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STUDIES ON DEIODO-SULFINATION PART. II. THE REACTIONS OF PERFLUOROALKANESULFINATES WITH HALOGEN AND HALOGEN ACIDS AND A NEW METHOD FOR THE SYNTHESIS OF PERFLUOROSULFONIC ACID

WEI-YUAN HUANG, BING-NAN HUANG and CHANG-MING HU

Shanghai Institute of Organic Chemistry, Academia Sinica
345 Lingling Lu Shanghai 200032 (China)

SUMMARY

In the presence of a small amount of hydroquinone, reaction of potassium 3-oxaoctafluoropentane-1,5-disulfinate (I), 5-iodo-3-oxa-octafluoropentanesulfinate (VII) or 7-iodo-3-oxa-dodecafluoroheptanesulfinate (XII) with hydriodic acid gives the corresponding perfluorocarboxylic acid 3-oxahexafluoropentanedioic acid (II), 5-iodo-3-oxahexafluoropentanoic acid (III) or 7-iodo-3-oxadecafluoroheptanoic acid (XIII), respectively. The formation of 1,5-diiodo-3-oxaoctafluoropentane (IV) or 1,5-dibromo-3-oxaoctafluoropentane (VIII) from the reaction of I or VII with I_2 or Br_2, respectively, has not been previously recorded in the literature. In the case of iodine this can be regarded as a retro-deiodo-sulfination. However, the reaction of the sulfinate with Cl_2 stops at the sulfonyl chloride stage. Deiodo-sulfination provides a new method for the synthesis of perfluorocarboxylic acids, perfluoroalkyl bromide and perfluorosulfonic acid from R_FI.

INTRODUCTION

The properties of both alkane- and fluoroalkane-sulfonic acid and their derivatives have been widely investigated. There are few studies in the properties of perfluorosulfinic acids however (1) and

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the discovery of deiodo-sulfination (2) prompted us to further studies of the reactions of perfluorosulfinates and in particular of their synthetic applications.

RESULTS AND DISCUSSION

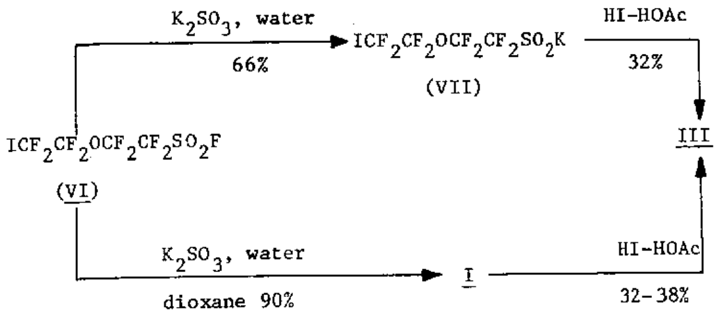
1 The reaction of perfluorosulfinates with halogen acids

The reaction product of perfluorosulfinates $R_FCF_2SO_2M$ (M=K, Na with hydrobromic or hydriodic acid was perfluorocarboxylic acids R_FCO_2H (3) (4). However, the expected 3-oxahexafluoropentanedioic acid (II) was formed only in 8-10% yield when potassium 3-oxaoctafluoropentane-1.5-disulfinate (I) was treated with hydriodic acid. Interestingly, the major product was 5-iodo-3-oxahexafluoropentanoic acid (III) together with 1.5-diiodo-3-oxaoctafluoropentane (IV) and a small amount of 5-H-3-oxahexafluoropentanoic acid (V):

$$\underset{(\underline{I})}{KO_2SCF_2CF_2OCF_2CF_2SO_2K} + HI \xrightarrow[HOAc]{\Delta} \underset{(\underline{II})\ 8\text{-}10\%}{HO_2CCF_2OCF_2CO_2H} +$$

$$\underset{(\underline{III})\ 32\text{-}38\%}{ICF_2CF_2OCF_2CO_2H} + \underset{(\underline{IV})\ 12\text{-}14\%}{ICF_2CF_2OCF_2CF_2I} + \underset{(\underline{V})\ \text{a small amount}}{HCF_2CF_2OCF_2CO_2H}$$

By this new route, III was prepared from 5-iodo-3-oxaoctafluoropentanesulfonyl fluoride (VI) and the yield was slightly higher than that of the alternative route (4) (Scheme 1).



Scheme 1

Evidently, there were two concurrent transformations in the reaction of disulfinate I with hydriodic acid. The first was the expected conversion of perfluorosulfinate $R_FCF_2SO_2K$ to perfluorocarboxylic acid R_FCO_2H:

$$R_FCF_2SO_2K + 2HI \longrightarrow KHF_2 + I_2 + R_FCO_2H + S$$

The other reaction must be the transformation of $-CF_2SO_2K$ to $-CF_2I$. It is suggested that the $-CF_2I$ group was formed through the reaction of the sulfinate with iodine liberated from the former reaction, thus :

$$R_FCF_2SO_2K + I_2 \longrightarrow R_FCF_2I + SO_2 + KI$$

If the rates of these two reactions were nearly identical then the molar ratio of the main products should be II : III : IV = 1 : 2 : 1, which agreed quite well with our experimental results. V was produced from the reduction of III.

Similarly, when hydrobromic acid was used as the reducing agent, II, 1.5-dibromo-3-oxaoctafluoropentane (VIII) and 5-bromo-3-oxahexafluoropentanoic acid (IX) were formed, thus :

$$\underline{I} + HBr \xrightarrow{HOAc} \underset{(\underline{II})\ 10\text{-}15\%}{\underline{II}} + \underset{(\underline{VIII})}{BrCF_2CF_2OCF_2CF_2Br} + \underset{(\underline{IX})\ 20\text{-}25\%}{BrCF_2CF_2OCF_2CO_2H}$$

Variation of the ratio of I to hydrobromic acid causes a change in the product distribution, for example, with HBr : I = 6 : 1, the molar ratio of IX to II was 2.5:1, and with HBr:I=10:1 the ratio became 1:1.25. The dibromide VIII was formed only in a small amount probably because the sulfonyl bromide is thermally more stable than the corresponding sulfonyl iodide (See Section 2).

Since hydrochloric acid has no reducing power, its reactions with I and VII gave only 3-oxaoctafluoropentane-1.5-disulfinic acid(X) and 5-iodo-3-oxaoctafluoropentanesufinic acid (XI) respectively in quantitative yields. When the reaction was run at over 70^{0}C, decomposition products were also formed besides the major products X and XI.

Addition of a small amount of hydroquinone to the reaction system of I, hydriodic acid and acetic acid improved the yield of the diacid II considerably (53%). In a similar way, the yields of perfluorocarboxylic acid III and 7-iodo-3-oxa-decafluoroheptanoic acid (XIII) respectively from VII and potassium 7-iodo-3-oxa-dodecafluoroheptanesulfinate (XII) also increased significantly (50-60%). Furthermore, the addition of hydroquinone seems to be able to protect the $-CF_2I$ group from reduction as no 5-H-3-oxa-hexafluoropentanoic acid (V) nor 7-H-3-oxadecafluoroheptanoic acid (XIV) were formed from these reactions. In contrast, compound VII reacted with hydriodic acid in the absence of hydroquinone to give III, IV and V in 32, 30 and 10% yields respectively. Similarly, in the absence of hydroquinone XII afforded XIII only in 30% yield. It is interesting that the ratios of XIII : XIV and III : V were nearly 3 : 1 in the reactions without hydroquinone. These results suggested that the conversion of $-CF_2SO_2K$ to $-CF_2I$ as well as that from $-CF_2I$ to $-CF_2H$ under such conditions are both free radical reactions whereas the conversion of $-CF_2SO_2K$ to -COOH is an ionic reaction.

Previous workers (3) carried out the reaction of perfluoroalkane sulfonyl fluorides with sodium sulfite followed by reaction with hydrobromic acid to obtain perfluorocarboxylic acids in 20% yield without the isolation of the intermediate sulfinate. Through the replacement of HBr with the more powerful reducing agent hydriodic acid and the addition of a free radical inhibitor, hydroquinone, to block the side-reactions, we were able to improve the yield of the desired R_FCO_2H considerably, thus rendering these reactions to be of synthetic significance. The reaction sequence of deiodosulfination followed by HI treatment furnished a new alternative route for the preparation of perfluorocarboxylic acids from perfluoroalkyl iodides.

2 The reactions of perfluorosulfinates with halogens

In the preceding section the transformation of $R_FCF_2SO_2K$ to R_FCF_2I has been interpreted as the reaction between $-CF_2SO_2K$ group and elementary iodine. To verify this assumption, the reaction of perfluorosulfinates with bromine or iodine in glacial acetic acid was studied. It was found that the diiodide IV and dibromide VIII were formed in 40-50% from the reactions of I or VII with iodine and bromine respectively.

It has been reported (1) (5) that perfluorosulfinic acids or their salts reacted with Cl_2 or Br_2 in many solvents such as glacial acetic acid at room temperature to give the corresponding sulfonyl halides, however, with I_2 the reaction was very slow or no reaction occured. That fluorinated sulfonyl halides underwent a radical SO_2 extrusion to yield alkyl halides when heated has also been recorded (6). However the direct conversion of $R_FCF_2SO_2K$ to R_FCF_2X (X=Br, I), desufinato-halogenation, is presently unknown. When X=I, the transformation, desulfinato-iodination can be regarded as a retro-deiodo-sulfination reaction. Thus, desulfinato-halogenation should be the consequence of thermal SO_2 extrusion of the unstable intermediate, sulfonyl halide, produced from sulfinate and halogen. Desulfinato-iodination was shown to be a free radical reaction for it can be stopped by adding a small amount of an inhibitor such as hydroquinone (See Section 1). Moreover, it probably went through a transition state of a tight free radical pair since no hydrogen-abstraction product was detected in desulfinatoiodination of I or VII.

On the other hand, the reaction of perfluorosulfinate with chlorine can stop at the sulfonyl chloride stage because a higher temperature was required for the cleavage of the S-Cl bond, which is more stable than a C-I or C-Br bond. Hence, when I, VII or 5-H-3-oxa-octafluoropentanesulfinic acid (XVI) was treated with chlorine at room temperature, the corresponding 3-oxa-octafluoropentane-1.5-disulfonyl chloride (XVII), 5-iodo-3-oxaoctafluoropentanesulfonyl chloride (XV) or 5-H-3-oxa-octafluoropentanesulfonyl chloride (XVIII) was formed in 80-85% yield. Among these, the disulfonyl chloride (XVII) has been employed as a monomer for the synthesis of fluorinated polysulfonamide (7).

Perfluorosulfonic acids are usually synthesized by electrochemical fluorination of alkanesulfonyl halides, but the yield decreases markedly with an increased length of the carbon chain in the starting materials. They can also be obtained from the oxidation of corresponding sulfide, disulfide (8) or sulfinic acid (1). However all the other known methods for the synthesis of perfluorosulfinates require the interaction of sulfur dioxide with organometallic compounds such as Mg (9), Zn (10), (11), Ni, Fe, Co (12), derived from perfluoroalkyl iodides. Therefore with the introduction of deiodosulfination a new and better method for the synthesis of perfluorosulfonic acids from perfluoroalkyl iodides is realized.

EXPERIMENTAL

All boiling and melting points are uncorrected. IR spectra were measured on Carl Zeiss Specord 75 IR spectrometer using NaCl windows. NMR spectra were taken on a Varian EM-360 spectrometer at 60 MHz using TMS for ^{1}H and TFA for ^{19}F as external standard respectively, δ_{CFCl_3} (positive upfield) were calculated by $\delta_{CF_3CO_2H}$ + 76.8. MS spectra were taken on a Finnigan GC-MS-4021 spectrometer.

The reaction of potassium 3-oxa-octafluoropentane-1,5-sulfinate (I) with hydriodic acid

A mixture of 52 g (0.11 mole) I, 90 ml 55-57% hydriodic acid (ca. 0.68 mole) and 40 ml glacial acetic acid was allowed to reflux for 11 hrs. with stirring. On cooling, a saturated $NaHSO_3$ solution was added until the mixture became colorless. After repeated extraction with ethyl ether the organic phase was dried over $MgSO_4$ and filtered. After the removal of ether, fractionation under reduced pressure gave the first fraction (below 100°C/500 mm), which was separated into two phases on standing. Redistillation of the heavier liquid yielded a colorless product (IV) 4.9 g (12% yield) b.p. 135-136°C (literature value (13) 138-140°C). Continuous fractionation gave the second fraction (III) 12.6 g (34% yield), a colorless liquid b.p. 77-79°C/1.0 mm and the third (II) 1.6 g (9% yield), a colorless liquid with b.p. 116-119°C/1.0 mm, which solidified to a white waxy solid in the receiver. m.p. 75-77°C (Cited in (14) 76-79°C),

To identify the by-product V, the 42-45°C/5 mm fraction (compound V contaminated with ca. 20% of III) was esterified by the chloroform-alcohol esterification method (4) to give ethyl 5-H-3-oxahexafluoropentanoate (XIX), a colorless liquid with b.p. 56-58°C/36 mm. Compound XIX was identified through comparison of its b.p., IR and ^{19}F NMR spectra with authentic samples (4).

Analysis : Calculated for $C_4F_8I_2O$ (IV): F, 32.34% Found : F, 32.01. 31.99%.

IR (film) : No peak appears above 1300 cm^{-1}. There are very strong peaks around 1200 cm^{-1} (C-F) (these peaks appear in all the following compounds).

^{19}F NMR (neat) : δ =65.8 (s, ICF_2), 88.0 (s, OCF_2) ppm. both of equal intensity.

Mass spectrum ; 470 (M), 227 (base peak, ICF_2CF_2). 343 (M-I) 177 (ICF_2) 100 (C_2F_4) 127 (I).

IR of II(film) : 3400-2700(broad, O-H), 1760 (s, C=O) cm^{-1}.

^{19}F NMR (neat) : δ=78.1 (s, $-OCF_2CO_2H$) ppm

Diethyl 3-oxatetrafluoropentanedioate (XX), a colorless liquid with b.p. 80-83°C/6 mm, (cited in (14) 80-84°C/6 mm, was prepared from II in the usual way.

IR (film) : 2995-2850 (C-H), 1780 (s, C=O); 1420-1350 (C-H) cm^{-1}

^{19}F NMR (neat) : δ =77.0 (s, OCF_2COOEt) ppm.

MS : 263 (base peak, M+1), 243 (M-F), 235 (M+1-CO). 207 (M+1-2CO), 73 (COOEt), 45 (OEt).

The reaction of I with hydrobromic acid

A mixture of 22.9 g (50 mmole) I, 37 ml ca. 45% hydrobromic acid (ca. 0.3 mole) and 20 ml glacial acetic acid was refluxed for 14 hrs. On cooling a saturated $NaHSO_3$ solution was added to destroy the bromine formed. The resulting mixture was extracted with ether and distilled under reduced pressure to give the first fraction (b.p. below 100°C/50 mm), from which a small amount of compound VIII (nc) was isolated as a colorless liquid, b.p. 95-98°C by distillation. The residuce was shown by ^{19}F NMR spectroscopy to be a mixture of IX and II in a molar ratio of ca. 2.5:1 and continuous fractionation gave IX (nc) (3.2 g, 22% yeild) as a colorless liquid with b.p. 74-77°C/2 mm and compound II (0.9 g, 9% yield).

Analysis : Calculated for $C_4F_8Br_2O$ (VIII): C, 12.78; F, 40.44%. Found : C, 12.92, 13.03; F, 40.66, 40.78%

IR (film) : No peak appears above 1300 cm^{-1}

^{19}F NMR (neat) : δ =69.2 (s, $BrCF_2$), 86.9 (s, CF_2O) ppm, both of the same intensity.

Analysis : Calculated for $C_4HF_6BrO_3$ (IX): C, 16.51; F, 39.18%. Found : C, 16.46, 16.78; F, 39.18, 38.92%

IR (film) : 3140 (broad OH), 1780 (vs, C=O) cm^{-1}.

^{19}F NMR (neat) : δ =69.5 (s, $BrCF_2$), 87.6 (s, CF_2O), 80.1 (t, OCF_2COOH) ppm, all of equal intensity.

Compound IX was converted to the corresponding ester, ethyl 5-bromo-3-oxahexafluoropentanoate (XXI), a colorless liquid b.p. 72-74°C/40 mm (nc).

Analysis : Calculated for $C_6H_5F_6BrO_3$ (XXI): C, 22.59; H, 1.58; F, 35.73%; Found : C, 22.31, 22.13; H, 1.09, 1.03; F, 36.22, 36.24%

IR (film) : 2955-2850 (C-H), 1780 (s, C=O) cm^{-1}

^{19}F NMR (neat) : δ =69.2 (t, $BrCF_2$), 87.3 (m, OCF_2), 79.4 (t, OCF_2CO_2Et) ppm, all of the same intensity.

MS : 319, 321 (M+1), 179, 181 (base peak $BrCF_2CF_2$), 129, 131 ($BrCF_2$), 100 (C_2F_4), 245, 247 ($BrCF_2CF_2OCF_2$), 73 (COOEt), 45 (OEt).

The reaction of I with hydrochloric acid

A mixture of 8.1 g (18 mmole) I, 20 ml conc. hydrochloric acid (excess) and 10 ml glacial acetic acid was stirred below 70°C under a stream of nitrogen for 6 hrs. The solution was extracted with ether, after the removal of solvents the residue was kept at 65°C under a pressure of 1.0 Torr for 6 hrs. to give a colorless viscous liquid (X) (6.6 g, quantitative) (nc).

Analysis : Calculated for $C_4H_2F_8O_5S_2$ (X) : C, 13.88; F, 43.91% Found : C, 14.04, 14.16; F, 43.81, 43.89%.

^{19}F NMR : (neat) : δ =81.6 (s, OCF_2), 128.4 (s, CF_2SO_2H) ppm, both of equal intensity.

Compound X was further characterized through conversion to the corresponding disulfonyl chloride (XVII).

The reaction of potassium 5-iodo-3-oxaoctafluoropentanesulfinate (VII) with hydrochloric acid

In a similar manner 3.0 g of a colorless viscous liquid (nc) (XI) was obtained from the reaction of 3.5 g (7.5 mmole) VII, 15 ml conc. hydrochloric acid and 8 ml glacial acetic acid.

Analysis : Calculated for $C_4HF_8IO_3S$ (XI) : C, 11.78; F, 37.25; S, 7.86%. Found : C, 11.58, 11,47; F, 37.37, 37.41; S, 7.70, 7.52%

^{19}F NMR : (neat) : δ =66.0 (s, ICF_2), 82.8 (s, $O\underline{CF_2}CF_2SO_2H$); 86.1 (s, $ICF_2\underline{CF_2}O$); 127.1 (s, CF_2SO_2H) ppm, all of the same intensity.

The preparation of compound II

A mixture of 16.2 g (35 mmole) I, 55 ml (ca. 0.42 mole) 55-57% hydriodic acid, 25 ml glacial acetic acid and 0.2 g hydroquinone (1.2% of I by weight) was allowed to reflux for 12 hrs. to give a colorless liquid with b.p. 116-119°C/1.0 mm (II) (3.8 g, 53% yield), which solidified to a white waxy solid m.p. 75-77°C.

The preparation of compound III

Method A : A mixture of 46.4 g (0.10 mole) VII, 50 ml glacial acetic acid and 80 ml 55-57% hydriodic acid (ca. 0.60 mole) was heated to 120°C for 18 hrs. with stirring to give two colorless liquids of b.p. 77-79°C/1.0 mm (10.8 g, 32% yield) (III) and b.p. 135-136°C (IV) (11 g, 30% yield) respectively.

Method B : A mixture of 38.2 g (82 mmole) VII, 65 ml (ca. 0.5 mole) 55-57% hydriodic acid, 30 ml glacial acetic acid and 0.5 g hydroquinone (1.3% of VII by weight) was allowed to reflux for 12 hrs. with stirring to give a colorless liquid with b.p. 77-79°C/1.0 mm (III) (16.8 g, 60% yield)

The preparation of 7-iodo-3-oxadecafluoroheptanoic acid (XIII)

Method A : A mixture of 40 g (74 mmole) XII, 60 ml (ca. 0.45 mole) 55-57% hydriodic acid and 30 ml glacial acetic acid was allowed to reflux for 14 hrs. After collecting the fraction of b.p. below 100°C/150 mm, the residue was shown by ^{19}F NMR spectrum to contain XIII and XIV in a molar ratio of ca. 3:1. Working up gave XIII (nc) as a colorless liquid with b.p. 88-89°C/0.6 mm (9.7 g, 30% yield), d_4^{25}= 1.980.

Analysis : Calculated for $C_6HF_{10}IO_3$: C, 16.44; H, 0.23; F, 43.38%. Found : C, 17.00, 16.77; H, 0.24, 0.27; F, 42.97, 43.04%

IR (film) : 3130 (broad OH), 1780 (vs, C=O) cm^{-1}

^{19}F NMR (neat) : δ =59.3 (m, ICF_2); 112.8, 123.6 (m, CF_2CF_2) 83.1 (m, OCF_2), 78.3 (t, OCF_2CO_2H) ppm, all of equal intensity.

Method B : A mixture of 42.4 g (79 mmole) XII, 63 ml (ca. 0.47 mole) 55-57% hydriodic acid, 30 ml glacial acetic acid and 0.5 g hydroquinone (1.2% of XII by weight) was stirred at 120°C for 14 hrs. Distillation gave XIII, colorless liquid of b.p. 88-89°C/0.6 mm (17.9 g, 52% yield), which shown the same IR and ^{19}F NMR as the sample from method A.

The reaction of VII with iodine

A mixture of 2.5 g VII (5.4 mmole), 1.5 g (5.9 mmole) iodine and 5 ml glacial acetic acid was heated to 105°C with stirring for 9 hrs. and compound IV was obtained as a colorless liquid (1.0 g, 50% yield) b.p. 135-137°C.

The reaction of I with iodine

A mixture of 12.5 g (27 mmole) I, 4 ml glacial acetic acid and 15.2 g (60 mmole) iodine was allowed to react at 110°C for 10 hrs. to give IV as a colorless liquid b.p. 135-136°C (4.8 g, 48% yield).

The reaction of I with bromine

A mixture of 18 g (39 mmole) I, 5 ml glacial acetic acid and 15.2 g (95 mmole) bromine was refluxed for 10 hrs. to give compound VIII as a colorless liquid. b.p. 95-98°C (4.5 g, 42% yield).

The reaction of VII with chlorine

Chlorine gas was bubbled through a solution of 18.6 g (40 mmole) VII in 20 ml water for 4 hrs. when the mixture was separated into two phases. Distillation of the lower layer gave compound XV as a colorless liquid (nc) (15 g, 85%) b.p. 95-96°C/100 mm.

Analysis : Calculated for $C_4F_8ClIO_3S$ (XV) : C, 10.85; F, 34.35; S, 7.25%. Found : C, 10.57, 10.25; F, 34.41, 34.72; S, 7.52, 7.66%.

IR (film) : 1425 (s, SO_2Cl) cm^{-1}.

^{19}F NMR (neat) : δ =65.2 (t, ICF_2); 80.5, 85.3 (m, CF_2OCF_2); 108.5 (t, CF_2SO_2Cl) ppm, all of the same intensity.

The reaction of compound XVI with chlorine

A mixture of 15 g (50 mmole) 5-hydro-3-oxa-octafluoropentanesulfonyl fluoride (XXII), 9.5 g (60 mmole) anhydrous potassium sulfite, 9 ml water and 3 ml dioxane was reacted at 80°C for 9 hrs. Then, 10 ml conc. hydrochloric acid was added and the mixture was extracted with ether. After removal of solvents from the organic layer, the resulting residue was kept at 75°C for 5 hrs. under a pressure of 1 Torr to give a viscous liquid (XVI) (12 g), to which 10 ml water was added and chlorine gas was bubbled through the solution for 3 hrs. Working up gave compound XVIII as a colorless liquid (nc), b.p. 48-50°C/660 mm (11 g, 82% yield based on the sulfinic acid).

Analysis : Calculated for $C_4HF_8ClO_3S$ (<u>XVIII</u>) : C, 15.18; S, 10.13; F, 48.01%. Found : C, 15.11, 15.31; S, 10.32, 10.31; F, 47.91, 48.36%.

IR (film) : 1425 (s, SO_2Cl) cm^{-1}

^{19}F NMR (neat) : δ=138.3 (d-t, HCF_2); 89.1, 80.0 (both m, CF_2OCF_2), 109.5 (t, CF_2SO_2Cl) ppm, all of equal intensity.

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