(the Mo(III) stage). The temperature rose to 75 °C during electrolysis and the final colour of the reduced electrolyte was red. The reduced electrolyte was removed from the cell without any protective atmosphere and was placed in the refrigerator for crystallization after filtration. (A small amount (1 to 2 g) of a brownish material of unknown composition separated. This was filtered off and washed with ethanol. Before washing with ethanol this precipitate began to change to a bluish colour on the surface as soon as the mother liquor had drained off.)

Ethanol was added to the filtrate and a yellowish brown precipitate formed. This precipitate was filtered off, washed with ethanol, and dried at 40 °C, yielding a light brown product (Found: Mo, 14·5; OX, 53·3; NH_4, 10·8 per cent. Calc. for $(NH_4)_4Mo(OX)_4.8H_2O$: Mo, 14·5; OX, 53·6; NH_4, 10·8 per cent).

The conductance for 10^{-3}M is 730 mhos at 25 °C and this is comparable with the double salt $(NH_4)_3MoCl_6.NH_4Cl.2H_2O$, 730 mhos (Steele 1955).

The oxalato complex charred at 60 °C. It is very soluble in water, giving a reddish brown solution, but is insoluble in common organic solvents.

References

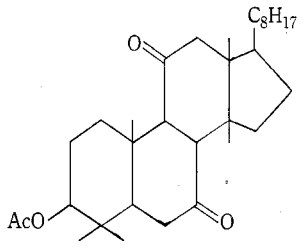
CHILESOTTI, A. (1906).—*Z. Electrochem.* **12**: 146.
FOERSTER, F., and FRICKE, E. (1923).—*Z. angew. Chem.* **36**: 458.
SPITTLE, H. M., and WARDLAW, W. (1929).—*J. Chem. Soc.* **1929**: 792.
STEELE, M. C. (1955).—M.Sc. Thesis, N.S.W. University of Technology.

METHYLSTEROIDS*†

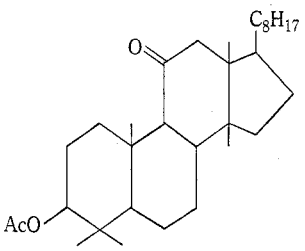
IV. WOLFF-KISHNER REDUCTIONS OF DIKETONES DERIVED FROM LANOSTEROL

By C. S. BARNES‡

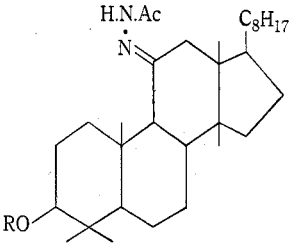
Wolff-Kishner reduction of the diketone I, under conditions designed to give the 7-deoxy compound II after acetylation, gave also a compound more strongly absorbed on alumina. By analogy with the works of Elks and Phillipps (1956) and on the basis of the ultraviolet absorption spectrum and method of formation it is formulated as the acetylhydrazone of 3β-acetoxylanostan-11-one (III ; R=Ac).



(I)

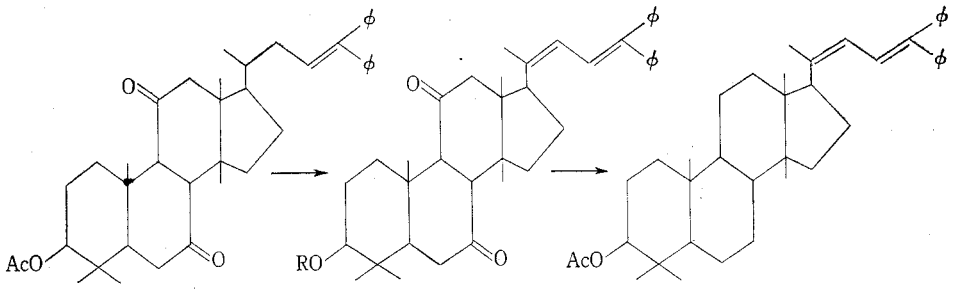


(II)



(III)

The phenylbutadiene (VI) has already been reported (Barnes 1956). It has now been prepared by a variation of the original route.



(IV) (V) (VI)

The diphenylethylene (IV) was converted with *N*-bromosuccinimide to give V (R=Ac) characterized also as the alcohol (V ; R=H) and benzoate (V ; R=Bz). Vigorous Wolff-Kishner reduction and acetylation of the product then gave VI.

* Manuscript received March 26, 1957.

† Part III. Barnes and Palmer (1957).—*Aust. J. Chem.* **10** : 334.

‡ Division of Industrial Chemistry, C.S.I.R.O., Melbourne.

Experimental

(*a*) *General.*—As in Part III (Barnes and Palmer 1957).

(*b*) *Wolff-Kishner Reduction of 7,11-Dioxolanostan-3β-yl Acetate* (*I*).—Sodium (8 g) was treated with diethylene glycol (200 ml) and the diketone I (8 g) and hydrazine hydrate (20 ml; 90%) added. After heating to 180 °C for 18 hr, the product was isolated in the usual way and acetylated. Crystallization gave 11-oxolanostan-3β-yl acetate (II) (4 g). The remainder was chromatographed on alumina to give with benzene, more II. Benzene-ether mixtures eluted fractions which on crystallization gave *11-oxolanostan-3β-yl acetate 11-acetylhydrazone* (*III*; *R*=*Ac*) (1 g) which crystallized from chloroform-methanol to have m.p. 230–231 °C, $[\alpha]_D$ +71° (*c*, 1·3); $\lambda_{max.}$ 217 mμ, ε 14,000, $\lambda_{inflex.}$ c. 235 mμ, ε 8000 (Found: C, 75·2; H, 10·7; N, 5·3%. Calc. for $C_{34}H_{58}O_3N_2$: C, 75·3; H, 10·7; N, 5·1%).

Hydrolysis with methanolic potassium hydroxide gave the derived *alcohol* (*III*; *R*=*H*) crystallizing from methanol to have m.p. 218–220 °C, $\lambda_{max.}$ 217 mμ, ε 14,300; λ 235, ε 9000 (Found: C, 76·2; H, 11·0; N, 5·8%. Calc. for $C_{32}H_{56}O_2N_2$: C, 76·7; H, 11·3; N, 5·6%).

(*c*) *7,11-Dioxo-24,24-diphenyl-25,26,27-trisnorlanosta-20(22),23-dien-3β-ol* (*V*; *R*=*H*) *and Derivatives.*—The diphenylethylene (IV) (3 g) was oxidized in the usual way (Barnes 1956) with *N*-bromosuccinimide (1·2 g) in carbon tetrachloride solution (150 ml). Acetylation of the product gave *7,11-dioxo-24,24-diphenyl-25,26,27-trisnorlanosta-20(22), 23-dien-3β-yl acetate* (V; R=Ac) which crystallized from chloroform-methanol to have m.p. 237–240 °C, $[\alpha]_D$+26° (*c*, 1·76); $\lambda_{max.}$ 230 mμ, ε 14,000; $\lambda_{max.}$ 303 mμ, ε 26,000 (Found: C, 81·0; H, 8·3; O, 10·7%. Calc. for $C_{41}H_{50}O_4$: C, 81·2; H, 8·3; O, 10·6%).

Hydrolysis by methanolic potassium hydroxide gave the derived *alcohol* (V; R=H) which crystallized from chloroform-methanol to have m.p. 236–239 °C, $[\alpha]_D$ +2° (*c*, 1·4); $\lambda_{max.}$ 305 mμ, ε 30,000 (Found: C, 82·7; H, 8·4%. Calc. for $C_{39}H_{48}O_3$: C, 82·9; H, 8·5%).

Benzoylation of the alcohol with benzoyl chloride in pyridine for 1 hr (100 °C) gave the *benzoate* (V; R=Bz) crystallizing from chloroform-methanol to have m.p. 262–264 °C, $\lambda_{max.}$ 230 mμ, ε 29,000; $\lambda_{max.}$ 305 mμ, ε 29,000 (Found: C, 82·7; H, 7·5%. Calc. for $C_{46}H_{52}O_4$: C, 82·6; H, 7·8%). The constants (m.p. 236–237 °C, $[\alpha]_D$ +2°; $\lambda_{max.}$ 310 mμ, log ε 4·52) recorded by McGhie *et al.* (1951) for this compound suggest they may have had the alcohol (V; R=H).

(*d*) *Wolff-Kishner Reduction of 7,11-Dioxo-24,24-diphenyl-25,26,27-trisnorlanosta-20(22), 23-dien-3β-yl Acetate* (*V*; *R*=*Ac*).—The dione (V; R=Ac) (2·8 g) and anhydrous hydrazine (5 ml) were heated to 180 °C in diethylene glycol (100 ml) for 1 hr. A solution of the alkoxide made by reacting sodium (3 g) with diethylene glycol (100 ml) was added and heating continued for 18 hr. Working up in the usual way, acetylating, and crystallizing gave the 7,11-deoxy compound VI having m.p. 234–236 °C undepressed on mixing with that obtained previously (Barnes 1956). Chromic acid oxidation of VI gave the 20-ketone with identical m.p. and mixed m.p. with that obtained previously (Barnes 1956).

References

Barnes, C. S. (1956).—*Aust. J. Chem.* **9**: 228 (see Corrigendum p. 436).

Barnes, C. S., and Palmer, A. (1957).—*Aust. J. Chem.* **10**: 334.

Elks, J., and Phillipps, G. H. (1956).—*J. Chem. Soc.* **1956**: 4326.

McGhie, J. F., Pradhan, M. K., Cavalla, J. F., and Knight, S. A. (1951).—*Chem. & Ind.* **1951**: 1165.

AUSTRALASIAN MEDICAL PUBLISHING CO. LTD.
SEAMER AND ARUNDEL STS., GLEBE, SYDNEY