3,3,3-TRIFLUOROPROPYL(METHYL)CYCLOSILOXANES

I. Isolation and Identification of Trifluoropropyl(methyl)dimethylcyclosiloxanes

E. G. Kagan, Yu. A. Yuzhelevskii, A. L. Klebanskii, O. N. Larionova, and A. V. Kharlamova

Khimiya Geterotsiklicheskikh Soedinenii, Vol. 3, No. 5, pp. 819–822, 1967

UDC 547.79'128:543.544

Mixtures of cyclosiloxanes containing 3,3,3-trifluoropropyl(methyl)- and dimethylcyclosiloxanes units, are separated by vacuum distillation and GLC. Three hitherto undescribed compounds are isolated and characterized. Six new cyclosiloxanes are identified by indirect methods, in cuts which are mixtures. Chromatography and fractional distillation give results which are in satisfactory agreement.

It was previously reported that a mixture of cyclosiloxanes, consisting of 3,3,3-trifluoropropyl(methyl)siloxane components (Φ) and dimethylsiloxane ones (D) can be obtained by catalytic rearrangement of the products of joint hydrolysis of 3,3,3-trifluoropropyl(methyl)dichlorosilane and dimethyldichlorosilane (mole ratio 1:1). From the mixture of products were isolated [1] the following individual cyclotetrasiloxanes: ΦD_3, Φ_2D_2, Φ_3D, and the cyclopentasiloxane Φ_3D_2. Subsequently conditions for analyzing this mixture by high temperature GLC were chosen, and of the 18 peaks on the chromatograms only 12 could be interpreted.

In the present work the above mixture of cyclosiloxanes was separated by vacuum distillation. The starting mixture and all the cuts were analyzed chromatographically. The individual compounds were isolated, and among them 1,3-bis(3,3,3-trifluoropropyl)-1,3,5,5-tetramethylcyclotrisiloxane (Φ_2D), bis(3,3,3-trifluoropropyl)octamethylcyclopentasiloxane (Φ_2D_3), and 1,3,5,7-(3,3,3-trifluoropropyl)-1,3,5,7,9,9-hexamethylcyclopentasiloxane (Φ_4D) (Table 1). From the chromatographic analysis data previously given [1], 3,3,3-trifluoropropylheptamethylcyclotetrasiloxane (ΦD_3), 1,3,5-tris(3,3,3-trifluoropropyl)-1,3,5,7,7-pentamethylcyclotetrasiloxane (Φ_3D), and tris(3,3,3-trifluoropropyl)heptamethylcyclopentasiloxane (Φ_3D_2) are obtained purer. Table 1 gives their properties.

Comparison of the boiling points of some cyclosiloxanes shows that on passing from Φ_mD_n to $\Phi_{m+1}D_{n-2}$ (i.e. on replacing 2 units D by one unit Φ) there is little change in the boiling point. At the same time it

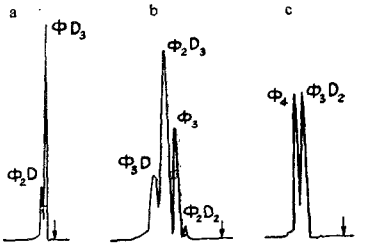

Fig. 1. Chromotagrams of intermediate cuts (Griffin chromatograph, He rate 1.9 *l*/hr; pressure at column outlet 30 mm): a) 55.7° (1 mm) cut; band rate 5 mm/min; column temperature 172°; b) mixture of cuts 86.3–97.6° (1 mm) and 100.2–103.6° (1 mm); 15 mm/min, column temperature 203°; c) cut 106.6–118.3° (0.2 mm), band rate 5 mm/min; column temperature 202°.

emerged that $\Phi_{m+1}D_{n-2}$ comes off the chromatograph column immediately after Φ_mD_n. This made it possible to make assumptions regarding the unknown components of some mixed cuts, obtained by fractional distillation (Fig. 2). The specific refraction R_D, mean molecular weight M, and elemental composition calculated using these assumptions are in satisfactory agreement with the experimental data (Table 2).

Thus, all the components of the mixture of 3,3,3-trifluoropropyl(methyl)dimethylcyclosiloxanes investigated were either isolated pure or identified in

Table 1

Properties of 3,3,3-Trifluoropropyl(methyl)dimethylcyclosiloxanes

Compound	Bp, °C (pressure mm)	n_D^{20}	d_4^{20}	M		MR_D		Elemental composition, %							
								C		H		F		Si	
				Found	Calculated	Found	Calculated	Found	Calculated	Found	Calculated	Found	Calculated	Found	Calculated
Φ_2D*, $C_{10}H_{20}F_6O_3Si_3$	102(20)	1.3697	1.1685	390.0	386.5	74.76	74.62	31.7	31.2	5.2	5.2	28.8	29.6	21.9	21.7
Φ_2D_3*, $C_{14}H_{22}F_6O_5Si_5$	98.5(1)	1.3830	1.1131	529.4	534.7	112.07	111.90	31.3	31.4	6.3	6.0	21.1	21.3	25.2	26.2
Φ_4D*, $C_{18}H_{34}F_{12}O_5Si_5$	126.5(0.2)	1.3773	1.2327	698.5	698.8	130.48	130.60	30.8	31.0	5.8	6.3	31.9	32.6	20.1	20.0
ΦD_3, $C_{10}H_{25}F_3O_4Si_4$	99(20)	1.3840	1.0598	376.5	378.5	83.51	83.91	31.2	31.7	6.4	6.6	16.0	15.1	28.9	29.6
Φ_3D, $C_{14}H_{27}F_9O_4Si_4$	105 5(1)	1.3738	1.2086	540.0	542.6	102.49	102.61	30.6	31.0	5.0	5.0	31.7	31.5	20.8	20.7
Φ_3D_2, $C_{16}H_{33}F_9O_5Si_5$	118(0.9)	1.3800	1.1752	610.0	616.6	121.51	121.25	31.8	31.2	5.5	5.4	28.2	27.7	23.0	22.7

*New compound

Table 2

Assigning Unknown Components of Mixed Cuts

Fraction number	Bp, °C (pressure mm)	n_D^{20}	d_4^{20}	Cut composition, component *, %** 1	2	3	Formula proposed for X_n	M mean Found	M mean Calculated	R_D Found	R_D Calculated	Elemental composition, % C Found	C Calculated	H Found	H Calculated	F Found	F Calculated	Si Found	Si Calculated
I	71.2—71.8 (20)	1.3787	1.0494	D_4 (15)	X_1 (85)	—	ΦD_2	305.5	303.2	0.2201	0.2200	31.4	31.7	6.7	6.4	29.7	29.2	16.8	15.9
II	122.2—122.4 (20)	1.3849	1.0810	X_2 (60)	Φ_2D_2 (40)	—	ΦD_4	454.4	458.0	0.2167	0.2169	31.1	31.6	6.4	6.4	17.8	17.5	27.9	28.4
III	114.8—115.2 (1)	1.3855	1.1301	Φ_3D (14)	X_3 (69)	Φ_3D_2 (17)	Φ_2D_4	585.0	600.9	0.2076	0.2089	31.0	31.4	5.9	6.0	22.7	22.0	26.1	25.9
IV	117 (0.2)	1.3755	1.2371	Φ_4 (70)	X_4 (30)	—	Φ_3D_3	657.0	644.5	0.1853	0.1862	30.8	30.9	4.7	4.9	33.5	33.0	20.0	19.9
V	150—152 (0.5)	1.3771	1.2254	X_5 (28)	Φ_5 (72)	—	Φ_4D_2	788.0	778.6	0.1836	0.1831	31.4	30.8	4.6	4.7	33.9	34.5	20.0	19.0

* In order of yield on the chromatograph column; X_n = unknown components.

** Calculated from the chromatogram (see Fig. 2).

Table 3

Composition of a Mixture of 3,3,3-Trifluoropropyl(methyl)dimethylcyclosiloxanes

Component	Content, % In the mixture charged (from the results of fractional distillation)	Calculated on the sum of the rings to Φ_4D inclusive: From fractional distillation results	By chromatographing the starting mixture	Difference, %
D_3	0.49	0.51	0.18	−0.33
D_4	1.04	1.07	0.84	−0.23
D_5	0.16	0.17		−0.17
ΦD_2	2.14	2.21	1.55	−0.66
ΦD_3	12.56	12.98	13.43	+0.45
ΦD_4	2.39	2.47	2.89	+0.42
Φ_2D	2.93	3.03	2.89	−0.14
Φ_2D_2	30.47	31.49	30.75	−0.74
Φ_2D_3	6.05	6.25	6.78	+0.53
Φ_2D_4	0.29	0.30	traces	−0.30
Φ_3	1.10	1.14	1.69	+0.55
Φ_3D	22.28	23.03	22.96	−0.07
Φ_3D_2	6.22	6.43	7.45	+1.02
Φ_3D_3	0.77	0.80	traces	−0.80
Φ_4	5.39	5.57	6.37	+0.80
Φ_4D	2.47	2.55	2.22	−0.33
Φ_4D_2	0.17	—	—	—
Φ_5	0.13	—	—	—
Still residue	1.19	—	—	—
Losses	1.76	—	—	—
Total	100.00	100.00	100.00	—
Mean difference				±0.47

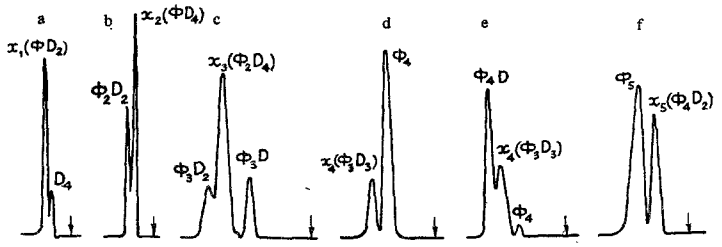

Fig. 2. Chromatograms of mixed cuts (see Table 2): a–e) Griffin chromatograph; He rate 1.9 *l*/hr; band speed 5 mm/min; pressure at column exit: a) 300 mm; b–e) 30 mm; a) cut I; column temperature 132°; b) cut II; column temperature 172°; c) cut III; column temperature 172°; d) cut IV; column temperature 202°; e) cut 122–126° (0.2 mm); column temperature 202°; f) fraction V; Pye chromatograph; Ar rate 9 *l*/hr; column temperature 160°; pressure at column outlet 760 mm.

mixed cuts. The data on the quantitative composition of the mixture (Table 3) shows satisfactory agreement between results of chromatographic analysis of all mixtures, and results of fractional distillation.

EXPERIMENTAL

Vacuum fractionation was carried out in argon through a column with a rating of 38 theoretical plates. Most of the chromatographic analyses were run on a Griffin chromatograph, column diameter 6 mm, length 1740 mm, stationary phase SKTFT-50 rubber on Celite 545, carrier gas helium, catharometer detector.

Three of the highest boiling fractions were analyzed with a Pye chromatograph, column diameter 4 mm, length 1524 mm, stationary phase polyethylene glycol adipate on Celite 545, argon ionization detector.

Molecular weights were found cryoscopically in Freon-112 (standard chromatographically pure Φ_3 [3]). In calculating the fractional distillation results, the content of each component in all the fractions, pure, intermediate, and mixed, was taken into account.

The authors thank R. A. Mogilevskaya and coworkers who made the elementary analyses.

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27 December 1965

Lebedev All-Union Scientific Research Institute for Synthetic Rubber, Leningrad