

IONIC HYDROGENATION OF Δ^4 -3-KETOSTEROIDS IN ANDROSTANE SERIES

T. A. Serebryakova, A. V. Zakharychev,
S. N. Ananchenko, and I. V. Torgov

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The same as previously [1, 2], a high stereodirectivity of the ionic hydrogenation was observed in the reduction of the Δ^4 -3-keto grouping in the androstane series. Testosterone (I) and its derivatives (I) (II) and (III) when treated with CF_3COOH and Et_3SiH give predominantly compounds of the 5β -series (Table 1).

The 19-CH_3 group exerts an effect on the stereodirectivity of the reduction of the Δ^4 -3-ketosteroids. Thus, the yield of the 5α -epimer is increased to 40% in the reduction of 19-nortestosterone (IV). The reduction of the Δ^1 double bond occurs initially in the hydrogenation of $\Delta^{1,4}$ -androstadien-3-one, with the formation of the Δ^4 -3-keto compound, which is then hydrogenated further to the corresponding 5β -derivative, as mentioned above.

TABLE 1

Starting compound	Solvent	Time, h	Ratio* of isomers 5β : 5α , %
Testosterone (I)	CH_2Cl_2	44	86:14
Δ^4 -Androsten-3, 17-dione (II)	CH_2Cl_2	60	83:17
Testosterone propionate (III)	CH_2Cl_2	48	86:14
19-Nortestosterone (IV)	CF_3COOH	30	96:4
	CH_2Cl_2	42	60:40

* The ratio of the isomers was determined by GLC.

LITERATURE CITED

1. T. A. Serebryakova, A. V. Zakharychev, S. N. Ananchenko, and I. V. Torgov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1679 (1972).
2. T. A. Serebryakova, A. V. Zakharychev, R. N. Chigir, S. N. Ananchenko, and I. V. Torgov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1917 (1973).

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