Silicon Tetrafluoride, a New Fluorinating Agent

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Silicon tetrafluoride is a new, low cost fluorinating agent for organic chlorine compounds. The application of the reaction is limited by the thermal stability of the chlorinated starting materials. The new method is especially useful for the preparation of fluorochloromethanes and carbonyl fluorochloride.

Many attempts have been made in the past to utilize the fluorine values of silicon tetrafluoride, a waste product of fertilizer manufacture, for fluorination reactions. Processes are known in which the silicon tetrafluoride is converted into hexafluorosilicates and used in this form as fluorinating agents.[1–3] These processes, however, involve troublesome operations (corrosion and filtration problems), which prevent their industrial application. Recently the formation of ethyl fluoride from ethyl orthoformate and silicon tetrafluoride was reported,[4] but this reaction is run in the liquid phase with catalysts and does not seem to be generally applicable. Apparently it is limited to highly reactive compounds such as ortho esters.

The use of silicon tetrafluoride as fluorinating agent in the vapor phase at elevated temperatures was investigated for both inorganic[5] and organic compounds. The reactions of the following organic compounds with silicon tetrafluoride were studied: carbon tetrachloride, chloroform, phosgene, carbon dioxide, perchloroethylene, pentachloroethane, hexachloropropylene, chlorobenzene, and hexachlorobenzene. The silicon tetrafluoride is hereby converted to fluorochlorosilanes.

All reactions were carried out by passing the vapors of the chlorine compound together with an excess of silicon tetrafluoride through an electrically heated quartz tube. In most reactions the quartz tube was filled with Hengar quartz granules, in order to achieve a better heat transfer. In a few cases the use of catalysts was investigated, but no catalytic effects were observed. The reaction products were condensed in cold traps and analyzed by gas chromatography and infrared spectroscopy.

Table I gives a summary of the results obtained. It shows that SiF_4 is able to replace chlorine by fluorine in $-CCl_3$ groups of high enough thermal stability. In the case of carbon tetrachloride as starting material a mixture of the different fluorochloromethanes is obtained in good yields. At lower temperatures the formation of $CFCl_3$ is favored; at higher temperatures that of CF_2Cl_2. Therefore it is possible to use this process for the production of either fluorochloromethane by selecting the most suitable temperature range for each fluorocarbon.

Hexachloropropylene can be fluorinated under much milder conditions, due to the activation of the allylic chlorine atoms. The fluorination occurs exclusively in the $-CCl_3$ group.

In the case of chloroform there are two competitive reactions: the fluorination and the thermal decomposition of $CHCl_3$. At lower temperatures the yield of $CHFCl_2$ is higher, but the conversion of the starting material is low. At higher temperatures the conversion of the starting material increases, but at the same time thermal decomposition starts. Among other products carbon tetrachloride was formed and, therefore, the occurrence of $CFCl_3$ and CF_2Cl_2 in the reaction mixture can be explained.

Phosgene gives fluorochlorophosgene in 100% yield and conversions higher than 40% per pass. No difluorophosgene is formed under these conditions. This reaction proceeds at temperatures as low as 400°. At higher temperatures the yield of COFCl stays at 100%, but the conversion of the starting material drops. This can be explained by the shifting of the equilibrium between $CO + Cl_2 \rightleftharpoons COCl_2$ above 500° toward the left side. This fact apparently influences the fluorination reaction. A carbonyl group cannot be fluorinated, as can be shown by the reaction of $COCl_2$ and CO_2 with SiF_4.

Perchloroethylene gives high yields of $CFCl{=}CCl_2$, but the conversion of the starting material remains low, due to the relatively unreactive chlorine atoms in this compound. Attempts to achieve higher conversions by the use of different catalysts, such as HCl, BF_3, and AlF_3, were not successful. Pentachloroethane does not possess a high enough thermal stability, since it is dehydrohalogenated at relatively low temperature to perchloroethylene.

The fluorination of aromatic compounds such as monochlorobenzene and hexachlorobenzene was attempted, but no fluorine-containing products could be obtained. Apparently the chlorine atom in these compounds is too unreactive.

Experimental

Materials.—Silicon tetrafluoride, phosgene, hydrogen chloride, boron trifluoride, and carbon dioxide were purchased from Matheson. The quartz granules, used as filling material of the reactor, were purchased from Hengar. The aluminum trifluoride catalyst on asbestos as a carrier was prepared in our laboratory. All the other chemicals were purchased from chemical supply houses.

Fluorination of CCl_4.—A stream of silicon tetrafluoride measured with a flowmeter was passed through a vessel containing CCl_4. The temperature of the CCl_4 container was kept with an oil bath at about 50° corresponding to a vapor pressure of CCl_4 of 300 mm. The SiF_4–CCl_4 mixture was subsequently passed through an electrically heated quartz tube, which was filled with Hengar quartz granules. The length of the heated zone was 33 cm. and the diameter of the tube was 2.5 cm. The reaction products were scrubbed with aqueous sodium hydroxide solution in order to eliminate all the silicon-containing compounds and analyzed by gas chromatography and infrared spectroscopy. The aqueous solution was checked for Cl^-. Four qualitative reactions were run with a contact time of 10 sec. at different temperatures. The products showed the following composition: 500°, only starting materials; 600°, 20% CF_2Cl_2, 80% $CFCl_3$, and unreacted CCl_4; 700°, 25% CF_2Cl_2, 75% $CFCl_3$, and unreacted CCl_4; and

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(1) J. Dahmlos, U. S. Patent 2,935,531 (1960).

(2) J. Dahmlos, U. S. Patent 3,113,157 (1963).

(3) Wasag-Chemie A. G. British Patent 909,078 (1962).

(4) K. G. Mason, J. A. Sperry, and E. S. Stern, *J. Chem. Soc.*, 2558 (1963).

(5) K. O. Christe and A. E. Pavlath, *ibid.*, in press.

TABLE I

VAPOR PHASE FLUORINATION OF ORGANIC COMPOUNDS WITH SILICON TETRAFLUORIDE[a]

Starting material	Temp., °C.	Contact time, sec.	Vapor pressure of starting material, (mm. Hg)	Conversion of starting material, (%)	Yield, %						
CCl_4					CF_3Cl	CF_2Cl	$CFCl_3$				
	600	10	300	57.8	...	18.9	81.1				
	800	10	300	77.1	17.2	51.3	31.5				
$CCl_3CCl{=}CCl_2$					$CF_2ClCCl{=}CCl_2$	$CFCl_2CCl{=}CCl_2$					
	420	10	100	83	59.1	25.5					
	520	7	100	87	56.8	31.0					
$CHCl_3$					$CHFCl_2$	CF_2Cl_2	$CFCl_3$	CCl_4	$CHCl{=}CCl_2$	$CCl_2{=}CCl_2$	$CHCl_2{-}CCl_3$
	450	10	100	3.2	47.0	...	...	trace	...	...	...
	500	10	100	4.25	34.7	...	...	26.7	6.8	5.6	...
	550	10	100	7.1	31.1	...	...	24.0	8.5	9.9	...
	670	4	100	71.7	...	1.4	8.2	39.6	1.5	39.5	9.9
$COCl_2$					$COFCl$[b]	Dec. of $COCl_2 \rightarrow CO + Cl_2$					
	360	15	380	3.66	100	0					
	420	15	380	42.4	100	0					
	500	15	380	37.5	100	0.15					
	600	15	380	15.4	100	1.4					
	700	15	380	11.1	100	35.3					
CO_2	750–850	4–7	150	No reaction							
$CCl_2{=}CCl_2$					$CFCl{=}CCl_2$	CCl_4	Cl_2				
	500	6	200	0.3	100	...	...				
	600	6	200	0.4	100	...	...				
	800	6	200	2.9	82.9	13.8	2.7				
$CHCl_2CCl_3$	400–650	7–3	200	Only dehydrohalogenation, but no fluorination							
Chlorobenzene	480–700	5	100	No reaction or decomposition							
Hexachlorobenzene	500–800	10	200	No reaction or no fluorination							

[a] In all cases the quartz tube was filled with Hengar quartz granules in order to achieve a better heat exchange. All reactions were run at atmospheric pressure. [b] The amount of $CO + Cl_2$ formed was considered for the calculation of the yield as starting material and not as reaction product, since $CO + Cl_2$ can be easily recombined to phosgene.

800°, 17% CF_3Cl, 52% CF_2Cl_2, 31% $CFCl_3$, and unreacted CCl_4. The results of two quantitative runs at 600 and 800° are included in Table I.

Fluorination of $CCl_3CCl{=}CCl_2$.—The reactions were run in the same way as described above for the CCl_4. The $CCl_3CCl{=}CCl_2$-containing vessel was kept by an oil bath between 130 and 140° and the inlet to the reactor was heated by an infrared lamp in order to avoid condenstion of the starting material. Two reactions were run at 420 and 520°. The conversions and yields are given in Table I.

Fluorination of $CHCl_3$.—The reactions were run in the same way as described above for the CCl_4. The $CHCl_3$ container was kept at room temperature. Table I shows the results of four reactions between 450 and 670°.

Fluorination of $COCl_2$.—A 1:1 mixture of $COCl_2$ and SiF_4 was passed through an electrically heated quartz tube, filled with Hengar quartz granules. The reactions were run at different temperatures and the reaction products were condensed in two cold traps at −78 and −196°. The condensed products were transferred to the vacuum line and analyzed by gas chromatography, fractionation, and infrared spectroscopy. Three qualitative reactions at 500, 650, and 850° and five quantitative reactions between 360 and 700° were run. The results of the quantitative reactions are given in Table I.

Fluorination of CO_2.—Two reactions between CO_2 and SiF_4 were run in the same way as described above for $COCl_2$. Infrared analysis and gas chromatographic investigation of the reaction products showed that no reaction had occurred between the starting materials.

Fluorination of $CCl_2{=}CCl_2$.—The reactions were run in the same way as described for CCl_4. The $CCl_2{=}CCl_2$ container was kept at 80°. Four reactions were run with Hengar quartz granules as filling material. The results of these four reactions are given in Table I. In addition, three reactions between 500 and 800° were run using 15% of gaseous HCl as a catalyst. No improvement of the results could be obtained. In the same way, the addition of 10% BF_3 to the starting materials did not increase the amount of fluorinated products, as could be shown by three reactions between 500 and 800°. In another attempt the filling material of the reaction tube was replaced by an aluminum trifluoride catalyst on asbestos as carrier and three reactions were run between 550 and 850°, but also in this case no improvement of the results could be obtained.

Fluorination of $CHCl_2CCl_3$.—The reactions were run in the same way as described for CCl_4. The vapor pressure of $CHCl_2CCl_3$ was kept at 200 mm. Three reactions were carried out and showed the following results: at 400°, 7-sec. contact time—1.6% $CHCl{=}CCl_2$, 30.8% $CCl_2{=}CCl_2$, and 67.6% starting material; at 500°, 6-sec. contact time—3.6% $CHCl{=}CCl_2$, 91.2% $CCl_2{=}CCl_2$, 3.9% starting material, and 1.3% CCl_4; at 650°, 3-sec. contact time—0.3% $CHCl{=}CCl_2$, 84.7% $CCl_2{=}CCl_2$, 14.5% starting material, and 0.5% CCl_4. No fluorinated products were observed.

Fluorination of Aromatic Chlorine Compounds.—Three reactions between chlorobenzene and SiF_4 were run in the same way as described for CCl_4. At 480 and 600° no reaction occurred; at 700° the starting material started to decompose. Four reactions between hexachlorobenzene and SiF_4 were run. The hexachlorobenzene was placed in a quartz boat at the entrance of the tubular reactor and sublimed through the hot reaction tube. The reactions were run at 500, 650, 750, and 800°, but no fluorinated aromatic compounds could be obtained, as could be shown by n.m.r., infrared spectroscopy, and gas chromatography.

The Meerwein Arylation of Vinyl Sulfones[1]

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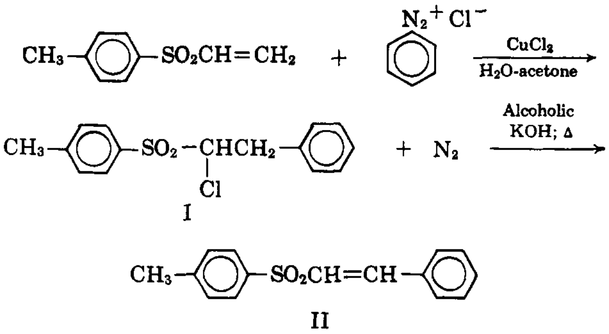
Meerwein arylation of vinyl sulfones with aromatic diazonium salts was shown to yield α-halo-β-aryl sulfones. Despite low yields, the reaction provides a convenient route to these comparatively inaccessible compounds.

The Meerwein arylation of vinyl sulfones was investigated as a synthetic approach to α-chloro-β-aryl sulfones [$RSO_2CH(Cl)CH_2Ar$], since methods for preparing such compounds are limited. The Meerwein reaction[2] normally gives a product in which the incoming halo substituent occupies a position α, and the incoming aryl group occupies a position β, to the activating, electron-withdrawing substituent.

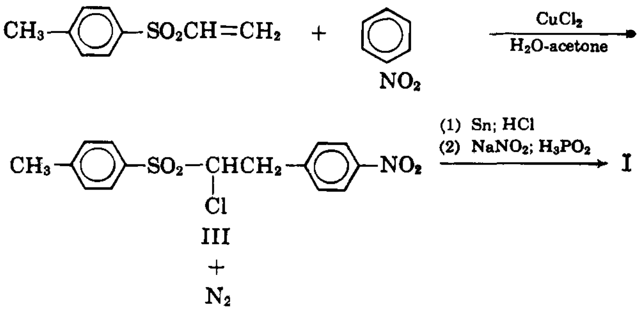
$$Z{-}CH{=}CH_2 + ArN_2^+X^- \longrightarrow Z{-}CH(X)CH_2Ar + N_2$$

Although a wide variety of olefins has been subjected to the Meerwein reaction, at the beginning of our investigation there were no reports in the literature of Meerwein arylations of vinyl sulfones.

Arylation of *p*-tolyl vinyl sulfone with benzenediazonium chloride produced an adduct in 15–20% yield. The 1-chloro-2-phenylethyl *p*-tolyl sulfone structure (I) was assigned to this product on the basis of its dehydrohalogenation product, ω-styryl *p*-tolyl sulfone. This dehydrohalogenation was smoothly effected by refluxing I in alcoholic potassium hydroxide.



Arylation of *p*-tolyl vinyl sulfone with *p*-nitrobenzenediazonium chloride produced an adduct in 20–30% yield, which was assigned the 1-chloro-2-(*p*-nitrophenyl)ethyl *p*-tolyl sulfone structure (III). Compound III was converted into I by removal of the nitro group as indicated.



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[1] Abstracted from the Ph. D. Thesis of J. E. Tracy Purdue University, 1965.

[2] C. S. Rondestvedt, Jr., *Org. Reactions*, **11**, 189 (1960).