

Preparation of α,ω -Ditriazinylperfluoroalkane Derivatives (I)

Yung K. Kim, George A. Grindahl, John R. Greenwald, and Ogden R. Pierce

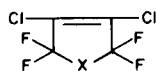
Research Department, Dow Corning Corporation, Midland, Michigan 48640

Received November 19, 1973

The synthesis of 2-oxa and 2-thiaperfluoroglutaric acids and their corresponding ethyl esters, amides, nitriles, acid chlorides, and also 2-thiaperfluoroglutaric anhydride are described. These compounds were prepared as precursors to α,ω -ditriazinylperfluoroalkane derivatives containing a heteroatom in the perfluoroalkylene chain. The ditriazinylpropanes were prepared most satisfactorily from the diacid chlorides rather than the dinitriles.

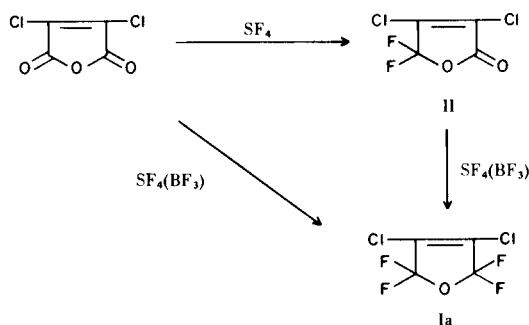
Previous work in this laboratory (2) has demonstrated the feasibility of preparing fluorocarbon-substituted *s*-triazines containing reactive sites which could be used for subsequent reactions. In continuation of work on the preparation of new fluorocarbon-substituted *s*-triazines, we have extended our work to α,ω -ditriazinylperfluoroalkanes containing oxygen or sulfur as a heteroatom in the alkane portion of the molecule.

The required 2-oxa- and 2-thiaperfluoroglutaric acids were conveniently prepared by oxidation of 3,4-dichloroperfluoro-2,5-dihydrofuran (Ia), and 3,4-dichloroperfluoro-2,5-dihydrothiophene (Ib), respectively.



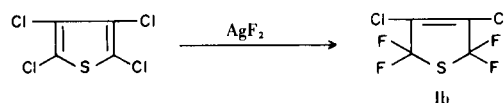
Ia, X = O
Ib, X = S

The dihydrofuran, Ia, is reported to be obtained in 46% yield by fluorination of dichloromaleic anhydride with sulfur tetrafluoride (3). Attempts to repeat this reaction in our laboratory with no catalyst present gave only α,β -dichloro- γ,γ -difluoro- γ -crotonolactone (II) in 71% yield. However, with the use of boron trifluoride as a catalyst, the lactone, II, and dichloromaleic anhydride were both fluorinated to give the expected dihydrofurans, Ia, in 31% and 21% yields respectively. A number of side



products were formed in each case. The predominant one (10%) was identified as 1,2-dichloroperfluorocrotonyl fluoride (isolated as the ethyl ester).

The fluorination of tetrachlorothiophene with silver difluoride is known to afford 3,4-dichloroperfluoro-2,5-dihydrothiophene (Ib) in 45% yield (4). Repetition of this reaction in our laboratory gave yields as high as 63% when the reaction temperature was maintained at 0°.

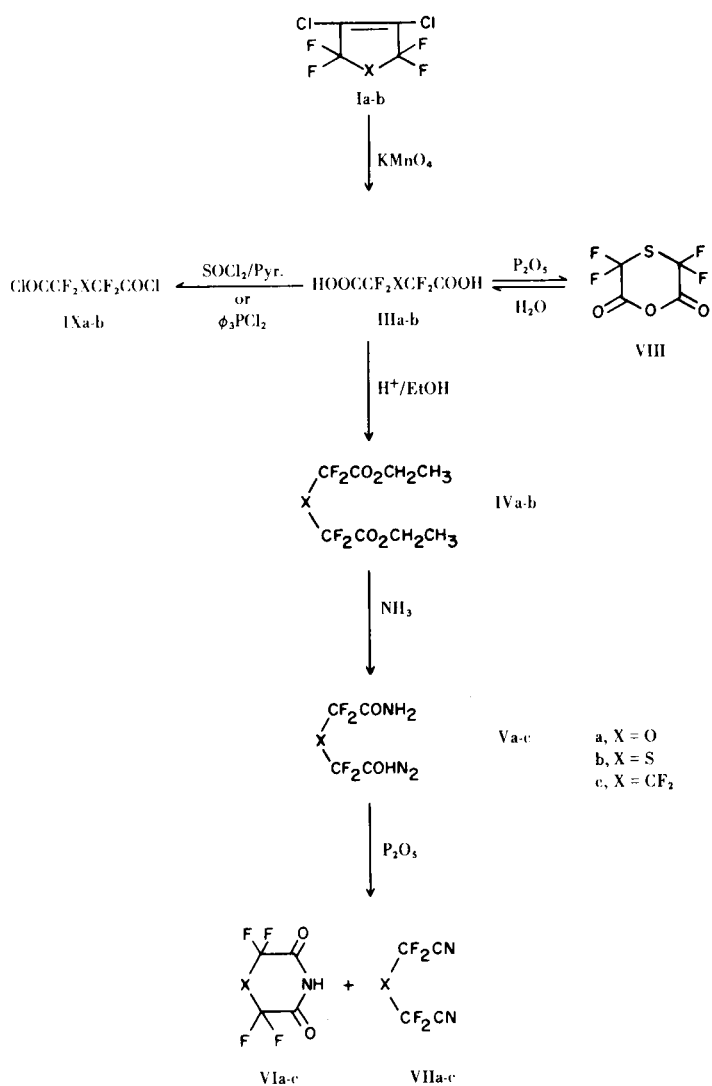


Compounds Ia and Ib were readily oxidized by potassium permanganate solution to give the 2-oxa- and 2-thiaperfluoroglutaric acids (IIIa-b). When ammonia was passed through ice-cooled ether solutions of the esters, nearly quantitative yields of the diamides (Va-b) were obtained.

The dehydration of perfluoroglutaramide is known to be complicated by the tendency of this material to form perfluoroglutarimide (VIc) along with perfluoroglutaronitrile (VIIc) (5). It has also been reported that only the imide VIc was formed when sulfuric acid was used as a dehydrating agent (6). However, we have found that the addition of the heteroatom diamides Va-b to a large excess of hot phosphorus pentoxide either under reduced pressure or with a nitrogen sweep gave the expected dinitrile VIIa-b in good yield.

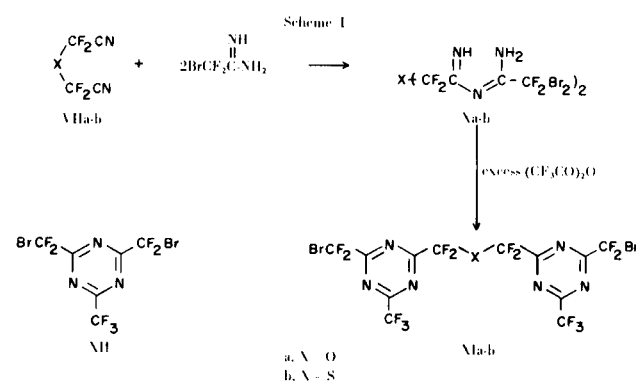
Preparation of 2-oxaperfluoroglutaryl chloride (IXa) from the crude acid (IIIa) was accomplished with the use of dichlorotriphenylphosphorane or thionyl chloride. Although a higher yield (63%) was obtained from the phosphorane reagent, its relatively poor volume efficiency made thionyl chloride (41%) the more attractive reagent.

MIDL - 029



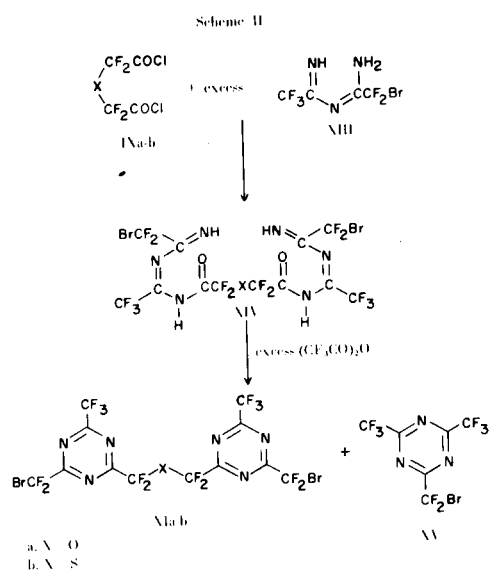
A similar reaction produced 2-thiaperfluoroglutaryl chloride (IXb) in 93% yield from the pure acid IIIb which had been obtained in nearly quantitative yield from the stoichiometric hydrolysis of the corresponding anhydride (VIII).

In view of the possibility that the dinitriles VIIa-b may form the corresponding cyclic imidine in preference to the diamidine, even in the presence of a large excess of ammonia, it was decided to prepare bromodifluoroacetamide and react it with the dinitriles VIIa-b to form the required intermediates Xa-b (Scheme I). When VIIb was added to an excess of bromodifluoroacetamide, followed by acylation and cyclodehydration with excess trifluoroacetic anhydride (7), the only product isolated was 2,4-bis(bromodifluoromethyl)-6-trifluoromethyl-*s*-triazine (XII) (2). There was also an intractable residue. A similar procedure was followed with VIIa except the intermediate reaction solution was rapidly added to a



large excess of trifluoroacetic anhydride. Subsequent isolation procedures yielded a small amount (6%) of material assumed to be the desired α,ω -di-(4-bromodifluoromethyl)-6-trifluoromethyl-*s*-triazinyl)- β -oxaperfluoropropane (XIa). Since some ditriazinyl propane was formed when the reaction sequence was completed quickly (10 minutes) and none was formed when a slightly longer time (30 minutes) was used, it seems that the diimidoylamidines (Xa-b) are formed initially but rapidly undergo decomposition under the reaction conditions.

After unsuccessful attempts to prepare XIa-b by the route shown in Scheme I, an alternate synthetic route described in Scheme II was investigated. The required unsymmetrical imidoylamidine XIII was prepared by addition of bromodifluoroacetonitrile to excess ammonia, removal of the ammonia, and combination of a dry ice cooled methylene chloride slurry of the resultant material with trifluoroacetonitrile. A large excess of XIII was used for the synthesis shown in Scheme II with the intent that the unused portion would scavenge the hydrogen chloride released when condensation took place with the diacid chloride IX. Acylation of the excess XIII and the total



cyclodehydration were effected with trifluoroacetic anhydride. From this synthetic sequence, the desired ditriazines XIa-b and co-product, XV, were obtained as the major products along with several other possible scrambled byproducts, most of which were not characterized thoroughly. The desired ditriazines XIa-b were isolated by distillation and characterized by elemental and spectroscopic analyses.

EXPERIMENTAL.

All boiling points and melting points are uncorrected. Melting points were determined on a Thomas Hoover melting point apparatus. Gas phase chromatography was conducted on an F and M Model 720 and 810 apparatus using 10' x 1/4" stainless steel columns containing 20% FS[®] 1265 Fluid, 10,000 cs, on Anakrom 90-100 mesh ABS. Infrared spectra were obtained with a Perkin Elmer Model 137 Infracord.

Pressure reactions were carried out in a 1.4 l. stainless steel pressure vessel. Solid reactants were placed in the bomb which was then sealed, cooled in dry ice-acetone and evacuated. Liquid or gaseous reactants were then added. At the conclusion of the reaction, gaseous products were vented to an evacuated recovery cylinder before opening the bomb.

Dichloromaleic anhydride, thionyl chloride, sulfur tetrafluoride, triphenyl phosphine, boron trifluoride, tetrachlorothiophene, silver difluoride, trifluoroacetonitrile and trifluoroacetic anhydride were all obtained commercially and were used without further purification. Bromodifluoroacetonitrile was prepared as described previously (2).

α,β -Dichloro- γ,γ -difluoro- γ -crotonolactone (II).

Using the pressure reaction apparatus, dichloromaleic anhydride, 167 g. (1.0 mole) and sulfur tetrafluoride, 235 g. (2.2 mole) were heated to 245° with rocking for 21 hours. The gaseous products (199 g.) were vented and the clear yellow liquid (193 g.) was poured onto sodium fluoride and distilled under reduced pressure to give 134 g. (0.71 mole, 71% yield) of II: b.p. 50-51° (35 mm); F^{19} nmr (neat, fluorotrichloromethane reference): +85.5 ppm (s, difluoromethylene); ir (carbon tetrachloride): 5.49 μ (carbonyl) and 6.14 μ (double bond).

Anal. Calcd. for $C_4Cl_2F_2O_2$: C, 25.4; Cl, 37.5; F, 20.1. Found: C, 25.5; Cl, 37.2; F, 20.2.

3,4-Dichloroperfluoro-2,5-dihydrofuran (Ia).

Method A.

The pressure vessel was charged with 167 g. (1.0 mole) of dichloromaleic anhydride, 238 g. (2.2 mole) of sulfur tetrafluoride and 5 g. (0.07 mole) of boron trifluoride and was heated to 300° for 56 hours. On cooling, gaseous material was vented and the dark liquid (175 g.) was poured over glass wool and fractionated. The material boiling at 25-80° was collected and added to an equal volume of absolute ethanol. After water washing and drying (calcium chloride), the material was combined with that obtained from two similar runs and fractionated. This gave 136 g. (0.65 mole, 21% yield) of Ia, b.p. 70-74° [lit. (3) b.p. 73-74°]. A portion of this material, b.p. 73°, which showed one peak by glc had n_D^{25} 1.3607; F^{19} nmr (neat, fluorotrichloromethane reference): δ +76.4 ppm (s); ir (carbon tetrachloride): 6.10 μ (double bond).

Anal. Calcd. for $C_4Cl_2F_4O$: C, 22.8; Cl, 33.7; F, 36.0. Found: C, 22.7; Cl, 33.8; F, 36.3.

Method B.

The fluorination of II was carried out using 485 g. (2.57 mole) of II, 332 g. (3.08 mole) of sulfur tetrafluoride and 10 g. (0.15 mole) of boron trifluoride. The pressure vessel was heated to 290° for 40 hours. On cooling, 285 g. of gases and 514 g. of black liquid were recovered. The liquid was stored over glass wool and fractionated to give 246 g. of colorless liquid, b.p. 58-78° which was treated with 100 ml. of absolute ethanol, washed with water, and dried (calcium sulfate). Filtration and fractionation gave 178 g. (0.85 mole, 33% yield) of Ia, b.p. 70-74° and 53 g. (0.22 mole, 8.5% yield) of ethyl 1,2-dichloroperfluorocrotonate: b.p. 62.5-64° (20 mm); n_D^{25} 1.3982; ir (carbon tetrachloride): 5.72 μ (carbonyl) and 6.17 μ (double bond).

Anal. Calcd. for $C_6H_5Cl_2F_3O_2$: C, 30.4; H, 2.1; Cl, 29.9; F, 24.1; m.w. 237. Found: C, 30.4; H, 2.2; Cl, 29.8; F, 24.2; m.w. (mass spec.) 236.

Diethyl 2-Oxaperfluoroglutarate (IVa).

About 178 g. (0.85 mole) of Ia was slowly added to a stirred mixture of 350 g. (2.22 mole) of potassium permanganate in 2 l. of distilled water. The mixture was allowed to stir 40 hours, acidified with 200 ml. of concentrated sulfuric acid and decolorized with sulfur dioxide. This mixture was continuously extracted with ether for four days. The ether solution was dried (calcium sulfate), filtered and volatile material removed on a rotary evaporator, leaving 130 g. (0.63 mole, 74% yield) of white solid presumed to be 2-oxaperfluoroglutaric acid (IIIa).

About 120 g. (0.58 mole) of the crude IIIa was combined with 400 ml. of absolute ethanol and 25 ml. of concentrated sulfuric acid, refluxed for three days and poured into 1 l. of water. The organic phase was taken up in ether, water washed, dried (calcium chloride), filtered and solvent removed by distillation. The residue was fractionated under reduced pressure to give 56.4 g. (0.215 mole, 32.5% yield) of IVa; b.p. 80-84° (6 mm); n_D^{25} 1.3612 [lit. (8) b.p. 52-54° (2 mm)]; F^{19} nmr (neat, fluorotrichloromethane): +78.0 ppm (s); ir (carbon tetrachloride): 5.63 μ (carbonyl).

Anal. Calcd. for $C_8H_{10}F_4O_5$: C, 36.7; H, 4.1; F, 29.0. Found: C, 36.7; H, 3.9; F, 29.1.

The residue from the above distillation (26.8 g.) was mixed with 100 ml. of absolute ethanol and 1 ml. of concentrated sulfuric acid and refluxed for 20 hours. The cooled reaction mixture was then poured into water, the organic layer was taken up in ether and the ether solution was washed with water and dried (calcium chloride). Subsequent fractionation gave an additional 20 g. (0.077 mole, 13% yield) of IVa, b.p. 85.5° (7 mm).

2-Oxaperfluoroglutaramide (Va).

A solution of 70.1 g. (0.267 mole) of IVa in 400 ml. of anhydrous ether was cooled in an ice-water bath and anhydrous ammonia was bubbled through the solution for 4 hours. The clear solution was refluxed for a few minutes to remove ammonia, cooled and filtered to give 37.5 g. of white solid amide. Approximately one-half of the ether was removed and the solution again filtered to give 7.2 g. of white solid amide. The remaining solvent was removed and the resulting solid was triturated with 25 ml. of ether and filtered leaving 6.0 g. of white solid. A total of 50.7 g. (0.248 mole, 93% yield) of Va, m.p. 148-150°, was obtained; F^{19} nmr (acetone, fluorotrichloromethane reference): +78.1 ppm (s); ir (halocarbon: nujol mull): 5.8 μ (carbonyl).

Anal. Calcd. for $C_4H_4F_4N_2O_3$: C, 23.5; H, 2.0; F, 37.2; N, 13.7. Found: C, 23.6; H, 2.2; F, 37.4; N, 13.6.

2-Oxaperfluoroglutaronitrile (VIIa).

The apparatus consisted of a 1 liter, 3-necked flask fitted with a nitrogen inlet, solid addition device, mechanical stirrer, thermometer and a gas outlet connected to a series of two dry ice-cooled traps. Into the flask was placed 380 g. of phosphorus pentoxide which was heated to 210°. Then 23.8 g. (0.117 mole) of Va was added to the hot stirred solid over a 30 minute period. After heating the mixture for 2 hours, the material in the dry ice-cooled traps was collected using vacuum line techniques. This gave 8.8 g. (0.053 mole, 45% yield) of VIIa; b.p. 38-40° (capillary); n_D^{25} 1.290; ir (10 cm gas cell, 10 mm): 4.40 μ (cyano); F^{19} nmr (neat, fluorotrichloromethane reference): +58.4 ppm.

Anal. Calcd. for $C_4F_4N_2O$: C, 28.6. Found: C, 28.3.

2-Oxaperfluoroglutaryl Chloride (IXa).

Method A.

A sample of dichlorotriphenylphosphorane was prepared by adding chlorine, 30 g. (0.42 mole), to a dry ice-cooled solution of 101 g. (0.385 mole) of triphenylphosphine in methylene chloride. This mixture was allowed to warm to ambient temperature and solvent was removed under reduced pressure. Because the dichlorotriphenylphosphorane was caked, an additional 100 ml. of methylene chloride was added to make a slurry. To this mixture, 25.5 g. (0.124 mole) of the diacid IIIa was slowly added. After stirring overnight, the volatile material was removed under vacuum. Distillation gave 19 g. (0.078 mole, 63% yield) of IXa, b.p. 95°. This material contained approximately 10% methylene chloride.

Method B.

About 126 g. (0.61 mole) IIIa was slowly added to a mixture of 1 ml. of wet pyridine and 400 g. (3.36 mole) of thionyl chloride. The mixture was heated to reflux for several hours and allowed to stand at room temperature for 3 days. Since some solid remain in the flask, the material was again heated to reflux for 6 hours. The mixture was then fractionated to give 61 g. (0.25 mole, 41% yield) of IXa, b.p. 93-97°.

Refractionation gave pure IXa, b.p. 95°; n_D^{25} 1.3537; ir (carbon tetrachloride): 5.6 μ (carbonyl); F^{19} nmr (neat, fluorotrichloromethane): +76.6 ppm (s).

Anal. Calcd. for $C_4Cl_2F_4O_3$: C, 19.8; F, 31.3. Found: C, 19.8; F, 31.4.

3,4-Dichloroperfluoro-2,5-dihydrothiophene (Ib).

Tetrachlorothiophene, 250 g. (1.1 mole), was melted and slowly added to an ice water-cooled flask containing 841 g. (5.75 mole) of silver difluoride. The mixture was well stirred during the 4 hours required for addition. After allowing the reaction mixture to warm to room temperature overnight, volatile material was removed under vacuum. This liquid was combined with material from a similar reaction and fractionated to give 316 g. (1.4 mole, 63% yield) of Ib; b.p. 115-117°; n_D^{25} 1.4293 (lit. (4) b.p. 117-119°, n_D^{31} 1.4269).

Diethyl 2-Thiaperfluoroglutarate (IVb).

A solution of Ib, 56.6 g. (0.25 mole), in 180 ml. of acetone and 20 ml. of water was cooled in an ice bath and treated with 77 g. (0.49 mole) of potassium permanganate, incrementally. The reaction mixture was treated with 1 ml. of concentrated sulfuric acid and decolorized with sulfur dioxide. The clear solution was extracted continuously with ether for two days, the organic layer dried (calcium sulfate), and the solvent removed by distillation. The residue was treated with 20 ml. of concentrated sulfuric acid and 60 ml. of absolute ethanol, first in an ice bath and finally at

reflux for 1 hour. The reaction mixture was then quenched with ice, the organic layer separated, washed and dried to yield 23 g. of a brown liquid. The reaction was repeated, omitting the water solvent and using only 52.7 g. (0.33 mole) of potassium permanganate, to yield 20.0 g. of an orange liquid. The products were combined and fractionated to yield 21.8 g. (0.079 mole, 16% yield) of IVb, b.p. 89-90.5° (5 mm); n_D^{25} 1.4023; F^{19} nmr (neat, fluorotrichloromethane reference): +78.8 ppm (s).

Anal. Calcd. for $C_8H_{10}F_4O_4S$: C, 34.5; H, 3.6; F, 27.3; S, 11.5. Found: C, 34.5; H, 3.8; F, 27.2; S, 11.5.

2-Thiaperfluoroglutaramide (Vb).

About 21.8 g. (0.079 mole) of IVb was dissolved in 100 ml. of ether, cooled in an ice bath and treated with ammonia for 3 hours. Absence of starting material was verified by gas chromatography. The solution was reduced in volume on a steam bath to yield 12.3 g. of white crystals, m.p. 163.5-164°; ir (carbon tetrachloride): 5.95 μ (carbonyl); F^{19} nmr (fluorotrichloromethane reference): +71.8 ppm.

Anal. Calcd. for $C_4H_4F_4N_2O_2S$: C, 21.8; H, 1.8; N, 12.7; S, 14.6. Found: C, 21.8; H, 1.9; N, 12.5; S, 14.4.

Further removal of solvent afforded an additional 4.7 g. of tan crystals, m.p. 159-162°. Total yield of Vb was 17.0 g. (98.5% yield).

2-Thiaperfluoroglutaronitrile (VIIb).

About 17.0 g. (0.077 mole) of Vb was added to 226 g. (1.59 mole) of well stirred, hot (200°) phosphorus pentoxide at 570 mm. The liquid product which collected in the dry ice-cooled trap was transferred to an ampoule using vacuum line techniques. The liquid, 7.0 g. (0.038 mole, 49% yield), was found to be 97% pure according to gas chromatographic analysis; b.p. 75-76°; ir (carbon tetrachloride): 4.50 μ (cyano).

Anal. Calcd. for $C_4F_4N_2S$: C, 26.1; F, 41.3; N, 15.2. Found: C, 26.2; F, 41.6; N, 15.2.

2-Thiaperfluoroglutaric Anhydride (VIII).

A solution of 283 g. (1.25 mole) of Ib in 950 ml. of dry (calcium sulfate) acetone was treated with 410 g. (2.6 mole) of potassium permanganate incrementally over a period of 6 hours. A mild exotherm was controlled with an ice bath. After stirring at room temperature for 16 hours, the reaction mixture was acidified with a solution of 250 g. of concentrated sulfuric acid in 250 ml. of water. During this addition, 500 ml. of water was added to facilitate stirring. Following decoloration with sulfur dioxide, the aqueous layer was devolatilized to remove acetone and extracted continuously with ether for 60 hours. The extract was dried (calcium sulfate) and concentrated by distilling the ether. The brown, semi-solid residue was added to 300 g. of phosphorus pentoxide (exothermic) and the product was removed by distillation at reduced pressure. The orange liquid, 87.3 g., was fractionated from phosphorus pentoxide to give 67.3 g. (26.5% yield, based on Ib) of VIII, b.p. 96-97°; ir (carbon tetrachloride): 5.38 μ , 5.53 μ (carbonyl).

Anal. Calcd. for $C_4F_4O_3S$: F, 37.9. Found: F, 37.5.

2-Thiaperfluoroglutaric Acid (IIb).

About 62.5 g. (0.31 mole) of VIII was dissolved in 50 ml. of ether and treated with 5.6 g. (0.31 mole) of water. Cooling with an ice-water bath was required to control the vigorous reaction and maintain the temperature between 10° and 20°. The reaction mixture was stirred at 0° for 1 hour, heated to 50° briefly and devolatilized by distilling ether at reduced pressure. The crystalline residue, 66.1 g. (97% yield) was triturated with warm methylene

chloride and filtered under nitrogen to yield 61.8 g. (91% yield) of white, dry IIIb, m.p. 95-96°; F^{19} nmr (neat, fluorotrifluoromethane reference): +77.0 ppm (s).

Anal. Calcd. for $C_4H_2F_4O_4S$: C, 21.6; H, 0.9; F, 34.2. Found: C, 21.6; H, 1.0; F, 34.6.

2-Thiaperfluoroglutaryl Chloride (IXb).

The diacid IIIb, 61.4 g. (0.276 mole) was added incrementally to 100 ml., 162 g. (1.36 mole) of thionyl chloride at 10°. The solid was insoluble in thionyl chloride and no reaction was noted after stirring at room temperature for 1 hour, adding 50 μ l. of pyridine, heating for 30 minutes at 45° and at 65° for 1 hour. When 0.5 ml. of wet pyridine was added and the reaction mixture refluxed for 6 hours, the system became homogeneous and remained so after cooling. Unreacted thionyl chloride was distilled and the residue was fractionated to give 66.7 g. (93% yield) of IXb, b.p. 57-58° (45 mm), 136.5° (micro); ν (carbon tetrachloride): 5.6 μ (carbonyl).

Anal. Calcd. for $C_4Cl_2F_2O_2S$: C, 18.6; Cl, 27.4; F, 29.3. Found: C, 18.3; Cl, 26.9; F, 29.7.

α,ω -Di(4-bromodifluoromethyl-6-trifluoromethyl-*s*-triazinyl)- β -oxaperfluoropropane (XIa).

Scheme I.

A pool of 200 ml. of ammonia was condensed into the flask and allowed to warm to reflux. About 88 g. (0.56 mole) of bromodifluoroacetonitrile was distilled into the flask. Excess ammonia was removed under water aspirator vacuum and the remaining solid was pulverized with the stirring paddle under vacuum. Methylene chloride (200 ml.) was added and this slurry stirred while 21.7 g. (0.13 mole) of VIIa in 100 ml. of methylene chloride was rapidly added. The addition took 5 minutes and some warming was evident, so the mixture was intermittently cooled to maintain the temperature near 25°. The entire reaction mixture was poured into an addition funnel and rapidly added to a mixture of 430 g. (2.1 moles) of trifluoroacetic anhydride and 200 ml. of methylene chloride which had been previously cooled to -10°. The addition took 5 minutes during which time the temperature rose from -10° to 15°. This mixture was allowed to stir for one-half hour and poured into 2 l. of water at 0°. The organic layer was washed three times with water, dried (calcium sulfate), filtered and concentrated by distilling solvent. The residue was distilled under reduced pressure to give 3.8 g. (0.0075 mole, 6% yield) of XIa; b.p. 95-97° (1 mm); n_D^{25} 1.4175; ν (carbon tetrachloride): 6.47 μ (carbon-nitrogen double bond); F^{19} nmr (neat, fluorotrifluoromethane reference): +59.6 ppm (s, bromodifluoromethyl), +72.0 ppm (s, trifluoromethyl), +73.5 ppm (s, difluoromethylene adjacent to oxygen).

Anal. Calcd. for $C_{12}Br_2F_{14}N_6O$: C, 21.5; F, 39.7. Found: C, 21.9; F, 39.3.

Scheme II.

To a pool of 200 ml. of ammonia at reflux temperature, 200 g. (1.28 mole) of bromodifluoroacetonitrile was slowly added. The mixture was stored overnight at dry ice temperature, then ammonia was removed under water aspirator vacuum. With the flask still under reduced pressure, the solid amidine was powdered and stirred. With the flask at atmospheric pressure, the amidine was cooled in dry ice-acetone and 900 ml. of dry methylene chloride was added. Then 133 g. (1.4 mole) of trifluoroacetonitrile was slowly added and the mixture was allowed to warm to room temperature. There was still solid present in the reaction mixture so the trifluoroacetonitrile which had collected in the dry ice

trap, with 50 g. of new material, was added to the mixture. This operation was repeated several times until a total of 235 g. (2.5 moles) of trifluoroacetonitrile had been added. With the reaction mixture cooled in ice-water, a solution of 77 g. (0.316 mole) of IXa in 100 ml. of methylene chloride was slowly added. This mixture was stirred overnight with ice-water cooling. Then, 514 g. (2.44 moles) of trifluoroacetic anhydride was added and the mixture heated to reflux for one hour. After cooling, the reaction mixture was poured into 1 l. of water at 0°, and the layers were separated. The water layer was extracted with 200 ml. of methylene chloride and the combined methylene chloride layers were washed four times with 1 l. portions of distilled water, then dried over calcium sulfate. After filtration, the solvent was removed and the residue was fractionated. There was obtained 113 g. (0.38 mole, 67% yield) of 2,4-bis(trifluoromethyl)-6-bromodifluoromethyl-*s*-triazine (XV); b.p. 70-72° (75 mm); [lit. (2) b.p. 52-53° (31 mm)]; 34.5 g. (0.085 mole) of 2,4-bis(bromodifluoromethyl)-6-trifluoromethyl-*s*-triazine (XII); b.p. 105-106° (80 mm); [lit. (2) b.p. 82° (28 mm)]; and 54.4 g. (0.081 mole, 26% yield) of XIa, b.p. 88-97° (0.5-0.75 mm); n_D^{25} 1.4097; infrared: 6.47 μ (carbon-nitrogen double bond); F^{19} nmr (fluorotrifluoromethane reference): +59.8 ppm (s, bromodifluoromethyl); +72.0 ppm (s, trifluoromethyl); +73.6 ppm (s, difluoromethylene adjacent to oxygen).

Anal. Calcd. for $C_{12}Br_2F_{14}N_6O$: C, 21.5; Br, 23.9; F, 39.7; N, 12.6. Found: C, 21.6; Br, 23.4; F, 40.0; N, 12.5.

α,ω -Di(4-bromodifluoromethyl-6-trifluoromethyl-*s*-triazinyl)- β -thiaperfluoropropane (XIb).

Scheme I.

Excess ammonia was condensed into a dry flask under nitrogen and 25.2 g. (0.162 mole) of bromodifluoroacetonitrile was swept into the liquid ammonia with a stream of nitrogen. Unreacted ammonia was allowed to evaporate and residual ammonia was removed at 0° under reduced pressure while the white, solid bromodifluoroacetamide was powdered with the stirring paddle. The dry amidine was cooled to -70°, slurried with 65 ml. of dry methylene chloride and treated with a solution of 6.0 g. (0.033 mole) of nitrile VIIb in dry methylene chloride. A reaction ensued immediately. When this addition was completed, the cloudy slurry was warmed to 0° briefly, cooled to -20° and treated with trifluoroacetic anhydride, 80 g. (0.38 mole). The solution was then allowed to warm to 25°. The final, clear solution was refluxed (38°) momentarily, cooled and poured onto crushed ice. The organic phase was separated, washed with an equal volume of water, dried (calcium sulfate) and fractionated on an 18" spinning band column at reduced pressure to give 30.5 g. (78% yield) of 2,4-bis(bromodifluoromethyl)-6-trifluoromethyl-*s*-triazine XII, b.p. 54-55° (6 mm) [lit. (2) b.p. 51-52° (6 mm)]. Continued fractionation to 115° gave several highly colored, multi-component cuts and a carbonaceous residue. None of the desired product was obtained.

Scheme II.

Bromodifluoroacetamide, 1.24 moles, was prepared by adding 194 g. (1.24 moles) of bromodifluoroacetonitrile to an excess of anhydrous ammonia at -65° and distilling the unreacted ammonia. Last traces of ammonia were removed with the aid of a partial vacuum at 25°. The white, free-flowing solid amidine was slurried with 500 ml. of dry (molecular sieves) methylene chloride and treated with trifluoroacetonitrile at temperatures from -75° to 25° until a solution resulted. The supposed imidoamidine XIII in methylene chloride was cooled to 5° and treated with 59.8 g.

(0.24 mole) of IXb by drops over a period of 1 hour. An additional 50 ml. of methylene chloride was required to facilitate stirring. After standing at 0° overnight, the solid mass was treated with 440 g. (2.1 moles) of trifluoroacetic anhydride. The resulting clear solution was refluxed briefly, cooled, poured onto ice and the organic layer was collected, washed once with water and dried over calcium sulfate. Solvent was removed by distillation and the residue was fractionated to give the following principal fractions.

Fraction A, 129 g. (0.37 mole, 49% yield, based on excess imidoamidine XIII) of 2,4-bis(trifluoromethyl)-6-bromodifluoromethyl-*s*-triazine (XV), b.p. 45° (18 mm) [lit. (2) b.p. 130°].

Fraction B, 40 g. (0.1 mole) of 2,4-bis(bromodifluoromethyl)-6-trifluoromethyl-*s*-triazine (XII), b.p. 57-62° (10 mm) [lit. (2) b.p. 51-52° (6 mm)].

Fraction C, 46.8 g. (0.068 mole, 28.4% yield, based on IXb) of XIb, b.p. 75-76° (0.15-0.20 mm); ir (carbon tetrachloride): 6.46 μ (carbon-nitrogen double bond) 8.0-8.5 μ (carbon-fluorine); F¹⁹ nmr (neat, fluorotrichloromethane internal reference): +59.9 ppm (s, bromodifluoromethyl), +72.2 ppm (s, trifluoromethyl), +75.5 ppm (s, difluoromethylene adjacent to sulfur).

Anal. Calcd. for C₁₂B₂F₁₄N₆S: C, 21.0. Found: C, 21.0.

REFERENCES

- (1) This work was performed under Contract No. F33615-67-C-1350, Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio 45433.
- (2) G. A. Grindahl, W. X. Bajzer, and O. R. Pierce, *J. Org. Chem.*, **32**, 603 (1967).
- (3) W. R. Hasek, W. C. Smith, and V. A. Engelhardt, *J. Am. Chem. Soc.*, **82**, 543 (1960).
- (4) H. Ulrich, E. Kober, R. Ratz, H. Schroeder, and C. Grundmann, *J. Org. Chem.*, **27**, 2593 (1962).
- (5) E. T. McBee and P. A. Wiseman, U. S. Patent No. 2,515,246 (1950); *Chem. Abstr.*, **44**, 9475e (1950).
- (6) A. L. Henne and W. F. Zimmer, *J. Am. Chem. Soc.*, **73**, 1103 (1951).
- (7) For a more thorough discussion of the preparation of perfluoroalkyl-*s*-triazines, see reference 2 and H. C. Brown, P. D. Shuman and J. Turnbull, *J. Org. Chem.*, **32**, 231 (1967).
- (8) R. E. Banks and E. D. Burling, *J. Chem. Soc.*, 6077 (1965).