ESTERS AND URETHANES WITH TRIOXOIMIDAZOLIDINE RING

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Abstract:
Hydroxyalkyl derivatives of parabanic acid obtained from the acid and oxiranes, react with carboxylic acid or isocyanates to give esters and urethanes with trioxoimidazolidine ring. The optimized conditions for their synthesis avoiding the linear products formed due to ring-opening reactions were established. The esters and urethanes were isolated at high yield and identified on the basis of elemental analysis, IR and ^{1}H NMR spectroscopy, acidic number and saponification number as well.

Introduction:

Here we report that esters **(7, 8)** and urethanes **(9, 10)** containing trioxoimidazolidine ring can be obtained in reaction between bis(N-hydroxyalkyl) derivatives **(6)** of parabanic acid (PA) with carboxylic acids or isocyanates, respectively (scheme **I**). However, the starting hydroxyalkyl derivatives of parabanic acid are obtainable from oxiranes **(4)** in demanding procedure [2] due to accompanying side-reaction of ring-opening of parabanic acid resulting in formation of linear polymers with ester and amide groups. High yield for hydroxyalkyl derivatives of parabanic acid (HAPA) was achieved when 1:1 (or 1:2) molar ratio of PA and oxirane, 0.03 mol catalytic Et_3N per mole of PA, at 30-40°C temperature were used [2, 3].

Here we have found that ring-opening related side-reactions can be avoided by azeotropic removal of water during not more than 4 hour esterification under reflux. Synthetic routes to HAPA and its precursor PA were described previously [1,4].

Results and Discussion:

Our preliminary attempts to synthesize ester from N,N'-bis(2-hydroxyethyl) parabanate **6 (R= H, HEPA)** and acetic acid in presence of formic acid as catalyst at 90°C in heptane resulted in formation of 2,2'-(1,3-trioxoimidazolidine)diethyl diacetate **8 (R = H-, R_1 = -CH_3, DEDA)** with low yield, long time of reaction (16 hours) and polymeric products containing hydroxyl and amide groups demonstrated by their characteristic resonances at 4.8 ppm (OH) and 8.4 -9.2 ppm (NH_2) in the ^{1}H NMR spectrum and amide IR bands at 1667 cm^{-1} and

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Scheme I

where:

$R = R' = H$-, CH_3-, CH_2Cl-,

$R_1 = CH_3$-, $CH_2=CH$-, $CH_3=C(CH_3)$-, $C_{17}H_{35}$-

1514 cm ^{1}and ν(OH and NH) vibrations at 3200 - 3500 cm^{-1} [2]. Here we have modified the procedure leading to **DEDA** by the use of concentrated sulfuric acid as catalyst and toluene as azeotropic agent for water removal. Due to high boiling point of this reaction mixture (115°C) the reaction proceed faster (4 hours). Analytical procedure at alkaline conditions led to ring opening and in that way we were able to determine the acidic number [2] and saponification number of the product. The results of this simple determination allowed us to identify fast the esters formed from acetic, stearic, methacrylic, and acrylic acids.

In the series of experiments we have found that HEPA reacted within 4-5 hours with two equivalents of acrylic or methacrylic acids to give diesters **8** (**R= H-, R_1= CH_2=CH-** and **R_1 = CH_2=C(CH_3)-**, respectively), whereas N,N'-bis(2-hydroxypropyl) parabanate **6** (**R= CH_3, HPPA**) in the same procedure resulted in mono-esters with mentioned acids. Monoesters were identified by their N-CH_2-CH_2-OH (3.5 ppm) and N-CH_2-CH_2-O-C(O)-R (3.8 ppm) resonances at ^{1}H NMR spectrum.

The diester product was formed when stoichiometric excess of methacrylic acid (4 equivalents) was applied and the diester was the only product when 6 equivalents of acid was used. The low yield of diester was caused by consumption of the acid in its polymerization despite the use of phenothiazine as inhibitor. Analogous procedure with HPPA and 4 equivalents of acrylic acid gave diester.

Reactions of HAPA with 1 or 2 equivalents of phenyl isocyanates in presence of Et_3N led to mono- and bis-N-(phenylcarbamates) **9** (**R = H**, and **CH_3-**) and **10** (**R = H**, and **CH_3-**), respectively. The products were identified by their elemental analysis, acidic numbers and characterized by ^{1}H NMR spectroscopy. In the equimolar reaction between HPPA and phenyl isocyanate the ^{1}H NMR and IR spectra suggested the formation of mono-ester, which was confirmed by GC MS experiment by molecular ion 349 m/e.

Experimental:

General procedure for the synthesis of esters

In a typical procedure the reaction mixture containing 10.5 g of HEPA (or 11.5 g HPPA 0.05 mol), 0.1-0.6 mol of acid (acetic, methacrylic, acrylic, or stearic), 150 cm^3 of toluene, and 0.25 cm^3 conc. H_2SO_4 was heated for 5-6 hours with continues removal of toluene/water. After cooling the reaction mixture was washed with 10% Na_2CO_3 (aq) until CO_2 evolution ceased, followed by washing with water. The solvents were stripped out to give oily products, which were dried under reduced pressure (t = 60°C, p = 2·10^{-3} MPa = 15 mm Hg). In case of reaction with methacrylic and acrylic acids the phenothiazine (2% w/w) inhibitor of polymerization was used.

General procedure for the synthesis of urethane

In a typical procedure the reaction mixture containing 0.02 mol of HEPA (or HPPA) dissolved in 40 cm^3 of dioxane, phenyl isocyanate (2.38 or 4.76 g; 0.02 or 0.04 mol, respectively), and 0.05 cm^3 Et_3N was heated at 60-70°C until isocyanate number was zero.

Analyses

Acidic number was monitored by alkalimetric titration with 0.1 M KOH (aq) [6], while saponification number and isocyanate groups were monitored by known methods [6,7]. ^{1}H NMR spectra were recorded with Brucker AMX300 spectrometer, IR spectra were taken with the use of Perkin Elmer (PARAGON 1000 FT) spectrophotometer.

Elemental analyses were performed with EA 1108 (Carlo-Erba) analyzer and GC-MS experiments were conducted with Hewlett Packard 6890N chromatograph equipped with 5973 Network mass detector.

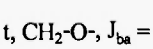
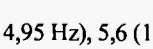
Analytical data

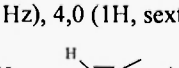
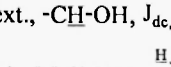
2,2'-(1,3-trioxoimidazolidine)diethyl diacetate (DEDA), (8, R = H-, R_1 = CH_3-), $C_{11}H_{14}N_2O_7$;

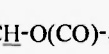
Yield - 80 %; AN [mg KOH/g], Calcd.: 196, Found: 182; SN [mg KOH/g], Calcd.: 588, Found: 593; elemental analysis - % Calcd.: C 46,15; H 4,90; N 9,79; % Found: C 45,50; H 4,83; N 9,34; IR (capillary film) [cm^{-1}], 1724 (C=O), 1440 - 1400 (CH_2), 1222, 1144 (-C-O-), ^{1}H-NMR (d_6-acetone), δ [ppm] 1,9 (3H, s, CH_3), 3,7 (2H, t, N-CH_2-, J_{ab} = 5,1 Hz), 4,1 (2H, t, -CH_2-O-, J_{ba} = 5,2 Hz).

2,2'-(1,3-trioxoimidazolidine)diethyl distearate (DEDS), (8, R = H-, R_1 = CH_3-$(CH_2)_{14}$-CH_2(d)-CH_2(c)-), $C_{43}H_{78}N_2O_7$; Yield - 75 %; m.p. = 70 - 71°C; AN [mg KOH/g] - Calcd.: 76, Found: 78; SN [mg KOH/g] - Calcd.: 228, Found: 222; elemental analysis - % Calcd.: C 69,73; H 10,54; N 3,78; % Found: C 69,36; H 10,88; N 3,48; IR (KBr) [cm^{-1}], 1745 (C=O) 1472 - 1409 (CH_2), 1262, 1173 (C-O): ^{1}H-NMR ($CDCl_3$), δ [ppm] 0,8 (3H, t, -CH_3), 1,0 - 1,7 (30 H, m, $(CH_2)_{15}$), 2,2 (2H, t, CH_2-(CO)O-, J_{cd} = 7,6 Hz), 3,85 (2H, t, N-CH_2-, J_{ab} = 5,3 Hz), 4,25 (2H, t, CH_2-O-, J_{ba} = 5,2 Hz).

2,2'-(1,3-trioxoimidazolidine))dipropyl distearate (DPDS), (8, R = CH_3(e), R_1 = CH_3-$(CH_2)_{14}$-CH_2(d)-CH_2(c)), $C_{45}H_{82}N_2O_7$; Yield - 72 %, m.p. = 47 - 48°C; AN [mg KOH/g], Calcd.: 73, Found: 77; SN [mg KOH/g], Calcd.: 222, Found: 227; elemental analysis - % Calcd.: C 70,31; H 10,68; N 3,65; % Found: C 69,72; H 11,02; N 3,85; IR (KBr), [cm^{-1}]; 1737 (C=O) 1472 - 1414 (CH_2), 1194, 1104 (C-O), ^{1}H-NMR ($CDCl_3$), δ [ppm]. = 0,8 (3H, t, CH_3-), 1,0 - 1,7 (33 H, m, $(CH_2)_{15}$, CH_3-CH-O-), 2,2 (2H, t, CH_2-(CO)O-, J_{cd} = 7,5 Hz), 3,7 (2 H, d, -N-CH_2-, J_{ab} = 5,2 Hz), 5,1 (2H, sext., CH-O-, $J_{ba, be}$ = 6,3 Hz).

2,2'-(1,3-trioxoimidazolidine)diethyl dimethacrylate (DEDM) (8, R= H-, R_1 = -$C(CH_3)$=CH_2), $C_{15}H_{18}N_2O_7$; Yield - 72%; AN [mg KOH/g], Calcd.: 160, Found: 166; SN [mg KOH/g], Calcd.: 498, Found: 492; elemental analysis - % Calcd.: C 53,25; H 5,33; N 8,28; % Found: C 53,63; H 5,26; N 8,36; IR (capillary film), [cm^{-1}]: 1727 (C=O), 1636 (C=C) 1437-1400 (CH_2), 1294, 1153 (C-O-(CO): ^{1}H-NMR (d_6-acetone), δ [ppm]: 1,8 (3H, s, =C-CH_3), 3,75 (2H, t, N-CH_2-, J_{ab} = 4,95 Hz), 4,2 (2H, t, CH_2-O-, J_{ba} = 4,95 Hz), 5,6 (1H, m, ), 6,0 (1 H, s, ).

2-[3-(2-hydroxypropyl)-1,3-trioxoimidazolidine]propyl methacrylate (PM), (7, R' = CH_3(e), R= CH_3(f), R_1 = -$C(CH_3)$=CH_2) $C_{13}H_{18}N_2O_6$;, Yield - 70 %; AN [mg KOH/g], Calcd.: 188, Found: 180; SN [mg KOH/g], Calcd.: 377, Found: 351; elemental analysis - % Calcd.: C 52,35; H 6,04; N 9,40; % Found: C 52,5; H 5,98; N 9,32; IR (capillary film), [cm^{-1}]: 3536 (OH), 1727 (C=O), 1636 (C=C), 1437-1400 (CH_2), 1294 (C-O-(CO)), 1153 (C-O-(CO)-, -OH); ^{1}H-NMR (d_6-acetone), δ [ppm]; 1,05 (3H, d, CH_3-CH-OH, J_{ed} = 6,4 Hz), 1,15 (3H, d, CH_3-CH-O(CO)-, J_{fb} = 6,4 Hz), 1,8 (3H, s, =C-CH_3), 3,5 (2H, d, -N-CH_2-CH-OH, J_{cd} = 6,6 Hz), 3,8 (2H, d, -N-CH_2-CH-O(CO)-, J_{ab} = 5,6 Hz), 4,0 (1H, sext., -CH-OH, $J_{dc, de}$ = 5,3 Hz), 4,15 (1H, s, OH), 5,1 (1H, sext., -CH-O(CO)-, $J_{ba, bf}$ = 5,0 Hz), 5,6 (1H, m, ), 6,0 (1 H, s. ).

2,2'-(1,3-trioxoimidazolidine)dipropyl dimethacrylate (DPDM), (8, R= CH_3(c), R_1 = -$C(CH_3)=CH_2$), $C_{17}H_{22}N_2O_7$; Yield - 78%; AN [mg KOH/g], Calcd.: 153, Found: 157; SN [mg KOH/g], Calcd.: 471, Found: 458; elemental analysis - % Calcd.: C 55,74; H 6,01; N 7,65; % Found: C 55,80; H 5,99; N 7,15; IR (capillary film) [cm^{-1}]; 1733 (s, C=O), 1635 (C=C), 1438-1404 (CH_2), 1294, 1161 (C-O-(CO)): ^{1}H-NMR (d_6-acetone), δ [ppm] 1,25 (3H, d, CH_3-CH-O(CO)-, J_{cb} = 6,6 Hz), 1,85 (3H, s, =C-CH_3), 3,85 (2H, d, -N-CH_2-CH-O(CO)-, J_{ab} = 6,4 Hz), 5,2 (1H, sext., -CH-O(CO)-, $J_{ba,\ bc}$ = 6,3 Hz), 5,7 (1 H, m, ), 6,0 (1H, s.,).

2,2'-(1,3-trioxoimidazolidine)diethyl diacrylate (DEDA), (8, R= H-, R_1 = -CH=CH_2), $C_{13}H_{14}N_2O_7$; Yield -72 %; AN [mg KOH/g], Calcd.: 181, Found: 189; SN [mg KOH/g], Calcd.: 543, Found: 573; elemental analysis - % Calcd.: C 50,32; H 4,52; N 9,03; % Found: C 50,47; H 4,18; N 8,66; IR (capillary film) [cm^{-1}]; 1718 (C=O), 1635 (C=C), 1439-1404 (CH_2), 1260, 1174 (C-O-(CO)); ^{1}H-NMR (d_6-acetone), δ [ppm]; 3,85 (2H, t, -N-CH_2-, J_{ab} = 5,2 Hz), 4,25 (2H, t, -CH_2-O-, J_{ba} = 5,2 Hz), 5,8 - 6,6 (3H, m, CH_2=CH-).

2,2'-(1,3-trioxoimidazolidine)dipropyl diacrylate (DPDA), (8, R= CH_3(c), R_1 = -CH=CH_2), $C_{15}H_{18}N_2O_7$; Yield - 70 %; AN [mg KOH/g], Calcd.: 168, Found: 168; SN [mg KOH/g], Calcd.: 498, Found: 494; elemental analysis - % Calcd.: C 53,25; H 5,33; N 8,28; % Found: C 53,15; H 5,27; N 8,07; IR capillary film) [cm^{-1}]; 1732 (C=O), 1636 (C=C),1439-1402 (CH_2), 1263, 1187 (C-O-(CO)-) [cm^{-1}];^{1}H-NMR (d_6-acetone), δ [ppm] = 1,25 (3H, d, CH_3-, J_{cb} = 6,6 Hz), 3,85 (2H, d, -N-CH_2-, J_{ab} = 5,5 Hz), 5,15 (1H, sext., -CH-, $J_{ba,\ bc}$ = 5,5 Hz), 5,8 - 6,5 (3H, m, CH_2=CH-).

2-[3-(2-hydroxyethyl)-1,3-trioxoimidazolidine]ethyl N-phenylcarbamate (EPC), (9, R' = R = H), $C_{14}H_{15}N_3O_6$; Yield - 85 %; AN [mg KOH/g], Calcd.: 175, Found: 167; elemental analysis - % Calcd.: C 52,34; H 4,67; N 13,08; % Found: C 52,07; H 4,91; N 12,54; IR (KBr), [cm^{-1}]; 3550-3300 (OH), 3300-3150 (NH), 1740 (C=O), 1596 (N-H and C-N),1536, 1499 (CH in phenyl ring), 1444-1405 (CH_2), 1215 (C-O-(CO)NH-), 1050 (O-H); ^{1}H-NMR (d_6-DMSO), δ [ppm]; 3,5 (4H, s, -N-CH_2-CH_2-OH), 3,8 (2H, t, -N-CH_2-, J_{ab} = 5,3 Hz), 4,2 (2H, t, -CH_2-O-(CO), J_{ba} = 5,3 Hz), 4,8 (1H, s, OH), 6,8 - 7,6 (5H, in phenyl ring), 9,6 (1H, s, -NH).

2-[3-(2-hydroxypropyl)-1,3-trioxoimidazolidine]propyl N-phenylcarbamate (PPC), (9, R = CH_3(e) R' = CH_3,), $C_{16}H_{19}N_3O_6$; Yield - 84 %; AN [mg KOH/g], Calcd.: 161, Found: 161; elemental analysis % Calcd.: C 57,27; H 4,77; N 12,73; % Found: C 57,79; H 4,62; N 12,22; IR (KBr), [cm^{-1}]; 3550-3300 (O-H), 3300-3150 (N-H), 1735 (C=O), 1599 (N-H and C-N), 1542, 1502 (phenyl ring), 1448-1414 (CH_2), 1227 (-C-O-(CO)NH-), 1086 (OH); ^{1}H-NMR (d_6-DMSO), δ [ppm]; 0,9 (3H, d, CH_3-CH-OH), 1,2 (3H, d, CH_3-CH-O(CO)), 3,35 (2H, d, -N-CH_2-CH-O-H, J_{cd} = 6,3 Hz), 3,7 (2H, d, N-CH_2-CH-O-(CO), J_{ab} = 5,7 Hz), 3,8 (1H, m, -CH-OH), 5,0 (H, sext., -CH-O- (CO), $J_{ba,\ be}$ = 6,3 Hz), 5,1 (1H, s, -OH), 6,8 - 7,6 (5H, m, in phenyl ring), 9,65 (1H, s, -NH).

2,2'-(1,3-trioxoimidazolidine)diethyl bis(N-phenylcarbamate) (DEPC) (10, R = H-), $C_{21}H_{20}N_4O_7$; Yield - 86 %; m.p.= 145 - 146°C; AN [mg KOH/g], Calcd.: 127, Found: 128; elemental analysis - % Calcd.: C 55,01; H 5,44; N 12,03; % Found: C 55,55; H 5,88; N 12,04; IR (KBr), [cm^{-1}]; 3374-3307 (N-H), 1735, 1703 (C=O), 1598 (N-H and C-N), 1541, 1515 (phenyl ring), 1443-1404 (CH_2), 1238, 1116 (C-O-(CO)NH-),^{1}H-NMR (d_6-DMSO), δ [ppm]: 3,8 (2H,t, -N-CH_2-,J_{ab}=5,4 Hz), 4,2 (2H, t, -CH_2-O-, J_{ba} = 5,4 Hz), 6,8 -7,6(5H,m,in phenyl ring), 9,6 (1H, s, NH).

2,2'-(1,3-trioxoimidazolidine)dipropyl bis(N-phenylcarbamate) (DPPC) (10, R = CH_3(c)), $C_{23}H_{24}N_4O_7$; Yield - 82 %; AN [mg KOH/g], Calcd.: 120, Found: 124; elemental analysis - % Calcd.: C 58,97; H 5,13; N 11,97; % Found: C 58,80; H 5,13; N 11,76; IR (KBr), [cm^{-1}]; 3400-3200 (NH), 1714, 1743 (C=O), 1596 (N-H and C-N),

1542, 1501 (phenyl ring)), 1443-1409 (CH_2), 1227, 1126 (C-O-(CO)NH); ^{1}H-NMR (d_6-DMSO), δ [ppm] 1,2 (3H, d,CH_3,, J_{cb} = 6,1 Hz), 3,7 (2H, d, -N-CH_2-, J_{ab} = 5,6 Hz), 5,0 (1H, sext., CH-O, $J_{ba,\ bc}$ = 6,3 Hz), 6,8 - 7,6 (5H, in phenyl ring), 9,65 (1H, s, -NH).

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