

EFFICIENT SYNTHESIS OF REARRANGED CHOLEST-13(17)-ENES

CATALYSED BY MONTMORILLONITE-CLAY

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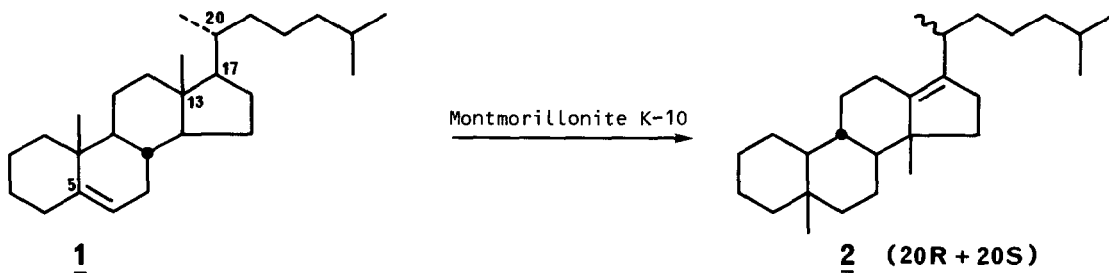
ABSTRACT.

Backbone rearranged cholest-13(17)-enes are obtained quantitatively from cholest-5-ene in the presence of K-10 montmorillonite clay.

Past studies^{1,2} have shown that cholest-5-ene 1 undergoes a backbone rearrangement to a mixture of 20R and 20S rearranged cholest-13(17)-enes 2 (5 β ,14 β -dimethyl-18-19-dinor-8 α ,9 β ,10 α -cholest-13(17)-enes) when heated at reflux in acetic acid in the presence of toluene-p-sulfonic acid. The reported yields were in the range of 50% and the two isomers could be separated on AgNO₃-silica gel³.

In the present study we showed that it is possible to obtain 2 nearly quantitatively as a 1:1 mixture of 20R and 20S isomers by treating 1 for 1 h. in cyclohexane at room temperature in presence of K-10 montmorillonite clay. A simple decantation followed by a flash chromatography⁴ over AgNO₃-silica gel delivered the pure isomers.

Alternatively the montmorillonite can also be deposited on top of the AgNO₃-silica gel column and a solution of cholest-5-ene in cyclohexane added. After 1 h. the isomers of 2 can then be separated as described above.



In our experience this method is by far the most convenient way of preparing rearranged cholest-13(17)-enes ; it is nearly quantitative and operative on the gram scale.

Experimental.

Typically 750 mg of cholest-5-ene, 1⁵, pure by GC, were added to 750 mg of dry montmorillonite K-10 (FLUKA) in 6 ml of dry cyclohexane in a round bottom flask and the mixture stirred for 1 h. at room temperature. After removing the clay by decantation and washing it twice with cyclohexane, the solution was evaporated to yield an oily product (739 mg) which displayed only two peaks in GC in an approximately 1:1 ratio. Separation of the two isomers performed by flash chromatography⁴ on a 10% AgNO₃-silica gel column (20 x 4 cm ; Kieselgel 60, 0.040-0.063 mm, MERCK) with hexane as an eluent yielded 343 mg of the first eluting 20S isomer and 349 mg of the 20R isomer, both pure by GC (total yield of 20R + 20S isomers : 92%). Spectral and analytical data of the two isomers were in agreement with those reported for 20R and 20S rearranged cholest-13(17)-enes 2¹⁻³.

References.

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