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Synthesis of SF_5–benzene ($SF_5C_6H_5$) by the SF_5–halide method

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Abstract

Several significant and useful syntheses of pentafluorothiobenzene ($SF_5C_6H_5$) from SF_5–halides (SF_5X, X = Cl, Br) and cyclohexene or derivatives of cyclohexene are presented.

Keywords: Pentafluorothiobenzene; SF_5–organoaromatic systems

1. Introduction

The original synthesis of pentafluorothiobenzene ($SF_5C_6H_5$) was reported by Sheppard over 40 years ago [1]. This method employs AgF_2 and diphenyl disulfides in a chlorofluorocarbon solvent and is carried out in a copper vessel. More recently, it has been found that elemental fluorine in various solvents (such as CH_3CN) can be used to prepare SF_5–aromatic derivatives such as (3- or 4-nitrophenyl) sulfur pentafluoride in 39–41% yields [2]. A brief overview covering the use of AgF_2 and F_2 is given in a recent article [3]. We have found that SF_5Br, when photolysed in benzene, yields $SF_5C_6H_5$ in small quantities [4]. Other approaches to preparing SF_5–aromatic compounds include catalytic dehydrogenation of the Diels–Alder product obtained from $SF_5C{\equiv}CH$ and butadiene or from the cyclotrimerization of $SF_5C{=}CH$ [5,6].

2. Results and discussion

In applying the SF_5–halide (SF_5X) method it was recognized from previous studies with hydrocarbon alkenes that, in general, SF_5Br is much more reactive than SF_5Cl; with SF_5Br addition, another pathway giving SF_4 and a BrF addition product also occurs [7]. With cyclohexene, SF_5Cl addition results in a mixture of SF_5Cl and ClF adducts [8]; it should be pointed out that recently the ClF addition part of this reaction has been suppressed by using a $(CH_3CH_2)_3B$-catalyst at low temperature [9]. Since cylcohexene is a reactive olefin while allyl acetate is a poorly reactive olefin with SF_5Cl [7], it was thought that placing acetate groups on the cyclohexene ring in allylic positions would moderate the addition of SF_5Br. We have found that SF_5Br will add quantitatively to 1,4-diacetoxy-2-cylcohexene and that the adduct will lose in a two-step manner HBr and two molecules of $CH_3C(O)OH$; thermolysis of the *trans*-diacetate derivative, in diphenylether (bp 259 °C), gave $SF_5C_6H_5$ in about 40% yield (Scheme 1).

Alternatively, the 1,4-diacetoxy-2-SF_5-2-cyclohexene can be converted to the corresponding diol which on treatment with P_4O_{10} produces $SF_5C_6H_5$ (Scheme 2) in 88% yield; the diol can be quantitatively prepared either by the catalytic transesterification of **2** in methanol or by hydrolysis of **2**.

We have also found a way to prepare $SF_5C_6H_5$ through the use of SF_5Cl and cyclohexene. Using the method of Aït-Mohand and Dolbier [9], SF_5Cl was added to cyclohexene; the adduct underwent HCl elimination giving the known 1-SF_5-1-cyclohexene which was brominated with *N*-bromosuccinimide. The dibromo-adduct was then dehdyrobrominated producing $SF_5C_6H_5$ in 68% yield. The reaction sequence is given in Scheme 3.

The last method has the advantage of using cyclohexene and SF_5Cl, the latter of which can be easily prepared from SF_4, KF, and Cl_2.

The spectral data are included in Section 3 and confirm the molecular structures and chemical transformations for the compounds. The GC–MS and the HRMS spectra contained the parent ions or the MH^+ species; appropriate fragmentation patterns were also found for the compounds. The infrared (IR) spectra contained the characteristic

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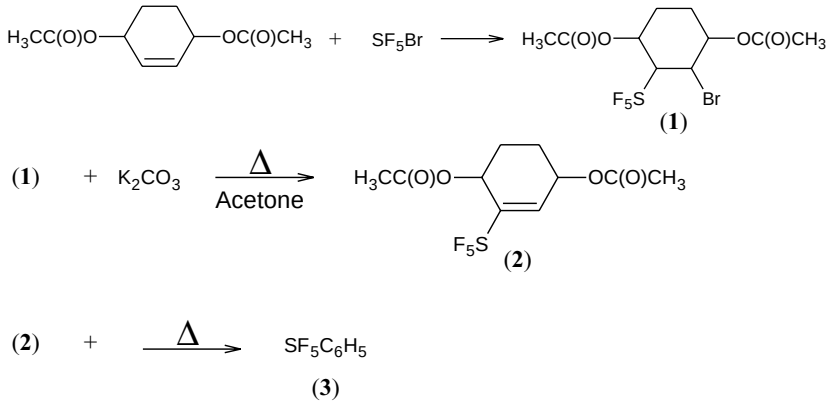
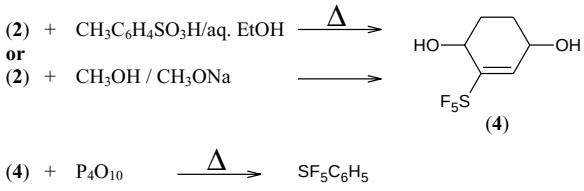


Scheme 1.



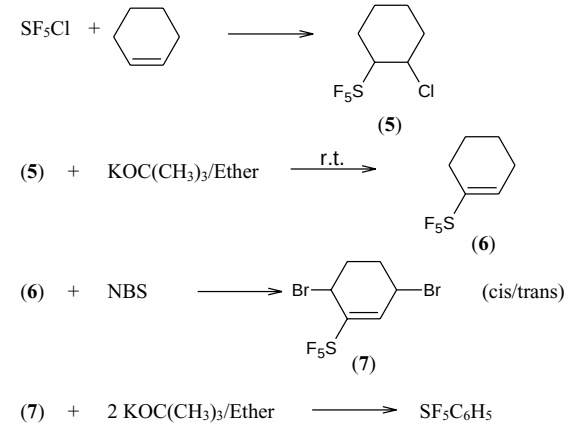
Scheme 2.

absorption bands for the C–H, O–H, C=O, C=C, SF_5 groups; for example, the very strong S–F stretching mode occurs in the 861–803 cm^{-1} range while a deformation band occurs in the 593–598 cm^{-1} region. In the ^{19}F NMR spectra, the chemical shifts for the SF_5-group (AB_4 pattern) are found in the 82.5–86.0 ppm range (A) and in the 55.1–61.0 ppm range (B).

3. Experimental

3.1. General methods

The *cis*- and *trans*-1,4-diacetoxy-2-cyclohexene were separately made from 1,3-cyclohexadiene [10], the latter of which was readily prepared in large quantities by modifying the procedure that employs acid-catalyzed elimination of alcohol from 3-alkoxycyclohexene [11]. It should be noted that a mixture of *cis*- and *trans*-1,4-diacetoxy-2-cyclohexene can be prepared by a patented procedure that employs oxidative acetoxylation of cyclohexene [12]. The 1-SF_5-2-Cl-cyclohexane (**5**) was prepared according to the method of Aït-Mohand and Dolbier [9]. The IR spectra were obtained using a Perkin-Elmer 2000 FTIR system operating at 2.0 cm^{-1} resolution. The NMR spectra were obtained using a Varian EM-390 spectrometer operating at 84.6 MHz for ^{19}F and at 90 MHz for ^{1}H (also a Bruker instrument operating at 500 MHz was used for ^{1}H). The standards $CFCl_3$ and $(CH_3)_4Si$ were used as internal standards in $CDCl_3$. Mass spectra (GC–MS) were obtained with using a Hewlett-Packard HP 5890 series II chromatograph equipped with a HP 5970 mass selective detector operated at 70 eV and a 30m DB-5 column. For a standard run, the column was maintained at 50 °C for 2 min, followed by an increase in temperature of 11 °C/min until the temperature of the column reached 280 °C. The precise molecular weight determination for compounds: *cis*/*trans*-(**2**), *trans*-(**4**) were obtained on a Kratos MS 50TC by chemical ionization with methane.



Scheme 3.

3.1.1. Addition of SF_5Br to trans- and cis-1,4-diacetoxy-2-cyclohexene (*1*)

To a 400 ml Pyrex Carius vessel (previously subjected to an acid wash and dried under vacuum) equipped with a Teflon valve and stirring bar, 15.17 g (76.6 mmol) of *trans*-1,4-diacetoxy-2-cyclohexene was added and dried in vacuo. To the reaction vessel, 300 ml of CH_2Cl_2 was added and then cooled to −196 °C and evacuated; 16.89 g (81.6 mmol) of SF_5Br was then added under vacuum. The reaction vessel was placed in an ice bath and irradiated while stirring with three 250-W sunlamps at a distance of 30 cm for 60 h. A GC–MS analysis showed that all of the cyclohexene reactant was consumed. The solvent was removed under vacuum leaving 31 g (76.5 mmol, ∼100% yield) of the *trans*-adduct as a light yellow oil. The adduct was found via GC–MS to contain three SF_5-compounds present in the ratio 67:25:3. When reaction of *cis*-1,4-diacetoxy-2-cyclohexene with

SF_5Br is carried out in a similar fashion, the *cis*-product was obtained in 100% yield. The *trans*- and *cis*-adducts were not further characterized but used to prepare **2** and **3**.

3.1.2. Preparation of trans/cis-1,4-diacetoxy-2-SF_5-2-cyclohexene (2)

In a 500-ml round-bottomed vessel equipped with a Teflon stirring bar, 5.94 g (14.7 mmol) of *trans*-(**1**) (from reaction above), 75 ml of acetone and 7.5 g of finely ground K_2CO_3 were refluxed for 28 h. The solids were removed by suction filtration; evaporation of the filtrate gave the *trans*-product, *trans*-(**2**), 4.65 g (14.4 mmol, yield of 98%) as an off-white crystalline solid which when recrystallized from ethanol or isopropanol gave large colorless crystals, mp 109–110 °C. When the *cis*-compound (**1**) was reacted in a similar fashion, the product *cis*-1,4-diacetoxy-2-SF_5-2-cyclohexene, *cis*-(**2**) was produced in 70% yield; mp 139–140 °C.

3.1.2.1. Trans-derivative. IR spectrum (neat, KBr, cm^{-1}): 3016 (vw), 2968 (w), 2948 (w), 2862 (vw), 1740 (vs), 1690 (w), 1657 (w), 1436 (w), 1375 (m), 1365 (m), 1304 (w), 1241 (s), 1222 (vs), 1199 (m-s), 1122 (w), 1094 (w), 1051 (w), 1015 (s, sh 1029), 987 (s, sh 974), 923 (w-m), 822 (vs,b), 737 (m), 672 (w), 647 (w-m), 593 (m), 558 (w-m), 492 (w), 468 (w-m).

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.86 (t, $J = 3.1$ Hz, 1H), δ 6.90 (d, $J = 4.68$ Hz, 1H), δ 5.51 (s, 1H), δ 1.8–2.1 H(5) + H(6) (m, overlap with CH_3CO, 2s at 2.08, 2.09, comb. 10H).

^{19}F NMR ($CDCl_3$, CCl_3F): Φ_A 82.3 (nine line pattern, 1F), Φ_B 57.5 (d-m, 4F, $J = 149.0$ Hz).

3.1.2.2. Cis-derivative. IR spectrum (neat, KBr, cm^{-1}): 3074 (vw), 2969 (w), 2928 (w), 2880 (w), 1738 (vs), 1693 (w), 1676 (w), 1656 (w), 1449 (w), 1430 (w), 1371 (m), 1304 (w), 1233 (vs, sh 1246), 1205 (m-s), 1147 (w), 1093 (w), 1049 (m), 1020 (m), 993 (m), 959 (m), 920 (w), 861 (s), 851 (vs), 833 (vs), 821 (vs), 745 (s), 669 (w), 647 (m), 615 (w), 598 (m), 572 (w-m), 537 (w-m), 514 (w), 483 (w).

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.79 (t, br., 1H), δ 6.72 (d, $J = 2.8$ Hz, 1H), δ 5.53 (s, br., 1H), δ 1.75–2.1 (m, overlap with CH_3CO, s at 2.2, 2.09, comb. 10H).

^{19}F NMR ($CDCl_3$, CCl_3F): Φ_A 82.5 (nine line pattern, 1F), Φ_B 58.0 (d-m, 4F), $J = 149.0$ Hz.

High-resolution mass spectrum (HRMS): The *trans*-isomer $(M - H)^+ = 323.03883$; Calc. = 323.03765 and $(MH)^+ = 325.05447$; Calc. = 325.05330. The *cis*-isomer $(M - H)^+ = 323.03716$; Calc. = 323.03765; and $(MH)^+ = 325.05246$; Calc. = 325.05330.

3.1.3. Preparation of $SF_5C_6H_5$ (3) via thermolysis of 2

Into a 50-ml round-bottomed flask equipped with a Teflon stirring bar and three stacked Vigerux columns (air condenser), 3.29 g (10.2 mmol) of *trans*-(**2**), and 25 ml of diphenylether were added. The mixture was heated to 265–270 °C (temperature of sand bath); after 15 h, the volatile materials were removed under vacuum by heating the reaction mixture to 100 °C for 7 h and collecting the volatile materials in a −78 °C trap (trap was attached to top of Vigerux columns). To the condensate (2.5 g) a 20% NaOH solution was added dropwise until the pH was 10–11; the lower layer was removed, dried over Na_2SO_4, giving 0.81 g (3.97 mmol, yield of 39%) of pure $SF_5C_6H_5$ (**3**) as shown by GC–MS.

GC–MS spectrum: 204 $(M)^+$, 185 $(M - F)^+$, 127 $(SF_5)^+$, 108 $(SF_4)^+$, 96 $(SC_5H_4)^+$, 89 $(SF_3)^+$, 77 $(C_6H_3)^+$, 70 $(SF_2)^+$, 51 $(SF)^+$.

IR spectrum (neat, KBr, cm^{-1}): 3079 (w), 2361 (w), 2337 (w), 1487 (m), 1454 (m), 1098 (m), 831 (s, sh 871), 756 (ms), 688 (m), 646 (m), 596 (m), 580 (m).

^{1}H NMR (500 MHz, $CDCl_3$, $(CH_3)_4Si$): $\delta_{2,6}$ 7.75 (d, $J = 7.95$ Hz), $\delta_{3,5}$ 7.45 (t, $J = 7.33$ Hz), δ_4 7.50 (t, $J = 7.33$ Hz).

^{19}F NMR ($CDCl_3$, CCl_3F): Φ_A 84.0 (nine line pattern, 1F), Φ_B 61.9 (d-m, 4F), $J = 149.3$ Hz.

3.1.4. Preparation of trans-1,4-dihydroxy-2-SF_5-cyclohexene (4)

3.1.4.1. Hydrolysis method. Into a 100-ml round-bottomed flask equipped with a Teflon stirring bar, 2.16 g (6.67 mmol) of *trans*-(**2**), 10 ml of ethanol, 50 ml of water and 1.0 g of *p*-toluenesulfonic acid monohydrate were added; the mixture was refluxed for 20 h. The reaction was cooled to RT and extracted six times with 15 ml of *t*-butylmethyl ether. Evaporation of the extract left behind 1.58 g (6.58 mmol) of an oil (99% yield) that slowly solidified; the product **4** was shown to be pure by GC–MS and was recrystallized from a mixture of methylene chloride and *t*-butylmethylether. The mp was 129–130 °C.

3.1.4.2. Transesterfication method. In a 500-ml round-bottomed flask, 21.00 g (64.8 mmol) of *trans*-(**2**), 250 ml of CH_3OH and CH_3ONa (50 mg of Na in 3 ml of CH_3OH, 2.17 mmol) were mixed together. After ~18 h, a GC–MS spectrum showed complete conversion to the *trans*-diol. Several drops of 6N HCl were added until the solution was slightly acidic. The volatile components were removed under vacuum leaving behind 15.84 g of product (includes NaCl and traces of water). The *trans*-diol (**4**) can be recrystallized as shown above.

IR spectrum (neat, KBr, cm^{-1}): 3225 (b, m), 2966 (w), 2938 (w), 2855 (w), 2707 (w), 1441 (w), 1415 (w), 1354 (w), 1305 (w), 1278 (w), 1260 (w), 1196 (w-m), 1090 (w-m), 1028 (m-s), 997 (s), 952 (w), 920 (w-m, sh 929), 831 (vs, sh 848, 865), 803 (vs), 749 (m), 715 (w), 652 (w-m), 629 (w-m), 598 (w-m), 569 (w-m), 478 (w).

^{1}H NMR (d_6-acetone, $(CH_3)_4Si$): δ_1 4.60 (br. s, 1H), δ_4 4.40 (br. s, 1H), δ_3 6.60 (d, $J = 4.17$ Hz, 1H), $\delta_{5,6}$ 2.0 (m, 4H, D_2O), δ_{OH} 4.15 (s, 2H).

^{19}F NMR ($CDCl_3$, CCl_3F): Φ_A 85.5 (nine line pattern, 1F), Φ_B 58.7 (d-m, 4F), $J = 149.9$ Hz.

High-resolution mass spectrum: $(M-1)^+ = 239.01695$. Calc. = 239.01652.

*3.1.5. Preparation of $SF_5C_6H_5$ (**3**) by dehydration of **4***

Into a 100-ml round-bottomed flask equipped with a Teflon stirring bar, 3.83 g (16.0 mmol) of **4**, 8.4 g (29.6 mmol) of P_4O_{10} and 50 ml of CH_2Cl_2 were added and refluxed for 4 days; analysis of the reaction showed that all of **4** was consumed and that $SF_5C_6H_5$ was present. Water was added dropwise (50 ml) to the mixture and stirred for 1 h; the organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 (2×20 ml). The volume of the combined organic phases was reduced via distillation to 10 ml. The residue was pumped on through a trap cooled to −78 °C; upon warming the trap to −40 °C and pumping again through another trap cooled to −78 °C left behind 2.87 g (14.1 mmol) of the product $SF_5C_6H_5$ (**3**), 88% yield). A GC–MS spectrum showed the product to be pure.

*3.1.6. Preparation of 1-SF_5-1-cyclohexene (**6**)*

In a 250-ml round-bottomed flask equipped with a Teflon stirring bar, 17.3 g (70.8 mmol) of **5** was dissolved in 150 ml of diethyl ether; to this solution, cooled in an ice-bath, was added 9.5 g (85 mmol) of potassium butoxide in small portions over a 0.5 h period. The reaction mixture was warmed to RT and stirred an additional 14 h; analysis of the solution showed the reaction to be complete. The mixture was poured into 500 ml of water; the lower phase was separated. The remaining aqueous phase was extracted with ether (1×40 ml) and the ether solution was added to the original lower phase. The ether was removed under reduced pressure and the residue distilled through a trap cooled to −196 °C.

The fraction collected at 50–52 °C/8 mmHg was the product **6**; 50.3 mmol, yield was 71%. Some of the product was also present in the −196 °C trap.

IR spectrum (neat, KBr, cm^{-1}): 2946 (s), 2867 (m), 2833(w), 1659 (vw), 1451(w), 1443 (m), 1428 (w), 1365 (w), 1352 (vw), 1273 (w), 1180 (vw), 1147 (w) 1086 (vw), 1060 (w), 944 (s), 931 (m), 827 (vs, sh 850), 812 (vs), 715 (s), 656 (s), 593 (m), 578 (m), 573 (w-m), 532 (w), 514 (w-m), 464 (w).

GC–MS spectrum: 208 $(M)^+$, 127 $(SF_5)^+$, 89 $(SF_3)^+$, 82 $(C_6H_9)^+$, 79 $(C_6H_7)^+$, 53 $(C_4H_5)^+$.

^{1}H NMR (500 MHz, $CDCl_3$, $(CH_3)_4Si$): δ_2 6.50 (distort. T, 1H), $\delta_{3,6/6,3}$ 2.55, 2.31 (2m, 4H), $\delta_{4,5}$ 1.67 (m, 4H).

^{19}F NMR (84.7 MHz, $CDCl_3$, CCl_3F): Φ_A 86.0 (nine line pattern, 1F), Φ_B 55.1 (d-m, 4F), $J = 147.0$ Hz.

*3.1.7. Preparation of trans/cis-1,4-dibromo-2-SF_5-2-cyclohexene (**7**)*

Into a 100-ml round-bottomed flask equipped with a Teflon stirring bar, 2.29 g (11.0 mmol) of **6**, 6.7 g (37.6 mmol) of *N*-bromosuccinimide and 50 ml of CCl_4 were added. The reaction mixture was refluxed for 5 h. After filtration, washing the filtrate with water (50 ml), back-extracting the water with CCl_4 (10 ml), and condensing away the solvent from the combined CCl_4 phases, a light brown oil (3.85 g, 10.1 mmol, 92% yield) was obtained. The GC–MS spectrum showed the absence of **6** and the presence of two new compounds of similar retention time (the dibromo isomers, **7**) with some minor contaminants.

Retention times: first isomer, 12.99 min (27%); second isomer, 13.10 min (73%).

GC–MS spectrum: 287, 285 $(M - Br)^+$, 206 $(M - 2Br)^+$, 205 $(M - H - 2Br)^+$, 185 $(M - H_2F - 2Br)^+$, 127 $(SF_5)^+$, 97 $(C_5H_5S)^+$, 79 $(C_6H_7)^+$, 78 $(C_6H_6)^+$, 77 $(C_6H_5)^+$, 51 $(SF)^+$.

*3.1.8. Dehydrobromination of **7** to give **3***

In a 150-ml round-bottomed vessel equipped with a Teflon stirring bar, 2.75 g (7.5 mmol) of **7** was dissolved in 60 ml of ether and cooled to −78 °C; 2.0 g of potassium butoxide was added over 0.5 h. The mixture warmed to room temperature over a 2 h period where the GC–MS spectrum showed the absence of **7** and the presence of **3**. The solution was poured into 150 ml of a 10% NaCl solution contained in a separatory funnel; after shaking, the ether portion was removed. The aqueous phase was extracted twice more with 20 ml portions of ether. The ether extracts were combined, cooled to 0 °C, and the ether portion was removed under vacuum. The remaining oil (2.8 g) was passed through a short column of silica gel (10 g); 1.51 g of a light brown oily product was recovered. The product was cooled to −30 °C and pumped through a trap cooled to −78 °C; 1.05 g (5.1 mmol, 68% yield) of **3** was found in the −78 °C trap and shown by GC–MS to be pure.

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