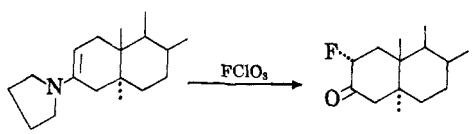
Communications TO THE EDITOR

2α-Fluorocholestanone

Sir:

We wish to report the synthesis of a 2α-fluoro-3-ketosteroid by a novel chemical reaction, the treatment of a 3-ketosteroid enamine with perchloroyl fluoride.



Cholestan-3-one pyrrolidyl enamine[1] (3.0 g.) was dissolved in dry thiophene-free benzene (900 ml.), and perchloroyl fluoride[2] was bubbled into the orange-colored solution until the color was discharged (about 30 sec.). After washing with saturated sodium bicarbonate and then with water, the benzene was removed by evaporation at reduced pressure, and the residual yellow crystals were taken up in 100 ml. of a 1:1 mixture of benzene and petroleum ether. This solution was filtered through 10 g. of Florisil and the filtrate evaporated to dryness *in vacuo*. Recrystallization of the residue from *n*-hexane afforded 2α-fluorocholestan-3-one as colorless glistening plates, 2.0 g., 72%, m.p. 170–173° (uncorr.), $[\alpha]_D^{25}$ + 60° (c = 1.00, $CHCl_3$). *Anal.* Calcd. for $C_{27}H_{45}OF$: C, 80.15; H, 11.21; F, 4.70. Found: C, 79.83; H, 11.20; F, 4.93

The infrared spectrum of 2α-fluorocholestan-3-one (KBr pellet) was compared with that of cholestan-3-one. The position of the carbonyl band was found to have shifted from 5.88μ for cholestanone to 5.79μ for the fluorocholestanone. A rather strong band at 9.23μ was shown by the fluorocholestanone but was completely absent in the spectrum of cholestanone; this 9.23μ band, therefore, was assigned to the C—F stretching of the fluoro ketone. Otherwise the spectrum of 2α-fluorocholestan-3-one was quite similar to that of cholestan-3-one.

2α-Fluorocholestanone can be sublimed without decomposition at its melting point (170°) under 0.1 mm. Hg. pressure. This remarkable thermal stability, as well as the shift in the position of the carbonyl band by 0.09μ (26 $cm.^{-1}$),[3] indicates that the fluorine atom at position 2 is equatorial (α) and not axial (β).

Syntheses of other steroidal α-fluoroketones by the foregoing method are in progress, and the results will be discussed more completely in a forthcoming publication.

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(1) F. W. Heyl and M. E. Herr, *J. Am. Chem. Soc.*, **75**, 1918 (1953).

(2) Pennsylvania Salt Manufacturing Co., Three Penn Center Plaza, Philadelphia 2, Pa.

(3) R. N. Jones, D. A. Ramsay, F. Herling, and K. Dobriner, *J. Am. Chem. Soc.*, **74**, 2828 (1952).