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The chlorination of 1,2-difluoroethane (HFC-152)

Mario J. Nappa* and Allen C. Sievert

E. I. du Pont de Nemours and Co., Du Pont Chemical, Jackson Laboratory, Chambers Works, Deepwater, NJ 08023 (USA)

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Abstract

The photochlorination of CH_2FCH_2F yields CH_2FCCl_2F and CHClFCHClF, both of which were considered to be potential replacements for CFC-113 (CCl_2FCF_2Cl) based on their boiling points (48 °C and 59 °C, respectively). The CHClFCHClF/CH_2FCCl_2F ratio can be controlled by the choice of solvents. In aromatic solvents, the reactivity of the chlorine radical is reduced, increasing the amount of CH_2FCCl_2F produced. Relative rates in CCl_4 and in the presence of water were compared to rates in aromatic solvents. Both CH_2FCCl_2F and CHClFCHClF failed in early toxicity tests and will thus not be pursued as HCFC replacements for CFC-113.

Introduction

The search for suitable replacements for chlorocarbons and chlorofluorocarbons (CFCs) has intensified in recent years with the adoption of the Montreal Protocol and increasing international pressure to eliminate the use of CFCs by 1996 or sooner [1, 2]. Preferred replacements for CFCs contain hydrogen; these compounds have reduced atmospheric lifetime and ozone depletion potential (ODP). Many of the first wave of replacements also contain chlorine and are known as HCFCs (hydrochlorofluorocarbons). HCFCs themselves are considered to be interim products due to their expected phase-out early in the 21st century [3].

A possible route to HCFCs is the chlorination of hydrofluorocarbons (HFCs), many of which are available via classical chemistry such as the addition of HF to unsaturated compounds or via the Swarts reaction. Examples are (1) the chlorination of HFC-152a (CH_3CHF_2) to make HCFC-142b (CH_3CClF_2), an alternate blowing agent for foams [4], and (2) the chlorination of HFC-143a (CH_3CF_3) or HCFC-133a (CH_2ClCF_3) to make HCFC-123 ($CHCl_2CF_3$), a possible replacement for CFC-11 ($CFCl_3$) and, for some applications, CFC-113 (CCl_2FCF_2Cl) [5].

Due to its low toxicity and many applications, CFC-113 (b.p. 47.6 °C) has proven to be a particularly difficult compound to replace [6]. Although

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*Author to whom all correspondence should be addressed at Central Research and Development Dept., Experimental Station, E.I. du Pont de Nemours and Co., P.O. Box 80262, Wilmington, DE 19880-0262, USA.

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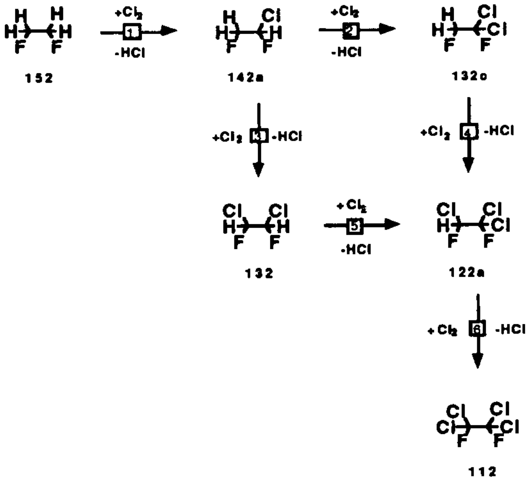
blends of HCFC-141b (CH_3CCl_2F) and HCFC-123 are being touted as replacements for CFC-113, the blends are not drop-in replacements due to their lower boiling points and requirement for new equipment in cleaning agent applications [7]. Two potential replacements for CFC-113 based on their boiling points are HCFC-132 (CHClFCHClF, b.p. 59 °C) and HCFC-132c (CH_2FCCl_2F, b.p. 48 °C).

Several preparations of HCFC-132 and HCFC-132c have been described in the literature; none are particularly suited for large-scale reactions. HCFC-132 has been prepared by the addition of fluorine across the double bond of *trans*-1,2-dichloroethylene using PbO_2/HF [8], AgF_2 [9], CoF_3 [9], PbO_2/SF_4 [10] and F_2 [11]. HCFC-132c has been prepared by the reaction of vinylidene chloride with the PbO_2/SF_4 reagent [10]; other metal fluorides were reported to be unsuccessful in adding fluorine [9]. Both HCFC-132 and -132c were formed as by-products from the reaction of SF_5OF with *cis*-1,2- and 1,1-dichloroethylene, respectively [12].

In this paper, we describe a convenient route for the synthesis of both HCFC-132 (a mixture of diastereomers) and HCFC-132c via the chlorination of HFC-152 (CH_2FCH_2F).

Results and discussion

The photochlorination of CH_2FCH_2F had been reported by Yano and coworkers; however, the reaction was carried out with excess hydrofluorocarbon (low hydrofluorocarbon conversion), and the dichloro species were not reported [13]. The focus of these works was the determination of the absolute rate parameters for the initial chlorination step for a series of hydrofluorocarbons. The stepwise chlorination of CH_2FCH_2F to yield ultimately CCl_2FCCl_2F is shown below (Scheme 1):



Scheme 1.

In our initial experiments, we carried out the chlorination of CH_2FCH_2F in CCl_4 to minimize losses of starting material due to the evaporation of the volatile components of the reaction. The chlorination reaction whose course is depicted in Fig. 1 occurs in the stepwise manner as outline above. The initial concentration of CH_2FCH_2F was 51% by weight, the temperature being 8–10 °C to minimize evaporative loss. Despite these conditions, we obtained only 48% recovery of products derived from the chlorination.

We did not measure the absolute rate constant for the chlorination of HCFC-152, but it is reported to be 13.8×10^{-13} cm^3 s^{-1} at 0 °C [13]. It has been reported that the rate constant for the chlorination of the secondary hydrogens in CH_2FCH_2F is 29-times greater than the secondary hydrogens in $C\mathit{H}_2FCHF_2$ and 14.2-times greater than the tertiary hydrogen in $CH_2FC\mathit{H}F_2$ [13]. The replacement of a hydrogen by a fluorine (or chlorine in our case) reduces the rate of subsequent chlorinations. The tertiary hydrogen in $CH_2FC\mathit{H}F_2$ is 2.1-times more reactive in photochlorinations than each of its secondary hydrogens [14]. If both types of hydrogen in $CH_2FCHClF$ reacted at the same rate, we would generate twice as much $CHClFCHClF$ as CH_2FCCl_2F in the early stages of the chlorination, since there are twice as many secondary hydrogens; from the graph shown in Fig. 1 this is clearly not the case.

While substitution of a hydrogen in CH_2FCH_2F with a chlorine to make $CHClFCH_2F$ results in an overall decrease in the rate of subsequent chlorinations, geminal hydrogens are activated by the chlorine relative to the vicinal hydrogens. This effect was also measured for the chlorination of 2,2-difluoropropane, where the relative reactivities of the hydrogens are as follows [13]:

$CH_3\text{–}CF_2C\mathit{H}_3$	$C\mathit{H}_3\text{–}CF_2C\mathit{H}_2Cl$		$C\mathit{H}_3\text{–}CF_2C\mathit{H}Cl_2$	
1.0	0.11	4.1	0.11	4.4

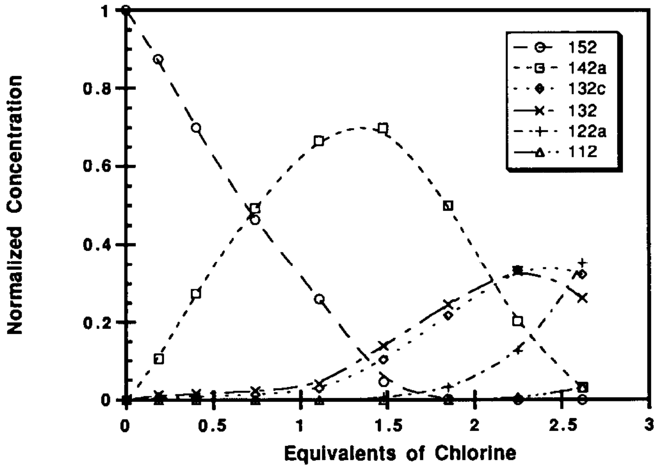


Fig. 1. The photochlorination of CH_2FCH_2F in CCl_4.

In general, solvents reduce the amount of evaporative loss of volatile components, such as CH_2FCH_2F or $CH_2FCHClF$ in our case, because they reduce the partial pressures of these components. Whilst the use of a solvent was helpful, we ultimately reduced evaporative loss by using a reflux condenser chilled to −30 °C. In another attempt to minimize the amount of evaporative loss, CH_2FCH_2F was chlorinated in the presence of water to trap the HCl; in this case, there was no solvent (e.g. CCl_4) except for water. The internal cooling coils of our reactor were kept at 6–7 °C, and recovery was improved to 63%. Initially, we had thought that the presence of water would increase the reactivity of the chlorine radical and reduce selectivity, but the only side-effect is the production of more CCl_2FCCl_2F from the chlorination of $CHClFCCl_2F$.

It is known that the use of aromatic solvents in photochlorination reactions can affect the selectivities by reducing the reactivity of the chlorine radical, making it more selective [15–17]. Common aromatic solvents which affect the selectivities are chlorobenzene, fluorobenzene and dichlorobenzene. We have carried out a reaction in chlorobenzene (1.5 wt.%) at 5 °C and the results are shown graphically in Fig. 2.

At low conversion of $CH_2FCHClF$, the $CH_2FCCl_2F/CHClFCHClF$ ratio should be equal to the k_2/k_3 ratio, which was observed to be 1.4 compared to 0.9 for the reaction in CCl_4 indicating that chlorobenzene does moderate the reactivity of the chlorine radical making it more selective. Unfortunately, however, the rate of chlorination is reduced significantly, and from the shallow slope of the disappearance of $CH_2FCHClF$ we have determined that much of the chlorine is emerging unreacted; moreover, 10-times as much chlorine needs to be added as in the CCl_4 reaction for similar conversions of CH_2FCH_2F. Chlorination of CH_2FCH_2F was also carried out in fluorobenzene, when a k_2/k_3 ratio equal to 1.5 was obtained, which is also better than in CCl_4 or neat CH_2FCH_2F solution. The use of aromatic solvents enabled us to vary the split of CH_2FCCl_2F and $CHClFCHClF$ from the case where no solvent

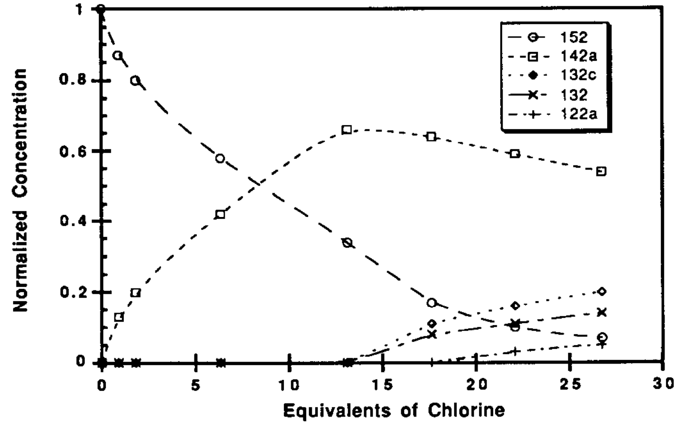


Fig. 2. The photochlorination of HCFC-152 in chlorobenzene solution.

or when CCl_4 was used to yield a product which was predominantly $CHClFCHClF$ to one which was predominantly CH_2FCCl_2F.

We have utilized a photochlorination technique to convert CH_2FCH_2F to CH_2FCCl_2F and $CHClFCHClF$, both candidates for the replacement of CFC-113. Unfortunately, both failed in toxicity studies: CH_2FCCl_2F exposure produced degeneration and necrosis of seminiferous epithelial cells in the testes of exposed male rats. $CHClFCHClF$ was reported to have a low LC_{50} value [18] and this has been confirmed. Although useful laboratory reagents, these are not being pursued as commercial solvent replacements for CFC-113 (which has an acceptable exposure limit of 1000 ppm) because of their acute toxicity.

Experimental

Carbon tetrachloride was purchased from Baker; chlorobenzene and fluorobenzene were purchased from Aldrich, and all were used as received. Chlorine (Linde) was purified by passing through a Balston (Lexington, MA) cartridge filter to remove entrained ferric chloride. Chlorine was metered using either Teledyne Hastings mass flow controllers (CST-50MG) or Matheson rotometers. All rotometers were calibrated with nitrogen and corrected for chlorine using a factor of 0.66.

CAUTION! In inhalation studies on male rats, CH_2FCH_2F was found to be highly toxic: all rats exposed to average concentrations of 75 ppm or greater died during exposure or within a 24 h period after exposure [19]. CH_2FCH_2F should only be handled under conditions where exposure to personnel is minimized by proper protective equipment and adequate ventilation. CH_2FCH_2F was prepared via ethylene glycol as previously described [20]. CH_2FCCl_2F and $CHClFCHClF$ were characterized by GC–MS (CH_2FCCl_2F *m/e*: 66; 79; 99; 101; 103 $CHClFCHClF$ *m/e*: 67; 69; 79; 99; 101) and NMR spectroscopy (see below). In the NMR spectral studies, all the spectra were recorded in CD_2Cl_2. ^1H and ^{13}C spectra were referenced to internal TMS; ^{19}F spectra were referenced to external CCl_3F.

$CH_2FCHClF$: ^{19}F NMR δ: -146.1 (m, $-CHCl\mathit{F}$); -221.05 (tdd, $^2J_{HF}=46.6$ Hz, $^3J_{FF}=20.6$ Hz, $^3J_{HF}=9.8$ Hz, $-CH_2\mathit{F}$) ppm.

$CHClFCHClF$: ^1H NMR δ: 6.23 (m) ppm. ^{13}C NMR δ: 98.58 (ddd, $J_{CF}=251.68$ Hz, $^1J_{CH}=218.7$ Hz, $^2J_{CF}=31.1$ Hz) ppm. ^{19}F NMR δ: -146.28 (m); -147.97 (m) ppm.

CH_2FCCl_2F: ^1H NMR δ: 4.70 (dd, $^2J_{HF}=46.4$ Hz, $^3J_{HF}=3.6$ Hz) ppm. ^{13}C NMR δ: 86.6 (dtd, $^1J_{CF}=193.5$ Hz, $^2J_{CF}=26.5$ Hz, $^1J_{CH}=159.4$ Hz, $-\mathit{C}H_2F$); 116.6 (dd, $^1J_{CF}=299.1$ Hz, $^2J_{CF}=22.9$ Hz, $-\mathit{C}Cl_2F$) ppm. ^{19}F NMR δ: -66.84 (dt, $^3J_{HF}=14.0$ Hz, $^3J_{FF}=22.2$ Hz, $-CCl_2\mathit{F}$); -210.31 (dt, $^2J_{HF}=46.6$ Hz, $^3J_{FF}=22.8$ Hz, $-CH_2\mathit{F}$) ppm.

$CHClFCCl_2F$: ^{19}F NMR δ: -69.47 (d, $^3J_{FF}=21.9$ Hz, $-CCl_2\mathit{F}$); -139.74 (dd, $^2J_{HF}=48.3$ Hz, $^3J_{FF}=22.6$ Hz, $-CHCl\mathit{F}$) ppm.

CCl_2FCCl_2F: ^{19}F NMR δ: -67.66 (s) ppm.

Photochlorination in CCl_4

CH_2FCH_2F (110 g, 1.67 mol) and CCl_4 (108 g, 0.70 mol) were added to a modified 1 l Ace® photochemical reactor shown in Fig. 3. The reactor was modified to allow for expansion of the solution which occurred during the chlorination process. Chlorine (125 g, 1.76 mol) was added over 7.1 h whilst keeping the temperature of the solution between 8–10 °C. At the end of the reaction, 207 g (including CCl_4) was isolated and the absolute yields were calculated by GPLC methods: ($CHClFCCl_2F$, 19%; $CHClFCHClF$, 14%; CH_2FCCl_2F, 11%; $CHClFCH_2F$, 2%; CCl_2FCCl_2F, 2%; we assume the remainder was lost due to evaporation of the low-boiling CH_2FCH_2F (30.7 °C) and $CHClFCH_2F$ (~35 °C)). See Fig. 1 for concentration profiles. The loss of more than one-half of the organic material during the run explains the need for only slightly more than 1 equiv. of chlorine to prepare the dichloro species as shown in Fig. 1.

Photochlorination in the presence of water

CH_2FCH_2F (20.0 g, 0.30 mol) and H_2O (54.8 g, 3.04 mol) were added to a photofluorinator described elsewhere [21]. Chlorine (90.9 g, 1.28 mol) was added over 8 h whilst stirring vigorously and keeping the temperature of the solution between 6–8 °C. A total of 37 g of over-chlorinated material was isolated with the following overall yields calculated by GPLC methods: (CH_2FCCl_2F, 3%; $CHClFCl_2F$, 25%; CCl_2FCCl_2F, 36%).

Photochlorination in chlorobenzene

CH_2FCH_2F (1.0 g, 0.015 mmol) and C_6H_5Cl (58.1 g, 0.606 mol) were added to a small cylindrical Pyrex reactor with internal cooling coils and containing a small Teflon® stir bar. The chlorine (7.74 g, 0.11 mmol) was added over 3.5 h whilst keeping the temperature of the solution at 10 °C.

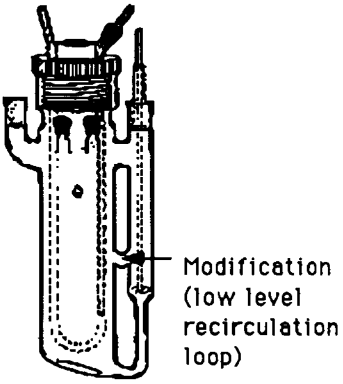


Fig. 3. Ace® photochemical reactor.

See Fig. 2 for concentration profiles. During the chlorination, the outside of the reactor was irradiated with an RMS UV tanning lamp*.

Large-scale photochlorination

To a 10 l version of the Ace photochlorinator shown in Fig. 3, equipped with an Allihn condenser operated at -27 °C, was added CH_2FCH_2F (1.02 kg, 16.5 mol). Whilst keeping the solution at 7–12 °C, chlorine was added for 9 h at a flow rate of 1.5 l min^{-1} (2.32 kg, 33.1 mol). The organic product (1936 g) isolated was analyzed as follows by GPLC methods: $CHClFCH_2F$, 497 g (4.9 mol); CH_2FCCl_2F, 578 g (4.3 mol); CHClFCHClF, 600 g (4.5 mol); $CHClFCCl_2F$, 224 g (1.3 mol); CCl_2FCCl_2F, 37 g (0.2 mol); this results in an overall yield of 89%. Because of the large difference in boiling points and the lack of azeotrope formation, the products of the chlorination are easily isolable by fractional distillation.

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*A commercial Sylvania RMS sunlamp has a Pyrex-type glass lens so that there is very little light generated below 280 nm wavelength. Over the range 280–320 nm, a typical 250 W RS type sunlamp generates 1.2 W, from 320–380 nm that generated is 2.9 W, with 1.0 W being generated from 380–500 nm, 1.7 W from 500–600 nm and 0.26 W from 600–700 nm.

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