5α-Cholestan-6-one Tosylhydrazone

This was prepared in the same manner as the 3-tosylhydrazone. Crystallized from ethanol-hexane it had m.p. 151-152° (dec.). Yield 1.3 g (92%) (Found: C, 73.6; H, 9.7; N, 5.25. Calc. for C_{24}H_{44}N_{2}O_{3}S: C, 73.6; H, 9.8; N, 5.05%).

5α-Cholest-1-en-3-one Tosylhydrazone

5α-Cholest-1-en-3-one (1.5 g, 3.9 mmoles) was dissolved in 10 ml glacial acetic acid and 1.5 g (8.1 mmoles) p-toluenesulphonylhydrazine added. The solution was kept at 30° for 5 hr. The product began to precipitate after about 5 min. The precipitate was filtered off, washed with cold hexane, and air-dried. Crystallization first from ethanol and then from chloroform-hexane gave 1.85 g (89%) of product, m.p. 168-170° (dec.) (Found: C, 72.5; H, 8.9; N, 5.3. Calc. for C_{24}H_{44}N_{2}O_{3}S·H_{2}O: C, 72.6; H, 8.24; N, 5.0%).

Preparation of the Steroid Olefins

The tosylhydrazone (2 g), dissolved in 20 ml dry tetrahydrofuran, was cooled in an ice-bath in an atmosphere of nitrogen and 8 ml 2Н-methyllithium in hexane (Aldrich) added dropwise with stirring. After 2 hr of reaction, the mixture was precipitated on ice, dilute HCl added, and the steroid extracted with pentane. To separate the olefins from the saturated by-product the reaction mixture was chromatographed on silica gel impregnated with 25% silver nitrate. The saturated alkylcholestanes eluted with cyclohexane, the olefins with n-hexane.

Ozonization of the Steroidal Olefins

About 50 mg of olefin were dissolved in 10 ml methylene chloride and ozone from a Welsbach ozonizer bubbled through the solution at -70° until the blue colour of dissolved ozone appeared. The solution was then evaporated in vacuum at as low a temperature as possible and the residue treated with a solution of 100 mg LiAlH_{4} in 10 ml tetrahydrofuran for 1 hr at room temperature. The excess hydride was destroyed by addition of ethyl acetate and aqueous acid. The steroid was extracted with ether, the solvent evaporated, and the residue transformed into the trimethylsilyl derivative in the usual way.

Corrigenda

VOLUME 22, NUMBER 10
Page 2255: Structure (IV) should have ring A aromatic

VOLUME 22, NUMBER 11
Page 2493, line 1: For 1,2-dienes read 1,3-dienes
Page 2494, third paragraph, line 1: For 1,4-dienes^{2} read 1,4-dienes^{1}
Page 2495, first paragraph, line 8: Between \( \log \epsilon 4 \cdot 13 \) and \( 3 \cdot 28 \) insert 295 μ
Page 2495, fourth paragraph, line 2: For nitrobenzene read nitrosobenzene
Page 2495, fourth paragraph, line 10: For 4127 read 4 \cdot 27 and for 2180 read 2 \cdot 80

VOLUME 23, NUMBER 1
Page 124: There should be no equivalent sign between formulae (12) and (13)