vealed the absence of epidioxide and the presence of pyro- and isopyrocalciferol$_3$ (> 96%). TLC (ether) showed only one spot with R_f 0.45 (Vitamin D_3).
2) A similar experiment, using 100 mg of *trans*-Vitamin D_3 (**4**) in 30 ml of methanol, afforded a residue with maximum absorption at 270 nm. GC showed the presence of epidioxide (~ 20%), R_{rel} 2.98, and *trans*-Vitamin D_3. TLC (ether) showed two spots, R_f 0.30 (epidioxide) and 0.55 (*trans*-Vitamin D_3).

Preparation of trans-*Vitamin D_3* (**4**) *by photosensitization*
A stirred emulsion of 5 g of sensitox in 1700 ml of dry, freshly distilled, benzene was purged with nitrogen overnight. After addition of 5 g of Vitamin D_3 (**3**) and a few drops of pyridine the vigorously stirred solution was irradiated in a pyrex flask at 5° in a reactor equipped with four Philips TL 8W/33 lamps. After 2.5 hours GC showed the mixture to contain 62% of *trans*-Vitamin D_3 (**4**). Sensitox was removed by filtration through a sintered glass funnel G4 covered with a layer of alumina. The solvent was removed by evaporation under reduced pressure at room temperature. Chromatography at 5° on alumina (Woelm neutral act. II-III, eluent hexane/ether 7 : 3 → 1 : 1) afforded 2.5 g (50%) of *trans*-Vitamin D_3 (**4**) as a colourless oil of purity > 95% (GC). It crystallized from light petroleum (b.p. 40–60°) at −30°, m.p. 91–93° (lit.[17] 90.5–91.5°).

Preparation of Vitamin D_3 acetate by photosensitization
A solution of 100 mg of *trans*-Vitamin D_3 (**4**), in 250 ml of dry, freshly distilled, benzene was purged with nitrogen for two hours. After addition of 400 mg of phenazine the solution was irradiated with light from four RUL-3500 Å lamps for one hour, after which time GC showed the ratio of *cis*- to *trans*-isomer to be 9 : 1. The solvent was evaporated, the residue was dissolved in 1 ml of pyridine and 0.2 ml of acetic anhydride were added. After standing overnight, followed by the usual work-up, the sensitizer was removed by short-column chromatography (Merck silica H 60, eluent hexane/ether 2 : 1 → 1 : 1). The yield of Vitamin D_3 acetate (purity ~ 90%) was 76 mg (69%).

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An approach to 11β-isopropoxymethyl steroids

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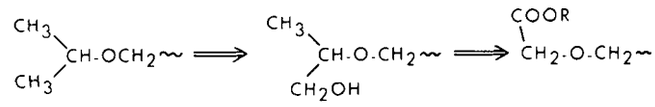
Abstract. A route for the preparation of 11β-isopropoxymethyl derivatives of steroids is exemplified by the preparation of (11β,17α)-17-hydroxy-11-(isopropoxymethyl)-19-norpregn-4-en-20-yn-3-one (**1**). To this end (11β)-11-(hydroxymethyl)-3-methoxyestra-1,3,5(10)-trien-17-one cyclic ethylene acetal (**2**) was converted into its 11β-(2-hydroxyethoxy)methyl derivative **5**. Oxidation of **5** to the corresponding 11β-(carboxymethoxy)methyl derivative **7**, followed by methylation and subsequent reduction gave (11β)-3-methoxy-11-[(1-methylethoxy)methyl]estra-1,3,5(10)-trien-17-one cyclic ethylene acetal (**13**). Birch reduction and ethinylation provided **1**.

Introduction

The synthetic modification of the steroid skeleton may lead to molecules which either display stronger potency than their natural predecessors or even behave as selective antagonists in hormonal events. This discovery has aroused the development of vast numbers of therapeutically valuable hormonal products[1-3].
Continuous interests in our laboratories in steroid molecules with specific hormonal properties prompted us to synthesize some 11β-isopropoxymethyl steroids. Since the preparation of these derivatives is not as straightforward as a first glance might suggest, we would like to present here the synthesis of 11β-isopropoxymethyl norethisteron (**1**).

Synthesis

The ready available[4] (11β)-11-(hydroxymethyl)-3-methoxyestra-1,3,5(10)-trien-17-one cyclic ethylene acetal (**2**) was used as starting material. Our initial attempts to convert **2** into its isopropyl ether with either 2-iodopropane or 2-bromopropane under the variety of basic conditions usually employed for such reactions (sodium hydride or butyllithium in organic solvents like DMSO, DMF, THF) or with the aid of phase transfer catalysis were met with failure. Presumably the alkoxide derived from such an 11β-hydroxymethyl group is too hindered and preferably effects elimination reactions only. At the same time we observed that upon treatment of **2** with sodium hydride and ethyl bromide in DMF the ethyl ether was formed, though in a very moderate yield (~ 35%). Based on this observation we reasoned that an alternative approach to an isopropyl group might consist in the initial creation of an ether bond with a primary halide, provided with a suitable functionality which could finally be modified into the desired isopropyl group *e.g.* according to the following retrosynthetic scheme:



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An attempt to alkylate **2** with methyl bromoacetate proved to be unsuccessful due to the high acidity of the ester α-protons[5]. Bromoacetaldehyde diethyl acetal proved to be an unsuitable substrate too. The THP ether of 2-bromoethanol (**4**) proved to be a convenient alkylating agent. Treatment of **2** with sodium hydride in DMF followed by reaction with **4** provided the required derivative **3** in a rather low yield, but since the starting material could be easily recycled by simple chromatography an acceptable net conversion of **2** into **3** could be achieved. Treatment of **3** with 3N aq. HCl in THF at room temperature easily removed the protecting groups to provide **5**. Since oxidation of **5** with chromic acid, in order to obtain a carboxylate group in the 11β ether chain, produced a complex mixture, a two-step oxidation reaction via the aldehyde was investigated. The conversion of **5** into the aldehyde **6** proved to be unexpectedly difficult. Frequently used oxidizing agents such as pyridinium chlorochromate[6], *Pfitzner–Moffat* conditions[7] or silver carbonate on *Celite*[8] produced only intractable tars. On treatment of **5** with dimethyl sulfide/N-chlorosuccinimide complex[9] the desired aldehyde **6** could be obtained in 46% yield as a labile oily substance. Upon treatment of **6** with silver oxide[10] in aqueous THF the carboxylic acid **7** was readily obtained. Subsequent esterification with methanol in the presence of a catalytic amount of sulphuric acid furnished the corresponding methyl ester **8**. For further elaboration the carbonyl group at C-17 was protected next by conversion into the ethylene acetal **9** by treatment with ethylene glycol and trimethyl orthoformate.

Upon treatment of **9** with lithium diisopropylamide and methyl iodide in THF initially in very low yields the required **10** was obtained as a 1 : 1 mixture of diastereoisomers. However on carrying out the methylation in the presence of HMPA a substantial improvement of the yield up to 65% was achieved. Subsequent reduction with $LiAlH_4$ provided the alcohol **11** which was converted into its tosylate **12** and then with $LiAlH_4$ into the desired isopropoxy derivative **13** (84% from **10**). Good quality $LiAlH_4$ and thoroughly dry THF proved to be necessary for smooth conversion of **12** into **13**, since otherwise substantial amounts of **11** were formed. The enone system **14** was easily obtained by a *Birch* reduction[11] with sodium in liquid ammonia. Protection of the enone system prior to ethinylation could be brought about conveniently by conversion into the thioacetal **15** by means of ethanedithiol and BF_3 etherate[12]. The alternative way to protect the enone system via an enol ether with triethyl

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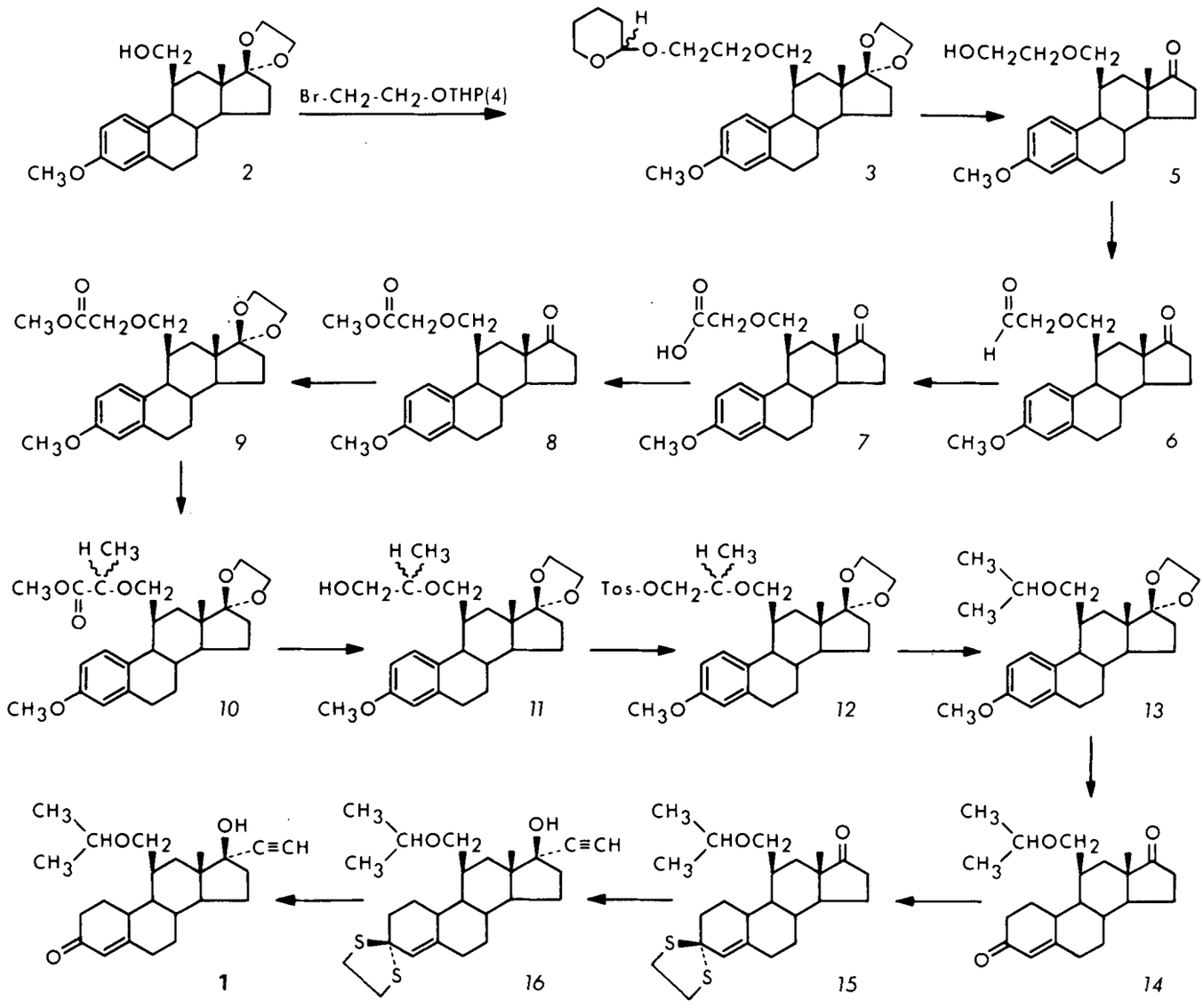

orthoformate produced many side-products and was therefore abandoned.
Ethinylation of **15** was readily brought about by potassium acetylide in THF to afford **16**. Subsequent hydrolytic cleavage[13,14] of the thioacetal with methyl iodide in aqueous ethanol finally afforded the desired **1**.

Experimental part

General
Melting points are uncorrected and measured on a Büchi melting point apparatus. ^{1}H-NMR spectra were recorded in $CDCl_3$ solutions on a Bruker Hx-90 E spectrometer, using tetramethylsilane as an internal standard. Infrared spectra were obtained on a Perkin-Elmer 580 spectrometer. Organic solvents were dried on molecular sieves prior to use (Linde, 4A). Dry THF was obtained by distillation from $LiAlH_4$ prior to use. Silicagel and silica thin-layer plates were purchased from Merck (Darmstadt).

2-(2-Bromoethoxy)-tetrahydro-(2H)-pyran (**4**)
To a solution of 37.5 g (0.3 mol) of 2-bromoethanol in 200 ml of methylene chloride, containing 200 mg of toluenesulphonic acid, was added dropwise with stirring at 0–5° a solution of 27.7 g (0.33 mol) of dihydropyran in 100 ml of methylene chloride. After stirring for an additional $\frac{1}{2}$ h the reaction mixture was washed twice with 200 ml of 10% $NaHCO_3$ solution, dried and evaporated to give 58 g of **4** as an essentially pure oil. Distillation gave 53.3 g (85%) of **4**, b.p. 62–65° (1 mm) [lit.[15] 94° (14 mm)].

(11β)-11-[[2-[(Tetrahydro-2H-pyran-2-yl)oxy]ethoxy]methyl]-3-methoxyestra-1,3,5(10)-trien-17-one cyclic ethylene acetal (**3**)
To a solution of 17.9 g (0.05 mol) of **2** in 150 ml of DMF under N_2 was added 2.3 g (~ 0.05 mol) of NaH (50% dispersion in oil). The suspension was stirred and heated on an oil bath up to the temperature where a vigorous gas evolution commenced (~ 85–90°). The mixture was then kept at this temperature for 15 min, after which time hydrogen evolution had ceased, and was then cooled to room temperature. A solution of 10.45 g (0.05 mol) of **4** in 10 ml of DMF was added and stirring was prolonged for 16 h. The reaction mixture was poured into 1 l of water and extracted twice with ether. The mixture which remained after washing, drying and evaporation of the organic solvent was chromatographed on silica gel, using toluene/5% ethyl acetate as eluent.
This gave 4.3 g (17%) of **3** as a viscous oil. NMR (90 MHz) δ 1.01 (s, 3, 18-CH_3), 3.78 (s, 3, OCH_3), 3.96 (s, 4, O–CH_2–CH_2–O), 4.65 (m, 1, CH (THP)), 6.60–6.80 (m, 2, H-2 and H-4), 7.20 (m, 1, H-1). (No distinct signals of the diastereoisomers were observed.)

(11β)-11-[(2-Hydroxyethoxy)methyl]-3-methoxyestra-1,3,5(10)-trien-17-one (**5**)
To a solution of 23.3 g (0.05 mol) of **3** in 200 ml of THF was added 200 ml of 3N HCl. The mixture was stirred at room temperature while monitoring the hydrolysis by TLC. After 5 h the reaction mixture was diluted with 1.2 l of 10% $NaHCO_3$ solution and extracted with ether. Upon washing, drying and concentrating, the resulting crude product was chromatographed through a short silicagel column (toluene/10% ethyl acetate as eluent). This gave 15.8 g (89%) of **5** as a white solid; m.p. (tol./hex.) 98–99°. Analysis: $C_{22}H_{28}O_4$; calcd. C, 73.71; H 8.44; found: C, 73.70; H, 8.60. NMR: δ 1.00 (s, 3, 18-CH_3), 3.20–3.50 (m, 4, 11β CH_2–O–CH_2–), 3.65 (t, 2, –CH_2OH), 3.78 (s, 3, OCH_3). IR (CCl_4): 1742 cm^{-1} (CO).

(11β)-3-Methoxy-11-[(2-oxoethoxy)methyl]estra-1,3,5(10)-trien-17-one (**6**)
To a solution of 800 mg (~ 6 mmol) of *N*-chlorosuccinimide in 30 ml of dry toluene was added dropwise with stirring at 0° 500 mg (8 mmol, ~ 0.6 ml) of dimethyl sulfide. After stirring for an additional 15 min the mixture was cooled to −25° and a solution of 1.43 g (4 mmol) of **5** in 5 ml of toluene was added and stirring was continued for $2\frac{1}{2}$ h at −25°. Then 1 ml of triethylamine was added and the mixture was stirred for an additional 20 min while allowing the temperature to rise gradually to room temperature. After addition of 40 ml of ether the reaction mixture was washed subsequently with 10 ml 1% HCl solution, and twice with water. The oil which resulted after washing, drying and evaporation was chromatographed on silicagel using toluene/ethyl acetate (8/2) as eluent. This gave 0.65 g (46%) of **6** as an oil. This product proved to be unstable and decomposed on standing at room temperature for several days. NMR: δ 1.01 (s, 3, 18-CH_3), 3.42 (d, 2, 11β-CH_2), 3.77 (s, 3, OCH_3), 3.89 (d, 2, CH_2CHO), 9.62 (t, 1, CHO). IR (CCl_4): 1741 cm^{-1} (CO).

(11β)-11-[(Carboxymethoxy)methyl]-3-methoxyestra-1,3,5(10)-trien-17-one (**7**)
Fresh silver oxide was prepared by adding dropwise with stirring 5 ml of 2N NaOH (0.01 mol) to a solution of 1.01 g (6 mmol) of silver nitrate in 10 ml of water. The resulting suspension was stirred for an additional 10 min and then a solution of 710 mg (2 mmol) of **6** in 3 ml of THF was added dropwise. After 1 h the reaction mixture was filtered through Celite, diluted with water and acidified with 2N HCl. The carboxylic acid which precipitated, was taken up in ether. Upon washing, drying and concentrating 600 mg (92%) of **7** was obtained as a solid; m.p. (i-Pr_2O) 190–192°. NMR: δ 1.02 (s, 3, 18-CH_3), 3.45 (d, 2, 11β-CH_2), 3.75 (s, 3, OCH_3), 3.96 (s, 2, OCH_2COOH), 8.30 (s, 1, COOH). IR (CH_2Cl_2): 1736 cm^{-1} (COO).

(11β)-3-Methoxy-11[[(methoxycarbonyl)methoxy]methyl]estra-1,3,5(10)-trien-17-one (**8**)
A solution of 7.60 g (0.02 mol) of **7** in 100 ml of methanol, containing 0.5 ml of conc. sulphuric acid, was refluxed for 1 h. Then the reaction mixture was concentrated to ~ 20 ml and then poured into 150 ml of water. The product was extracted twice with ether. The combined organic phases were washed once with 10% aq. $NaHCO_3$ solution and once with water. Upon drying and evaporation 7.30 g (85%) of **8** was obtained as a solid; m.p. (tol/hex) 122–124°; Analysis: $C_{23}H_{30}O_5$; calcd. C, 71.48; H, 7.82; found C, 71.11; H, 7.89. NMR: δ 1.02 (s, 3, 18-CH_3), 3.40 (d, 2, 11β-CH_2), 3:67 (s, 3, $COOCH_3$) 3.77 (s, 3, OCH_3), 3.95 (s, 2, OCH_2COOCH_3). IR (CCl_4): 1743 cm^{-1}, 1760 cm^{-1} (CO).

(11β)-3-Methoxy-11-[[(methoxycarbonyl)methoxy]methyl]estra-1,3,5(10)-trien-17-one cyclic ethylene acetal (**9**)
A mixture consisting of 7.7 g (0.02 mol) of **8**, 50 ml of ethylene glycol, 50 ml of methylene chloride, 15 ml of trimethyl orthoformate and 50 mg of *p*-toluenesulfonic acid was refluxed for 2 h while monitoring the reaction by TLC. Then the mixture was poured onto 100 ml of water. The product was extracted with methylene chloride. Upon washing, drying and evaporation the resulting oil was chromatographed over a short silicagel column (toluene/ethyl acetate 95/5 as eluent). This afforded 8.5 g (98%) of **9** as a solid; m.p. (ether/hexane) 112–114°. NMR: δ 1.02 (s, 3, 18-CH_3), 3.45 (m, 2, 11β-CH_2), 3.70 (s, 3, OCH_3), 3.78 (s, 3, OCH_3), 3.90 (s, 4, OCH_2CH_2O), 3.95 (s, 2, OCH_2COOCH_3). Analysis: $C_{25}H_{34}O_6$; calcd., C, 69,74; H, 7.96; found, C, 70.01; H, 7.88.

(11β)-3-Methoxy-11-[[1-(methoxycarbonyl)ethoxy]methyl]estra-1,3,5(10)-trien-17-one cyclic ethylene acetal (**10**)
To a cooled solution of 5 mmol of lithium diisopropylamide in dry THF (prepared from 0.75 ml of diisopropylamine and 3.3 ml of 15% butyllithium in 10 ml of THF) was added dropwise in ~ 5 min with stirring at −70° a solution of 2.14 g (5 mmol) of **9** in 5 ml of THF. After stirring for an additional 5 min at −70° a solution of 800 mg (ca. 5.5 mmol) of methyl iodide in 1 ml of HMPA was introduced by syringe. Stirring was prolonged for an additional 15 min at −70° and then external cooling was removed and the mixture was allowed to come to room temperature. After 1 h the reaction mixture was poured into 50 ml of water and the product was extracted with ether. After washing, drying and evaporation of the organic solvents the crude material was chromatographed over a short silicagel column (using toluene/5% eth. ac. as eluent). This gave 1.44 g (65%) of **10** as a viscous oil and as a mixture of diastereoisomers.
NMR: δ 1.01 (s, 3, 18-CH_3), 1.29 and 1.38 (d, 3, –$CH(CH_3)$-$COOCH_3$), 3.68 (s, 3, CH_3), 3.80 (s, 3, CH_3), 3.95 (s, 4, OCH_2CH_2O).

(11β)-3-Methoxy-11-(isopropoxymethyl)estra-1,3,5(10)-trien-17-one cyclic ethylene acetal (**13**)
A solution of 4.42 g (0.01 mol) in 10 ml of THF was added dropwise with stirring to a suspension of 380 mg (0.01 mol) of $LiAlH_4$ in

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10 ml of THF. The reaction mixture was stirred for an additional hour and then worked up by adding subsequently 0.38 ml of water, 0.38 ml of 15% NaOH and 1.20 ml of water. The resulting mixture was filtered through Celite and evaporated to give 4.05 g of essentially pure **11** as an oil; R_f (tol/25% EtOAc) 0.20 and 0.22 two diastereoisomers. NMR: δ 1.0 (s and 2d, 6, 18-CH_3 and CH_3CHCH_2OH), 3.78 (s, 3, OCH_3), 3.95 (s, 4, OCH_2CH_2O).

The crude **11** was taken up in 30 ml of pyridine and 3.7 g (0.02 mol) of *p*-toluenesulphonyl chloride were added. The mixture was stirred overnight and then poured into 200 ml of water. The product was extracted twice with ether. The pyridine was removed from the organic phase by washing twice with 100 ml of 2N HCl, followed by washing once with 10% aq. $NaHCO_3$ and once with water. Upon drying and evaporation 5.4 g of tosylate were obtained as a colourless oil and more than 95% pure according to NMR; R_f (tol./25% EtOAc) 0.75. NMR: δ 0.97 (s, 3, 18-CH_3), 1.05 (dd, 3, $-OCH(CH_3)-$), 2.43 (s, 3, CH_3 tosylate), 3.80 (s, 3, OCH_3), 3.93 (s, 4, $-OCH_2CH_2O-$).

This crude tosylate was dissolved 20 ml of THF and then 1 g of $LiAlH_4$ was added. The mixture was stirred at room temperature while monitoring the reaction by TLC. After 5 h the conversion proved to be complete and work-up was performed by subsequent addition of 1 ml of water, 1 ml of 15% NaOH and 3 ml of water. After filtration through Celite the organic solution was concentrated. The oil which remained was chromatographed through a short silicagel column (tol./5% EtOAc as eluent) and afforded 3.35 g (84%) of **13** as an oil. NMR: δ 1.02 (s, 3, 18-CH_3), 1.05 (dd, 3, isopr. CH_3), 0.78 (s, 3, OCH_3), 3.92 (s, 4, OCH_2CH_2O), 6.70 (m, 2, H-2 and H-4), 7.20 (d, 1, H-1). R_f (tol./25% EtOAc) 0.85.

(11β)-11-(Isopropoxymethyl)estr-4-ene-3,17-dione (**14**)

A solution of 4.0 g (0.01 mol) of **13** in 20 ml THF was added dropwise in 10 min to a solution of 1.5 g of lithium in 150 ml of liquid NH_3 at −60°. The reaction mixture was stirred for an additional 4 h at −33° and then excess lithium was destroyed by careful addition of 70 ml of ethanol. After evaporation of the ammonia 100 ml of water was added to the mixture and the product was extracted with ether. The oil which left after work-up was taken up in 30 ml of THF. Then 25 ml of 4N HCl was added and stirring was prolonged for 3 h. At this time the enol ether and the acetal had been hydrolysed. The mixture was diluted with 100 ml of water and the product was extracted with ether. The crude **14** which was obtained after washing, drying and evaporation of the organic phase, was chromatographed through a short silicagel column (tol./10% EtOAc as eluent) and yielded 2.6 g (76%) of pure **14** as a solid; m.p. [toluene/hexane] 105–107°. NMR: δ 0.90 (s, 3, 18-CH_3), 1.17 (d, 6, isopropyl CH_3), 5.86 (s, 1, H-4). Analysis: $C_{22}H_{32}O_3$; calcd. C, 76.70; H, 9.36; found: C, 76.39; H, 9.43. IR (CCl_4): 1679, 1742 cm^{-1} (CO).

(11β)-11-(Isopropoxymethyl)estr-4-ene-3,17-dione cyclic 3-ethylene dithioacetal (**15**)

To a cooled solution (0°) of 1.72 g (0.005 mol) of **14** in 20 ml of methanol were added successively 1.5 ml of ethanedithiol and 1.5 ml BF_3 etherate. After stirring for 1 h at 0° the product which had precipitated was filtered and washed with cold methanol. This gave 2.0 g (95%) of **15** as a white solid; m.p. (diisopropylether/hexane) 173–174°. NMR: δ 0.90 (s, 3, 19-CH_3), 1.15 (d, 6, isopropyl CH_3), 5.63 (s, 1, H-4). IR (CCl_4): 1747 cm^{-1} (CO). Analysis: $C_{24}H_{36}OS_2$; calcd. C, 71.25; H, 8.97; found: C, 71.18; H, 8.98.

(11β,17α)-17-Hydroxy-11-(isopropoxymethyl)-19-norpregn-4-en-20-yn-3-one cyclic ethylene dithioacetal (**16**)

A stream of acetylene gas was bubbled through a solution of 1.2 g (ca. 0.01 mol) of potassium *tert*-butoxide in 25 ml of THF at −10°, during a period of 1 h. Then a solution of 2.10 g (5 mmol) of **15** in 10 ml of dry THF was added dropwise in 15 min followed by bubbling acetylene gas through the solution for another 1 h at −10°. The mixture was worked up by pouring into 150 ml of water, followed by extraction of the product with ethyl acetate. Upon washing, drying and concentrating 2.1 g (94%) of essentially pure **16** was obtained as a foam; R_f (tol/30% acetone) 0.77; for **15**: 0.05. NMR: δ 0.90 (s, 3, 18-CH_3), 1.17 (d, 6, isopropyl CH_3), 2.60 (s, 1, C≡C−H), 5.62 (s, 1, H-4).

(11β,17α)-17-Hydroxy-11-(isopropoxymethyl)-19-norpregn-4-en-20-yn-3-one (**1**)

To a solution of 2.23 g (5 mmol) of **16** in 30 ml of 96% ethanol were added 3 ml of water and 3 ml of methyl iodide. This mixture was refluxed for 10 h. Then the reaction mixture was concentrated, and 50 ml of a 1% aqueous sodium thiosulfate solution was added and the product was extracted with methylene chloride. The crude product was chromatographed over a short silicagel colum (toluene/10% EtOAc as eluent) and provided 1.55 g (84%) of pure **1**; m.p. (diisopropyl ether) 135–137°. Analysis: $C_{24}H_{34}O_3$; calcd. C, 77.80; H, 9.25; found C, 77.90; H, 9.52. NMR: δ 0.88 (s, 3, 18-CH_3), 1.14 (d, 6, isopropyl CH_3), 2.60 (s, 1, C≡CH), 3.40–3.70 (t, 2, 11β-CH_2 and m, 1, $CH(CH_3)_3$), 5.86 (s, 1, H-4). IR (CCl_4): 1672 cm^{-1} (CO). $[\alpha]_D^{20}$ (CH_2Cl_2) +31° (*c* 1.00).

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Nickel(II) complexes of deprotonated thiourea; Crystal structure of $Ni[(C_6H_5)NC(S)N\{(C_2H_4)_2O\}]_2$

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Abstract. Nickel(II) complexes with deprotonated trisubstituted thiourea were prepared. The crystal structure of $Ni[PhNC(S)N\{(C_2H_4)_2O\}]_2$ showed that the nickel atom is centrosymmetrically square planar coordinated through the N and S of the thioureido ligands. The diamagnetic compound crystallizes in the monoclinic space group *C2/c* [a = 24.146(3), b = 10.480(2), c = 9.473(3) Å, β = 106.38(1)°] and contains four formula units per unit cell.

Introduction

A large number of complexes of thiourea have been reported[1]. Only a few complexes in which a thioamide nitrogen of thiourea is deprotonated are known. Most of these are prepared by insertion of an organic isothiocyanate in a

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