A Selective Monodehydration of C_{4-14}-α,ω-Alkanediols with Stearic and/or Palmitic Acids

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Synopsis. The formation of monoesters of the C_{4-14}-α,ω-alkanediol(**1**) with stearic and/or palmitic acids and the consecutive pyrolysis of the monoesters to an ω-alken-1-ol(**2**) were effected at 320—350 °C under 260—760 mmHg** in a backmix flow reactor of a constant volume equipped with a fractionating column, through which the unchanged **1** was partially recycled. The selectivity in the preparations of **2**(C_6, C_{10}, and C_{14}) was greater than 79%.

We found a useful synthetic method to prepare a C_{4-14}-ω-alken-1-ol(**2**) from the corresponding α,ω-alkanediol(**1**). Acid catalyzed dehydrations of an

$$\underset{\mathbf{1}}{\mathrm{HOCH_2(CH_2)_\mathit{n}CH_2OH}} \longrightarrow \underset{\mathbf{2}}{\mathrm{CH_2{=}CH(CH_2)_{\mathit{n}-1}CH_2OH}} + \mathrm{H_2O} \qquad (1)$$

alkanol to form the corresponding alkene are generally accompanied by migration of the double bond and the intermolecular and/or the intramolecular ether formations.[1] These reactions can not be applied to **1** in the substantial yield, without the formations of alkadienes, the double bond-isomers of **2**, and the polyethers.

The vapor phase pyrolysis of acetates at 300—600 °C is known to be effective for the preparation of alkenes from the corresponding alkanols without migration of the double bond.[2] Preparation of any ω-alken-1-ol *via* the esters of alkanediols has not been reported. The selective preparation of the monoacetate of **1** without accompanying the formation of the diacetate will be difficult. We used high boiling saturated fatty acids **3** *i.e.*, palmitic acid, stearic acid, or the mixture of them so that the ester formation (Eq. 2) and the subsequent pyrolysis (Eq. 3) to give the ω-alken-1-ols might be induced concurrently at 320—350 °C. These steps were operated by means

$$\mathbf{1} + \underset{\mathbf{3}}{\mathrm{RCOOH}} \longrightarrow \mathrm{RCOOCH_2(CH_2)_\mathit{n}CH_2OH} + \mathrm{H_2O} \qquad (2)$$

$$\mathrm{RCOOCH_2(CH_2)_\mathit{n}CH_2OH} \longrightarrow \mathbf{3} + \mathbf{2} \qquad (3)$$

of a backmix[3] flow reactor of a constant volume of a liquid phase. While H_2O and **2** are being taken out through the rectification column, **1** is continuously supplied to the reactor. Compound **3** initially introduced into the reactor steadily functions like a catalyst throughout the operation period.

Experimental

TABLE 1. IR AND NMR DATA FOR ω-ALKEN-1-OLS(**2**)

2	IR(neat) ν_{max}/cm^{-1}	NMR(20% in CCl_4 solution) δ
$n=2$	915, 990, 1643, 3070	4.85—6.09(ABX, 3H, $\mathrm{C\underline{H}_2{=}C\underline{H}}$-), 3.56 (t, $J=6$ Hz, 2H, $\mathrm{-CH_2-C\underline{H}_2OH}$), 2.44(t, d, $J=6$ Hz, 2H, $\mathrm{{=}CH-C\underline{H}_2-CH_2OH}$), 3.29(s, 1H, $\mathrm{-CH_2O\underline{H}}$)
$n=4$	910, 995, 1643, 3070	4.75—6.07(ABX, 3H, $\mathrm{C\underline{H}_2{=}C\underline{H}}$-), 3.48 (t, $J=7$ Hz, 2H, $\mathrm{-CH_2-C\underline{H}_2OH}$), 2.05 (t, d, $J=7$ Hz, 2H, $\mathrm{{=}CH-C\underline{H}_2-CH_2-}$), 1.48(m, 4H, $\mathrm{-CH_2(C\underline{H}_2)_{\mathit{n}-2}-CH_2-}$), 3.58 (s, 1H, $\mathrm{CH_2O\underline{H}}$)
$n=8$	910, 995, 1643, 3070	4.74—6.04(ABX, 3H, $\mathrm{C\underline{H}_2{=}C\underline{H}}$-), 3.45 (t, $J=6$ Hz, 2H, $\mathrm{-CH_2-C\underline{H}_2OH}$), 2.02 (t, d, $J=6$ Hz, 2H, $\mathrm{{=}CH-C\underline{H}_2-CH_2-}$), 1.28(b, s, 12H, $\mathrm{-CH_2-(C\underline{H}_2)_{\mathit{n}-2}-CH_2-}$), 4.23(s, 1H, $\mathrm{CH_2O\underline{H}}$)
$n=12$	910, 995, 1643, 3060	4.74—6.05(ABX, 3H, $\mathrm{C\underline{H}_2{=}C\underline{H}}$-), 3.46 (t, $J=6$ Hz, 2H, $\mathrm{-CH_2-C\underline{H}_2OH}$), 2.01 (t, d, $J=6$ Hz, 2H, $\mathrm{{=}CH-C\underline{H}_2-CH_2-}$), 1.27(b, s, 20H, $\mathrm{-CH_2-(C\underline{H}_2)_{\mathit{n}-2}-CH_2-}$), 4.13(s, 1H, $\mathrm{CH_2O\underline{H}}$)

A mixture of 24.3 g of stearic acid and 30.9 g of palmitic acid, and 61.5 g of 1,10-decanediol(purity 98.2 wt%) were placed in a 200-ml flask equipped with a 20 mmϕ × 200 mm-Vigreux fractionating column of *ca.* three theoretical plates connected with a reflux condenser, and refluxed at 330—350 °C, under 700 mmHg.** The temperature at the top of the column initially indicated 295 °C and gradually lowered to 265 °C. Then the effluent vapor was started to be taken out from the column at a rate of 10 g/h. Concurrently, 1,10-decanediol was started to be fed to the flask at the same rate. The temperature of the effluent vapor was maintained by regulating the temperature in the flask between 330 and 350 °C as well as by regulating the feed rate. From 1500 g of 1,10-decanediol, 126 g of the H_2O layer and 1372 g of the oily part were obtained as the distillate.

The oily part was analyzed by gas chromatography using a Shimadzu GC 6A apparatus on a 2 mmϕ × 3 m column packed with 5 wt% of FFAP on Chromosorb W, AW-DMCS (80—100 mesh). The column temperature was elevated from 100 to 230 °C by 10 °C/min, N_2 was used as the carrier at 50 ml/min, and the injection temperature was 280 °C.

The oily part was fractionated by a further distillation. The main fraction of 869 g was identified to be 9-decen-1-ol; IR and NMR data are shown in Table 1. Each fraction was characterized by its boiling point and the main components were distinguished by their retention times in its gas chromatogram by comparison with those of the corresponding authentic samples.

In the same way as above, we prepared 3-buten-1-ol, 5-hexen-1-ol, and 13-tetradecen-1-ol from the corresponding 1,4-butanediol(purity 96.9 wt%), 1,6-hexanediol (99.0 wt%), and 1,14-tetradecanediol(81.3 wt%) in the presence of

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**1 mmHg≈133.3 Pa.

TABLE 2. RESULTS OF CONTINUOUS DEHYDRATIONS

1	$n=2$	$n=4$	$n=8$	$n=12$
(**1**/**3**)[a]	0.8	0.8	1.7	1.7
Temperature/°C				
reactor	330—345	330—350	330—350	330—340
effluent vapor	170	204—215	265	235—240
Pressure/mmHg**	760	760	700	260
Operation time/h	32	24	150	19
Distillate composition[b]				
H_2O	0.58[f]	0.85	0.81	0.64
2	0.36	0.64	0.73	0.49
tetrahydrofuran	0.06[f]	—	—	—
double bond-isomers of **2**	0.13	0.05	0.07	—
alkadienes	(0.06[g])	0.12	0.01	0.05
1(unreacted)	0.37	0.19	0.18	0.46
Bp of **2**/°C(mmHg**)[c]	102(760)	74(28)	74(1)	120—122(2.5)
Selectivity/%[d]	57	79	89	91
Yield of **2**/%[e]	50	71	80	83

a) Starting mole ratio of **1** to **3**. b) Each content shows the ratio to 1 mol of **1** continuously supplied; a corrected value for the purity of a starting material. c) All boiling points are uncorrected. d) $100\times\{(\text{content of } \mathbf{2})/(1.0-\text{content of } \mathbf{1})\}$ in the distillate. e) $100\times\{\mathbf{2}_{\text{isolated}}/(\mathbf{1}_{\text{fed}}-\mathbf{1}_{\text{recovered}})\}$ after the fractionation. f) Prior to the fractional distillation, tetrahydrofuran containing H_2O was separated from the oily part. g) No butadiene was found. This value denotes twice the amount of dimers of butadiene.

palmitic acid.

Results and Discussion

Results are shown in Tables 1 and 2. By means of increasing the mole ratio **1**/**3** in the reactions of C_6- and C_{10}-alkanediol, the formation of the by-products such as double bond isomers of ω-alken-1-ol and the alkadienes were suppressed, although the conversions of **1** were decreased. However, the ratio should be reduced to the range 0.8—1.0 in order to maintain the reaction temperature at 320—350 °C in the reactions of 1,4-butanediol and 1,6-hexanediol, because boiling points of them were 230 and 250 °C respectively at an ordinary pressure. On the whole, the decrease of the carbon number of the alkanediol increased the difficulty in the application of this reaction.

In the case of 1,4-butanediol, the selectivity was exceptionally low. There tetrahydrofuran was formed as the smaller part of the by-products. However, it should be noticed that this result stands in contrast to the fact that tetrahydrofuran was a primary product in the dehydration of 1,4-butanediol catalyzed by HCl.[4]

ω-Alken-1-ols thus produced are important in perfumery; *e.g.*, 1-decen-1-ol has been used as the component of a rosy odor and 5-hexen-1-ol has a verdurous odor.

References

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