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Department of Chemistry,
University of Manitoba,
Winnipeg, Manitoba.

Δ^{11}-STEROIDS

P. Ziegler and A. A. Amos

During attempts at introduction of a Δ^{11} double bond into some steroids, we had occasion to prepare 3,20-dioxo-12α-tosyloxypregnane. This compound has previously been reported as having m.p. 130–132° (1, 2), 120–125° (3), 129–131° (4), but has otherwise not been characterized satisfactorily. In this laboratory, 3,20-dioxo-12α-hydroxypregnane was treated with *p*-tosyl chloride to yield 90% of crystalline material which, after purification, had m.p. 155–156.5°. Elemental analyses and ultraviolet absorption data indicated that our compound is authentic 3,20-dioxo-12α-tosyloxypregnane. The discrepancy in melting point might be due to polymorphism, which is known (3) to occur in this particular series of steroids. The steroid tosylate was then converted to 3,20-dioxo-12α-tosyloxypregnane bis-ethylene ketal, a crystalline compound which gave correct analyses and exhibited the expected ultraviolet absorption data (ϵ = 12,900 at 224 mμ in isooctane). This compound, obtained in the form of an amorphous solid, has been reported (4) to have ϵ = 25,120 at 225 mμ in ethanol.

Dehydrotosylation of 3,20-dioxo-12α-tosyloxypregnane to 3,20-dioxo-Δ^{11}-pregnene has been effected (1) by refluxing with collidine, but the yields of product were low (32%). A more recently developed procedure (2, 3, 4), consisting of dehydrotosylation by chromatography through a column of activated alumina, gave much improved yields (70–85%). In order to carry out this conversion on a larger scale, it seemed desirable to find an alternative method which would avoid chromatography and, at the same time, provide adequate yields. It has now been found that this can be accomplished (50–60% yield) by dehydrotosylating in N-methylpyrrolidone containing a small amount of water and 10% potassium acetate. It seems that this reaction proceeds readily in a slightly basic medium of high dielectric constant.

EXPERIMENTAL

3,20-Dioxo-12α-tosyloxypregnane

3,20-Dioxo-12α-hydroxypregnane (4 g), m.p. 182.5–184.5° and $[\alpha]_D^{25}$ +135.8° (*c*, 0.41, ethanol), was dissolved in dry pyridine (8 ml). After addition of *p*-tosyl chloride (4.5 g) the mixture was kept at 37° for 5 days. By that time the solution had turned brown and long crystals of pyridine hydrochloride had deposited. The solution was then cooled to 0°, the excess reagent was destroyed by addition of water (1 ml) and the mixture was poured into dilute hydrochloric acid. The products were extracted with ether, the solvent extract was washed with dilute acid, then with water until neutral. After it was dried over sodium sulphate, filtered, and evaporated, there remained 5.72 g of residue which crystallized from ether–hexane. In two crops, 5.17 g (89%) of crystals, m.p. 148–153°, were obtained. Three further recrystallizations from ether–hexane provided the analytical specimen, m.p. 155–156.5° (decomp. at 160°), $[\alpha]_D^{25}$ +66.1° (*c*, 0.61, ethanol), $\lambda_{max}^{isooctane}$ 224 mμ (ϵ 12,020). Calculated for $C_{28}H_{38}O_5S$: C, 69.10; H, 7.87; S, 6.59. Found: C, 69.14; H, 7.84; S, 6.43.

3,20-Dioxo-12α-tosyloxypregnane Bis-ethylene Ketal

3,20-Dioxo-12α-tosyloxypregnane (10 g) and *p*-toluenesulphonic acid (0.35 g) were stirred and refluxed for 7 hours in benzene (160 ml) and ethyleneglycol (30 ml). A Dean–Stark trap was used to separate the water formed. The mixture was cooled, neutralized with sodium bicarbonate, and diluted with water; the benzene extract was separated, then washed with water, dried, and evaporated. The residue (12.5 g) crystallized from ether to provide 9.3 g (85%) of ketal, m.p. 148–150° (decomp.). Repeated recrystallizations from ether gave the pure compound, m.p. 150° with decomp. (the melting point depends on the rate of heating), $[\alpha]_D^{25}$ +66.4° (*c*, 0.76, ethanol), and $\lambda_{max}^{isooctane}$ 224 mμ (ε 12,900). Calculated for $C_{32}H_{46}O_7S$: C, 66.87; H, 8.07; S, 5.58. Found: C, 67.03; H, 8.12; S, 5.49. This compound has been described (4) to be amorphous with $\lambda_{max}^{ethanol}$ 225 mμ (ε 25,120).

3,20-Dioxo-Δ¹¹-pregnene

Potassium acetate (3.75 g), water (1.25 ml), and N-methylpyrrolidone (37.5 ml) were stirred and heated to 110°. After addition of 3,20-dioxo-12α-tosyloxypregnane (5 g), the temperature was kept at 115–120° for 3.5 hours. The reaction mixture was then poured into water, the products were extracted with ether, the solvent extract was washed, dried, and evaporated. The residue crystallized from ether–hexane to yield, in two crops, 1.77 g (55%) of material, m.p. 130–133°. Two recrystallizations gave the pure compound, m.p. 138.5–140° and $[\alpha]_D^{25}$ +94.0° (*c*, 0.424, ethanol).

When 3,20-dioxo-Δ^{11}-pregnene was dissolved in methanol containing traces of mineral acid, the corresponding 3-dimethylketal precipitated as white crystals. Repeated recrystallization from ether gave m.p. 137–139° and $[\alpha]_D^{26}$ +89.0° (*c*, 0.551, chloroform). Calculated for $C_{23}H_{36}O_3$: C, 76.62; H, 10.04; O, 13.31. Found: C, 76.45; H, 10.04; O, 13.49.

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Research and Development Laboratories,
Canada Packers Limited,
Toronto 9, Ontario.

REACTIONS OF BENZYLIDENETRIPHENYLPHOSPHORANE WITH SOME DICARBONYL COMPOUNDS

J. Parrick

The reactions of Wittig reagents with certain dicarbonyl compounds is of proved synthetic utility (1). We have found that the reaction of benzylidenetriphenylphosphorane (I) with some 1,2-dicarbonyl compounds gave 2-benzylidene ketones, even when 2 molar equivalents of the phosphorane were used.

Phosphorane (I) reacted with phenanthraquinone to give 9,10-dihydro-9-benzylidene-10-oxophenanthrene but no reaction was observed with anthraquinone, and only intractable tars were obtained with diacetyl, *p*-benzoquinone, and 1,2- and 1,4-naphthoquinone. A mixture of what was assumed to be the two geometrically isomeric 1,2,3-triphenylprop-1-en-3-ones was obtained from benzil.

The reaction of Wittig reagents with compounds having a carbonyl group in a heterocyclic ring has been little investigated. Isatin was found to react readily with 1 molar equivalent of benzylidenetriphenylphosphosphorane to give 3-benzylidene oxindole, the same as that prepared from oxindole and benzaldehyde. Thus, the two reactions give the same pure stereoisomer. Reduction of 3-benzylidene oxindole with lithium aluminum hydride gave 3-benzylindole.

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