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Synthesis of *tert*-Alkylperoxy-substituted Derivatives of 2-Propanol, Dioxolane, and Thiirane

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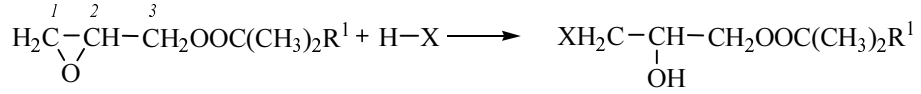
Abstract—Treatment of *tert*-alkyl-2-oxiranylmethyl peroxides with compounds containing an active hydrogen, with ketones, chlorosilanes, and potassium thiocyanate furnished a series of functionally-substituted dialkyl peroxides.

Organic peroxides with functional groups are widely used in the chemistry of macromolecular compounds as initiators of the radical polymerization.

The alteration of substituents makes it possible to prepare initiators of various activity and solubility in the water and organic phases. The latter opportunity ensures the free choice of a necessary initiator both for the processes carried out in bulk, in emulsion, or in suspension.

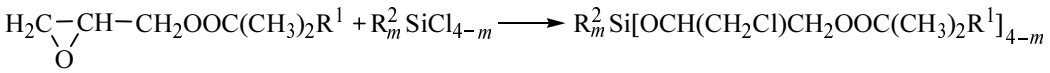
We performed a series of syntheses of functionally-substituted primary-tertiary dialkyl peroxides from the formerly prepared [1] 3-*tert*-alkylperoxy-1,2-epoxypropanes **Ia** and **Ib**. Epoxyperoxide **I** was treated with concn. hydrochloric and hydrobromic acids, with alcohols, phenol, and methyl alkyl ketones in the presence of boron trifluoride etherate, with alkylchlorosilanes, and with potassium thiocyanate dispersion in anhydrous ethanol. As a result functionalized peroxide **II–IX** were obtained.

The mentioned syntheses and also the workup and purification of the target products were carried out under conditions ensuring the preservation of the peroxy moiety.



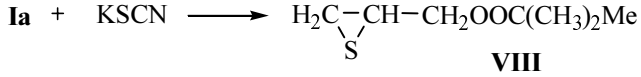
Ia **II–Va–Ve, VI**

X = Cl (**II**), Br (**III**), OH (**IV**), R^2O (**V**), $R^2{}_3COO$ (**VI**); R^1 = Me (**Ia, II–VI**); R^2 = Me (**Va, VI**), Et (**Vb**), Pr (**Vc**), *t*-Bu (**Vd**), Ph (**Ve**).

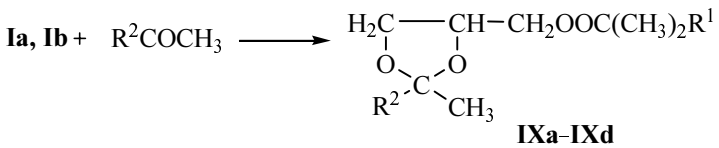


Ia, Ib **VIIa–VIIe**

R^1 = Me (**Ia, VIIa–d**), Et (**Ib, VIIe**); R^2 = Me (**VIIa, VIIb, VIId, VIIe**), Et (**VIIc**); *m* = 1 (**VIId**), 2 (**VIIb, VIIc**), 3 (**VIIa, VIIe**).



VIII



IXa–IXd

IX, R^1 = Me (**a–c**), Et (**d**); R^2 = Me (**a, d**), Et (**b**), Pr (**c**).

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Taking into account the expected high boiling points of all the substances and the relatively low temperature of the homolytic cleavage of the dialkylperoxy group we purified compounds obtained by preparative column chromatography on aluminum oxide.

In reactions with compounds containing active hydrogen the epoxy ring opened as expected in conformity to Krasussky rule [2, 3], namely, with prevailing formation of substituted 2-propanols **II–VI**; chloroalkylsilanes afforded in good yields 1-chloro-2-alkylsiloxy-substituted derivatives **VIIa–VIIe**; with ketones the process resulted in alkylperoxymethyl derivatives of dioxolanes **IXa–IXd** presumably as mixtures of *cis*- and *trans*-isomers.

The composition of compounds obtained was confirmed by elememtal analysis, cryoscopic measurements, and by refractometry, and their structure was proved by IR and ^{1}H NMR spectroscopy and by chemical methods. Compounds **IV** and **V** besides the preparation from epoxyperoxide **Ia** and the corresponding alcohol were also obtained by an independent synthesis from glycidol and its ethers by treatment with *tert*-butyl hydroperoxide. Chloroalkylsilane derivatives were hydrolyzed in acid medium to alkylsilanols and alkylperoxy ethers of glycerol monochlorohydrin **II**.

The relatively low yield of 2-propanol derivatives is due to their fairly high solubility in water and to the required purification by column chromatography.

IR spectra unambiguously show that the opening of the epoxy ring and formation of the hydroxy group is accompanied by disappearance from the spectrum of the absorption bands in the region 3070 cm^{-1} (vibrations of the methylene group of the epoxy ring) and 910 cm^{-1} (asymmetrical stretching vibtations of the ring) and with appearance of a band in the region 3500 cm^{-1}. More ambiguous are assignments of the absorption bands belonging to the *tert*-alkylperoxy groups. Sometimes [4–6] the band at 870 cm^{-1} is assigned to the symmetric stretching vibrations of the oxygen–oxygen bond. However in the dialkyl peroxides because of the symmetry of vibrations and also due to the close values of masses and force constants for groups O–O and C–O, C–C the appearance of this characteristic band is hardly probable [7]. Moreover, just in this region a strong band is observed belonging to a tertiary alkoxy group [7]. At least in the spectrum of *tert*-butyl ether of the glycerol monochlorohydrin $ClCH_2CHOHCH_2OC(CH_3)_3$ (**X**) lacking peroxy group the same bands were observed as in the spectrum of compound **II**.

Table 1. Yields, physical constants, and elemental analyses of substituted dialkyl peroxides **II–IX**

Compd. no.	*m*	Yield, %	n_D^{20}	d_4^{20}, g/cm^3	M		MR_D		$[O]_{act}$	
					found	calculated	found	calculated	found	calculated
II	–	53	1.4440	1.0911	179.3	182.7	44.48	44.88	9.40	8.75
III	–	64	1.4630	1.3015	206.4	227.1	47.97	47.77	7.85	7.04
IV	–	31	1.4440	1.048	178.7	164.2	41.61	41.58	11.45	9.72
Va	–	46	1.4310	1.000	187.8	178.2	46.26	46.45	9.40	8.97
Vb	–	56	1.4296	0.9720	180.0	192.3	51.06	51.10	8.30	8.32
Vc	–	58	1.4309	0.9624	212.2	206.3	55.48	55.74	7.40	7.76
Vd	–	39	1.4320	0.9546	247.8	220.3	59.86	60.42	7.55	7.26
Ve	–	32	1.4870	1.0531	218.7	240.3	65.63	66.15	7.20	6.66
VI	–	28	1.4260	0.9688	251.0	236.3	62.48	62.61	14.35	13.50
VIIa	3	54	1.4300	0.9757	244.8	254.8	67.47	67.71	6.50	6.30
VIIb	2	82	1.4408	1.0625	403.6	421.4	104.7	105.2	7.00	7.60
VIIc	2	73	1.4462	1.0520	434.3	449.5	114.0	114.5	7.80	7.10
VIId	1	98	1.4512	1.1130	569.4	588.0	142.4	142.7	8.20	8.20
VIIe	3	59	1.4340	0.9700	247.9	268.9	72.18	72.36	5.80	6.00
VIII	–	49	1.4760	1.3590	158.1	162.3	44.25	44.43	9.50	9.90
IXa	–	42	1.4319	0.9748	199.3	204.3	54.05	53.86	8.40	7.80
IXb	–	36	1.4292	0.9675	211.4	218.3	58.19	58.50	7.60	7.30
IXc	–	28	1.4378	0.9690	226.6	232.3	62.91	63.15	7.30	6.90
IXd	–	32	1.4333	0.9718	209.7	218.3	58.42	58.50	7.60	7.30

Table 2. IR spectra of substituted 2-propanols **Ia, II–IV, Va, Ve, VI, X**

Compd. no.	OH	$\nu_{as}(CH_2)$ in epoxide	ν(CH)	$\nu_{as}(CH_3)$	$\nu_s(CH_3)$	$\delta(CH_2)$	$\delta_{as}(C–CH_3)$	$\delta_s[C(CH_3)_2]$		Skeletal $CC(CH_3)_2R$		$COOC(CH_3)_2$ and $COC(CH_3)_2$
Ia	–	3072	3008	2942	2891	1492	1473	1395	1372	1248	911	880
II	3490	–	3011	2960	2890	1484	1459	1395	1372	1246	–	873
III	3510	–	3008	2960	2914	1485	1470	1390	1372	1245	–	869
IV	3480	–	2997	2968	2911	1484	1469	1395	1373	1246	–	877
Va	3490	–	3009	2960	2889	1495	1474	1396	1373	1242	–	880
Vb	3490	–	3009	2962	2893	1480	1448	1383	1361	1240	–	880
VI	3490	–	2998	2958	2898	1489	1465	1385	1370	1245	–	886
X	3500	–	3009	2957	2889	1478	1478	1392	1361	1236	–	870

Table 3. ^{1}H NMR spectra of epoxyperoxide **Ia**, its adducts **IV, Va, Ve, VIIa, VIII**, and **IX**, and of phenylglycidol (**XI**), δ, ppm (^3J, ^2J, Hz)

Compd. no.	$(CH_3)_3$, s (9H)	$2H^1$, d.d (1H)	(1H)	H^2, m (1H)	$2H^3$, d.d (1H)	(1H)	Other protons
Ia	1.24	2.62 (*J* 2.5, *J* 4.5)	2.85 (*J* 4.5, *J* 4.5)	3.23–3.28	3.91 (*J* 6, *J* 13)	4.09 (*J* 4, *J* 13)	
IV	1.24	3.40–3.70 m	3.70–3.85	3.98–4.05 m	4.05–4.15 m	2.20 br.s (2H, 2OH)	
Va	1.24	3.43 (*J* 4, *J* 10)	3.49 (*J* 4, *J* 10)	3.90–4.05	4.03 (*J* 4, *J* 12)	4.05–4.15 m	2.40 br.s (1H, OH), 3.387 s (3H, SH_3O)
Ve	1.24	4.14	4.17	3.70–3.85	4.08	4.14	2.40 br.s (1H, OH), 6.94 d (2H, *O*-H in Ph), 6.99 t (1H, *p*-H in Ph), 7.32 t (2H, *m*-H in Ph)
VIII	1.22	2.18	2.48	3.00–3.08	3.51	4.17	
VIIa	1.14	3.36–3.52 m	3.56–3.72 m	3.80–3.95	3.59 d	3.36 s	0.05 s [9H, $(SH_3)_3Si$]
IXa	1.14	3.82 s	3.83 s	3.92–4.08	3.60–3.75 m	3.79 d	1.40 s (6H, $2SH_3$)
XI	–	2.78 (*J* 5, *J* 5)	2.93 (*J* 5, *J* 5)	3.30–3.45	3.98–4.05 m	4.05–4.15 m	6.94 d (2H, *O*-H in Ph), 6.99 t (1H, *p*-H in Ph), 7.32 t (2H, *m*-H in Ph)

The opening of the epoxy ring led to considerable changes also in the ^{1}H NMR spectra. The destruction of the rigid three-membered ring provides a possibility of rotation around the carbon–carbon bond previously included into the ring. This fact results in increased number of possible rotamers and therefore in a complication of the spectrum. The addition of water to peroxide **Ia** furnished glycerol monoalkylperoxy ether **IV**, and the addition of methanol and phenol afforded 1,3-disubstituted ethers of glycerol **Va** and **Ve**.

The comparison of spectra of compounds **I, IV, Va**, and **Ve** shows that in all cases the signals of the methylene protons in the moiety $CH_2OC(CH_3)_3$ appear virtually at the same chemical shift, $\delta(CH_2)$ ~3.9–4.2 ppm (Table 3). Matching the spectra of peroxides **I** and **Ve** with that of phenylglycidol (**XI**) revealed the effect of replacing the *tert*-butoxy by the phenyl group on the chemical shifts of the other protons in these molecules. Apparently the phenoxy goup is a stronger acceptor of the electron density than the *tert*-alkylperoxy one, therefore the protons H^1, H^2, and H^3 in the phenoxy derivatives **Ve** and **XI** suffer deshielding. Therewith the signal of one of protons H^1 in compound **Ve** the most spatially approached to the phenoxy group underwent the largest downfield shift [δ_{H^3} ~3.9 ppm for epoxyperoxide **I**, δ_{H^1} ~4.1 ppm for peroxide **Ve**, and δ_{H^3} ~4.0 ppm for

phenylglycidol (**XI**) lacking peroxy group]. The chemical shifts of protons attached to C^2 atom in the fragment C–CHOH–C essentially depend on the alkoxy substituents at the atoms C^1 and C^3. For instance, in epoxyperoxide **I** and in glycidol, i.e., in compounds containing an epoxy ring, the signal of the proton belonging to the mentioned group appears in a relatively strong field (δ ~3.25 and ~3.38 ppm). In noncyclic compounds, namely, in 1-mono- and 1,3-disubstituted glycerols this proton signal is displaced downfield ((δ ~3.8 ppm for compounds **IV** and **Ve**, and ~4.1 ppm for compound **Va**). The position of the signals from the methylene protons which prior to the addition reaction were included into the epoxy ring (H^1) depends mainly on the character of the alkyl substituent at the oxygen atom linked to this methylene group. The characteristic feature of these signals is the magnetic nonequivalence of these protons that is also observed for the protons of the methylene group in the $CH_2OC(CH_3)_3$ moiety.

EXPERIMENTAL

IR spectra were recorded on a double-beam spectrophotometer IKS-14 (LiF prism). All measurement were carried out at 293 K in a drop layer (condensed phase) of nonfixed thickness; CCl_4 was used as solvent.

^1H NMR spectra were registered from solutions in $CDCl_3$ on a spectrometer Bruker at operating frequency 400 MHz in a pulse mode; internal reference TMS.

Initial epoxyperoxides **Ia** and **Ib** were prepared from epichlorohydrin, the corresponding *tert*-alkyl hydroperoxides, and KOH as described in [1]. The content of active oxygen was measured iodometrically.

3-*tert*-Butylperoxy-1-chloro-2-propanol (II). At stirring to 0.05 mol of 3-*tert*-butylperoxy-1,2-epoxypropane (**Ia**) heated at 35–40°C was added dropwise within 30–40 min 0.06 mol of concn. HCl. The stirring at the same temperature was continued for 30 min, and then the reaction mixture was diluted with a double volume of the saturated water solution of $(NH_4)_2SO_4$. The separated organic layer was thrice washed with the water solution of $(NH_4)_2SO_4$ and dried over Na_2SO_4. The purification of the product was carried out on a column packed with Al_2O_3 of the II grade of activity using acetone as eluent.

Similarly from 0.05 mol of epoxyperoxide **Ia** and 0.06 mol of 60% hydrobromic acid was obtained compound **III**.

1-*tert*-Butylperoxy-2,3-propanediol (IV). *a.* At stirring to 5 ml 0.5 N sulfuric acid heated at 35–40°C was added dropwise within 30–40 min 0.05 mol of peroxide **Ia**. The stirring at the same temperature was continued for 30 min, and then the reaction mixture was saturated with $(NH_4)_2SO_4$, and the target product was extracted into ether. The ether extract was washed with saturated solution of $(NH_4)_2SO_4$ and dried over $MgSO_4$. The product was purified as described above.

b. At cooling 40% water solution of 0.01 mol of KOH was mixed with 0.06 mol of 80% *tert*-butyl hydroperoxide. At 35–40°C while stirring was added dropwise within 30–40 min 0.05 mol of glycidol. The stirring at the same temperature was continued for 30 min. The separation and purification of the product was performed as in experiment *a*.

3-*tert*-Butylperoxy-1-methoxy-2-propanol (Va). *a.* At stirring to 5 ml 0.5 N solution of sulfuric acid in methanol heated at 35–40°C was added dropwise within 30–40 min 0.05 mol of peroxide **Ia**. Further workup was carried out as described in the synthesis of compound **IV**.

b. At cooling 40% water solution of 0.01 mol of KOH was mixed with 0.06 mol of 80% *tert*-butyl hydroperoxide. At 35–40°C while stirring was added dropwise within 30–40 min 0.05 mol of glycidyl methyl ether. The stirring at the same temperature was continued for 30 min. The separation and purification of the product was performed as in the synthesis of compound **IV**.

Compounds **Vb** and **Vc** were prepared in a similar way along both procedures.

Peroxide **Vd** was prepared only along procedure *b* from *tert*-butyl glycidyl ether because in the acid medium the tertiary alcohol added to the epoxy group only at the temperature where the peroxy group might decompose.

3-*tert*-Butylperoxy-1-phenoxy-2-propanol (Ve). At 40–45°C while stirring was added to 40% solution of 0.56 g of KOH in water 0.15 mol of phenol. At the same temperature was added dropwise while stirring within 30–40 min 0.05 mol of peroxide **Ia** and within next 30 min 40% water solution of 2.24 g of KOH. The stirring at the same temperature was continued for 30 min, and then the reaction mixture was saturated with $(NH_4)_2SO_4$, and the target product was extracted into ether. The ether extract was twice washed with 5% water solution of NaOH, twice with water, and dried over Na_2SO_4. The purification was performed as described above.

1,3-Di-*tert*-butylperoxy-2-propanol (VI). At cooling 40% water solution of 0.01 mol of KOH was mixed with 0.06 mol of 80% *tert*-butyl hydroperoxide. At 35–40°C

while stirring was added dropwise within 30–40 min 0.05 mol of peroxide **Ia**. The stirring at the same temperature was continued for 30 min, and then additionally was added dropwise within 30–40 min 0.05 mol 40% water solution of KOH. The mixture was diluted with the same volume of water, the organic layer was separated and washed twice with 5% water solution of NaOH, twice with water, and dried over Na_2SO_4. The purification was performed as described above.

Trimethyl(3-*tert*-butylperoxy-1-chloro-2-propyloxy)silane (VIIa). At 30–35°C while stirring was added dropwise to 0.1 mol of trimethylchlorosilane within 3–4 h 0.1 mol of peroxide **Ia**. The stirring at the same temperature was continued for 30 min, and then reaction mixture was maintained for 1–2 h at reduced pressure (1–2 mm Hg) while heating at 40–50°C. The chromatographic purification was carried as above using hexane for eluent.

In the same fashion by treating epoxyperoxide **Ia** with dimethyldichlorosilane, dimethyldichlorosilane and methyltrichlorosilane compounds **VIIb–VIId**, and from epoxide **Ib** with trimethylchlorosilane was prepared compound **VIIe**.

Hydrolysis of peroxide VIIa. At 20–25°C 0.05 mol of compound **VIIa** was gradually added while stirring to 1.6 ml of concn. HCl in 32 ml of water. After stirring for 30 min the mixture was thrice extracted with ether. The combined extracts were washed with water, 2% water solution of NaOH, and again with water. On drying over Na_2SO_4 and evaporating the solvent the residue was purified as described above using hexane as eluent. We obtained 8.6 g of compound that by the refraction index and the IR spectrum was identified as compound **II**.

3-*tert*-Butylperoxy-1,2-epithiapropane (VIII). To 0.05 mol of peroxide **Ia** in 25 ml of anhydrous ethanol was added in one portion 5 g of KSCN. The dispersion was stirred for 40 h at 25–30°C, then it was diluted with 50 ml of water, and the target product was extracted into ether. The extract was dried on $MgSO_4$. On evaporating ether the residue was subjected to column chromatography on Silicagel 60 (0.063–0.100 mm) using benzene as eluent.

4-(*tert*-Butylperoxymethyl)-2,2-dimethyl-1,3-dioxolane (IXa). To 0.2 mol of acetone was poured swiftly a solution of 0.004 mol of $SnCl_4$ in 3.6 ml of CCl_4, and then dropwise while stirring was added at 30–40°C in 50–60 min 0.1 mol of peroxide **Ia**. The stirring at the same temperature was continued for 1 h, and then reaction mixture was diluted with an equal volume of water, and the organic layer was separated. The water layer was extracted with ether, the combined organic solution was washed with 5% solution of NaOH and with water. On removing the solvent the product was subjected to column chromatography on Al_2O_3 of **II** activity grade, eluent hexane.

In the same way from epoxyperoxide **Ia** by treating with 2-butanone and 2-pentanone were prepared compounds **IXb** and **IXc** respectively, from epoxyperoxide **Ib** and acetone was obtained dioxolane **IXd**.

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