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Journal of Fluorine Chemistry 128 (2007) 552–556
JOURNAL OF FLUORINE CHEMISTRY
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Short communication

Thermal chlorofluorination of propyne and propadiene II

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Received 11 December 2006; received in revised form 22 January 2007; accepted 24 January 2007
Available online 31 January 2007

Abstract

Propyne and propadiene have been previously reported to readily undergo vapor phase catalyzed chlorofluorination at temperatures to 285 °C to form $C_3F_4Cl_4$ mixtures that are primarily $CFCl_2$–CF_2–$CFCl_2$. Continued fluorination at temperatures up to 485 °C produce the rearranged $C_3F_6Cl_2$ isomers CF_3–CCl_2–CF_3 and CF_2Cl–$CFCl$–CF_3.

Keywords: Chlorofluorination; Propyne; 1,2-Propadiene; Dichlorohexafluoropropane

1. Introduction

In a previous publication [1], we reported that propyne and propadiene readily undergo vapor phase chlorofluorination at temperatures up to 285 °C. The principal products of this reaction are saturated tetrachlorotetrafluoropropanes, with the major isomer being 1,1,3,3-tetrachloro-1,2,2,3-tetrafluoropropane ($CFCl_2$–CF_2–$CFCl_2$) (see Scheme 1). This selectivity contrasted with the terminally fluorinated products obtained from either propane or propene. The present study was undertaken to push this reaction further to produce more highly fluorinated products. The objective was to determine whether the reversed selectivity would hold or whether rearrangements would ensue and alter the stereoselectivity back to that seen for propane and propene.

The precedent for high temperature thermal chlorofluorination of propane and propene can be found in processes that have been developed by E.I. Du Pont de Nemours [2–4] and Great Lakes Chemical Corp. [5]. Both cases use chromium based catalysts to produce 2,2-dichlorohexafluoropropane (CF_3–CCl_2–CF_3) as the nearly exclusive $C_3F_6Cl_2$ product. More strenuous conditions further fluorinate the products to 2-chloro-1,1,1,2,3,3,3-heptafluoropropane (CF_3–$CFCl$–CF_3). The processes diverge at this point to produce hexafluoropropene and 1,1,1,2,3,3,3-heptafluoropropane, respectively. As the chloroheptafluoropropane is simply the product of harsher fluorination conditions and involves fully expected chemistry, the extent of fluorination that would be considered "full" for this project was hexafluorination to $C_3F_6Cl_2$ product. From there one may choose to follow either the Du Pont or the Great Lakes methodologies.

It is indicated in Fig. 3 of Webster et al. [2] that the hexafluoro isomer CF_2Cl–$CFCl$–CF_3 will isomerize to CF_3–CCl_2–CF_3 under reaction conditions over 350 °C. The heptafluoro isomer CF_2Cl–CF_2–CF_3 isomerizes to CF_3–$CFCl$–CF_3 according to Fig. 1 of Webster et al. [2] and paragraph 0105 of Iikubo et al. [5]. The propensity for these reactions all along is to produce terminally fluorinated products either directly or by rearrangement. Therefore, it is anticipated that although chlorofluorination of propyne and propadiene produces the internally fluorinated $CFCl_2$–CF_2–$CFCl_2$, rearrangement could likely change the nature of the hexafluorinated product. Kvicala et al. [6] performed $FeCl_3$ catalyzed fluorinations in the presence of chlorine on various tri-, tetra-, and pentafluorinated propanes at 360–390 °C. The pentafluoropropane $CFCl_2$–$CFCl$–CF_3 rearranged 38% to CF_2Cl–CCl_2–CF_3 at 390 °C. The hexafluorinated material that was isolated had rearranged only 12% further (i.e. was mostly CF_2Cl–$CFCl$–CF_3). The only example containing an internally difluorinated substrate (Expl. 7) reacted a mixture of tetrafluorides containing 42% internally difluorinated (mostly CCl_3–CF_2–CF_2Cl) and 50% internally monofluorinated (mostly CCl_3–$CFCl$–CF_3) propanes. This reaction at 365 °C shows pentafluorinated products that are about 28% monoisomerized and hexafluorinated products that are 54% diisomerized (from $CFCl_2$–CF_2–CF_2Cl to CF_3–CCl_2–CF_3, see

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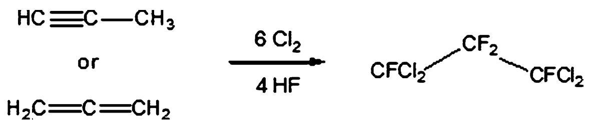
doi:10.1016/j.jfluchem.2007.01.010



Scheme 1.

Scheme 2). At these temperatures, neither conversion nor isomerization is complete.

The initial goal of this project was to determine whether propyne could, in fact, serve as a viable feedstock for high temperature vapor phase chlorofluorination. With that already established in the previous communication [1], it became the next goal to press the fluorination to the hexafluorodichloropropane family of products. Evaluation of the isomer content would follow.

2. Results and discussion

2.1. Reaction conditions

Reactions were performed in a single 1 in. (2.5 cm) diameter tubular reactor, 24 in. (61 cm) long, with two electrically heated temperature zones of equal length. As described in the literature [5], it is advisable to perform chlorofluorination reactions of hydrocarbons in two stages. A first stage reaction is performed at a lower temperature of between 225 and 285 °C in order to mitigate the exotherm of initial chlorination. A second stage reaction is then performed at a higher temperature of approximately 450–500 °C to encourage more complete fluorine for chlorine exchange. In the previous study, the conditions for the lower temperature, first stage chlorofluorination reaction of propyne and propadiene had been established. The inlet temperature would be moderated to about 225 °C by controlling the feeds and the outlet temperature would be allowed to achieve 285 °C. A molar ratio of HF to hydrocarbon of ~30:1 effectively controlled the exotherm for the temperatures and feed rates of the examples. A chlorine to hydrocarbon molar ratio of 9–12:1 ensured full chlorine-for-hydrogen exchange. Thorough dilution of the hydrocarbon and chlorine feeds in the HF is essential for minimizing by-product formation. As such, the HF feed was split into two equal streams. One stream was mixed with propyne and the other stream was mixed with chlorine. The two streams were vaporized each in a separate vaporizer. The two streams were recombined at the entrance to the reactor. The outflow of this first reactor, which has been established above to be principally tetrachlorotetrafluoropropanes, was then passed on through a short length of heated tubing to a second reactor, of identical dimensions as the first. This reactor tube was held at a constant temperature, equal or higher than the first reactor (285–485 °C, see Table 1). The pressure of the reactor was held at 50 psi. Both reactor beds were charged with chromium oxide-on-carbon catalyst that was activated with HF and 2% oxygen before use.

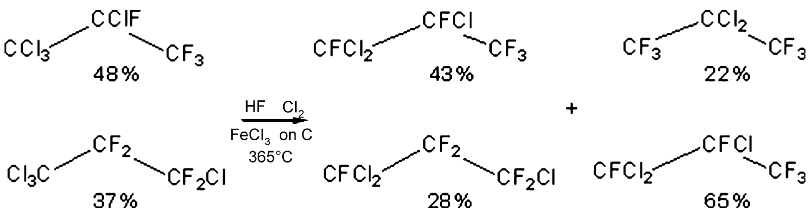
Table 1
GC percentage of chlorofluoropropanes from chlorofluorination of propyne

Temperature	$C_3F_6Cl_2$	$CF_2Cl–CFCl_2$	$C_3F_5Cl_3$	$C_3F_4Cl_4$
285 °C	–	–	12	83
385 °C	10	1	17	66
435 °C	18	5	33	43
485 °C	34	36	26	3
Propane (435 °C)	43	1.7	19.2	31.4

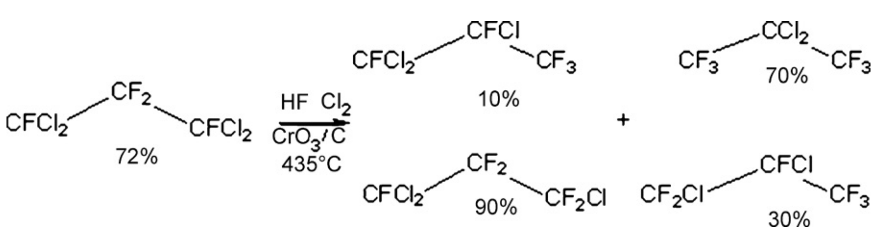
2.2. Fluorination experiments on propyne

Propyne was fed into the first chlorofluorination reactor under the same conditions used to produce tetrachlorotetrafluoropropane. Preheaters brought both feeds to approximately 200 °C. With an HF:Cl_2:propyne molar ratio of 30:10:1, the reaction ran adiabatically and the temperature of the inlet zone stabilized around 230 °C while the outlet zone leveled-out at 285 °C. The outflow of this first reactor passed through a 1/2 in. diameter transfer tube, heated to the temperature of the second reactor, and entered the second reactor at the top. Several temperatures were tested for the second reactor. Initially, 285 °C (the same temperature as the first reactor's outlet) was tried in order to establish the effectiveness of simply longer residence time. Feed composition as it came from the first reactor would be 14% $C_3F_5Cl_3$, 70% $C_3F_4Cl_4$ and 7% $C_3F_3Cl_5$. Little additional reaction occurred in the second reactor. Reactions were then performed with the second reactor at 385, 435 and 485 °C. The results are shown in Table 1.

With all the literature precedents for chlorofluorination of propane, it is no surprise that temperatures near 450 °C are necessary for conversion to hexafluorinated products. What was surprising was the amount of fragmentation encountered, as evidenced by the observation and isolation of the C-2 component $CFCl_2–CF_2Cl$ (CFC-113). It had been anticipated that most fragmentation would occur in the first reactor during the exothermic reaction of hydrogen containing intermediates. Rather, it was occurring with the more-or-less stable fully halogenated materials. As a control experiment, propane was reacted under identical conditions on the same bed of catalyst.



Scheme 2.



Scheme 3.

As shown in Table 1, propane exhibited much less fragmentation while undergoing appreciably more conversion.

The 435 °C sample of hexafluorinated and pentafluorinated materials was analyzed for their isomeric composition. Whereas GC/MS with a 60 M DB-1 column had been a useful tool for analyzing $C_3F_3Cl_5$, $C_3F_4Cl_4$ and $C_3F_5Cl_3$ isomeric compositions, the $C_3F_6Cl_2$ isomers were not separated. ^{13}C NMR, however, made quick work of identifying the isomers and ^{19}F NMR integration quantified their relative amounts. The pentafluorotrichloropropane fraction is 90% 1,1,3-trichloro-1,2,2,3,3-pentafluoropropane ($CFCl_2–CF_2–CF_2Cl$) and 10% 1,2,3-trichloro-1,1,2,3,3-pentafluoropropane ($CF_2Cl–CFCl–CF_2Cl$), correlating to 90% unrearranged and 10% mono-rearranged product. The target dichlorohexafluoro- fraction is 70% 2,2-dichloro-1,1,1,3,3,3-hexafluoropropane ($CF_3–CCl_2–CF_3$) and 30% 1,2-dichloro-1,1,2,3,3,3-trifluoropropane ($CF_2Cl–CFCl–CF_3$).

It had been hoped that the extent of fluorination would increase stepwise at some temperature to produce predominantly pentafluorinated product, just as tetrafluorinated product predominated at 285 °C. This was not the case. So, the question of when rearrangement occurs is still somewhat open. Clearly, the majority of pentafluorinated material observed was non-rearranged. However, this may be because rearranged material was quicker to fluorinate on to hexafluoro-material (and generate $–CF_3$ groups). What is evident is that no appreciable amount of the hexafluoro- material had retained the internal-CF_2– substitution (see Scheme 3). For the most part, double isomerization had occurred. This leads one suspect that, in slight contrast to the example of Kvicala et al. [6] most pentafluoro- material was double isomerizing to a species ($CF_2Cl–CCl_2–CF_3$) that was quickly fluorinated further. Note that Kvicala used a less active $FeCl_3$ based catalyst but did operate with much longer residence time (larger reactor, less HF, Cl_2, and HCl) which should have allowed substantial opportunity for rearrangements to occur.

The fragmentation of the C-3 compounds to $CCl_2F–CF_2Cl$ is indeed a problem. As evidenced by the lack of fragmentation in the propane product, this is the direct result of trying to react species that are more sensitive to chlorine radical attack. The pathways available to these species for releasing energy are either rearrangement or fragmentation. At 485 °C, it is almost a 50/50 split. It is possible that changing the catalyst or fine tuning the conditions may decrease the rate of fragmentation (but this is not likely if fragmentation is free radical induced). However, since rearrangement is occurring to generate the same product as that obtained more readily from propane, that effort is not worthwhile.

2.3. *Initial chlorofluorination steps*

With the endgame of the chlorofluorination of propyne evaluated, some study was made into the earlier stages of this reaction, particularly into the selectivity of this reaction to produce 2,2-*gem* fluorinated tri-, and tetrafluorinated products. It seems odd that HF addition across the triple bond of propyne or the allenic bonds of propadiene should be so much more facile than addition of chlorine, or propargylic chlorine substitution. Actually, it is odd that the chlorination part of this reaction did not fragment the feedstock outright via unstable chloroacetylenes.

However, it was observed that the HF/propyne preheater was exotherming and required very little power input once the propyne feed was started. Modifications to the reactor system were made to allow sampling between the preheater and the mixing point at the inlet of the first reactor tube. Samples taken at this point were 100% 2,2-difluoropropane. At 200 °C, an empty 1/2 in. tube was extremely efficient at hydrofluorinating propyne and apparently propadiene. Apparently, hydrofluorination of propene was not as efficient as its products were terminally fluorinated. This ‘‘prefluorination’’ of the propyne is not so surprising, but only liquid phase preparations had been noticed in the literature [7].

3. Conclusions

High temperature vapor phase chlorofluorination of propyne is predisposed to forming 2,2-*gem* fluorinated products, under the conditions described, due to the initial formation of 2,2-difluoropropane in the preheating stage of the process. Up to 285 °C, 1,1,3,3-tetrachloro-1,2,2,3-tetrafluoropropane is the predominant product. Subjected to further fluorination at temperatures above 435 °C, isomerization accompanies fluorination and the major product becomes 2,2-dichloro-1,1,1,3,3,3-hexafluoropropane. Fragmentation to $CFCl_2–CF_2Cl$ also ensues. As propadiene also forms identical tetrafluorinated intermediate product, it is fully expected to achieve the same results with that alternative feedstock.

4. Experimental

4.1. *General*

Anhydrous hydrogen fluoride was Matheson-Trigas CP grade. Chlorine was Matheson-Trigas HP grade. Propyne was 98% pure from Sigma–Aldrich. Chromium catalyst was prepared as per Ref. [5], Example 2, using a chromium oxide rather than chromium chloride solution. Chromium oxide was Baker ACS grade. GC/MS was performed on an HP 5890/5971A spectrometer with a 60M DB-1 capillary column. Chemical shifts of ^{1}H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded in ppm downfield from Me_4Si (δ 0.00) in $CDCl_3$ using a Bruker ARX300 instrument. ^{19}F NMR (282 Hz) were recorded in ppm downfield from internal standard $CFCl_3$ (δ 0.00) in $CDCl_3$. Hydrogen fluoride was pumped directly and the flow monitored by loss of mass from the feed cylinder. Chlorine and hydrocarbons were flowed as vapor through a rotameter and the flow monitored by loss of mass from the feed cylinder.

Cautionary note: Anhydrous HF causes severe burns to the skin and mucous membranes. HF should be handled with full PPE protection. An ample supply of HF antidote gel should be kept on hand before handling HF. See the reference for burn treatment procedures [8].

4.2. Catalyst bed preparation

The first reactor constituted a 1 in. (2.54 cm) diameter nickel alloy tube 24 in. (61 cm) in length fitted with a five-point thermocouple running through the center of the reactor. The reactor was mounted vertically and fed from the bottom. Pressure control was achieved with a Teflon diaphram gas regulator valve at the outlet end of a vertical chilled water condenser. The reactor was charged with catalyst and purged with N_2 at 200 °C until no water vapor was detectable at the outlet with a cold mirror. Anhydrous hydrogen fluoride was then introduced at 1 mL/min for 1 h. The temperature was raised to the anticipated reaction temperature for 1 h. The N_2 stream was enriched to 2% O_2 for 2 h. The oxidant flow was stopped and the temperature stabilized to the desired reaction temperature.

The second reactor was identical to the first, mounted vertically and fed from the top. It was connected to the first reactor with a short 0.5 in. tube, mounted in its own heating block. This reactor was charged with catalyst and the catalyst bed activated just as was the first bed.

At the beginning of each reaction, anhydrous hydrogen fluoride was flowed at 70 g/h into the first reactor bed, maintaining an inlet reactor section temperature of 220 °C and an outlet reactor section temperature of 285 °C. The second reactor temperature was maintained at the desired temperature (i.e. 485 °C) in both the upper and lower heated sections. A backpressure of 50 psi was allowed to build. After 0.5 h, a second HF flow was started at 70 g/h.

4.3. Chlorofluorination of propyne (at 435 °C)

Into the first HF stream, propyne was flowed at 10.2 g/h. Into the second HF stream, chlorine was flowed at 136 g/h. The temperature at the first thermocouple stabilized at about 235 °C. The temperature of the last thermocouple stabilized at 280 °C. The overall HF:Cl_2:propyne ratio for the reaction was 36:8:1. The outflow stream was condensed and collected under pressure and upon completion of the reaction, passed into crushed ice and separated. The clear, colorless liquid product was analyzed by gas chromatography. Product composition was 17.5% $C_3F_6Cl_2$, 33.0% $C_3F_5Cl_3$, 43.1% $C_3F_4Cl_4$ and 5.4% $C_2F_3Cl_3$. ^{13}C and ^{19}F NMR analysis [9–12] further defined the composition of the $C_3F_6Cl_2$ fraction to be 70% 2,2-dichloro-1,1,1,3,3,3-hexafluoropropane and 30% 1,2-dichloro-1,2,3,3,3-tetrafluoropropane [13]. NMR analysis defined the $C_3F_5Cl_3$ fraction to be 90% 1,1,3-trichloro-1,2,2,3,3-pentafluoropropane and 10% 1,2,3-trichloro-1,1,2,3,3-pentafluoropropane.

4.4. Chlorofluorination of propane (at 435 °C)

Into the first HF stream, propane was flowed at 6.1 g/h. Into the second HF stream, chlorine was flowed at 122 g/h. The temperature at the first thermocouple stabilized at about 249 °C. The temperature of the second thermocouple remained at 280 °C. The overall HF:Cl_2:propane ratio for the reaction was 67:12:1. The outflow stream was condensed and collected under pressure and upon completion of the reaction, passed into crushed ice and separated. The clear, colorless liquid product was analyzed by gas chromatography. Product composition was 43.4% $C_3F_6Cl_2$, 19.2% $C_3F_5Cl_3$, 31.4% $C_3F_4Cl_4$ and 1.7% $C_2F_3Cl_3$.

4.5. Spectral data (see Refs. [9–12] for literature values)

4.5.1. 2,2-Dichloro-1,1,1,3,3,3-hexafluoropropane (CF_3–CCl_2–CF_3)

^{19}F NMR (282 MHz, $CDCl_3$): δ −75.9 (s, 6F, CF_3), ^{13}C NMR (75 MHz, $CDCl_3$): δ 78.7 (hept, $J = 37.0$ Hz, CCl_2), 121.9 (q, $J = 284.4$ Hz, CF_3); MS *e/z* (%): 201 (12), 151 (47), 132 (29); 101 (18); 85 (35); 69 (100) [14].

4.5.2. 1,2-Dichloro-1,1,2,3,3,3-hexafluoropropane (CF_2Cl–$CFCl$–CF_3)

^{19}F NMR (282 MHz, $CDCl_3$): δ −64.7 (dd, $J = 173.6$, 9.5, 2.3, 1F, CF_2Cl), −65.9 (dd, $J = 173.6$, 11.6, 1F, CF_2Cl), −77.0 (ddd, $J = 11.4$, 9.5, 6.5, 3F, CF_3), −134.5 (ddd, $J = 6.5$, 1F, CFCl); ^{13}C NMR (75 MHz, $CDCl_3$): δ 102.3 (dq, $J = 35.7$, 35.7 Hz, CFCl), 118.8 (dq, $J = 286.6$, 30.2 Hz, CF_3), 122.2 (dt, $J = 301.0$, 32.0 Hz, CF_2Cl); MS *e/z* (%): 85 (18) [15].

4.5.3. 1,1,3-Trichloro-1,2,2,3,3-pentafluoropropane ($CFCl_2$–CF_2–CF_2Cl)

^{19}F NMR (282 MHz, $CDCl_3$): δ −64.6 (d, 2F, $J = 3.7$ Hz, CF_2Cl), −70.9 (hept, 1F, $J = 3.7$, 2.0 Hz, CF_2Cl), −113.8 (d, 2F, $J = 2.0$ Hz, CF_2Cl); ^{13}C NMR (75 MHz, $CDCl_3$): δ 109.5 (tq, $J = 269.6$, 99.1 Hz, CF_2), 113.9 (dt, $J = 305.1$, 35.5 Hz, $CFCl_2$), 122.5 (tt, $J = 302.4$, 74.6 Hz, CF_2Cl); MS *e/z* (%): 201 (20), 116 (31), 101 (66); 85 (100); 66 (23).

4.5.4. 1,2,3-Trichloro-1,1,2,3,3-pentafluoropropane (CF_2Cl–$CFCl$–CF_2Cl)

^{19}F NMR (282 MHz, $CDCl_3$): δ −62.5 (dm, $J = 40.8$, 1F, CF_2Cl), −62.9 (dd, $J = 1.6$, 1.6 Hz, 1F, CF_2Cl), −63.3 (ddd, $J = 3.3$, 1.6, 1F, CF_2Cl), −63.7 (dm, $J = 40.8$, 1F, CF_2Cl), −127.6 (hept, $J = 6.1$, 1F, CFCl), ^{13}C NMR (75 MHz, $CDCl_3$):

δ 105.4 (dpent, $J = 269.0$, 33.0 Hz, CFCl), 124.0 (td, $J = 303.8$, 33.4 Hz, CF_2Cl); MS *e*/*z* (%): 201 (16), 147 (6), 131 (15); 116 (20); 85 (100).

Acknowledgements

This project was funded by Louisiana Board of Regents Industrial Ties Grant LEQSF (2004-07)-RD-B-08, Cox-Walker Engineering, Baton Rouge LA and Futago LLC, W. Lafayette, IN.

NMR studies were made possible by an instrumentation grant from The Louisiana Board of Regents LEQSF 045UG-02.

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[13] Authentic $CF_2Cl–CFCl–CF_3$ was also made for NMR comparison purposes by photochlorinating hexafluoropropene.
[14] Major component of unseparated MS peak. Fragments reported match authentic sample.
[15] Minor component of unseparated MS peak. Authentic sample prepared from photochlorination of hexafluoropropene has MS *e*/*z* (%): 201 (3), 185 (23), 85 (100), 69 (50).