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Short communication

The addition of $(CF_3SO_2)_2CHBr$ to vinylidene fluoride

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Abstract

It has been found that a mixture of $(CF_3SO_2)_2CH_2$ and $(CF_3SO_2)_2CBr_2$ can be used instead of $(CF_3SO_2)_2CHBr$ in the radical addition to $H_2C{=}CF_2$; the 1:1 and 1:2 adducts have been isolated and characterized. An improved synthesis of $(CF_3SO_2)_2CBr_2$ is also reported.

Keywords: Bis(trifluoromethanesulfonyl) derivatives; Vinylidene adducts with $(CF_3SO_2)_2CHBr$

1. Introduction

The fact that $SF_5CH_2CF_2SO_3Li$ (prepared from $SF_5CH_2CF_2Br$) formed the first organic superconductor with bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) [1] has prompted us to try to prepare the structural congener $(CF_3SO_2)_2CHCH_2CF_2SO_3Li$ from $(CF_3SO_2)_2CHCH_2CF_2Br$, which in turn is prepared from $(CF_3SO_2)_2CHBr$; this compound is not as readily prepared as was expected [2]. The previous work found that treating $(CF_3SO_2)_2CHK$ with Br_2 in CCl_4 only formed $(CF_3SO_2)_2CHBr$ [2]; in our laboratory with CH_2Cl_2 as the solvent, a mixture of $(CF_3SO_2)_2CH_2$, $(CF_3SO_2)_2CHBr$ and $(CF_3SO_2)_2CBr_2$, was obtained in the molar ratio of 8:19:4 (^{19}F NMR).

Koshar and Mitsch reported in their original work that the monobromo-compound would add in a free-radical process to several terminal olefins [2]. Their work did not encompass fluorinated olefins and they reported only mono-addition products. In a preliminary run with this mixture, we found that $H_2C{=}CF_2$ and benzoyl peroxide heated to about 80 °C for 1 week showed (^{19}F NMR analysis) that the crude product contained the 1:1 adduct, $(CF_3SO_2)_2CHCH_2CF_2Br$, and very little $(CF_3SO_2)_2CH_2$ and $(CF_3SO_2)_2CBr_2$. It was concluded from this result that a 1:1 mixture of $(CF_3SO_2)_2CH_2$ and $(CF_3SO_2)_2CBr_2$ could be used in lieu of $(CF_3SO_2)_2CHBr$. Also, since the dibromo-compound was needed, a simplified procedure for its preparation was developed.

2. Results and discussion

A 1:1 mixture of $(CF_3SO_2)_2CH_2$ (**1**) and $(CF_3SO_2)_2CBr_2$ (**2**) rapidly converts into a mixture of $(CF_3SO_2)_2CHBr$ (**3**, 66%), 17% (**1**) and 17% (**2**) as determined from ^{19}F NMR; each compound appears as a singlet at −78.0 (**1**), −63.5 (**2**), and −72.0 (**3**) ppm. This ratio is found 15 min after mixing and is unchanged after heating at 80 °C for 5 days. The ^{1}H NMR spectrum of the 1:1 mixture of (**1**) and (**2**) contains two singlets at 4.97 (**3**) and 6.18 (**1**) ppm with a respective molar ratio of 77:23 (Fig. 1). Attempts at obtaining pure (**3**) by repeatedly acidifying re-crystallized $(CF_3SO_2)_2CBrNa$ or treating the mercurial salt $[(CF_3SO_2)_2CH]_2Hg$ with bromine in F-113 resulted in mixtures.

In order to simplify the preparation of (**2**), it was found that several additions and removal of a small amount of water to a CH_2Cl_2 solution containing (**1**) and a slight excess of bromine resulted in a yield of (**3**) near 100%. Previous attempts at this preparation using an alkaline bromine solution gave a yield of only 47% [2]. It appears that the water removes HBr from the equilibrium shown below thereby favoring the formation of the dibromo-product (**2**):

$$\underset{(\mathbf{1})}{(CF_3SO_2)_2CH_2}2Br_2\ \underset{(\mathbf{2})}{(CF_3SO_2)_2CBr_2}2HBr$$

Similar equilibria were investigated by Altschul and Bartlett [3] and the same type of reaction is evident with $(CF_3SO_2)_3CCl$ which oxidizes iodide [4].

With a high yield preparation of $(CF_3SO_2)_2CBr_2$ (**2**) in hand, it was possible with $(CF_3SO_2)_2CH_2$ (**1**) to generate in situ $(CF_3SO_2)_2CHBr$ (**3**) and study its addition to $H_2C{=}CF_2$. In this

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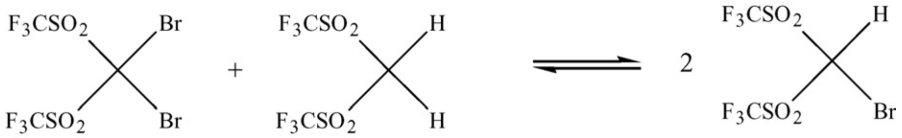

(**2**) (**1**) (**3**)

Fig. 1. Equilibrium of the three bis(trifluoromethanesulfonyl)methane compounds.

manner the mono- and di-adducts were formed (see equation below). It was found that increasing the reaction temperature from ≈80 °C to 90–100 °C led to a greater degree of formation of the di-adduct. The best results were obtained when a slight molar excess (≈5%) of (**2**) was used which simplified the otherwise difficult separation from unreacted reactants due to co-distillation. Also, addition products were not formed when the free-radical initiator was absent:

$$\begin{matrix} (CF_3SO_2)_2CHBr \\ \underset{(\mathbf{3})}{\times\ (1\text{ or }2)\ CH_2CF_2} \end{matrix} \qquad \begin{matrix} \underset{(\mathbf{4})}{(CF_3SO_2)_2CHCH_2CF_2Br} \\ \underset{(\mathbf{5})}{(CF_3SO_2)_2CHCH_2CF_2CH_2CF_2Br} \end{matrix}$$

Both adducts are soluble in water, producing a strongly acidic solution; adduct (**4**) is a liquid and adduct (**5**) is a solid.

Unfortunately, treatment of $(CF_3SO_2)_2CHCH_2CF_2Br$ (**4**) with an excess of one equivalent of sodium sulfite at 115–135 °C for 2 weeks failed to give $(CF_3SO_2)_2CHCH_2CF_2SO_3Na$.

The infrared spectra for the new adducts (**4 and 5**) exhibit strong absorption bands in the C–F region (1100–1400 cm^{-1}) [5]. The SO_2 asym. and sym. stretching bands for compounds (**4** and **5**) are located in the 1391–1399 and 1111–1119 cm^{-1} region [6]. The C–H absorption bands for (**4 and 5**) are located near 3000 cm^{-1}.

The ^1H, ^{19}F and ^{13}C NMR values for the new adducts (Tables 1 and 2) are in agreement with a structures resulting from the attachment at the methylene portion of the vinylidene fluoride molecule. An interesting feature in the ^{19}F NMR spectra (**4** and **5**) is the splitting of the CF_3 groupings. These are usually recorded as singlets but for both adducts triplet splitting is found; there is a long-range interaction which is larger (4.4 Hz) for $^6J_{FF}$ in the di-adduct then in the mono-adduct (3.2 Hz). While for the pentane derivative the $C(3)F_2$-unit appears as a symmetric multiplet and its long-range interaction can only be inferred by the CF_3-splitting in the bis(trifluoromethanesulfonyl) methyl grouping, the reciprocity of splitting between CF_2Br and $(CF_3SO_2)_2C$ is clearly seen in the propane derivative. Gutowsky and Belford [7] found such long-range coupling with six intervening bonds in the compound $(CF_3)_2NCF_2CFBrCF_3$ and attributed the coupling observed between the propyl-CF_3 and the amine-CF_3 groups to a close spatial approach between the two centers. The chemical shifts and splittings of our telomers are correspondingly in close agreement with those found for $CCl_3CH_2CF_2Cl$ and $CCl_3CH_2CF_2CH_2CF_2Cl$ [8] and for $CCl_3CH_2CF_2Br$ [9].

The mass spectrum contained fragments that support the assigned structure.

3. Experimental

The compound $(CF_3SO_2)_2CH_2$ was obtained from 3M company and was sublimed prior to use. The vinylidene fluoride was obtained from PCR while the bromine was obtained from the Aldrich Chemical Co.; both chemicals were used as received.

The infrared spectra of the compounds were obtained on a Perkin-Elmer 2000 FTIR spectrometer operating at 1.0 cm^{-1} resolution using KBr windows. The NMR spectra were recorded in $CDCl_3$-solutions on a Varian EM-390 spectrometer for fluorine (84.7 MHz, CCl_3F (internal) = 0) and on a GE-500 spectrometer (500 (^1H) and 100 (^{13}C) MHz, $Si(CH_3)_4$ (internal) = 0). Gas chromatography–mass spectroscopy (GC–MS) results were obtained using a Hewlett-Packard HP5890 mass selective detector (operating at 70 eV) and a DB5 column. Elemental analysis by Mikroanalytisches Laboratorium Beller, Göttingen, Bundesrepublik Deutschland.

3.1. $(CF_3SO_2)_2CBr_2$

A vigorously stirred mixture of bis(trifluoromethanesulfonyl)methane (20.06 g, 71.6 mmol), methylene chloride (25 ml) and water (15 ml) was treated with bromine (9.5 ml, 184 mmol) in five equal portions during a 5 min period; initially, the bromine color lightened quickly and warming was noted. After 15 min of stirring, a brown two-phase mixture was obtained. The lower layer was drawn off with a separatory funnel and the aqueous phase extracted with 5 ml of methylene chloride (which was now the upper layer). The organic phases were combined and stirred with 15 ml of water for (1/2) h, where a lightening of the color was observed. There were still three species observed in the ^{19}F NMR spectrum with a strongly increased singlet at −63.5 ppm for the dibromo-compound, as compared to the first reaction step. Separating the organic layer and stirring with another 15 ml of water for 0.5 h again led to completion of the bromination (there was only the signal for $(CF_3SO_2)_2CBr_2$ in the ^{19}F NMR spectrum). Drying of the organic phase overnight with anhydrous magnesium sulfate, filtering by suction, washing the $MgSO_4$ with CH_2Cl_2 (25 ml), removal of the methylene chloride by atmospheric distillation and vacuum-distilling the product gave 30.06 g (96% of theory) of $(CF_3SO_2)_2CBr_2$, boiling at 68–72 °C/2.0 Torr, as a light-brown oil. The lit. value is 107–108 °C/17 Torr [2]. The purity >98%, the impurity is $(CF_3SO_2)_2CHBr$ by ^{19}F NMR spectroscopy and was present after but not before drying; storage over K_2CO_3 prevents formation of (**3**). ^{19}F NMR spectrum: $\varphi_1 = -63.5$ ppm, s.

Table 1
NMR data on 1-bromo-1,1-difluoro-3,3-bis(trifluoromethanesulfonyl)-propane

	$(CF_3SO_2)_2$	CH	CH_2	CF_2Br
^{1}H NMR		$\delta = 5.06$, t, 1.0H, $J = 4.45$ Hz	$\delta = 3.28$, d-t, $^3J_{23} = 4.49$, $^3J_{12} = 13.51$, 2.0H	
^{19}F NMR	$\varphi = -73.8$, t, $^6J_{FF} = 3.1$, 6.0F			$\varphi = -49.0$, t-sept., $^3J_{12} = 14.1$, $^6J_{FF} = 3.2$, 2.0F
^{13}C NMR ^{1}H-decoupled	$\delta = 119.41$, q, $J = 329.5$	$\delta = 72.83$, s	$\delta = 31.33$, t, $J = 25.50$	$\delta = 116.46$, t, $J = 305.73$

3.2. Bis(trifluoromethanesulfonyl)bromomethane

The compound was initially synthesized according to the directions given by Koshar and Mitsch with the exception that the potassium salt of bis(trifluoromethanesulfonyl)methane was made in methanol instead of in ethanol and brominated in methylene chloride instead of carbon tetrachloride. In this way, 22.68 g of the dry potassium salt was obtained from 20.00 g of bis(trifluoromethanesulfonyl)methane. 15.57 g of the potassium salt gave 13.95 g of bromination product. This boiled at 64–68 °C/2.5 Torr and consisted (^{19}F NMR spectrum) of an 8:19:4 molar mixture of $(CF_3SO_2)_2CH_2$, $(CF_3SO_2)_2CHBr$ and $(CF_3SO_2)_2CBr_2$.

3.3. Run 1: preparation of $(CF_3SO_2)_2CHCH_2CF_2Br$ (4)

The above mixture containing 8 parts $(CF_3SO_2)_2CH_2$, 19 parts $(CF_3SO_2)_2CHBr$ and 4 parts $(CF_3SO_2)_2CBr_2$ (total wt., 7.77 g) was heated in a 75 ml steel bomb tube with 2.7 g vinylidene fluoride and 100 mg of $(PhCOO)_2$ for 1 week at 75–85 °C. The crude product, 8.79 g of a pale brown liquid, contained very little $(CF_3SO_2)_2CH_2$ and $(CF_3SO_2)_2CBr_2$ and a new compound (^{19}F NMR spectroscopy). Distillation at 1–2 Torr and 63–66 °C, gave 7.32 g (≈80% yield of a clear, colorless, oily liquid, identified as 1-bromo-1,1-difluoro-3,3-bis(trifluoromethanesulfonyl)-propane (**4**). A careful examination of the ^{19}F NMR spectrum of the reaction mixture revealed that there was also present a very small amount of 1-bromo-1,1,3,3-tetrafluoro-5,5-bis(trifluoromethanesulfonyl)-pentane (**5**). Analytical data of (**4**) are given below.

3.4. Run 2: preparation of $(CF_3SO_2)_2CHCH_2CF_2CH_2CF_2Br$ (5)

15.50 g of a 1:1 (molar) mixture of $(CF_3SO_2)_2CH_2$ and $(CF_3SO_2)_2CBr_2$, corresponding to 43.2 mmol of $(CF_3SO_2)_2CHBr$), 210 mg of $(PhCOO)_2$ and 11.28 g of vinylidene fluoride (176 mmol) were added to a 75 ml steel bomb tube and heated (3d, 105–110°). After cooling, the excess vinylidene fluoride was condensed into a cold trap (−196°) and the bomb tube opened. A dark liquid was found, consisting of some $(CF_3SO_2)_2CH_2$, $(CF_3SO_2)_2CBr_2$, $(CF_3SO_2)_2CHBr$, $(CF_3SO_2)_2$ $CHCH_2CF_2Br$ and what was afterwards identified as $(CF_3SO_2)_2CHCH_2CF_2CH_2CF_2Br$ (^{19}F NMR ratio = 4:1:5:23:11, in the above sequence).

After re-sealing the steel tube, and without adding any more benzoyl peroxide, the vinylidene fluoride previously collected in the cold trap was re-introduced into the reaction vessel at −196 °C and heating was continued for three more days at 105–110 °C. After bleeding off of the olefin, practically no change in the composition of the mixture was noted. The crude product was vacuum-distilled at ≈70 °C/3.5–4 Torr, yielding 11.42 g of a clear liquid, consisting ≈60% of 1-bromo-1,1-difluoro-3,3-bis(trifluoromethanesulfonyl)-propane, the rest was bis(trifluoromethanesulfonyl)methane (18%), bis(trifluoromethanesulfonyl)bromomethane (18%) and bis(trifluoromethanesulfonyl)-dibromomethane (4%) by ^{19}F NMR spectroscopy. Further distillation of the pot residue at 75–93°/1 Torr gave a product that solidified in the condenser. The water flow was interrupted and the condenser warmed up with a heat gun in order to melt the solid; distillation was continued with these conditions. This resulted in 6.01 g (28.5% yield) of a semi-solid in the collection flask. Separation from 1-bromo-1,1-difluoro-3,3-bis(trifluoromethanesulfonyl)-propane was achieved by sublimation at 30 μm and ambient temperature overnight (the cold finger, held at 3–4 °C, was initially wrapped in cellulose paper to absorb the collecting liquid and prevent it from falling back into the sample); the paper is removed and the sublimation temperature is raised to 55 °C. At 55 °C, any additional propane derivative is removed by wiping until a solid is collected. The solid obtained contained a small amount of the propane derivative and was

Table 2
NMR data on 1-bromo-1,1,3,3-tetrafluoro-5,5-bis(trifluoromethanesulfonyl)-pentane

	$(CF_3SO_2)_2$	CH	CH_2	CF_2	CH_2	CF_2Br
^{1}H NMR		$\delta = 5.19$, t, 1.0H, $J = 4.39$ Hz	$\delta = 3.23$, d-t, $^3J_{45} = 4.49$, $^3J_{34} = 13.69$		$\delta = 3.29$, t-t, $^3J_{12} = {}^3J_{23} = 13.77$; $\delta_2 + \delta_4 = 4.0$H	
^{19}F NMR	$\varphi = -74.2$, t, 6.0F, $^6J_{FF} = 4.4$			$\varphi = -96.3$, m, 2.0F		$\varphi = -45.7$, t-t, $^3J_{12} = 14.7$, $^4J_{13} = 9.6$, 2.0F
^{13}C NMR ^{1}H-decoupled	$\delta = 119.45$, q, $J = 329.59$	$\delta = 71.36$, s	$\delta = 32.32$, t, $J = 23.89$	$\delta = 117.41$, t, $J = 248.50$	$\delta = 50.39$, quintet, $J = 25.02$ (av.)	$\delta = 115.39$, t, $J = 305.23$

re-sublimed in the same manner at 40 °C. Finally, 1-bromo-1,1,3,3-tetrafluoro-5,5-bis(trifluoromethanesulfonyl)-pentane (2.82 g, 13.4% yield) was obtained as a white solid. This material developed a pinkish tint after a few weeks.

3.5. *1-Bromo-1,1-difluoro-3,3-bis(trifluoromethanesulfonyl)-propane* $(CF_3SO_2)_2CHCH_2CF_2Br$ (**4**)

Infrared spectrum (neat sample on KBr): 3012, vw; 2947, vw; 2898, vw; 1428, w-m; 1399, s; 1216, vs; 1111, vs; 1019, w-m; 948, m; 907, w; 823, vw; 814, vw; 791, vvw; 771, vw; 741, vw; 713, w; 701, w,sh; 661, vw; 643, w; 630, w; 591, w; 582, w; 552, vvw; 542, vvw; 509, m; 501, m; 488, m.

Gas chromatogram–ass spectrum (DB5, 12 m, 50 °C/4 min, then at 18 °C/min to 280 °C, injection block temperature = 250 °C): $R_t = 5.95$ min; mass, %, fragment: 229, 4.3%, $C_5H_3F_2O_4S_2^+$; 209, 3.0%, $(M\text{-}CF_3SO_2\text{-}HBr)^+$; 133, 3.2%, $CF_3SO_2^+$; 125, 11.4%, $C_3F_3S^+$, $C_3H_3F_2OS^+$; 121, 3.8%, $C_3H_2FS_2^+$; 93, 8.2%, $C_2H_2FOS^+$; 91, 14.2%, $C_2H_3O_2S^+$, C_2FOS^+; 77, 17.9%, $C_3H_3F_2^+$, CHO_2S^+; 76, 5.1%, $C_3H_2F_2^+$, CO_2S^+; 75, 13.9%, $C_3HF_2^+$; 69, 100%, CF_3^+; 64, 4.0%, SO_2^+, $C_2H_2F_2^+$; 57, 3.6%, C_2HS^+, $C_3H_2F^+$.

B.p. = 63–66 °C (1–1(1/2) Torr). Anal. calcd.: for $C_5H_3BrF_8O_4S_2$: C, 14.19; H, 0.71; S, 15.15; F, 36.0. Found: C, 14.10; H, 0.70; S, 15.00; F, 35.9%.

3.6. *1-Bromo-1,1,3,3-tetrafluoro-5,5-bis(trifluoromethanesulfonyl)-pentane* $(CF_3SO_2)_2CH(CH_2CF_2)_2Br$ (**5**)

Infrared spectrum (neat sample on KBr): 3019, w; 2994, w; 2974, w; 2967, w; 2941, m; 1439, w; 1403, m-s; 1391, m-s; 1382, s; 1370, m-s; 1329, w; 1252, m-s; 1226, vs; 1209, vs; 1200, s-vs; 1183, m; 1148, m-s; 1119, s; 1100, vs; 1040, w; 1002, w-m; 972, vvw; 942, m; 905, vvw; 888, m-s; 828, m-s; 805, w; 777, w-m; 773, w,sh; 748, m; 715, m; 669, vvw; 649, w; 633, vvw; 611, m; 599, m; 576, w-m; 557, w; 554, w; 539, vvw; 508, m; 489, m; 481, w-m,sh; 448, m.

Gas chromatogram–mass spectrum (DB5, 12 m, 50 °C/4 min, then at 18 °C/min to 280 °C, injection block temperature = 250 °C): $R_t = 8.31$ min; mass, %, fragment: 265, 263, 0.6, 0.6%, $CSCCH_2CF_2CH_2CF_2Br^+$; 253, 27.1%, $CF_3SO_2CCH_2CF_2CHCF^+$; 229, 11.6%, $C_5H_3F_2O_4S_2^+$; 135, 6.8%, $C_4HF_2OS^+$; 113, 11.0%, $C_2F_3S^+$; 91, 5.9%, $C_4H_5F_2^+$; 77, 16.0%, $C_3H_3F_2^+$; 75, 14.5%, $C_3HF_2^+$; 69, 100%, CF_3^+; 51, 15.2% $(CF_2 + H)^+$.

M.p. = 57–58 °C. Anal. calcd.: for $C_7H_5BrF_{10}O_4S_2$: C, 17.26; H, 1.03; S, 13.16; F, 39.0. Found: C, 17.35; H, 1.09; S, 13.04; F, 38.8%.

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