Rhodium-catalysed Isomerisation of Some Unsaturated Organic Substrates

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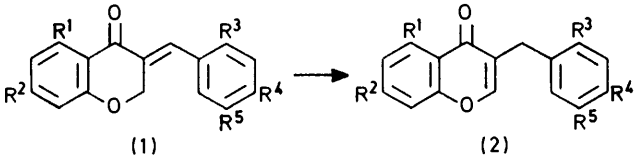
The versatile rhodium trichloride trihydrate has been employed in catalytic amounts to promote double-bond migration. This method allows good yields in otherwise difficult, or impossible, exocyclic–endocyclic isomerisations. The rearrangement of ergosterol was found to be more complex. Besides known isomers a new *cis*-AB-ergosterol isomer has been isolated.

MIGRATION of a double bond may be difficult to bring about when the molecule concerned is fragile. The classical methods usually require drastic conditions, *i.e.* strong bases or acids or high temperature heterogeneous catalysis.[1] The recent discovery that several transition metal complexes, used as homogeneous catalysts, can isomerise double bonds in simple olefinic systems [2,3] has been applied to a few more sophisticated molecules.[4-6] The potential interest of these reagents in organic chemistry lies in their selectivity and ability to bring about reaction under mild conditions. We were looking for a simple and efficient catalytic system for exocyclic–endocyclic migration of the double bond in arylmethylenechroman-4-ones. Although other types of reagent proved unsuccessful, rhodium chloride trihydrate catalysed this reaction efficiently. Several other examples have been studied; they are described below.

A method for exocyclic–endocyclic migration of the double bond in arylmethylenechroman-4-one would allow ready access to the homoisoflavone skeleton. This nucleus must otherwise be built up from the appropriate dihydrochalcones and formic esters.[7] In basic medium compounds of type (1) are degraded. They are unreactive towards acids. However, treatment of (1a)



(1) (2)

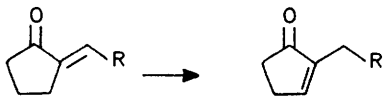
a; $R^1 = R^2 = R^3 = R^4 = R^5 = H$
b; $R^1 = R^2 = H$, $R^3 = R^4 = R^5 = OMe$
c; $R^1 = Me$, $R^2 = R^3 = R^4 = R^5 = OMe$

with Raney nickel afforded a mixture of the endocyclic double bond isomer (2a) and the reduced homoisoflavone.[8]

Ready transposition of this double bond has been reported in only two cases: during condensation of

[1] A. J. Hubert and H. Reimlinger, *Synthesis*, 1969, 97; 1970, 405.
[2] G. C. Bond, *Ann. Reports*, 1966, **63**, 27.
[3] R. Cramer, *Accounts Chem. Res.*, 1968, **1**, 186.
[4] J. F. Biellmann and M. J. Jung, *J. Amer. Chem. Soc.*, 1958, **90**, 1673.
[5] A. J. Birch and G. S. R. Subba Rao, *Tetrahedron Letters*, 1968, 3797.
[6] E. J. Corey and J. W. Suggs, *J. Org. Chem.*, 1973, **38**, 3224; *Tetrahedron Letters*, 1975, 3775.
[7] L. Farkas, A. Gottsegen, M. Nogradi, and J. Strelisky, *Tetrahedron*, 1971, **27**, 5049.
[8] J. N. Chatterjea, S. C. Shaw, and J. N. Singh, *J. Indian Chem. Soc.*, 1974, 281.

chroman-4-one with phthalaldehyde [9] and during hydration of a flavylium perchlorate.[10] However in our hands the transformation (1) ⟶ (2) occurred simply on adding a catalytic amount of the rhodium salt to a solution of (1) in ethanol–chloroform. After refluxing for 24 h a nearly quantitative yield of (2) was obtained.



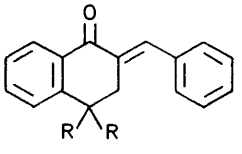
(3) (4)

a; R = $[CH_2]_2 \cdot CH_3$

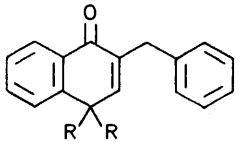
b; R = $[CH_2]_3 \cdot CH_3$

c; R = Ph

The 2-substituted cyclopentenones (4), useful intermediates in the synthesis of several natural products,[11] are difficult to prepare.[12,13] For example, exocyclic–endocyclic double bond rearrangement of alkylidene- or benzylidene-cyclopentanones (3) catalysed by acids gives poor or moderate yields.[14] However, with the help of the rhodium catalyst, compounds of type (4) were obtained in good yield; since the exocyclic isomers are easily prepared, this process offers a convenient route to these compounds. Appropriate model experiments showed that these rearrangements were not due to hydrochloric acid released by rhodium trichloride. The same catalytic system converted the benzylidenetetralone (5a) quantitatively into 2-benzyl-1-naphthol. Compounds of type (5) have been reported to be un-



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



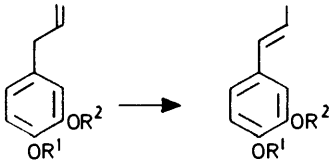
(6)

reactive towards acids and bases,[15] or at least very resistant [16] to isomerisation. The 4,4-dimethylnaphthalenone (6; R = Me), readily obtained by isomerisation of (5b) (also inert to acids and bases), was previously obtainable only by a three-step synthesis.[17]

Isomerisation occurs readily when the migrating double bond moves into conjugation with an aromatic nucleus. In contrast to the fact that allyl groupings are isomerised by strong bases with formation of significant amounts of *cis*-isomer,[1] eugenol (7a) and safrole (7b) gave predominantly the *trans*-isomers (8a) and (8b). The 1 : 9 *cis–trans* ratio in isoeugenol was altered neither by the amount of catalyst nor by the reaction time, but was slightly sensitive to an increase of the reaction temperature, as recently noted.[18]

The commercially available isoeugenol contains approximately 40% of *cis*-isomer. The *cis–trans* ratio remained unchanged even after a long period of contact with the rhodium catalyst. It has been reported that the ratio of *cis*- to *trans*-isosafrole was 4 : 6 when chlorotristriphenylphosphinerhodium was used as catalyst.[5]

It was of interest to investigate the behaviour of a typical conjugated diene like ergosterol towards rhodium trichloride. The hydrochloric acid-promoted rearrangement of the 5,7-diene into ergosterols B_1, B_2, and B_3 is classic.[19] We have found that on adding a catalytic amount of rhodium trichloride to an ethanolic solution



(7) (8)

a; R^1 = H, R^2 = Me a; R^1 = H, R^2 = Me

b; R^1R^2 = CH_2 b; R^1R^2 = CH_2

of ergosterol it was partially transformed into the dimeric rhodium(I)-complex (9) and the previously unknown coprostatrienol (10), accompanied by ergosterols B_2 (11) and B_1 (12).

Convenient experimental conditions were defined for preparing the dimer selectively, or to avoid as far as possible its formation in order to get the maximum yield of (10). For instance, by adding regularly small quantities of rhodium trichloride to an ethanolic solution of ergosterol all the starting material was transformed after 30 h at 70 °C affording 25% of (10), 45% of (11), and 30% of (12). Almost no reaction occurred in chloroform unless enough ethanol was added, and in that case compound (10) was obtained in a much lower yield. Structure (10) was assigned on the basis of spectroscopic data, particularly its n.m.r. spectrum, showing an equatorial 3α-proton [20] and a characteristic pattern for the 6- and 7-hydrogen atoms. In agreement, the alcohol (10) was much more rapidly oxidised to the ketone (13) than its isomer (11) to the corresponding ketone (14). Finally, the AB-*cis*-ring junction for (10) was proved after parallel oxidation of the *p*-nitrophenylhydrazones (15) and (16)

[9] D. H. R. Barton, P. D. Magnus, and J. I. Okogun, *J.C.S. Perkin I*, 1972, 1103.
[10] J. Andrieux, unpublished observations.
[11] E. Demole, E. Lederer, and D. Mercier, *Helv. Chim. Acta*, 1962, **45**, 685.
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[13] M. F. Ansell and J. W. Ducker, *J. Chem. Soc.*, 1959, 329.
[14] J. M. Conia and J. Amice, *Bull. Soc. chim. France*, 1968, 3327.
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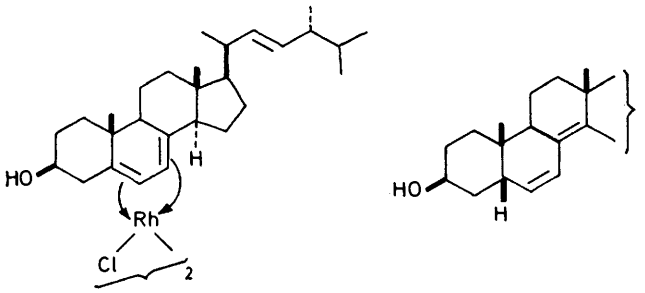
[16] D. H. R. Barton, J. H. Bateson, S. C. Datta, and P. D. Magnus, *J.C.S. Perkin I*, 1976, 503.
[17] A. Hassner and N. H. Cromwell, *J. Amer. Chem. Soc.*, 1958, **80**, 893.
[18] Ger. Pat., 2,508,347.
[19] L. F. Fieser and M. Fieser, ' Steroids,' Reinhold, New York, 1954.
[20] L. M. Jackman and S. Sternhell, 'Application of NMR Spectroscopy in Organic Chemistry,' Pergamon, London, 1969, p. 288.

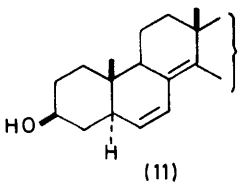
to the same product (17), according to a previously published procedure.[21]

Formation of the *cis*-AB-steroid was intriguing in view of our earlier results [22] showing that a transition metal complex, for steric reasons, will specifically bind to the



(9)

(10)



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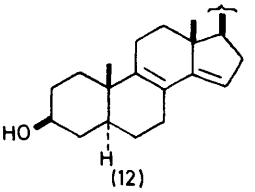

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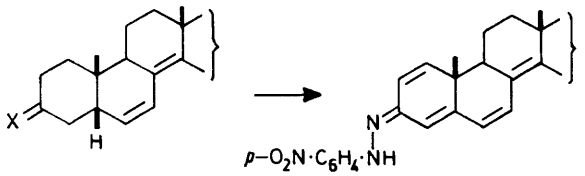
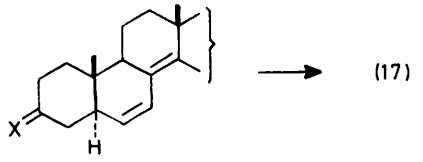


(13) X = O

(15) X = *p*-$O_2N \cdot C_6H_4 \cdot NH \cdot N$

(17)



(17)

(14) X = O

(16) X = *p*-$O_2N \cdot C_6H_4 \cdot NH \cdot N$

α-face of ergosterol. Decomplexation of the dimer (9) with cyanide anion gave a quantitative yield of ergosterol, proving that at that stage no rearrangement had occurred. The dimer was stable in air and was unchanged after prolonged refluxing in ethanol or chloroform, but it decomposed rapidly when a catalytic amount of hydrochloric acid was added, affording a mixture of ergosterols B_1 and B_2. Since it has been found [23] that rhodium trichloride oxidizes ethanol to give a catalytically active rhodium hydride species with concomitant production of hydrogen chloride, such a process could have been responsible for the observed isomerisation.[24] In order to remove the possibility of hydrogen chloride being involved, an excess of potassium carbonate was added to a solution of ergosterol and rhodium trichloride in ethanol. After 48 h all the starting material was consumed and the major product by far was ergosterol B_1, thus indicating that a rhodium hydride species was able to bring about the isomerisation independently of the production of hydrogen chloride. In the last two experiments compound (10) was not detected. A last experiment was conducted by adding a catalytic quantity of hydrochloric acid to a solution of ergosterol in ethanol; after 30 h at reflux the respective amounts of compounds (10), (11), and (12) were *ca.* 21, 60, and 19%.

Thus, at least two competitive mechanisms are involved in the isomerisation. The first is the result of the protonation at C-5 on both faces in the approximate ratio 5 : 1 (α : β), leading to the isomeric alcohols (10) and (11). Compound (10) was relatively inert when exposed to rhodium salt or to hydrochloric acid; in contrast ergosterol B_2 rearranges easily. This migration of the double bond proceeds at least partially because there is some hydrogen chloride present, but on the basis of our experiments catalysis by an active rhodium species can certainly not be excluded.

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus, i.r. spectra for Nujol mulls with a Perkin-Elmer 257 spectrophotometer, u.v. spectra (unless indicated to the contrary) for solutions in ethanol with a Unicam SP 800 spectrophotometer, and n.m.r. spectra for solutions in $CDCl_3$ (Me_4Si as internal standard) with a Varian T60 spectrometer. Optical rotations were determined for solutions in $CHCl_3$. Both thin-layer and plate chromatography were carried out on silica gel G254. Silver nitrate plates refer to silica gel plates impregnated (10%) with silver nitrate. Light petroleum refers to the fraction of b.p. 40—60°. Anhydrous magnesium sulphate was used for drying solutions. All the reactions described were carried out under nitrogen. Rhodium chloride trihydrate was purchased from Johnson-Matthey Chemicals. Neutral alumina (grade I) was always used.

3-Benzylchromone (2a).—The benzylidenechromanone (1a) (0.2 g), m.p. 112—113° (lit.,[8] 112—113°) in chloroform (2 ml) and ethanol (2 ml) was treated with $RhCl_3,3H_2O$ (10 mg) and water (0.2 ml). After 24 h stirring at 70 °C the red solution was poured into water. Extraction with chloroform and usual work-up gave, after filtration through alumina (elution with Et_2O) an essentially quantitative yield of (2a), m.p. 111° (from MeOH) (lit.,[8] 110—111°).

3-(2,4,5-Trimethoxybenzylidene)chroman-4-one (1b).[25]—2,4,5-Trimethoxybenzaldehyde (1 g) was added to chroman-4-one (0.8 g) in benzene (30 ml) and piperidine (1 ml). The solution was heated at reflux for 24 h, the water being drained from the condenser. The addition of benzene and piperidine was repeated and the mixture was refluxed for 2 h. If t.l.c. showed incomplete transformation the treatment was repeated. The crude mixture was eluted with benzene through a column of alumina to give the *chroman-4-one* (1b) (84%), m.p. 136—138° (from benzene–light petroleum), τ

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[22] D. H. R. Barton and H. Patin, *J.C.S. Perkin I*, 1976, 829.

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6.15 (6 H, s), 6.08 (3 H, s), 4.72 (2 H, d, *J* 3 Hz), and 2—3.5 (7 H) (Found: C, 69.9; H, 5.5. $C_{19}H_{18}O_5$ requires C, 69.9; H, 5.6%).

7-Methoxy-5-methyl-3-(2,4,5-trimethoxybenzylidene)chroman-4-one (1c).[25]—2,4,5-Trimethoxybenzaldehyde (1 g) and 5-methyl-7-methoxychroman-4-one [26] (1 g) in dry benzene and piperidine (1.5 ml) were refluxed for 24 h. The same treatment as above afforded the *chroman-4-one* (1c) (86%), m.p. 130—132°, τ 7.23 (3 H, s), 6.20 (9 H, s), 6.10 (3 H, s), 4.93 (2 H, d, *J* 3 Hz), 3.62 (1 H, s), 3.70 (1 H, s), 3.54 (1 H, s), and 2.12 (1 H, s) (Found: C, 68.0; H, 5.7. $C_{21}H_{22}O_6$ requires C, 68.1; H, 6.0%).

3-(2,4,5-Trimethoxybenzyl)chromone (2b).—Under the same conditions as described for (2a), the benzylidenechromanone (1b) gave a nearly quantitative yield of the *chromone* (2b) (n.m.r. control), m.p. 117—118° (from ether–light petroleum), τ 6.17 (3 H, s), 6.20 (3 H, s), 6.22 (3 H, s), 6.25 (2 H, s), and 3.4—1.7 (7 H) (Found: C, 70.1; H, 5.7. $C_{19}H_{18}O_5$ requires C, 69.9; H, 5.6%).

7-Methoxy-5-methyl-3-(2,4,5-trimethoxybenzyl)chromone (2c).—For complete transformation of (1c) (0.2 g) *ca.* 10% of $RhCl_3,3H_2O$ was needed during 48 h, but otherwise the same conditions were used as described for (2a). This afforded a nearly quantitative yield (n.m.r. control) of the *chromone* (2c), m.p. 124—125° (from ether–light petroleum), τ 7.2 (3 H, s), 6.3 (2 H, s), 6.2—6.08 (12 H), and 3.4—2.5 (6 H) (Found: C, 68.1; H, 6.05. $C_{21}H_{22}O_6$ requires C, 68.1; H, 6.0%).

Rearrangement of 2-Substituted Cyclopentanones (3).—Butylidenecyclopentanone (3a) [2,4-dinitrophenylhydrazone m.p. 162—163° (lit.,[27] 158—159°)], pentylidenecyclopentanone (3b) [2,4-dinitrophenylhydrazone, m.p. 122—123° (lit.,[27] 121°)], and benzylidenecyclopentanone (3c), m.p. 71° (lit.,[28] 71—72°) were prepared according to ref. 28.

To cyclopentanone (3) (10 g) in ethanol (10 ml) were added water (1 ml) and $RhCl_3,3H_2O$ (0.35 g). After 3 days under reflux the mixture was poured into water and extracted with ether. The usual work-up gave an oil containing more than 90% (n.m.r. control) of compound (4). The crude product was filtered through a short column of alumina (elution with ether) and then distilled under reduced pressure to give 2-n-butylcyclopent-2-enone (4a) [the yield of the fraction b.p. 105—107° at 15 mmHg was 72%; 2,4-dinitrophenylhydrazone, m.p. 131—132° (lit.[13] 128—130°)]; 2-n-pentylcyclopent-2-enone (4b) [the yield of the fraction b.p. 100—102° at 4 mmHg was 64%; 2,4-dinitrophenylhydrazone, m.p. 104—105° (lit.,[13] 99—100°)]; or 2-benzylcyclopent-2-enone (4c) [the yield of the fraction b.p. 161—163° at 15 mmHg was 79%; 2,4-dinitrophenylhydrazone, m.p. 190—191° (lit.,[14] 177—178°)].

2-Benzyl-1-naphthol.—To 2-benzylidene-1-tetralone (5a) (1 g) [15] in ethanol–chloroform (1 : 1; 10 ml) were added water (0.5 ml) and $RhCl_3,3H_2O$ (50 mg). After 48 h at 70 °C and the usual work-up the yield was nearly quantitative; m.p. 72—74° (lit.,[15] 73—74°).

2-Benzyl-4,4-dimethylnaphthalen-1(4H)-one (6; R = Me).—To the benzylidenetetralone (5b) [17] [m.p. 110° (lit.,[17] 110°)] (1 g) in 1 : 1 ethanol–chloroform (15 ml) were added water (1.5 ml) and $RhCl_3,3H_2O$ (4 × 20 mg, one portion every 12 h; n.m.r. then showed complete transformation). The mixture was poured into water; extraction with chloroform followed by the usual work-up and filtration through alumina afforded 93% of product, m.p. 113—114° (from methanol) (lit.,[17] 112—113°), τ 8.6 (6 H, s), 6.22 (2 H, s), 3.43 (1 H, s), and 2.9—1.7 (9 H).

Isomerisation of Eugenol.—To eugenol (20 g) in ethanol (5 ml) was added $RhCl_3,3H_2O$ (0.1 g). The temperature was maintained at 20 °C by cooling and after 2 h the mixture was poured into water and extracted with ether. The usual work-up was followed by distillation; the yield of the fraction b.p. 140—142 °C at 15 mmHg was 92%. The minimum amount of catalyst for 20 g of eugenol is 5 mg; complete transformation requires 24 h in this case. The amount of the *trans*-isomer of eugenol was always at least 90%.

Isomerisation of Safrole.—Under the same conditions safrole (20 g) was converted into isosafrole, b.p. 130—132° at 15 mmHg (93%). The amount of *trans*-isomer was about 80%.

Bis[(chloro)(ergosterol)rhodium] (9).—To ergosterol (0.6 g) in ethanol (70 ml) was added $RhCl_3,3H_2O$ (0.4 g). The red mixture was stirred at 70 °C; the yellow dimer was deposited progressively and after 6 h the u.v. spectrum indicated that all the starting material was consumed. The mixture was cooled and the complex (9) was filtered off, and washed with ethanol, and dried under vacuum to give the yellow *dimer* (9) (0.68 g, 67%), m.p. 178—180° (decomp.), $\nu_{max.}$ 3 340, 1 640, 1 100, 970, and 890 cm^{-1}, τ 9.37 (13-Me), 9.24, 9.12, and 9.04 (other Me), 6.37 (H-3), 5.47—5.1 (H-6 and -7, m), and 4.83 (H-22 and -23) [Found: C, 62.7; H, 8.15; Cl, 6.5%; *M* (osmometric in $CHCl_3$), 1 126. $C_{56}H_{88}Cl_2Rh_2$ requires C, 62.8; H, 8.3; Cl, 6.6%; *M*, 1 069].

The mixture obtained after distillation of the ethanolic solution was fractionated by p.l.c. (ether–light petroleum, 1 : 2). The compound R_F 0.32 (47 mg) was later identified as coprosta-6,8(14),22-trien-3β-ol (see below). The more polar fraction (63 mg) was ergosterol B_1, m.p. 137—138° (after two crystallisations from $CHCl_3$–MeOH) (lit.,[19] m.p. 136°), $[\alpha]_D$ 40° (*c* 1.05), $\lambda_{max.}$ 252 nm (ε 19 000).

Decomposition of the Complex (9).—To the complex (9) (0.25 g) in $CHCl_3$ (12 ml) was added a solution of KCN (0.6 g) in water (6 ml). Stirring was maintained for 2 h, then an excess of water was added and the mixture was extracted with ether. The usual work-up afforded, after filtration through a short column of alumina (elution with ether), ergosterol (0.157 g, 85%), identical with authentic material.

Reaction of the Complex (9) *with Hydrogen Chloride.*—To the complex (9) (0.25 g) in $CHCl_3$ (10 ml) was added aqueous 32% hydrochloric acid (50 mg). The mixture was refluxed for 4 h, then poured into water and treated in the usual way. The u.v. spectrum showed no ergosterol, and the n.m.r. spectrum was consistent with the presence of a 1 : 1 mixture of ergosterols B_1 and B_2.

Coprosta-6,8(14),22-trien-3β-ol (10).—To ergosterol (1.2 g) in ethanol (150 ml) was added $RhCl_3,3H_2O$ (60 mg). The solution was stirred at 70 °C and two more portions (60 mg) of catalyst were added at 8 h intervals. After 30 h the u.v. spectrum indicated complete disappearance of the starting material. The mixture was cooled and the dimer (9) (80 mg) was filtered off. The solvent was removed under vacuum and the residue in $CHCl_3$ (10 ml) was fractionated by p.l.c. (ether–light petroleum, 1 : 2). The fraction of R_F 0.32 afforded the trienol (10) (0.24 g) and the fraction of R_F 0.23 (0.72 g) was shown to be a mixture of ergosterols B_1 and B_2 (60% of the latter by n.m.r.). The *trienol* (10) had m.p. 88°

[26] D. H. R. Barton, L. Cottier, K. A. Freund, F. Luini, P. D. Magnus, and I. Salazar, *J.C.S. Perkin I*, 1976, 499.

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(from MeOH–$CHCl_3$), $[\alpha]_D$ +75° (*c* 0.81), $\lambda_{max.}$ 252 and 236sh nm (ε 17 000 and 15 000), $\nu_{max.}$ 3 260, 1 650, 1 615, 1 170, 1 040, 970, and 760 cm^{-1}, τ, 9.23, 9.08, 9.02, and 8.9 (methyls), 5.95 (H-3, $W_{\frac{1}{2}}$ 7 Hz), 4.80 (H-22 and -23), 4.52 (H-6, d of d, $J_{6,7}$ 10 Hz, $J_{5,6}$ 5.5 Hz), and 3.93 (H-7, *J* 10 Hz), *m/e* 396 (M^+) and 271 (100%) (Found: C, 84.9; H, 11.15. $C_{28}H_{44}O$ requires C, 84.8; H, 11.2%). The *trienol* (10) *acetate* had m.p. 115—116° (from MeOH), $[\alpha]_D$ 73° (*c* 0.89), $\lambda_{max.}$ 250 nm (ε 23 000) (Found: C, 82.1; H, 10.6. $C_{30}H_{46}O_2$ requires C, 82.1; H, 10.5%). The mixture of ergosterol isomers was benzoylated and the crude mixture of benzoates was treated with the Cookson reagent [29] in order to remove traces of ergosterol. Separation on silver nitrate plates eluted several times with ether–light petroleum (1 : 9) afforded the less polar ergosterol B_2 benzoate (0.28 g), m.p. 135°, $[\alpha]_D$ −115° (*c* 2.3). A portion (0.1 g) was treated with KOH in MeOH–dioxan to afford ergosterol B_2, m.p. 123—124° (lit.,[19] 124°), $[\alpha]_D$ −100° (*c* 1.1). The more polar fraction was ergosterol B_1 benzoate, m.p. 140—141° (lit.,[30] 140°), $[\alpha]_D$ −31° (*c* 0.83).

Reaction of Ergosterol in the Presence of Potassium Carbonate.—To ergosterol (1.2 g) in ethanol (150 ml) were added K_2CO_3 (0.3 g) and $RhCl_3,3H_2O$ (0.1 g). The mixture was stirred at 70 °C for 24 h, more catalyst (0.1 g) was added, and the mixture was stirred for 24 h more. The solvent was removed under vacuum and the mixture chromatographed on alumina (elution with ether). The crude product was treated with the Cookson reagent [29] then crystallised to give ergosterol B_1 (0.66 g), m.p. 138°.

Reaction of Ergosterol with Hydrogen Chloride.—To ergosterol (1.2 g) in ethanol (150 ml) was added aqueous 32% hydrochloric acid (0.13 g) and the mixture was refluxed for 30 h. The solvent was distilled off and the mixture was fractionated by p.l.c. (ether–light petroleum, 1 : 2). The less polar fraction (0.205 g) was compound (10) and the more polar (0.788 g) contained *ca.* 75% (n.m.r.) of ergosterol B_2, which was obtained pure after treatment with the Cookson reagent [29] and crystallisation.

Coprosta-6,8(14),22-trien-3-one (13).—To the trienol (10) (0.7 g) in acetone (25 ml) at 0 °C, Jones reagent (0.5 ml) was added dropwise. After 2 min the cooling bath was removed and the mixture stirred for 10 min, then poured into water and extracted with ether. The usual work-up followed by p.l.c. and crystallisation (MeOH–$CHCl_3$) afforded plates (0.46 g, 65%) of the *ketone* (13), m.p. 114°, $[\alpha]_D$ +35° (*c* 1.72), $\lambda_{max.}$ 254 and 235 nm (ε 17 000 and 14 000), $\nu_{max.}$ 1 740, 1 145, 985, and 780 cm^{-1}, τ 9.17, 9.1, 9.04, 9.0, and 8.73 (methyls), 4.80 (H-22 and -23), 4.6 and 4.43 (H-6), and 3.85 (H-7 d, *J* 10 Hz), *m/e* 394 (M^+) and 269 (100%) (Found: C, 85.0; H, 10.5. $C_{28}H_{42}O$ requires C, 85.2; H, 10.7%).

The ketone (0.3 g) was converted [21] into the p-*nitrophenylhydrazone* (15). Cooling afforded 0.27 g of product, and dilution of the mother liquor with water, extraction with ether, and conventional work-up followed by t.l.c. gave a further 64 mg. Purification by t.l.c. and careful crystallisation under nitrogen (ether–light petroleum) gave a sample, m.p. 145—146°, $[\alpha]_D$ +239° (*c* 0.12), $\lambda_{max.}$ 250 nm (ε 28 000), *m/e* 529 (M^+) (Found: C, 77.2; H, 8.7; N, 7.9. $C_{34}H_{47}N_3O_2$ requires C, 77.1; H, 8.9; N, 7.9%).

Ergosta-6,8(14),22-trien-3-one (14).—To a solution of ergosterol B_2 (1 g) [31] in acetone (50 ml), Jones reagent (1 ml) was added at 0 °C. The mixture was stirred for 30 min at 0° C and for 3 h at room temperature, then poured into water. Extraction with ether followed by the usual work-up, p.l.c., and crystallisation (MeOH–$CHCl_3$) gave the *ketone* (14) (0.52 g), m.p. 156—157°, $[\alpha]_D$ −61° (*c* 0.92), $\lambda_{max.}$ 252 nm (ε 19 000), $\nu_{max.}$ 1 735, 985, and 780 cm^{-1}, τ 9.22, 9.17, 9.12, 9.05, and 9.0 (methyls), 4.82 (H-6, -22, and -23), and 3.82 (H-7, d, *J* 10 Hz) (Found: C, 85.1; H, 10.7%). The p-*nitrophenylhydrazone* (16), prepared and purified as described above, had m.p. 156—158°, $[\alpha]_D$ −9° (*c* 0.16), $\lambda_{max.}$ 252 nm (ε 30 000), *m/e* 529 (M^+) (Found: C, 77.4; H, 9.0; N, 8.1%).

Oxidation of the p-*Nitrophenylhydrazones* (15) *and* (16).—To the hydrazone (15) (0.2 g) in dimethoxyethane (20 ml) were added *p*-nitrobenzoic acid (0.7 g) and potassium butoxide (1.4 g). The purple mixture was stirred for 1 h at room temperature, then quenched with aqueous 5% acetic acid (100 ml) and extracted with ether. The organic layer was washed with aqueous sodium carbonate then with water. Distillation left a red solid p-*nitrophenylhydrazone* (17) (182 mg) which was purified by t.l.c. and crystallised under nitrogen (ether–light petroleum); m.p. 160—162°, $[\alpha]_D$ +572° (*c* 0.14), $\lambda_{max.}$ 433 nm (ε 47 000), *m/e* 525 (M^+) (Found: C, 77.9; H, 8.3; N, 7.6. $C_{34}H_{43}N_3O_2$ requires C, 77.7; H, 8.2; N, 8.0%).

Compound (16), submitted to the same treatment for 2 h gave a red solid, m.p. 160—162° [mixed m.p. with (17) showed no depression], with the same characteristics as listed for (17) (Found: C, 77.7; H, 8.2; N, 7.7%).

We thank the S.R.C. and the C.N.R.S. for financial support. We are grateful to Roussel-Uclaf for a gift of ergosterol.

[6/1217 *Received*, 23*rd July*, 1976]

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