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PRELIMINARY NOTE

Dehydration of 2-Trifluoromethyl-3,3,3-trifluoropropanol with Base*

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SUMMARY

2-Trifluoromethyl-3,3,3-trifluoropropanol gave 2-trifluoromethyl-3,3,3-trifluoroprop-1-ene in good yield by the action of base under mild conditions.

During the study of making 2-trifluoromethyl-3,3,3-trifluoroprop-1-ene (1), we found a base, especially potassium hydroxide, acted unusually as a dehydrating reagent upon 2-trifluoromethyl-3,3,3-trifluoropropanol (2) under mild conditions to yield (1).

Compound (1) is a useful monomer for the synthesis of fluoropolymers. It is polymerized itself and also is used as a comonomer in the synthesis of various fluoropolymers [1].

It is an unexpected reaction that a base acts as a dehydrating reagent for such a polyfluoroalcohol.
Usually dehydration of polyfluoroalcohols is known to be difficult and only drastic conditions using reagents such as phosphorus pentaoxide [2] or sulphuric acid [3] give the dehydrated compounds.

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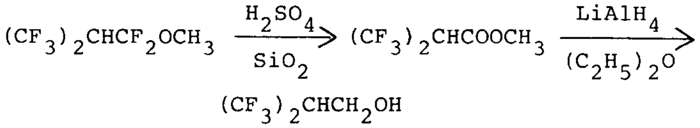
The starting alcohol was synthesized in good yield by the following route:



$$(CF_3)_2CHCF_2OCH_3 \xrightarrow[SiO_2]{H_2SO_4} (CF_3)_2CHCOOCH_3 \xrightarrow[(C_2H_5)_2O]{LiAlH_4} (CF_3)_2CHCH_2OH$$

$(CF_3)_2CHCOOCH_3$

$(CF_3)_2CHCF_2OCH_3$; 34.8 g (0.15 mole), H_2SO_4 ; 6 g, SiO_2 ; 3.5 g (0.058 mole), Reaction temperature ; 65-90 °C, Reaction time ; 1 hr., Yield ; 30 g (95%).
BP. 88 °C ; MS, m/e = 210(M^+), 190(M^+-HF), 179(M^+-OCH_3) ; ^{1}H NMR ($CDCl_3$) ; δ 3.9(s,CH_3), 3.8-4.3(m,CH), ^{19}F NMR (CCl_4, ext. TFA) ; δ 12.7(d,CF_3, J = 8.5 Hz).

$(CF_3)_2CHCH_2OH$

$(CF_3)_2CHCOOCH_3$; 50 g (0.238 mole), $LiAlH_4$; 6.5 g (0.171 mole), ether ; 150 ml, Reaction temperature ; -15∿-10 °C, Reaction time ; 2.5 hrs. Yield ; 30.3 g (70%).
BP. 102 °C ; MS, m/e = 181(M^+-H), 163(M^+-F), 113(M^+-CF_3), 31 (CH_2OH), ^{1}H NMR ($CDCl_3$) ; δ 3.7(d,CH_2 J = 4.5 Hz), 2.6-3.2 (m,CH), 3.0(s,OH), ^{19}F NMR (CCl_4, ext. TFA) ; δ 12.6(d,CF_3, J = 8.5 Hz).

The dehydration was carried out using a large excess of powdered base with or without solvent at room temperature to 50 °C. As the base potassium hydroxide gave the best yield and sodium hydroxide was next, as shown in Table 1.

Table 1

Dehydration of compound (2) with various bases

Base	KOH	NaOH	LiOH	$Ca(OH)_2$
Yield (%)	57.9	26.4	0	0

$(CF_3)_2CHCH_2OH$; 1.1 mmole, Base ; 11 mmole
CCl_4 ; 5 ml, Reaction temperature ; 20 °C,
Reaction time ; 5 min.

$(CF_3)_2C{=}CH_2$ (1)

BP. 14 °C ; MS, m/e = 164(M^+), 145(M^+-F), 95(M^+-CF_3), ^{1}H NMR ($CDCl_3$) ; δ 6.3(s,CH_2) ; ^{19}F NMR (CCl_4, ext. TFA) ; δ 13.5(s,CF_3).

Table 2

Dehydration of compound (2) with various solvents

Solvent	CCl_4	$CHCl_3$	CH_2Cl_2	CH_3CHCl_2	CH_2ClCH_2Cl
Yield (%)	57.9	60.7	66.4	80.0	45.1

Solvent	$CHCl_2CH_2Cl$	$CHCl_2CHCl_2$	CH_2ClCCl_3	$CCl_2{=}CHCl$
Yield (%)	54.6	52.9	57.0	61.2

Solvent	$CF_2ClCFCl_2$	Dioxane	n-Propanol	NEAT
Yield (%)	52.9	44.8	0	52.0

$(CF_3)_2CHCH_2OH$; 1.1 mmole, KOH ; 11 mmole, Solvent ; 5 ml
Reaction temperature ; 20 °C, Reaction time ; 5 min.

To extend the procedure to other polyfluoroalcohols, we tried to dehydrate $(CF_3)_2CFCH_2CH_2OH$ and $(CF_3)_2CFHCH_2OH$ but these compounds did not give the dehydrated products under the same reaction conditions.

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