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DERIVATIVES OF UNDECAN-X-ONES (X = 2 – 6) SYNTHESIS AND SPECTRAL DATA

Review: **dr hab. Krzysztof Śmigielski**

Undecan-x-ones (x = 2 – 6) have been used as starting materials in the synthesis of ethylene and propylene acetals, undecan-x-ols and their acetates. Acetals were prepared in the reaction between ketones and ethane-1,2-diol or propane-1,2-diol in toluene in the presence of sulfosalicylic acid as a catalyst. Alcohols were synthesised in the reduction of ketones with sodium borohydride in water/propan-2-ol. Acetates were prepared by esterification of alcohols with acetic anhydride in the presence of sodium acetate. All derivatives were prepared in a 2 – 5 g scale. Ethylene acetal of undecan-3-one and all propylene acetals are newly prepared compounds. Physical properties (boiling point, refractive index) and spectral data (IR, ^1H NMR) for all the synthesized derivatives of undecan-x-ones have been determined.

1. Introduction

The direct transformation of carboxylic acids into ketones in the presence of metal oxide catalysts (catalytic ketonization) has been known since 1895 [1]:

$$2\ RCOOH \rightarrow RCOR + CO_2 + H_2O$$

The ketonization of two different acids (cross-ketonization) leads to the formation of three ketones or if formic acid is used to aldehyde and ketone.

Recently, we studied the ketonization reaction in a continuous mode under flow conditions in the presence of many metal oxides as catalysts [2-4]. Esters were employed as precursors of acids, when the use of acid was inconvenient or not feasible. Various aliphatic [5, 6] and aralkyl [7, 8] ketones can be obtained in the cross-ketonization of the appropriate esters. The ketonization of esters of dicarboxylic acids (cyclo-ketonization) leads to the formation of cyclic ketones [9-11].

Ketones are raw materials for the preparation of many valuable derivatives. The relation between the structure of organic compounds and their odor properties has been studied for many years. In our two former works, we have demonstrated the dependence of the structure of straight-chain symmetric aliphatic C_7-C_{15} ketones and also straight-chain metameric C_{13} aliphatic ketones and the derivatives of both groups of ketones on their odor [12, 13]. In this work, we report the details of the synthesis of a group of undecan-x-one (x=2-6) derivatives, such as ethylene and propylene acetals, undecan-x-ols and their acetates. Their odor characteristics and odor threshold concentrations have been determined very recently and will soon be reported by us [14].

2. Exsperimental

Ketones: A series of undecan-x-ones, where x = 2 – 6, was prepared directly from carboxylic acids in a single step synthesis, according to the method described elsewhere [15]. All ketones were purified by distillation under reduced pressure prior to use. The purity of the synthesised ketones, their physical properties and spectral data were also determined by us [15].

Diols: Ethane-1,2-diol (p.a. POCH Gliwice, Poland) and propane-1,2-diol (p. a.. VEB Laborchemie APOLDA) were used as received.

Other reagents: Sulfosalicylic acid (purum p.a., Fluka), toluene (p.a. POCH Gliwice, Poland), $NaBH_4$ (98%, Aldrich), acetic anhydride (p.a. International Enzymes Ltd), sodium acetate (anhydrous, p.a., POCH Gliwice, Poland) and propan-2-ol (p.a., POCH Gliwice, Poland) were used as received.

Methods: The ^1H NMR spectra were recorded on a Bruker 250 DPX spectrometer, in $CDCl_3$ using TMS as internal standard. The IR spectra were measured using Specord M 80 spectrometer (film or KBr pellet). Microanalyses were performed on a Perkin Elmer 2400 CHN elemental analyser. Melting points (uncorrected) were determined on Boetius apparatus. The purity of compounds was confirmed by GC/MS, IR, ^1H NMR and the measurements of refractive index.

3. Results

Ethylene and propylene acetals of undecan-x-ones, undecan-x-ols and undec-x-yl acetates were prepared starting from undecan-x-ones. The details of the synthesis are summarized briefly for each group of compounds in four general procedures given below:

Synthesis of ethylene acetals of undecan-x-ones (2e–6e)[**]

A mixture of ketone (4.26 g, 0.025 mole), ethylene glycol (2.33 g, 0.0375 mole), 1 g of sulfosalicylic acid and 70 cm^3 of toluene was heated under reflux for 1.5 h. Water was separated as heteroazeotrope with toluene in a Dean-Stark trap. After cooling, water (100 cm^3) was added to the reaction mixture and the layers separated. The water layer was extracted (3 x 20 cm^3) with toluene and organic layers were collected, washed with brine and with 5% Na_2CO_3 solution and dried over $MgSO_4$. After decantation from above the drying agent the solvent was evaporated in a rotatory evaporator. The crude product was distilled under reduced pressure.

Propylene acetals of undecan-x-ones (2p –6p)

A mixture of ketone (4.26 g, 0.025 mole), propylene glycol (2.85 g, 0.0375 mole), 1 g of sulfosalicylic acid and 70 cm^3 of toluene was heated under reflux for 1.5 h. Water was separated as heteroazeotrope with toluene in a Dean-Stark trap. After cooling, water (100 cm^3) was added to the reaction mixture and the layers separated. The water layer was extracted (3 x 20 cm^3) with toluene and organic layers were collected, washed with brine and with 5% Na_2CO_3 solution and dried over $MgSO_4$. After decantation from above the drying agent the solvent was evaporated in a rotatory evaporator. The crude product was distilled under reduced pressure.

Undecan-x-ols (2u-6u)

To the stirred solution of (4.26 g, 0.025 mole) of undecan-x-one in 100 cm^3 of propan-2-ol a solution of $NaBH_4$ (1.00 g, 0.026 mole) in 30 cm^3 50/50 v/v water – propan-2-ol was slowly dropped at room temperature. The mixture was stirred for 10 h, 150 cm^3 of water added and 2-propanol was distilled off in a rotatory evaporator. The resulted mixture was separated, the water layer extracted with hexane (3 x 20 cm^3) and extracts collected. The organic layer was washed with brine, water until neutral and dried over $MgSO_4$. After decantation from above the drying agent the solvent was evaporated in a rotatory evaporator. The crude product was distilled under reduced pressure.

[**] the number refers to the position of carbonyl group in the starting ketone, the letter is assigned to the type of derivative; e – ethylene acetal, p – propylene acetal, u – undecanol, a- acetate.

Undec-x-yl acetates (2a-6a)

A mixture of undecan-x-ol (2.58 g, 0.015 mole), acetic anhydride (1.60 g, 0.016 mole) and anhydrous sodium acetate (0.50 g, 0.006 mole) was heated under reflux for 5-6 h. To the cold mixture 50 cm^3 of water was added and heated under reflux for 15 min. After cooling, the layers were separated, the water layer was extracted with toluene (3 x 30 cm^3). The organic layers were collected, washed with brine and with 5% $NaHCO_3$ solution until neutral and dried over $MgSO_4$. After decantation from above the drying agent toluene was removed in a rotatory evaporator. The crude product was distilled under reduced pressure.

Physical properties and spectral data for all synthesized compounds are collected in Tables 1-4.

Table1

Physical properties of ethylene and propylene acetals of undecan-x-ones

Code No.	Bp [°C/mm Hg]	n^{20}_D (exp)	n^{20}_D (lit)	Yield [%]
2e	80-2/0.5	1.4288	--	73
3e[x]	84-8/0.6	1.4301	--	65
4e	82-4/0.6	1.4289	--	63
5e	78-80/0.4	1.4288	--	63
6e	84-5/1.0[a]	1.4296	--	58
2p[x]	80-1/0.5	1.4374	--	70
3p[x]	81-2/0.5	1.4372	--	63
4p[x]	75-6/0.4	1.4378	--	58
5p[x]	84-6/0.7	1.4380	--	61
6p[x]	86-8/1.0	1.4351	--	58

[x] – newly prepared compound;
[a] – 131-3°C/25 mm Hg [16].

Table 2

Physical properties of undecan-x-ols and their acetates

Code No.	Bp [°C/mm Hg]	n^{20}_D (exp)	n^{20}_D (lit)	Yield [%]
2u	78-9/0.5[a]	1.4382	1.4400[a]	91
3u	82-4/0.6[b]	1.4357	1.4367[b]	84
4u	76-7/0.4[c]	1.4351	1.4345[c]	86
5u	87/0.8[d]	1.4262	1.4248[d]	86
6u	77-9/0.6[e]	1.4362	1.4355[e]	84
2a	66-7 /0.5[f]	1.4260	1.4256[b]	88
3a	63-4/0.4[g]	1.4259	1.4254[g]	81
4a[x]	70-3/0.6	1.4261	--	81
5a	60-2/0.3[h]	1.4265	--	75
6a[x]	71-4/0.8	1.4262	--	78

[x] – newly prepared compound; [a] – b.p. 79-81°C/1 mm Hg [17]; [b] – b.p. 117°C/16 mm Hg [18];
[c] – b.p. 78-80°C/1 mm Hg [19]; [d] – b.p. 139-40°C/17 mm Hg [20]; [e] – b.p. 130-2°C/28 mm Hg [21];
[f] – b.p. 109-110°C/6 mm Hg [22]; [g] – b.p. 125°C/18 mm Hg [23]; [h] – b.p. 239.3- 240.8°C [24].

Table 3

Spectral data for the obtained ethylene and propylene acetals of undecan-x-ones

Code No.	GC purity [%]	IR [cm^{-1}]	^{1}H NMR[a] [δ ppm]
2e	98.9	3000, 2850, 1480, 1380, 1110;	0.82 (3H, t, J = 6.9), 1.16 (3H, s), 1.30 (14H, m), 1.56 (2H, m), 3.89 (4H, s);
3e	99.3	3000, 2850, 1490, 1330, 1120;	0.89 (6H, m), 1.31 (12H, m), 1.62 (4H, m), 3.92 (4H, s);
4e	99.1	3000, 2850, 1480, 1360, 1100;	0.88 (6H, m), 1.33 (12H, m), 1.54 (4H, m), 3.90 (4H, s);
5e	99.2	3050, 2860, 1500, 1350, 1120;	0.89 (6H, m), 1.29 (12H, m), 1.60 (4H, m), 3.93 (4H, s);
6e	99.2	3000, 2850, 1480, 1360,1120;	0.88 (6H, m), 1.31 (12H, m), 1.59 (4H, m), 3.92 (4H, s);
2p	99.2	3000, 2850, 1480, 1370, 1110;	0.84 (3H, t, J = 7.0), 1.19 (14H, m), 1.33 (3H, m), 1.56 (2H, m), 3.36 (3H, m), 4.02 (2H, m), 4.15 (1H, m);
3p	99.3	3000, 2850, 1490, 1370, 1110;	0.83 (6H, m), 1.19 (12H, m), 1.55 (4H, m), 3.33 (3H, m), 3.99 (2H, m), 4.12 (1H, m);
4p	99.6	3000, 2850, 1480, 1370, 1100;	0.89 (6H, m), 1.24 (12H, m), 1.58 (4H, m), 3.31 (3H, m), 4.01 (2H, m), 4.11 (1H,m);
5p	99.3	3000, 2850, 1480, 1350, 1110;	0.88 (6H, m), 1.30 (12H, m), 1.59 (4H, m), 3.32 (3H, m), 4.02 (2H, m), 4.14 (1H,m);
6p	99.4	3000, 2850, 1480, 1360, 1110;	0.88 (6H, m), 1.30 (12H, m), 1.56 (4H, m), 3.33 (3H, m), 4.01 (2H, m), 4.16 (1H,m);

[a] - J in [Hz]

Table 4

Spectral data for the obtained undecan-x-ols and their acetates

Code No.	GC purity [%]	IR [cm^{-1}]	^1H NMR[a] [δ ppm]
2u	98.9	3380, 3000, 2850, 1480, 1160;	0.91 (3H, t, J = 7.5), 1.19 (3H, t, J = 7.5), 1.46 (16H, m), 1.90 (1H, s), 3.52 (1H, m);
3u	99.8	3380, 3000, 2850, 1480, 1150;	0.91 (6H, m), 1.30 (12H, m), 1.46 (5H, m), 3.52 (1H, m);
4u	98.8	3380, 3000, 2850, 1480, 1150;	0.90 (6H, m), 1.33 (12H, m), 1.46 (5H, m), 3.52 (1H, tt, $J_1 = J_2 = 7.5$);
5u	99.1	3400, 3000, 2850, 1480, 1150;	0.90 (6H, tt, $J_1 = J_2 = 7.5$), 1.48 (16H, m), 1.70 (1H, s), 3.40 (1H, tt, $J_1 = J_2 = 7.5$);
6u	99.2	3350, 3000, 2850, 1480, 1160;	0.88 (6H, tt, $J_1 = J_2 = 7.5$), 1.48 (16H, m), 1.84 (1H, s), 3.52 (1H, tt, $J_1 = J_2 = 7.5$);
2a	99.1	3000, 2850, 1740, 1480, 1245;	0.89 (3H, t, J = 7.0), 1.14 (3H, d, J = 4.3), 1.26 (16H, m); 1.94 (3H, s), 5.10 (1H, m);
3a	99.1	3000, 2850, 1740, 1480, 1270;	0.84 (6H, m), 1.22 (12H, m), 1.46 (4H, m), 1.97 (3H, s), 4.74 (1H, m);
4a	99.3	3000, 2850, 1740, 1480, 1260;	0.89 (6H, m), 1.22 (12H, m), 1.44 (4H, m), 1.99 (3H, s), 4.67 (1H, m);
5a	98.9	3000, 2800, 1735, 1480, 1280;	0.88 (6H, m), 1.26 (12H, m), 1.59 (4H, m), 2.03 (3H, s), 4.81 (1H, m);
6a	99.2	3000, 2850, 1740, 1480, 1260;	0.89 (6H, m), 1.22 (12H, m), 1.51 (4H, m), 1.99 (3H, s), 4.89 (1H, m);

[a] – J in [Hz].

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POCHODNE UNDEKAN-X-ONÓW (X = 2 – 6): SYNTEZA I CHARAKTERYSTYKA SPEKTRALNA

Streszczenie

W artykule opisano wykorzystanie undekan-x-onów (x=2-6) do syntezy pochodnych, takich jak acetale etylenowe i propylenowe, undekan-x-ole i ich octany. Syntezę acetali wykonywano poddając ketony reakcji odpowiednio z glikolem etylenowym i propylenowym w toluenie w obecności kwasu toluenosulfonowego jako katalizatora. Alkohole otrzymywano w reakcji redukcji ketonów wodorkiem borowosodowym w wodnym propan-2-olu. Octany undekanoli otrzymywano w reakcji estryfikacji alkoholi bezwodnikiem octowym wobec octanu sodowego. Wszystkie pochodne otrzymywano w skali 5g. Acetale etylenowe i propylenowe otrzymano z wydajnościami rzędu 55-73%, a undekanole i ich octany z wydajnościami 75–91%. Acetal etylenowy undekan-3-onu i wszystkie acetale propylenowe undekanonów nie są opisane w literaturze chemicznej. Określono właściwości fizyczne (temperatura wrzenia, współczynnik załamania światła) i spektralne (IR, ^{1}H NMR) otrzymanych związków.

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