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Tertiary Alcohols Based on 1-Acetylpyrene

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Abstract—From 1-acetylpyrene by reactions with butyllithium, lithium alkylacetylenides and peroxyacetylenides previously unknown tertiary alcohols were synthesized.

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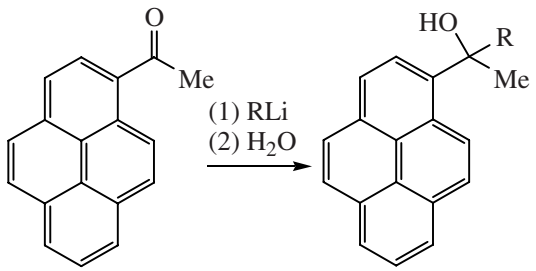
A convenient procedure for preparation peroxy group containing tertiary acetylene alcohols by treating with lithium peroxyacetylenides 1-and 2-acetonaphthone was formerly described [1,2].



I **II**–**VIII**

R = Bu (II), $C{\equiv}C(CH_2)_4Me$ (**III**), $C{\equiv}C(CH_2)_{15}Me$ (**IV**), $C{\equiv}CCMe_2OOCMe_3$ (**V**), $C{\equiv}CCMe_2OOCMe_2Et$ (**VI**), $C{\equiv}CCMe_2OOCMe_2Pr$ (**VII**), $C{\equiv}CCMe_2OOCMe_2C_6H_5$ (**VIII**).

In this study a preparative synthesis was carried out of previously unknown tertiary alcohols **II–VIII** by treating 1-acetylpyrene (**I**) with butyllithium, lithium alkylacetylenides and peroxyacetylenides obtained by reacting butyllithium with the corresponding monosubstituted alkynes and peroxyalkynes [2]. The tertiary alcohols containing in their structure alongside the aromatic pyrene fragment also acetylene (**III–VIII**) and peroxy (**V–VIII**) groups were synthesized in 80–90% yields. They were purified by column chromatography on aluminum oxide. Compounds **II–VIII** are yellow viscous pasty substances well soluble in common organic solvents and insoluble in water. We failed to obtain compounds **II–VIII** in the crystalline state. They are stable at storage at 0–5°C in the dark. The structure of alcohols **II–VIII** was confirmed by elemental analysis, molecular weight measurement by cryoscopy, UV, ^{1}H NMR, and IR spectroscopy. The spectral data are in good agreement with the data published for related compounds [3]. The purity of compounds obtained was 95 ± 1% according to ^{1}H NMR spectra.

EXPERIMENTAL

IR spectra were recorded on a Fourier spectrophotometer Protege-460 (Nicolet) from thin films. UV spectra were measured on a spectrophotometer Specord UV Vis from solutions of compounds in methanol of concentration 1×10^{-4} M. ^{1}H NMR spectra were registered on a spectrometer Tesla BS-587A (100 MHz) from 5% solutions in $CDCl_3$, chemical shifts were measured from internal reference TMS. Molecular weights were measured by cryoscopy in benzene. Column chromatography was carried out on neutral aluminum oxide L 40/250 μm of II grade Brockmann activity (eluent hexane–ethyl ether mixture).

1-Acetylpyrene (**I**) used was of 97% purity, mp 86–89°C [3]. Initial peroxyalkynes and butyllithium were prepared by procedures [4] and [5] respectively.

Tertiary alcohols based on 1-acetylpyrene II–VIII. To a solution of 5.5 mmol of butyllithium (or lithium alkylacetylenide or lithium peroxyacetylenides obtained by reacting butyllithium with the corresponding monosubstituted alkynes and peroxyalkynes) in 50 ml of benzene mixture with anhydrous ethyl ether cooled to –20°C was added under argon atmosphere in one portion at vigorous stirring 4 mmol of 1-acetylpyrene (**I**). The reaction temperature was slowly raised to 20–23°C, and

the stirring was continued for 2–3 h till complete dissolution of the crystals of compound **I**. The reaction mixture was left standing for 15–20 h at 20–23°C, then it was diluted with 100 ml of hexane and washed with water 3–4 times. The organic layer was separated and dried over $CaCl_2$. The solvent was removed, and the residue was kept under a vacuum. Tertiary alcohols **II–VIII** were purified by column chromatography on aluminum oxide.

2-(1-Pyrenyl-2-hexanol) (II). Yield 80%. IR spectrum, ν, cm^{-1}: 3440 (OH), 3115, 3090, 3040 (CH_{Ar}), 2955, 2929, 2869 (CH_{Alk}), 1625, 1595, 1584, 1540, 1507, 1383, 1253, 1231 (Ar), 1131 (C–O), 848, 820, 758, 721, 684, 670, 635 (CH_{Ar}). UV spectrum , λ_{max}, nm (ε): 204 (26000), 209 (18000), 233 (42000), 243 (70000), 255 (14000), 265 (28000), 277 (49000), 313 (13000), 328 (30000), 343 (47000). ^{1}H NMR spectrum, δ, ppm: 0.73 t (3H, Me), 1.00–1.35 m [4H, $(CH_2)_2$], 1.86 s (3H, Me), 2.15 q (2H, CH_2), 2.90 s (1H, OH), 7.60–9.05 m ($9H_{arom}$). Found, %: C 87.64; H 7.45. *M* 290.7. $C_{22}H_{22}O$. Calculated, %: C 87.28; H 7.33. *M* 302.4.

2-(1-Pyrenyl)-3-nonyn-2-ol (III). Yield 84%. IR spectrum, ν, cm^{-1}: 3420 (OH), 3115, 3092, 3040 (CH_{Ar}), 2955, 2930, 2870, 2860 (CH_{Alk}), 2240 (C≡C), 1625, 1595, 1580, 1510, 1380, 1255, 1231 (Ar), 1460 (CH_2), 1083 (C–O), 844, 820, 760, 720, 684 (CH_{Ar}). UV spectrum , λ_{max}, nm (ε): 204 (25000), 209 (18000), 233 (43000), 243 (70000), 255 (14000), 265 (28000), 277 (50000), 300 (6000), 313 (13000), 328 (30000), 343 (47000). ^{1}H NMR spectrum, δ, ppm: 0.74 t (3H, Me), 1.00–1.65 m [6H, $(CH_2)_3$], 2.04 s (3H, Me), 2.15 q (2H, CH_2), 2.95 s (1H, OH), 7.45–9.05 m ($9H_{arom}$). Found, %: C 88.67; H 7.35. *M* 324.4. $C_{25}H_{24}O$. Calculated, %: C 88.20; H 7.10. *M* 340.5.

2-(1-Pyrenyl)-3-eicosyn-2-ol (IV). Yield 85%. IR spectrum, ν, cm^{-1}: 3420 (OH), 3114, 3087, 3041 (CH_{Ar}), 2924, 2852 (CH_{Alk}), 2240 (C≡C), 1620, 1594, 1580, 1510, 1383, 1253, 1231 (Ar), 1465 (CH_2), 1085 (C–O), 846, 830, 820, 760, 721, 682 (CH_{Ar}). UV spectrum , λ_{max}, nm (ε): 205 (24000), 209 (18000), 233 (42000), 243 (70000), 255 (13000), 265 (27000), 277 (50000), 300 (6000), 313 (12000), 328 (30000), 343 (46000). ^{1}H NMR spectrum, δ, ppm: 0.86 t (3H, Me), 1.05–2.65 m [28H, $(CH_2)_{14}$], 2.13 s (3H, Me), 2.18 q (2H, CH_2), 2.75 s (1H, OH), 7.75–9.20 m ($9H_{arom}$). Found, %: C 87.85; H 9.42. *M* 481.9. $C_{36}H_{46}O$. Calculated, %: C 87.40; H 9.37. *M* 494.8.

5-*tert*-Butylperoxy-5-methyl-2-(1-pyrenyl)-3-hexyn-2-ol (V). Yield 82%. IR spectrum, ν, cm^{-1}: 3422 (OH), 3115, 3090, 3040 (CH_{Ar}), 2979, 2931, 2865 (CH_{Alk}), 1630, 1600, 1580, 1510, 1375, 1362, 1247 (Ar), 1154, 1082 (C–O), 867 (O–O), 847, 827, 819, 760, 723, 683 (CH_{Ar}). UV spectrum , λ_{max}, nm (ε): 204 (25000), 209 (18000), 233 (45000), 243 (70000), 255 (15000), 265 (28000), 277 (50000), 300 (6000), 313 (13000), 328 (30000), 345 (48000). ^{1}H NMR spectrum, δ, ppm: 1.23 s (9H, Me_3COO), 1.49 s (6H, Me_2C), 2.13 s (3H, Me), 2.74 s (1H, OH), 7.85–9.15 m ($9H_{arom}$). Found, %: C 81.16; H 7.19. *M* 388.2. $C_{27}H_{28}O_3$. Calculated, %: C 80.97; H 7.05. *M* 400.5.

5-Methyl-5-*tert*-pentylperoxy-2-(1-pyrenyl)-3-hexyn-2-ol (VI). Yield 84%. IR spectrum, ν, cm^{-1}: 3420 (OH), 3115, 3090, 3041 (CH_{Ar}), 2981, 2935, 2869 (CH_{Alk}), 1630, 1600, 1580, 1510, 1376, 1363, 1247 (Ar), 1461 (CH_2), 1154, 1083 (C–O), 865 (O–O), 848, 826, 820, 761, 723, 682 (CH_{Ar}). UV spectrum , λ_{max}, nm (ε): 204 (25000), 210 (18000), 233 (44000), 243 (70000), 255 (15000), 265 (28000), 277 (50000), 300 (5000), 313 (13000), 328 (30000), 345 (48000). ^{1}H NMR spectrum, δ, ppm: 0.90 t (3H, Me), 1.11 s (6H, Me_2COO), 1.42 q (2H, CH_2), 1.45 s (6H, CH_2), 2.08 s (3H, Me), 2.88 s (1H, OH), 7.65–9.07 m ($9H_{arom}$). Found, %: C 81.45; H 7.42. *M* 403.6. $C_{28}H_{30}O_3$. Calculated, %: C 81.13; H 7.29. *M* 414.5.

5-Methyl-5-(2-methyl-2-pentylperoxy)-2-(1-pyrenyl)-3-hexyn-2-ol (VII). Yield 90%. IR spectrum, ν, cm^{-1}: 3405 (OH), 3115, 3090, 3040 (CH_{Ar}), 2983, 2959, 2935, 2871 (CH_{Alk}), 1630, 1598, 1580, 1510, 1377, 1362, 1249 (Ar), 1460 (CH_2), 1153, 1083 (C–O), 865 (O–O), 849, 828, 760, 724, 684 (CH_{Ar}). UV spectrum , λ_{max}, nm (ε): 204 (24000), 210 (18000), 233 (44000), 243 (70000), 255 (15000), 265 (28000), 277 (50000), 300 (6000), 313 (13000), 328 (30000), 345 (48000). ^{1}H NMR spectrum, δ, ppm: 0.89 t (3H, Me), 1.15 s (6H, Me_2COO), 1.25–1.55 m [4H, $(CH_2)_2$], 1.45 s (6H, CH_2), 2.07 s (3H, Me), 2.92 s (1H, OH), 7.65–9.07 m ($9H_{arom}$). Found, %: C 81.70; H 7.61. *M* 410.3. $C_{29}H_{32}O_3$. Calculated, %: C 81.27; H 7.53. *M* 428.6.

5-Methyl-2-(1-pyrenyl)-5-(2-phenylprop-2-ylperoxy)-3-hexyn-2-ol (VIII). Yield 86%. IR spectrum, ν, cm^{-1}: 3420 (OH), 3112, 3090, 3065, 3040, 3030, 3012 (CH_{Ar}), 2983, 2933, 2870 (CH_{Alk}), 1630, 1605, 1590, 1447, 1515, 1377, 1360, 1253 (Ar), 1151, 1083 (C–O), 862 (O–O), 849, 820, 762, 720, 699, 680 (CH_{Ar}). UV spectrum , λ_{max}, nm (ε): 205 (31000), 210 (20000), 234 (43000), 244 (70000), 255 (14000), 265 (28000), 277 (50000), 300 (6000), 314 (13000), 328 (30000), 343

(48000). ^{1}H NMR spectrum, δ, ppm: 1.45 s (6H, Me_2COO), 1.49 s (6H, Me_2C), 2.12 s (3H, Me), 2.78 s (1H, OH), 7.00–9.12 m (14H, Ar). Found, %: C 83.38; H 6.55. *M* 449.0. $C_{32}H_{30}O_3$. Calculated, %: C 83.09; H 6.54. *M* 462.6.

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