Tetrahedron Vol. 42, No. 15, pp. 4259 to 4265, 1986
Printed in Great Britain.

0040-4020/86 $3.00+.00
Pergamon Journals Ltd.

OXIDATION OF AROMATIC SUBSTRATES PART VII[1]. THE SELECTIVE OXIDATION OF PHENOLIC ALKENES WITH RUTHENIUM TETROXIDE

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(*Received in UK* 13 *May* 1986)

ABSTRACT - Whereas free phenols are rapidly oxidised by ruthenium tetroxide with fragmentation, the aromatic nuclei of their O-trifluoroacetates are unaffected by the reagent in dry conditions. This has led to a method for the controlled oxidation of functionalised phenols which is demonstrated here by the selective cleavage of hydroxyarylalkenes, coumarins and aromatic steroidal alkenes.

INTRODUCTION

The applications of this powerful reagent are limited by its lack of specificity and aromatic nuclei with electron-donating substituents are rapidly and completely degraded by it. Methods for the selective oxidation of complex phenols are desirable both as an aid to the determination of new structures and also to the modification of known compounds which are pharmacologically active. The recent literature shows[2] that there is considerable activity in both these areas of research.

In the one recorded instance[3] of protection of a phenol from the action of the tetroxide by acetylation the A ring of estradiol diacetate (9; X=Ac; 17α-H, 17β-OAc for keto) survived in the minor product, to give 9α-hydroxy-6-oxoestradiol diacetate. The major product was still the dicarboxylic acid (11; H, AcO for keto) obtained by cleavage of ring A and we therefore felt that our purpose would be better served if trifluoroacetates were used. A considerable increase in the oxidation potential of O-trifluoroacetates is expected in view of the positive Hammett constants observed[4] in the trifluoroacetylaminobenzoic acids. This is illustrated by the successful trapping of monohydric phenols as their trifluoroacetates when aromatic hydrocarbons and ketones are subjected[5] to electrolytic hydroxylation. The action of the tetroxide resembles electrosynthesis in that both proceed through an intermediate radical cation.

A number of simple trial oxidations show that in the readily prepared trifluoroacetates the aromatic nucleus was effectively protected. Thus when phenol reacted with a deficit of the tetroxide at 20°C all the oxidant was consumed within one minute, whilst under comparable conditions some oxidant survived after five hours contact with phenyl trifluoroacetate. In a related experiment 4-biphenyl trifluoroacetate (1, X=CF_3.CO, Scheme A) was treated with ruthenium tetroxide (8 oxygen equivalents) when 35% of the starting material was recovered together with 55% of acidic products. After removal of the protecting group comparative IR

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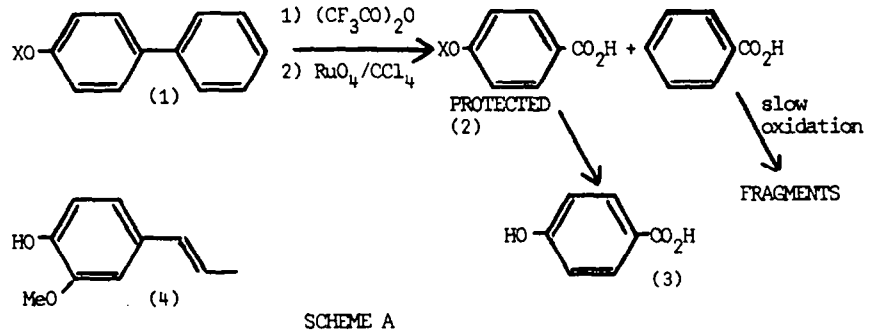
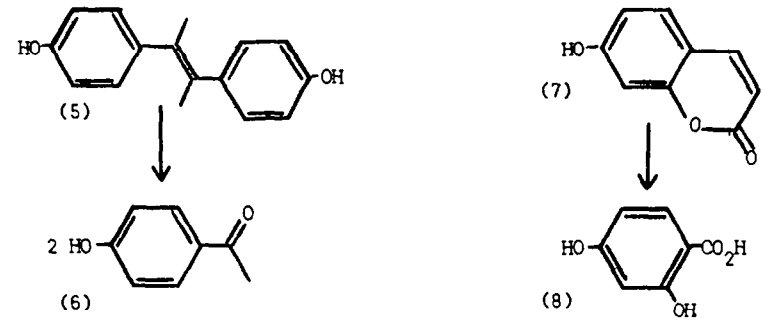
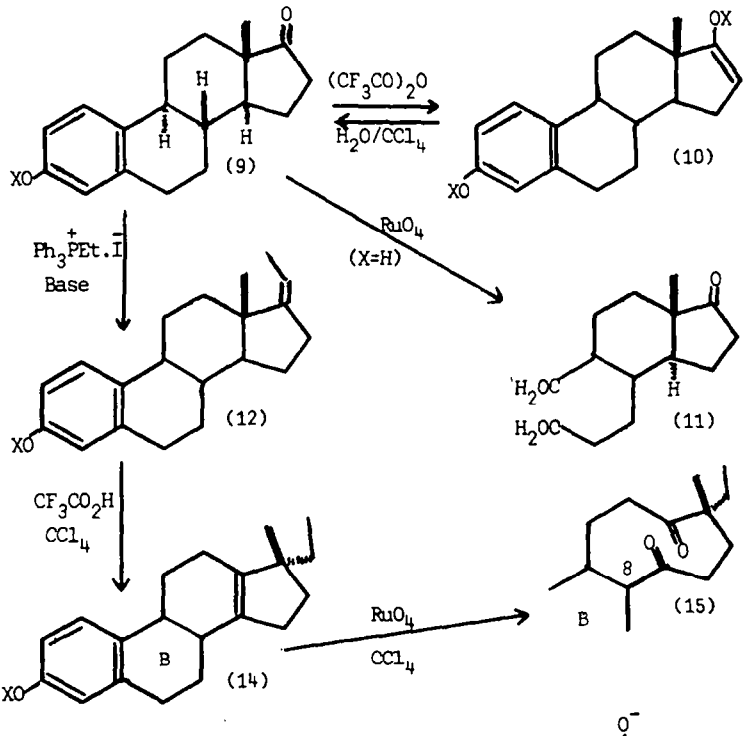


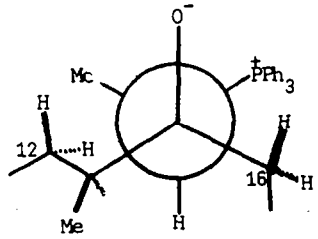
SCHEME A





SCHEME B

AROMATIC STEROIDS



spectroscopy and paper chromatography[6,7] showed that the mixture contained only 4-hydroxybenzoic and benzoic acids in a molar ratio of 9:1. Acetylation also diverted the oxidation towards survival of the phenolic ring in 4-acetoxybiphenyl, but this was less marked since the ratio of 4-hydroxybenzoic:benzoic acid in the product was reduced to 3:1. Evidently the trifluoroacetyl group affords considerably more protection than does acetyl, both in directing attack to the oxygen-free ring and also in ensuring the survival of its cleavage product (2, X=CF_3CO, Scheme A) and indirectly the phenolic product (3).

RESULTS

Phenolic alkenes were studied initially because the tetroxide is a superior reagent to others in common use for the oxidation of monofunctional alkenes. Although alkenes are attacked by cations derived from the heterolysis of unsymmetrical acyl trifluoroacetates[8], this cleavage is precluded in the symmetrical trifluoroacetic anhydride. This reagent can therefore be used in excess for the selective O-trifluoroacetylation of phenolic alkene models, which may then be oxidised in carbon tetrachloride solution without further manipulation. If the alkene is especially sensitive to acid-catalysis then the liberated trifluoroacetic acid may be neutralised by the addition of pyridine[9]. Isoeugenol (4) was taken as typical of the naturally occurring propenylphenols and it was converted into the O-trifluoroacetate in almost quantitative yield. In the ^{1}H-NMR spectrum of this derivative the three aromatic protons were deshielded by about 0.2 ppm compared with those in the spectrum of the parent phenol; this provided further evidence of the deactivating power of the trifluoroacetate group and absorption typical of allylic and vinylic protons showed that the alkene function was retained.

Oxidation of isoeugenyl trifluoroacetate by ruthenium tetroxide in carbon tetrachloride solution was complete within five minutes and afforded vanillin (16%) and a further useful yield of vanillic acid (57%) by the alkaline extraction of precipitated ruthenium dioxide.

The stilboestrol analogue, 4,4'-dihydroxystilbene (5), was oxidised without isolation of the bis-trifluoroacetate, to afford 4-hydroxyacetophenone (6) in an overall yield of 62%. The second stage of this trifluoroacetylation is more difficult than the first, as the remaining conjugated hydroxyl group is a weak nucleophile; more forcing conditions are therefore needed to ensure its complete protection. In a similar one-pot synthesis umbelliferone (7) was converted into 2,4-dihydroxybenzoic acid (8) in 81% yield.

Derivatives of estrone were used to demonstrate the selective oxidation of remotely placed alkene groups. In the protection of estrone both the phenol and the enol form were trifluoroacetylated to give a mixture of (9, X=CF_3CO, Scheme B) and the bis-derivative (10, X=CF_3CO), which was characterised in the IR spectrum by absorption at 1740 cm^{-1} (ketone C=O), by a broad band at 1790–1800 cm^{-1} arising[10] from the trifluoroacetate groups and by peaks at 1690 cm^{-1} (enol C=C) and 700 cm^{-1} (vinyl CH). We have found no record of the formation of enol trifluoroacetates from ketones in trifluoroacetic anhydride, although androst-4-ene-3,17-dione affords the mono-enolate at C3 on treatment with heptafluorobutyric anhydride[11]. 17-Oxosteroids are known[12] to react with silylating agents to form trimethylsilyl ethers. When a solution of the mixed estrone derivatives in carbon tetrachloride was shaken with cold

water, the enol trifluoroacetate was preferentially and completely hydrolysed: the peaks at 700 cm^{-1} due to the vinyl group were discharged, the ketone carbonyl absorption was enhanced and the ester carbonyl resolved as a sharp singlet at 1800 cm^{-1}. Estrone trifluoroacetate was obtained from the organic layer in 78% yield and was recovered unchanged after treatment with ruthenium tetroxide, in favourable contrast to the behaviour[3] of estradiol diacetate mentioned above. This result showed that the estrone nucleus was a suitable vehicle for the synthesis of model phenolic alkenes.

The pregnenol [(Z)-norpregna-1,3,5(10),17(20)-tetraen-3-ol (12, X=H)], was obtained (75% yield) by the Wittig procedure using a modification of the method of Krubiner and Oliveto[13]. This geometry in the product is consistent with reaction under kinetic control, in which the solvated 'ylide attacks the α-face, to give an intermediate betaine (13) where the bulky phosphonium group has the minimal interaction with the steroid skeleton[14]. The norpregna-tetraen-3-ol (12, X=H) was converted into its O-trifluoroacetate (12, X=CF_3CO, mp 70°) in almost quantitative yield in the presence of pyridine and its solution in carbon tetrachloride was immediately treated with ruthenium tetroxide. The reaction was complete within five minutes but time was allowed for the adsorption of acid fragments by coagulated ruthenium dioxide. This process was then essentially complete since the IR spectrum of the supernatant solution was identical with that of estrone trifluoroacetate, which was isolated and converted into estrone (mp 256°) in 59% yield with respect to the unprotected phenol (12, X=H).

The tetrasubstituted alkene (14, X=H) provided an exacting test of the selective oxidation procedure. A sample was obtained by trifluoroacetylation of the (Z)-pregnenol (12, X=H) in the absence of pyridine, when exposure to trifluoroacetic acid induces a cis-1,2-shift of the 18-methyl group to give the protected phenol (14, X=CF_3CO). In (12) the rearrangement reduces steric interactions of both methyl groups and is of a type common in steroid reactions which proceed through an incipient C-17 carbocation[15].

The structural differences between the trifluoroacetates of the norpregnenol (12) and its rearrangement product (14) were defined by differences in their ^{1}H-NMR spectra. In the precursor (12) the vinyl proton appeared as a quartet (J=7 Hz) centred at δ 5.15, with the allylic 21-methyl group resonance a doublet (J=7 Hz) at δ 1.69 and that of the 18-methyl group a singlet at δ 0.91. In the product (14) the vinylic ^{1}H-resonance was lost, the 21-methyl signal occurred upfield at δ 0.79 and the migrated methyl group, now deshielded relative to its original position, resonated as a singlet at δ 1.00. Homonuclear decoupling at δ 0.79 showed that the 21-methyl group was coupled to a methylene quartet (J=7 Hz, 20-Hz) centred at δ 1.35 and that it was evidently not allylic.

The trifluoroacetate of the highly hindered alkene (14, X=CF_3CO) was oxidised within five minutes by ruthenium tetroxide and afforded the seco-diketone (15, X=CF_3CO) in 67% yield. The absence of any vinylic resonance in the NMR spectrum of (14) or of any aldehydic resonance in the spectrum of its oxidation product (15) confirmed that the former was a tetrasubstituted alkene. These characteristics and IR absorption typical of strain-free aliphatic carbonyl groups in the diketone (15) exclude ring B as a site for the cleaved double bond and bar

a location exocyclic to ring B or ring D. The NMR spectrum of (15) included three aromatic protons deshielded by the trifluoroacetoxy function: of six or seven protons in the range of δ 2.31-2.87 three must be benzylic, hence the others (3H or 4H) can only result from deshielding by two carbonyl groups. The remaining carbonyl-deshielded resonance (1H, δ 3.15-3.48) was at the lowest field of this group consistent with the location of this proton at the bridgehead (C8). The breadth of the signal (33 Hz) correlates with two periplanar ($J_{H8,H9}$, $J_{H8,H7}$) and one smaller coupling ($J_{H8,H7}$).

CONCLUSION

The characterisation of the seco-diketone (15), and of estrone (9, X=H) from the action of ruthenium tetroxide on the trifluoroacetylated steroidal alkenes shows that skeletal oxygenation is restricted to the point of cleavage. The course of these reactions and those of the other protected hydroxyarylalkenes indicates that the procedure could be extended to the selective oxidation of other functional groups in complex phenols.

EXPERIMENTAL

Uncorrected melting points were determined with a hot-stage microscope and are reported in degrees centigrade. Infrared spectra were recorded with a Pye Unicam SP3-200 instrument and UV spectra were taken with a Unicam SP 800. ^{1}H-NMR spectra were obtained by Dr. R.D. Farrant using a Jeol FX-100 spectrometer and the mass spectra were taken by the Physico-Chemical Measurements Unit, Harwell and by the ULIRS at Queen Elizabeth College, London. HPLC was carried out using Spectra-Physics SP 8700 equipment.

Preparation of O-Trifluoroacetates; General Procedure: Each phenol (ca 20 mmol) or phenolic steroid (2 mmol) was dissolved in carbon tetrachloride or chloroform with trifluoroacetic anhydride (ca fivefold excess) and the solution was left to stand overnight at ambient temperature to ensure completion. The O-trifluoroacetates were purified by distillation or by recrystallisation. When this derivative was extremely susceptible to hydrolysis the best overall yields were obtained with solvent-free crude material charcterised by IR[10] and ^{1}H-NMR spectroscopy, followed by the full characterisation of the oxidation product.

Phenyl Trifluoroacetate[16], 4-Biphenyltrifluoroacetate[17] (1, X=CF_3CO), 4-Biphenylacetate[18] and Isoeugenyl Trifluoroacetate[19] were obtained in good yield as described previously.

Oxidation with Ruthenium Tetroxide: This followed previously published procedures[4], and therefore only in the first following experiment is the oxidation described in detail.

4-Biphenyl Trifluoroacetate (200 mg, 0.75 mmol) in carbon tetrachloride (30 ml) was treated with a solution of ruthenium tetroxide (3 mmol) in carbon tetrachloride (10 ml), prepared from hydrated ruthenium dioxide (630 mg, 3 mmol) and aqueous sodium periodate (0.45M, 30 ml). The oxidation proceeded steadily until after 1 h no tetroxide remained. After coagulation of the ruthenium dioxide starting material (70 mg, 35%) was recovered from solution, whilst acidic products were obtained by extraction of the dioxide with hot aqueous sodium hydroxide (0.2M, 30 ml). The extract was acidified (pH=2) with hydrochloric acid (1M), centrifuged to remove a further quantity of ruthenium dioxide and extracted with ether (3 x 20 ml). Evaporation of the dry ($MgSO_4$) organic layer afforded a mixture of acids (37 mg, 55% allowing recovery) whose IR spectrum compared closely with that of a mixture of 4-hydroxybenzoic and benzoic acids in a molar ratio of 9:1.

4-Acetoxybiphenyl (210 mg, 1 mmol) on treatment with ruthenium tetroxide (5 mmol) led to recovery of starting material (27 mg, 12%) and the isolation of 4-hydroxybenzoic acid containing 28 ± 5% of benzoic acid, as shown by comparative IR spectroscopy. Quantitative paper chromatography[20] of the product and of six mixtures containing a range of compositions of the two pure components indicated that benzoic acid formed 19 ± 7% of the mixture. In this work ultraviolet detection was used in conjunction with a spray[17] containing bromocresol purple indicator.

Isoeugenyl Trifluoroacetate (520 mg, 2 mmol) consumed the tetroxide (4 mmol) within 1 min to leave a residue in solution, which was treated with aqueous-methanolic sodium carbonate (1M in 8 ml of mixed solvent) to remove the protecting group. Acidification gave crude material (59 mg) which was extracted with petroleum ether (bp 60-80°) to give vanillin mp 77° (48 mg, 16%), identical (mp, IR spectrum) with reference material.

Precipitated ruthenium dioxide was extracted with alkali as above to give vanillic acid (192 mg, 57%), mp 211° (lit.[21] 210°).

4,4-Dihydroxy-α,β-dimethylstilbene† (178 mg, 0.75 mmol) was trifluoroacetylated in boiling trifluoroacetic anhydride for 2 h; the crude product in carbon tetrachloride (4 ml) was treated with ruthenium tetroxide (from the hydrated dioxide, 142 mg, 0.93 mmol) in carbon tetrachloride (4 ml). A dense precipitate of ruthenium dioxide was rapidly formed and any excess of tetroxide was quenched after 20 mins by the addition of benzene (1 ml). The filtrate afforded a pale yellow crystalline residue (219 mg) of the trifluoroacetylated product, which on solvolysis in methanol gave 4-hydroxyacetophenone (125 mg, 62%). This was shown to be free from significant impurities by HPLC on a Nucleosil column (5 μm spherical silica, 25 cm x 5 mm i.d.) by elution with petroleum ether-ethyl acetate (60:40). On recrystallisation from benzene/cyclohexane (1:1) the product had an IR spectrum and melting point (107-109°) identical with those of a reference sample.

7-Hydroxycoumarin† (320 mg, 2 mmol) was refluxed with trifluoroacetic anhydride (4.2 ml, 30 mmol) and the crude product in carbon tetrachloride (40 ml) was treated with ruthenium tetroxide (from $RuCl_3.3H_2O$, 4 mmol), when ruthenium dioxide was immediately precipitated. Filtration and evaporation of solvent afforded a small quantity (4 mg) of product. The major quantity of 2,4-dihydroxybenzoic acid (272 mg) was determined by HPLC (Hypersil 5 ODS, eluent 30:70, MeOH:H_2O) against a reference standard, after extraction of the precipitated dioxide with hot sodium hydroxide (2 g in 10 ml of water).

Trifluoroacetylation of Estrone: Under the usual conditions this compound (0.54 g, 2 mmol) gave a crystallised (petroleum ether, bp 40-60°) product which was evidently a mixture (665 mg) melting largely between 95-7° and 103-8° and with IR absorption characteristic of a mixture of the required compound (9) and of the enol trifluoroacetate (10, see above). Estrone trifluoroacetate was obtained (78%, allowing recovery) by briefly shaking a carbon tetrachloride solution of the mixture with water, followed by the immediate separation, drying ($MgSO_4$) and evaporation of the organic layer. This material was quite satisfactory for the subsequent oxidation; its IR spectrum was typical[10] but lacked absorption due to the enol derivative. The ^{1}H-NMR spectrum ($CDCl_3$) showed peaks at δ 7.32 (d, J=8 Hz, 1-ArH), 6.95 (d, H=8 Hz, 2-ArH), 6.91 (s, 4-ArH), 1.1-3.0 (steroid skeleton), 0.92 (s, 18-CH_3). On a small scale estrone trifluoroacetate was recrystallised (petroleum ether, bp 40-60°) to give material of mp 130-133° with an IR spectrum identical with that obtained previously.

(Z)-Norpregna-1,3,5(10),17(20)-tetraen-3-ol (12, X=H): This was prepared from estrone (2.03 g, 7.5 mmol) and ethyltriphenylphosphonium iodide (14.6 g, 35 mmol) by the method of Krubniner and Oliveto[13]. Crude product (4.2 g) could not be crystallised following the published chromatography procedures. The gum was therefore taken up on silica gel (Crosfield M60, 5 g) from solution in dichloromethane; elution (petroleum ether/ethyl acetate 3:1) of this charged material through a column of silica gel gave a solid (2.36 g, mp 125-130°, 85% yield) on trituration with petroleum ether (bp 60-80°). Final recrystallisation (ethanol-water) afforded pure tetraen-3-ol (12) (1.58 g, 75%), mp 132-5° (lit.[13] 137-9°), further characterised by the IR spectrum and by the ^{1}H-NMR absorption (δ, $CDCl_3$) at 7.13 (d, J=8 Hz, 1-H), 6.58 (d, J=8 Hz, 2-H). 6.54 (s, 4-H), 4.52 (s, 3-OH), 3.0-1.0 (steroid skeleton) and as above.

Trifluoroacetylation: The tetraen-3-ol (12, 560 mg, 2 mmol) was converted into the trifluoroester, mp 64-70°, in 96% yield by the procedure used for isoeugenol. The IR spectrum (CCl_4) showed ν_{max} (cm^{-1}) 2940 and 2870 (C-H); 1797 (C=O); 1605, 1585 and 1490 (aromatic C-C); 1380 (methyl); 1360 (ester C-O); 1230 (C-F sym stretch); 1180 and 1155 (C-F asym stretch); 1130 (Ph-O). ^{1}H-NMR absorption was at δ 7.32 (d, J=8 Hz, 1-H), 6.93 (d, J=8 Hz, 2-H), 6.89 (s, 4-H), 5.15 (q, J=7 Hz, 20-H), 3.0-1.0 (steroid skeleton), 1.69 (d, J-7 Hz, 21-H_3), 0.91 (s, 18-H_3). These characteristics showed that reaction was essentially complete and the next step was begun immediately.

Oxidation: Crude trifluoroacetylated material (12, X=CF_3CO) in carbon tetrachloride (20 ml) reacted completely with ruthenium tetroxide (3 mmol in 30 ml of CCl_4) within 5 min. The IR spectrum of the filtrate closely resembled that previously recorded for estrone trifluoroacetate; the solvent and washings of the precipitated dioxide were therefore evaporated and the solid residue solvolysed in methanol (10 ml). The product in chloroform was finally washed with water to remove traces of ruthenium-containing impurities and gave estrone (320 mg, 59% with respect to the unprotected phenol, (12) X=H), mp 256° (lit.[22] mp 256°) with typical IR absorption.

17β-Methyl-18,19-dinor-17β(H)-pregna-1,3,5(10),13-tetraen-3-yl trifluoroacetate (14, X=CF_3CO): The tetraen-3-ol (12, 564 mg, 2 mmol) was dissolved in carbon tetrachloride (10 ml) containing trifluoroacetic anhydride (1.5 ml, 11 mmol) and left overnight at ambient temperature. Solvent and trifluoroacetic acid were removed by passage of nitrogen, brief evacuation with a water pump and re-evaporation of carbon tetrachloride (3 ml, dried by ignited $MgSO_4$). This crude trifluoroacetate (706 mg, 93%) had mp 4-8°, its IR spectrum differed only in minor details from that of the isomer (12, X=CF_3CO); the NMR spectrum was also similar save for significant details discussed above. This substance was finally characterised by its solvolysis to give the parent alcohol (14, X=H).

Solvolysis: The trifluoroacetate (14, X=CF_3CO, 270 mg, 0.7 mmol) was heated under reflux with methanol (5 ml) for 30 min. Evaporation of solvent and methyl trifluoroacetate (bp 43°) afforded crystalline 17α-methyl-18,19-dinor-17β-pregna-1,3,5(10),13-tetraen-3-ol (14, X=H), mp

†Kindly donated by Professor D.N. Kirk from the collection of Mr. W. Lawson, Middlesex Hospital Medical School.

138° (cyclohexane). The NMR spectrum was similar to that of the trifluoroacetate but the aromatic resonances were at higher field and an additional signal appeared at δ 4.5 (3-OH). The mass spectrum showed the required molecular ion [m/e 282, $C_{20}H_{26}O$] with a fragment ion at m/e 253 ($M^+-C_2H_5$).

Oxidation: The crude trifluoroacetate (14, X=CF_3CO, from the precursor X=H, 188 mg, 0.66 mmol) in carbon tetrachloride (1 ml) reacted almost immediately with ruthenium tetroxide (from 118 mg of RuO_2, 0.76 mmol). An excess of oxidant was destroyed by the addition of ether (1 ml) and the filtrate shaken briefly with saturated sodium bicarbonate solution. Evaporation of the dry ($MgSO_4$) layer gave crude crystalline product (177 mg, 67% from (14), X=H) contaminated by colloidal ruthenium compounds. The inorganic impurities were removed from an aged (3 days) solution in cyclohexane by centrifugation, followed by crystallisation of the organic product from the supernatant liquor. The pure trifluoroacetate of 3-hydroxy-17β-methyl-18,19-dinor-13,14-seco-17β-pregna-1,3,5(10)-triene-13,14-dione (15, X=CF_3CO) had mp 110-113°, IR absorption (CCl_4) showed ν_{max} (cm^{-1}) 1785 (ester C=O); 1695 (both ketone C=O) and other peaks typical [10] of a trifluoroacetate. ^{1}H-NMR absorption ($CDCl_3$) was as given above together with δ 1.10 (s, 17-H_3), 0.78 (t, J=7 Hz, 21-H_3). Mass spectrometry gave a molecular ion of 410.1703 ($C_{22}H_{25}O_4F_3$ requires 410.17050).

Acknowledgement: We acknowledge the tenure of an SERC research studentship (to D.P.L.).

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