

Table 1. Yields, physical constants, and elemental analyses of peroxides **I**, **III**, **VIIa–q**, **VIIIa, b**

Compd. no.	Yield, %	bp, °C, (p, mm Hg)	d_{20}^{20}	n_D^{20}	Found, %		Formula	Calculated, %		<i>M</i>	
					C	H		C	H	found	calc.
I ^a	55	46–47 (2)	0.9350	1.4230	64.68	11.16	C ₁₀ H ₂₀ O ₃	63.80	10.71	179.7	188.3
III ^a	60	59–60 (5 × 10 ⁻²)	0.8488	1.4415	68.67	12.43	C ₁₄ H ₃₀ O ₃	68.25	12.27	232.8	246.4
VIIa	70	50–51 (5 × 10 ⁻²)	0.9473	1.4390	67.66	10.51	C ₁₂ H ₂₂ O ₃	67.26	10.35	204.9	214.3
VIIb	81	81–82 (5 × 10 ⁻²)	0.8541	1.4540	71.44	11.32	C ₁₆ H ₃₀ O ₃	71.07	11.18	259.0	270.4
VIIc	61	72–73 (5 × 10 ⁻²)	0.8442	1.4460	71.37	11.40	C ₁₆ H ₃₀ O ₃	71.07	11.18	260.7	270.4
VIIId	80	98–99 (5 × 10 ⁻²)	0.8848	1.4555	72.91	11.72	C ₁₈ H ₃₄ O ₃	72.44	11.48	284.6	298.5
VIIe	82	–	0.8875	1.4570	74.88	12.11	C ₂₂ H ₄₂ O ₃	74.53	11.94	338.1	354.6
VIIIf	88	–	0.8985	1.4605	76.55	12.51	C ₂₇ H ₅₂ O ₃	76.36	12.34	411.3	424.7
VIIg	66	–	0.8884	1.4615	77.02	12.58	C ₂₈ H ₅₄ O ₃	76.65	12.41	411.0	438.7
VIIh	73	107 × 108 (5 × 10 ⁻²)	0.9174	1.5120	75.00	9.11	C ₁₈ H ₂₆ O ₃	74.45	9.02	273.6	290.4
VIIi	61	–	1.0778	1.4745	64.22	10.23	C ₁₃ H ₂₄ O ₄	63.91	9.90	241.9	244.3
VIIj	73	–	1.0018	1.4620	66.78	10.57	C ₁₅ H ₂₈ O ₄	66.14	10.36	270.8	272.4
VIIk	79	–	1.0651	1.4510	66.70	10.68	C ₁₉ H ₃₆ O ₅	66.25	10.53	331.7	344.5
VIII	83	–	1.0290	1.4520	67.61	10.78	C ₂₀ H ₃₈ O ₅	67.00	10.68	341.4	358.5
VIIIm	73	–	0.9244	1.4520	78.11	11.03	C ₂₁ H ₄₀ O ₅	67.71	10.82	360.8	372.5
VIIIn	84	–	0.9675	1.4520	69.40	11.14	C ₂₃ H ₄₄ O ₅	68.97	11.06	388.1	400.6
VIIo	64	–	0.9938	1.4695	70.13	10.87	C ₂₄ H ₄₄ O ₅	69.87	10.74	401.3	412.6
VIIp	77	–	0.9965	1.4900	71.32	9.70	C ₂₄ H ₃₈ O ₅	70.90	9.42	388.6	406.6
VIIq	81	–	1.1851	1.5535	77.30	8.26	C ₃₄ H ₄₂ O ₅	76.95	7.98	511.7	530.7
VIIIa	66	–	0.958	1.4500	72.03	11.50	C ₁₇ H ₃₂ O ₃	71.79	11.34	277.1	284.4
VIIIb	62	–	1.0057	1.4945	74.10	9.32	C ₂₃ H ₃₄ O ₄	73.76	9.15	359.6	374.5

^a O_{act}, %, found,calculated: 8.39, 8.50 (**I**) 6.28, 6.49 (**III**).

chloride under similar conditions apparently due to steric hindrances.

The structure of compounds synthesized was confirmed by ¹H NMR, IR, and UV spectra. Yields, physical constants, and elemental analyses of compounds **I**, **III**, **VIIa–c**, **VIIIa, b** are given in Table 1, ¹H NMR data in Table 2, IR and UV spectra in Table 3.

The thermal stability of peroxides obtained was evaluated by derivatography [8]. Peroxy group containing alcohols **III**, **VIIa, b, d–q**, ether **VIIIa**, and ester **VIIIb** are relatively thermally stable compounds that start to decompose with notable rate and obvious heat evolution only at 117–140°C; the original ketone, fairly volatile at heating, starts to decompose already at 108°C.

On the DTG and TG curves appear from one (compounds **I**, **III**, **VIIa**) to two (**VIIb, i, j–p**, **VIIIa**) and three (**VIIId–g, f**, **VIIIb**) stages of mass loss. The data on the thermal stability of peroxides obtained corresponding to the first stage of decomposition are presented in Table 4.

As seen from Table 4, disubstituted acetylene monoperoxyalcohols **VIIb, d–h** are slightly more heat resistant than unsubstituted acetylene peroxyalcohol **VIIa**: The decomposition onset for the latter is at 117°C, by 5–23°C lower than for compounds **VIIb, d–h**. Peroxy group containing diols **VIIi, j** decompose at 122 and 126°C respectively, also by 5–9°C higher than unsubstituted peroxyalcohol **VIIa**. In the series of monoperoxyalcohols **VIIb, d–h** the heat resistance grows with elongation of the hydrocarbon chain of the substituent attached to the triple bond. The most thermally stable are compounds with long pentadecyl (**VIIIf**) and hexadecyl (**VIIg**) substituents at the triple bond (Table 4). Among the acetylene diperoxyalcohols **VIIj–p** the most heat resistant are the diperoxides with two alkylperoxy groups **VIIk–n**. Diperoxides with alkylperoxy and cycloalkyl(aralkyl)-peroxy groups **VIIo, p** are less thermally stable and decompose at 115–116°C, by 6–12°C lower than start to decompose diperoxides **VIIk–n** (Table 4). Note also somewhat higher thermal resistance of diperoxyalcohol **VIIId** with two *tert*-butylperoxy groups as compared to that of diperoxides containing one

Table 2. ¹H NMR spectra of peroxides **I**, **III**, **VIIa–q**, **VIIIa, b**

Compd. no.	¹ H NMR spectrum, δ, ppm
I	1.23 s (9H, Me ₃ COO), 1.27 s (6H, Me ₂ C), 1.21 s (3H, Me), 2.69 s (2H, CH ₂)
III	0.91 t [3H, Me(CH ₂) ₃], 1.23 s (9H, Me ₃ COO), 1.27 s [3H, MeC(OH)], 1.33 d (6H, Me ₂ C), 1.79 q (2H, CH ₂), 3.55 s (1H, OH)
VIIa	1.23 s (9H, Me ₃ COO), 1.31 s [3H, MeC(OH)], 1.54 d (6H, Me ₂ C), 2.03 q (2H, CH ₂), 2.46 s (1H, C≡CH), 4.72 s (1H, OH)
VIIb	0.91 t [3H, Me(CH ₂) ₃], 1.23 s (9H, Me ₃ COO), 1.29 s [3H, MeC(OH)], 1.35–1.58 m [4H, (CH ₂) ₂], 1.50 d (6H, Me ₂ C), 1.97 q (2H, CH ₂), 2.17 t (2H, CH ₂ C≡C), 4.42 s (1H, OH)
VIIc	1.19 s (9H, Me ₃ CC≡C), 1.24 s (9H, Me ₃ COO), 1.29 s [3H, MeC(OH)], 1.50 d (6H, Me ₂ C), 1.95 q (2H, CH ₂), 4.42 s (1H, OH)
VII d	0.90 t [3H, Me(CH ₂) ₅], 1.23 s (9H, Me ₃ COO), 1.30 s [3H, MeC(OH)], 1.30–1.60 m [8H, (CH ₂) ₄], 1.51 d (6H, Me ₂ C), 1.97 q (2H, CH ₂), 2.19 t (2H, CH ₂ C≡C), 4.45 s (1H, OH)
VII e	0.91 t [3H, Me(CH ₂) ₉], 1.17–1.45 m [28H, MeC(OH), Me ₃ COO, (CH ₂) ₈], 1.53 d (6H, Me ₂ C), 1.98 q (2H, CH ₂), 2.17 t (2H, CH ₂ C≡C), 4.46 s (1H, OH)
VII f	0.89 t [3H, Me(CH ₂) ₁₄], 1.20–1.57 m [38H, MeC(OH), Me ₃ C, (CH ₂) ₁₃], 1.52 d (6H, Me ₂ C), 1.99 q (2H, CH ₂), 2.18 t (2H, CH ₂ C≡C), 4.49 s (1H, OH)
VII g	0.88 t [3H, Me(CH ₂) ₁₅], 1.15–1.90 m [30H, CH ₂ and CH ₂) ₁₄], 1.23 s (9H, Me ₃ COO), 1.29 s [3H, MeC(OH)], 1.52 d (6H, Me ₂ C), 2.18 t (2H, CH ₂ C≡C), 4.47 s (1H, OH)
VII h	1.25 s (9H, Me ₃ COO), 1.32 c [3H, MeC(OH)], 1.60 s (6H, Me ₂ C), 2.10 q (2H, CH ₂), 4.75 s (1H, OH), 7.18–7.48 m (5H, Ph)
VII i	1.23 s (9H, Me ₃ COO), 1.32 s [3H, MeC(OH)], 1.53 s (6H, Me ₂ C), 2.04 q (2H, CH ₂), 2.20 s (1H, CH ₂ OH), 4.29 s (2H, CH ₂ C≡C), 4.79 s (1H, MeCOH)
VII j	1.23 s (9H, Me ₃ COO), 1.31 s [3H, MeC(OH)], 1.49 s (6H, Me ₂ CC≡C), 1.51 d (6H, Me ₂ CCH ₂), 1.99 q (2H, CH ₂), 2.64 s (1H, Me ₂ COH), 4.70 s (1H, MeCOH)
VII k	1.24 s (18H, 2Me ₃ COO), 1.29 s [3H, MeC(OH)], 1.45 s (6H, Me ₂ CC≡C), 1.52 d (6H, Me ₂ CCH ₂), 1.98 q (2H, CH ₂), 4.55 s (1H, OH)
VII l	0.88 t (3H, MeCH ₂), 1.19 s (6H, Me ₂ COO), 1.23 s (9H, Me ₃ COO), 1.29 s [3H, MeC(OH)], 1.44 s (6H, Me ₂ CC≡C), 1.50 q (2H, CH ₂ Me), 1.52 d (6H, Me ₂ CCH ₂), 1.98 q (2H, CH ₂ CMe ₂), 4.52 s (1H, OH)
VII m	0.91 [3H, Me(CH ₂) ₂], 1.19 s (6H, Me ₂ COO), 1.24 s (9H, Me ₃ COO), 1.29 s [3H, MeC(OH)], 1.44 s (6H, Me ₂ CC≡C), 1.53 d (6H, Me ₂ CCH ₂), 1.40–1.57 m [4H, (CH ₂) ₂], 1.97 q (2H, CH ₂ CMe ₂), 4.54 s (1H, OH)
VII n	0.89 t [3H, Me(CH ₂) ₄], 1.19 s (6H, Me ₂ COO), 1.22 s (9H, Me ₃ COO), 1.30 s [3H, MeC(OH)], 1.44 s (6H, Me ₂ CC≡C), 1.52 d (6H, Me ₂ CCH ₂), 1.42–1.60 m [8H, (CH ₂) ₄], 1.99 q (2H, CH ₂), 4.54 s (1H, OH)
VII o	1.15 s (6H, Me ₂ COO), 1.23 s (9H, Me ₃ COO), 1.29 s (3H, MeC(OH)), 1.40–1.90 m [11H, C ₆ H ₁₁], 1.44 s (6H, Me ₂ CC≡C), 1.52 d (6H, Me ₂ CH ₂), 1.99 q (4H, CH ₂), 4.51 s (1H, OH)
VII p	1.22 s (9H, Me ₃ COO), 1.28 s [3H, MeC(OH)], 1.44 s (6H, Me ₂ COO), 1.55 d (6H, Me ₂ CCH ₂), 1.60 s (6H, Me ₂ CC≡C), 2.01 q (2H, CH ₂), 4.59 s (1H, OH), 7.20–7.55 m (5H, Ph)
VII q	1.20 s (9H, Me ₃ COO), 1.22 s (6H, Me ₂ CC≡C), 1.25 s [3H, MeC(OH)], 1.49 d (6H, Me ₂ CCH ₂), 1.99 q (2H, CH ₂), 4.50 s (1H, OH), 7.15–7.45 m (15H, Ph ₃ C)
VIII a	0.93 t [3H, Me(CH ₂) ₃], 1.19 s (9H, Me ₃ COO), 1.25–1.60 m [4H, (CH ₂) ₂], 1.34 d (6H, Me ₂ C), 1.49 s [3H, MeC(OMe)], 1.99 s (2H, CH ₂), 2.21 t (2H, CH ₂ C≡C), 3.30 s (3H, MeO)
VIII b	0.89 t [3H, Me(CH ₂) ₃], 1.20 s (9H, Me ₃ COO), 1.30–1.55 m [4H (CH ₂) ₂], 1.39 d (6H, Me ₂ C), 1.91 s [3H, MeCO(O)Ph], 2.21 t (2H, CH ₂ C≡C), 2.44 d (2H, CH ₂), 7.30–8.07 m (5H, Ph)

tert-butylperoxy group and *tert*-pentylperoxy (**VIII**), 2-methyl-2-pentylperoxy (**VIII m**), and 2-methyl-2-heptylperoxy (**VIII n**) groups. Replacing of hydroxy group by methoxy and benzyloxy ones in peroxyalcohol **VIII b** considerably increased the heat resist-

ance of the corresponding ether **VIII a** and ester **VIII b**. Compound **VIII a** starts to decompose at 127°C, compound **VIII b** at 132°C, by 10 and 15°C respectively higher than the onset of decomposition of the original peroxyalcohol **VIII b**.

Table 3. IR and UV spectra of peroxides **I**, **III**, **VIIa-q**, **VIIIa, b**

Compd. no.	IR spectrum, ν , cm^{-1}	UV spectrum, λ_{max} , nm (ϵ)
I	2975, 2930, 2875 (CH alkyl); 1705 (C=O); 1470 (CH_2); 870 (O-O)	207 (400)
III	3460 (OH); 2980, 2930, 2875 (CH alkyl); 1470 (CH_2); 870 (O-O)	203 (130), 235 (60), 275 (30)
VIIa	3490 (OH); 3310 ($\text{C}\equiv\text{CH}$); 2980, 2940, 2875 (CH alkyl); 2110 ($\text{C}\equiv\text{C}$); 1470 (CH_2); 1060 (C-OH); 870 (O-O)	204 (170)
VIIb	3475 (OH); 2980, 2930, 2875 (CH alkyl); 2235 ($\text{C}\equiv\text{C}$); 1470 (CH_2); 1065 (C-OH); 870 (O-O)	204 (250)
VIIc	3490 (OH); 2975, 2930, 2870 (CH alkyl); 2225 ($\text{C}\equiv\text{C}$); 1470 (CH_2); 1060 (C-OH); 870 (O-O)	204 (200)
VIIId	3460 (OH); 2975, 2955, 2925, 2875, 2855 (CH alkyl); 2230 ($\text{C}\equiv\text{C}$); 1470 (CH_2); 1060 (C-OH); 870 (O-O)	204 (300)
VIIe	3475 (OH); 2975, 2955, 2925, 2855 (CH alkyl); 2235 ($\text{C}\equiv\text{C}$); 1470 (CH_2); 1060 (C-OH); 870 (O-O)	203 (250)
VIIIf	3490 (OH); 2990, 2940, 2860 (CH alkyl); 2245 ($\text{C}\equiv\text{C}$); 1470 (CH_2); 1070 (C-OH); 870 (O-O)	202 (200)
VIIg	3470 (OH); 2980, 2960, 2930, 2860 (CH alkyl); 2240 ($\text{C}\equiv\text{C}$); 1470 (CH_2); 1065 (C-OH); 870 (O-O)	203 (200), 222 (150), 270 (100)
VIIh	3470 (OH); 3080, 3060, 3040, 3025 (CH aryl); 2980, 2930, 2875 (CH alkyl); 2225 ($\text{C}\equiv\text{C}$); 1600, 1490 (aryl); 1470 (CH_2); 870 (O-O); 755, 690 (CH aryl)	205 (12000), 241 (11000), 251 (10000)
VIIi	3390 (OH); 2980, 2940, 2870 (CH alkyl); 2240 ($\text{C}\equiv\text{C}$); 1470 (CH_2); 1055 (MeC-OH); 1010 ($\text{H}_2\text{C-OH}$); 870 (O-O)	202 (1000), 222 (700), 265 (500)
VIIj	3400 (OH); 2985, 2940, 2875 (CH alkyl); 2250 ($\text{C}\equiv\text{C}$); 1470 (CH_2); 1065 (C-OH); 870 (O-O)	204 (300), 255 (150)
VIIk	3510 (OH); 2980, 2930, 2870 (CH alkyl); 2110 ($\text{C}\equiv\text{C}$); 1470 (CH_2); 1055 (C-OH); 870 (O-O)	204 (300)
VIIl	3475 (OH); 2980, 2940, 2875 (CH alkyl); 2110 ($\text{C}\equiv\text{C}$); 1470 (CH_2); 1060 (C-OH); 870 (O-O)	203 (300)
VIIm	3510 (OH); 2985, 2940, 2875 (CH alkyl); 2120 ($\text{C}\equiv\text{C}$); 1065 (C-OH); 870 (O-O)	204 (300)
VIIIn	3475 (OH); 2985, 2960, 2940, 2875 (CH alkyl); 2150 ($\text{C}\equiv\text{C}$); 1470 (CH_2); 1060 (C-OH); 870 (O-O)	204 (400)
VIIo	3500 (OH); 2980, 2930, 2855 (CH alkyl); 2120 ($\text{C}\equiv\text{C}$); 1470 (CH_2); 1065 (C-OH); 870 (O-O)	204 (1000), 230 (500)
VIIp	3500 (OH); 3095, 3070, 3030 (CH alkyl); 2990, 2940, 2875 (CH alkyl); 2120 ($\text{C}\equiv\text{C}$); 1600, 1495, 1450 (aryl); 1470 (CH_2); 1060 (C-OH); 870 (O-O); 770, 705 (CH aryl)	208 (5000)
VIIq	3480 (OH); 3090, 3060, 3040, 3025 (CH alkyl); 2985, 2940, 2875 (CH alkyl); 1595, 1490, 1450 (aryl); 1470 (CH_2); 1065 (C-OH); 870 (O-O); 760, 700 (CH aryl)	205 (41000)
VIIIa	2980, 2940, 2875, 2825 (CH alkyl); 2240 ($\text{C}\equiv\text{C}$); 1470 (CH_2); 1085 (C-O-C); 870 (O-O)	204 (300), 229 (200), 268 (100)
VIIIb	3090, 3070, 3030 (CH aryl); 2980, 2960, 2940, 2875 (CH alkyl); 2245 ($\text{C}\equiv\text{C}$); 1725 (C=O); 1600, 1580, 1450 (aryl); 1470 (CH_2); 870 (O-O); 755, 710 (CH aryl)	202 (9000), 231 (9000)

EXPERIMENTAL

IR spectra of compounds were measured on spectrophotometer Specord 75IR from thin film. ^1H NMR spectra were registered on Tesla BS-567A instrument from solutions in CDCl_3 , internal reference tetramethylsilane, UV spectra were recorded on

spectrophotometer Specord UV Vis from solutions in methanol of 1×10^{-3} M concentration (compounds **I**, **III**, **VIIa-g**, **i-o**, **VIIIa**) or of 1×10^{-4} M concentration (compounds **VIIh**, **p**, **q**, **VIIIb**). Molecular weight of compounds was determined by cryoscopy in benzene.

Table 4. Derivatographic evaluation of heat resistance of peroxides **I**, **III**, **VIIa, b, d–q**, **VIIIa, b** (first stage of decomposition)

Compd. no.	Temperature, °C			Mass loss, %
	onset	final	maximum	
I	108	172	164	88
III	118	203	165	79
VIIa	117	200	153	63
VIIb	122	188	162	44
VIIc	128	192	165	42
VIIe	132	197	165	27
VIIg	138	195	165	20
VIIh	140	192	166	17
VIIi	133	190	163	28
VIIj	122	175	152	49
VIIk	126	175	160	42
VIIl	127	187	157	55
VIIm	125	195	162	63
VIIo	122	195	155	53
VIIp	122	182	162	47
VIIq	116	187	158	50
VIIIa	115	190	160	52
VIIIb	125	182	158	20
VIIIc	127	202	165	51
VIIId	132	185	165	32

Thermal characteristics of compounds obtained were evaluated on a Paulik-Paulik-Erdey derivatograph in argon atmosphere at a linear heating rate 7 deg min⁻¹. Weighed portions of compounds were 100 mg, DTA 1/10, DTG 1/10. The homogeneity of compounds was checked by TLC on Silufol plates 20 cm high, eluent hexane-ether, 3:1, development with *N,N*-dimethyl-*p*-phenylenediamine hydrochloride. The column chromatography was carried out on neutral Al₂O₃ L 40/250 μ, II grade Brockmann activity. The content of active oxygen in peroxides **I**, **III** was measured by iodometry with the use of concn. HCl [9]; with acetylene peroxides **VIIa–q**, **VIIIa, b** the results were overestimated [10]. The original peroxides were prepared by known methods: **I**, [11]; **IVk, l**, [12]; **IV m–q**, [13]. Butyllithium was obtained along procedure [14].

2-tert-Butylperoxy-4-hydroxy-2,4-dimethyloctane (III). To a cooled to -40 ÷ -20°C and vigorously stirred solution of 0.01 mol of 2-*tert*-butylperoxy-2-methylpentan-4-one (**I**) in 20 ml of anhydrous THF was added within 0.5 h 0.01 mol of butyllithium in hexane solution, The mixture was stirred for 1 h at,

gradually warmed to 20–23°C within 1–2 h, and the stirring was continued for another 3 h. The arising lithium peroxyalcoholate **II** was hydrolyzed with 100 ml of water, peroxyalcohol **III** was extracted into hexane, dried with CaCl₂. On removing the solvent the product was purified by vacuum distillation.

2-tert-Butylperoxy-4-hydroxy-2,4-dimethylhex-5-yne (VIIa). A solution of 0.03 mol of lithium monoacetylide **Va** obtained by dropwise addition within 0.5 h of 0.03 mol of butyllithium in hexane solution to 50 ml THF cooled to -70°C at constant bubbling through THF of dry acetylene **IVa** was mixed with 0.02 mol of peroxyketone **I**. The reaction mixture was stirred for 1 h, then it was warmed to 20–23°C within 1–2 h and stirred for 3 h more. The arising lithium peroxyalcoholate **VIa** was hydrolyzed with 100 ml of water, peroxyalcohol **VIIa** was extracted into hexane, dried with CaCl₂. On removing the solvent the product was purified by vacuum distillation.

2-tert-Butylperoxy-4-hydroxy-2,4-dimethyl[dec- (VIIb), dodec- (VIIc), hexadec- (VIIe), heneicos- (VIIg), docos- (VIIh)]-5-yne, 2-tert-butylperoxy-4-hydroxy-2,4,7,7-tetramethyl-oct-5-yne (VIIc), 2-tert-butylperoxy-4-hydroxy-2,4-dimethyl-6-phenylhex-5-yne (VIIh), 4-hydroxy-2,7-di(*tert*-butylperoxy)2,4,7-trimethyloct-5-yne (VIIk), 2-tert-butylperoxy-4-hydroxy-2,4,7-trimethyl-7-[*tert*-pentyl- (VIII), [(2-methyl-2-pentyl)- (VIIl), (2-methyl-2-heptyl)- (VIIm), (2-cyclohexyl-2-propyl)- (VIIp), (triphenylmethyl)- (VIIq)]peroxyoct-5-yne. (General procedure). To a cooled to -40 ÷ -20°C and vigorously stirred solution of 0.13 mol of alkyne **IVb–h, k–q** in 20 ml of anhydrous THF was added dropwise under argon within 0.5 h a hexane solution of 0.011 mol of butyllithium. The mixture was stirred for 1 h, then 0.01 mol of peroxyketone **I** was added, the temperature was raised to 20–23°C within 1–2 h, the mixture was stirred for 3–4 h more, and left overnight (for 18 h). The arising lithium peroxyalcoholate **VIIb–h, k–q** was hydrolyzed with 100 ml of water, peroxyalcohol **VIIb–h, k–q** was extracted into hexane, dried with CaCl₂. On removing the solvent the products were either purified by vacuum distillation (**VIIb–d, h**) or after keeping in a vacuum they (**VIIe–g, k–q**) were subjected to column chromatography on Al₂O₃ with elution first with 100 ml of hexane to remove unreacted alkynes **IVb–h, k–q** and then with a mixture of 30 ml of ethyl ether and 200 ml of hexane. The solvent was evaporated, and the products were dried in a vacuum.

2-tert-Butylperoxy-4,7-dihydroxy-2,4-dimethylhept-5-yne (VIIi), 2-tert-Butylperoxy-4,7-dihydr-

oxy-2,4,7-trimethyloctyne (VIIj). To a cooled to $-40\text{...}-20^{\circ}\text{C}$ and vigorously stirred solution of 0.03 mol of hydroxyalkyne **VIi, j**, in 100 ml of anhydrous THF was added dropwise under argon within 0.5 h a hexane solution of 0.06 mol of butyllithium. The mixture was stirred for 1 h, then 0.01 mol of peroxyketone **I** was added, the temperature was raised to $20\text{--}23^{\circ}\text{C}$ within 1–2 h, the mixture was stirred for 3–4 h more, and left overnight (for 18 h). The arising lithium peroxyalcoholate **VIi, j** was hydrolyzed with 300 ml of water, peroxydiols **VIIIi, j** were extracted into hexane, dried with CaCl_2 . On removing the solvent the product was kept in a vacuum and then subjected to column chromatography on Al_2O_3 , elution with a mixture of 70 ml of ethyl ether and 200 ml of hexane. The solvent was evaporated, and the products were dried in a vacuum.

2-tert-Butylperoxy-4-[methoxy- (VIIIa) or benzyloxy-(VIIIb)]-2,4-dimethyldec-5-yne. To a solution containing 0.01 mol of lithium peroxyalcoholate **VIb** was added 0.011 mol of methyl iodide and 3 ml of hexamethylphosphoramide (in the synthesis of compound **VIIIa**) or 0.012 mol of benzoyl chloride (in the synthesis of compound **VIIIb**). The reaction goes to completion within 18 h at $20\text{--}23^{\circ}\text{C}$. Then to reaction mixture was added 100 ml of hexane, the organic solution was washed with water (in case of **VIIIa**) or with saturated aqueous NaHCO_3 (in case of **VIIIb**), and dried with CaCl_2 . The methyl ether **VIIIa** and benzoate **VIIIb** were purified by chromatography on a column charged with Al_2O_3 , eluent hexane.

REFERENCES

1. Dikumar, E.A., Yuvchenko, A.P., Kozlov, N.G., Popova, L.A., and Moiseichuk, K.L., *Zh. Org. Khim.*, 2000, vol. 36, p. 245.
2. Dikumar, E.A., Yuvchenko, A.P., Zhukovskaya, N.A., Murashko, V.L., and Moiseichuk, K.L., *Zh. Obshch. Khim.*, 1997, vol. 67, p. 1556.
3. Yuvchenko, A.P., Dikumar, E.A., and Moiseichuk, K.L., *Zh. Obshch. Khim.*, 1994, vol. 64, p. 81.
4. Yuvchenko, A.P., Dikumar, E.A., Gurinova, E.S., and Moiseichuk, K.L., *Zh. Obshch. Khim.*, 1994, vol. 64, p. 1692.
5. Dikumar, E.A., Yuvchenko, A.P., Murashko, A.P., Murashko, V.L., Makhnach, S.A., and Moiseichuk, K.L., *Zh. Obshch. Khim.*, 2000, vol. 70, p. 791.
6. Ol'dekop, Yu.A., Churkina, L.A., and Zvereva, T.D., *Vestsi Akad. Nauk BSSR, Ser. Khim.*, 1976, no. 3, p. 84.
7. Ol'dekop, Yu.A., Zvereva, T.D., and Churkina, L.A., *Vestsi Akad. Nauk BSSR, Ser. Khim.*, 1981, no. 2, p. 126.
8. Wendlandt, W. Wm., *Thermal Methods of Analysis*, New York: Interscience, 1964.
9. Adams, D.B., *Analyst.*, 1966, vol. 91, no. 1083, p. 397.
10. Mair, R.D. and Graupner, A.J., *Anal. Chem.*, 1964, vol. 36, p. 194.
11. US Patent 3642755, 1972; *Chem. Abstr.*, 1972, vol. 76, no. 24, 141543k.
12. Ol'dekop, Yu.A., Moiseichuk, K.L., and Yuvchenko, A.P., *Vestsi Akad. Nauk BSSR, Ser. Khim.*, 1978, no. 4, p. 85.
13. Yuvchenko, A.P., Moiseichuk, K.L., Dikumar, E.A., and Ol'dekop, Yu.A., *Vestsi Akad. Nauk BSSR, Ser. Khim.*, 1985, no. 2, p. 65.
14. Talalaeva, T.V. and Kocheshkov, K.A., *Metody elementoorganicheskoi khimii. Litii, natrii, kalii, rubidii, tsezii* (Methods of Organoelemental Chemistry: Lithium, Sodium, Potassium, Rubidium, Cesium), Moscow: Nauka, 1971, vol. 99, p. 554.