(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; NH₄, 10·8 per cent. Calc. for (NH₄)₂Mo(OX)₄·8H₂O: Mo, 14·5; OX, 53·6; NH₄, 10·8 per cent).

The conductance for 10⁻⁹M is 730 mhos at 25 °C and this is comparable with the double salt (NH₄)₂MoCl₆·NH₄Cl·2H₂O, 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

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 3α-acetoxylanostan-11-one (III; \( R = Ac \)).

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

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.

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‡ 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-Dioxolano-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-oxolano-3β-yl acetate (II) (4 g). The remainder was chromatographed on alumina to give benzene-ether mixtures eluted fractions which on crystallization gave 11-oxolano-3β-yl acetate 1-acetylhydrazone (I) (1 g) which crystallized from chloroform-methanol to have m.p. 230–231 °C, [α]D +71° (c, 1.3); λmax 217 μm, ε 14,000, λmax 235 μm, ε 14,000, λmax 235 μm, ε 235 μm, ε 8000 (Found: C, 76.2; H, 10.7; N, 5.3%). Calc. for C49H44O2N4: 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, λmax 217 μm, ε 14,300, λmax 305 μm, ε 26,000 (Found: C, 81.0; H, 8.3; O, 10.7%.) Calc. for C49H44O4: C, 81.2; H, 8.3; O, 10.6%.

(c) 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 diphenylethylene (IV) (3 g) was oxidized in the usual way (Barnes 1966) with 2,3-dibromosuccinimide (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, [α]D +11° (c, 1.76); λmax 230 μm, ε 14,000; λmax 303 μm, ε 26,000 (Found: C, 76.2; H, 11.0; N, 5.8%). Calc. for C49H44O4: C, 76.7; H, 11.3; N, 5.6%.

Hydrolysis by methanolic potassium hydroxide gave the derived alcohol (V; R=H) which crystallized from chloroform-methanol to have m.p. 236–239 °C, [α]D +2° (c, 1.4); λmax 305 μm, ε 30,000 (Found: C, 82.7; H, 8.4%). Calc. for C49H44O4: C, 82.9; H, 8.6%.

(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 (3 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 glyccl (100 ml) was added and heating continued for 18 hr. Working up in the usual way, acetylation, and crystallizing gave the 20-ketone with identical m.p. and mixed m.p. 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