

ISOPROPYL ALCOHOL AS A HYDROGEN DONOR IN THE CATALYTIC REDUCTION OF UNSATURATED STEROID COMPOUNDS

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The property of certain alcohols to be hydrogen donors in the catalytic hydrogenation of unsaturated compounds [1, 2] was used by us to reduce steroids of the androstane and estrone series.

On the example of testosterone and 19-nortestosterone we established that in aqueous isopropanol solution, in the presence of Raney Ni catalyst, Δ^4 -3-keto systems undergo exhaustive reduction to the corresponding androstanediols (Table 1).

TABLE 1

Compound	Time, h	Conversion, %	Ratio of isomers 5 β : 5 α , % *
Testosterone	3	100	62 : 38
Testosterone (in presence of Py)	6	95	80 : 20
19-Nortestosterone	3	100	33 : 67

* Here and in Tables 2 and 3 the ratio of the reaction products was determined by GLC.

TABLE 2

Compound	Time, h	Catalyst	Ratio of isomers 14 α : 14 β , % *
3-Methyl ether of 8(9), 14-bisdehydroestrone	6	PtO ₂	99 : 1
	2	Ni/Re	93 : 7
3-Methyl ether of 8(9), 14-bisdehydroestradiol	3	PtO ₂	100
	3	Ni/Re	90 : 10
Acetate of 3-methyl ether of 8(9), 14-bisdehydroestradiol	6	PtO ₂	98 : 2
	2	Ni/Re	87 : 13
Acetate of 3-methyl ether of 8(9), 14-bisdehydro-17 α -estradiol	8	PtO ₂	No reaction
	2	Ni/Re	33 : 67

TABLE 3

Compound	Time, h	Reaction products	Amount in mixture, %
3-Methyl ether of 6-dehydroestrone	3	3-Methyl ether of estrone	90
3-Methyl ether of 6-dehydroestradiol	4	3-Methyl ethers of estrone and estradiol	40 and 50
Acetate of 3-methyl ether of 6-dehydroestradiol	3	Acetate of 3-methyl ether of estradiol	92
3-Methyl ether of 9(11)-dehydroestrone	8	3-Methyl ether of estrone	25

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The derivatives of 8(9),14-bisdehydroestrone (or of estradiol) are reduced stereoselectively in aqueous isopropanol solution, in the presence of either Raney Ni or PtO₂ catalyst, to give the derivatives of 8(9)-dehydroestrone (or of estradiol), predominantly of the 14 α series, in an overall yield of ~90% (Table 2). Both the nature of the catalyst and the stereochemistry of the substituent at C¹⁷ affect the course of the reaction and its stereoselectivity. In compounds of the dehydroestrone and dehydroestradiol series the Δ^6 and $\Delta^{9(11)}$ double bonds are reduced in aqueous isopropanol solution, in the presence of either PtO₂ or Raney Ni catalyst, to give estrone (or estradiol) derivatives with a natural configuration (Table 3).

LITERATURE CITED

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