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A new oxidation process. Transformation of *gem*-bishydroperoxides into esters

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Abstract: A new oxidation process has been found where α,ω-dicarboxylic acid esters and ω-hydroxycarboxylic acid esters are formed on heating *gem*-bishydroperoxides in alcohol in the presence of $BF_3 \cdot Et_2O$. By addition of H_2O_2 to this reaction α,ω-dicarboxylic acid esters are formed almost selectively.

Keywords: Oxidation, gem-*bishydroperoxides,* α,ω*-dicarboxylic acid esters,* ω*-hydroxycarboxylic acid esters, hydrogen peroxide, boron trifluoride*

1 Introduction

In recent years, interest in organic *gem*-bishydroperoxides has increased sharply with respect to the cyclic peroxides possessing high antimalarial activity [1–9]. Previously we reported a new effective method for the synthesis of *gem*-bishydroperoxides based on a reaction of ketals with hydrogen peroxide catalyzed by boron trifluoride complexes [10]. This methodology has readily made these compounds accessible and has opened an opportunity for their wider use in organic synthesis. Presently, the chemistry for the use's of *gem*-bishydroperoxides has been insufficiently studied. Furthermore these substances possess a high content of active oxygen not being used in oxidation processes.

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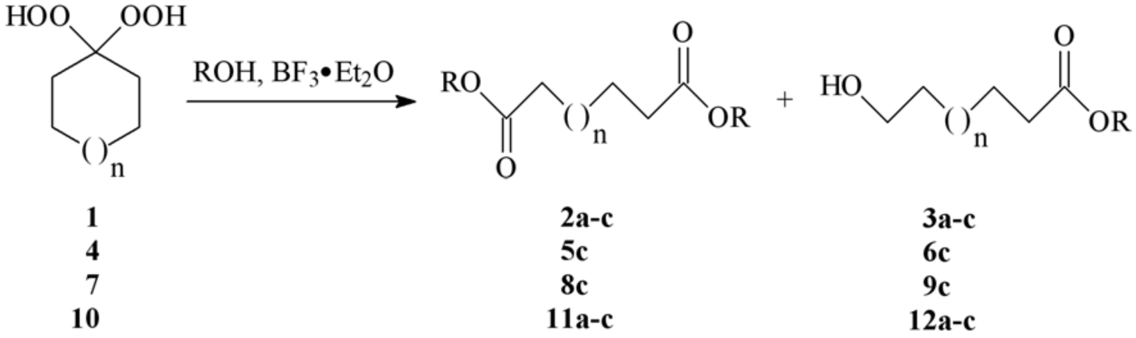
2 Results and discussion

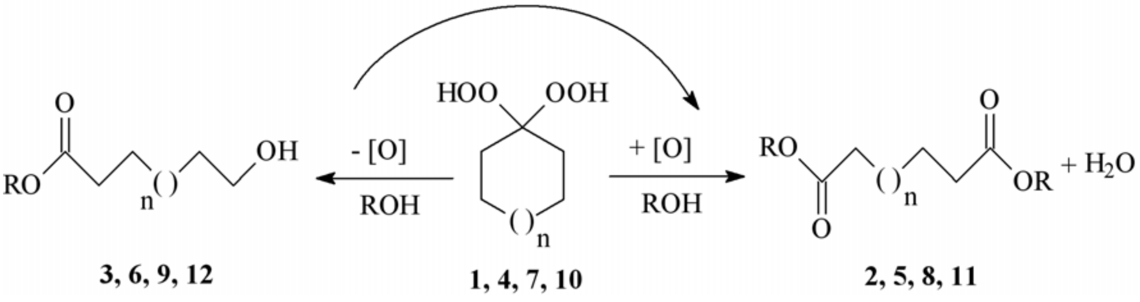
In this paper we report a new oxidation process where *gem*-bishydroperoxides **1**, **4**, **7**, **10** are transformed into α,ω-dicarboxylic acid esters **2**, **5**, **8**, **11** and ω-hydroxycarboxylic acid esters **3**, **6**, **9**, **12**. This transformation proceeds by refluxing the *gem*-bishydroperoxide in alcohol with $BF_3{\cdot}Et_2O$ (Scheme 1). The reaction is of further interest since the $BF_3{\cdot}Et_2O$ complex has also been used for the synthesis of *gem*-bishydroperoxides in Et_2O as solvent.



n = 1 (**1**, **2**, **3**), 2 (**4**, **5**, **6**), 3 (**7**, **8**, **9**), 7 (**10**, **11**, **12**)
R = Et (**a**), Pr (**b**), Bu (**c**)

Scheme 1 Boron trifluoride catalyzed transformation of gem-bishydroperoxides into esters.

An important feature of the transformation of *gem*-bishydroperoxides into α,ω-dicarboxylic acid esters and ω-hydroxycarboxylic acid esters is that in accordance with the reaction stoichiometry the preparation of α,ω-dicarboxylic acid esters **2**, **5**, **8**, **11** cannot simply be a monomolecular reaction. The synthesis of these esters from bishydroperoxides **1**, **4**, **7**, **10** demands an additional atom of oxygen plausibly donated by a second molecule of bishydroperoxide via intermolecular transfer (Scheme 2).



Scheme 2 α,ω-Dicarboxylic acid esters synthesis via transfer of active oxygen.

A number of the experiments have shown, that the yields of α,ω-dicarboxylic acid esters **2**, **5**, **8**, **11** and ω-hydroxycarboxylic acid esters **3**, **6**, **9**, **12** are comparable with each other (Table 1). In the reaction mechanism, one molecule of bishydroperoxide is a donor of active oxygen, and the other molecule is an acceptor. The ω-hydroxycarboxylic acid esters **3**, **6**, **9**, **12** are probably formed as the result of a Baeyer-Villiger rearrangement. The requirement for this rearrangement is that the molecule contains only one O-O fragment.

Consequently, the bishydroperoxide must undergo transformation into the monoperoxide with a loss of oxygen before a Baeyer-Villiger rearrangement is possible in this reaction.

The mechanism for the synthesis of α,ω-dicarboxylic acid esters **2**, **5**, **8**, **11** is probably similar to the mechanism suggested earlier [11] and differs mainly in that the obtained acids are esterified during the reaction.

Table 1 The synthesis of α,ω-dicarboxylic acid esters **2**, **5**, **8**, **11** α,ω-hydroxycarboxylic acid esters **3**, **6**, **9**, **12** from *gem*-bishydroperoxides **1**, **4**, **7**, **10**[a].

Run	Bishydro-peroxide	Solvent	$BF_3 \cdot Et_2O$, eqv	Yields of α,ω-dicarboxylic acid esters, %[b]	Yields of ω-hydroxycarboxylic acid esters, %[b]
1	**1**	EtOH	1	**2a**, 26	**3a**, 32
2	**1**	EtOH	5	**2a**, 35	**3a**, 32
3	**1**	PrOH	1	**2b**, 21	**3b**, 37
4	**1**	PrOH	2	**2b**, 23	**3b**, 31
5	**1**	PrOH	5	**2b**, 36	**3b**, 35
6	**1**	BuOH	1	**2c**, 29	**3c**, 35
7	**1**	BuOH	5	**2c**, 36	**3c**, 45
8	**1**	BuOH	- [c]	**2c**, 17	**3c**, 21
9	**4**	BuOH	5	**5c**, 35	**6c**, 41
10	**7**	BuOH	5	**8c**, 32	**9c**, 37
11	**10**	EtOH	5	**11a**, 34	**12a**, 31
12	**10**	PrOH	5	**11b**, 42	**12b**, 40
13	**10**	BuOH	5	**11c**, 41	**12c**, 37

[a] Reaction conditions: reaction temperature for; EtOH - 76-78 °C, PrOH - 92-94 °C, BuOH - 106-108 °C; overall reaction time was 20 minutes.

Eqv=mol($BF_3 \cdot Et_2O$) / mol(bishydroperoxide)

[b] The yields were calculated from the isolated products.

[c] $BF_3 \cdot Et_2O$ was not used.

The results from Table 1 show that the major factors influencing the yields of esters are $BF_3 \cdot Et_2O$ concentration and the ring size of gem-bishydroperoxide. The ester yields increased slightly with increasing $BF_3 \cdot Et_2O$ concentration and ring size. In reaction run 8, which was carried out in the absence of $BF_3 \cdot Et_2O$, esters **2c** and **3c** yields were approximately halved in comparison with other experiments with bishydroperoxide **1** (run 7). The maximum total yield of esters **11b**+**12b** (82 %) for run 12 was observed in the transformation of 1,1-bishydroperoxicyclododecane (**10**) in propanol.

A number of experiments were carried out with the addition of 5 eqv H_2O_2 with the purpose of studying the influence of an additional oxidizer on the ratio and yields of the esters (Table 2).

This resulted in the dibutylalkanedioats being the main products, where yields were 72-84 % and the formation of butyl ω-hydroxyalkanoats was almost completely suppressed; yields were less than 7 %.

Thus, in this study a new transformation of *gem*-bishydroperoxides is reported. The

Table 2 The synthesis of dibutylalkanedioats and butyl ω-hydroxyalkanoats from bishydroperoxides **1**, **4**, **7**, **10** with use of $H_2O_2^a$.

Run	Bishydroperoxide	Yields of dibutylalkanedioats, %[b]	Yields of butyl ω-hydroxyalkanoats, %[b]
1	1	**2c**, 72	**3c**, 6
2	4	**5c**, 81	**6c**, 7
3	7	**8c**, 84	**9c**, 6
4	10	**11c**, 80	**12c**, traces

[a] Reaction conditions: solvent - BuOH, temperature 106-108 °C, total reaction time 20 minutes, H_2O_2 - 5 eqv, $BF_3{\cdot}Et_2O$ - 1 eqv. Eqv=mol($BF_3{\cdot}Et_2O$ or H_2O_2) / mol(bishydroperoxide)

[b] The yields were calculated from the isolated products.

gem-bishydroperoxides on heating in alcohols in the presence of $BF_3{\cdot}Et_2O$ gave α,ω-dicarboxylic acid esters and ω-hydroxycarboxylic acid esters with approximately equal yields. Addition of H_2O_2 to the reaction results in suppression of ω-hydroxycarboxylic acid esters formation. The reaction conditions are mild and do not demand the use of proton acids.

This transformation opens an opportunity for the application of *gem*-bishydroperoxides as oxidizers. From a practical point of view this reaction can find applications in the synthesis of complicated α,ω-dicarboxylics acid esters and ω-hydroxycarboxylics acid esters and for the preparation of anticorrosion compositions.

3 Experimental part

^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AC-200, Bruker WM-250, Bruker AM-300. Analytical TLC: Silufol UV-254, Silpearl as the sorbent, starch as the binder. Column chromatography was performed on silica gel (63-200 mesh, Merk).

Melting points were determined on a Kofler hot stage.

Cycloalkanones and $BF_3{\cdot}Et_2O$ (all of reagent grade) were used without additional purification. Solutions of H_2O_2 in Et_2O are prepared according to [12]. Solvents: petroleum ether, diethyl ether, ethanol, propanol and butanol were distilled before use.

Acetals for synthesis of bishydroperoxides were prepared in accordance with [11].

Bishydroperoxides **1, 4, 7, 10** were prepared in accordance with [10].

CAUTION. Bishydroperoxides **1**, **4** are shock and friction sensitive and consequently should be handled with care. These compounds are decomposed explosively on heating to 100 °C and above.

General procedure for α,ω-dicarboxylic acid esters 2, 5, 8, 11 and ω-hydroxycarboxylic acid esters 3, 6, 9, 12 synthesis from bishydroperoxides 1, 4, 7, 10

Gem-bishydroperoxide 0.5 g **1** (3.38 mmol), **4** (3.09 mmol), **7** (2.84 mmol), **10** (2.16 mmol) was dissolved in 5 ml of alcohol (EtOH, PrOH, BuOH). $BF_3{\cdot}Et_2O$ (1, 2 or 5 eqv) was added (in run 8, Table 1, $BF_3 \cdot Et_2O$ was not used) and the mixture was heated to reflux (temperature EtOH - 76-78 °C, PrOH - 92-94 °C, BuOH - 106-108 °C) for 20 minutes. Dry potassium carbonate (fivefold molar excess as compared with $BF_3 \cdot Et_2O$) was added and the mixture was stirred for 20 minutes. The inorganic salts were filtered. The liquid was thoroughly evaporated for removal of alcohols traces. The esters were isolated by column chromatography using petroleum ether/diethyl ether (with an increasing diethyl ether gradient from 2 to 25 %).

Procedure for dibutylalkanedioats and butyl ω-hydroxyalkanoats synthesis from bishydroperoxides 1, 4, 7, 10

Gem-bishydroperoxide 0.5g **1** (3.38 mmol), **4** (3.09 mmol), **7** (2.84 mmol), **10** (2.16 mmol) was dissolved in BuOH (5ml). A 6 % ether solution of H_2O_2 (5 eqv) was added. The ether was evaporated at 10-15 Torr. $BF_3 \cdot Et_2O$ (1 eqv) was added and the mixture was refluxed (106-108 °C) for 20 minutes. The esters were isolated as described above.

Diethylhexanedioate (2a) [13]

NMR ^1H, 250 MHz (δ, $CDCl_3$): 1.18 (t, 6H, CH_3, J=7.2 Hz), 1.53-1.65 (m, 4H, $\underline{CH_2}CH_2COOEt$), 2.18-2.32 (m, 4H, CH_2COOEt), 4.05 (q, 4H, OCH_2, J=7.2 Hz).

Ethyl 6-hydroxyhexanoate (3a) [14]

NMR ^1H, 500 MHz (δ, $CDCl_3$): 1.14 (t, 3H, CH_3, J=7.0 Hz), 1.24-1.32 (m, 2H, CH_2), 1.40-1.48 (m, 2H, CH_2), 1.49-1.57 (m, 2H, CH_2), 2.19 (t, 2H, CH_2COOEt, J = 7.3 Hz), 3.04-3.16 (br. s., 1H, OH), 3.49 (t, 2H, CH_2OH, J = 6.7 Hz), 4.01 (q, 2H, $COOCH_2$, J=7.0 Hz).

NMR ^{13}C, 125 MHz (δ, $CDCl_3$): 13.9 (CH_3), 24.4, 25.1, 32.0, 34.0 (CH_2), 60.0, 61.9 ($O\underline{CH_2}CH_3$, CH_2OH), 173,8 (C=O).

Dipropylhexanedioate (2b) [15]

NMR ^1H, 300 MHz (δ, $CDCl_3$): 0.93 (t, 6H, CH_3, J=7.3 Hz), 1.53-1.71 (m, 8H, CH_2), 2.24-2.38 (m, 4H, CH_2COOPr), 4.02 (t, 4H, $COOCH_2$, J=6.6 Hz).

NMR ^{13}C, 75.47 MHz (δ, $CDCl_3$): 10.4 (CH_3), 22.0, 24.5, 33.9 (CH_2), 66.0 (OCH_2Et), 173.5 (C=O).

Propyl 6-hydroxyhexanoate (3b) [16]

NMR ^1H, 300 MHz (δ, $CDCl_3$): 0.92 (t, 3H, CH_3, J=7.3 Hz), 1.28-1.71 (m, 8H, CH_2), 2.31 (t, 2H, CH_2COOPr, J = 7.0 Hz), 3.10-3.40 (br. s., 1H, OH), 3.72 (t, 2H, CH_2OH, J = 6.5 Hz), 4.03 (t, 2H, $COOCH_2$, J=6.6 Hz).

NMR ^{13}C, 62.9 MHz (δ, $CDCl_3$): 10.0 (CH_3), 21.6, 24.4, 25.2, 31.9, 33.8 (CH_2), 61.8 (CH_2OH), 65.5 (OCH_2Et), 173.6 (C=O).

Dibutylhexanedioate (2c) [17]

NMR ^1H, 250 MHz (δ, $CDCl_3$): 0.90 (t, 6H, CH_3, J=7.1 Hz), 1.21-1.72 (m, 12H, CH_2), 2.25-2.35 (m, 4H, CH_2COOBu), 4.04 (t, 4H, $COOCH_2$, J=6.8 Hz).

Butyl 6-hydroxyhexanoate (3c) [18]

NMR ^1H, 200 MHz (δ, $CDCl_3$): 0.90 (t, 3H, CH_3, J=7.1 Hz), 1.22-1.67 (m, 10H, CH_2), 2.29 (t, 2H, CH_2COOBu, J=7.4 Hz), 3.2-3.4 (br.s, 1H, OH), 3.64 (t, 2H, CH_2OH, J=6.6 Hz), 4.02 (t, 2H, $COOCH_2$, J=6.6 Hz).

NMR ^{13}C, 62.9 MHz (δ, $CDCl_3$): 13.2 (CH_3), 18.7, 24.3, 25.0, 30.2, 31.8, 33.8 (CH_2), 61.6, 63.7 (OCH_2Pr, CH_2OH), 173,5 (C=O).

Dibutylheptanedioate (5c) [19]

NMR ^1H, 200 MHz (δ, $CDCl_3$): 0.89 (t, 6H, CH_3, J=7.1 Hz), 1.20-1.66 (m, 14H, CH_2), 2.26 (t, 4H, CH_2COOBu, J=7.4 Hz), 4.02 (t, 4H, $COOCH_2$, J=6.6 Hz).

NMR ^{13}C, 62.9 MHz (δ, $CDCl_3$): 13.5 (CH_3), 19.0, 24.5, 28.4, 30.5, 33.9, (CH_2), 63.9 (OCH_2Pr), 173.3 (C=O).

Butyl 7-hydroxyheptanoate (6c)

NMR ^1H, 250 MHz (δ, $CDCl_3$): 0.89 (t, 3H, CH_3, J=7.2 Hz), 1.26-1.70 (m, 12H, CH_2), 2.26 (t, 2H, CH_2COOBu, J = 7.2 Hz), 2.65-2.75 (br. s, 1H, OH), 3.57 (t, 2H, CH_2OH, J = 7.1 Hz), 4.03 (t, 2H, $COOCH_2$, J=6.7 Hz).

NMR ^{13}C, 62.9 MHz (δ, $CDCl_3$): 13.6 (CH_3), 19.0, 24.8, 25.3, 28.8, 30.5, 32.4, 33.9 (CH_2), 62.5, 64.0 (OCH_2Pr, CH_2OH), 173,8 (C=O).

Found (%): C, 65.61; H, 11.15. $C_{11}H_{22}0_3$. Calculated (%): C, 65.31; H, 10.96.

Dibutyloctanedioate (8c) [17]

NMR ^1H, 250 MHz (δ, $CDCl_3$): 0.90 (t, 6H, CH_3, J=7.2 Hz), 1.24-1.69 (m, 16H, CH_2), 2.26 (t, 4H, CH_2COOBu, J=7.4 Hz), 4.03 (t, 4H, $COOCH_2$, J=6.6 Hz).

NMR ^{13}C, 62.9 MHz (δ, $CDCl_3$): 13.4 (CH_3), 19.0, 24.6, 28.6, 30.6, 34.0, (CH_2), 63.9 (OCH_2Pr), 173.4 (C=O).

Butyl 8-hydroxyoctanoate (9c)

NMR ^1H, 250 MHz (δ, $CDCl_3$): 0.89 (t, 3H, CH_3, J=7.2 Hz), 1.21-1.68 (m, 14H, CH_2), 2.25 (t, 2H, CH_2COOBu, J = 7.2 Hz), 3.25-3.37 (br. s, 1H, OH), 3.54 (t, 2H, CH_2OH, J = 7.1 Hz), 4.02 (t, 2H, $COOCH_2$, J=6.8 Hz).

NMR ^{13}C, 62.9 MHz (δ, $CDCl_3$): 13.5 (CH_3), 18.9, 24.7, 25.4, 28.6, 28.9, 30.5, 32.5, 34.1 (CH_2), 62.4, 63.9 (OCH_2Pr, CH_2OH), 173.8 (C=O).

Found (%): C, 66.90; H, 11.39. $C_{12}H_{24}0_3$. Calculated (%): C, 66.63; H, 11.18.

Diethyldodecanedioate (11a) [20]

M.p. = 15.5-16.5 °C. (m.p. = 16.7-17.2 °C [20])

NMR ^1H, 250 MHz (δ, $CDCl_3$): 1.17-1.65 (m, 22H, CH_2, CH_3), 2.25 (t, 4H, CH_2COOEt, J=7.3 Hz), 4.09 (q, 4H, $COOCH_2$, J=7.2 Hz).

Ethyl 12-hydroxydodecanoate (12a) [21]

M.p. = 23-24.5 °C. (m.p. = 24-25 °C [21])

NMR ^1H, 200 MHz (δ, $CDCl_3$): 1.16-1.70 (m, 21H, $CH_{2,}CH_3$), 2.28 (t, 2H, CH_2COOEt, J=7.3 Hz), 2.36-2.56 (br. s., 1H, OH), 3.63 (t, 2H, CH_2OH, J=6.7 Hz), 4.12 (q, 2H, $COO\underline{CH_2}CH_3$, J=6.7 Hz).

Dipropyldodecanedioate (11b) [20]
M.p. = 11.5-12.5 °C. (m.p. = 12.7 - 13.4 °C [20]).

NMR ^{1}H, 300 MHz (δ, $CDCl_3$): 0.92 (t, 6H, CH_3, J=7.3 Hz), 1.20-1.69 (m, 20H, CH_2), 2.30(t, 4H, CH_2COOPr, J=7.3 Hz), 4.03 (t, 4H, OCH_2, J=6.7 Hz).

NMR ^{13}C, 75.47 MHz (δ, $CDCl_3$): 10.4 (CH_3), 22.0, 25.0, 29.1, 29.2, 29.3, 34.3 (CH_2), 65.7 (OCH_2Et), 173.8 (C=O).

Propyl 12-hydroxydodecanoate (12b)
NMR ^{1}H, 300 MHz (δ, $CDCl_3$): 0.92 (t, 3H, CH_3, J=7.3 Hz), 1.10-1.75 (m, 20H, CH_2), 2.30 (t, 2H, CH_2COOPr, J = 7.0 Hz), 2.30-2.50 (br. s., 1H, OH), 3.53 (t, 2H, CH_2OH, J = 6.6 Hz), 4.03 (t, 2H, $COOCH_2$, J=6.7 Hz).

NMR ^{13}C, 75.47 MHz (δ, $CDCl_3$): 10.4 (CH_3), 22.1, 25.1, 29.2-29.8 (7C), 30.9, 34.5 (CH_2), 64.1 (CH_2OH), 65.8 (OCH_2Et), 174.0 (C=O).

Found (%): C, 69.95; H, 11.49. $C_{15}H_{30}0_3$. Calculated (%): C, 69.72; H, 11.70.

Dibutyldodecanedioate (11c) [20]
NMR ^{1}H, 200 MHz (δ, $CDCl_3$): 0.92 (t, 6H, CH_3, J=7.1 Hz), 1.21-1.68 (m, 24H, CH_2), 2.27 (t, 4H, CH_2COOBu, J=7.5 Hz), 4.06 (t, 4H, $COOCH_2$, J=6.5 Hz).

Butyl 12-hydroxydodecanoate (12c)
NMR ^{1}H, 200 MHz (δ, $CDCl_3$): 0.93 (t, 3H, CH_3, J=7.2 Hz), 1.18-1.70 (m, 22H, CH_2), 2.29 (t, 2H, CH_2COOBu, J=7.4 Hz), 2.59-2.81 (br. s., 1H, OH), 3.65 (t, 2H, CH_2OH, J=6.8 Hz), 4.06 (t, 2H, $COOCH_2$, J=6.6 Hz).

NMR ^{13}C, 50.32 MHz (δ, $CDCl_3$): 13.7 (CH_3), 19.1, 24.9, 29.1-29.8 (8C), 30.6, 34.3 (CH_2), 62.9, 64.1 (OCH_2Pr, CH_2OH), 174.0 (C=O).

Found (%): C, 70.63; H, 11.51. $C_{16}H_{32}0_3$. Calculated (%): C, 70.54; H, 11.84.

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