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Preparation of 2,3,3,3-tetrafluoropropene from trifluoroacetylacetone and sulphur tetrafluoride

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Abstract

Practical details are presented for the laboratory preparation of 2,3,3,3-tetrafluoropropene in good yield from trifluoroacetylacetone and sulphur tetrafluoride in the presence of hydrogen fluoride. The gas-phase IR spectrum of the tetrafluoropropene (b.p., −28 °C) is reproduced and a detailed analysis of the olefin's nuclear magnetic resonance (NMR) spectra (^1H, ^{13}C, ^{19}F) is provided. © 1997 Elsevier Science S.A.

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1. Introduction

Needing to establish quickly a procedure for making 2,3,3,3-tetrafluoropropene (**1**), we chose to try the unusual [1] fluorination-cum-cleavage reaction $CF_3COCH_2COCH_3$ (**2**) + $SF_4 \rightarrow CF_3CF{=}CH_2$ (**1**) + SOF_2 [2] rather than seemingly more attractive methods [3], since not only were trifluoroacetylacetone (**2**) and sulphur tetrafluoride immediately available, but we were also well versed in the use of the latter reactant. Importantly, too, we have long been fully equipped at UMIST to pursue work with anhydrous hydrogen fluoride (AHF) which we suspected from the outset might be needed as a catalyst/solvent. The results of successful pilot experiments carried out on three times (0.14 mmol of **2**) the literature scale [2] are reported here.

2. Results and discussion

The Russian work [2] being followed established that 1,1,1-trifluorinated β-diketones CF_3COCH_2COR ($R \equiv CH_3$ (**2**), C_2H_5 or $(CH_3)_2CH$) react with about a two molar excess of SF_4 at 20 °C during 12 h to provide approximately 65 : 35 mixtures (by gas–liquid chromatography (GLC) (uncalibrated) analysis of alkali-washed products) of 2,3,3,3-tetrafluoropropene (**1**) and the corresponding alkanoyl fluoride (RCOF). The tetrafluoropropene (**1**) was isolated in unstated yields [1,2] by a sketchily described methodology culminating in preparative GLC, and its identity was confirmed by nuclear magnetic resonance (NMR) (^1H, ^{19}F) spectroscopy.

In our experience, adventitious hydrogen fluoride is difficult to avoid when working with sulphur tetrafluoride owing to facile hydrolysis of this reagent. However, it should be noted that in the original work summarized above, no HF was deliberately added to CF_3COCH_2COR–SF_4 reaction mixtures. By contrast, the same workers found that SF_4 fluorination of the bistrifluoromethyl analogue of **2** proceeded only in anhydrous hydrogen fluoride [2]: $CF_3COCH_2COCF_3 + SF_4/HF \rightarrow CF_3CF{=}CHCF_2CF_3$ (80%).

Finding in our work that the fluorination of **2** with SF_4 in the absence of added HF proceeded sluggishly, reactions were run on a 21 g scale (see Table 1) at 60 °C in the presence of HF, considered not to be absolutely anhydrous owing to the method used to load the Monel reaction vessel (see Section 3.2). The best (gas chromatography (GC)-estimated) yield of 2,3,3,3-tetrafluoropropene (**1**) (82%, with no SF_4 detected chromatographically in the crude gaseous product) was achieved with a **2** to SF_4 to HF molar ratio of 1.0 : 1.7 : 0.6, and after combining products from several similar experiments which had been largely or completely freed from HF, SF_4, SOF_2 and CH_3COF using a KF–H_2O–NaOH–$CaCl_2$ scrubbing train, the fluoroalkene (b.p., −28 °C) was isolated in 75% yield and better than 99% GC purity by precise fractional distillation. The identity of the product

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Table 1
Details of the conversion of $CF_3COCH_2COCH_3$ (**2**) to $CF_3CF{=}CH_2$ (**1**) with SF_4–HF mixtures in a Monel autoclave[a]

2 (g; mol)	SF_4 (g; mol)	HF (g; mol)	Temperature (°C)[b]	Time (h)	Crude product (g)[c]	Yield of **1** (%)[d]
21.0; 0.14	39.0; 0.36	20; 1.0	60	15	28	70
21.0; 0.14	30.0; 0.27	20; 1.0	60	15	30	76
21.0; 0.14	26.0; 0.24	16; 0.8	60	18	24	82
21.0; 0.14	29.0; 0.265	16; 0.8	60	18	30	76

[a] After each run, the autoclave lid was removed and the black volatile acrid liquid lying in the cup was treated with 4 M aqueous KOH (left in the vessel overnight). The cup was then washed out thoroughly with water, cleaned with a mild abrasive and polished ready for use again.

[b] Autoclave wall temperature; headspace value, 50 °C.

[c] Determined by weighing collection traps from the purification train.

[d] According to GC peak areas (uncalibrated detector).

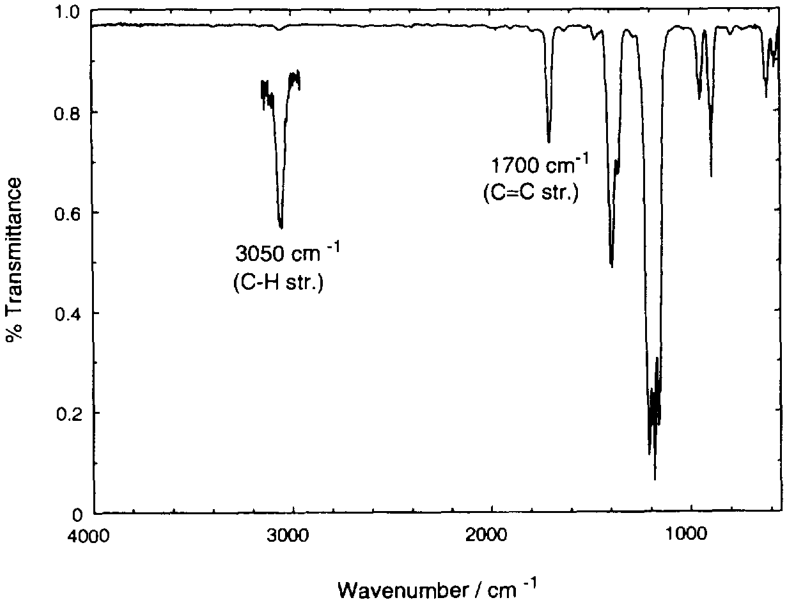


Fig. 1. Gas-phase FTIR spectrum of 2,3,3,3-tetrafluoropropene (**1**; $CF_3CF{=}CH_2$).

was confirmed spectroscopically (mass spectrometry (MS), IR (see Fig. 1) and NMR (see Fig. 2)).

The ^1H and ^{19}F NMR spectra for a solution of **1** in $CDCl_3$ comprise an $ABPX_3$ system in which one proton (H_A, to lower field) shows no resolved coupling to the CF_3 group fluorines, whereas the other (H_B) does ($|^4J_{HF}| = 1.4$ Hz; relative sign not clear cut). A complete set of data is provided in Fig. 2(a), the analysis being performed by Corio's methods [4], and the assignment of H_A and H_B being based on the magnitudes of the $^3J_{HF}$ coupling constants ($J_{trans} > J_{cis}$ [5]).

3. Experimental details

3.1. Starting materials

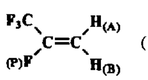
3.1.1. Sources

Trifluoroacetylacetone (**1**; 99%), sulphur tetrafluoride (technical grade) and AHF (99.8% or better) were used as received from Fluorochem Ltd. (UK), Air Products and Chemicals Inc. (USA) and ICI (UK) respectively.

3.1.2. Hazards

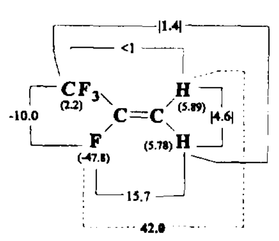
Trifluoroacetylacetone (b.p., 105–107 °C) is classed as a flammable irritant and its manipulation presents no special problems. By marked contrast, sulphur tetrafluoride (b.p., -38 °C) is highly toxic, its inhalation toxicity being comparable with that of phosgene [6]; this property, coupled with its susceptibility towards hydrolysis at room temperature with the liberation of hydrogen fluoride ($SF_4 + H_2O \rightarrow$ (fast) $2HF + SOF_2$; $SOF_2 + H_2O \rightarrow$ (slow) $2HF + SO_2$), demands that it should be used only by appropriately well-trained personnel in dedicated work areas of appropriate design (Ref. [6] contains useful information on the methods of handling). The hazardous nature of AHF is legendary [7] and anyone using this material must acquaint themselves thoroughly with acceptable safe practices; these must include making adequate prior arrangements for medical treatment [7].

Hudlický's much-used manual [8] contains some useful information on how to transfer AHF (b.p., 19.5 °C) from a normal (no dip pipe) commercial metal cylinder to a polyethylene (PE) receiver, but gives inadequate detail about heating the cylinder gently to ensure a reliable discharge of the contents. When necessary (which proved not to be the



(1)

(*a*) ^{1}H and ^{19}F data (ν_A-ν_b = 21.3 Hz)[a,b]



(*b*) ^{13}C data[c,d]

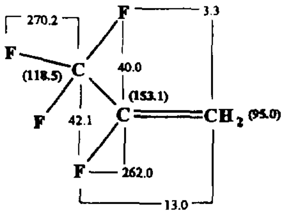


Fig. 2. NMR chemical shifts (ppm, in parentheses) and coupling constants (Hz) for 2,3,3,3-tetrafluoropropene (1). [a]^{1}H at 300 MHz (Bruker AC-300 instrument; ext. Me_4Si ref.); ^{19}F at 188.8 MHz (Bruker AC-200; ext. CF_3CO_2H ref., positive assignment downfield). [b]Stepanov et al. [2] carried out a simplistic analysis of the spectra of **1** in CCl_4 on the basis of an AA′XX′-type system, quoting δ_H (HMDS ref.) 5.44 ppm (J_{HF} = 46 Hz) and δ_F ($CFCl_3$ ref.) −72.2 (d, CF_3, J_{FF} = 11 Hz), −124.65 (m, CF) ppm. [c]^{13}C at 75.5 MHz (Bruker AC-300; ^{1}H decoupled, ext. Me_4Si ref.). [d]Not all the weaker lines of the multiplets were listed on the print-out, but quartets (from coupling to *C*F_3) were usually easily distinguished from doublets (from *C*F).

case in the present work, since a cylinder fitted with a dip pipe was used), we adhere strictly to the manufacturer's (ICI) instructions to heat AHF cylinders in a shroud supplied with warm air ducted from a small electric fan heater, so that in no circumstances can the temperature exceed 45 °C (35 °C is the prescribed normal value) [9].

No hazards data appear to be available for 2,3,3,3-tetrafluoropropene (1), and hence care was taken to avoid inhalation of the pure gas [10]. Inhalation of crude material containing (after removal of HF) SOF_2, SF_4 and CH_3COF was strictly avoided.

3.2. Preparation of 2,3,3,3-tetrafluoropropene

3.2.1. Transfer of AHF and SF_4 from commercial storage cylinders to secondary containers

3.2.1.1. Anhydrous hydrogen fluoride (with A.E. Laing)

A steel AHF cylinder (capacity 22 kg; dip pipe type used regularly in our laboratories to fill Simons ECF cells) was connected via flexible copper tubing to a robust semi-transparent PE bottle (500 cm^3) fitted with a screw top carrying copper inlet and outlet tubes (0.6 mm i.d.); the former reached halfway down the length of the bottle, while the latter led from the lid into a fume hood to carry away HF fumes. Once the PE bottle had been chilled to approximately −5 °C in an ice/salt bath, the valve on the storage cylinder was opened carefully (smooth working of the valve should be checked before making the connection to the PE bottle) and an appropriate amount of liquid AHF was collected (as judged visually with the aid of volume calibration marks made with a wax crayon; density of HF = 1.0015 g cm^{-3} at 0 °C [11]). The relatively small known amount of AHF used in each fluorination experiment (see Section 3.2.2) was obtained by transferring material from the cold PE collection vessel to a smaller chilled (ice/salt) pre-weighed stout PE bottle equipped with a tight-fitting lid. Samples assembled in this manner can be stored, if necessary, in a refrigerator until required.

The operations described above were carried out in a laboratory dedicated to work with AHF conjointly by two well-trained chemists wearing appropriate personal protective equipment [9].

3.2.1.2. Sulphur tetrafluoride

For each fluorination experiment (Section 3.2.2), a fresh sample of SF_4 was transferred, using standard vacuum techniques, from a double-valved (important: for safety reasons, a fine-control stainless steel valve must be fitted to back up the main valve) commercial cylinder directly to a thoroughly dried, calibrated (volume scale; density of SF_4 = 1.9190 g cm^{-3} at −73 °C [12]), pre-weighed Pyrex tube (150 cm^3) cooled in liquid nitrogen (connections were made with the aid of copper, Pyrex and Viton® fluorubber tubing, as appropriate). Once charged, the cold Rotaflo™ tube was quickly weighed to ascertain the approximate amount of SF_4 present (this determined the amount of trifluoroacetylacetone (**2**) placed in the fluorination vessel (see Section 3.2.2)), and then returned to its bath of liquid nitrogen to await use in a fluorination experiment. The whole operation, including weighing of the Rotaflo™ tube, was conducted in an efficient dedicated fume cupboard.

3.2.2. Fluorination of trifluoroacetylacetone (2)

In a typical experiment, cold (approximately −5 °C) hydrogen fluoride (20 g, 1.0 mol) was poured from a PE storage bottle (Section 3.2.1.1) into a Monel autoclave (250 cm^3) containing trifluoroacetylacetone (21.0 g, 0.14 mol). The vessel's lid carrying a closed valve, bursting disc assembly (nickel disc protected by a 0.1 mm thick PTFE membrane, 150 atm rating and a 0–250 atm gauge) was then quickly bolted on and standard vacuum transference techniques (autoclave cooled in liquid nitrogen) were used to charge it with sulphur tetrafluoride (39.0 g, 0.36 mol) from a Rotaflo tube container (Section 3.2.1.2). The autoclave's valve was then closed and the vessel was allowed to warm to room temperature in a fume cupboard before it was heated electrically at 60 °C (outside wall temperature; vessel head-space temperature, 50 °C) for 15 h in a properly ventilated blast-proof cubicle. The autoclave was allowed to cool somewhat, and was then transferred to a fume cupboard and connected to a product recovery train, comprising an acid gas scrubbing section (a glass tube (40 cm × 2.5 cm) loosely packed with dry granular KF leading to three Drechsel bottles in series, the first being empty ("suck-back" trap), the second containing H_2O (200 cm^3) and the third charged with 2 M aqueous NaOH (200 cm^3)), a drying tube ($CaCl_2$; 40 cm × 2.5 cm) and finally two cold Pyrex traps (−78 °C) which were connected (via a protective −196 °C trap) to a vacuum system. Gaseous products were bled slowly and completely from the autoclave by careful use of the vessel's needle valve, in conjunction (in the later stages) with a judicious reduction of the pressure (to minimize the transfer of water vapour from the scrubbing train). The volatile material (33.0 g) collected at −78 °C was shown by GC-IR analysis (1.5 m Porapak Q, 80 °C, N_2 carrier, uncalibrated katharometer detector) to comprise (in order of elution; percentage composition estimated from peak areas) SOF_2 (6%), SF_4 (8%), $CF_3CF{=}CH_2$ (**1**; 70%), CH_3COF (12%) and three unidentified products (total, 4%).

The results of other experiments, all carried out in the same manner using the same quantity of trifluoroacetylacetone, are given in Table 1. Products from these runs were combined and the material (85.0 g) was rectified using an adiabatic low-temperature column (1 m × 15 mm packed with 2.5 mm Fenske glass rings) similar to that described previously [13] to provide 47.6 g (0.42 mol, 75%) of 2,3,3,3-tetrafluoropropene (GC purity, better than 99%), b.p. −28.0 °C (literature [14], −28.3 °C); MS data (70 eV EI; VG 7070 EP instrument) *m/z*: 114 (M^+, 90% (accurate mass: found, 114.0088; calculated for $C_3H_2F_4$, 114.0092)), 113 ($(M-1)^+$, 22%), 95 [$(M-F)^+$, 34%), 75 ($C_3HF_2^+$, 11%), 69 (CF_3^+, 100%), 65 (8%), 64 ($C_2H_2F_2^+$, 96%), 45 ($C_2H_2F^+$, 48%), 44 (C_2HF^+, 8%), 31 (CF^+, 9%); IR (10 cm gas cell, NaCl optics; Nicolet 250 FTIR spectrophotomer) λ_{max}: 3050vw (=C–H str.), 1700m (C=C str.), 1396s, 1388s, 1357m, 1209vs, 1190vs, 1181vs, 1160vs, 1153vs (C–F str.), 948m, 892m (=C–H out-of-plane bending) cm^{-1} (see Fig. 1).

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[3] For example: $CF_3CF_2CH_2OH$ (Aldrich) → $CF_3CF_2CH_2OTs$ → $CF_3CF_2CH_2I$ → (with Zn in $MeCO_2H$)$CF_3CF{=}CH_2$ (E.T. McBee, D.H. Campbell and C.W. Roberts, *J. Am. Chem. Soc.*, *77* (1955) 3149); $CF_3CF_2CH_2OH + H_2/C$ → (hot act. C)$CF_3CF{=}CH_2$ (K. Ihara, F. Yamaguchi and S. Yamane, EP 328148 A1 890816 (to Daikin Ind.); *Chem. Abs.*, *112* (1989) 78156f).

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