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Synthesis of Peroxy Bond Containing Acetylene Alcohols, Ethers, and Esters, Derivatives of 2-Octanone*

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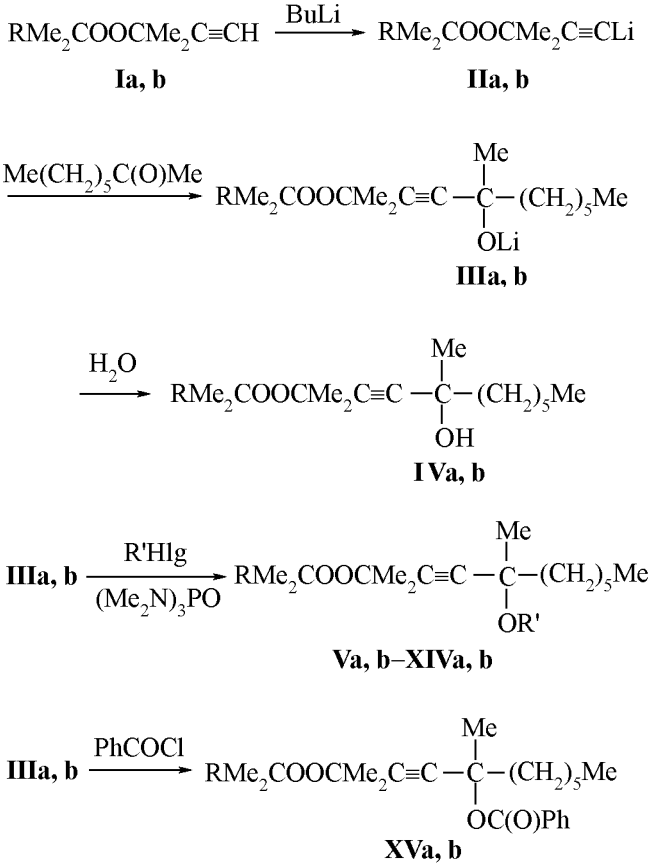
Abstract—A synthesis was developed of 2,5-dimethyl-2-tert-alkylperoxy-5-lithiumoxy-3-undecynes by treating the corresponding peroxyalkynes with butyllithium followed by reaction of the arising lithium peroxyacetylides with 2-octanone. The lithium peroxyalcoholates undergo hydrolysis with water to furnish peroxy bond containing alcohols. They also react with methyl and ethyl iodides, alkyl and benzyl bromides in the presence of hexamethylphosphoramide to afford the corresponding 2,5-dimethyl-2-tert-alkylperoxy-5-alkyl(benzyl)oxy-3-undecynes, with benzoyl chloride they yield peroxy bond containing benzoates. The thermal stability of the peroxides obtained was estimated by derivatography.

We showed [1] that lithium peroxyacetylides in the presence of hexamethylphosphoramide (HMPA) as catalyst could be applied to the synthesis of disubstituted peroxyalkynes.

In the present communication we report on preparation procedure for acetylene primary-tertiary ethers **Va, b–XVa, b** that we developed by an example of peroxy bond containing compounds. Ethers **Va, b–XVa, b** were obtained from 2-octanone with the use of solutions of lithium peroxyacetylides **IIa, b** in tetrahydrofuran in the presence of HMPA as catalyst. The synthesis was carried out without isolation and additional purification of the intermediately arising compounds **IIa, b, IIIa, b**. To our knowledge the direct synthesis of acetylene ethers containing peroxy bond from ketones was nowhere described [2–4].

2,5-Dimethyl-2-*tert*-alkylperoxy-5-lithiumoxy-3-undecynes (**IIIa, b**) were prepared by reaction with 2-octanone of lithium peroxyacetylides (**IIa, b**) obtained by treating 3-methyl-3-tert-alkylperoxy-1-butynes (**Ia, b**) with butyllithium [5]. Lithium peroxyalcoholates **IIIa, b** that form on the intermediate stage are used in solution without isolation. They possess high reactivity. The hydrolysis of compounds **IIIa, b** with water gave rise to peroxyalcohols **IVa, b** in 70% yield.



I–**XV**, R = Me (**a**), Et (**b**); **V**–**XIV**, **R'** = **Me (V)**, Et (**VI**), $Me(CH_2)_3$ (**VII**), $Me(CH_2)_5$ (**VIII**), $Me(CH_2)_9$ (**IX**), $Me(CH_2)_{11}$ (**X**), $Me(CH_2)_{14}$ (**XI**), $Me(CH_2)_{15}$ (**XII**), $Me(CH_2)_{17}$ (**XIII**), $PhCH_2$ (**XIV**); **Hlg = I (V, VI)**, Br (**VII**–**XIV**).

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Table 1. Yields, physical constants and elemental analysis of peroxides **IVa, b**–**Va, b**

Compd. no.	Yield,	bp, °C (p, mm Hg)	d_{20}^{0}	n_D^{20}	Found, %		Formula	Calculated, %		M	
					C	H		C	H	found	calcd.
IVa	70	70–71 (0.03)	0.9846	1.4390	71.94	11.40	$C_{17}H_{3203}$	71.79	11.34	278	284.4
IVb	70	81–82 (0.03)	0.9218	1.4510	72.47	11.53	$C_{18}H_{34}O_3$	72.44	11.48	292	298.5
Va	67	78–79 (0.03)	0.8527	1.4390	72.51	11.55	$C_{18}H_{34}O_3$	72.44	11.48	294	298.5
Vb	71	86–87 (0.03)	0.8448	1.4420	73.23	11.73	$C_{19}H_{36}O_3$	73.03	11.61	310	312.5
VIa	77	82–83 (0.03)	0.9292	1.4380	73.14	11.74	$C_{19}H_{36}O_3$	73.03	11.61	306	312.5
VIb	78	87–88 (0.03)	0.9002	1.4435	73.74	11.81	$C_{20}H_{38}O_3$	73.57	11.73	319	326.5
VIIa	65	92–93 (0.03)	0.9204	1.4440	74.28	12.03	$C_{21}H_{40}O_3$	74.07	11.84	333	340.5
VIIb	66	97–98 (0.03)	0.9055	1.4415	74.68	12.11	$C_{22}H_{42}O_3$	74.52	11.94	346	354.6
VIIIa	64	104–105 (0.03)	0.9266	1.4420	75.12	12.31	$C_{23}H_{44}O_3$	74.95	12.03	356	368.6
VIIIb	74	108–109 (0.03)	0.8281	1.4515	75.61	12.24	$C_{24}H_{46}O_3$	75.34	12.12	370	382.6
IXa	72	–	0.9859	1.4570	76.84	12.50	$C_{27}H_{52}O_3$	76.36	12.34	412	424.7
IXb	74	–	0.8774	1.4560	76.91	12.53	$C_{28}H_{54}O_3$	76.65	12.41	414	438.7
Xa	61	–	0.9829	1.4505	77.25	12.64	$C_{29}H_{56}O_3$	76.93	12.47	433	452.8
Xb	62	–	0.9763	1.4560	77.34	12.61	$C_{30}H_{58}O_3$	77.19	12.52	450	466.8
XIa	66	–	0.9327	1.4525	78.03	12.78	$C_{32}H_{62}O_3$	77.67	12.63	470	494.8
XIb	76	–	0.8949	1.4550	78.11	12.84	$C_{33}H_{64}O_3$	77.89	12.68	490	508.9
XIIa	66	–	0.8760	1.4555	78.14	12.79	$C_{33}H_{64}O_3$	77.89	12.68	494	508.9
XIIb	69	–	0.9029	1.4550	78.44	12.83	$C_{34}H_{66}O_3$	78.10	12.72	498	522.9
XIIIa	67	–	0.8787	1.4550	78.42	12.87	$C_{35}H_{68}O_3$	78.30	12.76	523	536.9
XIIIb	71	–	0.9749	1.4575	78.66	12.93	$C_{36}H_{70}O_3$	78.48	12.81	532	550.9
XlVa	60	–	0.9793	1.4940	77.12	10.42	$C_{24}H_{38}O_3$	76.96	10.23	362	374.6
XIVb	61	–	0.9807	1.4950	77.46	10.41	$C_{25}H_{40}O_3$	77.27	10.37	371	388.6
XVa	65	–	1.0163	1.4890	74.25	9.43	$C_{24}H_{36}O_4$	74.19	9.34	377	388.5
XVb	73	–	0.9473	1.4880	74.83	9.66	$C_{25}H_{38}O_3$	74.59	9.51	388	402.6

Table 2. ^{1}H NMR spectra of compounds **IVa, b**–**XVa, b**

Compd. no.	δ, ppm
IVa	0.90 t (3H, Me), 1.20–1.65 m [10H, $(CH_2)_5$], 1.24 s (9H, Me_3COO), 1.47 s (9H, Me_2C and MeCC≡C), 2.20 s (1H, OH)
IVb	0.89 t (6H, 2$\underline{Me}CH_2$), 1.20 s (6H, Me_2COO),1.23–1.74 m [12H, CH_2 and $(CH_2)_5$], 1.45 s (9H, Me_2C and MeCC≡C) 2.00 s (1H, OH)
Va	0.89 t (3H, $\underline{Me}CH_2$), 1.25 s (9H, Me_3COO), 1.26–1.75 m [10H, $(CH_2)_5$], 1.37 s (3H, MeCC≡C), 1.48 s (6H, Me_2C), 3.34 s (3H, MeO)
Vb	0.89 t (6H, 2$\underline{Me}CH_2$), 1.20 s (6H, Me_2COO), 1.23–1.85 m [12H, CH_2 and $(CH_2)_5$], 1.36 s (3H, MeCC≡C), 1.47 s (6H, Me_2C), 3.34 s (3H, MeO)
VIa	0.89 t [3H, $\underline{Me}(CH_2)_5$], 1.19 t (3H, $\underline{Me}CH_2$), 1.25 s (9H, Me_3COO), 1.25–1.80 m [10H, $(CH_2)_5$], 1.37 s (3H, MeCC≡C), 1.47 s (6H, Me_2C), 3.60 q (2H, $\underline{CH_2}Me$)
VIb	0.88 t (3H, $\underline{Me}CH_2C$), 0.93 t [3H, $\underline{Me}(CH_2)_5$], 1.17 t (3H, $\underline{Me}CH_2O$), 1.19 s (6H, Me_2COO), 1.23–1.90 m [12H, $MeCH_2C$ and $(CH_2)_5$], 1.37 s (3H, MeCC≡C), 1.47 s (6H, Me_2C), 3.60 q (2H, $MeCH_2O$)
VIIa	0.90 t (6H, 2$\underline{Me}CH_2$), 1.25 s (9H, Me_3COO), 1.25–1.75 m [14H, $(CH_2)_2$ and $(CH_2)_5$], 1.37 s (3H, MeCC≡C), 1.47 s (6H, Me_2C), 3.54 t (2H, CH_2O)
VIIb	0.89 t (9H, 3$\underline{Me}CH_2$), 1.19 s (6H, Me_2COO), 1.22–1.75 m [16H, CH_2, $(CH_2)_2$ and $(CH_2)_5$], 1.36 s (3H, MeCC≡C), 1.46 c (6H, Me_2C), 3.54 t (2H, CH_2O)
VIIIa	0.89 t (6H, 2$\underline{Me}CH_2$), 1.20–1.75 m [18H, $(CH_2)_4$ and $(CH_2)_5$], 1.25 s (9H, Me_3COO), 1.36 s (3H, MeCC≡C), 1.46 s (6H, Me_2C), 3.53 t (2H, CH_2O)
VIIIb	0.89 t (9H, 3$\underline{Me}CH_2$), 1.19 s (6H, Me_2COO), 1.20–1.75 m [20H, CH_2, $(CH_2)_4$ and $(CH_2)_5$], 1.37 s (3H, MeCC≡C), 1.47 s (6H, Me_2C), 3.53 t (2H, CH_2O)
IXa	0.88 t (6H, 2$\underline{Me}CH_2$), 1.17–1.70 m [26H, $(CH_2)_5$ and $(CH_2)_8$], 1.25 s (9H, Me_3COO), 1.35 s (3H, MeCC≡C), 1.46 s (6H, Me_2C), 3.52 t (2H, CH_2O)
IXb	0.88 t (9H, 3$\underline{Me}CH_2$), 1.18 s (6H, Me_2COO), 1.20–1.75 m [28H, CH_2, $(CH_2)_5$ and $(CH_2)_8$], 1.36 s (3H, MeCC≡C), 1.46 s (6H, Me_2C), 3.53 t (2H, CH_2O)
Xa	0.89 t (6H, 2$\underline{Me}CH_2$), 1.20–1.70 m [30H, $(CH_2)_5$ and $(CH_2)_{10}$], 1.25 s (9H, Me_3COO), 1.36 s (3H, MeCC≡C), 1.47 s (6H, Me_2C), 3.52 t (2H, CH_2O)
Xb	0.90 t (9H, 3$\underline{Me}CH_2$), 1.19 s (6H, Me_2COO), 1.15–1.75 m [32H, CH_2, $(CH_2)_5$ and $(CH_2)_{10}$], 1.36 s (3H, MeCC≡C), 1.46 s (6H, Me_2C), 3.52 t (2H, CH_2O)
XIa	0.89 t (6H, 2$\underline{Me}CH_2$), 1.15–1.65 s [36H, $(CH_2)_5$ and $(CH_2)_{13}$], 1.25 s (9H, Me_3COO), 1.35 s (3H, MeCC≡C), 1.45 s (6H, Me_2C), 3.52 t (2H, CH_2O)
XIb	0.90 t (9H, 3$\underline{Me}CH_2$), 1.20 s (6H, Me_2COO), 1.15–1.75 m [38H, CH_2, $(CH_2)_5$ and $(CH_2)_{13}$], 1.36 s (3H, MeCC≡C), 1.47 c (6H, Me_2C), 3.52 t (2H, CH_2O)
XIIa	0.88 t (6H, 2$MeCH_2$), 1.20–1.65 m [38H, $(CH_2)_5$ and $(CH_2)_{14}$], 1.25 s (9H, Me_3COO), 1.35 s (3H, MeCC≡C), 1.46 s (6H, Me_2C), 3.52 t (2H, CH_2O)
XIIb	0.89 t (9H, 3$\underline{Me}CH_2$), 1.20 s (6H, Me_2COO), 1.22–1.75 m [40H, CH_2, $(CH_2)_5$ and $(CH_2)_{14}$], 1.36 s (3H, MeCC≡C), 1.46 s (6H, Me_2C), 3.52 t (2H, CH_2O)
XIIIa	0.88 t (6H, 2$\underline{Me}CH_2$), 1.15–1.75 m [42H, $(CH_2)_5$ and $(CH_2)_{16}$], 1.25 s (9H, Me_3COO), 1.37 s (3H, MeCC≡C), 1.49 s (6H, Me_2C), 3.50 t (2H, CH_2O)
XIIIb	0.88 t (9H, 3$\underline{Me}CH_2$), 1.20 s (6H, Me_2COO), 1.20–1.70 m [44H, CH_2, $(CH_2)_5$ and $(CH_2)_{16}$], 1.36 s (3H, MeCC≡C), 1.45 s (6H, Me_2C), 3.51 t (2H, CH_2O)
XIVa	0.89 t (3H, $\underline{Me}CH_2$), 1.15–1.75 m [10H, $(CH_2)_5$], 1.22 s (9H, Me_3COO), 1.43 s (3H, MeCC≡C), 1.46 s (6H, Me_2C), 4.62 d (2H, CH_2O), 7.13–7.40 m (5H, Ph)
XIVb	0.89 t (6H, 2$\underline{Me}CH_2$), 1.19 s (6H, Me_2COO), 1.20–1.80 m [12H, CH_2 and $(CH_2)_5$], 1.40 s (3H, MeCC≡C), 1.49 s (6H, Me_2C), 4.63 d (2H, CH_2O), 7.15–7.45 m (5H, Ph)
XVa	0.89 t (3H, $\underline{Me}CH_2$), 1.20–1.65 m [10H, $(CH_2)_5$], 1.20 s (9H, Me_3COO), 1.49 s (6H, Me_2C), 1.80 s (3H, MeCC≡C), 7.30–8.05 m (5H, Ph)
XVb	0.90 t (6H, 2$\underline{Me}CH_2$), 1.15 s (6H, Me_2COO), 1.20–1.70 m [12H, CH_2 and $(CH_2)_5$], 1.47 s (3H, Me_2C), 1.80 s (3H, MeCC≡C), 7.30–8.10 m (5H, Ph)

The solutions of lithium peroxyalcoholates **IIIa, b** react with methyl and ethyl iodides, alkyl bromides and benzyl bromide in the presence of HMPA as catalyst giving rise to the corresponding 2,5-dimethyl-2-*tert*-alkylperoxy-5-alkyl(benzyl)oxy-3-undecynes (**Va, b–XVa, b**) in 61–78% yield. The reaction fails to occur without HMPA. With 1-bromo-2-phenylethane formed styrene, peroxyalcohols **IVa, b**, and LiBr instead of ethers with a peroxy bond.

Lithium peroxyalcoholates **IIIa, b** with benzoyl chloride afford peroxyesters of benzoic acid **XVa, b** in 65–73% yield.

Compounds **IVa, b–XVa, b** obtained are colorless or lightly colored fluids well soluble in the common organic solvents and insoluble in water. Compounds **IVa, b–XVa, b** are stable to storage at 0–5°C. Physical constants and yields of peroxides **IVa, b–XVa, b** are listed in Table 1, their ^{1}H NMR spectra in Table 2.

In the IR spectra of compounds **IVa, b–XVa, b** were identified the absorption bands supporting their structure. The absorption bands of C=O and C≡C–H groups of the initial 2-octanone and 3-methyl-3-*tert*-alkyl-1-butynes (**Ia, b**) are lacking in the IR spectra of peroxides **IVa, b–XVa, b**. In the IR spectra of peroxyalcohols **IVa, b** appears the absorption band of associated OH groups at 3395 ± 5 cm^{-1}. Ethers **Va, b–XIVa, b** are characterized by the absorption band of stretching vibrations of C–O–C bonds at 1100 ± 10 cm^{-1}, in the spectra of esters **XVa, b** is observed the absorption band of C=O stretching vibrations at 1730cm^{-1}. The phenyl groups in the IR spectra of compounds **XIVa, b, XVa, b** appear as three bands of stretching vibrations of C–H bonds in the benzene ring at 3095 ± 5, 3065 ± 5 and 3040 ± 5 cm^{-1}; absorption bands of bending vibrations of the benzene ring in the regions 1660 ± 10, 1600 ± 5, 1580 ± 5 (**XVa, b**), 1500 ± 5, 720 ± 5, 700 ± 5 cm^{-1} [6].

In the UV spectra of peroxides synthesized the absorption maxima are present at the following wavelengths: [λ_{max}, nm (ε)]: 204 ± 1 (200 ± 50) (**IVa, b–VIa, b**); 205 (350), 227 (200) (**VIIa, b**); 204 ± 1 (1500 ± 500), 240 ± 10 (1500 ± 500) (**VIIIa, b–XIIIa, b**); 205 ± 1 (11000), 248 ± 1 (4000) (**XIVa, b**); 202 (18000), 230 ± 1 (20000) (**XVa, b**).

The thermal stability of compounds synthesized was estimated by derivatography. Peroxides **IVa, b–XVa, b** are relatively heat resistant. Peroxyalcohols **IVa, b** start to decompose with a notable rate and a pronounces heat evolution only at 138–140°C, ethers **Va, b–XIVa, b** are somewhat more thermally stable, and their decomposition begins at 140–146°C. Peroxybenzoates **XVa, b** are stable up to 136–139°C.

EXPERIMENTAL

IR spectra of compounds were recorded on Specord 75IR instrument from thin films. ^{1}H NMR spectra were registered on spectrometer Tesla BS-567A from solutions in $CDCl_3$, internal reference TMS. UV spectra were obtained on spectrometer Specord UV-Vis from solutions in methanol at concentration 1×10^{-2} M for compounds **IVa, b–XIIIa, b** or 1×10^{-4} for compounds **XIVa, b, XVa, b**. The molecular weights were determined cryoscopically in benzene.

Thermal stability of compounds synthesized was measured on derivatograph of Paulik-Paulik-Erdei system under argon, the heating rate 7°C per min. The precisely weighed amount of compound was 100 mg, DTA 1/10, DTG 1/10. The homogeneity of compounds was checked by TLC on Silufol plates, plate height 20 cm. eluent hexane–ether, 3 : 1, development with *N*,*N*-dimethyl-*p*-phenylenediamine dihydrochloride. In column chromatography was used neutral Al_2O_3 of II grade Brockmann activity. The determination of the active oxygen in peroxides **IVa, b–XVa, b** by iodometry with the use of conc. HCl [8] gave overestimated results. Initial peroxyalkynes **a, b** and butyllithium were prepared along procedures [9, 10] respectively.

2,5-Dimethyl-2-[*tert*-butyl- and *tert*-pentyl]-5-lithiumoxy-3-undecynes (IIIa, b). General procedure. To a hexane solution of butyllithium (0.011 mol) cooled to –40…–20°C while vigorous stirring under an argon flow was added within 0.5 h 0.13 mol of peroxyalkyne **Ia, b** in 20 ml of anhydrous tetrahydrofuran. The mixture was stirred for another 1 h, and 0.01 mol of 2-octanone was added thereto. Then the temperature was raised to 20–23°C within 1–2 h, and the stirring was continued for 3–4 h more. Then the reaction mixture was left standing for 18 H. Compounds **IIIa, b** were used as obtained, without isolation in individual state.

2,5-Dimethyl-2-[*tert*-butyl- and *tert*-pentyl]-5-hydroxy-3-undecynes (IVa, b). General procedure. To a solution of 0.01 mol of lithium peroxyalcoholates **IIIa, b** was added 100 ml of water, peroxyalcohols **IVa, b** were extracted into hexane, and the extract was dried on $CaCl_2$, the solvent was removed, and the reaction product was purified by vacuum distillation.

2,5-Dimethyl-2-[*tert*-butyl- (Va–XIVa) and *tert*-pentyl (Vb–XIVb)]peroxy-5-[methyl- (Va, b), ethyl- (VIa, b), butyl- (VIIa, b), hexyl- (VIIIa, b), decyl- (IXa, b), dodecyl- (Xa, b), pentadecyl- (XIa, b), hexadecyl- (XIIa, b), octadecyl- (XIIIa, b), benzyl- (XIVa, b)]oxy-3-undecynes. General procedure. To a solution of 0.01 mol of lithium peroxyalcoholates **IIIa, b** was added 0.01 mol of methyl or ethyl iodides or 0.008 mol of alkyl bromides or benzyl bromide, and then 3 ml of hexamethylphosphoramide. At the use of methyl and ethyl iodides the reaction completed at 20–23°C within 18 h. With bromides the reaction mixture was heated under reflux for 50–70 h in an argon atmosphere. To the reaction mixture was added 100 ml of hexane, the organic solution was washed with water, 30% aqueous NaOH, and dried on $CaCl_2$. The solvent was removed. Peroxides **Va, b–VIIIa, b** were vacuum-distilled. Compounds **IXa, b–XIVa, b** were purified by column chromatography on Al_2O_3, eluent hexane.

2,5-Dimethyl-2-[*tert*-butyl- and *tert*-pentyl]-5-benzoyloxy-3-undecynes (XVa, b). General procedure. To a solution of 0.01 mol of lithium peroxyalcoholates **IIIa, b** was added in one portion 0.012 mol of benzoyl chloride. The reaction mixture was stirred for 3–4 h and left standing for 18 h. Then 100 ml of water was added, the product was extracted into hexane, the organic layer was washed with water, saturated water solution of $NaHCO_3$, and dried on $CaCl_2$. The solvent was removed, and compounds **XVa, b** were purified by column chromatography on Al_2O_3, eluent hexane.

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