

Chlorosulfate (III) was obtained in 18.4% yield, bp 135-137°C,  $d_4^{20}$  1.796,  $n_D^{20}$  1.3990. Found: C 10.75; Cl 21.25; F 34.30; S 19.27%.  $C_3Cl_2F_6O_3S_2$ . Calculated: C 10.81; Cl 21.32; F 34.23; S 19.22%.

Fluorosulfate (IV) was obtained in 2.8% yield, bp 119-120°C,  $d_4^{20}$  1.776,  $n_D^{20}$  1.3588 [5].

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#### REACTIONS OF ALIPHATIC ALDEHYDES AND ALCOHOLS CATALYZED BY A GIANT PALLADIUM CLUSTER

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The oxidation-reduction disproportionation of acetaldehyde (I) to ethanol and acetic acid proceeds in neutral aqueous solutions of binuclear rhodium iridium, and ruthenium complexes [1]. We have discovered that the giant micelle-like palladium cluster with the idealized formula  $[Pd_{561}Phen_{60}](OAc)_{180}$  (II) [2] catalyzes the Tischenko disproportionation of (I):



The reaction rate at 60°C in an argon atmosphere with 2-4% (I) in ethanol is about 1000 moles/mole (II)·h. In addition to the disproportionation, (I) is also acetalized: the yield of  $MeCH(OEt)_2$  is 30-50% relative to converted (I). In an oxygen atmosphere, (I) is accumulated due to the reaction



also catalyzed by cluster (II) in addition to the above-mentioned reactions. The oxidation, which is accompanied by subsequent disproportionation to the ester and acetalization of the aldehyde formed, proceeds in the presence of (II) also in the case of 1-propanol and other higher alcohols. However, neither  $CH_2O$  nor formalin were found upon the oxidation of methanol in the presence of (II), and the only product of the conversion is  $HCO_2Me$ . Secondary alcohols are oxidized to ketones, which do not undergo further transformations. Thus, cluster (II) catalyzes not only the oxidative substitution of the  $\alpha$ -hydrogen atom in alcohols but also the acetalization of aldehydes and their disproportionation to give esters.

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