

TRITIATION OF STEROIDS BY EXCHANGE WITH TRITIATED ALCOHOLS

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DURING the tracer investigation of the isomerization of bile acids in amyl alcohol-t solution of sodium amyloxide the incorporation of tritium into the unreacted hyodeoxy cholic acid has been observed³. In a number of papers a simple transfer of deuterium from labeled t-butanol-d onto the tertiary carbon atoms of organic compounds in the presence of alkoxide ions has been reported⁴. Exchange reactions between tritiated water and the hydrogen atoms of organic molecules also take place in the presence of

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³ I.Weisz, unpublished results.

⁴ D.J.Cran and coworkers, J.Amer.Chem.Soc. 83, 3683 (1961); 84, 4358 (1962).

heterogenous catalysts⁵.

It has been found in our Laboratory, that tritium exchange between certain steroids and aliphatic alcohols containing tritium in their hydroxyl groups also taken place without the presence of any basic catalysts. 500 mg progesterone was dissolved in 10 ml of *n*-amyl alcohol and 3 ml of H₂O (10 mCi/ml) and refluxed for 2 hrs. The products were separated by chromatography and then re-crystallised. The pure compound showed a constant specific activity of 3400 cpm/mg⁶. The specific activity of this progesterone did not decrease during boiling for 1 hr. in ethanol or 15 min. in methanol-water in the presence of sodium carbonate, but it decreases to about one-third value by boiling in the same solution for 5 hrs.

These experiments show that the remaining tritium is most probably located in other positions than the α -methylene groups to the carbonyl function.

By repeating the labeling procedure twice the specific activity of progesterone sample rose up to 10800 cpm/mg.

⁵ B.E.Gordon and J.A.Van-Klaveren, Int.J.Appl.Rad. and Isotopes 13, 103 (1962).

⁶ Measured by EKO liquid scintillation counter. Counting efficiency 2,45 %.

This spontaneous exchange reaction may be promoted by alkaline carbonates or in case of anhydrous tritiated ethanol or amyl-alcohol either by alkoxide ions or by aluminium oxide.

An aliquot sample of tritiated progesterone has been converted into tritiated corticosterone and aldosterone by means of incubation with adrenal gland quarters of rats.

Similar results have been achieved in case of cholesterol and hydrocortisone.

Investigations on the position of incorporated tritium as well as a further study of its mobility are in progress.