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Fluorinated Ketenedithioacetals.
5. A New Synthesis of Perfluoroketenedithioacetals from alkyl perfluoroalkanedithiocarboxylates

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Abstract: The title compounds were synthesized by reaction of organometallic reagents with alkyl perfluoroalkanedithiocarboxylates via a thiophilic attack and a subsequent elimination of the α-fluoride.

Thiocarbonyl derivatives are able to react with aliphatic organometallic reagents via a thiophilic attack giving rise to sulfur stabilized carbanions.[1] Such reactivity has found several applications in the case of dithioesters.[2,3] The presence of a withdrawing perfluoroalkyl group enchance the electrophilicity of the thiocarbonyl function. As an example, alkyl perfluorodithiocarboxylates are very efficient dienophiles.[4] We assumed that these dithioesters would be good candidates for thiophilic organometallic addition, owing to the possibility of a subsequent fluoride elimination which would be a further driving force for the reaction. Such process would be an interesting methodology for the preparation of perfluoroketenedithioacetals, since a new synthesis of the parent dithioesters has just been proposed.[4b] Perfluoroketenedithioacetals, previously prepared from perfluoroaldehyde hydrates, are versatile intermediates for the synthesis of various fluorosubstituted compounds.[5] A complementary methodology for their synthesis would be useful especially for higher homologues for which perfluoroaldehydes are not commercially available. We describe in this paper such synthesis via the reaction of organomagnesium and lithium reagents with alkyl perfluoroalkanedithiocarboxylates.

Dithioesters **1a**-**1e** reacted in very mild conditions (-50°C) with organomagnesium reagents to give the corresponding ketenedithioacetals **2a**-**2e** in good yields (fig 2, table I).The reaction worked with lithium reagent as well, as examplified by the preparation of compound **2f** from reaction with butyllithium.

As a typical procedure, an equimolar amount of RMgBr (R = Et, Pr) (solution in Et_2O) or Buli (solution in hexane) was added to a solution of 0.005 mol of the dithioester **1** in diethyl ether (15 ml) cooled to -50°C. The mixture was stirred 0.5 h at -50°C and slowly heated to 20°C (2 h). The reaction solution was washed with water (2x10 ml) and dryied over sodium sulfate. After removing the solvent compound **2** was distilled in vacuo.[6]

In contrast to a previously reported synthesis of compounds **2**,[5a] this methodology allows to prepare unsymetrical dithioacetals. In such case a mixture of two diastereomers (1/1.5-2) was obtained. The overal transformation can be viewed as a S_N' process begining by the thiophilic attack. Although we have not carried out a kinetic study, a concerted process is probable as previous attempt to trap an intermediate anion failed.[7]

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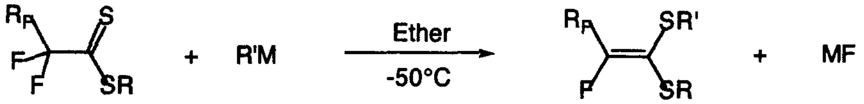

Starting compound	R_F	R	R'	M	Ketene dithioacetal	Yield %
1a	F	$CH_2C_6H_5$	C_2H_5	MgBr	2a	86
1b	CF_3CF_2	C_2H_5	C_2H_5	MgBr	2b	69[5a]
1c	CF_3CF_2	$CH_2C_6H_5$	C_2H_5	MgBr	2c	70
1d	CF_3CF_2	n-C_3H_7	C_2H_5	MgBr	2d	60
1e	$H(CF_2)_3$	n-C_3H_7	n-C_3H_7	MgBr	2e	70[5b]
1a	F	$CH_2C_6H_5$	n-C_4H_9	Li	2f	69

The products **2** were isolated by distillation. **It is crucial to remove the magnesium salts before distillation** to avoid a thermal transformation. In the course of the first experiment with organomagnesium reagent, the crude was distilled without any aqueous treatment, in order to simplify the procedure. The distillate recovered a deep red color characteristic of a thiocarbonyl group. According to preliminary investigations the compound formed is a new dithioester containing bromine.[8] After removing the salts by washing with water, distillation gave the pure ketenedithioacetal in good yields without transformation.

These results constitutes a new complementary methodology for the synthesis of perfluoroketenedithioacetals which allows the preparation of unsymetrical analogues. A new reaction of these perfluoroketenedithioacetals with magnesium bromide was found, which is currently under investigation.

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6 Compounds **2** were characterized by NMR and elemental analysis. They have spectral features in accordance with the already reported compounds **2b**[3a] and **2e**[3b]. Compounds **2c**, **2d** and **2f** were isolated as a mixture of Z and E diastereomers (1/1.5-2).

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8 The same compound was obtained by warming the pure ketene dithioacetal in the presence of $MgBr_2$. According to preliminary NMR analysis, it is probably an α,β-unsaturated compound resulting from a former bromide attack on the alkyl group and displacement of a β-fluorine.

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