H (3 × H-18); 1.18 s, 9 H ($(CH_3)_3CCOO$); 2.04 s, 3 H (CH_3COO); 3.05 narrm, 1 H (H-6α); 3.64 s, 2 H (2 × H-19); 4.53 dd, 1 H, J = 9.8, J' = 7.3 (H-17α); 4.83 brm, 1 H (H-3α). For $C_{26}H_{39}BrO_5$ (511.5) calculated: 61.05% C, 7.69% H; found: 60.88% C, 7.80% H.

Reaction of 19-Bromo Epoxides **16** and **18** with Sodium Phenylsulfinate

19-Bromo-5α,6-epoxide **16** (102 mg, 0.20 mmol) and $PhSO_2Na$ (44.5 mg, 0.27 mmol) in anhydrous DMF (1 ml) were heated at 65 °C for 24 h. The reaction mixture was poured into water and extracted three times with methylene chloride. The combined extracts were washed with saturated $NaHCO_3$ and water, dried and evaporated to give a dark yellow oily residue which was subjected to column chromatography on silica. Elution with benzene–ether (98 : 2) yielded unreacted substrate (16 mg) and pure product **17**.

19-(Phenylsulfonyl)-5α,6-epoxy-5α-androstane-3β,17β-diyl 3-acetate 17-pivalate (**17**) (90.1 mg, 79%; 93% based on recovered **16**), m.p. 172–175 °C (hexane–acetone), $[\alpha]_D^{22}$ –83.2 (*c* 0.5). IR spectrum (KBr): 1 727, 1 481, 1 447, 1 368, 1 322, 1 309, 1 288, 1 244, 1 170, 1 147, 1 090, 1 037. ^{1}H NMR spectrum: 0.94 s, 3 H (3 × H-18); 1.19 s, 9 H ($(CH_3)_3CCOO$); 2.01 s, 3 H (CH_3COO); 3.19 d, 1 H, J = 3.9 (H-6β); 3.29 d, 1 H, J = 14.7 (H-19); 3.48 d, 1 H, J = 14.7 (H-19); 4.57 dd, 1 H, J = 9.0, J' = 7.6 (H-17α); 5.02 brm, 1 H (H-3α); 7.63 m, 2 H (2 × H_m-Ar); 7.70 m, 1 H (H_p-Ar); 7.97 m, 2 H (2 × H_o-Ar). For $C_{32}H_{44}O_7S$ (572.8) calculated: 67.11% C, 7.74% H; found: 67.01% C, 7.79% H.

An analogous reaction of the isomeric 19-bromo-5β,6-epoxide **18** resulted in an isolation of the unchanged substrate only.

Reduction of Epoxide **17** with Aluminium Triiodide

To a solution of epoxide **17** (14.3 mg, 0.025 mmol) in anhydrous acetonitrile (0.4 ml), a freshly prepared 0.35 M benzene solution of AlI_3 (1 ml) was added. The reaction mixture was stirred at room temperature for 20 h, quenched with cold water, diluted with dichloromethane and poured into water. The water layer was extracted with dichloromethane and the combined organic extracts were washed with 5% $NaHSO_3$ and water, dried and evaporated. The residue was subjected to flash chromatography. Elution with hexane–ethyl acetate (80 : 20) afforded 19-phenylsulfonyl olefin **10** (6.9 mg, 50%) identical with product described above.

Preparation of 19-(Phenylsulfonyl)androsta-5,7-diene-3β,17β-diyl 3-Acetate 17-Pivalate (**20**) by Bromination–Dehydrobromination

A mixture of olefin **10** (38.4 mg, 0.07 mmol) and $NaHCO_3$ (30 mg, 0.33 mmol) in benzene–hexane (1 : 1, 1 ml) was heated under reflux, and the hot solution was treated with 1,3-dibromo-5,5-dimethylhydantoin (14 mg, 0.05 mmol). The mixture was refluxed for 30 min, cooled and filtered. The solution was evaporated and the residue containing the allylic bromides **19** was redissolved in anhydrous THF (0.5 ml). Tetrabutylammonium bromide (2 mg) was added and the mixture was stirred for 30 min at room temperature. Then, it was treated with 2,4,6-trimethylpyridine (20 ml) and a 1 M THF solution of tetrabutylammonium fluoride (400 ml). The mixture was stirred at room temperature for 3 h. The solution was diluted with ether, washed with water, cold 5% HCl, and saturated $NaHCO_3$, dried and evaporated. The residue was chromatographed on a silica gel column. Elution with benzene–ether (99 : 1) yielded slightly impure 19-phenylsulfonyl diene **20** which after rechromatography in the same solvent system gave analytically pure oily product (3.4 mg, 9%), $[\alpha]_D^{22}$ –60.0 (*c* 0.5). UV spectrum: 287 (9 500), 275 (10 100), 267 (9 200), 223 (7 900). ^{1}H NMR spectrum: 0.83 s, 3 H (3 × H-18); 1.21 s, 9 H ($(CH_3)_3CCOO$); 2.05 s, 3 H (CH_3COO); 3.29 d, 1 H, *J* = 14.7 (H-19); 3.43 d, 1 H, *J* = 14.7 (H-19); 4.70 brm, 2 H (H-3α and H-17α); 5.45 m, 1 H (H-7); 5.66 d, 1 H, *J* = 5.9 (H-6); 7.49–7.68 brm, 3 H (2 × H_m-Ar and 1 × H_p-Ar); 7.89 m, 2 H (2 × H_o-Ar). For $C_{32}H_{42}O_6S$ (554.7) calculated: 69.29% C, 7.63% H; found: 69.19% C, 7.52% H.

7-Oxo-19-(phenylsulfonyl)androst-5-ene-3β,17β-diyl 3-Acetate 17-Pivalate (**21**)

Olefin **10** (516 mg, 0.93 mmol) in dry dichloromethane (6 ml) was added to a solution of CrO_3–(pyridine)$_2$ complex, prepared from CrO_3 (2.2 g, 22 mmol) and pyridine (3.5 ml, 44 mmol) in CH_2Cl_2 (44 ml), and the mixture was stirred for 48 h at room temperature. The solution was poured into saturated $NaHCO_3$. A black tarry precipitate was dissolved in saturated $NaHCO_3$ and extracted with CH_2Cl_2. The combined organic layers were washed several times with saturated $NaHCO_3$, 5% HCl, 5% $NaHCO_3$ and brine, dried and evaporated. The residue was subjected to flash chromatography. Elution with hexane–ethyl acetate (6 : 4) gave pure enone **21** (323 mg, 61%) as a glass: m.p. 108–110 °C, $[\alpha]_D^{22}$ –113.3 (*c* 0.8). IR spectrum (KBr): 1 728, 1 669, 1 480, 1 447, 1 364, 1 323, 1 309, 1 291, 1 241, 1 164, 1 151, 1 089, 1 033. ^{1}H NMR spectrum: 1.04 s, 3 H (3 × H-18); 1.21 s, 9 H ($(CH_3)_3CCOO$); 2.05 s, 3 H (CH_3COO); 3.24 dd, 1 H, *J* = 12.2, *J*′ = 10.7 (H-8β); 3.32 d, 1 H, *J* = 14.7 (H-19); 3.55 d, 1 H, *J* = 14.7 (H-19); 4.64 dd, 1 H, *J* = 8.8, *J*′ = 7.8 (H-17α); 4.74 brm, 1 H (H-3α); 5.96 s, 1 H (H-6); 7.61 m, 2 H (2 × H_m-Ar); 7.70 m, 1 H (H_p-Ar); 7.94 m, 2 H (2 × H_o-Ar). For $C_{32}H_{42}O_7S$ (570.7) calculated: 67.34% C, 7.42% H; found: 67.21% C, 7.34% H.

Conversion of Enone **21** into Tosylhydrazone **22**

A solution of enone **21** (171 mg, 0.3 mmol) and tosylhydrazide (223 mg, 1.2 mmol) in anhydrous methanol (3.6 ml) was heated at 55 °C for 14 h. The mixture was cooled and poured into 5% HCl.

The white precipitate was filtered off washed on the filter with water and air dried. After drying overnight in the desiccator (over P_2O_5), the crude product was sufficiently pure (a single spot on TLC) to be used for the next step without any further purification. Yield of tosylhydrazone **22** was 217 mg (98%), m.p. 132–137 °C. IR spectrum (KBr): 3 210, 1 726, 1 666, 1 480, 1 448, 1 324, 1 306, 1 292, 1 241, 1 169, 1 154, 1 088, 1 036. ^{1}H NMR spectrum: 1.03 s, 3 H (3 × H-18); 1.21 s, 9 H ($(CH_3)_3CCOO$); 2.06 s, 3 H (CH_3COO); 2.44 s, 3 H (CH_3-Ar); 3.14 dd, 1 H, J = 12.2, J' = 10.3 (H-8β); 3.22 d, 1 H, J = 14.7 (H-19); 3.49 d, 1 H, J = 14.7 (H-19); 4.61 brm, 2 H (H-3α and H-17α); 6.22 s, 1 H (H-6); 7.28–7.93 brm, 10 H (9 × H-Ar and 1 × H-N).

Reduction of Tosylhydrazone **22**

The crude tosylhydrazone **22** (185 mg, 0.25 mmol) was dissolved in dry toluene (6 ml) and lithium hydride (52 mg, 6.5 mmol) was added. The mixture was refluxed for 45 min under argon atmosphere. Fast filtration of the cooled reaction mixture into ice-cold 2% H_2SO_4 followed by washing of the organic layer with saturated $NaHCO_3$ solution and water, drying and concentration *in vacuo* yielded an oily residue which was subjected to flash chromatography. Elution with hexane–ethyl acetate (80 : 20) gave oily diene **20** (93 mg, 67%), identical with the product described above.

Photochemical Reaction of 19-Phenylsulfonyl Diene **20**

A solution of diene **20** (33 mg, 0.06 mmol) in benzene–ether (1 : 4, 300 ml) was cooled to 0 °C and degassed by an argon purge for 30 min. The mixture was irradiated for 15 min through a water-cooled (0 °C) quartz inner well with a 350 W Hanau S 81 lamp. The solvents were evaporated and the complex mixture of irradiation products was initially separated by column chromatography on silica using benzene–ethyl acetate (99 : 1) as an eluent. The first chromatographical separation provided the mixture of **23** and **24**, mixture of **25** and **26**, and impure **27**. Further separation and purification of these photoproducts were achieved by repeated chromatography on silica using benzene–ethyl acetate (199 : 1 → 99 : 1) solvent systems. Yields and R_F (benzene–ethyl acetate, 9 : 1) of the analytically pure compounds were as follows: **23** (6.7 mg, R_F 0.51), **24** (1.5 mg, R_F 0.49), **25** (0.8 mg, R_F 0.47), **26** (2.8 mg, R_F 0.44), **27** (1.5 mg, R_F 0.37).

19-(Phenylsulfonyl)-8α-phenyl-8α-androst-5-ene-3β,17β-diyl 3-acetate 17-pivalate (**23**): m.p. 135–138 °C (hexane–acetone). IR spectrum ($CHCl_3$): 1 719, 1 480, 1 448, 1 370, 1 324, 1 317, 1 308, 1 289, 1 251, 1 171, 1 152, 1 033. ^{1}H NMR spectrum: 1.11 s, 3 H (3 × H-18); 1.23 s, 9 H ($(CH_3)_3CCOO$); 2.02 s, 3 H (CH_3COO); 2.96 dd, 1 H, J = 12.5, J' = 3.8 (H-9α?); 3.17 d, 1 H, J = 14.9 (H-19); 3.53 d, 1 H, J = 14.9 (H-19); 4.64 brm, 1 H (H-3α); 4.69 dd, 1 H, J = 9.0, J' = 6.9 (H-17α); 5.40 d, 1 H, J = 5.2 (H-6); 7.13 m, 2 H (2 × H_o-Ar); 7.19 m, 1 H (H_p-Ar); 7.28 m, 2 H (2 × H_m-Ar); 7.55 m, 2 H (2 × H_m-Ar′); 7.63 m, 1 H (H_p-Ar′); 7.91 m, 2 H (2 × H_o-Ar′). Mass spectrum, *m/z* (%): 495 (58, M – AcOH – Ph), 393 (16, 495 – Me_3CCOOH), 353 (100, 495 – $PhSO_2H$), 251 (35, 353 – Me_3CCOOH), 57 (56). For $C_{38}H_{48}O_6S$ (632.9) calculated: 72.12% C, 7.65% H; found: 72.56% C, 8.16%.

19-(Phenylsulfonyl)-8β-phenylandrost-5-ene-3β,17β-diyl 3-acetate 17-pivalate (**24**): IR spectrum ($CHCl_3$): 1 718, 1 480, 1 378, 1 307, 1 288, 1 253, 1 175, 1 151, 1 036. ^{1}H NMR spectrum: 1.05 s, 3 H (3 × H-18); 1.22 s, 9 H ($(CH_3)_3CCOO$); 2.00 s, 3 H (CH_3COO); 2.89 d, 1 H, J = 14.7 (H-19); 3.00 d, 1 H, J = 14.7 (H-19); 3.05 dd, 1 H, J = 13.2, J' = 2.9 (H-9α?); 4.56 ≈ tt, 1 H, J = 11.5, J' = 4.5 (H-3α); 4.63 dd, 1 H, J = 9.3, J' = 7.3 (H-17α); 5.37 narrm, 1 H (H-6); 7.05 m, 2 H (2 × H_o-Ar); 7.14 m, 1 H (H_p-Ar); 7.19 m, 2 H (2 × H_m-Ar); 7.59 m, 2 H (2 × H_m-Ar′); 7.67 m, 1 H (H_p-Ar′); 7.89 m, 2 H (2 × H_o-Ar′). Mass spectrum, *m/z* (%): 495 (41, M – AcOH – Ph), 393 (19, 495 – Me_3CCOOH), 353 (100, 495 – $PhSO_2H$), 251 (40, 353 – Me_3CCOOH), 57 (55).

(6E)-5α-(Phenylsulfonyl)-9,10-secoandrosta-6,8,10(19)-triene-3β,17β-diyl 3-acetate 17-pivalate (**25**): ^{1}H NMR spectrum: 0.83 s, 3 H (3 × H-18); 1.19 s, 9 H ($(CH_3)_3CCOO$); 2.02 s, 3 H (CH_3COO); *ca*

4.7 brm, 2 H (H-3α and H-17α); 5.33 s, 1 H (H-19); 5.47 d, 1 H, *J* = 16.3 (H-7); 5.71 m, 1 H (H-9); 5.79 s, 1 H (H-19); 6.08 d, 1 H, *J* = 16.3 (H-6); 7.49 m, 2 H (2 × H_m-Ar); 7.62 m, 1 H (H_p-Ar); 7.77 m, 2 H (2 × H_o-Ar).

*(5Z,7S)-7-(Phenylsulfonyl)-9,10-secoandrosta-5,8,10(19)-triene-3*β*,17*β*-diyl 3-acetate 17-pivalate* (**26**): IR spectrum (CCl_4): 1 729, 1 462, 1 447, 1 378, 1 320, 1 307, 1 286, 1 240, 1 162, 1 151, 1 032. ^{1}H NMR spectrum: 0.75 s, 3 H (3 × H-18); 1.19 s, 9 H ((CH_3)$_3$CCOO); 2.02 s, 3 H (CH_3COO); 4.34 d, 1 H, *J* = 10.7 (H-7); 4.65 dd, 1 H, *J* = 9.3, *J*′ = 7.3 (H-17α); 4.70 ≈ tt, 1 H, *J* = 10, *J*′ = 4.5 (H-3α); 4.75 brs, 1 H (H-19); 4.97 brs, 1 H (H-19); 5.69 dd, 1 H, *J* = 10.7, *J*′ = 1.0 (H-6); 5.86 m, 1 H, *W* = 9 (H-9); 7.52 m, 2 H (2 × H_m-Ar); 7.62 m, 1 H (H_p-Ar); 7.82 m, 2 H (2 × H_o-Ar). Mass spectrum, *m/z* (%): 554 (4, M^+), 412 (2, M^+ – $PhSO_2H$), 353 (72, M^+ – AcOH - $PhSO_2$), 251 (41, 353 – Me_3CCOOH), 57 (100). HR-MS, for $C_{32}H_{42}O_6S$ calculated: 554.2702; found: 554.2729.

*(5Z,7R)-7-(Phenylsulfonyl)-9,10-secoandrosta-5,8,10(19)-triene-3*β*,17*β*-diyl 3-acetate 17-pivalate* (**27**): IR spectrum (CCl_4): 1 730, 1 480, 1 447, 1 377, 1 321, 1 308, 1 286, 1 242, 1 161, 1 151, 1 036. ^{1}H NMR spectrum: 0.75 s, 3 H (3 × H-18); 1.20 s, 9 H ((CH_3)$_3$CCOO); 1.96 s, 3 H (CH_3COO); 4.36 d, 1 H, *J* = 10.7 (H-7); 4.44 ≈ tt, 1 H, *J* = 6.4, *J*′ = 3.2 (H-3α); 4.69 dd, 1 H, *J* = 9.3, *J*′ = 7.3 (H-17α); 4.73 d, 1 H, *J* = 1.1 (H-19); 4.94 brs, 1 H (H-19); 5.73 d, 1 H, *J* = 10.7 (H-6); 5.88 m, 1 H, *W* = 9 (H-9); 7.52 m, 2 H (2 × H_m-Ar); 7.63 m, 1 H (H_p-Ar); 7.81 m, 2 H (2 × H_o-Ar). Mass spectrum, *m/z* (%): 554 (5, M^+), 494 (1, M^+ – AcOH), 412 (2, M^+ – $PhSO_2H$), 353 (100, M^+ – AcOH – $PhSO_2$), 251 (66, 353 – Me_3CCOOH), 57 (41). HR-MS, for $C_{32}H_{42}O_6S$ calculated: 554.2702; found: 554.2730.

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