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Short communication

The reaction of SF_5Br with select 1,2-dihaloethylenes

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ABSTRACT

SF_5Br 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 $SF_5CH{=}CHBr$ and $CHBr_2CHBr_2$ is found. The mechanism for this reaction is discussed.

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1. Introduction

The first SF_5-containing alkyl bromide was prepared by reaction of SF_5Br with ethylene [1]. Since 1966, our laboratory has successfully added SF_5Br to a number of fluorinated and chlorofluorinated olefins [2]. In most cases the reaction is a one-to-one addition of SF_5Br to alkenes or alkynes; in some cases oligomers or polymers are formed [3]. In 1996, the first successful addition of SF_5Br to the brominated olefins $CH_2{=}CHBr$ CHBr and $CF_2{=}CFBr$ was reported [4]. However, when SF_5Br is added to 1,2-dibromoethlylene a new reaction pathway is revealed that should be useful in preparing a large number of interesting SF_5-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 SF_5Br or SF_5Cl to alkenes and alkynes, only one study has examined the reaction of SF_5Br with 1,2-dihaloolefins; in this study, the stereochemistry of the products formed from the reaction of SF_5Br with *cis*- and *trans*-1,2-difluoroethylene was examined. The results of this study were that SF_5Br reacts with *cis*- and *trans*-1,2-difluoroethylene to give nearly the same mixture of erythro- and threo-forms for the addition product $SF_5CHFCHFBr$ [5].

When SF_5Br is reacted with 1,2-dichloroethylene, the expected simple addition occurs giving $SF_5CHClCHBrCl$:

$$SF_5Br + ClCH{=}CHCl \rightarrow SF_5CHClCHBrCl \tag{1}$$

This result is similar to that found for additions of SF_5Br to other chlorinated olefins [6] and to the reaction of CCl_3Br with $CHCl{=}CHCl$ [7].

However, when SF_5Br is reacted with 1,2-dibromoethylene, a more complex reaction occurs:

$$SF_5Br + 2CHBr{=}CHBr \rightarrow SF_5CH{=}CHBr + CHBr_2CHBr_2 \tag{2}$$

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 CCl_3Br with allylbromide, leading to a 1:1-mixture of $CH_2BrCHBrCH_2Br$ and $(CCl_3CH_2)_2CHBr$, and similarly the reaction with $CHBr{=}CHBr$, resulting in $CCl_3CH{=}CHBr$ and sym-$C_2H_2Br_4$ in the ratio of 1:1 [7]. It should be noted that CCl_3Br 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:

$$SF_5Br = SF_5^{\bullet} + Br^{\bullet}$$

$$CHBr = CHBr + SF_5^{\bullet} \rightarrow [CHBrCHBrSF_5]^{\bullet}$$

$$[CHBrCHBrSF_5]^{\bullet} \rightarrow CHBr = CHSF_5 + Br^{\bullet}$$

$$(\text{or } CHBrCHBrSF_5^{\bullet} + CHBr = CHBr \rightarrow CHBr = CHSF_5 + CHBrCHBr_2^{\bullet})$$

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$$CHBr=CHBr + Br^{\bullet} \rightarrow [CHBrCHBr_2]^{\bullet}$$

$$[CHBrCHBr_2]^{\bullet} + SF_5Br \rightarrow SF_5^{\bullet} + CHBr_2CHBr_2$$

The above scheme accounts for all products and the exchange of bromine for the SF_5-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 SF_5Br with acetylene also produces $SF_5CH=CHBr$ 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 $SF_5CH=CHBr$ (bp 86–89 °C) into a cold trap leaving behind the non-volatile $CHBr_2CHBr_2$; 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 SF_5Br (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 $SF_5CH=CHBr$ ($R_t = 2.2$ 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*-$SF_5CH=CHBr$ (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*-$SF_5CH=CHBr$ 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 SF_5-radical; the intermediate radical ($F_5SCHBrCHBr^{\bullet}$) may then rotate about the C–C single bond to the preferred configuration from which the $Br^{\bullet}$ would be lost, resulting in the formation of the *trans*-product. The product from reaction (2) is the same as that of SF_5Br with C_2H_2, 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 $SF_5CH=CHBr$ 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 $CDCl_3$ with either CCl_3F or $Si(CH_3)_4$ as internal standards. ^1H NMR spectra were run on a GE-500 instrument (500 MHz), ^{19}F 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 $SF_5CHClCHClBr$ was determined on a Kratos MS 50TC spectrometer; chemical ionization with methane.

3.1. Reaction of 1,2-dibromoethylene and SF_5Br

A mixture of 1,2-dibromoethylene (a mixture of ≈40:60 of the two isomers) and SF_5Br 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 $F_5SCH=CHBr$ and $CHBr_2CHBr_2$. A minor product (≪1%) was also present and had a mass spectrum very similar to that of $F_5SCH=CHBr$. 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 $CHBr_2CHBr_2$ (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 $SF_5CH = CHBr$ a pale tan liquid and which had a tendency to take on a pinkish hue with time.

^1H NMR spectrum: $\delta_1 = 7.07$ (dp, $J_{12} = 13.09$ Hz, 1H); $\delta_2 = 7.30$ (d, $J_{12} = 13.09$ Hz, 1H). ^{19}F NMR spectrum (AB_4): $\delta_A = 80.8$ (nine line pattern, 1F); $\delta_B = 64.6$ (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, SF_5^+; 124, 126, 59, 57, $C_2H_2BrF^+$ (rearr.); 105, 107, 84, 82, $C_2H_2Br^+$; 104, 106, 8, 10, C_2HBr^+; 96, 2, $SF_2C_2H_2^+$; 89, 65, SF_3^+; 79, 81, 2,2, Br^+; 70, 20, SF_2^+; 58, 5, $C_2H_2S^+$; 57, 4, C_2HS^+; 56, 2, C_2HS^+; 51, 3, SF^+; 45, 22, CHS^+; 43, 4, C_2F^+ (rearr.); 26, 21, $C_2H_2^+$.

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 SF_5Br

A mixture of 1,2-dichloroethylene (9.58 g, 99 mmol), 50 ml of methylene chloride and 17.86 g of SF_5Br (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: $\delta_1 = 5.74$ (dp, $J_{SF4} = 4.69$ Hz, 1H); $\delta_2 = 6.50$ (d, $J_{HH} = 1.90$ Hz, 1H). ^{19}F NMR spectrum (AB_4): $\delta_A = 75.3$ (nine line pattern, 1F); $\delta_B = 55.7$ (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, $(M-SF_5)^+$, ratio = 10 (25%):15:7:1; 140, 142, 144, $(M-SF_5-Cl)^+$, ratio = 3 (1.6%):4:<1; 139, 141, 143, $(M-SF_5-Cl-H)^+$, ratio = 10 (9%):14:1; 129, 131, $(F_2SC_2Cl))^+$, ratio 4 (12%):1; 127 SF_5^+, 30%; 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, SF_3^+, 34%; 70, SF_2^+, 5%; 61, 63, $C_2H_2Cl^+$, ratio = 3 (24%):1; 60, 62, C_2HCl^+, ratio = 3 (10%):1.

High-resolution mass spectrum: $^{12}C_2{}^{1}H_2{}^{79}Br^{35}Cl_2{}^{19}F_5{}^{32}S$, Fd.: 301.83580. Calcd.: 301.83578.

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