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An Improved Procedure for the Preparation of Very Pure Ethanol-OD

Short Communication

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Changed molar ratio of starting materials and prolonged reaction times in the deuterolysis of tetraethylorthosilicate gave yields of pure (> 99.5%) ethanol-OD (relative to starting D_2O) nearly twice of that of a literature procedure.

*(Keywords: Deuterolysis; Ethanol-*OD*; Methanol-*OD*; Tetraethylorthosilicate)*

*Eine verbesserte Vorschrift zur Herstellung von hochreinem Ethanol-*OD
(Kurze Mitteilung)

Verändertes molares Verhältnis der Ausgangsverbindungen und längere Reaktionszeit bei der Deuterolyse von Orthokieselsäuretetraethylester führt zur nahezu zweifachen Ausbeute einer Literaturmethode an reinem (> 99.5%) Ethanol-OD (relativ zu eingesetztem D_2O).

In the course of the synthesis of multideuterated heterocyclic compounds[1] we needed large amounts of completely D_2O-free ethanol-OD. Of the various published[2] syntheses the procedure of *Pasto* and *Meyer*[3] has the advantage of simplicity and of relatively inexpensive starting materials: tetraethylorthosilicate (0.5 mol) is reacted with 2 mol of D_2O and the resulting ethanol-OD is distilled off at reduced pressure. The product was reported to contain 0.2% D_2O (by GLC).

In our hands this method showed a number of shortcomings: 1. The speed of the uncatalyzed deuterolysis varied, but occasionally was very slow. This could be overcome by the addition of catalytic amounts of thionyl chloride to the reaction mixture[4]. 2. The resulting ethanol-OD contained varying amounts of D_2O (> 1%); in every instance attempted drying by $Mg/Mg(OC_2H_5)_2$ was quenched by the D_2O. 3. With the proposed[3] molar ratio only half of the deuterium of the used D_2O is found in the ethanol-OD. The rest remains in the various silicic acids [between $Si(OD)_4$ and SiO_2] or is reconverted to D_2O. Since D_2O is the most expensive component of the procedure we attempted to find modifications for eliminating these disadvantages.

A change of the molar ratio to 1.2 mol $Si(OC_2H_5)_4$ vs. 2 mol D_2O, catalyzation with $SOCl_2$ and prolonged reaction times ($\geqslant$ 4 weeks) resulted in a yield of $> 90\%$ ethanol-OD (relative to starting deuterium), nearly twice the amount of the original procedure[3]. The product was found by GLC to be essentially free of D_2O; traces could be eliminated with $Mg/Mg(OC_2H_5)_2$.

The procedure of *Pasto* and *Meyer* has been used for the synthesis of methanol-OD[5]. Employing the modifications presented above we obtained (with tetramethylorthosilicate) comparable yields of D_2O-free CH_3OD.

Preparation of Ethanol-OD. To 250 g (1.2 mol) of tetraethylorthosilicate* 40 g (2 mol) of D_2O were added, and the mixture was cooled to 0°. A few drops $SOCl_2$ were added, and the mixture was stirred for 1 hour at 0°, then 2 hours at ambient temperature and finally at reflux (bath temp. 100°) for 4 weeks. After 10 days another few drops of $SOCl_2$ were added**. When the deuterolysis was complete, the mixture was distilled at ~ 6–2 kPa into a receiver cooled with dry ice/isopropanol. Average yield was 175 g (3.7 mol). D_2O-content by GLC (column: 2 mm i. d. glass; 10% Carbowax 400 on Chromosorb W, acid washed, 80–100 mesh; carrier gas He; thermoconductivity detector) was $\ll 0.5\%$. After drying over Mg (1.2 g/100 ml *Et*OD, activated with 0.2 ml CCl_4) for 12 hours and distillation no D_2O could be detected.

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* The commercial material was found to contain ethanol and toluene, and was distilled over a fractionating column before use.

** The progress of the deuterolysis can be checked by drawing samples and testing them by GLC after distillation on a *Kugelrohr* apparatus.

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