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FLUORINATION OF 1,4-DIOXAN WITH SULFUR TETRAFLUORIDE IN HYDROGEN FLUORIDE

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SUMMARY

Reaction of sulfur tetrafluoride with 1,4-dioxan in anhydrous hydrogen fluoride in the presence of small additions of sulfur chlorides or chlorine results in the replacement of several hydrogen atoms in dioxan ring by fluorine atoms. Depending on various conditions, 2,3,3-trifluoro-1,4-dioxan, 2,3,3,5,6-pentafluoro-1,4-dioxans as well as 1,2,2,2,2′-pentafluoroethyl ether can be obtained as major products in a good yield.

The reaction appeared to proceed via initial chlorination followed by the replacement of chlorine atoms by fluorine atoms.

INTRODUCTION

Sulfur tetrafluoride is known to have been used as an selective fluorinating agent for replacement of the oxygen atoms in the carbonyl and hydroxyl groups by fluorine atoms [1,2]. Formation of products corresponding to replacement of hydrogen atoms by fluorine atoms in the reactions of sulfur tetrafluoride was observed only in a few cases, for example, on treatment of anthrone [3] and adamantane derivatives [4-6] with SF_4.

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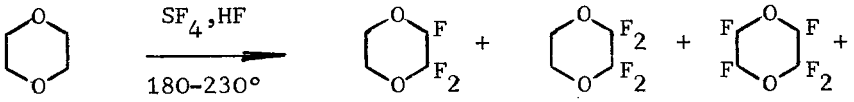
RESULTS AND DISCUSSION

We have found that on heating of 1,4-dioxan with SF_4 in anhydrous hydrogen fluoride at 180-230°, several hydrogen atoms are replaced by fluorine, forming a mixture of 2,3,3-trifluoro-1,4-dioxan (I), 2,2,3,3-tetrafluoro-1,4-dioxan (II), two stereoisomeric 2,3,3,5,6-pentafluoro-1,4-dioxans (III a,b) and 1,2,2,2,2'-pentafluoroethyl ether (IV) in a high yield. Linear ether (IV) is apparently formed as a result of ring cleavage in trifluorodioxan(I). This reaction is also accompanied by release of elementary sulfur.



(I) (II) (III a,b)

+ $CF_3CHFOCH_2CH_2F$

(IV)

However, the yields and ratios of the products obtained varied when different samples of sulfur tetrafluoride were used. This made us assume that the unusual reaction of SF_4 with 1,4-dioxan took place due to the presence of small quantities of sulfur chlorides or chlorine in sulfur tetrafluoride obtained from SCl_2 and NaF [7]. These impurities are often present in SF_4 inspite of low-temperature distillation.

To verify this assumption, SF_4 was thoroughly purified by 48-hour storage at 20° in a stainless steel cylinder containing amalgamated copper chips. This represents a slight modification of the method described in the literature [8] .

It was found that SF_4 purified in this way did not convert 1,4-dioxan into polyfluorodioxans when heated up to 185° in hydrogen fluoride. Instead, tar was formed and some unchanged dioxan recovered. On the other hand, under similar conditions the addition of 0.3-0.5% SCl_2, S_2Cl_2 or chlorine into pure SF_4 resulted in the formation of fluorinated products (I-IV) from dioxan in a high yield.

It should be noted, that the reaction of sulfur tetrafluoride in hydrogen fluoride with 1,4-dioxan is sensitive even to slight traces of above-mentioned chlorinating agents which remain after purification of SF_4, but heating to 220-230° is necessary for fluorination to occur and yields of fluorinated products are very small.

We have also found that an identical influence upon the reaction course of 1,4-dioxan with SF_4 in HF was exerted by hydrogen chloride present in the reaction mixture when hydrogen fluoride of technical grade was employed.

The facts observed allow us to make an assumption that the reaction of sulfur tetrafluoride in hydrogen fluoride with 1,4-dioxan in the presence of sulfur chlorides or chlorine may involve initial chlorination of dioxan followed by the replacement of chlorine atoms by fluorine atoms. Some reactions of halogen exchange with SF_4 are described in the literature [9].

Chlorination of 1,4-dioxan at elevated temperatures is known to proceed in succeeding reactions of the replacement of hydrogen atom by chlorine followed by dehydrohalogenation and addition of chlorine to the double bond [10]. This results in products containing chlorine atoms at adjacent carbon atoms. Probably analogous chlorination processes accompanied by halogen exchange take place on heating of dioxan with SF_4 and HF in the presence of chlorinating agents, which finally results in the formation of 2,3,3-trifluorodioxan (I). Then the latter is converted into pentafluorodioxans (III a,b).

Tetrafluorodioxan (II) is obtained in marked quantities when the contents of sulfur chlorides in SF_4 do not exeed 0.1%. It is possible that under such conditions at 200-220° the removal of HCl from intermediate Cl,F-containing 2,3,3-trisubstituted dioxan occurs followed by addition of Cl_2 and the replacement of chlorine atoms by fluorine atoms. It is doubtful that in this process trifluorodioxan (I) can be an intermediate product, since it was found[11] that 2,3,3-trifluorodioxan cannot be dehydrohalogenated even under very severe conditions.

The possibility to obtain highly fluorinated dioxan derivatives in high yields in the presence of merely small amounts of sulfur chlorides or chlorine is explained by the fact that HCl formed in the reactions of dioxan chlorination and halogen exchange easily reacts with sulfur tetrafluoride [12] recovering chlorinating agents.

$$SF_4 + HCl \longrightarrow [SCl_4] \longrightarrow SCl_2 + Cl_2$$

The nature of fluorinating agent is unknown. Probably, sulphonium ion SF_3^+ known to be formed from SF_4 in the HF medium[13] takes part in the replacement reaction of chlorine by fluorine. In the absence of significant quantities of HF, 1,4-dioxan fails to react with SF_4 even in the presence of sulfur chlorides or Cl_2 in the reaction mixture. The heating of dioxan with HF and chlorides only does not result in the replacement of hydrogen atoms by fluorine atoms.

The data obtained on the role of chlorine in the reaction of dioxan with SF_4 allow us to assume that also other reactions of oxidative fluorination, such as reactions of SF_4 with anthrone [3] and adamantane derivatives[4-6] actually proceed in the same manner. For example, we have found that under conditions described in the literature [6] adamantane fails to react with pure SF_4 and is quantitatively recovered. Under the same conditions, the addition of 0.3% of S_2Cl_2 into SF_4 results in the formation of mono- and difluoroadamantanes in a high yield.

Thus, the above mentioned data on the effective influence of small additions of chlorinating agents upon reactions of some organic compounds with SF_4 can extend the synthetic utility of sulfur tetrafluoride.

EXPERIMENTAL

NMR spectra were taken on a Tesla BS-497 NMR Spectrometer at 100 MHz for ^1H and 94.075 MHz for ^{19}F using HMDS as internal and CF_3COOH as external standards and d_6-acetone as solvent. Gas-liquid chromatography was carried out on "ΠAXB-07" Chromatograph with thermal conductivity detector and helium as a carrier gas. The flow rate was 60 ml/min., and a stainless steel column (5 m × 10 mm) with 15% of Silicon FS-1265 on Chromosorb W(AW-DMCS) was used. The separation temperature was 105°.

Chemicals

Sulfur tetrafluoride was prepared according to the literature [7] and purified as described above.

Treatment of 1,4-dioxan with SF_4 and HF

1,4-Dioxan, SF_4 and HF (with or without addition of SCl_2, S_2Cl_2 or Cl_2) were heated in a stainless steel cylinder at selected temperatures. On cooling to room temperature volatile products were removed, the liquid from the cylinder was poured on ice followed by steam distillation. The mixture obtained was separated by GLC method.

The reaction conditions, yields and percentage of products obtained are listed in Table I. Physical properties, analytical

TABLE I

Treatment of 1,4-dioxan with sulfur tetrafluoride in anhydrous hydrogen fluoride

Starting materials, g			Reaction conditions		Yield, g	Products			
						Percentage in the mixture			
1,4-Dioxan	SF_4 [1]	HF	Temp.,°C	Time, hrs		I	II	III a,b	IV
2.5	15	5	185	8		No reaction			
2.5	15	5	230	8	0.6	36	25	2	37
2.5	15	5 [2]	220	8	1.3	56	14	4	26
2.5	15 [3]	5	185	8	2.8	89	1	2	8
2.5	15 [4]	5	185	8	2.6	85	2	3	10
2.5	15 [5]	5	190	12	2.6	13	-	51	36
3.3	28 [5]	10	190	22	4.0	-	-	73	27
2.5	15 [6]	5	220	10	2.4	20	24	6	50
4.4	30 [6]	10	240	6	5.3	4	34	-	62

[1] SF_4 purified as described above. [2] HF(technical) contained 0.1% of HCl. [3] S_2Cl_2(0.06 g)was added. [4] SCl_2(0.06 g.) was added. [5] 1-2% Cl_2 was added. [6] Nearly 0.1% S_2Cl_2 was added.

TABLE II

Physical properties, analytical and NMR data of fluorinated products (I-IV)

Pro-duct	B.p., °C	n_D^{24}	Found F %	Formula	Req. F %	NMR ^1H, δ ppm, J,Hz	NMR ^{19}F, δ ppm, J,Hz
I	120-121	1.3540	40.08, 40.10	$C_4H_5F_3O_2$	40.14	CHF,5.34(d), J_{HF}52; CH_2-CH_2,3.52-4.55(m)	CF_2,8.02,ΔAB,4.46, J_{AB}160; CHF,70.58(dt), J_{FH}52,J_{FF}14
II	119 [14]		47.67, 47.95	$C_4H_4F_4O_2$	47.50	CH_2CH_2, 4.22(s)	CF_2CF_2, 15.30(s)
III a	99-100*	1.3260	53.27, 53.69	$C_4H_3F_5O_2$	53.37	3CHF, 5.74(m)	CF_2,5.25,ΔAB,3.02, J_{AB}156; 3CHF,57.68(dm), J_{FH}50; 62.43(dm), J_{FH}50; 72.39(dm), J_{FH}51
III b	101-102*	1.3260	53.50, 53.87	$C_4H_3F_5O_2$	53.37	3CHF,5.58(dm),J_{HF}48; 5.65(dm), J_{HF}50; 5.82(dm), J_{HF}48	CF_2,3.16,ΔAB,15.58,J_{AB}164; 3CHF,56.42(dd), J_{FH}48,J_{FF}22; 58.43(dd),J_{FH}48, J_{FF}12; 61.39(m), J_{FH}50
IV (nc)	96-97	1.3030	57.80, 58.14	$C_4H_5F_5O$	57.93	CHF,5.56(dk), J_{HF}60; CH_2F,4.51(dm),J_{HF}47; CH_2,4.12(dm), J_{HF}28	CF_3,6.44(dd), J_{FH}3, J_{FF}6; CHF,65.73(dk),J_{FH}60, J_{FF}6; CH_2F,148.67(tt),J_{FH}47,J_{FH}28

*Sivolobov's method.

and NMR data of cyclic and linear fluorinated ethers (I-IV) are listed in Table II. NMR data of trifluorodioxan (I), tetrafluorodioxan (II) and pentafluorodioxans (III a,b) are close to the data described in the literature [14,15] . In accordance with the paper [15] pentafluorodioxan (III a) seems to be 2$\underline{H}$,5$\underline{H}$/3$\underline{H}$ isomer and (III b) - 2$\underline{H}$/3$\underline{H}$,5$\underline{H}$ isomer.

Treatment of adamantane with SF_4

a) With SF_4 purified from sulfur chlorides and chlorine

In a similar manner to that described above, adamantane (4.0 g) and purified SF_4 (25 g) were heated for 6 h at 100°. Sublimation of the crude product gave unchanged adamantane (3.9g). M.p. and NMR ^1H were identical with authentic sample.

b) In the presence of S_2Cl_2

Under the same conditions adamantane (4.0 g), purified SF_4 (25 g) and S_2Cl_2 (0.08 g) gave the mixture (~1:1 by GLC) of mono- and difluoroadamantanes (3.7 g), which after sublimation were separated by GLC method. The temperature of the column was 150°. Monofluoroadamantane, m.p. 259° and difluoroadamantane, m.p. 264-265° were identical with authentic samples. The NMR ^1H and ^{19}F data for fluoroadamantanes obtained did not differ from that previously reported [6] .

REFERENCES

1 W.R.Hasek, W.C.Smith, V.A.Engelhardt, J.Am.Chem.Soc., 82 (1960) 543.

2 L.M.Yagupolskii, A.I.Burmakov, L.A.Alexeeva, Reakzii i metodi issledovania org. soedinenii, Khimia, Moscow, 22 (1971) 40.

3 D.E.Applequist, R.Searle, J.Org.Chem., 29 (1964) 987.

4 A.M.Alexandrov, G.I.Danilenko, E.V.Konovalov, A.P.Krasnoschek, T.P.Medvedeva, Zh.Org.Khim., 10 (1974) 1548.

5 A.M.Alexandrov, V.P.Kuhar, G.I.Danilenko, A.P.Krasnoschek, Zh.Org.Khim., 13 (1977) 1629.

6 A.P.Hardin, A.D.Popov, P.A.Protopopov, Zh.Vses.Khim.Obshchestva im. D.I.Mendeleeva, 22 (1977) 116.

7 F.S.Fawcett, C.W.Tullock, Inorg.Synth., 7 (1963) 119.

8 G.E.Arth, J.Fried, U.S.Pat. 3,046,094 (1962); C.A., 57 (1962) 9460.

9 C.W.Tullock, R.A.Carboni, R.J.Harder, W.C.Smith, D.D.Coffman, J.Am.Chem.Soc., 82 (1960) 5107.

10 L.A.Briyan, M.W.Smedley, R.K.Summerbell, J.Am.Chem.Soc., 72 (1950) 2206; R.K.Summerbell, D.R.Berger, J.Am.Chem.Soc., 79 (1957) 6504.

11 P.L.Coe, P.Dodman, J.C.Tatlow, J.Fluorine Chem., 6 (1975) 115.

12 D.K.Padma, Phosphorus and Sulfur, 3 (1977) 19.

13 M.Azeem, M.Brownstein, R.J.Gillespie, Can.J.Chem., 47 (1969) 4159.

14 W.Schweztfeger, G.Siegemund, Angew.Chem., 92 (1980) 123.

15 J.Burdon, I.W.Parsons, Tetrahedron, 27 (1971) 4533, 4553.