A New, Promising Route to Functionalized 1,2-Dioxetanes

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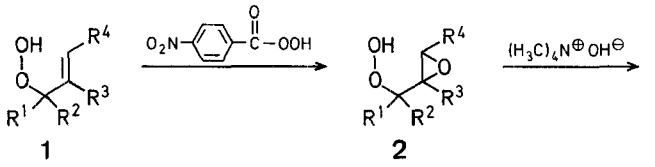
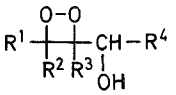
While it is known that five- and six-membered cyclic peroxides may result from intramolecular cyclisation of hydroperoxyoxiranes[1], the scope of this reaction has not been fully explored. We have found that the hydroperoxyoxiranes **2** are converted to the 3-α-hydroxyalkyl-1,2-dioxetanes **3** by treatment with a tetraalkylammonium hydroxide in a two-phase water/diethyl ether medium.



1 **2**



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The compounds **3** are isolated as light-yellow, crystalline solids and exhibit the special features of 1,2-dioxetanes[2]. First, they cleave thermally to give the two expected carbonyl-containing fragments. Secondly, they emit a visible bluish light when heated suddenly to 180 °C (chemiluminescence is also observed in solution at 60 °C). Further evidence of structure is provided by ^{1}H- and ^{13}C-N.M.R. data and mass spectra. It is worth note that none of the possible five-membered ring isomer **4** has been detected.

Table. 3-(1-Hydroxyalkyl)-1,2-dioxetanes **3a–k**

Product No.	R^1	R^2	R^3	R^4	Yield[a] [%]	m.p. [°C]	Molecular formula[b]	^{1}H-N.M.R. (CCl_4/TMS)[c] δ [ppm]
3a	CH_3	CH_3	CH_3	H	62	35°	$C_6H_{12}O_3$ (132.2)	3.83 (s, 2H); 2.89 (s, OH); 1.58 (s, 3H); 1.40 (s, 3H); 1.35 (s, 3H)
3b	—$(CH_2)_5$—		—$(CH_2)_4$—		79	119°	$C_{12}H_{20}O_3$ (212.3)	4.55 (s, 1H); 4.40 (s, OH); 2.4–1.0 (m, 18H)
3c	—$(CH_2)_5$—		H	H	64	70°	$C_8H_{14}O_3$ (158.2)	4.67 (t, 1H); 3.83 (d, 2H); 2.90 (s, OH); 2.4–0.9 (m, 10H)
3d	—$(CH_2)_5$—		CH_3	H	74	75°	$C_9H_{16}O_3$ (172.2)	4.40 (s, OH); 3.78 (s, 2H); 2.2–0.95 (m, 10H); 1.30 (s, 3H)
3e	—$(CH_2)_5$—		H	CH_3	70	82°	$C_9H_{16}O_3$ (172.2)	4.39 (s, 1H); 4.38 (q, 1H); 2.6–1.0 (m, 11H); 1.11 (d, 3H)
3f	CH_3	CH_3	—$(CH_2)_4$—		77	90°	$C_9H_{16}O_3$ (172.2)	4.3 (m, 1H); 2.00 (s, OH); 2.0–1.2 (m, 14H)
3g[e]	C_6H_5—CH_2	CH_3	CH_3	H	78	70°	$C_{12}H_{16}O_3$ (208.3)	7.25 (m, 5H); 4.12 (s, 2H); 3.61, 2.87 (ν_A, ν_B, J_{AB} = 14 Hz, C_6H_5—CH_2); 2.58 (s, OH); 1.47 (s, 3H); 1.41 (s, 3H)
3h[e]	C_6H_5—CH_2	CH_3	CH_3	H	80	68°	$C_{12}H_{16}O_3$ (208.3)	7.0 (m, 5H); 3.87, 3.49 (ν_A, ν_B, J_{AB} = 11.25 Hz, CH_2OH); 3.33, 2.90 (ν_A, ν_B, J_{AB} = 13.75 Hz, C_6H_5—CH_2); 2.41 (s, OH); 1.68 (s, 3H); 1.42 (s, 3H)
3i	CH_3	CH_3	C_6H_5—CH_2	H	77	68°	$C_{12}H_{16}O_3$ (208.3)	7.0 (m, 5H); 3.89, 3.50 (ν_A, ν_B, J_{AB} = 11.00 Hz, CH_2OH); 3.36, 2.93 (ν_A, ν_B, J_{AB} = 13.75 Hz, C_6H_5—CH_2); 2.16 (s, OH); 1.69 (s, 3H); 1.43 (s, 3H)
3j[e]	C_6H_5—CH_2	H	CH_3	H	75[d]	—	—	7.0 (m, 5H); 5.40 (ABX); 3.62–2.62 (ABX and AB); 1.40 (s, 3H)
3k[e]	C_6H_5—CH_2	H	CH_3	H	80[d]	—	—	7.09 (m, 5H); 5.53 (ABX); 3.93–2.73 (ABX and AB); 1.39 (s, 3H)

[a] Yield of isolated and crystallised product.
[b] Satisfactory microanalyses obtained (C ±0.33, H ±0.11).
[c] ^{1}H-N.M.R. spectra were taken on a Varian A 60 A spectrometer.
[d] Not isolated in pure form owing to low stability.
[e] *cis*- or *trans*-stereoisomer.

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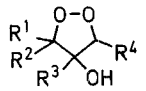

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In comparison with the classical Kopecky[2] route to 1,2-dioxetanes from β-bromohydroperoxides, this new approach leads to various functionalized 1,2-dioxetanes[3,4]. So, we have been able to transform the alcoholic moiety of compounds **3** with preservation of the cyclic peroxide framework[5]. Further major advantages of this method are the good yields under safe conditions and the ease of isolation of the products. At the present time the main limitation is the availability of the allylic hydroperoxides **1**, the epoxidation of which affords the hydroperoxyoxiranes **2**.

2-(1-Hydroperoxyalkyl)-oxiranes 2; General Procedure:
To a magnetically stirred solution of allylic hydroperoxide **1**[7] (20 mmol) in chloroform (75 ml) is added *p*-nitroperbenzoic acid (20 mmol), temperature being kept below 20 °C. Completion of the reaction is checked by ^{1}H-N.M.R. (disappearance of the signal due to the olefinic protons). The *p*-nitrobenzoic acid is then filtered on a sintered glass and the chloroform solution stirred with anhydrous potassium carbonate (20 g). After 2 h, the suspension is filtered and the solvent removed under vacuum at room temperature. The crude hydroperoxyalkyloxirane **2** is used without further purification.

3-(1-Hydroxyalkyl)-1,2-dioxetanes 3; General Procedure:
To an efficient mechanically stirred solution of the hydroperoxyalkyloxirane **2** (10 mmol) in ether (50 ml) cooled at 10 °C is added a 25% aqueous solution of tetramethylammonium hydroxide[6] (25 mmol). A yellow colour goes from aqueous phase into organic phase as the cyclisation proceeds. After completion (2–4 h, ^{1}H-N.M.R. monitoring) the ether layer is decanted and the aqueous phase extracted with ether (2 × 30 ml). The combined ether portions are washed with brine (30 ml), dried with sodium sulfate, and evaporated to dryness under reduced pressure at 0 °C. The yellow residual product is taken in anhydrous pentane (70 ml) and the product **3** is allowed to crystallise at −20 °C.

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