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PRELIMINARY NOTE

The Electrophilic Thionation and Chlorination of Polyfluorinated α-Keto Esters

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SUMMARY

The methyl ester of trifluoropyruvic acid reacts with phosphorus pentachloride at the keto carbonyl as well as at the ester carbonyl group. The reaction of polyfluorinated α-keto esters with Davy's reagent occurs regioselectively at the keto carbonyl and is accompanied by reduction and thiomethylation.

Interaction of polyfluorinated α-keto esters with electrophilic reagents has not been studied previously. In this paper we describe the electrophilic chlorination and thionation of polyfluorinated α-keto esters with phosphorus (V)-containing reagents, i.e. phosphorus pentachloride, tetraphosphorus decasulphide and derivatives of perthiophosphonic acid anhydrides, namely 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane 2,4-disulphide (Lawesson's reagent) and 2,4-bis(methylthio)-1,3,2,4-dithiadiphosphetane 2,4-disulphide (Davy's reagent). Both of the last two are more efficient then tetraphosphorus decasulphide [1-3].

The reaction of pyruvic acid with phosphorus pentachloride yields the acid chloride of 2,2-dichloropropionic acid [4], while the ethyl ester of pyruvic acid gives a mixture of tri- and tetra-chloropropionic esters [5]. So no reactions at carboxyl or ester carbonyl functions were realized.

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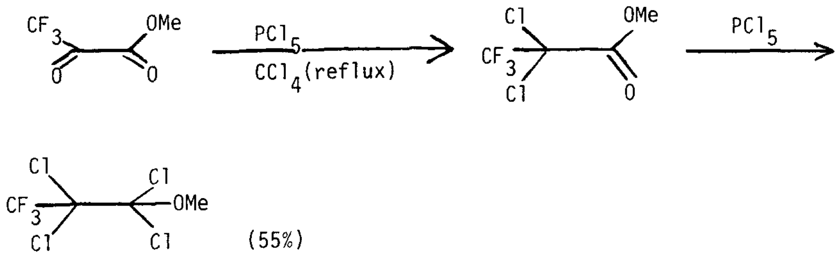
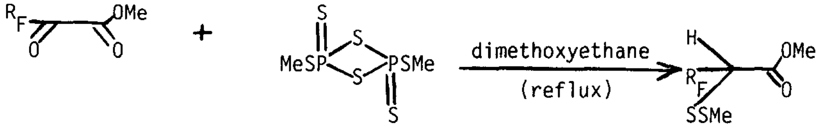
Treatment of the methyl ester of trifluoropyruvic acid with phosphorus pentachloride in boiling carbon tetrachloride solution leads to 3,3,3-trifluoro-1,1,2,2-tetrachloro-1-methoxypropane. Thus both carbonyl groups react. We studied the reaction using IR spectroscopy. The absorption band of keto group was found to disappear first.



Data are lacking on the thionation of α-keto esters with tetraphosphorus decasulphide or Lawesson's/Davy's reagents. Neither tetraphosphorus decasulphide nor Lawesson's reagent react with polyfluorinated α-keto esters at temperatures below 140 °C (polyfluorinated α-keto esters are unstable above this temperature). However, the more efficient Davy's reagent reacts with polyfluorinated α-keto esters at the acceptable temperature of 80 °C. In this case attack occurs regioselectively at the keto carbonyl group and is accompanied by reduction, presumably hydride transfer from solvent. The esters of α-methyldithiofluorocarboxylic acids, but no expected [1-3] esters of α-thioxofluorocarboxylic acids, are formed in this reaction.



$R_F = CF_3$ (55%) , $H(CF_2)_2$ (60%)

$CF_3CCl_2CCl_2OCH_3$

To a solution of 9.2 g (0.044 mol) PCl_5 in 50 ml of refluxing carbon tetrachloride was added dropwise, and with stirring, 6.2 g (0.04 mol) of methyl trifluoropyruvate. The mixture was refluxed for 16 hr and then cooled to room temperature. The reactants were decomposed with crushed ice and the organic layer separated and washed quickly with cold aqueous Na_2CO_3, water and saturated brine. The extract was dried over anhydrous magnesium sulfate and evaporated. The residue was distilled to yield 5.8 g (55%) of 3,3,3-trifluoro-1,1,2,2-tetrachloro-1-methoxypropane: bp 80-81 ^{o}C (15 mm Hg). IR (liquid film): no carbonyl bonds; ^{1}H NMR (100 MHz, $CDCl_3$) δ 3.88(s, 3H,OCH_3); ^{19}F NMR (94.1 MHz, C_6F_6) δ 85.2 (s, 3F, CF_3). Analysis: found C 18.36, H 1.07, Cl 53.18, F 21.16%; calcd. for $C_4H_3Cl_4F_3O$: C 18.07, H 1.13, Cl 53.33, F 21.43%.

$CF_3CH(SSCH_3)COOCH_3$

To a suspension of 11.4 g (0.04 mol) Davy's reagent in 70 ml of dimethoxyethane was added dropwise , and with stirring, 6.2 g (0.04 mol) of methyl trifluoropyruvate. The mixture was refluxed for 2 hr with stirring and then cooled to room temperature. Dimethoxyethane was evaporated and the residue was extracted by chloroform. The chloroform was evaporated and the residue distilled to yield 4.8 g (55%) of methyl 3,3,3-trifluoro-2-(methyldithio)propanoate: bp 58 ^{o}C (5 mm Hg). IR (liquid film) ν max (cm^{-1}) 1750 (CO), 700(C-S), 535 (S-S); Raman spectrum ν (cm^{-1}) 697 (C-S), 530 (S-S); ^{1}H NMR (100 MHz, $CDCl_3$) δ 2.5 (s, 3H, SCH_3), 3.84 (s, 3H, OCH_3), 4.08 (q, J= 8.0 Hz, 1H, CH); ^{13}C NMR (25.4 MHz, $CDCl_3$) δ 23.9 (s, SCH_3), 53.3 (s, OCH_3), 57.0 (q, J= 30.0 Hz, CH), 123.5 (q, J= 80.0 Hz, CF_3), 164.6 (s, CO); Mass spectrum (rel.intensity/%) m/z 222 $M+2^{+}$(9), 221 $M+1^{+}$ (12), 220 M^{+}(92), 161 $CF_3CHSSCH_3^{+}$(100), 80 $HSSCH_3^{+}$(90), 69 CF_3^{+}(68), 66 $H_2S_2^{+}$(60), 59 CH_3OCO^{+}(87), 47 SCH_3^{+}(80). Analysis: found C 27.29, H 2.84, F 26.04, S 29.11%; calcd. for $C_5H_7F_3O_2S_2$: C 27.27, H 3.20, F 25.88, S 29.12%.

$HCF_2CF_2CH(SSCH_3)COOCH_3$

This ester was prepared as above in 60% yield; bp 84 °C (20 mm Hg). IR (liquid film) νmax (cm^{-1}) 1750 (CO), 720 (C-S), 550 (S-S); ^1H NMR (100 MHz, $CDCl_3$) δ 2.49 (s, 3H, SCH_3, 3.83 (s, 3H, OCH_3), 4.03 (m, 1H, CH) 6.12 (t.t, ^2J= 53.0 Hz, ^3J= 4.9 Hz, 1H, HCF_2CF_2). Analysis: found C 28.33, H 3.13, F 30.40, S 25.74%; calcd. for $C_6H_8F_4O_2S_2$: C 28.57, H 3.19, F 30.13, S 25.42%.

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