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The reduction of carboxylic acid chlorides to aldehydes

$$RCOCl + H_2 \rightarrow RCHO + HCl \tag{1}$$

was carried out and studied by Zaitsev [1] at 220-230° in the vapor phase and by Rosenmund [2] at 100-150° in the liquid phase in the presence of Pd-black. The aldehyde formed can be partially reduced to an alcohol or saturated hydrocarbon with liberation of water. The alcohol and water react with the acid chloride to give an ester or acid, respectively. The acid chloride and hydrogen can also react in the direction of reac-tion (2) to form a saturated hydrocarbon and carbon monoxide.

$$RCOCl + H_2 \rightarrow RH + CO + HCl$$
 (2)

Minimizing all these side reactions is achieved by partial poisoning of the catalyst, for example with sulfur compounds, or by decreasing the contact time. The corresponding aldehydes were obtained in 90-95% yield [3] by vapor-phase reduction of the acid chlorides of isovaleric and benzoic acids in the presence of Pd-asbestos at $190-220^\circ$. We have synthesized neopentane and neohexane aldehydes in the same yields from the acid chlorides of C₅ and C₆ neo-acids in the presence of Pd-activated charcoal at 190° [4].

In the present work we have made an attempt to extend reaction (1) to the acid chlorides of some cyclic acids: cyclopentane-, cyclohexane-, 1-methylcyclopentane-, and 1-methylcyclohexanecarboxylic acids. Under analogous conditions, cyclopentane- and cyclohexanecarbonyl chlorides react mainly (70-85%) according to scheme (1) to form cyclopentane- and cyclohexanealdehydes, which were obtained in the form of the solid cyclic trimers, which are easily depolymerized into the monomers on heating in the presence of acidic reagents. Reaction (2) also occurs to the extent of 12-16%, with reduction of the acid chlorides to cyclopentane or cyclohexane, respectively.

1-Methylcyclopentanealdehyde and 1-methylcyclohexanealdehyde were obtained, respectively, in 80-85% yield on reduction of 1-methylcyclopentanecarbonyl chloride or 1-methylcyclohexanecarbonyl chloride, according to reaction (1). These aldehydes were formed in the monomeric form. Polymerization to the trimer does not take place, in spite of the presence of HCl in the reaction zone, presumably because of steric hindrance created by the CH₃ group in the geminal position to the CHO group. Apparently for the same reason, a considerable decrease in extent of reaction (2) also occurs.

All of the aldehydes prepared were converted by the Kizhner reaction to the corresponding saturated naphthenic hydrocarbons, in 80-85% yield.

EXPERIMENTAL

The reduction reaction was conducted in the presence of 20% Pd on activated charcoal at 190°, with acid chloride and hydrogen space velocities of 0.3 and 100 h^{-1} , respectively. The reaction product was washed with alkali and with water, dried with anhydrous sodium sulfate, and distilled in a column of thirty theoretical plates efficiency. The order of carrying out the acid chloride reduction and converting the aldehydes obtained to hydrocarbons via the Kizhner reaction, and also the method of preparing the palladium catalyst, have been previously described [4]. The starting acid chlorides were synthesized in 90–95% yield by reaction of thionyl chloride with the appropriate carboxylic acids, which were prepared, in turn, by carbonylation of the appropriate alcohols [5].

N. D. Zelinskii Institute of Organic Chemistry of the Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5, pp. 1117-1120, May, 1968. Original article submitted August 16, 1967. <u>Cyclopentanealdehyde</u>. Cyclopentanecarbonyl chloride, bp 161-162°, d_4^{20} 1.1002, n_D^{20} 1.4631. Lit. [6]: bp 160-162°. The acid chloride was prepared from the acid, bp 103.3-104° (10 mm), d_4^{20} 1.0515, n_D^{20} 1.4538. Lit. [7]: bp 104° (10 mm) d_4^{20} 1.0510, n_D^{16} 1.4534. The acid chloride was converted in 97% yield into a mixture of solid and liquid products. The solid part of the catalyzate (85% yield) was the cyclic trimer of cyclopentanealdehyde, mp 128° (from hexane). Found: C 72.56, 72.56; H 10.47, 10.41%; mol. wt. 292; 288 (cryscopic, in benzene). C₁₈H₃₀O₃. Calculated: C 73.46; H 10.20%; mol. wt. 294. Lit. [8]: mp 117-117.5°. The trimer was depolymerized on heating with two drops of concentrated H₂SO₄ or with a few crystals of NaHSO₄ to form cyclopentanealdehyde, bp 136.7°, d_4^{20} 0.9283, n_D^{20} 1.4422. 2,4-Dinitrophenyl-hydrazone, mp 159°. Found: C 51.74, 51.69; H 5.07, 5.19; N 20.11, 20.27%. C₁₂H₁₄O₄N₄. Calculated: C 51.78; H 5.07; N 20.15%. Lit.: for aldehyde bp 135° [9]; d_4^{20} 0.9371, n_D^{20} 1.4432 [10]; for 2,4-dinitrophenyl-hydrazone, mp 158.7° [11]. The liquid part of the catalyzate (12% yield) consisted of 85% cyclopentane and 15% cyclopentene, and was converted into a single substance on hydrogenation over Pt/C.

Cyclopentanealdehyde was converted by the Kizhner reaction into methylcyclopentane, bp 72.0°, d_4^{20} 0.7491, n_D^{20} 1.4099.

<u>Cyclohexanealdehyde.</u> Cyclohexanecarbonyl chloride, bp 183-185°, d_4^{20} 1.0825, n_D^{20} 1.4766. Lit.: bp 184° [12], d_4^{15} 1.0962 [13], n_D^{20} 1.4766 [12]. The acid chloride was prepared from the acid, mp 30.5-31°. Lit. [13]: mp 30.5-31°. The acid chloride was reduced in 84% yield to a mixture of solid and liquid products. The solid product (68% yield) was the cyclic trimer of cyclohexanealdehyde, mp 198° (from benzene). Found: C 75.22, 75.40; H 10.75, 10.84%; mol. wt. 337, 338 (cryoscopic in benzene). C₂₁H₃₆O₃. Calculated: C 74.93; H 10.79%; mol. wt. 336. Lit. [14]; mp 196°. The trimer was depolymerized by the method indicated above into cyclohexanealdehyde, bp 159-160°, d_4^{20} 0.9263, n_D^{20} 1.4500. 2,4-Dinitrophenyl-hydrazone, mp 173°. Found: C 53.32, 53.42; H 5.58, 5.50%; N 19.28; 19.20%. C₁₃H₁₆O₄N₄. Calculated: C 53.41; H 5.52; N 19.18%. Lit.: bp 157° [15]; d_4^{20} 0.9270, n_D^{20} 1.4505 [16]. 2,4-Dinitrophenylhydrazone [17]: mp 172°. The liquid part of the catalyzate (16% yield) consisted of 70% cyclohexane and 30% cyclohexane, and contained only cyclohexane after hydrogenation over Pt/C.

The cyclohexanealdehyde was converted into methylcyclohexane, bp 100.9°, d_4^{20} 0.7692, n_D^{20} 1.4230 via the Kizhner reaction.

 $\frac{1 - Methyl cyclopentanealdehyde.}{1 - Methyl cyclopentanecarbonyl chloride, bp 52-55° (8 mm), d_4^{20} 1.0693, n_D^{20} 1.4618. Lit. [18]: bp 61° (15 mm). The acid chloride was synthesized from the acid, bp 219-220°, d_4^{20} 1.0220, n_D^{20} 1.4529. Lit. [19]: bp 219.0-219.5°, d_4^{20} 1.0218, n_D^{20} 1.4529 [18]. The acid chloride was reduced in 85% yield to 1-methyl cyclopentanealdehyde, bp 142.0-142.1°, d_4^{20} 0.9420, n_D^{20} 1.4533. 2,4-Dinitrophenyl hydrazone, mp 151.5°. Found: C 53.22, 53.11; H 5.68, 5.68; N 19.15; 18.99% C₁₃H₁₆O₄N₄. Calculated: C 53.41; H 5.52; N 19.18%. Lit.: bp 142-143° [20], n_D^{20} 1.4560 [21]. 2,4-Dinitrophenyl hydrazone, mp 153° [21]. By the Kizhner reaction the aldehyde was converted into 1,1-dimethyl cyclopentane, bp 87.9-88.1°, d_4^{20} 0.7550, n_D^{20} 1.4139. Lit.: bp 87.9° [22]; d_4^{20} 0.7548, n_D^{20} 1.4135 [23].$

<u>1-Methylcyclohexanealdehyde.</u> 1-Methylcyclohexanecarbonyl chloride, bp 75-77° (12 mm), d_4^{20} 1.0567, n_D^{20} 1.4678; it was synthesized from the acid, mp 37-38°. Lit. [24]: mp 37-38°. The acid chloride was reduced to 1-methylcyclohexanealdehyde in 80% yield, bp 166.5-167°, d_4^{20} 0.9051, n_D^{20} 1.4468. 2,4-Dinitrophenylhydrazone, mp 155°. Found: C 54.72, 54.80; H 5.84, 5.87; N 18.29, 18.19% C₁₄H₁₈O₄N₄. Calculated: C 54.89; H 5.92; N 18.31%. This aldehyde, which is not described in the literature, was converted by the Kizhner reaction into 1,1-dimethylcyclohexane, bp 119.8°, d_4^{20} 0.7813, n_D^{20} 1.4290. Lit. [23]: bp 119.8°, d_4^{20} 0.7819, n_D^{20} 1.4290.

CONCLUSIONS

1. The acid chlorides of cyclopentane-, cyclohexane-, 1-methylcyclopentane-, and 1-methylcyclohexanecarboxylic acids have been reduced to the corresponding aldehydes in 70-85% yield over Pd-charcoal catalyst in the vapor phase at 190°.

2. Cyclopentane- and cyclohexanealdehydes were obtained in the form of the solid cyclic trimers, but 1-methylcyclopentane- and 1-methylcyclohexane- aldehydes were obtained in the monomeric form.

3. The aldehydes synthesized have been converted into the corresponding naphthenic hydrocarbons in 80-85% yields by the Kizhner reaction.

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