

Catalytic Oxidation in Liquid-Phase of C₄-C₁₀ ALKYL- and C₅-C₇ Cycloalkyl Cyclohexanones to Alkylcaprolactones

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Abstract: *The liquid-phase oxidation of 2-alkyl- and cycloalkylcyclohexanones by aqueous solution of hydrogen peroxide in the presence of molybdenum compounds and dense acetic acid has been studied. The oxidation of ketones to lactone be proceed through an intermediate stage of generating peroxomolybdenum was established. The additives of acetic acid lead to accelerate the complex formation and promotion the selective oxidation of alkylcyclohexanones into the corresponding caprolactone. In the optimum conditions the yield of ε-caprolactone was 63,7-81,2%, however the selectivity of the process 79-86% was founded.*

Keywords: The liquid-phase oxidation, hydrogen peroxide, molybdenum compounds, carbamide adduct with hydrogen peroxide, 2-alkyl- and cycloalkylcyclohexanones, intermediate peroxomolybdenum, caprolactones.

1. Introduction

Lactones with alkyl and cycloalkyl substituents are of practical interest as medicinal, fragrant and flavoring compounds, as well as intermediate products to prepare polyurethanes, adipic acid and caprolactam [1, 2]. The known methods for their preparation are based on the reactions of hydrogenation of dicarboxylic acids and their anhydrides, cyclization of unsaturated, oxy- and halogen-substituted carboxylic acids, reductive cyclization of diols, carbonylation of unsaturated hydrocarbons, oxidation of various oxygen-containing compounds [3-6]. High yields of lactones were obtained by liquid-phase oxidation of alicyclic ketones with hydroperoxides, hydrogen peroxide [7-10] or molecular oxygen [11, 12] in the presence of complex compounds of transition metals.

Previously we have studied the oxidation of alicyclic ketones of the cyclopentane series corresponding to the δ - valerolactones [13]. Hydrogen peroxide of 30-34% concentration was used as an oxidizer, and molybdenum blue, prepared according to the method proposed in [14], was used as the catalyst.

In this paper, the results on the liquid-phase oxidation of C₄-C₁₀ alkyl- and C₅-C₇-cycloalkylcyclohexanones are given corresponding to the ε-alkylcaprolactones with the participation of homogeneous peroxocomplex molybdenum compounds.

2. Experimental Part

As raw materials C₄-C₁₀ alkyl- and C₅-C₇-cycloalkylcyclohexanone 98-99% degree of purity, obtained by the known method proposed in [15] were used. Oxidation of ketones was carried out in a thermostatic three-necked flask equipped with a mechanical stirrer, a thermometer, a

reflux condenser and a dropping funnel. Initial ketone, the catalyst and acetic acid were simultaneously loaded into a flask, and when a predetermined temperature was reached, 30-34% water solution of hydrogen peroxide or acetic solution of adduct of urea and H₂O₂ was instilled. The moment of contact of the oxidant with the raw material was fixed as the beginning of the reaction. At the end of the experiment, the oxide was extracted with toluene, separated from the aqueous phase, and each layer was analyzed separately. The composition of lactone and unreacted initial ketone were determined in the oxide.

As the catalyst the peroxocomplex compounds of molybdenum prepared by previously developed method [16], slow heating of spirit solution of a molybdenic blue or pentachloride of molybdenum with acetic acid before the termination of allocation of NBR or HCl and processing of the received connections by hydrogen peroxide during 1 h were used. The structure and composition of the obtained catalysts were determined by UV, IR method and EFR spectroscopy.

Urea peroxide was obtained by mixing 30-34% hydrogen peroxide and urea at a temperature of 26-30°C until the crystals dissolve completely. After cooling the resulting saturated solution at a temperature of 0-4°C, complex crystals being used as an oxidizer agent after filtration and drying drop out.

The synthesized lactones from the catalyst were isolated by toluene extraction, and then the extracts were combined and subjected to atmospheric-vacuum distillation. The purity and structure of these compounds were determined by the methods of GLC, IRS, NMR ¹H and ¹³C.

GLC analyzes were carried out on a chromatograph "Color-500M" (10% polyethylene glycol succinate (PEGS) on

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chromosorb W, the velocity of the helium gas carrier was 30 ml/min. Column temperature 120-160°C, evaporator temperature 280-300°C.

IR spectroscopic analysis was on an Alpha instrument in the range 400-4000 cm^{-1} .

^1H NMR spectra were taken at room temperature in solutions of carbon tetrachloride and deuterioacetone on "Bruker-AM-300".

3. Results and their Discussion

The preliminary experiments made for an assessment of efficiency of catalysts in urea peroxide disintegration reaction have shown their sufficient high activity in an interval temperature 20-30°C. The experiments on liquid-phase oxidation of alkyl cyclohexanones carried out in the presence of peroxocomplex compound of the molybdenum taken as the catalyst on the example of oxidation 2 hexylcyclohexanones have shown that in lack of carbonic acids conversion of initial connection at a temperature 50°C and duration of 4 h doesn't exceed 22-28%. Adding a little acetic acid into the system promotes the increase in conversion and selectivity of oxidation of a substratum. So, at a molar ratio 2 hexyl-cyclohexanones: CH_3COOH -1: 0.1 yield conversion of 2 alkyl-ketones reaches 67.4%, and selectivity of the reaction on a lactone of 79.0%. With the increase in the amount of acetic acid from 0.1 to 0.8 mole, the conversion of ketone increases from 67.4 to 81%, and the selectivity of the reaction decreases a little (from 79.0 to 68.3%). In the process of accumulation in a water oxydata the lactone is partially hydrolyzed in an oxyacid which is exposed further to an oligomerization. Apparently, under these conditions oxidation of ketone is followed by secondary transformation of a lactone and along with the main products of the reaction are formed also alkyl-derivative adipic and corresponding oxyacid. Optimum for obtaining ϵ -hexylcaprolactone is the ratio of ketone: acetic acid = 1: 0.2. Selectivity of the reaction on a lactone directly depends on the number of the used catalyst. The increase in concentration of Mo^{n+} from $2.5 \cdot 10^{-4}$ to $2 \cdot 10^{-3}$ g ions of Mo^{n+}/l leads to increase in conversion 2 hexyl-cyclohexanone and yield of caprolactone. It is assumed that oxidation of alkyl-cyclohexanones is preceded by interaction of compound of molybdenum with hydrogen peroxide and acetic acid with the formation of an intermediate peroxyacid complex. Reactionary ability of such complex is rather high and it is reflected in the increase of target products yield from 51.8 to 81.2%. At the same time the yield of lactone in the reacted ketone decreases from 88.4 to 63.5%. Peroxomolybdenic complexes in oxidation products was determined with spectrophotometric method on character of maximum absorption at 331 nanometers.

The significant effect on the direction of active oxygen transformation and selectivity formation of a lactone is rendered by reaction temperature. In an interval 20-40°C ketone oxidations proceeds with the induction period of 90-120 min. With temperature increase from 40 to 60°C active oxygen transformation proceeds selective and unproductive decomposition of H_2O_2 doesn't exceed 8-10%. However, at a

temperature higher than 80°C, the speed of unproductive decomposition of H_2O_2 increases, and the conversion of a substratum and selectivity process decreases.

At the found optimum temperature (40-60°C) the influence of initial concentration of H_2O_2 on conversion of 2 hexyl-cyclohexanones and the yield of corresponding lactone is investigated. The obtained data show that oxidation of ketone in the presence of 10-20% H_2O_2 solution is proceeded by the big induction period. Extent of the substratum transformation doesn't exceed 10.0-12.0 of%. Apparently, in the diluted hydrogen peroxide solution water participates in the formation of in situ of low-active aqua-complex of the catalyst. While using 26-33% H_2O_2 , higher conversion of ketone is reached 20-25%. Adding 95% of acetic acid or acetic anhydride into the system promotes sharp reduction of the induction period and increase in the yield of a lactone to 69.7%. It is explained by participation of acetic acid as a carrier of active oxygen from H_2O_2 to the sphere of a ligand environment of molybdenum and further in substratum molecules.

At oxidation 2 hexyl-cyclohexanone the adduct of urea and H_2O_2 in 90-95% acetic acid at a temperature 20°C and a molar ratio ketone: H_2O_2 = 1: 2 in the first 3 hours reaction proceeds, mainly, with the formation of ϵ -hexyl- ϵ -caprolactone content in which an oxidate reaches 54-58 of %, and in 5 hours of 62,8%. Within 6 hours full oxidation of the taken hexyl-cyclohexanone is obtained and the yield of the lactone forms 69,7%. The reaction with the use of this adduct proceeds more selectively at 10-20°C. A lactone yield under these conditions forms 80.0-81.2 of %. Oxidation of other alkyl-derivatives of cyclohexanone was carried out in conditions, optimum or close to it found at an oxidation reaction research of 2 hexyl-cyclohexanones in caprolactone. It is experimentally determined that, the change in length and structure of the alkyl radicals in the molecules of initial ketones affects reactionary ability of alkylcyclohexanone. Increase in the alkyl radical in the molecules of 2-n-alkylcyclohexanone C_4 - C_{10} leads to noticeable decrease in their reactionary ability (tab. 1). Some increase in the yield of a target product and selectivity is observed upon the transition from alkyl - and cycloalkyl derivatives of a cyclopentanone to the ketones containing a cyclohexanone fragment [17]. By the method of the competing reactions it was determined that the oxidation speed of alkyl- and cycloalkyl derivatives of cyclohexanone is higher than the speed of the oxidation of the corresponding alkyl-derivatives of a cyclopentanone (tab.1). It is possible to assume that the decrease in the yield of a lactone and consequently also reactionary ability of the corresponding alkyl cyclohexanone during the increase in the size of its alkyl deputy is caused by the increasing the effect of alkyl groups that complicates the attack of carbonyl group a peroxocomplex.

Table 1: Comparison of reactionary ability of alkyl-cyclanone by the method of the competing reactions

Taken	Quantity, gr	Obtained			
		Retrieval of ketones, gr	Lactone, gr	Molar ratio of lactones	
2-n.Butylcyclopentanone	6,39	4,9	0,81	1: 6,35	
2-n.Pentylcyclohexanone	7,03	3,8	5,6		
2-n.Pentylcyclopentanone	7,76	7,05	0,78	1: 5,93	
2-n.Pentylcyclohexanone	8,4	3,38	5,5		
2-n.Hexylcyclopentanone	8,4	7,7	0,75	1:6,6	
2-n.Hexylcyclohexanone	9,1	4,1	5,3		
2-n.Hexylcyclopentanone	8,4	7,7	0,75	1:6	
2-n.Hexylcyclohexanone	9,8	4,8	5,3		
2-n. Hexylcyclopentanone	8,4	7,6	0,85	1:5,0	
2-n.Octylcyclohexanone	10,5	5,6	5,2		
2-n.Hexylcyclopentanone	8,4	7,6	0,86	1:0,45	
2-n.Nonylcyclohexanone	11,2	6,4	5,0		
2-n.Hexylcyclopentanone	8,4	7,6	0,84	1:4,2	
2-n.Decylcyclohexanone	11,9	7,1	4,9		
2-Cyclopentylcyclopentanone	6,9	7,2	0,7	1:6,7	
2-Cyclopentylcyclohexanone	7,6	3,8	5,1		
2-Cyclohexylcyclopentanone	7,6	6,7	0,68	1:6,2	
2-Cyclopentylcyclohexanone	8,9	3,4	4,9		
2-Norbornylcyclopentanone	2,1	6,2	0,65	1:5,1	
2-Norbornylcyclohexanone	8,7	3,1	3,6		

Optimum condition for the reaction of liquid-phase oxidation of 2 alkyl-cyclohexanones in δ -alkyl- ϵ -caprolactone: temperature 40-50°C, molar ratio of ketone: CH₃COOH: H₂O₂ = 1: 0.1-0.2: 2, the number of the catalyst

- (5-7.5) • Mo's ^{+5/l} 10⁻⁴g-ion, reaction duration - 6 hours. Under these conditions the yield of caprolactoneforms 51.0-81.2 of %, and the selectivity of the process reaches 78.6-92.0 of %.

Physical and chemical indicators and the yield of the synthesized connections are given in tab. 2.

The structure of the obtained lactones is confirmed by the data of IR-, nuclear magnetic resonance ¹H and ¹³C-spectroscopy.

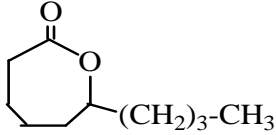
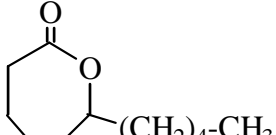
In IR - ranges of the synthesized connections intensive strips of absorption to the areas 1740-1730 and 1200-1050 of cm⁻¹ characterizing the groups of C=O and C-O-C are found. In the ranges of nuclear magnetic resonance ¹H of alkylcaprolactone in the strong fields there is a singlet of methyl group (1.1 m of), a multiple of CH₂ group (1.50-1.92m.d.), a doublet of CH₂ group at C=O (2.54 m d) and a triplet of CH group (4.45 m d). Ranges of nuclear magnetic resonance ¹³C are characterized by chemical shifts of carbon atoms, in m: 169.5-170.6 (C = O), 79.8-80.5 (C-O-C), 37 and 38.5 (CH₂, CH₂-C=O), 13.5-14.2 (CH₃), 18.0-31.5 (CH₂ of the cyclo and alkyl groups).

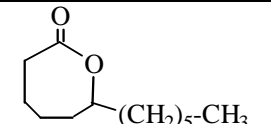
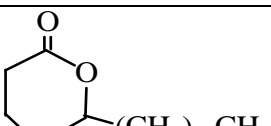
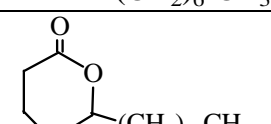
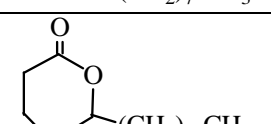
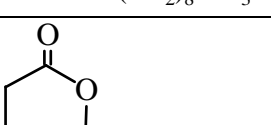
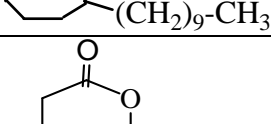
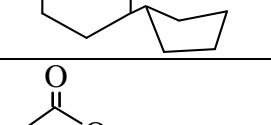
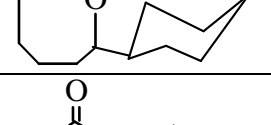
Obtained alkyl - and cycloalkylcaprolactona are characterized by pleasant smells of various directions and a shade and can be used as additives for the fragrant and flavoring compositions [18]. Organoleptic properties of the synthesized caprolactone are provided in table 3.

Table 2: Physical and chemical properties synthesized by ϵ -alkyl- ϵ -caprolactones

№	Name	Yield, %	Boiling temperature°C	d_4^{20}	n_D^{20}	MR _D		found, %		calculated, %	
						found	Calculated	C	H	C	H
1	ϵ -n.butyl- ϵ -caprolactone	63,7	120-123/2	0,9713	1,4606	48,07	47,68	70,66	10,49	70,58	10,59
2	ϵ -n.pentyl- ϵ -caprolactone	67,4	135-140/2	0,9646	1,4620	52,44	52,30	71,62	10,62	71,74	10,87
3	ϵ -n.hexyl- ϵ -caprolactone	69,7	150-155/2	0,9540	1,4630	57,15	56,53	72,73	11,10	72,73	11,11
4	ϵ -n.heptyl- ϵ -caprolactone	71,0	155-160/2	0,9462	1,4642	61,82	61,54	73,46	11,21	73,59	11,32
5	ϵ -n.octyl- ϵ -caprolactone	60,4	165-170/2	0,9335	1,4650	66,4	66,16	74,21	11,46	74,34	11,50
6	ϵ -n.nonyl- ϵ -caprolactone	59,4	175-180/2	0,9283	1,4664	71,2	70,78	74,89	11,58	75,00	11,67
7	ϵ -n.decyl- ϵ -caprolactone	55,3	185-190/2	0,9233	1,4670	76,3	75,39	75,40	11,84	75,59	11,81
8	ϵ -cyclopentyl- ϵ -caprolactone	49,5	138-140/2	1,0655	1,4953	53,9	54,7	73,50	10,23	73,47	10,20
9	ϵ -cyclohexyl- ϵ -caprolactone	81,2	130-132/2	1,1307	1,5330	57,65	56,99	74,90	9,51	75,00	9,62
10	ϵ -norbornyl- ϵ -caprolactone	51,0	134-136/2	1,0653	1,4910	49,48	50,01	72,33	9,62	72,53	9,89

Table 3: Organoleptic properties of synthesized alkyl-substituted caprolactones

№,	Name	Structural formulae	Smell
1.	ϵ -n.butyl- ϵ -caprolactone		fruit and Dihydromangane shade
2.	ϵ -n.pentyl- ϵ -capro-lactone		fruit-berry, with a hint of strawberry and dihydrozhasmona

3.	ϵ -H.n-hexyl- ϵ -caprolactone		a fruity and floral shade
4.	ϵ -H.heptyl- ϵ -caprolactone		The smell of dried mushrooms with a greenery shade
5.	ϵ -H.Octyl- ϵ -caprolactone		Dried mushrooms and prunes
6.	ϵ -H.Nonyl- ϵ -caprolactone		Fat withmusk shade
7.	ϵ -H.Decyl- ϵ -caprolactone		With a slight musk shade
8.	ϵ -Cyclopentyl- ϵ -capro-lactone		Slightly minty with a soft shade
9.	ϵ -Cyclohexyl- ϵ -capro-lactone		Fat, with a musk shade
10.	ϵ -Norbornyl- ϵ -caprolactone		Fat

References

- [1] Palm U., Askari Ch., HenerUwe et al. // Z.Lebensm-Untersuch und Forsch. 1991. 192. No 3. P. 209-213.
- [2] Soldatenko L.T., Kolyadina I.M., Shendrik V. The basis of organic chemistry of medicines. M.: 2003. 191 p.
- [3] Vasapollo G., Mele G., El Ali B. // J.Mol.Catal. (A). 2003. V. 204-205. P. 97.
- [4] Khusnutdinov R.I., Shadneva N.A., Lavrenteva Y.Y., Jamilov U.M. 2002104327/04 (2003) Russia. // Chemistry. 2005.№14.19H.159p.
- [5] Ji Hong-Bing,Wang Le-Fe, She Yuan-Bin. // HuaxueXuebao. 2005. V. 63. No 6. P. 1520. // Chemistry. 2006. №11. 19B4203.
- [6] Obara R., Szummy A., Zolnierczyk A. et al. // Pol. J. Chem. 2005. V. 79. N. 6. P. 981.
- [7] Finet L., Lena J.I., Candela K.T. et al. // Chem.Eur. J. 2003. 9. №16. P. 3813-3820
- [8] VilliamC.A. // J. Amer. Chem. Soc. 1964. V.86. 13. P.2638.
- [9] 19745-442. Germany. 1999. // Holderich W.P., Fishcer J., Schindler G., Edited. 2000. 12. 19H109p.
- [10] Murahashi S.I., Ono S., Imada Y. // Angew. Chem. Int. Ed. 2002. V.41. №13. P. 2366-2368.
- [11] Shinohara T., Fujioka S., Kotsuki H. // An Int. J. Rev. Commun. heterocycles Chem. 2001. 55. V.2. P.237-242.
- [12] Li X., Wang F., Lu X. et al. // Synth. Commun. 1997. 27.V.12. P. 2075-2079.
- [13] Abbasov M.F., Suleymanova E.T., Alimardanov X.M. // Applied Chemistry. 1997. T.70. № 4. p. 648-655.
- [14] Alimardanov X.M., Suleymanova E.T., Ismailov E.G., Akhundova A.A. // Petro-chemistry. 1994. T. 34. № 4. p. 344-350.
- [15] Abbasov M.F. Chemistry Journal of Azerbaijan. 1999. №2. P.32-35.
- [16] Alimardanov X.M., Abbasov M.F., Veliyeva F.M. and others. // Petro-chemistry. 2004. V.44. №3. P. 196-203.
- [17] Abbasov M.F., Suleymanova E.T, VelievF.G., JafarovaN.A. // petrochemical processing andoil refining. 2008. № 3-4. P. 264-268.
- [18] L.A.Kheifits, V.M. Dashunin. Fragrant substances and other products for perfumes.M.: Chemistry. 1994. 255 p.