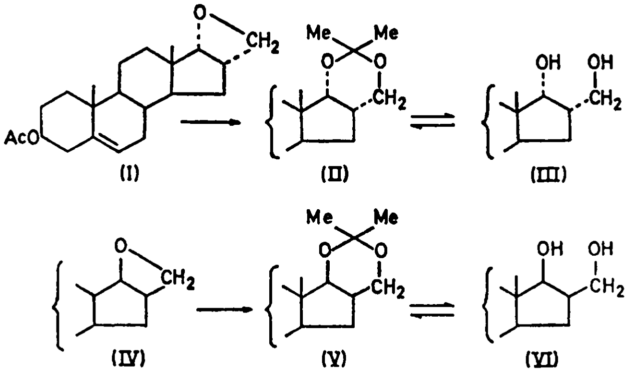
# Ring Expansion of Steroid Oxetans to Acetals

By Gy. Schneider,* I. Weisz-Vincze, A. Vass, and K. Kovács
(*Institute of Organic Chemistry, József Attila University, Szeged, Hungary*)

*Summary* Oxetan derivatives fused to the steroid skeleton react with carbonyl compounds in the presence of Lewis acids to give acetals with ring expansion.

Ethylene oxide and its substituted derivatives react with carbonyl compounds in the presence of Lewis acids[1] or in neutral medium[2] to give five-membered dioxolan derivatives.

In contrast, the four-membered oxetans readily undergo polymerisation under the effect of Lewis acids.[3]



(I) (II) (III)

(IV) (V) (VI)

We have found that oxetans fused to a steroid skeleton react in a different way and ring expansion occurs in the presence of Lewis acids to give six-membered dioxan derivatives in almost quantitative yield.

Thus, on adding dropwise a solution of 3-acetoxy-$16\alpha,17\alpha$-epoxymethyleneandrost-5-en-$3\beta$-ol (I) in dichloromethane to a solution of excess of acetone and boron trifluoride etherate or stannic chloride at room temperature, the less polar substance (II) is formed. In the case of boron trifluoride etherate the transformation proceeded within a few minutes, while with stannic chloride the reaction took 60 min. The product (II) was formed as the acetonide, m.p. 153°, $[\alpha]_D$ $-50 \pm 2°$ (*c* 0·5, $CHCl_3$). Treatment of (II) in methanol solution with aqueous toluene-*p*-sulphonic acid gave (III), which changed back to (II) with acetone diethyl acetal in the presence of boron trifluoride etherate catalyst. In alkaline methanol solution (II) was hydrolysed with loss of the 3-acetoxy-group, but the isopropylidene ring remained intact.

Under similar conditions, aliphatic and aromatic aldehydes such as acetaldehyde and benzaldehyde underwent a similar ring expansion reaction of oxetans to give the corresponding acetals. In the case of benzaldehyde the reaction was much slower.

(IV) behaved similarly to the α-compound (I) in the acetal formation reaction. It reacted with acetone in the presence of boron trifluoride etherate to give the acetonide (V), m.p. 172—174°, $[\alpha]_D$ $-17 \pm 2°$ (*c* 0·5, $CHCl_3$).

The same compound (V) was also obtained from the reaction of (VI) and acetone diethyl acetal.

We thank the Chemical Works of Gedeon Richter (Budapest) for support of this work.

(*Received, 5th April* 1972; *Com.* 565.)

---

[1] G. Willfang, *Ber.*, 1937, **70**, 2167; 1941, **74**, 145.
[2] F. Nerdel, J. Buddrus, G. Scherowsky, D. Klamann, and M. Fligge, *Annalen.*, 1967, **710**, 85.
[3] G. Dittus, in Houben-Weyl 'Methoden der organischen Chemie,' Bd. VI/3, G. Thieme Verlag, Stuttgart, 1965, pp. 493—515.