Unusual reaction of trifluoroacetone with benzenesulfenyl chloride

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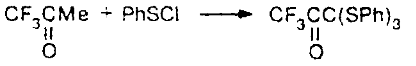
Aliphatic ketones and β-oxocarboxylates react vigorously (usually, with cooling) with alkane- and arenesulfenyl chlorides to give monosulfenylation products in almost quantitative yields.[1,2] Polyfluoroalkanesulfenyl chlorides react with carbonyl compounds with somewhat greater difficulty (at 20—70 °C),[3,4] and the reaction conditions are determined by the ability of a ketone to enolize. In the latter case, solvents that specifically solvate the S—Cl group (for example, acetonitrile) are sometimes used to enhance the rate of formation of sulfenylation products, or the reaction is conducted in the presence of acid or basic catalysts.

We found that, unlike nonfluorinated ketones, trifluoroacetone is not sulfenylated with benzenesulfenyl chloride when a mixture of the reagents is kept at 20 °C for a long time without a solvent, in solutions in hexane, dichloromethane, and even in acetonitrile, and in the presence of CF$_3$COOH. The reaction occurs vigorously only in the presence of organic bases, *e.g.*, in pyridine. In this case, the reaction does not stop at the stage of monosulfenylation, and even in excess of trifluoroacetone, triphenyl orthotrifluorotrithiopyruvate (**1**), the product of its complete sulfenylation, is formed.



$$CF_3C(=O)Me + PhSCl \longrightarrow CF_3C(=O)C(SPh)_3$$

1

Enoles, whose double bond is deactivated by the CF$_3$ group, seem to be unable to add sulfenyl chlorides. The sulfenylation in the reaction studied is determined by the possibility of formation of an enolate anion, which increases sharply as phenylthio groups are incorporated in the molecule of the carbonyl compound.

Triphenyl orthotrifluorotrithiopyruvate (1). Benzenesulfenyl chloride (4.34 g, 0.03 mol) was added dropwise to a solution of trifluoroacetone (3.36 g, 0.03 mol) in 5 mL of pyridine with stirring and cooling (0 °C). The reaction mixture was stirred at 0 °C for 1 h and left at 0—5 °C for 24 h. Unconsumed trifluoroacetone was removed and collected in a trap (2.24 g, 0.02 mol). The residue was mixed with 20 mL of ice water acidified with 5 mL of conc. HCl, the oil was separated and washed again with acidified ice water. After thrice-repeated washing, a solid product (4.35 g, 99%) was obtained, m.p. 82 °C (hexane). Found (%): C, 57.76; H, 3.57; S, 21.74; F, 12.85. C$_{21}$H$_{15}$F$_3$OS$_3$. Calculated (%): C, 57.80; H, 3.44; S, 22.02; F, 13.08. ^{1}H NMR (200 MHz, CDCl$_3$), δ: 7.4 (m, 3 Ph). ^{19}F NMR (183.3 MHz, CDCl$_3$), δ: −10.5 (s, CF$_3$). ^{13}C NMR {^{1}H} (200 MHz, CDCl$_3$), δ: 116.1 (q, CF$_3$, J = 294 Hz); 129.4 (CF$_3$CO$\underline{C}$); 128.8, 129.8, 135.2 (Ph); 180.9 (q, CF$_3\underline{C}$O, J = 32 Hz). IR, ν/cm^{-1}: 1720 (CO).

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References

1. T. N. Dubinina and U. S. Levchenko, *Zh. Org. Khim.*, 1979, **15**, 743 [*J. Org. Chem. USSR*, 1979, **15** (Engl. Transl.)].
2. I. V. Koval', *Usp. Khim.*, 1966, **64**, 781 [*Russ. Chem. Rev.*, 1966, **64** (Engl. Transl.)].
3. A. Yu. Sizov, A. F. Kolomiets, and A. V. Fokin, *Usp. Khim.*, 1992, **61**, 940 [*Russ. Chem. Rev.*, 1992, **61** (Engl. Transl.)].
4. A. Yu. Sizov, A. F. Kolomiets, and A. V. Fokin, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 1745 [*Russ. Chem. Bull.*, 1996, **45**, 1654 (Engl. Transl.)].

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