The best yield of II (5%, based on unrecovered dienone) was obtained with sodium methoxide in the cold and subsequent acidification and steam distillation, the other methods giving only traces. Care had been taken to make sure that the dienone used was a pure crystallized sample in which no II could be detected.

The formation of II from I can be best explained by assuming a bicyclic cyclobutane intermediate



This mechanism corresponds exactly to the results of Dodson and coworkers, who found an analogous bicyclic cyclobutane derivative to be an intermediate in their conversion of 1-methyl-1-dichloromethyl-2(1H)-naphthalenone to 1-methyl-3-naphthoic acid.

An alternative mechanism for the formation of II involving the primary formation of dichlorocarbene and *p*-cresoxide ion by deprotonation of I (retro-Reimer-Tiemann process)³ followed by reattachment of carbene to the ortho position of the *p*-cresoxide ion thus leading to II is unlikely on the following grounds: (a) An attempt to trap any intermediate dichlorocarbene by reacting I with sodium *t*-butoxide suspended in cyclohexene⁴ was unsuccessful, as no dichloronorcarane could be isolated, tars being the only products. (b) No *p*-cresol could be detected in the reaction mixtures, while it would have been expected to arise as a by-product under these assumptions.

EXPERIMENTAL

Reaction of I with sodium methoxide in methanol. A solution of 1.1 g. of I (0.0058 mole, m.p. 54-55°) in 15 ml. of absolute methanol containing 1.17 g. (0.217 mole) of sodium methoxide was left standing at room temperature for 20 hr. The solvent was then removed in vacuo and the residue, after the addition of 200 ml. of water, steam distilled. Thus 0.6 g. of I was recovered. After all distillable material had passed over the contents of the flask were acidified with dilute sulfuric acid and again steam distilled. The distillate now possessed the strong smell of II and gave its color reactions. It was extracted with ether, the ether layer evaporated, and the residue dissolved in ethanol. Upon addition of 2,4-dinitrophenylhydrazine reagent the derivative of II precipitated (0.040 g.-i.e. 5% of the theoretical amount based on unrecovered dienone, m.p. 261-264°, undepressed when mixed with an authentic sample showing the same m.p.).

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Conformational Analysis. XXIV. The Dipole Moment of 4-Fluorocoprostan-3-one¹

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The increasing interest in fluorinated steroids prompted us to study the conformation of the fluorine atom in compounds containing a fluorine on a carbon adjacent to a carbonyl group. It has been shown that the fluorine atom of α -fluorocyclohexanone prefers an equatorial conformation,^{3,4} and it was found earlier that the fluorine atom in the only known 2-fluorocholestan-3-one exists in the α (equatorial) configuration.⁵ In the present work the dipole moment of the only known 4-fluorocoprostan-3-one has been determined and allows an unambiguous assignment of the configuration at C-4 to be made.

Upon inspection of a model of 4-fluorocoprostan-3-one, it appeared that the α (equatorial) configuration of the fluorine would be the more stable, since an axial fluorine would interfere with one of the hydrogens of the C-7 methylene group. The nearest hydrogen is 1.7 Å from the axial fluorine as measured with Dreiding models. The repulsion energy was calculated according to the method of Hill,⁶ using the quantities $\alpha = 0.665$, and $\epsilon =$ 0.068 kcal./mole (the geometric mean of the F-F repulsion, obtained from fluorine gas (0.109 kcal./mole) and the H-H value). This repulsion energy was found to destabilize the axial configuration by 5.1 kcal./mole. For an equatorial fluorine the only interaction which does not occur in equatorial fluorocyclohexanone is that between the β -fluorine on C-4 and the equatorial hydrogen on C-6. As these atoms are 2.5 Å apart, the energy of this interaction is negligible. Only one isomer of 4fluorocoprostanone has been prepared, and from the energy considerations outlined, it seemed likely that it had the 4β -configuration. An unequivocal assignment of the configuration at C-4 was, however, made from the dipole moment.

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N_2	d_{12}	€12				
(Coprostan-3-one					
0.0000000	0.873090	2.2731				
0.00052308	0.873384	2.2798				
0,00074663	a	2.2829				
0.00104392	0.873591	2.2871				
0.00198058	0.874071	2.2998				
	N ₂ 0.00000000 0.00052308 0.00074663 0.00104392 0.00198058	$\begin{array}{c c c c c c c c c c c c c c c c c c c $				

TABLE I Dipole Moment Data

$ \begin{array}{l} \alpha = 13.523, \beta = 0.490, (P_{\theta} + P_{a}) = 130.60, \epsilon_{1} = 2.2729 \\ d_{1} = 0.87310, M_{R} = 118.73, P_{2\infty} = 315.8, \mu = 3.01 \\ D \end{array} $
A Elucroconnecton 2 one

4-1 Iuorocoprostan-5-one					
0.000000000	0.873050	2.2718			
0.000288442	0.873281	2.2792			
0.000493620	0.873510	2.2850			
0.000940493	0.873813	2.2966			
0.00136424	0.874025	2.3076			

 $\begin{array}{l} \alpha = 26.228, \beta = 0.734, (P_e + P_a) = 130.36, \epsilon_1 = 2.2719, \\ d_1 = 0.87308, M_R = 118.51, P_{2\infty} = 501.3, \mu = 4.26 \text{ D} \end{array}$

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	0.00000000	0.873172	2.2713
	0.00146111	0.873235	2.2783
	0.00298955	0.873326	2 2863
	0.00462863	0.873481	2.2946
	0.00591418	0.873550	2.3012
α	$= 5.074, \beta = 0.068$	$30, (P_e + P_a) = 30$	$0.25, \epsilon_1 = 2.2711$
	$d_1 = 0.87315$, M _R	$= 27.51, P_{2\infty} = 10$	$17.4, \mu = 1.94$

^a This point was discarded by the computer.

From the bond moments and the angles between the dipoles, the moments for the two epimeric fluoroketones were calculated. The methods and numerical values are those used earlier,⁵ except that a new value for the C—F dipole was obtained from cyclohexyl fluoride. The latter compound had a moment of 1.94 D (in benzene solution at 25°). The moment of coprostan-3-one was also measured and found to be 3.01 D. A value of 3.01 D was consequently used for the C-O dipole when the fluorine was axial, and 2.84 D was used when the fluorine was equatorial (taking into account the moment induced by the neighboring equatorial C-F dipole as described previously.⁵ The calculated values are as follows, 4α -fluorocoprostanone (axial fluorine) 2.97 D; 4β -fluorocoprostanone (equatorial fluorine), 4.32 D.

The moment of 4-fluorocoprostan-3-one was measured in benzene solution and found to be 4.26 D, and the configuration at C-4 is thus unequivocally established as β (equatorial).

EXPERIMENTAL

Coprostan-3-one Δ^4 -Cholestene-3-one was prepared from cholesterol in the usual manner via an Oppenhauer oxidation.⁷ Coprostan-3-one was prepared from Δ^4 -cholesten-3one by hydrogenation in ether with pallatium catalyst according to the procedure of Grosshof.⁸ M.p. 62-62.5° (reported m.p. 63°) from acetone.

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Cyclohexyl fluoride. The addition of anhydrous hydrofluoric acid to cyclohexene (in a polyethylene bottle) was carried out following essentially the literature procedure.¹⁰ The product had b.p. 64.5° (237 mm.), lit.¹⁰ b.p. 71.2° (300 mm.).

4-Fluorocoprostan-3-one. Used directly as received, m.p. 154.5-155° after drying 12 hr.

Measurements of dipole moments. The dipole moment apparatus used has been previously described.⁵ The dipole moments were measured in benzene solution, and the calculations were carried out by essentially the method of Halverstadt and Kumler¹¹ utilizing an IBM 650 computer programmed as described earlier.¹² As the coprostanone derivatives are of such high molecular weight, the usual neglect of atomic polarization may introduce some error.¹³ Unfortunately, there is no good simple method for determining the atomic polarization. What has been done in the present case is to set it equal to10% of the molar refractivity, for coprostanone, 4-fluorocoprostanone, and fluorocyclohexane. The effect of taking the atomic polarization into account was to lower the experimental moments slightly, of coprostanone from 3.10 to 3.01 D. and of cyclohexylfluoride from 1.98 to 1.94 D. These changes are not of great significance as the experimental error is about .03 D. The data are summarized in Table I.

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Bromination of Naphthalene in 60% Aqueous Acetic Acid¹

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In glacial acetic acid and other nonpolar solvents the bromination of aromatic compounds is usually second-, and sometimes third-, order in bromine,⁸

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