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Alcoholysis of malonyl peroxides to give peracids

Margarita A. Lapitskaya, Vera A. Vil', Elena D. Daeva, Alexander O. Terent'ev and Kasimir K. Pivnitsky

The numbers of the compounds are the same as those used in the main text.

Experimental (synthesis of reference samples)

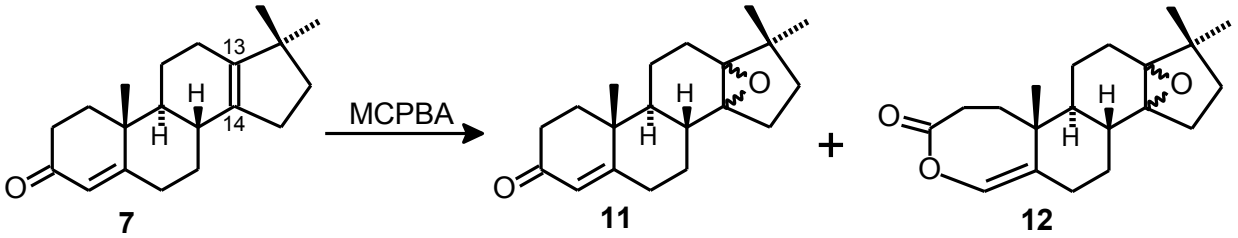
^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM instrument, 300.13 MHz. ESI mass spectra were obtained with a Bruker micrOTOF II spectrometer. Column chromatography was carried out on silica gel with 63-210 μm, while TLC was performed on Sorbfil-AF-A-UF plates (Russia).

Some compounds used in the study, namely spirocyclopropyl malonyl peroxide **1**[1], spirocyclobutyl malonyl peroxide **5a**[1], spirocyclopentyl malonyl peroxide **5b**[1], cyclopropane-1,1-dicarboxylic acid (**17**)[2] and 17,17-dimethyl-18-norandrosta-4,13-dien-3-one **7**,[3] were synthesized by the reported methods. 3β-Acetoxyandrost-5-en-17-one **8** (dehydroepiandrosterone acetate), its 5α,6α- and 5β,6β-epoxides **13**, as well as 5α,6α- and 5β,6β-epoxy-3β-acetoxy-17a-oxa-D-homoandrostan-17-ones **14** (oxidation products of epoxides **13** by Baeyer−Villiger) were used from the laboratory collection. The other reagents were obtained from Sigma-Aldrich. *m*-Chloroperoxybenzoic acid (MCPBA) of >95% purity was obtained by purification of the commercial sample.

Methyl hydrogen cyclopropane-1,1-dicarboxylate 3a. A solution of diacid **17** (130 mg, 1.00 mmol) in dry methanol (3 ml) was kept for 5 h at 50°C, then evaporated to dryness. The resulting crystalline mixture was extracted with benzene (5 ml), the extract was evaporated, and the semicrystalline residue was extracted with hexane (5 ml). The undissolved residue that remained after the extractions consisted of diacid **17** (99 mg, recovery 76%). The hexane extract was concentrated to give 34 mg (23%, ~100% with respect to non-recovered acid **17**) of monoester **3a** containing 7% of the corresponding diesters (according to NMR analysis), a colorless liquid.

Oxidation of olefin 7 by MCPBA.

Scheme 1'



7 **11** **12**

A solution of olefin **7** (60 mg, 0.21 mmol) and MCPBA (58 mg, 0.34 mmol) in CH_2Cl_2 (1 ml) was kept for 24 h at 25°C, diluted with ether and washed successively with 10% Na_2SO_3 and saturated $NaHCO_3$ aqueous solutions. Drying with $MgSO_4$ and concentration gave 64 mg of a light yellow oil. This oil was combined with 50 mg of the product from a similar experiment and chromatographed on silica gel (6 g) in benzene-ethyl acetate system (9 : 1). Elution gave successively a mixture of epoxylactones (α+β)-**12** (37 mg, 32%), R_f (CH_2Cl_2-t-BuOMe, 19:1) 0.60 and 0.67 (~1 : 1) (see Ref. 4 for an analogy) and a mixture of epoxides (α+β)-**11**[4] (50 mg, 42%), R_f 0.42 and 0.35 (37 : 63, respectively), light yellow oils.

Spectral data of compounds

All ^1H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded in $CDCl_3$ referring to added TMS (δ = 0.000 for ^1H) or $CDCl_3$ (δ = 77.10 for the central signal of $^{13}CDCl_3$). The underlined signals in the spectra descriptions indicate the reporter signals used in the analyses of the mixtures.

Compounds in Scheme 1'

7: ^1H NMR: 0.96 + 0.98 (2s, 6H, 17-Me_2), <u>1.16</u> (s, 3H, $C^{19}H_3$), <u>5.75</u> (s, 1H, 4-H) (Ref. 5).

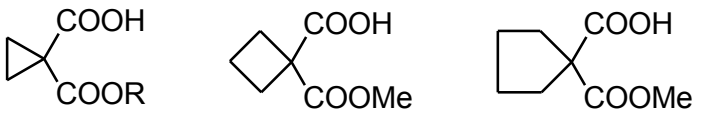
13α,14α-**11**: ^1H NMR: <u>0.89</u> + 1.03 (2s, 6H, 17-Me_2), <u>1.11</u> (s, 3H, $C^{19}H_3$), 5.74 (s, 1H, 4-H).

13β,14β-**11**: ^1H NMR: <u>0.94</u> + 1.02 (2s, 6H, 17-Me_2), 1.11 (s, 3H, $C^{19}H_3$), <u>5.75</u> (s, 1H, 4-H).

(α+β)-**12**: ^1H NMR: 0.90 + 0.92 + 1.01 + 1.02 (4s, 12H, 17-Me_2), 1.03 (s, 6H, $C^{19}H_3$), <u>6.05</u> (s, 2H, 4-H).

Alkyl hydrogen cycloalkane-1,1-dicarboxylates

Scheme 2'



3a,b,c **6a** **6b**

R = Me (**a**), Et (**b**), i-Pr (**c**)

3a: NMR ^{1}H: 1.75-1.86 [m AA'BB', 4H, $(CH_2)_2$], 3.80 (s, 3H, OMe), 11.5 (br.s, 1H, OH); ^{13}C: 22.01 [$(CH_2)_2$], 25.08 (C), 53.40 (OCH_3), 170.77 (*C*OOMe), 176.18 (COOH).

3b: NMR ^{1}H: 1.29 (t, 3H, CH_3, J = 7.2 Hz), 1.78-1.90 [m AA'BB', 4H, $(CH_2)_2$], 4.27 (q, 2H, OCH_2, J = 7.2.Hz), 10.7 (br.s, 1H, OH); ^{13}C: 13.88 (OCH_2CH_3), 22.38 [$(CH_2)_2$], 25.11 (C), 63.13 (OCH_2CH_3), 170.92 (*C*OOEt), 175.84 (COOH).

3c: NMR ^{1}H: 1.27 (d, 6H, $2CH_3$, J = 6.3 Hz), 1.71-1.86 [m AA'BB', 4H, $(CH_2)_2$], 5.12 (sept, 1H, OCH, J = 6.3 Hz), 7.9 (br.s, 1H, OH); ^{13}C: 22.06 [$(CH_2)_2$], 25.13 (C), 71.14 (OCH), 21.55 ($2CH_3$), 175.55 (COOH), 171.20 (*C*OOPr-i). Mass spectrum: m/z 173.0820, 195.0636, 217.0453. $C_8H_{12}O_4$. Calculated: M + H^+ 173.0808, M + Na^+ 195.0628, M – H + Na_2^+ 217.0448.

6a: NMR ^{1}H: 2.09 (quint, 2H, CH_2, J = 6.3 Hz), 2.60 [t, 4H, $C(CH_2)_2$, J = 8.1 Hz], 3.79 (s, 3H, OMe,), 10.2 (br.s, 1H, OH); ^{13}C: 16.23 [$CH_2(CH_2)_2$], 28.98 [$CH_2(CH_2)_2$], 52.45 [$C(CH_2)_2$], 52.90 (OCH_3), 172.32 (*C*OOMe), 176.74 (COOH) (Ref. 5).

6b: NMR ^{1}H: 1.69-1.75 [m, 4H, $(CH_2)_2$], 2.20-2.26 [m, 4H, $C(CH_2)_2$], 3.75 (s, 3H, OMe); ^{13}C: 25.61 [$(CH_2)_2$], 34.84 [$C(CH_2)_2$], 52.81 (OCH_3), 60.23[$C(CH_2)_2$], 173.08 (*C*OOMe), 177.67 (COOH).

Note: due to association of polar carboxyl-containing monoesters **3** and **6** and the corresponding peracids **2** and **5**, the NMR spectra of solutions of these compounds in $CDCl_3$ somewhat depend on solution concentration. This dependence is particularly pronounced for the signals of CH_2CH_2 moieties in compounds **2** and **3** with spin system AA'BB', the appearance of which strongly depends on the spectral parameters of the protons involved (see Figure S1).

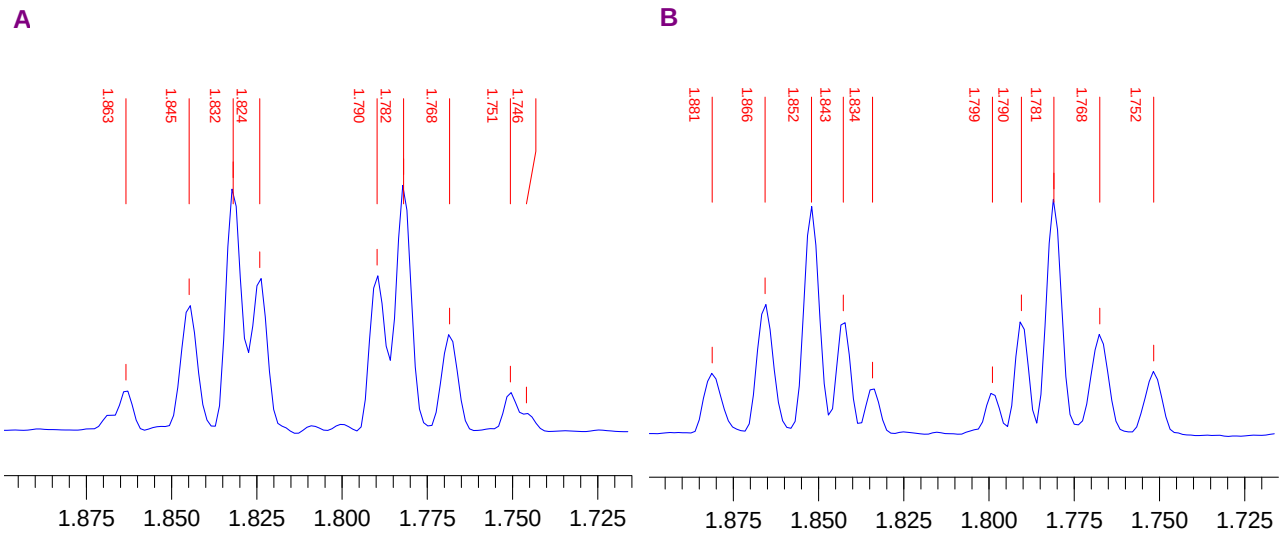
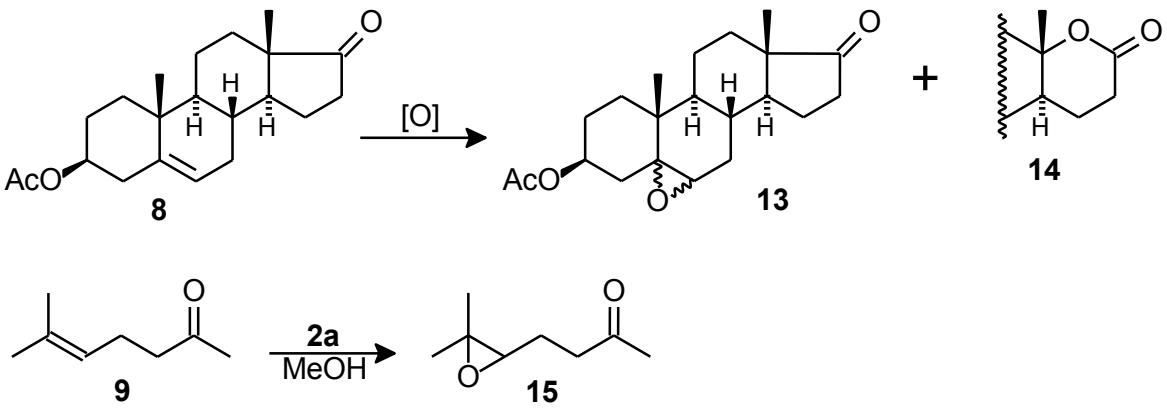


Figure S1 Multiplet signals of protons in the CH_2CH_2 moiety (spin system AA'BB') in the ^1H NMR spectra of solutions of monoester **3a** at various concentrations: **A** 0.35 mol·l^{-1}, **B** 0.07 mol·l^{-1}.

Products of epoxidation of olefins with peracids

Scheme 3'



8: ^1H NMR: 0.89 [s, 3H, Me(18)], 1.05 [s, 3H, Me(19)], 2.04 (s, 3H, OAc), 2.46 (dd, 1H, 16-H, J = 19.0, 8.8 Hz), 4.61 (tt, 1H, 3-H, J = 10.5, 5.3 Hz), 5.41 (d, 1H, 6-H, J = 4.8 Hz).

5α,6α-**13**: ^1H NMR: 0.82 [s, 3H, Me(18)], 1.10 [s, 3H, Me(19)], 2.02 (s, 3H, OAc), 2.43 (dd, 1H, 16-H, J = 19.0, 8.7 Hz), 2.94 (d, 1H, 6-H, J = 4.3 Hz), 4.95 (tt, 1H, 3-H, J = 11.0, 5.5 Hz).

5β,6β-**13**: ^1H NMR: 0.85 [s, 3H, Me(18)], 1.04 [s, 3H, Me(19)], 2.04 (s, 3H, OAc), 2.46 (dd, 1H, 16-H, J = 19.4, 8.5 Hz), 3.14 (br.d, 1H, 6-H, J = 2.0 Hz), 4.78 (tt, 1H, 3-H, J = 11.0, 5.5 Hz).

5α,6α-**14**: ^{1}H NMR: 1.00 [s, 3H, Me(19)], 1.26 [s, 3H, Me(18)], 2.02 (s, 3H, OAc), 2.56 (dd, 1H, J = 19.2, 3.3 Hz) + 2.65 (ddt, 1H, J = 19.2, 9.0, 3.3, C(16)H_2), 2.94 (d, 1H, 6-H, J = 4.2 Hz), 4.95 (tt, 1H, 3-H, J = 11.4, 5.1 Hz).

5β,6β-**14**: ^{1}H NMR: 1.05 [s, 3H, Me(19)], 1.28 [s, 3H, Me(18)], 2.04 (s, 3H, OAc), 2.56 (dd, 1H, J = 19.2, 3.3 Hz) + 2.65 [ddt, 1H, J = 19.2, 9.0, 3.3, C(16)H_2], 3.15 (d, 1H, 6-H, J = 2.7 Hz), 4.77 (tt, 1H, 3-H, J = 11.1, 4.8 Hz).

15: ^{1}H NMR: 1.28 + 1.30 [2s, 2 x 3H, Me(7) + Me(8)], 1.61-1.71 (m, 2H, C(4)H_2], 2.18 [s, 3H, Me(1)], 2.62 [m, 2H, C(3)H_2], 2.74 (dd, 1H, 5-H, J = 7.8, 4.5 Hz) (Ref. 7).

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