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Epoxyde Cleavage Reactions of $7\alpha,8\alpha$ - and $7\beta,8\beta$ -Epoxycholestanol Acetates*

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In a search for alternative synthetic route to 32-oxygenated sterol derivatives such as lanost-7-en-3,32-diol, $7\alpha,8\alpha$ - and $7\beta,8\beta$ -epoxycholestanol acetate (1 and 2) were subjected to various conditions of epoxyde cleavage. The *trans*-diaxial opening of the α -epoxyde 1 with lithium/ethylamine gave cholestan- $7\alpha,3\beta$ -diol, whereas cholestan- $8\beta,3\beta$ -diol was produced from the β -epoxyde 2 on reduction with lithium aluminum hydride. However, the *trans*-diaxial 8β -halo (or hydroxy)- 7α -ols were not obtained at all on treatment of the α -epoxyde 1 with various mineral acids or BF_3 -etherate in benzene. Under these conditions, the C-8 carbenium ion would be the intermediate, from which the 3β -acetoxy cholestan-7-one and a mixture of cholesta-6,8-, -7,9-, -7,14- and/or -8,14-dien- 3β -acetate, as well as 3β -acetoxycholest-8(9)- and -8-(14)-en- 7α -ol, were produced. The latter allylic alcohol, a possible synthetic precursor of 32-oxygenated sterol was prepared in 63% yield when benzene was replaced with tetrahydrofuran in the BF_3 -etherate-catalyzed reaction of the α -epoxyde 1.

* 本報告は *Chem. Pharm. Bull.*, 36, 2813 (1988) に発表.