FLUORINE-CONTAINING β-SULTONES.

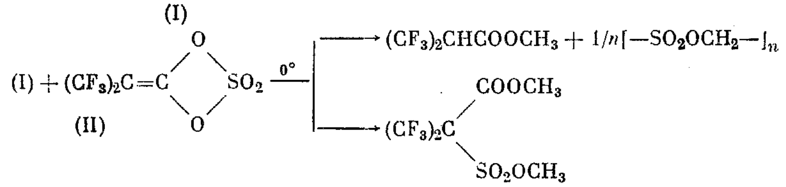
48. SULFOTRIOXIDATION OF HEXAFLUORODIMETHYLKETENALS

A. F. Eleev, G. A. Sokol'skii,
and I. L. Knunyants

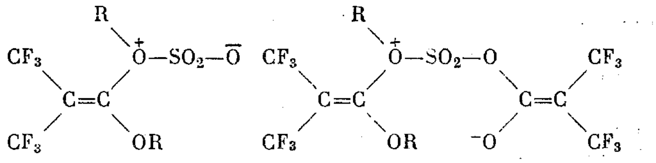
UDC 542.91:547.379.53'118

It has previously been shown that 1,1-bis(methoxy)hexafluoroisobutylene (I) reacts with SO_3 already at −60°C to form methyl α-H-hexafluoroisobutyrate (94% yield). If hexafluoroisobutenylidene sulfate (II) serves as the sulfotrioxidizing agent, the reaction begins at 0°C, is accompanied by the formation of hexafluorodimethylketene, and takes place along two pathways (50% each) [1]:

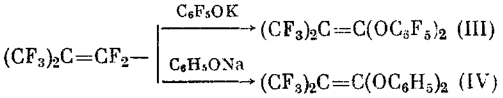
$$\underset{(I)}{(CF_3)_2C{=}C(OCH_3)_2} + SO_3 \xrightarrow{-60^\circ} (CF_3)_2CHCOOCH_3 + 1/n[-SO_2OCH_2-]_n$$



The observed exothermic nature of these reactions may be attributed to the strong electron-donor properties of the O atoms in ketenal I, owing to which the corresponding bipolar ions of the oxidation type, which undergo further conversions, form in the first stages of the processes:



In order to experimentally confirm this hypothesis, in the present work we made a comparison of the ability of two ketenals, whose molecules contain groups that are sterically similar, but differ with respect to their electronic effects on the O atoms to undergo sulfotrioxidation. The objects selected were 1,1-bis(pentafluorophenoxy)hexafluoroisobutylene (III) and 1,1-bis(phenoxy)hexafluoroisobutylene (IV), which were synthesized by reacting octafluoroisobutylene with the respective phenoxides:



$$(CF_3)_2C{=}CF_2 \xrightarrow{C_6F_5OK} (CF_3)_2C{=}C(OC_6F_5)_2\ (III)$$
$$(CF_3)_2C{=}CF_2 \xrightarrow{C_6H_5ONa} (CF_3)_2C{=}C(OC_6H_5)_2\ (IV)$$

As expected, the behavior of these ketenals under sulfotrioxidation conditions was different. Ketenal III is inert to SO_3 even at 100°C. This is due to the significant lowering of the electron-donor capacity of the O atoms. Conversely, ketenal IV, whose molecules contain electron-donor O atoms, react, with SO_3 at −60°C. This reaction results in the evolution of SO_2 and the formation of phenyl α-H-hexafluoroisobutyrate (73% yield):

$$(IV) + SO_3 \rightarrow (CF_3)_2CHCOOC_6H_5 + SO_2 + 1/n[-OC_6H_4-]_n$$

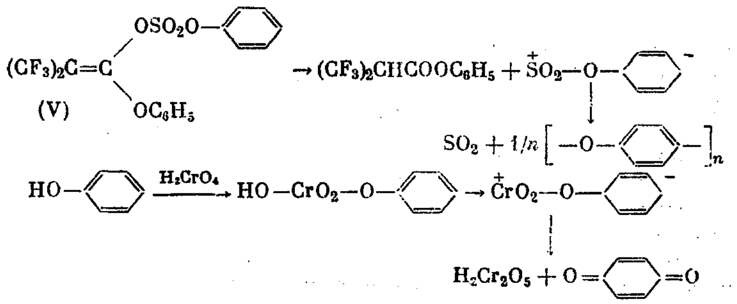
The evolution of SO_2 is probably due to the fact that the bipolar ion formed in the first step is stabilized by being converted into unstable sulfate V, which undergoes decomposition

---

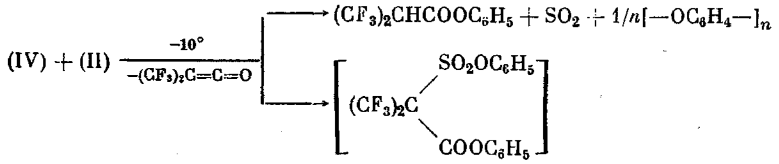
Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 10, pp. 2360-2366, October, 1978. Original article submitted June 14, 1977.

0568-5230/78/2710-2093$07.50

in an oxidation—reduction reaction similar to the reaction of phenol with chromic acid [2]:

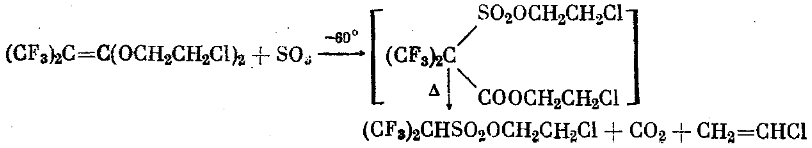


The nucleophilic properties of ketenal IV are so strong that when less active sulfate II is used instead of SO_3, the reaction takes place at $-10°C$. In this case, as in the case of ketenal I, the ketene is produced, and the conversions take place in several directions, the reaction mixture containing many residues products, from which it has not been possible to isolate the expected diester of α-sulfohexafluoroisobutyric acid:



$$(IV) + (II) \xrightarrow[-(CF_3)_2C=C=O]{-10^\circ} \begin{cases} (CF_3)_2CHCOOC_6H_5 + SO_2 + 1/n[-OC_6H_4-]_n \\ \left[(CF_3)_2C(SO_2OC_6H_5)(COOC_6H_5)\right] \end{cases}$$

Inasmuch as some common features are observed when ketenals I and IV are treated by various sulfotrioxidizing agents, it seemed wise to study these questions in the case of the sulfotrixoidation of other ketenals. It has previously been reported that 1,1-bis(β-chloroethoxy)hexafluoroisobutylene (VI) reacts with SO_3 at $-60°C$ and that thermolysis of the primary reaction product results in the formation of β'-chloroethyl 2-H-hexafluoropropane-2-sulfonate (94% yield) [3]:

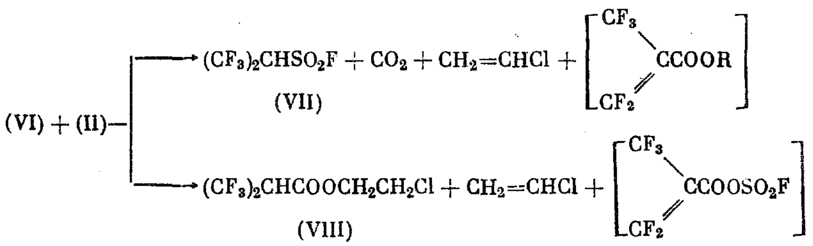


$$(CF_3)_2C=C(OCH_2CH_2Cl)_2 + SO_3 \xrightarrow{-60^\circ} \left[(CF_3)_2C(SO_2OCH_2CH_2Cl)(COOCH_2CH_2Cl)\right] \xrightarrow{\Delta} (CF_3)_2CHSO_2OCH_2CH_2Cl + CO_2 + CH_2=CHCl$$

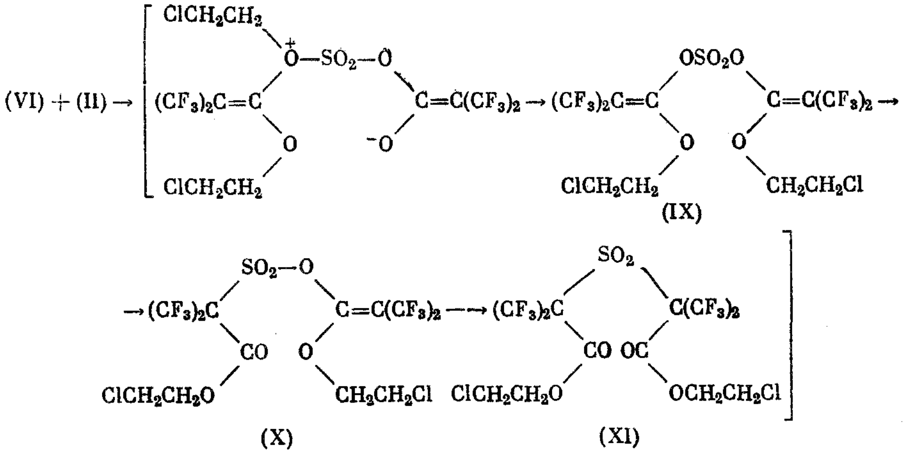
In the present work it was found that the reaction of ketenal VI with sulfate II takes place in a different direction. For example, if dry nitrogen preliminarily saturated with sulfate II (bp 50°C) is passed through ketenal VI, which has been cooled to 0°C, an exothermic reaction accompanied by the production of a mixture of gaseous and volatile liquid reaction products takes place, and the subsequent heating of the residue of the reaction mixture to 100°C is accompanied by more vigorous decomposition. The following compounds were found by GLC among the decomposition products blown off by nitrogen (the last of these compounds was found in the smallest quantity): CO_2, $CH_2=CHCl$, $(CF_3)_2C=C=O$, $(CF_3)_2CHCOF$, and $(CF_3)_2CHSO_2F$.

If the reactants indicated (VI and II) are taken in equimolar amounts and mixed at $-60°C$ in a Freon-22 solution, and the solvent is then distilled off (bp $-40°C$), and the reaction mixture is heated to 10-20°C, no visible signs of decomposition are observed. Nevertheless, a mixture of the aforementioned volatile products, among which the main one is 2-H-hexafluoropropane-2-sulfonyl fluoride (VII), is separated upon evacuation (down to 10 torr), the yield being 87%. β'-chloroethyl α-H-hexafluoroisobutyrate (VIII) (25%) is isolated from the residue of the reaction mixture by fractionation. Interestingly enough, if twice the molar amount of sulfate II is used inthe reaction with ketenal VI under the same conditions, the yield of sulfonyl fluoride VII is 65%, as calculated for the original sulfonyl-containing compound, and the yield of isobutyrate VIII is 30%, as calculated for the original ketenal.

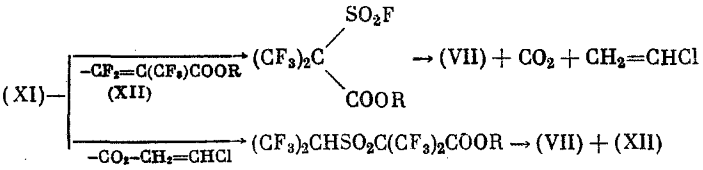
In all cases, after the removal of the products just enumerated, significant amounts of resinous residues remain. These residues are apparently formed by the polymerization and copolymerization of the unsaturated compounds accompanying those isolated. On the basis of stoichiometric arguments regarding the balance of the fluoride atoms and with consideration of the yields of VII and VIII, it may be postulated that the formation of the principal products isolated takes place in degradative processes taking place in parallel, e.g.,



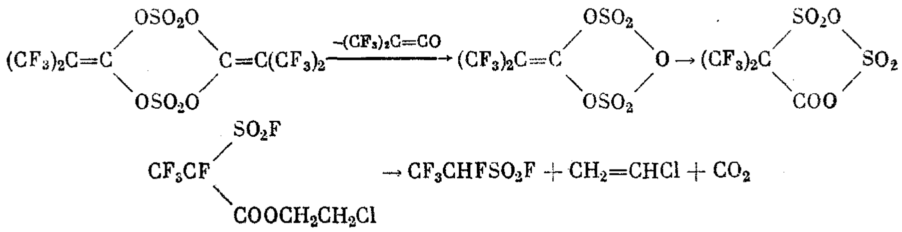
In analogy to the foregoing arguments, it may be suggested that the first stages of the reaction of VI with II include the formation of the corresponding bipolar ion, which is stabilized as symmetric sulfate IX, the latter being inclined to undergo isomerization to sulfonate X and then to sulfone XI:

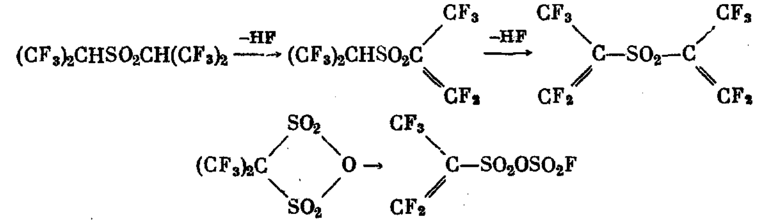


The main direction in the process under consideration, which results in the formation of sulfonyl fluoride VII, is apparently associated with further conversions of sulfone XI, for example, ($R = CH_2CH_2Cl$)



Sulfate IX, sulfonate X, and sulfone XI may participate in the formation of other reaction products and the formation of the resinous still residue. The basis for such an explanation is the existence of prototypes for most of the conversions represented in the form of analogous reactions, which were previously investigated in [3-5]:





Comparing the results of the sulfotrioxidation of hexafluorodimethylketenals I, IV, and VI, we may conclude that a common feature in all the cases is the initial attack of the O atom, which produces labile oxonium compounds that are stabilized by isomerization to the corresponding sulfates. The latter are capable of undergoing conversions, whose directions depend on the nature of the carbon fragment, which thus determines the result of the reaction. Of the sulfotrioxidation products obtained, the bis-esters of α-sulfohexafluoroisobutyric acid and 2-H-hexafluoropropane-2-sulfonyl fluoride are of greatest interest.

EXPERIMENTAL

The ^{1}H and ^{19}F NMR spectra were recorded on an Hitachi—Perkin—Elmer R-20 spectrometer at 60 and 56.456 MHz. The values of the chemical shifts, δ, which were measured relative to HMDS and CF_3COOH, and the values of the constants J are presented in Table 1.

1,1-Bis(pentafluorophenoxy)hexafluoroisobutylene (III). Potassium pentafluorophenoxide was obtained by treatment of pentafluorophenol with a calculated amount of $KHCO_3$ in CH_3CN followed by evaporation of the solvent, azeotrophic drying by benzene, and subjection to a vacuum. Preliminarily liquefied octafluoroisobutylene (32.0 g, 0.16 mole) was added to a suspension of 71.6 g (0.32 mole) of sodium pentafluorophenoxide in 300 ml of ether at −30°C with stirring. Then the temperature of the mixture was brought up to ∿ 20°C. The unreacted octafluoroisobutylene (12.0 g, 0.06 mole) was collected in a trap. The mixture was filtered, and the precipitate was washed with ether (two 50-ml portions). The subsequent fractionation of the combined mother solution and extracts yielded 20.4 g (59%) of pentafluorophenyl heptafluoroisobutenyl ether (IIIa), d_4^{20} 1.8686, n_D^{20} 1.3752, and 14.7 g (28%) of III.

1,1-Bis(phenoxy)hexafluoroisobutylene (IV). Octafluoroisobutylene (100 g, 0.5 mole) was added dropwise at −40°C with stirring to a suspension of sodium phenoxide in ether, which was obtained by adding a 30% ethereal solution of 94 g (1 mole) of phenol to 25 g of finely divided sodium in 500 ml of ether, in such a manner that the temperature of the mixture did not exceed −30°C. A technique similar to the isolation of III yielded 156.4 g (90%) of IV. IR spectrum (KBr, ν, cm^{-1}): 1670 (C=C), 1500, 1600 (C=C, C_6H_5).

Sulfotrioxidation of IV. A. A 3.5-g portion (1.82 ml, 0.0435 mole) of SO_3 was added dropwise over the course of 1 h at −60°C with stirring to a solution of 15.2 g (0.0435 mole) of IV in 80 ml of Freon-22. At the conclusion of the addition process, the solvent (bp −39°C) was distilled off. After the temperature was brought up to 20°C, the remaining mixture was a colorless, snow-like crystalline mass, which darkened and deliquesced upon heating or prolonged standing (12-15 h). Fractionation of the mixture yielded 8.6 g (73%) of phenyl 2-H-hexafluoroisobutyrate (IVa), d_4^{20} 1.3586, n_D^{20} 1.4123. The alkaline hydrolysis equivalent was 8.2, and the thoriometry equivalent was 6.18.

The SO_2 in the Freon distilled off was determined by GLC in a combined sample with a known specimen (2.5 g). The solid still residue (4.5 g), which was insoluble in water and organic solvents, was dissolved in a saturated solution of KOH. A yellow crystalline substance, which was soluble in organic solvents and corresponded to the composition $C_6H_4O_2$, was isolated upon acidification (∿ 4.1 g).

B. A 7.3-g portion (0.0283 mole) of hexafluoroisobutenylidene sulfate (II) was added dropwise with stirring at 0°C to a solution of 9.85 g (0.0283 mole) of IV in 60 ml of CCl_4. The mixture was heated for 1 h at 60-70°C. Hexafluorodimethylketene (4.2 g, 83%) and SO_2 (<1 g), which were identified by GLC, were condensed in a trap connected to the outlet reflux condenser. Then the solvent was distilled off, and the residue was fractionated in a vacuum. This yielded 2.3 g (30%) of phenyl 2-H-hexafluoroisobutyrate (IVa), which was identical to that already described. The residue was a nondistilling resin.

Sulfotrixidation of VI. A. Dry N_2 saturated with the vapor of 25.8 g (0.1 mole) of II was bubbled through 32.1 g (0.1 mole) of VI cooled to 0°C. An exothermic reaction accom-

TABLE 1

Compound	bp, °C (p, mm Hg) mp, °C	Found/Calculated, %			NMR				
					solvent (concentration, %)	^1H		^{19}F	
		C	H	F(Cl)		δ, ppm	J, Hz	δ, ppm	J, Hz
(IIIa)	70(18)	34,22 / 34,86	–	61,34 / 60,65	(100)	–	–	−17,0 s −17,4 s 78,5 d (*o*) 80,0 t (*p*) 85,5t (*m*)	24,5
(III)	148(18), 33	36,03 / 36,42	–	57,09 / 57,33	CCl_4 (50)	–	–	−17,5s 80–85 m	24,5
(IV)	137(5), 56	55,09 / 55,17	2,84 / 2,87	33,29 / 32,76	CCl_4 (50)	6,9 m	–	−21,1s	
(IVa)	50(4)	43,73 / 44,00	2,92 / 2,22	42,03 / 41,95	(100)	4,20 sept 7,20 m	7,0 –	−13,9 d	7,0
(VII)	80	15,63 / 15,39	0,51 / 0,43	56,45 / 56,84	(100)	4,65 m	6,7 1,5	−14,04 d.d −142,8 m	11,3 6,7 1,5
(VIII)	145	27,25 / 27,85	1,80 / 1,93	(13,05) / (13,73)	(100)	3,87 t 4,71t 4,35 sept	6,0 7,0	−12,8d	7,0

panied by the evolution of low-boiling products, which were condensed in a trap (−78°C), was observed. At the conclusion of the mixing of the reactants, the reflux condenser was replaced by a condenser set for distillation, and the reaction mixture was slowly heated to 160-170°C in a current of N_2. At 110-115°C vigorous decomposition of the reaction mixture accompanied by the evolution of gaseous and liquid products was observed in the still. After the exhaustive distillation of all the components of the mixture (180°C in the still), the products obtained were fractionated. The hexafluorodimethylketene (3.5 g, 0.02 mole) and 2-H-hexafluoroisobutyryl fluoride (4.1 g, 0.021 mole) isolated were identified by GLC and ^{19}F NMR. Sulfonyl fluoride VII (14.7 g, 0.063 mole) was identified by comparing its properties with those of a known specimen [6] and with the aid of the NMR spectrum. Isobutyrate VIII (7.8 g, 0.03 mole) is a colorless liquid, d_4^{20} 1.4849, n_D^{20} 1.3598. Found: MR, 38.40; Calculated: MR, 38.39.

B. A 25.8-g portion (0.1 mole) of II was added dropwise with stirring at −60°C to a solution of 32.1 g (0.1 mole) of VI in 80 ml of Freon-22. An exothermic reaction and the evolution of CO_2 (GLC) were observed. After the mixing of the reactants, the solvent was distilled off along with the vinyl chloride formed (GLC), and after a temperature of 0°C was reached, the reaction mass was evacuated to a residual pressure of 10 torr. The departing volatile components were condensed in a trap (−78°C), and their fractionation yielded 2-H-hexafluoroisobutyryl fluoride (5.5 g, 0.028 mole) and sulfonyl fluoride (VII) (20.4 g, 0.087 mole). Fractionation of the residue at atmospheric pressure resulted in the isolation of isobutyrate VIII (6.5 g, 0.025 mole), which was identical to that already described (see A).

C. A 19.6-g (0.0605 mole) portion of VI was slowly added dropwise at −60°C with stirring to a solution of 31.2 g (0.121 mole) of II in 80 ml of Freon-22. After the mixing of the reactants, the solvent was distilled off, and the residue was evacuated to 10 torr (residual pressure). The condensate obtained in the trap was washed with 50 ml of water, dried with $MgSO_4$, and distilled. This yielded 18.4 g (0.079 mole) of sulfonyl fluoride (VII).

CONCLUSIONS

1. The sulfotrioxidation of hexafluorodimethylketenals by sulfuric anhydride begins with the attack of an ethereal oxygen, the direction of the reaction being determined by the nature of the alkoxyl group.

2. 2-H-Hexafluoropropane-2-sulfonyl fluoride has been synthesized by reacting hexafluoroisobutenylidene sulfate with 1,1-bis(β-chloroethoxy)hexafluoroisobutylene.

LITERATURE CITED

1. A. F. Eleev, G. A. Sokol'skii, and I. L. Knunyants, Izv. Akad. Nauk SSSR, Ser. Khim., 1383 (1975).

2. J. D. Roberts and M. C. Caserio, Basic Principles of Organic Chemistry, W. A. Benjamin, New York (1964).
3. A. F. Eleev, G. A. Sokol'skii, and I. L. Knunyants, Izv. Akad. Nauk SSSR, Ser. Khim., 397 (1974).
4. V. M. Pavlov, V. N. Derkachev, G. A. Sokol'skii, and I. L. Knunyants, Khim. Geterotsikl. Soedin., 1321 (1973).
5. G. A. Sokol'skii, V. M. Pavlov, V. N. Golovkin, and I. L. Knunyants, Khim. Geterotsikl. Soedin., 472 (1974).
6. A. F. Eleev, G. A. Sokol'skii, and I. L. Knunyants, Izv. Akad. Nauk SSSR, Ser. Khim., 1573 (1977).

BROMINE- AND IODINE-CONTAINING (HALOALKYL)TRICHLOROSILANES AND METHYL(HALOALKYL)CHLOROSILANES AND THEIR CONVERSIONS

V. M. D'yakov, Yu. A. Lukina,
M. G. Voronkov, L. I. Gubanova,
G. A. Samsonova, and S. N. Tandura

UDC 542.91:547.1'128

Organosilicon compounds with the general formula $ICH_2(CH_3)_{3-n}SiCl_n$ (n = 1-3) are not known. The analogous bromine derivatives are compounds that are difficult to synthesize [1, 2]. Among them $BrCH_2SiCl_3$ [1] and $BrCH_2(CH_3)SiCl_2$ [2] could be obtained only with a very low yield. At the same time, the compounds named are reagents for the synthesis of many types of carbofunctional and silicofunctional organic compounds of silicon.

We have developed a simple and convenient method for obtaining such compounds by reacting the corresponding chloro derivatives with $AlBr_3$ [3] or AlI_3 [4] in a low-boiling inert solvent (C_2H_5Br or C_6H_6):

$$ClCH_2(CH_3)_{3-n}SiCl_n + {}^1/_3AlX_3 \rightarrow XCH_2(CH_3)_{3-n}SiCl_n + {}^1/_3AlCl_3$$
$$X = I, Br;\ n = 2, 3$$

When the number of chlorine atoms on the silicon is reduced, a decrease in the yields of the substitution products is observed, and when AlI_3 is reacted with dimethyl(chloromethyl)chlorosilane, disproportionation of the latter to form dimethyldichlorosilane and trimethylchlorosilane in a 3 : 1 ratio takes place instead of the substitution reaction. In the case of the reactions with AlI_3 in benzene, the silicoalkylation of benzene is not observed.* At the same time, when AlI_3 is reacted with (3-chloropropyl)trichlorosilane in benzene, two alkylation products of benzene, viz., (3-phenylpropyl)trichlorosilane and m-bis(3-trichlorosilylpropyl)benzene, form with 42.6 and 33.3% yields, respectively. This is due to the significantly higher reactivity of the (α-chloroalkyl)- and (β-chloroalkyl)chlorosilanes in Friedel—Crafts reactions in comparison to the corresponding (chloromethyl)chlorosilanes [6].

The reaction of (dichloromethyl)trichlorosilane with $AlBr_3$ in C_2H_5Br results in the formation of the heretofore unknown compound (dibromomethyl)trichlorosilane, which is then converted into (dibromomethyl)trimethoxysilane and, finally, into 1-(dibromomethyl)silatrane. It was not possible to obtain $I_2CHSiCl_3$ from $Cl_2CHSiCl_3$ and AlI_3 in an analogous manner.

Substitution of the chlorine atoms on the silicon by bromine or iodine atoms is not observed in the reaction under study. This is consistent with the "Eaborn series" [7], which forbids the replacement of the chlorine atoms attached to silicon. The difficulty in such exchange is due to the fact that the energy of the Si—Cl bond (85.8 kcal/mole) is significantly greater than the energy of Si—Br and Si—I bonds (69.3 and 51.1 kcal/mole, respectively).

---

*The silicoalkylation of benzene by $ClCH_2SiCl_3$ has been successfully carried out in the presence of $AlCl_3$ [5].

Irkutsk Institute of Organic Chemistry, Siberian Branch of the Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 10, pp. 2366-2372, October, 1978. Original article submitted May 25, 1977.

0568-5230/78/2710-2098$07.50