Photofragmentation Reactions of Ergosterol

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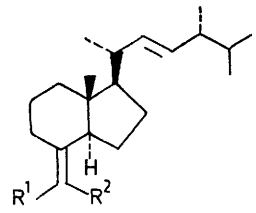
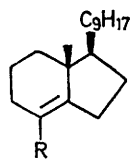
Summary The photochemical formation of de-AB-ergost-22-ene derivatives from ergosterol is described.

FRAGMENTATIONS during vapour-phase photolyses are documented.[1] We report the isolation and structural

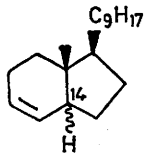
determination of the de-AB-ergost-22-ene derivatives (Ia)—(Ic), (IIa), (IIb), and (IIIa).



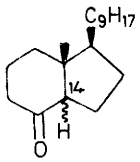
(I) a; $R^1=R^2=H$
b; $R^1=OEt, R^2=H$
c; $R^1=H, R^2=OEt$



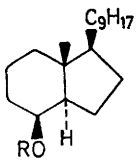
(II) a; R = H
b; R = Me



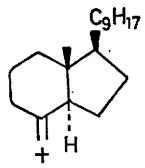
(III) a; 14α-H
b; 14β-H



(IV) a; 14α-H
b; 14β-H



(V) a; R = H
b; R = C(:O)C_6H_3-3,5$(NO_2)_2$
c; R = C(:S)SMe



(VI)

Irradiation of ergosterol (36 g) as before[2] and chromatography over alumina (Grade III, neutral), silica (Merck GF_{254}) and silica–$AgNO_3$ (10%) p.l.c. gave photofragments (Ia)—(IIIa) as in the Table. The structures of these compounds were confirmed by synthesis.

Wittig reactions of 'Grundmann's ketone' (IVa)[3] gave the diene (Ia) (74%) (with triphenylmethylenephosphorane) and the vinyl ethers (Ib) (25%) and (Ic) (25%) (with triphenylethoxymethylenephosphorane). The room temperature acid isomerisation (tetrahydrofuran–H_2O–H_2SO_4 100:21:9) of the diene (Ia) gave the diene (IIb) (100%). Reduction ($NaBH_4$) of the ketone (IV) gave de-AB-ergost-22-en-8β-ol (Va) (oil, 84%) isolated as its 3,5-dinitrobenzoate (Vb), m.p. 141–142°, (lit.,[4] 146°), $[\alpha]_D^{22}$ + 70°, (all $[\alpha]_D$ in $CHCl_3$ unless stated otherwise). Dehydration (methane sulphonic anhydride–pyridine) of (Va) gave the diene (IIa) (82%) and pyrolysis of the xanthate (Vc) (oil) gave the diene (IIIa) (55%). An attempt to synthesise (IIIa) from the ketone (IV) *via* its toluene-*p*-sulphonylhydrazone (m.p. 116—117°, 93%) and methyl-lithium gave the C-14 epimer (IIIb) (oil, 40%), alternatively prepared from the ketone (IVb)[5] by $NaBH_4$ reduction and dehydration (17%, overall, $[\alpha]_D^{22}$ 32°).

TABLE

Structure	Yield/mg	M.p.	$[\alpha]_D$ ($CHCl_3$)
(Ia)	76	Oil	+48°
(Ib)[b]	29	47—49°	+56° (cyclohexane)
(Ic)[b,c]	8	Oil	+49° (cyclohexane)
(IIa)	36	Oil	+9·8°
(IIb)	5	Oil	+12·4°
(IIIa)	14	Oil	+35°

[a] All new compounds gave satisfactory analytical and spectral data. [b] Stereochemistry may be reversed. [c] Tentative assignment (n.m.r., t.l.c. only).

The photolysis of ergosterol in cyclohexane gave the dienes (Ia), (IIa), (IIb), and (IIIa).

We favour vinyl carbonium ion (VI) intermediacy in the formation of the vinyl ethers (Ib) and (Ic) and a radical pathway for hydrocarbon fragment formation.

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[5] K. Dimroth and H. Jonsson, *Ber.*, 1941, **74**, 520.