ELECTROPHILIC REARRANGEMENT OF TRICHLOROALLYL ALCOHOL

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L. S. German and N. I. Delyagina

The rearrangement of trifluorovinylcarbinols to the acid fluorides of α -fluoro- α , β -unsaturated acids with the loss of hydrogen fluoride has been described by Knunyants et al. [1]. Such a reaction has not been reported for trichlorovinylcarbinols.

In the present work, we found that trichloroallyl alcohol, upon heating with H_2SO_4 , rearranges to the acid chloride of α -chloroacrylic acid. Apparently, the trichloroallyl cation is initially formed in this case. Under the reaction conditions, this species may be stabilized by reacting with H_2SO_4 at the dichloromethylene group. The subsequent elimination of chlorosulfonic acid shifts the reaction toward the formation of (I):

Shifts the reduction $\stackrel{H^+}{\longrightarrow} CCl_2 = CCl - CH_2 - \stackrel{\bullet}{\rightarrow} -H \xrightarrow[]{-H_2 \cap} \stackrel{H^+}{\longrightarrow} CCl_2 = CCl - CH_2 - \stackrel{\bullet}{\rightarrow} -H \xrightarrow[]{-H_2 \cap} \stackrel{H^-}{\longrightarrow} \stackrel{H^+}{\longrightarrow} \stackrel{H^+}{\longrightarrow} CCl_2 = CCl - CH_2 - \stackrel{H^-}{\longrightarrow} -H \xrightarrow[]{-H^+} \stackrel{H^-}{\longrightarrow} \stackrel{H^-}{\longrightarrow} \stackrel{H^+}{\longrightarrow} \stackrel{H^+}{\longrightarrow} \stackrel{H^+}{\longrightarrow} CCl_2 = CCl - CH_2 - \stackrel{H^-}{\longrightarrow} -OH \xrightarrow[]{-H^-} \stackrel{H^-}{\longrightarrow} \stackrel{H^-}$

A sample of 11 g trichloroallyl alcohol was added gradually to 10 ml conc. H_2SO_4 and then heated in vacuum (18 mm); a mixture of compounds was distilled off at 80°C bath temperature. Distillation of the mixture gave 3.9 g (59%) acid chloride of α -chloroacrylic acid, bp 26-29°C (20 mm), n_D^{20} 1.4742 [2], and also 2.5 g of starting trichloroallyl alcohol.

LITERATURE CITED

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A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, p. 951, April, 1986. Original article submitted November 10, 1985.