phenylpyrimidine (4d): 86%; (Me_2SO-d_6) δ 2.87 (m, 2, CH_2 pyrimidine), 3.30–4.57 (m, 6, C_1H, C_2H, C_3H, C_4H, CH_2OH), 5.85 (br s, OH), 6.29 (s, 1, C=CH), 7.58 (m, 3, *m*- and *p*-ArH), 8.17 (m, 2, *o*-ArH); ^{13}C NMR (Me_2SO-d_6) δ 37.77 (CH_2 pyrimidine), 61.66 (CH_2OH), 71.80, 72.05, 78.50, 81.95 (C_1, C_2, C_3, C_4 of carbohydrate), 110.40 (pyrimidine C_5), 127.68, 128.51, 131.32, 133.17 (aromatic), 157.30 (pyrimidine C_6), 164.29, 165.36 (pyrimidine C_2, C_4). Anal. Calcd for $C_{16}H_{18}N_2O_5 \cdot CH_3OH$: C, 58.28; H, 6.33; N, 8.00. Found: C, 58.70; H. 6.25; N, 7.93.

6-*C*-(α and β-D-Ribofuranosyl)methyl-4-hydroxypyrimidine (4e): 82%; NMR (D_2O) δ 2.87 (m, 2, CH_2 pyrimidine), 3.30–4.57 (m, 6, C_1H, C_2H, C_3H, C_4H, CH_2OH of carbohydrate), 6.51 (s, 1, pyrimidine C_5H), 8.92 (s, 1, pyrimidine C_2H); ^{13}C NMR (Me_2SO-d_6) δ 61.66 (CH_2OH), 71.73, 72.05, 78.24, 81.95 (C_1, C_2, C_3, C_4 of carbohydrate), 113.22 (pyrimidine C_5), 149.46 (pyrimidine C_2), 161.89, 164.95 (pyrimidine C_4, C_6), CH_2 pyrimidine obscured by Me_2SO peaks. Anal. Calcd for $C_{10}H_{14}N_2O_5 \cdot 0.8CH_3OH$: C, 48.43; H. 6.47; N, 10.46. Found: C, 48.08; H. 6.19; N, 10.62.

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Registry No.—**1**, 56752-57-9; α-**2**, 66358-76-7; β-**2**, 66358-77-8; α-**3a**, 66358-78-9; β-**3a**, 66358-79-0; α-**3b**, 66358-80-3; β-**3b**, 66358-81-4; α-**3c**, 66358-82-5; β-**3c**, 66358-83-6; α-**3d**, 66358-84-7; β-**3d**, 66358-85-8; α-**3e**, 66358-86-9; β-**3e**, 66358-87-0; α-**4a**, 66358-88-1; β-**4a**, 66358-89-2; α-**4b**, 66416-41-9; β-**4b**, 66358-90-5; α-**4c**, 66358-91-6; β-**4c**, 66358-92-7; α-**4d**, 66358-93-8; β-**4d**, 66358-94-9; α-**4e**, 66358-95-0; β-**4e**, 66358-96-1; guanidine hydrochloride, 50-01-1; acetamidine hydrochloride, 124-42-5; thiourea, 62-56-6; benzamidine hydrochloride, 1670-14-0.

References and Notes

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(7) See ref 4 for the first use of the shift positions in the ^{13}C NMR to assign anomeric configuration in *C*-nucleoside precursors.
(8) We have found that in the vast majority of cases $\Delta\delta$ for the β anomer is 1.89 ± 0.1 and for the α anomer 1.24 ± 0.1. Compound **3c** is slightly outisde this limit.
(9) H. Ohrui and S. Emoto, *J. Org. Chem.*, **42**, 1951–1957 (1977).
(10) Preliminary antibacterial screening on several of these compounds at the Lilly Research Laboratories has shown no significant activity.
(11) Spectral data are for the major anomer unless otherwise indicated for specific resonances.
(12) In all cases where analyses include methanol, the methyl protons were observed in the ^1H NMR spectrum.

Substitution Reactions of 17α-Vinyl-17β-trifluoroacetoxy Steroids

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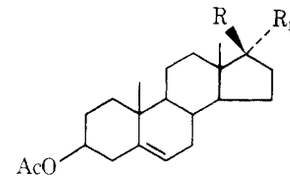
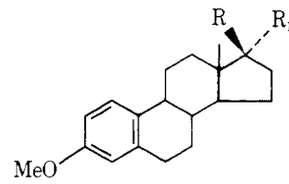
In continuation of our studies[1] on the trifluoroacetoxy group as a useful intermediate in the nucleophilic substitution of those steroid alcohols whose tosylates are difficult to obtain or isolate we became interested in the behavior of the 17α-vinyl-17β-trifluoroacetoxy derivatives 1 and **2**, prepared from the corresponding alcohols **1a**[2] and **2a**[3] with trifluoroacetic anhydride–pyridine at 0 °C.

Methanolysis of 1 in the presence of sodium acetate afforded 17α-methoxypregna-5,20-dien-3β-yl acetate (**1b**), (*E*)-21-methoxypregna-5,17(20)-dien-3β-yl acetate (**1c**), starting alcohol **1a**, and (*E*)-pregna-5,17(20)-dien-3β,21-diol 3-acetate (**1d**).[4]



1, R = $OCOCF_3$; R_1 = CH=CH_2
1a, R = OH; R_1 = CH=CH_2
b, R = CH=CH_2; R_1 = OMe
c, R = R_1 = =$CHCH_2OMe$[a]
d, R = R_1 = =$CHCH_2OH$[a]
e, R = R_1 = =$CHCH_2N_3$[a]
f, R = R_1 = =$CHCH_2OCOCF_3$[a]
g, R = R_1 = =$CHCH_2Cl$[a]
h, R = R_1 = =$CHCH_2OAc$[a]



2, R = $OCOCF_3$; R_1 = CH=CH_2
2a, R = OH; R_1 = CH=CH_2
b, R = R_1 = =$CHCH_2N_3$[a]
c, R = R_1 = =$CHCH_2Cl$[a]

[a] *E* isomers.

The structures **1b**, **1c**, and **1d** were inferred from their analytical and spectral (IR and ^1H-NMR) data.

The methoxy group in **1b** was assigned the 17α configuration on the basis of the upfield position of the 13-Me group compared with that of the 17β derivatives **1**, **1a**, and **2**.[1a]

Evidence for the trans stereochemistry at the 17(20) double bond in **1c** and **1d** was likewise obtained by comparison of their 13-Me shifts with those of compounds of known stereochemistry.[5]

1d was furthermore acetylated to give the known diacetate **1h**.[3]

The product pattern was nearly what one would expect from competing S_N1 and $B_{Ac}2$ mechanisms,[1a] the absence of a 17β-methoxy derivative being expected because of steric reasons.[1a]

The presence in high yield of the rearranged alcohol **1d** required nevertheless further investigation.

Isomerization of the initially formed alcohol **1a** appeared untenable since conversions of this type are acid catalyzed.[3]

1d could have instead resulted, via an acyl–oxygen cleavage, from the corresponding trifluoroacetate **1f**, in turn obtained by partial isomerization of 1 in the reaction medium.

That **1f** is probably the precursor of **1d** was supported by the fact that buffered methanolysis of **1f** in the same conditions as used for 1 afforded very quickly **1d** exclusively.

This fast consumption of **1f** joined to its probable slow formation (also see later) should account for our inability to detect it in the course of the methanolysis of **1**.

Bimolecular substitutions of **1** and **2** by azide ion in hexamethylphosphotriamide (HMPT) to give the 21-azido derivatives **1e** and **2b** proceeded in high yield (>70%).

1e and **2b** were assigned the trans stereochemistry on the same basis as discussed before.

As to the mechanism, these azidolyses cannot be regarded as pure S_N2' processes, since 1 has been found to rearrange partially into **1f** in HMPT and this latter was shown to afford quantitatively **1e** in the presence of NaN_3.

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From a synthetic point of view methanolysis of **1** (and likely similar unimolecular solvolyses) appears to be of limited usefulness. Solvolysis of **1** and **2** in aprotic solvents in the presence of strong nucleophiles should conversely represent a good alternative to the displacement of analogous 21-chloro derivatives **1g**[2] and **2c**[5] for the introduction of substituents at C-21.

Experimental Section[6]

17α-Pregna-5,20-dien-3β,17-diol 3-Acetate 17-Trifluoroacetate (1). A solution of 17α-pregna-5,20-dien-3β,17-diol 3-acetate (**1a**)[2] (0.36 g, 1 mmol) in pyridine (1.7 mL) was treated with trifluoroacetic anhydride (0.7 mL) at 0 °C for 15 min. Then cold 1 N HCl (11.7 mL) was added and the mixture was extracted with ether. The ether layers were washed to neutrality with cold water, dried (Na_2SO_4), and evaporated. The residue (0.45 g) was crystallized from *n*-hexane (0.33 g): mp 118–119 °C; $[\alpha]_D$ −39°; IR (CF_3COO) 1770 cm^{-1}; ^1H NMR δ 0.95 (3 H, s, 13-Me), 1.02 (3 H, s, 10-Me), 2.00 (3 H, s, 3β-OAc), 4.6 (1 H, m, 3α-H), 5.13 (1 H, dd, J_{trans} = 17 Hz, J_{gem} = 1.5 Hz, C-21 H), 5.33 (1 H, dd, J_{cis} = 10.5 Hz, J_{gem} = 1.5 Hz, C-21 H), 5.37 (1 H, m, C-6H), 5.91 (1 H, dd, J_{trans} = 17 Hz, J_{cis} = 10.5 Hz, C-20 H).[7] Anal. Calcd for $C_{25}H_{33}F_3O_4$ (454.5): C, 66.06; H, 7.32; F, 12.54. Found: C, 66.06; H, 7.32; F, 12.52.

Solvolysis of 1 in Methanol in the Presence of Sodium Acetate. A stirred solution of **1** (0.30 g, 0.66 mmol) and sodium acetate (0.11 g, 1.32 mmol) in 8 mL of methanol was heated at 60 °C for 4 h.[8] Methanol was then evaporated and the product was isolated with ether. The ethereal solution was washed twice with water and then dried (Na_2SO_4). The residue (0.25 g) was chromatographed on alumina (1.25 g). Elution with *n*-hexane–benzene (1:1) gave olefins (15 mg, 6%), followed by **17 α-methoxypregna-5,20-dien-3β-yl acetate (1b,** 23 mg, 9%): mp 137–138 °C (from methanol); $[\alpha]_D$ −83°; ^1H NMR δ 0.59 (3 H, s, 13-Me), 1.00 (3 H, s, 10-Me), 2.00 (3 H, s, 3β-OAc), 3.05 (3 H, s, 17α-OMe), 4.6 (1 H, m, 3α-H), 5.10 (1 H, dd, J_{trans} = 17 Hz, J_{gem} = 1.5 Hz, C-21 H), 5.25 (1 H, dd, J_{cis} = 10.5 Hz, J_{gem} = 1.5 Hz, C-21 H), 5.38 (1 H, m, C-6 H), 5.69 (1 H, dd, J_{trans} = 17 Hz, J_{cis} = 10.5 Hz, C-20 H).[7] Anal. Calcd for $C_{24}H_{36}O_3$ (372.5): C, 77.37; H, 9.74. Found: C, 77.31; H, 9.77.

Elution with benzene gave first **(*E*)-21-methoxypregna-5,17(20)-dien-3β-yl acetate** (1c, 53 mg, 21%): mp 87.5–88.5 °C (from methanol); $[\alpha]_D$ −63°; ^1H NMR δ 0.77 (3 H, s, 13-Me), 1.02 (3 H, s, 10-Me), 2.00 (3 H, s, 3β-OAc), 3.30 (3 H, s, 21-OMe), 3.90 (2H, d, *J* = 7 Hz, CH_2OMe), 4.6 (1 H, m, 3α-H), 5.21 (1 H, tt, *J* = 7, 2 Hz, C-20 H), 5.39 (1 H, m, C-6 H).[7] Anal. Calcd for $C_{24}H_{36}O_3$ (372.5): C, 77.37; H, 9.74. Found: C, 77.05; H, 9.75.

A second eluate with benzene gave the alcohol **1a** (22 mg, 9%).

Finally elution with benzene–ether (7:3) gave **(*E*)-pregna-5,17(20)-dien-3β,21-diol 3-acetate (1d,** 122 mg, 49%): mp 177–178 °C (from diisopropyl ether); $[\alpha]_D$ −61°; ^1H NMR δ 0.77 (3 H, s, 13-Me), 1.03 (3 H, s, 10-Me), 2.00 (3 H, s, 3β-OAc), 4.12 (2 H, d, *J* = 7 Hz, CH_2OH), 4.6 (1 H, m, 3α-H), 5.28 (1 H, tt, *J* = 7, 2 Hz, C-20 H), 5.38 (1 H, m, C-6 H).[7] Anal. Calcd for $C_{23}H_{34}O_3$ (358.5): C, 77.05; H, 9.56. Found: C, 76.80; H, 9.55.

(*E*)-Pregna-5,17(20)-dien-3β,21-diol 3-Acetate 21-Trifluoroacetate (1f). This was prepared in the same manner as **1** from 21-alcohol **1d** and crystallized from *n*-hexane: mp 99–101 °C; $[\alpha]_D$ −49°; IR (CF_3COO) 1770 cm^{-1}; ^1H NMR δ 0.78 (3 H, s, 13-Me), 1.02 (3 H, s, 10-Me), 2.00 (3 H, s, 3β-OAc), 4.6 (1 H, m, 3α-H), 4.82 (2 H, d, *J* = 7 Hz, CH_2OCOCF_3), 5.27 (1 H, tt, *J* = 7, 2 Hz, C-20 H), 5.39 (1 H, m, C-6H).[7] Anal. Calcd for $C_{25}H_{33}F_3O_4$ (454.5): C, 66.06; H, 7.32; F, 12.54. Found: C, 66.13; H, 7.48; F, 12.54.

Solvolysis of 21-trifluoroacetate 1f in methanol in the presence of sodium acetate under the same conditions as for **1** resulted, after 15 min,[8] in the formation of the 21-alcohol **1d** exclusively.

Solvolysis of 17β-Trifluoroacetate 1 in HMPT in the Presence of NaN_3. **1** (0.23 g, 0.5 mmol) and NaN_3 (0.32 g, 5 mmol) in 5 mL of HMPT were stirred at 60 °C for 5 h.[8] The mixture was poured into water and extracted with ether. The extract was washed with water to neutrality and dried (Na_2SO_4). The residue (0.19 g) was directly crystallized from *n*-hexane to afford 0.14 g (73%) of **(*E*)-21-azido-pregna-5,17(20)-dien-3β-yl acetate (1e):** mp 105–106 °C; $[\alpha]_D$ −56°; IR ($\overline{N_3}$) 2100 cm^{-1}; ^1H NMR δ 0.78 (3 H, s, 13-Me), 1.02 (3 H, s, 10-Me), 2.00 (3 H, s, 3β-OAc), 4.6 (1 H, m, 3α-H), 4.82 (2 H, d, CH_2N_3), 5.27 (1 H, tt, *J* = 7, 2 Hz, C-20 H), 5.39 (1 H, m, C-6H).[7] Anal. Calcd for $C_{23}H_{33}N_3O_2$ (382.5): C, 72.02; H, 8.67; N, 10.96. Found: C, 72.03; H, 8.76; N, 10.81.

The only other components found in the mother liquors were a relatively nonpolar substance (7%)[4] and alcohol **1d** in traces.

In the same manner as above solvolysis of **1f** was carried out in HMPT + NaN_3 to give **1e** in 1 h[8] in 100% yield.

When **1** was heated in HMPT at 60 °C partial isomerization into **1f** occurred. NMR analysis showed a **1**:**1f** = 85:15 ratio after 1 h. The ratio went down to a 66:34 value in 3 h.

3-Methoxy-19-nor-17α-pregna-1,3,5(10),20-tetraen-17-yl Trifluoroacetate (2). This was prepared in the same manner as **1** from 3-methoxy-19-nor-17α-pregna-1,3,5(10),20-tetraen-17-ol (**2a**) and crystallized from *n*-hexane: mp 124 °C; $[\alpha]_D$ +72°; IR (CF_3COO) 1770 cm^{-1}; ^1H NMR δ 0.98 (3 H, s, 13-Me), 3.75 (3 H, s, 3-OMe), 5.17 (1 H, dd, J_{trans} = 17 Hz, J_{gem} = 1.5 Hz, C-21H), 5.37 (1 H, dd, J_{cis} = 10.5 Hz, J_{gem} = 1.5 Hz, C-21 H), 5.97 (1 H, dd, J_{trans} = 17 Hz, J_{cis} = 10.5 Hz, C-20 H), 6.62–7.23 ppm (3 H, aromatic protons).[7] Anal. Calcd for $C_{23}H_{27}F_3O_3$ (408.5): C, 67.63; H, 6.66; F, 13.95. Found: C, 68.27; H, 6.82; F, 13.96.

Solvolysis of 2 in HMPT in the presence of NaN_3 in the same conditions as for **1** gave 0.17 g of a residue (from 0.20 g of **2**) which was chromatographed on PLC [benzene–*n*-hexane (1:2) as eluant] to afford 0.14 g (82%) of **(*E*)-3-methoxy-21-azido-19-norpregna-1,3,5(10),17(20)-tetraene (2b)** as an oil, pure by NMR analysis: $[\alpha]_D$ +51° (*c* 4.0); IR (N_3) 2100 cm^{-1}; ^1H NMR δ 0.81 (3 H, s, 13-Me), 3.73 (2 H, d, *J* = 7 Hz, CH_2N_3), 3.74 (3 H, s, 3-OMe), 5.23 (1 H, tt, *J* = 7, 2 Hz, C-20 H), 6.62–7.27 (3 H, aromatic protons).[7] Anal. Calcd for $C_{21}H_{27}N_3O$ (337.5): C, 74.74; H, 8.07; N, 12.45. Found: C, 74.58; H, 8.06; N, 12.27.

Registry No.—**1,** 65733-41-7; **1a,** 32782-36-8; **1b,** 65733-42-8; **1c,** 65733-43-9; **1d,** 65733-44-0; **1e,** 65733-45-1; **1f,** 65733-46-2; **2,** 65760-05-6; **2a,** 6885-48-9; **2b,** 65733-47-3.

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(6) Melting points were determined on a Kofler hot-stage apparatus. Rotations were taken with a Schmidt–Haensch polarimeter (1-dm cell) in 1% $CHCl_3$ solutions, unless otherwise specified. IR spectra ($CHCl_3$ solutions) were recorded on a Perkin-Elmer 521 spectrophotometer. ^1H-NMR spectra were measured for solutions in $CDCl_3$ (Me_4Si as internal standard) with a Varian EM-390 spectrometer. Column chromatography was carried out with deactivated (grade II) Woelm neutral alumina and preparative layer chromatography (PLC) on Merck HF_{254} silica gel (layers 0.5 mm thick). Hexamethylphosphotriamide (HMPT) was distilled in vacuo over sodium hydride; methanol was dried by treatment with magnesium.
(7) A convenient illustration of the features of systems of the type >CCH═CH_2 and >C═$CHCH_2X$ is found in: N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy to Organic Chemistry", Holden-Day, San Francisco, Calif., 1964, pp 85 and 112.
(8) The disappearance of starting material was monitored by TLC.

Photochemical Reduction and Decarboxylation of 2-Phenylquinoline-4-carboxylic Acids

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Though a variety of 2-phenylquinoline-4-carboxylic acids (cinchophens) and their derivatives have medicinal value,[2] some members of the family have been observed by Rothe[3] to cause phototoxicity in mice. We have previously found[5] that the phototoxicity of similar quinolinemethanol antimalarial compounds correlates with a surprisingly efficient photochemical fragmentation process. We have now studied five of the cinchophens and have discovered that, like the quinolinemethanols, these compounds also show unexpected photochemical reactivity.

Acids **1a–e** were prepared via Doebner condensations of the suitably substituted aniline and aldehyde. Irradiation led to

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