



Short communication

The reaction of SF₅Br with select 1,2-dihaloethylenes

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ABSTRACT

SF₅Br reacts with 1,2-haloethylenes (F, Cl, Br) in distinct ways. In the case of F- and Cl-olefins, the expected addition occurs while with 1,2-dibromoethylene a metathetical reaction yielding in a clean reaction a 1:1 mixture of SF₅CH=CHBr and CHBr₂CHBr₂ is found. The mechanism for this reaction is discussed.

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1. Introduction

The first SF₅-containing alkyl bromide was prepared by reaction of SF₅Br with ethylene [1]. Since 1966, our laboratory has successfully added SF₅Br to a number of fluorinated and chlorofluorinated olefins [2]. In most cases the reaction is a one-to-one addition of SF₅Br to alkenes or alkynes; in some cases oligomers or polymers are formed [3]. In 1996, the first successful addition of SF₅Br to the brominated olefins CH₂=CHBr CHBr and CF₂=CFBr was reported [4]. However, when SF₅Br is added to 1,2-dibromoethylene a new reaction pathway is revealed that should be useful in preparing a large number of interesting SF₅-compounds. Further work in this area is ongoing in our laboratory.

2. Results and discussion

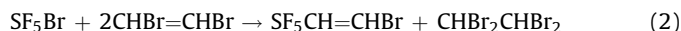
While a significant amount of research has been carried out with the addition of SF₅Br or SF₅Cl to alkenes and alkynes, only one study has examined the reaction of SF₅Br with 1,2-dihaloolefins; in this study, the stereochemistry of the products formed from the reaction of SF₅Br with *cis*- and *trans*-1,2-difluoroethylene was examined. The results of this study were that SF₅Br reacts with *cis*- and *trans*-1,2-difluoroethylene to give nearly the same mixture of erythro- and threo-forms for the addition product SF₅CHFCHFBr [5].

When SF₅Br is reacted with 1,2-dichloroethylene, the expected simple addition occurs giving SF₅CHClCHBrCl:



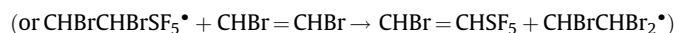
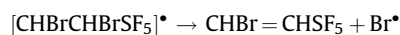
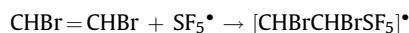
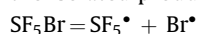
This result is similar to that found for additions of SF₅Br to other chlorinated olefins [6] and to the reaction of CCl₃Br with CHCl=CHCl [7].

However, when SF₅Br is reacted with 1,2-dibromoethylene, a more complex reaction occurs:



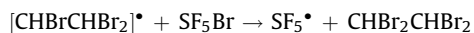
The above reaction with the bromoolefin (Eq. (2)) is interesting because we are aware of only two similar substituent exchanges in radical reactions; the γ -ray induced reaction of CCl₃Br with allylbromide, leading to a 1:1-mixture of CH₂BrCHBrCH₂Br and (CCl₃CH₂)₂CHBr, and similarly the reaction with CHBr=CHBr, resulting in CCl₃CH=CHBr and sym-C₂H₂Br₄ in the ratio of 1:1 [7]. It should be noted that CCl₃Br and 1,2-dichloro-ethylene undergo addition in the usual manner [7].

A rationalization may be provided by the following series of addition and abstraction reactions and agrees with the nature of the isolated products and starting materials:



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The above scheme accounts for all products and the exchange of bromine for the SF₅-group; a key factor is a weak C–Br bond that allows for the loss of a Br radical from an intermediate radical in a neighboring position. Since the C–Cl and C–F bonds are stronger than the C–Br bond, a similar addition–elimination process with CHX=CHX (X = F, Cl) does not occur.

The reaction of SF₅Br with acetylene also produces SF₅CH=CHBr and is an alternative method for preparing this compound [8]. The new method presented in this paper (see Eq. (2)) is a more convenient pathway and avoids the inherent dangers associated with the use of acetylene under pressure. Also, other benefits are that this reaction may be run on a larger scale, separation of products is easily achieved by pumping away the SF₅CH=CHBr (bp 86–89 °C) into a cold trap leaving behind the non-volatile CHBr₂CHBr₂; this stoichiometric by-product may be recycled to give the starting material, 1,2-dibromoethylene. The yield in reaction (2) is nearly quantitative and higher than in the acetylene reaction with SF₅Br (50–80%) [8]. It is interesting that, although the dibromoethylene used was a mixture of the geometric isomers (≈60:40, R_t = 2.95 and 3.36 min, respectively), essentially only one isomer of SF₅CH=CHBr (R_t = 2.2 min.) with the *trans*-configuration (NMR analysis) was obtained. However, when the crude product was injected into the GC–mass spectrometer, a second compound (R_t = 3 min) was present in very low amounts (less than 1%) and had a mass spectrum very similar to that of the main compound *trans*-SF₅CH=CHBr (it is thought that this compound in very low amounts is the *cis*-isomer). Since the 1,2-dibromoethylene isomers are separated (GC–MS) with a difference of almost one half minute, distinction between the *cis*- and *trans*-SF₅CH=CHBr should be possible. To account for the observation that essentially only the *trans*-isomer is present it is assumed that at some point of the reaction an isomerization occurs, most plausibly after addition of the SF₅-radical; the intermediate radical (F₅SCHBrCHBr[•]) may then rotate about the C–C single bond to the preferred configuration from which the Br[•] would be lost, resulting in the formation of the *trans*-product. The product from reaction (2) is the same as that of SF₅Br with C₂H₂, which produces almost exclusively the R_t = 2.2 min compound and trace quantities of the R_t = 3 min isomer [9].

The mass spectra for the compounds contained the parent ions and appropriate fragments. The proton NMR spectrum for SF₅CH=CHBr was obtained at 500 MHz; from analysis, a *trans*-configuration was deduced.

3. Experimental

The compound 1,2-dibromoethylene was prepared according to the literature [10] and the 1,2-dichloroethylene was purchased from TCI America.

All NMR spectra were run in CDCl₃ with either CCl₃F or Si(CH₃)₄ as internal standards. ¹H NMR spectra were run on a GE-500 instrument (500 MHz), ¹⁹F NMR spectra on a Varian 390 (84.7 MHz). Gas chromatography–mass spectroscopy (GC–MS) analysis was performed using a HP-Series 5970 instrument (electron impact, 70 eV), with a temperature program: 50 °C/2 min; then 11 °C/min → 280 °C on a DB-5 column of 30 m length, injection block at 250 °C.

The reactions were run with stirring (Teflon-coated magnetic stirring bar) in acid-washed and thoroughly dried (heating under high vacuum) Carius Pyrex tubes and were irradiated (250 W lamps) at ambient temperature and a distance of 25–40 cm. The

HRMS value for SF₅CHClCHClBr was determined on a Kratos MS 50TC spectrometer; chemical ionization with methane.

3.1. Reaction of 1,2-dibromoethylene and SF₅Br

A mixture of 1,2-dibromoethylene (a mixture of ≈40:60 of the two isomers) and SF₅Br was irradiated at a distance of 40 cm at ambient temperature by four sunlamps for 1 day after which a pinkish liquid was obtained. The crude product contained traces of the 1,2-dibromoethylenes and two main products as found by GC–MS; the main products found were F₅SCH=CHBr and CHBr₂CHBr₂. A minor product (<<1%) was also present and had a mass spectrum very similar to that of F₅SCH=CHBr. The Carius tube was heated to 95 °C and pumped on through a cold trap (–196 °C) for 2.5 h. The material that did not transfer was found to be virtually pure CHBr₂CHBr₂ (16.25 g, 98%, identified by IR spectrum and GC–MS). The condensed product (11.75 g), also practically pure, was distilled at atmospheric pressure to give 11.08 g of a pink liquid, bp = 86–89 °C; it was stirred for a few minutes with 5 drops of Hg to remove any coloration and twice vacuum-transferred, giving 10.96 g (97.1%) of SF₅CH=CHBr a pale tan liquid and which had a tendency to take on a pinkish hue with time.

¹H NMR spectrum: δ₁ = 7.07 (dp, J₁₂ = 13.09 Hz, 1H); δ₂ = 7.30 (d, J₁₂ = 13.09 Hz, 1H). ¹⁹F NMR spectrum (AB₄): δ_A = 80.8 (nine line pattern, 1F); δ_B = 64.6 (dm, J_{AB} = 154 Hz, 4F).

GC–MS; R_t = 2.22 min, (fragment, %, assignment): 232, 234, M⁺, 100%, 100%; 213, 215, 6,5, (M–F)⁺; 153, 6, (M–Br)⁺; 133, 1, (M–Br–HF)⁺; 127, 38, SF₅⁺; 124, 126, 59, 57, C₂H₂BrF⁺ (rearr.); 105, 107, 84, 82, C₂H₂Br⁺; 104, 106, 8, 10, C₂HBrF⁺; 96, 2, SF₂C₂H₂⁺; 89, 65, SF₃⁺; 79, 81, 2,2, Br⁺; 70, 20, SF₂⁺; 58, 5, C₂H₂S⁺; 57, 4, C₂HS⁺; 56, 2, C₂HS⁺; 51, 3, SF⁺; 45, 22, CHS⁺; 43, 4, C₂F⁺ (rearr.); 26, 21, C₂H₂⁺.

IR spectrum (neat sample on KBr): 3103, w-m; 1692, w; 1611, m-s; 1548, w; 1461, vw; 1385, w; 1304, vw; 1275, w; 1196, w-m; 1161, w; 1133, w; 1115, w; 919, s; 893, s; 869, s-vs, sh; 847, vs; 777, m; 734, vw; 708, m-s; 690, vw; 679, w; 632, m-s; 600, s; 570, m-s.

3.2. Reaction of 1,2-dichloroethylene with SF₅Br

A mixture of 1,2-dichloroethylene (9.58 g, 99 mmol), 50 ml of methylene chloride and 17.86 g of SF₅Br (86 mmol) was irradiated at ambient temperature at a distance of 25 cm for a total of 64 h. After removal of the solvent by distillation, 19.00 g of a light yellow liquid remained; distillation gave 16.5 g (63% of theory) bp 72–75 °C (48 Torr). This contained an impurity (GC–MS) and was probably CHBrClCHClF which could almost be completely removed by a second distillation.

¹H NMR spectrum: δ₁ = 5.74 (dp, J_{SF4} = 4.69 Hz, 1H); δ₂ = 6.50 (d, J_{HH} = 1.90 Hz, 1H). ¹⁹F NMR spectrum (AB₄): δ_A = 75.3 (nine line pattern, 1F); δ_B = 55.7 (dm, J_{AB} = 147 Hz, 4F).

Infrared spectrum (neat sample on NaCl): 3014, w; 2993, w-m; 1283, w; 1268, w-vw; 1228, vw; 1181, w-m; 1026, w-m; 886, sh, s; 851, vs; 824, s-vs; 748, m; 680, w-m; 671, w-m; 651, w; 622, w; 589, w-m; 562, w.

GC–mass spectrum; (e/z, fragment, %): 302, 304, 306, 308, M⁺, very feeble, ratio = 9 (0.1%):15:7:1; 223, 225, 227, (M–Br)⁺, ratio = 8 (1.5%):5.5:1; 175, 177, 179, 181, (M–SF₅)⁺, ratio = 10 (25%):15:7:1; 140, 142, 144, (M–SF₅–Cl)⁺, ratio = 3 (1.6%):4:<1; 139, 141, 143, (M–SF₅–Cl–H)⁺, ratio = 10 (9%):14:1; 129, 131, (F₂SC₂Cl)⁺, ratio 4 (12%):1; 127 SF₅⁺, 306; 115, 117, 119, (FCHClCHCl + H)⁺, ratio = 9 (100%):6:1; 96, 98, 100, (CHClCHCl + H)⁺, ratio 9 (39%):6:1; 95, 97, 99, CHClCHCl⁺, ratio = 9 (18%):6:1; 89, SF₃⁺, 34%; 70, SF₂⁺, 5%; 61, 63, C₂H₂Cl⁺, ratio = 3 (24%):1; 60, 62, C₂HCl⁺, ratio = 3 (10%):1.

High-resolution mass spectrum: $^{12}\text{C}_2^{1}\text{H}_2^{79}\text{Br}^{35}\text{Cl}_2^{19}\text{F}_5^{32}\text{S}$, Fd.:
301.83580. Calcd.: 301.83578.

References

- [1] C. Merrill, Ph.D. Thesis, University of Washington, 1962.
- [2] R.W. Winter, R.A. Dodean, G.L. Gard, ACS Symposium Series 911 on Fluorine-Containing Synthons, ACS Publications Division and Oxford University Press, Washington, DC, 2005, pp. 87–118, Chapter 4.
- [3] R.J. Terjeson, G.L. Gard, J. Fluor. Chem. 35 (1987) 653.
- [4] R.J. Terjeson, R. Willenbring, G.L. Gard, J. Fluor. Chem. 76 (1996) 63.
- [5] A.D. Berry, W.B. Fox, J. Org. Chem. 43 (1978) 365.
- [6] Q.C. Mir, R. Debuhr, C. Haug, H.F. White, G.L. Gard, J. Fluor. Chem. 16 (1980) 373.
- [7] E.A.I. Heira, L.C. Anderson, J. Am. Chem. Soc. 79 (1957) 4940.
- [8] J.M. Canich, M.M. Ludwig, W.W. Paudler, G.L. Gard, J.M. Shreeve, Inorg. Chem. 24 (1985) 3668.
- [9] In-house work done at Portland State University.
- [10] v.d. Walle, Bull. Soc. Chim. Belg. 27 (1913) 209.