ISSN 1070-4272, Russian Journal of Applied Chemistry, 2011, Vol. 84, No. 6, pp. 1046–1051. © Pleiades Publishing, Ltd., 2011.
Original Russian Text © Yu.K. Starobin, V.V. Berenblit, N.V. Lebedev, V.A. Gubanov, 2011, published in Zhurnal Prikladnoi Khimii, 2011, Vol. 84, No. 6, pp. 1025–1030.

Study of Liquid-Phase Photolysis of Perfluorinated Ketones

Yu. K. Starobin, V. V. Berenblit, N. V. Lebedev, and V. A. Gubanov

Federal State Unitary Enterprise S.Y. Lebedev Research Institute for Synthetic Rubber, St. Petersburg, Russia

Received November 29, 2010

Abstract—Liquid-phase photolysis of perfluorinated ketones under UV irradiation was examined.

DOI: 10.1134/S1070427211060255

Perfluoropolyoxaalkanes being highly chemically inert, heat resistant fluids are used as components in heat-resistant fluoropolymer formulations and gas transporting fluids in contemporary technology and medicine.

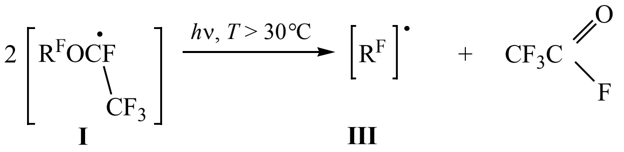
Perfluoropolyoxaalkanes can be obtained by the anodic dimerization according to Kolbe reaction in electrolysis of perfluoro-2-methyl-3-oxaalkanoic acids in acetonitrile medium [1–3] or by photolysis of perfluoroketones [4].

Earlier pyrolysis of derivatives of perfluoro-2-methyl-3-oxaalkanoic acids was investigated and conditions for obtaining the corresponding perfluoroketones in high yield were found [5].

In this regard, a research of the liquid-phase photolysis of perfluoroketones is promising in a wide temperature range in order to find optimal conditions for obtaining perfluoropolyoxaalkanes.

The liquid-phase decarbonylation of perfluoropolyoxaalkylketones under ultraviolet radiation at ambient temperature is accompanied by recombination of radicals formed and proceeds by Scheme 1.

We found that at photolysis temperature higher than 30° decarbonylation was accompanied by abstraction of trifluoroacetyl fluoride with formation of perfluoroalkyl or perfluorooxaalkyl radicals $[R_F]^{\cdot}$:

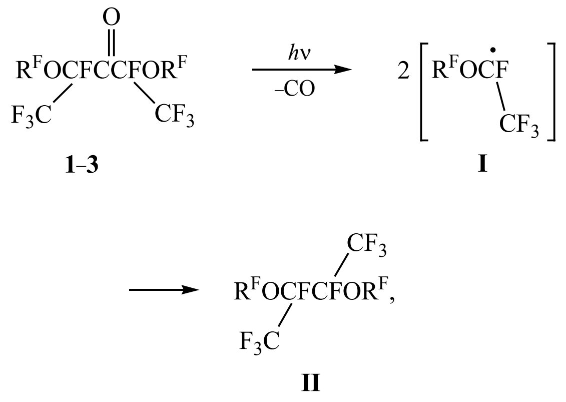


Interaction of radical **I** with radical **III** formed in photolysis leads to formation of “crossed” products, 2-perfluoroackoxyalkane (**IV**), and to recombination of perfluoroalkyl radical **III** to dimer **V** (Scheme 2).

Mass ratio of photolysis products **II**, **IV**, and **V** in a mixture for 1 h after the irradiation start at temperature up to 50°C was 1 : 1 : 1, however, for 10 h after the end of the process it reached 3 : 1 : 1. With increasing temperature higher than 120°C yield of dimer **V** was 60 wt %.

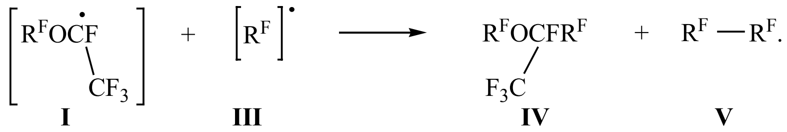
Boiling points in a series of dimers **II**, **IV,** and **V** containing oxygen in the structure decreased in increments of 30°. In particular, after photolysis of perfluoro-5,8,10,13-tetramethyl-4,7,11,14-tetraoxaheptadecan-9-one (**3**)

Scheme 1.



$R^F = CF_3CF_2CF_2–$ (**1**), $CF_3OCF_2CF_2CF_2–$ (**2**), $CF_3CF_2CF_2OCFCF_2–$ (**3**).

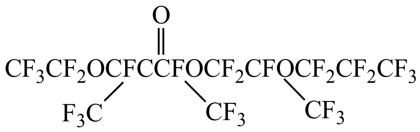
Scheme 2.



$$\left[R^FO\dot{C}F(CF_3)\right] + \left[R^F\right]^{\bullet} \longrightarrow R^FOCF(CF_3)R^F + R^F{-}R^F.$$

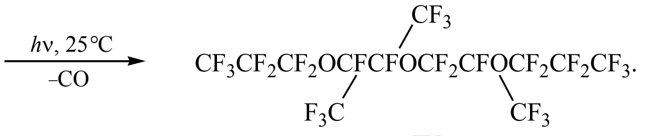
perfluoro-5,8,9,12-tetramethyl-4,7,10,13-tetraoxahexadecane (II_3), bp 216°C, perfluoro-5,8,10-trimethyl-4,7,11-trioxatetradecane (IV_3), bp 186°C, and perfluoro-5 ,7-dimethyl-4 ,8-dioxadodecane (V_3), bp 156°C were isolated by distillation and identified.

Unlike Kolbe cross-synthesis [1, 2], when both the dimerization of each of the radicals and their recombination to form an asymmetric dimer are revealed in the electrolysis products with comparable yields, in the asymmetric photolysis of the ketone **4** at 25°C almost exclusively asymmetric dimer is produced, which coincides with IV_3 by the structure:



$$CF_3CF_2O\underset{F_3C}{C}F\overset{\overset{O}{\|}}{C}\underset{CF_3}{C}FOCF_2\underset{CF_3}{C}FOCF_2CF_2CF_3$$

4



$$\xrightarrow[-CO]{h\nu,\ 25°C} CF_3CF_2CF_2O\underset{F_3C}{C}F\overset{CF_3}{C}FOCF_2\underset{CF_3}{C}FOCF_2CF_2CF_3.$$

IV_3

Recombination of radicals in the liquid phase takes place as if in a “cage,” directly in decarbonylation process, while in Kolbe electrosynthesis a mechanism of electrochemical desorption dictates the output of various products depending on the degree of filling of an anode surface by various radicals.

In an enlarged experience of decarbonylation of perfluoro-7,9-dimethyl-2,6,10,14-tetraoxapentadecan-8-one (**2**) at 40°C by the reaction on Scheme 3 a yield of dimer II_2 reached 95 mol %, whereas a total yield of dimers IV_2 and V_2 under these conditions was only 5 mol %.

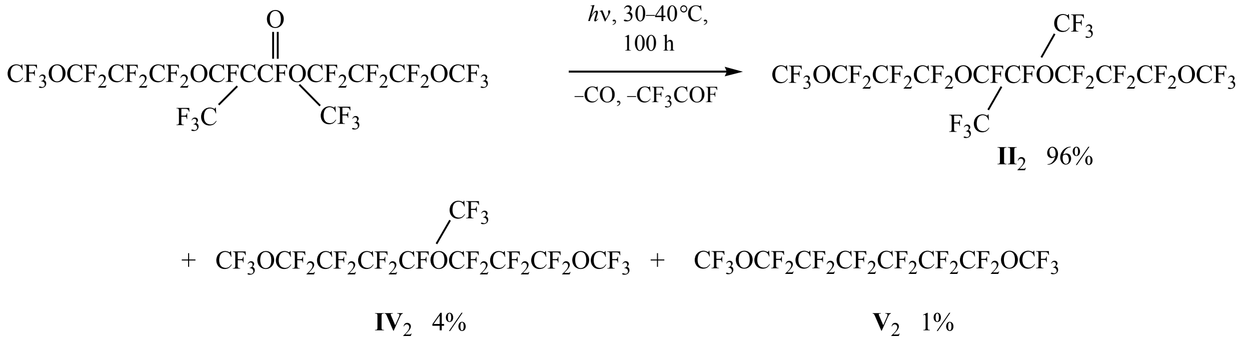
Figure 1 shows dependence of a composition of the products of photolysis of ketone **2** in the reaction mixture on time according to GLC data obtained by sampling in the course of the process.

Tables 1–3 show the structures, boiling temperatures and ^{19}F NMR spectra of the photolysis products, which reflect stereoisomerism of dimers **II** and **IV** associated with the presence of asymmetric fluoromethine carbon atoms with lateral trifluoromethyl groups.

EXPERIMENTAL

To study the photolysis reaction of perfluoroketones we used photochemical reactors with a capacity of 0.3 and 2 liters. A reactor (Fig. 2) consisted of a quartz cylindrical vessel with double walls with a height of 150 mm, an inner diameter of 50 mm, and an outer diameter of 140 mm equipped with a thermocouple and a reflux condenser connected to a nozzle for discharging the reaction gases. In the center of the reactor a high pressure mercury lamp (radiation in the ultraviolet region of 100–400 nm) was coaxially placed, which was cooled by air flow. The

Scheme 3.



$$CF_3OCF_2CF_2CF_2O\underset{F_3C}{C}F\overset{\overset{O}{\|}}{C}\underset{CF_3}{C}FOCF_2CF_2CF_2OCF_3 \xrightarrow[-CO,\ -CF_3COF]{h\nu,\ 30\text{–}40°C,\ 100\ h} CF_3OCF_2CF_2CF_2O\underset{F_3C}{C}F\overset{CF_3}{C}FOCF_2CF_2CF_2OCF_3\ \ II_2\ 96\%$$

$$+\ CF_3OCF_2CF_2CF_2\overset{CF_3}{C}FOCF_2CF_2CF_2OCF_3\ +\ CF_3OCF_2CF_2CF_2CF_2CF_2CF_2OCF_3$$

IV_2 4% V_2 1%

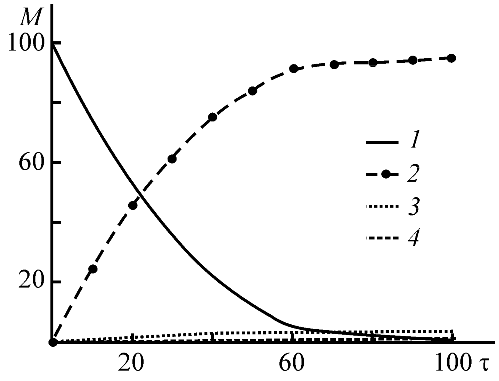


Fig. 1. Composition of the products of the photolysis of (*1*) perfluoro-7,9-dimethyl-2,6,10,14-tetraoxapentadecan-8-one (**2**) in the reaction mixture as function of a time τ of the synthesis according to GLC data. (*M*) Content of the photolysis products (wt %), (τ) time (h). Compound: (*2*) **II**, (*3*) **IV**, (*4*) **V**.

reactor was thermostated by water supply to the jacket. The reactor of the 0.3 l capacity was used for selection of the process temperature in the photolysis of perfluoroketones. The reactor of 2-liter capacity was used for the experiment enlarged.

Initial perfluoroketones, perfluoro-2,4-dipropoxypentan-3-one (**1**) and perfluoro-5,8,10,13-tetramethyl-

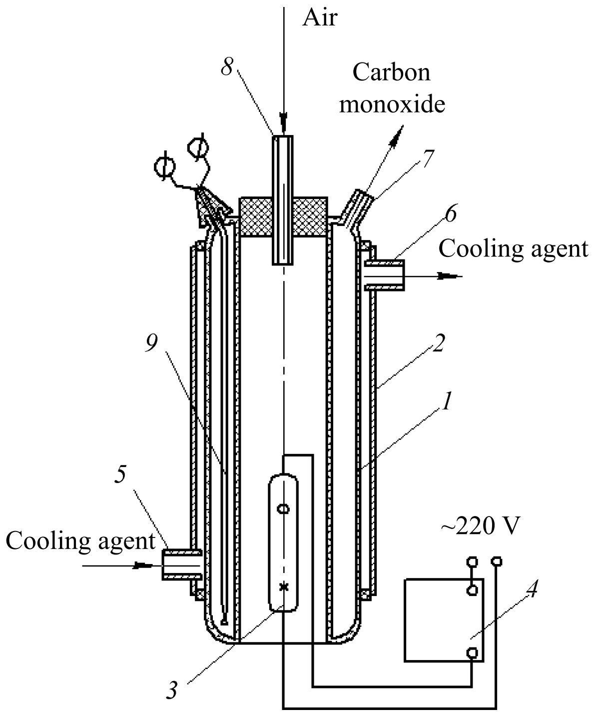


Fig. 2. Photochemical reactor. (*1*) Photochemical reactor made of quartz glass, (*2*) cooling jacket, (*3*) UV lamp, (*4*) device DRL-250 (SIP) for launching and controlling, (*5*) inlet of the cooling agent, (*6*) outlet of cooling agent, (*7*) fitting for carbon monoxide discharging, (*8*) inlet fitting for air, (*9*) thermocouple.

Table 1. ^{19}F NMR spectra of the products of the photolysis of perfluoro-2,4-dipropoxypentan-3-one (**1**)

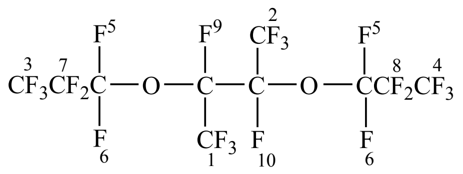
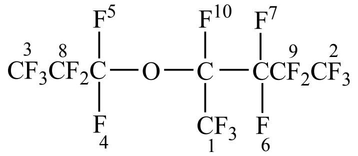
Compound structure	Atom no.	$-\delta_{\mathrm{CCl_2F}}$, ppm	Multiplet	$J_{\mathrm{F-F^*}}$, Hz
Perfluoro-5,6-dimethyl-4,7-dioxadecane (**II**$_1$) (bp 129–130°C)	1	76.6	d	J_{1-10} 8.5
	2	78.2	d	J_{2-9} 8.5
 $\mathrm{CF_3CF_2CF_2{-}O{-}CF(CF_3){-}CF(CF_3){-}O{-}CF_2CF_2CF_3}$	3	80.1	t	$J_{3-5;6}$ 9.0
	4	80.6	t	$J_{4-5;6}$ 9.0
	5	84.2	d.d.q	J_{5-6} 150; J_{5-9} 15; J_{5-3} 9.0
	6	84.8	d.d	J_{6-5} 150; J_{6-9} 15
	7	127.8	s	
	8	128.3	s	
	9	137.7	m	
	10	138.9	m	
Perfluoro-5-methyl-4-oxaoctane (**IV**$_1$) (bp 99–100°C)	1	77.1	t	$J_{1-6;7}$ 8.5
	2	80.7	t	$J_{2-6;7}$ 8.7
 $\mathrm{CF_3CF_2CF_2{-}O{-}CF(CF_3){-}CF_2CF_2CF_3}$	3	81.2		$J_{3-4;5}$ 9.0
	4	84.1		J_{4-5}148
	5	84.8		J_{5-4} 148
	6	117.2		J_{6-7} 286

Table 1 (Contd.)

Compound structure	Atom no.	$-\delta_{CCl_2F}$, ppm	Multiplet	J_{F-F^*}, Hz
	7	120.1	d.m	J_{7-6} 286
	8	127.5	s	
	9	128.6	s	
	10	137.9	m	
Perfluorohexane (**V**$_1$) (bp 58–60°C)	1	82.0	t	J_{1-3} 9.5
$\overset{1}{C}F_3\overset{2}{C}F_2\overset{3}{C}F_2\overset{4}{C}F_2\overset{5}{C}F_2\overset{1}{C}F_3$	2;5	127.3	t	J_{2-4} 8.5
	3;4	123.4	sext	$J_{3-1;5}$ 9.0

Table 2. ^{19}F NMR spectra of the products of the photolysis of perfluoro-7,9-dimethyl-2,6,10,14-tetraoxapentadeca-8-one (**2**)

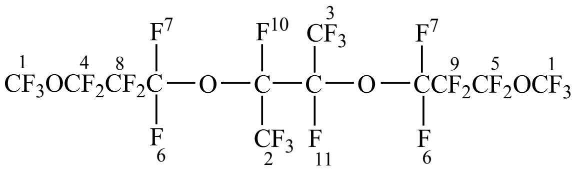
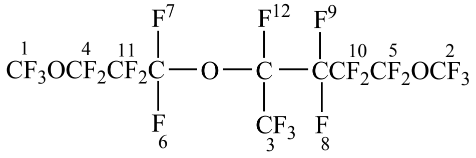
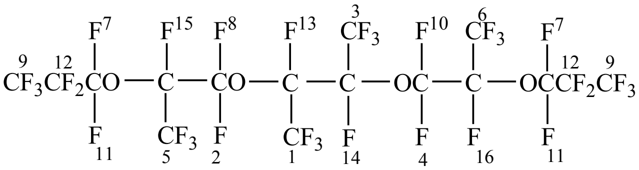
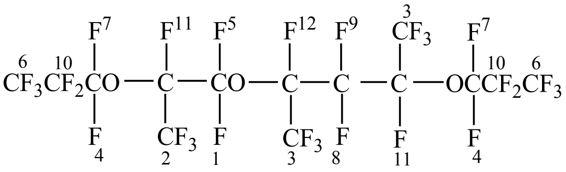
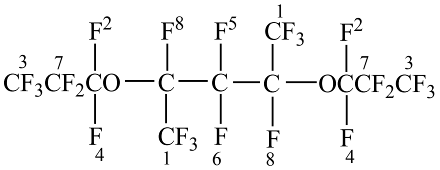
Compound structure	Atom no.	$-\delta_{CCl_2F}$, ppm	Multiplet	J_{F-F^*}, Hz
Perfluoro-7,8-dimethyl-2,6,9,13-tetraoxatetradecane (**II**$_2$) (bp 172°C)	1	54.7	t	$J_{1-4(5)}$ 10.0
 $\overset{1}{C}F_3O\overset{4}{C}F_2\overset{8}{C}F_2\overset{F^7}{\underset{F_6}{C}}-O-\overset{F^{10}}{\underset{CF_{3\,2}}{C}}-\overset{\overset{3}{CF_3}}{\underset{F_{11}}{C}}-O-\overset{F^7}{\underset{F_6}{C}}\overset{9}{C}F_2\overset{5}{C}F_2O\overset{1}{C}F_3$	2	76.5	d	J_{2-11} 8.6
	3	78.1	d	J_{3-10} 8.6
	4	83.4	sext	$J_{4-1;6;7}$ 9.0
	5	83.6	sext	$J_{5-1;6;7}$ 9.0
	6	84.2	d.m	J_{6-7} 147
	7	84.9	d.m	J_{7-6} 147
	8	127.8	s	
	9	128.3	s	
	10	137.7	m	
	11	138.9	m	
Perfluoro-7-metyl-2,6,11-trioxadodecane (**IV**$_2$) (bp 142°C)	1	54.5	t	J_{1-4} 10.0
 $\overset{1}{C}F_3O\overset{4}{C}F_2\overset{11}{C}F_2\overset{F^7}{\underset{F_6}{C}}-O-\overset{F^{12}}{\underset{CF_{3\,3}}{C}}-\overset{F^9}{\underset{F_8}{C}}\overset{10}{C}F_2\overset{5}{C}F_2O\overset{2}{C}F_3$	2	54.9	t	J_{2-5} F^2–F^5 9.8
	3	78.4	t	$J_{3-8;9}$ 8.7
	4	83.0	sext	$J_{4-1;6;7}$ 9.0
	5	83.8	sext	$J_{5-1;8;9}$ 9.2
	6	84.2	d.m	J_{6-7}147
	7	84.7	d.m	J_{7-6} 147
	8	117.2	d.m	J_{8-9}284
	9	120.1	d.m	J_{9-9} 284
	10	127.5	s	
	11	128.6	s	
	12	137.9	m	
Perfluoro-2,9-dioxadecane (**V**$_2$) (bp 112°C)	1	54.9	t	J_{1-2} 9.8
$\overset{1}{C}F_3O\overset{2}{C}F_2\overset{4}{C}F_2\overset{3}{C}F_2\overset{3'}{C}F_2\overset{4'}{C}F_2\overset{2}{C}F_2O\overset{1}{C}F_3$	2	83.9	sext	$J_{2-1;3}$ 9.0
	3	122.4	q	$J_{3-2;4}$ 8.5
	4	123.8	t	J_{4-3} 8.5

Table 3. ^{19}F NMR spectra of the products of the photolysis of perfluoro-5,8,10,13-tetrametyl-4,7,11,14-tetraoxaheptadecan-9-one (**3**)

Compound structure	Atom no.	$-\delta_{CCl_2F}$, ppm	Multiplet	J_{F-F^*}, Hz
Perfluoro-5,8,9,12- tetrametyl -4,7,10,13- tetraoxaheptadecane (**II**$_3$) (bp 216°C)  $CF_3CF_2CF_2O-CF(CF_3)-CF_2O-CF(CF_3)-CF(CF_3)-OCF_2-CF(CF_3)-OCF_2CF_2CF_3$	1	76.4	br.s	
	2	76.5	d.m	J_{2-8} ~ 150
	3	77.1	br.s	
	4	77.3	d.m	J_{4-7} ~ 150
	5	78.4	br.s	
	6	78.5	br.s	
	7	78.7	d.m	J_{7-4} ~ 150
	8	80.0	d.m	J_{2-8} ~ 150
	9	80.3	br.s	
	10	81.5	d.m	J_{10-11} ~ 150
	11	82.7	d.m	J_{11-10} ~ 150
	12	128.2	br.s	
	13	130.5	d	J_{13-x} 19
	14	138.2	d	J_{14-x} 19
	15	142.5	t	J_{15-x} 24
	16	142.8	t	J_{16-x} 24
Perfluoro-5,810-trimethyl-4,7,11-trioxatetradecane (**IV**$_3$) (bp 186°C)  $CF_3CF_2CF_2O-CF(CF_3)-CF_2O-CF(CF_3)-CF_2-CF(CF_3)-OCF_2CF_2CF_3$	1	76.6	d.m	J_{1-5} ~ 150
	2	77.1	br.s	
	3	78.2	br.s	
	4	78.7	d.m	J_{4-7} ~ 150
	5	80.0	d.m	J_{5-1} ~150
	6	80.3	br.s	
	7	81.5	d.m	J_{7-4} ~ 150
	8	118.0	d.m	J_{8-9} ~ 290
	9	120.5	d.m	J_{9-8} ~ 290
	10	128.2	br.s	
	11	142.3	t	J_{11-x}24
	12	142.8	t.d	J_{12-x}24; J_{12-x} 18
Perfluoro-5,7-dimethyl-4,8-dioxadodecane (**V**$_3$) (bp 156°C)  $CF_3CF_2CF_2O-CF(CF_3)-CF_2-CF(CF_3)-OCF_2CF_2CF_3$	1	78.2	br.s	
	2	78.7	d.m	J_{2-4}~150
	3	80.3	br.s	
	4	81.5	d.m	J_{4-2}~150
	5	118.0	d.m	J_{5-6}~290
	6	120.5	d.m	J_{6-7} ~290
	7	127.9	br.s	
	8	143.0	t.d	J_{8-x}24; J_{8-x} 18

4,7,11,14-tetraoxaheptadecan-9-one (**3**), were synthesized from the dimer and trimer of hexafluoropropenoxide respectively, perfluoro-7,9-dimethyl-2,6,10,14-tetraoxapentadecan-8-one (**2**) was obtained from perfluoro-2-(3-metoxy,propoxy)propionylfluoride [5]. Asymmetric perfluoro-5,7,10-dimethyl-4,8,11-trioxatetradecan-6-one (**4**) was obtained by condensation of the trimer of hexafluoropropenoxide with perfluoropropylvinyl ether in the presence of potassium fluoride in diglyme.

IR spectra were recorded on a spectrometer Perkin-Elmer FT Spectrum BX, UV spectra, on a spectrophotometer Perkin-Elmer Lambda 35 in a range of 50–400 nm. The structure of the photolysis products were determined by ^{19}F NMR spectra with a spectrometer Bruker Spectrospin AM-500 with a frequency of 470.6 MHz with hexafluorobenzene as an internal standard. Composition of the photolysis products were analyzed by gas-liquid chromatography (GLC) in a chromatograph LHM-8MD (Model 5, the thermal conductivity detector, temperature programming 30–200°C at 6 deg min^{-1}) with a column diameter d = 3 mm, length l = 3 m on a solid support Silohrom-2 (0.16–0.20 mm) with the stationary phase 5F4E (15 wt %), carrier gas helium, 40 ml min^{-1}.

In the 0.3 l reactor we charged 300 g of perfluoroketone, launched a temperature control of the reactor (a cooling agent temperature was set by setting its value on the thermostat) and cooling of the UV lamp by air flow supplied from a compressor. Then we switched on UV irradiation and monitored the process by the sampling from the reactor until complete disappearance in the products of the photolysis by IR spectrum of a band at 1780 cm^{-1} corresponding to the carbonyl group of perfluoroketone or by UV spectrum by disappearance of the absorption band of carbonyl group at 350 nm. The photolysis proceeded up to 10 hours, the temperature range was 30–120°C.

In the enlarged experiment, in the 2 l reactor 2900 g of perfluoro-7,9-dimethyl-2,6,10,14-tetraoxapentadecan-8-one (**2**) was charged and irradiated at 40°C with UV light for 100 hours. By distillation of 2800 g of the mixture of photolysis products we isolated 2650 g of perfluoro-7,8-dimethyl-2,6,9,13-tetraoxatetradecane (**II**$_2$) (bp 70.5–71.5°C/22 mm Hg) identified by ^{19}F NMR spectrum. From a head faction was isolated 25 g of perfluoro-2,9-dioxadexane (**V**$_2$) (bp 112°C/760 mm Hg) and from an intermediate fraction, 100 g of perfluoro-7-methyl-2,6,11-trioxadodecane (**IV**$_2$) (bp 142°C/760 mm Hg).

CONCLUSIONS

(1) Under the influence of UV irradiation at a temperature below 25°C, decarbonylation of perfluoro-2,4-dialkoxypentan-3-ones is accompanied by recombination of the resulting secondary perfluoroalkoxyethyl radicals to form the corresponding perfluoropolyoxaalkanes.

(2) When increasing the temperature of the photolysis decarbonylation of perfluoro-2,4-dialkoxypentan-3-ones accompanied by abstraction of trifluoroacetyl fluoride with the formation of the recombination products of perfluororadikals being formed.

(3) The photolysis of the asymmetric perfluoro-2,4-dialkoxypentan-3-ones at 25°C leads to the formation of only asymmetric perfluoropolyoxaalkanes.

ACKNOWLEDGMENTS

This work was supported by the Federal Agency for Science and Innovation, State Contract no. 02.523.12.3027.

REFERENCES

1. Levin, A.I., Sokolov, S.V., Chechina, O.N., and Bil'dinov, K.N., *Zh. Obshch. Khim.*, 1969, vol. 39, no. 2, pp. 440–442.
2. USSR Inventor's Certificate 1262890; *SSSR Byull. Izobr.,* no. 1262890.
3. Cherstkov, V.F., Grinberg, V.A., Sterlin, S.R. et al.; *Izv. Akad. Nauk SSSR, Ser. Khim.,* 1990, no. 10, pp. 2448–2449.
4. German Patent 2531511. *Verfahren zur Herstellung von Perfluoraethern.*
5. Lebedev, N.V., Berenblit, V.V., Starobin, Yu.K., and Gubanov, V.A., *Zh. Prikl. Khim.*, 2005, vol. 78, no. 10, pp. 1668–1673.