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Acetylenic Hydroperoxides Derived from 2*e*-Methyldecahydroquinolin-4-one

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Abstract — 2*e*-Methyldecahydroquinolin-4-one was reacted with lithium *tert*-alkylperoxy acetylides to prepare 4-hydroxy-2*e*-methyl-4-(2-methyl-2-*tert*-alkylperoxy-1-butyn-4-yl)decahydroquinolines. The latter readily react with carboxylic acids and methyl iodide, affording the corresponding salts.

In [1–5] we showed that lithium *tert*-alkylperoxy acetylides **IIa, IIb** can be applied for preparing hardly available heteroelement peroxides: acetylenic γ-silicon-containing peroxides, carborane-containing peroxy alcohols and esters, peroxy-containing alkynylphosphonates, and ferrocene-substituted acetylenic peroxy alcohols.

The aim of the present work was synthesis of previously unknown acetylenic peroxy-containing hydroxydecahydroquinolines **IVa, IVb, Va, Vb**. As starting compound we used the individual *trans* isomer of 2-methyldecahydroquinolin-4-one (**III**) with an equatorial methyl group. The structure of compound **III** was unambiguously established by ^{13}C NMR spectroscopy. The *trans*-decahydroquinolone structure of ketone **III** is confirmed by the coincidence of the chemical shifts of the characteristic C^3, C^8, C^9, and C^{10} atoms with those for model compounds, such as *trans*-*N*-R-decahydroquinolyl-2-ones [6, 7]. The equatorial arrangement of the methyl group was established by the value of its chemical shift (23.3 ppm), since were the methyl group axial, its chemical shift would not exceed 17 ppm [8].

Compounds **IVa, IVb, Va, Vb** were prepared by the reactions of 3-methyl-3-*tert*-alkylperoxy-1-butynes **Ia, Ib** with butyllithium at –40 to –20°C with subsequent reaction of the resulting lithium peroxy acetylides **IIa, IIb** with 2*e*-methyldecahydroquinolin-4-one (**III**) (molar ratio 1.2 : 1, temperature from 0°C to 20–23°C). The isolable yields of peroxides **IVa, IVb, Va, Vb** were 86–87%.

Peroxides **IVa, IVb, Va, Vb** are derivatives of the *trans*-decahydroquinoline series with an equatorial methyl group on C^2. Among the reaction products we identified a mixture of isomers, with an equatorial hydroxy group and, correspondingly, an axial peroxy-containing radical on C^4 (**IVa, IVb**) and with an axial hydroxy group (**Va, Vb**), in a 3 : 2 ratio.

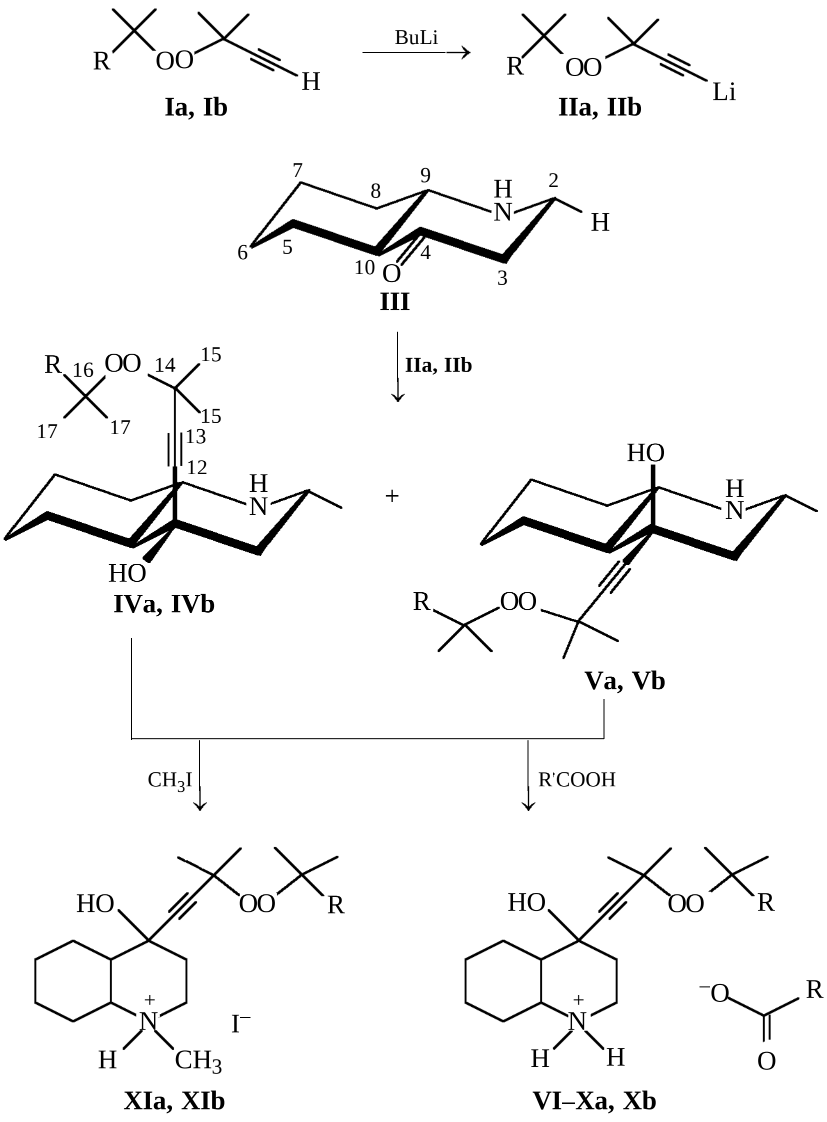
The *trans* configuration of peroxides **IVa, IVb, Va, Vb** is confirmed by the coincidence of the chemical shifts of the characteristic atoms C^3, C^8, C^9, and C^{10} with those for model compounds [6, 7].

We failed to isolate pure isomers **IVa, IVb, Va**, or **Vb** because of the inconsiderable difference in their physicochemical properties. However, assignment of signals in the ^{13}C NMR spectrum of the isomeric mixture is not difficult.

For reliable assignment one should take into account the chemical shifts of those carbon atoms whose steric environment is affected by 1,4-nonbonded interactions in going from one isomer to another. Thus, to assess the configuration of the OH group on C^4, one should consider the chemical shifts of C^2, C^3, C^8, C^9, and C^{10}. The strongest difference is observed for C^2 and C^9. Thus, in isomer **IVa** with an equatorial OH group the signals of C^2 and C^9 (δ_C 49.6 and 57.8 ppm) are shifted downfield by ~3 ppm because of the lack of 1,4-nonbonded interaction of C^2 and C^9 with the OH group, as compared with isomer **Va** with an axial OH group (δ_C 46.9 and 53.4 ppm). The chemical shifts of the other carbon atoms in the two isomers differ only slightly (within 1 ppm).

The ratio of isomeric peroxides **IVa, VIb** and **Va, Vb** in the mixture was determined by the integral intensity of downfield signals of C^2, C^3, C^8, C^9, and C^{10} in the ^{13}C NMR spectrum recorded with a relaxant.

4-Hydroxy-2*e*-methyl-4-(2-methyl-2-*tert*-alkylperoxy-3-butyn-4-yl)decahydroquinolines **IVa, IVb, Va, Vb** readily react with carboxylic acids and methyl iodide in diethyl ether at 20–23°C to give the corresponding salts. The isolable yields of peroxides **VIa, VIb**–**XIa, IXb** were 63–87%.



I, II, IV–**XI**, R = Me (**a**), Et (**b**); R' = H (**VI**), Me (**VII**), Ph (**VIII**), CH_2I (**IX**), *p*-BrC_6H_4 (**X**).

Peroxides **IVa, IVb**–**XIa, XIb** are while crystals stable on handling at 0–5°C. Compounds **IVa, IVb, Va, Vb** are readily soluble in ordinary organic solvents and insoluble in water. Salts **VIa, VIb**–**XIa, XIb** are readily soluble in methanol and ethanol and poorly soluble in chloroform. Compounds **VIa, VIb, VIIa, VIIb, IXa, IXb, XIa, XIb** are soluble in water.

The composition and structure of peroxides **IVa, IVb**–**XIa, XIb** were proved by elemental analysis (Table 1) and ^{1}H NMR (Table 2), IR, and UV spectroscopy (Table 3). The IR spectra of compounds **IVa, IVb, Va, Vb** lack bands at 1705 cm^{-1} due to the C=O group of the starting quinolone **III** and the ≡C–H and C≡C stretching absorption bands of the starting peroxy alkynes **Ia, Ib** at 3325 ± 5 and 2100 ± 5 cm^{-1} (Table 3).

EXPERIMENTAL

The IR spectra were obtained on a Specord IR-75 spectrometer in KBr pellets. The ^{1}H and ^{13}C NMR spectra were recorded on a Tesla BS-567A spectrometer in $CDCl_3$, internal reference TMS. The UV spectra were obtained on a Specord UV-Vis spectrophotometer for 1×10^{-3} M methanol solutions. The molecular weights of compounds **IVa, IVb, Va, Vb** were determined cryoscopically in benzene. The purity of the products was controlled by TLC on Silufol, eluent hexane–diethyl ether (3 : 1), developer *N*,*N*-dimethyl-*p*-phenylenediamine dihydrochloride. Analysis for active oxygen by iodometry with conc. HCl [9] gave overestimated values, probably because of the presence of the C≡C bond.

Table 1. Properties of compounds **IVa, IVb–XIa, IXb**

Comp. no.	Yield, %	mp, °C	Found, %				Formula	Calculated, %				Calculated *M*
			C	H	I (Br)	N		C	H	I (Br)	N	
IVa, Va	87	77–78	76.74	10.33	–	4.18	$C_{19}H_{33}NO_3$	70.55	10.28	–	4.33	323.5[a]
IVb, Vb	86	75–76	71.83	10.55	–	4.01	$C_{20}H_{35}NO_3$	71.18	10.45	–	4.15	337.55[a]
VIa	81	108–109	65.41	10.03	–	3.60	$C_{20}H_{35}NO_5$	65.01	9.55	–	3.79	369.5
VIb	82	175–176	66.12	9.84	–	3.40	$C_{21}H_{37}NO_5$	65.77	9.72	–	3.65	383.5
VIIa	77	184–185	65.74	9.75	–	3.97	$C_{21}H_{37}NO_5$	65.77	9.72	–	3.65	383.5
VIIb	82	173–174	66.88	9.93	–	3.40	$C_{22}H_{39}NO_5$	66.47	9.89	–	3.52	397.6
VIIIa	80	181–182	70.68	8.93	–	3.01	$C_{26}H_{39}NO_5$	70.08	8.82	–	3.14	445.6
VIIIb	85	173–174	70.93	9.30	–	2.81	$C_{27}H_{41}NO_5$	70.56	8.99	–	3.05	459.6
IXa	78	156–157	50.04	7.22	24.55	2.60	$C_{21}H_{36}NIO_5$	49.51	7.12	24.91	2.75	509.4
IXb	85	137–138	51.03	7.48	23.80	2.40	$C_{22}H_{38}NIO_5$	50.48	7.32	24.24	2.68	523.5
Xa	85	220–221	59.88	7.36	14.90	2.44	$C_{26}H_{38}NBrO_5$	59.54	7.25	15.23	2.67	524.5
Xb	87	117–118	60.54	7.88	14.19	2.30	$C_{27}H_{40}NBrO_5$	60.22	7.49	14.84	2.60	538.5
XIa	66	210–211	51.80	8.03	27.03	2.94	$C_{20}H_{36}NIO_3$	51.61	7.80	27.27	3.01	465.4
XIb	63	183–184	53.01	8.12	26.03	2.45	$C_{21}H_{38}NIO_3$	52.61	7.99	26.47	2.92	479.4

[a] Found *M*: 310.4 (**IVa, Va**), 318.8 (**IVb, Vb**).

Table 2. ^{1}H NMR spectra of compounds **IVa, IVb–XIa, XIb**

Comp. no.	δ, ppm
IVa, Va	1.03 d (3H, *Me*CH, *J* 6.5 Hz), 1.23 s (9H, Me_3COO), 1.45 s (6H, Me_2C), 1.15–2.65 m [13H, 2CH, OH, CH_2 and $(CH_2)_4$], 2.87–3.23 m (1H, C*H*Me)
IVb, Vb	0.88 t (3H, *Me*CH_2), 1.05 d (3H, *Me*CH, *J* 6.5 Hz), 1.21 s (6H, Me_2COO), 1.20–2.60 m [15H, 2CH, OH, $2CH_2$ and $(CH_2)_4$]
VIa	1.20 s and 1.00–1.20 d (12H, Me_3COO and *Me*CH), 1.20–2.25 m [13H, 2CH, OH, CH_2 and $(CH_2)_4$], 1.48 s (6H, Me_2C), 2.80–3.60 m (1H, C*H*Me), 5.35 br.s (2H, NH_2^+), 8.52 s [1H, HC(O)]
VIb	0.89 t (3H, *Me*CH_2), 1.18 s and 1.10–1.30 d (9H, Me_2COO and *Me*CH), 1.30–2.50 m [15H, 2CH, OH, $2CH_2$ and $(CH_2)_4$], 1.55 s (6H, Me_2C), 2.80–3.30 m (1H, CHMe), 4.35 br.s (2H, NH_2^+), 8.50 s [1H, HC(O)]
VIIa	1.20 s and 1.00–1.25 d (12H, Me_3COO and *Me*CH), 1.25–2.25 m [13H, 2CH, OH, CH_2 and $(CH_2)_4$], 1.45 s (6H, Me_2C), 1.99 s [3H, MeC(O)], 2.85–3.30 m (1H, C*H*Me), 4.35 br.s (2H, NH_2^+)
VIIb	0.87 t (3H, *Me*CH_2), 1.17 s and 1.10–1.25 d (9H, Me_2COO and *Me*CH), 1.30–2.55 m [15H, 2CH, OH, $2CH_2$ and $(CH_2)_4$], 1.45 s (6H, Me_2C), 1.97 s [3H, MeC(O)], 2.80–3.30 m (1H, C*H*Me), 5.45 br.s (2H, NH_2^+)
VIIIa	1.20 s and 1.00–1.20 d (12H, Me_3COO and *Me*CH), 1.20–2.20 m [13H, 2CH, OH, CH_2 and $(CH_2)_4$], 1.45 s (6H, Me_2C), 2.75–3.50 m (1H, C*H*Me), 5.75 br.s (2H, NH_2^+), 7.25–8.05 m (5H, Ph)
VIIIb	0.86 t (3H, *Me*CH_2), 1.15 s and 1.08–1.20 d (9H, Me_2COO and *Me*CH), 1.25–2.40 m [15H, 2CH, OH, $2CH_2$ and $(CH_2)_4$], 1.48 s (6H, Me_2C), 2.70–3.40 m (1H, C*H*Me), 6.25 br.s (2H, NH_2^+), 7.30–8.10 m (5H, Ph)
IXa	1.20 s and 1.00–1.27 d (12H, Me_3COO and *Me*CH), 1.27–2.25 m [13H, 2CH, OH, CH_2 and $(CH_2)_4$], 1.47 s (6H, Me_2C), 2.75–3.60 m (1H, C*H*Me), 3.68 s (2H, CH_2I), 5.65 br.s (2H, NH_2^+)
IXb	0.88 t (3H, *Me*CH_2), 1.18 s and 1.10–1.20 d (9H, Me_2COO and *Me*CH), 1.25–2.30 m [15H, 2CH, OH, $2CH_2$ and $(CH_2)_4$], 1.45 s (6H, Me_2C), 2.80–3.30 m (1H, C*H*Me), 3.70 s (2H, CH_2I), 5.85 br.s (2H, NH_2^+)
Xa	1.20 s and 1.10–1.22 d (12H, Me_3COO and *Me*CH), 1.27–2.30 m [13H, 2CH, OH, CH_2 and $(CH_2)_4$], 1.50 s (6H, Me_2C), 2.80–3.30 m (1H, C*H*Me), 5.65 br.s (2H, NH_2^+), 7.42–7.96 m (4H, *p*-C_6H_4)
Xb	0.87 t (3H, *Me*CH_2), 1.15 s and 1.10–1.22 d (9H, Me_2COO and *Me*CH), 1.25–2.30 m [15H, 2CH, OH, $2CH_2$ and $(CH_2)_4$], 1.50 s (6H, Me_2C), 2.80–3.20 m (1H, C*H*Me), 5.75 br.s (2H, NH_2^+), 7.40–7.95 m (4H, *p*-C_6H_4)
XIa	1.20 s and 1.15–1.30 d (12H, Me_3COO and *Me*CH), 1.30–2.30 m [13H, 2CH, OH, CH_2 and $(CH_2)_4$], 1.45 s (6H, Me_2C), 1.64 d (3H, NMe, *J* 6.5 Hz), 3.05–3.55 m (1H, C*H*Me)
XIb	0.88 t (3H, *Me*CH_2), 1.17 s and 1.10–1.20 d (9H, Me_2COO and *Me*CH), 1.20–2.60 m [15H, 2CH, OH, $2CH_2$ and $(CH_2)_4$], 1.53 s (6H, Me_2C), 1.55 d (3H, NMe, *J* 6.5 Hz), 2.80–3.50 m (1H, C*H*Me)

Table 3. IR and UV spectra of compounds **III, IVa, IVb–XIa, IXb**

Comp. no.	IR spectrum, ν, cm^{-1}	UV spectrum, λ_{max}, nm (ε)
III	3345 s, 2980 s, 2945 s, 2905 s, 2875 s, 1705 s, 770 m, 650 m	221 (600)
IVa, Va	3320 s, 2990 s, 2945 s, 2860 s	205 (300)
IVb, Vb	3300 s, 2980 s, 2940 s, 2860 s	205 (300)
VIa	2980 s, 2940 s, 2860 s, 2850–2350 br, s, 1640 s, 1605 s	204 (150)
VIb	2980 s, 2940 s, 2860 s, 2850–2350 br, s, 1640 s, 1580 s	204 (150)
VIIa	2980 s, 2940 s, 2860 s, 2840–2350 br, s, 1625 s, 1555 s	206 (150)
VIIb	2980 s, 2940 s, 2860 s, 2840–2350 br, s, 1625 s, 1550 s	205 (150)
VIIIa	3100 w, 3025 w, 2980 s, 2940 s, 2860 s, 2850–2350 br, s, 1625 s, 1555 s, 725 s, 675 m	205 (4500), 226 (8000)
VIIIb	3100 w, 3020 w, 2980 s, 2940 s, 2860 s, 2830–2350 br, s, 1640 s, 1620 s, 1550 s, 725 s, 675 m	204 (5000), 224 (8000)
IXa	2980 s, 2940 s, 2860 s, 2850–2350 br, s, 1630 s, 655 s	205 (3000), 264 (600)
IXb	2975 s, 2940 s, 2860 s, 2840–2350 br, s, 1640 s, 1620 s, 645 s	204 (3000), 264 (600)
Xa	3100 w, 3025 w, 2980 s, 2930 s, 2860 s, 2800–2350 br, s, 1620 s, 1575 s, 1525 s, 825 s, 765 s	205 (18000), 238 (15000)
Xb	3100 w, 3025 w, 2975 s, 2940 s, 2860 s, 2820–2350 br, s, 1640 s, 1620 s, 1590 s, 1520 s, 825 m, 775 s	204 (19000), 240 (19000)
XIa	3400 s, 2960 s, 2940 s, 2860 s, 2880–2400 br, s	205 (7000), 220 (15000)
XIb	3400 s, 2970 s, 2940 s, 2860 s, 2840–2350 br, s	203 (6000), 221 (14000)

The starting peroxides **Ia**–**Ic** and butyllithium were synthesized by the procedures in [10, 11], respectively. 2*e*-Methyldecahydroquinolin-4-one (**III**): mp 43°C; ^{13}C NMR spectrum, δ_C, ppm: 23.3 q (C^{11}), 24.2 t (C^7), 25.4 t (C^5), 25.7 t (C^6), 34.7 t (C^8), 51.1 t (C^3), 53.6 d (C^2), 56.1 d (C^{10}), 61.9 d (C^9), 210.1 s (C^4).

4-Hydroxy-2*e*-methyl-4-(2-methyl-2-*tert*-alkylperoxy-3-butyn-4-yl)decahydroquinolines IVa, IVb, Va, Vb. A solution of 0.025 mol of butyllithium in hexane was added under argon over the course of 0.5 h to a cooled (–40 to –20°C) and vigorously stirred solution of 0.03 mol of peroxy alkyne **Ia** or **Ib** in 50 ml of absolute ether. The mixture was stirred for an additional 1 h, and 0.02 mol of ketone **III** was added to it. The reaction mixture was allowed to warm to 20–23°C over the course of 1–2 h, stirred for an additional 3–4 h, and left to stand for 18 h at that temperature, after which it was diluted with 100 ml of hexane, washed with water, and dried with $MgSO_4$. Peroxides **IVa, IVb, Va, Vb** were purified by vacuum sublimation (T 70–75°C, p 0.02 mm). ^{13}C NMR spectrum, δ_C, ppm: compound **IVa**: 23.0 q (C^{11}), 25.6 t (C^7), 26.0 t (C^6), 26.5 t (C^5), 27.4 q ($3C^{17}$), 28.1 q ($2C^{15}$), 34.4 t (C^8), 49.2 t (C^3), 49.6 d (C^2), 55.4 d (C^{10}), 57.8 d (C^9), 68.9 s (C^4), 71.5 s (C^{16}), 74.9 s (C^{12}), 79.9 s (C^{13}), 86.8 s (C^{14}); compound **Va**: 23.0 q (C^{11}), 25.6 t (C^7), 26.0 t (C^6), 27.0 t (C^5), 27.4 q ($3C^{17}$), 28.1 q ($2C^{15}$), 34.7 t (C^8), 46.9 d (C^2), 50.2 t (C^3), 51.6 d (C^{10}), 53.4 d (C^9), 71.4 s (C^4), 71.5 s (C^{16}), 74.9 s (C^{12}), 79.9 s (C^{13}), 86.8 s (C^{14}).

Salts of 4-hydroxy-2*e*-methyl-4-(2-methyl-2-*tert*-alkylperoxy-3-butyn-4-yl)decahydroquinolines VIa, VIb–XIa, XIb were obtained by addition of a solution of 0.01 mol of formic, acetic, benzoic, iodoacetic, *p*-bromobenzoic, or methyl iodide in 10 ml of absolute ether at 20–23°C to a solution of 0.1 mol of compound **IVa, IVb, Va, Vb** in 10 ml of absolute ether. The reaction mixture was cooled to 0–5°C, and after 18 h white crystals of salts **VIa, Vb**–**XIa, XIb** formed and were filtered off, washed with a little cooled ether, and dried in a vacuum.

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