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OXIDATION OF NON-ACTIVATED C-H BONDS IN HYDROCARBONS AND STEROIDS

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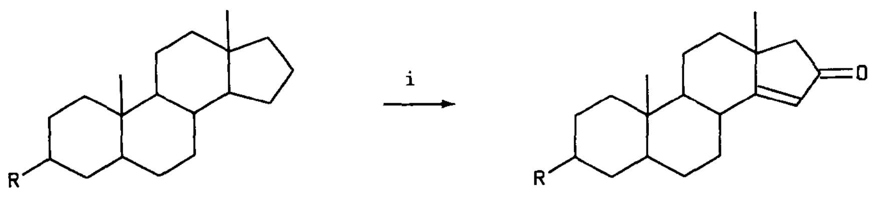
Summary. CrO_3 in $CH_2Cl_2/CH_3COOH/(CH_3CO)_2O$ oxidizes hydrocarbons to alcohols and ketones, 5α-androstane and 3β-acetoxy-5α-androstane are converted to 5α-androst-14-en-16-ones.

Regioselective oxidations of C-H bonds are desirable for the economic conversion of readily available natural products into higher value compounds. Useful methods to achieve this goal, more or less efficiently, are the template directed chlorination[1], the Gif system[2] or the anode[3].

We now found, that the convenient and inexpensive inorganic oxidant CrO_3 can be used, too, for such conversions. With CrO_3 in $CH_2Cl_2/CH_3CO_2H/(H_3CO)_2O$[4] adamantane has been oxidized to 62% 1-adamantol, norbornane to 29% (40%)[5] norbornanone, camphane to 30% (39%) epicamphor and 7% camphor, cis-decaline to 36% (59%) cis-9-decalol. These partially moderate selectivities improved with steroids. So 5α-androstane (1a) and 3β-acetoxy-5α-androstane (1b) were converted to 47% 2a and 68% 2b[6,7].



1 2

a: R=H; b: $R=O_2CCH_3$ (a: 47%, b: 68%)

i: CrO_3, CH_3CO_2H, $(CH_3CO)_2$, CH_2Cl_2

The steroids are identified by comparison of their mass spectra[8], the chemical shifts of the 18- and 19-H in the ^{1}H-NMR[9] and the C=O frequencies in the IR[10] with data from the literature. **2a** was converted by double bond hydrogenation[11] to 5α-androstan-16-one and **2b** was deacetoxylated to **2a** via its phenoxy thiocarbonate[12].

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5 Yields in parenthesis are based on conversion.
6 Conditions for oxidation: 0.4 mmol **1a** or **b** dissolved in 3 ml CH_2Cl_2, then addition of 1 ml CH_3CO_2H and 1 ml $(CH_3CO)_2O$.
7 Physical data of **2a** and **2b**:
2a IR (KBr): ν = 1680 cm^{-1} (C=O), 1605 (C=C). - ^{1}H-NMR ($CDCl_3$): δ = 5.85 (d, 1H, 15-H), 3.45 (m, 1H, 8-H), 2.25 (q, 2H, 17-H), 1.2 (s, 3H, 18-H), 0.9 (s, 3H, 19-H). - MS (70 eV): *m/z* (%) = 272 (100, M^+), 257 (80, M^+-CH_3), 163 (52), 109 (80), 97 (65).
2b IR (KBr): ν = 1720 cm^{-1}, 1680 (C=O), 1605 (C=C). - ^{1}H-NMR ($CDCl_3$): δ = 5.72 (d, 1H, 15-H), 4.65 (m, 1H, 3-H), 2.25 (q, 2H, 17-H), 2.0 (s, 3H, 21-H), 1.2 (s, 3H, 18-H), 0.9 (s, 3H, 19-H). - MS (70 eV): *m/z* (%) = 330 (11, M^+), 270 (100, M^+-CH_3COOH), 163 (41), 97 (55), 43 (81).
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