ISOMERIZATION OF PERFLUORINATED CYCLIC AMINES UNDER THE ACTION

OF ANTIMONY PENTAFLUORIDE

v.	Α.	Petrov, V. K. Kunanets,	UDC 542.952.1:547.592.1'161+
Κ.	N.	Makarov, and L. S. German	547.822.3:546.865'161

We previously showed [1, 2] that when perfluorinated tertiary amines, containing a substituent at the nitrogen atom, are heated in the presence of SbF₅, they are dealkylated with the formation of perfluorinated azaalkenes.

The given communication is devoted to the conversions of perfluorinated cyclic amines containing an alicyclic substituent at the nitrogen atom. Under the usual reaction conditions (100-120°C, 2 h), the perfluoro-N-cyclohexylpyrrolidine (I) remains unchanged; it isomerizes to the azomethine (II) under more drastic conditions (150°C, 12 h).



The heating of the mixture containing 80% of the perfluoro-N-cyclohexylpiperidine (III) and 20% of the perfluoro-N-cyclohexyl-3-methylpyrrolidine (IV) with catalytic amounts of SbF_5 only leads to the isomerization to the azomethine (V) of the amine (III), whereas the compound (IV) is unchanged under the conditions of the reaction (see scheme on following page). This is evidently explained by the presence of the CF_3 group in the heterocyclic fragment of the pyrrolidine (IV).

TABLE 1. Isomerization of the Amines (I), (III), (VI), and (VII)

Compound	Molar ratio	Reaction tempera- ture, °C	Reac- tion time, h	Compound obtained	Yield,	Bp, ℃	IR spec- trum, v C=N, cm^{-1}	Found/Calcu- lated, %	
	amine; SbF 5							C	F
(I)	1,60	145-150	12	(II)	42 *		1785	-	_
(III) * *	1,83	140–145	2	(V)	72	152-154	1785	$\frac{24.11}{24,22}$	73.02 73,21
(VI)	3,86	145-155	5	(VIII a,b)	84	150-155	1785	$\frac{24.14}{24,22}$	$\tfrac{74,15}{73,21}$
(VII)	3,55	150-160	6	(IXa,b)	81	169-1 72	1785	$\frac{24.30}{24,20}$	73.93 73,44

*The yield is presented according to the data of the GLC and the ¹⁹F NMR. **The initial amine (III) contained 20% of the amine (IV), which is unchanged under the reaction conditions according to the data of the GLC and the ¹⁹F NMR.

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 3, pp. 646-649, March, 1989. Original article submitted November 5, 1987.



At the same time, the presence of the trifluoromethyl group in the alicyclic substituent of the amine has virtually no influence on its reactivity. Thus, the heating of perfluoro-N-(4-methylcyclohexyl)piperidine (VII) and perfluoro-N-(4-methylcyclohexyl)pyrrolidine (VI) with SbF_5 results in their smooth isomerization to the azomethines (Xa, b) and (VIIIa, b), correspondingly.



The isomerization of the amines (I), (III), (VI), and (VII) under the action of SbF_5 is a stereospecific process. The anti-isomers of the corresponding azomethines are formed exclusively as the result of the reaction. However, in the case of the two last amines, the cleavage is also accompanied by the cis-trans isomerization in the cyclohexane fragment. Thus, the azomethine (VIII) with the 1:1 ratio of the isomers (VIIIa) and (VIIIb) is formed from the compound (VI) with the 3:1 ratio of the trans and cis isomers. The analogous picture is also observed in the case of the amine (VII), which is converted to the isomeric azomethines (IXa) and (IXb). The mechanism of this conversion is evidently analogous to that previously proposed [3] for the cleavage of perfluoro-N,N-diethylcyclohexylamine by the action of antimony pentafluoride.

EXPERIMENTAL

The ¹⁹F NMR spectra of the compounds (II) and (V) were taken on the Perkin-Elmer R-32 instrument (84.6 MHz); those of the compounds (IXa, b) and (VIIIa, b) were taken on the Bruker-WP-200SY instrument (188 MHz). The chemical shifts are presented in ppm from CF_3 -COOH (external); the SSCCs are presented in Hz. The IR spectra were obtained on the UR-20 spectrometer. The GLC analysis was performed on the LKhM-80 instrument with a column containing 20% FS-1265 on Chromosorb W, and the gas carrier was helium.

<u>Isomerization of the Amines (I), (III), (VI), and (VII) (General Method)</u>. The mixture of 10-20 g of the amine and 2-4 g of SbF_5 was heated at 140-160°C for 2-12 h; the monitoring of the course of the reaction was accomplished chromatographically. At the conclusion of the reaction, the mixture was cooled and poured onto ice; the lower layer was separated rapidly prior to drying it over CaCl₂ and distillation. The reaction conditions and the characteristics of the compounds obtained are presented in Tables 1 and 2. The ¹⁹F NMR spectra are as follows: 5.1 (a), 41.4 (b), 49.5 (c), -52.3 (d), 79.1 (e), and 44.0-51.04 (f) for (II), and 5.1 (a), 40.3 (b), 46.2 (c), 48.8 (g), -51.8 (d), 78.8 (e), and 51.04-54.3 (f) for (V).

The ¹⁹F NMR spectra of the compounds (VIIIa, b) and (IXa, b) are presented in Table 2.

The authors express their appreciation to M. V. Galakhov for the taking of the NMR spectra of the compounds (IXa, b) and (VIIIa, b).

			ssccs		2,6a,e=288,3,5a,e=285, 4a-d=20,	a-7=8(10) 2,6a,e=296,3,5a,e=290, 4a- d=24		2,6a,e=280, 3,5a,e=268, 4a-d=16,	$\alpha - 7 = 10(0)$, $1a - 4a = 44$, $2, be - 4a = 30$ 2, 6a, e = 296, $3, 5a, e = 274$, $4a - d = 23$, 1a - 4a = 76, $2, 6e - 4a = 32$	
			م		1	5,8		1	5,8	
(9			ą		-49,2	-49,2		-52,6	52,6	
(IXa, 1			Å		5,4	50,0		5,4	50,0	
and C-R	=Z	a (dXI	ß		51,1	47,0		51,1	47,0	
ч, b) Е	H H H	Ib), (dI	2		42,4	41,6		42,4	41,6	
s (VIIIa	Frank Frank	ra IIV)	Ie	somer	-6,0	-6,0	somer	-6,0	-6,0	
ethines			87. 7	trans I	87,5	86,0	cis I	73,0	73,0	
he Azon	R Fd		al		111,9	112,0		111,9	112,0	
ra of t	Fand Panel	r.a (IXa)	3,5e		59,7	59,7		58,8	58,7	
R Spect	Ferrar Ferrar	(VIIIa),	3,5a		43,8	43,8		45,2	45,3	
			2,6e		53,0	53,8		54,8	54,9	
of the			2,6a		41,5	41,4		40,3	40,2	
TABLE 2. Parameters			11.5		α β γ CF2CF2CF3	αβγο CF2CF2CF2CF3		αβγ CF2CF3	αβγδ	

ł 9 4 ¢ T U V II

CONCLUSIONS

When perfluorinated tertiary cyclic amines containing a substituent at the nitrogen atom are heated with antimony pentafluoride, they isomerize to the corresponding azomethines.

LITERATURE CITED

- V. A. Petrov, G. G. Belen'kii, and L. S. German, Izv. Akad. Nauk SSSR, Ser. Khim., 1935 (1985).
- V. A. Petrov, V. K. Kunanets, K. N. Makarov, and L. S. German, Summary of the 5th All-Union Conference on the Chemistry of Organofluorine Compounds, Zvenigorod (1986), p. 51.
- V. A. Petrov, V. K. Kunanets, B. A. Kvasov, et al., Izv. Akad. Nauk SSSR, Ser. Khim., No. 1, 122 (1988).

POLYSULFONYLETHENES.

5. THE REACTIONS OF TRIS(ORGANOSULFONYL)CHLOROETHENES WITH AMINES AND THIOLS

> N. E. Dontsova, V. P. Sergeeva, E. N. Prilezhaeva, and V. S. Bogdanov UDC 542.91:547.379.53:547.233.1:547.551

As a continuation of the systematic study of nucleophilic vinyl substitution in polysulfonylethenes [1-3], in the current work we investigate the interaction of tris(organosulfonyl)chloroethene (TSCE) (I), a new class of electron-deficient ethenes, with amines and thiols. In the previous report [3], we suggested that the formation of TSCE in the reaction of E-1,2-di(organosulfonyl)-1,2-dichloroethene (DSDCE) with amines apparently seemed to be caused by the "migration" of RSO₂-groups, forming products with a geminal arrangement of RSO₂-groups, N,N-aminyl disulfonylketenes.

Since the substitution reaction at the vinyl centre in tetrasubstituted, electronegative ethenes proceeds by a pathway of addition with elimination (Ad_N-E) [4-6], we propose a scheme for the interaction of TSCE (I) with the nucleophile which is supported by the compounds isolated, as described in the present work.



(1): R = Et (a); R = Ph (b); (II): R = Et, Nu = Et₂N (a), EtS (b), PhS (c): R = Ph. Nu = EtS(d); (III): R = Et, Nu = EtS (a), PhS (b); (IV): R = Et, Nu = n-BuHN (a), PhHN (b); R = Ph. Nu = PhHN (c); R = Et, Nu = EtS (d), PhS (e); (V): R = Et, Nu = Et₂N (a), PhS (b); (VI): R = Et, Nu = PhS; (VII): R = Et.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 3, pp. 649-653, March 1989. Original article submitted October 20, 1987.

0568-5230/89/3803- 0575\$12.50 © 1989 Plenum Publishing Corporation

575