Journal of Fluorine Chemistry, 8 (1976) 89–92

Received: June 9, 1975

SHORT COMMUNICATION

The Preparation of Perfluorinated Esters of Fluorine containing Tertiary Alcohols

N.J. BASSETT, G.H. ISMAIL, P. PIOTIS and B. TITTLE

Chemistry Department, University of the Witwatersrand, Jan Smuts Avenue,
Johannesburg (South Africa)

The reaction of an aromatic lithium reagent, LiR, with a perfluoroacid anhydride $(RfCO)_2O$, in ether solution at low temperatures, produces esters of composition $Rf(R)_2C\text{-}O\text{-}\underset{\overset{\|}{O}}{C}\text{-}Rf$ in addition to the expected ketone $Rf\underset{\overset{\|}{O}}{C}R$. Mixed esters of composition $Rf'(R)_2C\text{-}O\text{-}\underset{\overset{\|}{O}}{C}\text{-}Rf$ may be prepared by starting with a ketone $Rf'\underset{\overset{\|}{O}}{C}\,R$ and reacting with a lithium reagent LiR followed by perfluoroacid anhydride $(RfCO)_2O$. Hydrolysis of the esters provides a convenient route to tertiary alcohols of composition $Rf(R)_2C\text{-}OH$.

Recent publications have described the preparation of perfluoroesters of perfluorinated tertiary alcohols [1, 2, 3]. In this paper we describe the preparation of perfluoroesters of partially fluorinated tertiary alcohols of composition $Rf(R)_2C\text{-}OH$ and $Rf.R.R'.C\text{-}OH$.

Results and discussion

The reaction of an aromatic lithium reagent LiR with excess of a perfluoroacid anhydride $(RfCO)_2O$ in ether solution at low temperatures produces an ester of composition $RfR_2C\text{-}O\text{-}\underset{\overset{\|}{O}}{C}\text{-}Rf$ in addition to the expected ketone $Rf\underset{\overset{\|}{O}}{C}R$. The reaction appears to be general for perfluoroacid anhydrides and aromatic lithium reagents.

Esters containing mixed groupings may be prepared by starting with a ketone of composition $Rf\underset{\overset{\|}{O}}{C}R$. Reaction with an aromatic lithium reagent LiR' followed by reaction with a perfluoroacid anhydride $(Rf'CO)_2O$ at low temperatures in ether produces an ester of composition $Rf.R'.R.C\text{-}O\text{-}\underset{\overset{\|}{O}}{C}\text{-}Rf'$.

By this technique esters containing various Rf and R groupings have been prepared.

Hydrolysis of the esters provides a convenient route to the fluorine containing tertiary alcohols.

The structure of the ester produced by the reaction of Li phenyl with perfluoroacetic anhydride has been proved by ^{1}H and ^{19}F nmr spectroscopy, infrared spectroscopy, mass spectrometry and hydrolysis to the tertiary alcohol, a known compound of melting point 74°C [4]. Mass spectrometry indicates a parent ion current of m/e 348. This is in contrast to perfluorinated esters which are reported not to give a parent ion [5]. The infrared spectrum of the ester indicates a C=O stretching frequency at 1800 cm^{-1}. Spectroscopic data for the various esters and derivative tertiary alcohols are given in the experimental section.

Experimental

Preparation of 1,1,1-trifluoro-2,2-diphenyl ethyl trifluoracetate (nc)

In a typical preparation lithium phenyl was prepared from lithium (2.8 g) and bromobenzene (36.0 g) in diethyl ether (150 ml). The phenyl lithium solution was then cooled to -50°C and trifluoracetic anhydride (42.0 g) in diethyl ether (100 ml) was added dropwise over one hour. The final reaction product was quite clear. All volatiles were removed under vacuum and the resulting paste hydrolysed with 10 % sulphuric acid (140 ml). The resulting oil was extracted into ether, washed with sodium bicarbonate solution and then dried. The ether was distilled off to give a crude product (20.8 g). This was distilled under vacuum to yield $CF_3\underset{\overset{\|}{O}}{C}C_6H_5$ (6.4 g) and $CF_3(C_6H_5)_2C\text{-}O\text{-}\underset{\overset{\|}{O}}{C}\text{-}CF_3$ (7.6 g). There was a non-distillable residue as yet uncharacterised. The infrared spectrum of the ester indicated C=O at 1800 cm^{-1} and C-F at 1150 cm^{-1}, 1170 cm^{-1} and 1225 cm^{-1}. Mass spectrometry indicated a parent ion at m/e 348. ^{19}F nmr spectroscopy indicated two absorbtions of equal intensity at 70.1 ppm and 76.0 ppm with respect to $CFCl_3$ as standard.

Hydrolysis to 1,1,1,-trifluoro-2,2-diphenyl ethanol

The ester (2.0 g) was refluxed for two hours with ethanol (100 ml) containing KOH (3 g). The resulting white solid was filtered off. The melting point of 74°C was in agreement with the literature value for 1,1,1-trifluoro-2,2-diphenyl ethanol [4].

^{19}F nmr spectroscopy indicated one absorption at 75 ppm relative to $CFCl_3$.

Preparation of 1,1,1-trifluoro-2,2-di-p-tolyl ethyl trifluoroacetate (nc)

Procedure was as in above preparation: lithium (2.7 g) was reacted with p-bromotoluene (30.0 g) followed by reaction with trifluoracetic anhydride (42.0 g). The product ester was isolated as previously described b.p. 114°C at 10 mm Hg, (9.8 g). IR spectroscopy indicated C=O at 1808 cm^{-1} and C-F multiplet centred at 1180 cm^{-1}.

Hydrolysis to 1,1,1-trifluoro-2,2-di-p-tolyl ethanol (nc)

The ester (1.8 g) was hydrolysed with ethonolic KOH (100 ml). The resulting white solid melted over the range 130-135°C.

^{19}F nmr indicated one absorption at 65 ppm with respect to $CFCl_3$.

Preparation of 1,1,1-trifluoro-2-phenyl-2-p-tolyl ethyl trifluoracetate (nc)

Lithium phenyl was prepared from lithium (1 g) and homobenzene (12 g) in diethyl ether (150 ml). The reaction mixture was cooled to 0°C and the ketone $CF_3\underset{O}{C}C_6H_4CH_3$ (13 g) added dropwise over one hour. At the end of this period the reaction vessel was allowed to warm to room temperature and then cooled to -50°C. Trifluoracetic anhydride (15 g) in diethyl ether (75 ml) was then added slowly. The final product was a clear yellowish solution. This product was then treated as described above to isolate the ester (5.6 g). B.p. 92°C at 10 mm Hg. ^1H nmr indicated aromatic protons centred at τ 7.23 and CH_3 protons at τ 2.25. These were in intensity ratio of 3:1.

^{19}F nmr indicated two absorptions of equal intensity at 71.0 ppm and 76.0 ppm shift from $CFCl_3$ standard.

IR spectroscopy indicated a C=O frequency at 1804 cm^{-1} and C-F absorptions at 1130 cm^{-1}, 1175 cm^{-1} and 1230 cm^{-1}.

Hydrolysis of ester to 1,1,1-trifluoro-2-phenyl-2-p-tolyl ethanol (nc)

Ester (2.0 g) was hydrolysed with ethanolic KOH (100 ml). The resulting tertiary alcohol was precipitated in colloidal form by adding water followed by extraction into ether. The ether solution was dried and the ether removed under vacuum to give the tertiary alcohol (1.2 g). It was not possible to crystallise this tertiary alcohol, possibly due to traces of ethanol and ether.

IR spectroscopy indicated OH group 3540 cm^{-1} and C-F at 1160 cm^{-1}. ^{19}F nmr of the tertiary alcohol indicated a single absorption at 75 ppm from $CFCl_3$ standard. ^1H nmr indicated aromatic protons multiplet centred at τ 7.15 and CH_3 singlet 2.2 in the ratio of 3:1. A broad absorption at τ 4.0 exchanged readily with D_2O.

Preparation of 1,1,1-trifluoro-2,2-diphenyl ethyl perfluoro-propionate (nc)

Lithium phenyl was prepared by reacting bromobenzene (20 g) with lithium (2 g) in ether solution. Reaction was incomplete and 0.8 g lithium was recovered). This was reacted at 0°C with ketone $CF_3\underset{\overset{\|}{O}}{C}C_6H_5$ (25 g) in ether solution over a period of 1 hour. After warming up to room temperature for 15 minutes the reaction mixture was cooled to -50°C and perfluoropropioric anhydride (44 g) in ether solution added dropwise over a period of 1 hour. After allowing the clear solution to stand overnight the ester was isolated as described above, distilling at about 90°C at 5 mm Hg (8.2 g).

IR spectroscopy of the ester indicated C=O at 1802 cm^{-1} and C-F at 1140 cm^{-1}, 1175 cm^{-1}, 1225 cm^{-1} and 1290 cm^{-1}.

Preparation of 1,1,1-trifluoro-2-phenyl-2-p-tolyl ethyl perfluoro-propionate (nc)

The procedure was as in the previous preparation except that p-bromotoluene was used in place of bromobenzene. Quantities employed were lithium (1.5 g), p-bromotoluene (18.5 g), ketone $CF_3\underset{\overset{\|}{O}}{C}C_6H_5$ (13.0 g) and perfluoropropionic anhydride (23 g), yielding ester (14 g). B.p. 100°C at 5 mm Hg.

IR spectroscopy indicated C=O at 1800 cm^{-1} and C-F at 1140 cm^{-1}, 1170 cm^{-1}, 1225 cm^{-1} and 1290 cm^{-1}.

^1H nmr indicated aromatic protons centered at τ 7.23 and CH_3 group at τ 2.2 in the ratio of 3:1.

The authors wish to thank the CSIR for the ^{19}F nmr spectra.

1 I.S. Chang, J.T. Price, A.J. Tomlinson and C.J. Willis, Canad. J. Chem., 50 (1972) 512.

2 P.G. Johnson and B. Tittle, J. Fluorine Chem., 3 (1973/74) 1.

3 Nyal S. Walker and Darryl D. Desmarteau, J. Fluorine Chem., 5 (1975) 135.

4 T.F. McGrath and R. Levine, J. Amer. Chem. Soc., 77 (1955) 3656.

5 A. Majid and Jean'ne M. Shreeve, J. Org. Chem., 38 (1973) 4028.