COMMUNICATION

Alkylation of peroxyacids as a new method of peroxyester synthesis

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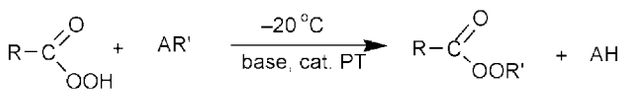
A new method for synthesis of short alkyl chain peroxyesters has been developed, which involves reaction of organic peroxyacids with alkyl trifluoromethanesulfonates, methyl chlorosulfonate, ethyl toluene-*p*-sulfonate, dimethyl sulfate and trialkyloxonium tetrafluoroborate performed under phase-transfer conditions.

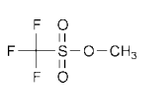
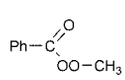
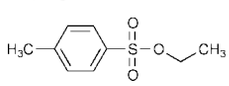
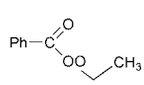
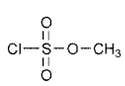
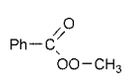
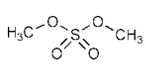
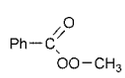
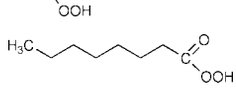
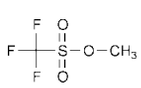
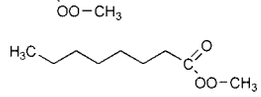
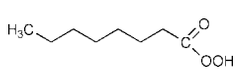
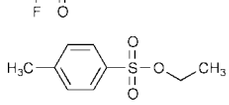
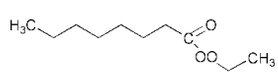
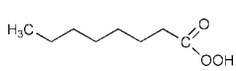
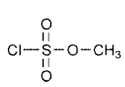
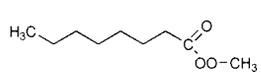
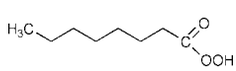
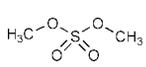
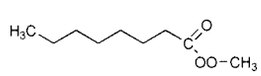
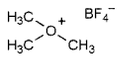
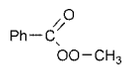
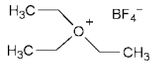
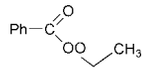
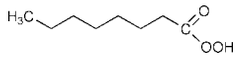
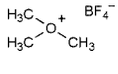
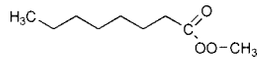
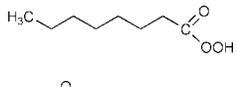
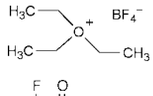
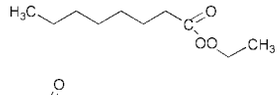
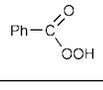
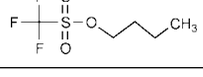
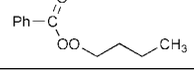
Peroxyesters easily decompose to give free radicals and therefore they find wide application as initiators of free-radical reactions, cross-linking agents, bleaching or oxidising agents and pharmaceutical additives.[1]

Alkyl peroxyesters have been synthesised until now by acylation of alkyl hydroperoxides only (Schotten–Baumann pro-

Table 1 Reactions of peroxyacid (**1**) with alkylating agent AR′ (**2**) in the presence of phase-transfer catalyst leading to formation of alkyl peroxyester (**3**)



1 **2** **3**

Peroxyacid **1**	Alkylating agent, AR′ **2**	Product **3**	Yield (%)
			98
			60
			58
			49
			73
			55
			49
			37
			98
			94
			90
			76
			38

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cedure[2]). The acylation takes place either in a homogeneous system in the presence of *e.g.* pyridine or triethylamine, or in a heterogeneous system in the presence of alkaline aqueous solutions. The acylation of primary alkyl hydroperoxides suffers from the problem of base-catalysed decomposition of the hydroperoxides. Moreover, few primary hydroperoxides are available; their preparation is difficult and unsafe. Instead of the hydroperoxides, under neutral conditions their barium salts can be employed.[3] Also these salts are of low stability, which limits their wider application. Only primary hydroperoxides with longer alkyl chains (C_4 and higher) react with ketenes[4] to yield peroxyesters.

We present a new approach to primary alkyl peroxyester synthesis involving alkylation of easily available organic peroxyacids by strong alkylating agents. It is worth mentioning that there are literature reports that claim alkylation of peroxyacids is not a possible process.[5,6]

The peroxyacid and alkylating agent dissolved in solvent provided the organic phase, while solid base formed the other phase. The syntheses were carried out at −20 °C in the presence of a phase-transfer catalyst (solid–liquid PTC). The results of the alkylation are shown in Table 1 and clearly indicate that the use of strong alkylating agents such as alkyl trifluoromethanesulfonates, methyl chlorosulfonate, ethyl toluene-*p*-sulfonate, dimethyl sulfate and trialkyloxonium tetrafluoroborate permits preparation of methyl peroxyesters in good yields. Methyl and ethyl peroxyesters are novel compounds, so far not described in the literature.

In summary, we have elaborated a new, efficient preparative method for the synthesis of short alkyl chain peroxyesters that has not been available before. In addition, we have shown that peroxyacids, in contrast to some earlier reports, can react with alkylating agents under mild conditions to give peroxyesters.

Experimental

Into a thermostated three-necked 100 cm^3 flask, equipped with a mechanical stirrer, a solution of peroxyacid (10 mmol) dissolved in toluene (30 cm^3), tetra-*n*-butylammonium hydrogen sulfate (0.2 mmol) and solid NaOH (15 mmol) were introduced at −20 °C. After stirring for 10 min at this temperature, a solution of alkylating agent (15 mmol) in toluene (20 cm^3) was added dropwise under nitrogen. Reactions with trialkyloxonium salts as alkylating agents (15 mmol) were carried out in methylene chloride (50 cm^3) and in the presence of solid K_2CO_3 (30 mmol). After stirring for up to 5 h (in the case of the butyl peroxybenzoate synthesis the reaction time was 40 h) at −20 °C the reaction mixture was washed with a solution of H_2O and saturated Na_2CO_3. The reaction progress was followed by HPLC.[7,8] The organic phase was dried over magnesium sulfate and evaporated to dryness; the residue was chromatographed (benzene–acetone, 7:1) to afford the alkyl peroxyesters.

The peroxyesters were characterised[9] by elemental analysis, mass spectrometry and ^1H and ^{13}C NMR spectroscopic analysis;[8] the active oxygen was determined according to the known procedure[10] by iodometric titration.

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Notes and references

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8 ^1H NMR and ^{13}C NMR spectra were recorded at 300 MHz in $CDCl_3$ (Varian Unity Inova plus, internal TMS). Mass spectra (ESI MS and EI MS) were recorded on a Mariner mass spectrometer (PerSeptive Biosystems). Elemental analyses were obtained on Perkin-Elmer analyser. HPLC was performed on a liquid chromatograph (Alliance, Waters 2690 system) with a Waters photodiode array detector and cartridge column (Nova-Pak C_{18} 4 μm); solvent system included methanol–water (70:30, 1 cm^3 min^{-1}).
9 Methyl peroxybenzoate: bp 40 °C/0.2 mmHg; ^1H NMR δ 4.14 (s, 1H), 7.41–7.95 (m, 5H); ^{13}C NMR: δ 64.7, 126.3, 127.7, 128.2, 133.3, 163.9; EI MS: 152 (M, 6%), 136 (2), 122 (4), 105 (99), 77 (100), 51 (64). Anal. calc. for $C_8H_8O_3$: C 63.16, H 5.26; found: C 63.11, H 5.20%. Active (O) calc.: 21.8; found: 20.8%.
Methyl peroxyoctanoate: bp 48 °C/0.5 mmHg; ^1H NMR : δ 0.88 (t, J = 7.6 Hz, 3H), 1.30 (m, 8H), 1.66 (q, J = 7.3 Hz, 2H), 2.29 (t, J = 7.8 Hz, 2H), 4.13 (s, 3H); ^{13}C NMR: δ 13.9, 22.5, 24.6, 28.7, 28.9, 30.4, 31.5, 64.0, 170.1; ESI MS: 175 (MH^+), 197 (MNa^+). Anal. calc. for $C_9H_{18}O_3$: C 62.07, H 10.34; found: C 62.00, H 10.20%. Active (O) calc.: 18.4; found: 18.2%.
Ethyl peroxybenzoate: ^1H NMR: δ 1.39 (t, J = 7.8 Hz, 3H), 4.41 (q, J = 7.4 Hz, 2H), 7.42–7.96 (m, 5H); ^{13}C NMR: δ 12.9, 72.5, 127.2, 128.5, 129.3, 133.4, 164.2. Anal. calc. for $C_9H_{10}O_3$: C 65.06, H 6.02; found: C 64.88, H 5.89%. Active (O) calc.: 19.2; found: 18.6%.
Ethyl peroxycaprylate: ^1H NMR: δ 0.88 (t, J = 7.6 Hz, 3H), 1.29 (m, 11H), 1.67 (quintet, J = 7.3 Hz, 2H), 1.29 (t, J = 7.8 Hz, 2H), 4.27 (quintet, J = 7.4 Hz, 2H); ^{13}C NMR: δ 12.8, 13.7, 22.3, 24.6, 28.6, 28.7, 30.8, 31.3, 72.0, 170.7. Anal. calc. for $C_{10}H_{20}O_3$: C 63.83, H 10.64%; found: C 63.77, H 10.55%. Active (O) calc.: 17.0; found: 16.0%.
Butyl peroxybenzoate: ^1H NMR: δ 0.98 (t, J = 7.6 Hz, 2H), 1.46 (s, J = 7.2 Hz, 2H), 1.72 (quintet, J = 7.3 Hz, 2H), 4.53 (t, J= 7.6, 2H), 7.39–8.06 (m, 5H); ^{13}C NMR: δ 13.6, 19.2, 31.0, 70.28, 128.2, 128.3, 129.4, 132.7, 166.4. Anal. calc. for $C_{11}H_{14}O_3$: C 68.04, H 7.22%; found: C 67.79, H 7.10%. Active (O) calc.: 16.5; found: 15.6%.
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