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OXIDATION OF SECONDARY CYCLIC ALCOHOLS BY Pb(OAc)$_4$ CATALYZED BY Cu(II) COMPOUNDS

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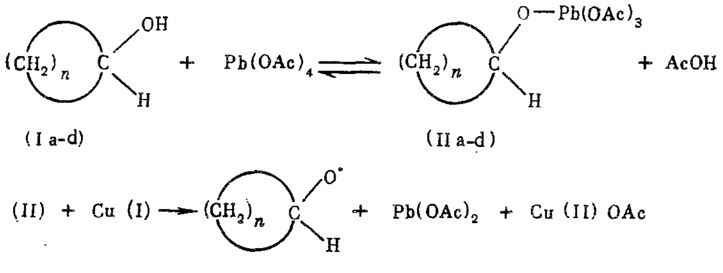
Cleavage of cycloalkanols in the presence of oxidative systems based on lead tetraacetate (LTA) is one of the most efficient methods for generation of alkyl radicals containing a carbonyl function in various positions with respect to the radical center [1, 2]. Generation of oxoalkyl radicals and their quantitative oxidation to ω-alkenones have been carried out by this method with the reaction of LTA–Cu(OAc)$_2$ with tertiary cyclic alcohols [3].

The main product of the reaction of secondary five- and six-membered cyclic alcohols with LTA (without the participation of Cu(II) compounds) is the acetate of the starting alcohol; in addition, β-fragmentation products and cycloalkanones are practically not formed (1-8% yield) [4]. In the oxidation of cycloheptanol and cyclooctanol, not only their acetates but also cyclic ketones and, in a significant amount, bicyclic ethers, epoxy compounds, are obtained [4, 5]. Previously we showed that the LTA–Cu(OAc)$_2$ system can be successfully used for the oxidation of unsubstituted five- and six-membered cycloalkanols to acyclic aldehydes [6].

In the present paper, we consider individual stages of the mechanism of this reaction and the effect of the structure of the alcohol on the direction of the oxidation process of C_5–C_8 secondary cyclic alcohols in the presence of LTA–Cu(II). In combination with LTA, we used copper diacetate, sulfate, and oxide. The reaction was carried out in benzene at 80°C, and the mole ratio alcohol:Pb(IV):Cu(II) was 1:1:0.1.

Being oxidized by the Pb(IV)–Cu(II) acetate system, secondary cycloalkanols (I) formed cycloalkoxy radicals (A), which fragmented with ring cleavage, giving ω-formylalkyl radicals (B). The latter were easily deprotonated by Cu(II) ions, being converted to ω-alkenals (III)



(I a-d) (II a-d)

•(A)

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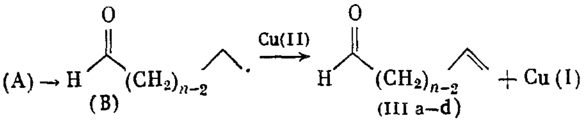
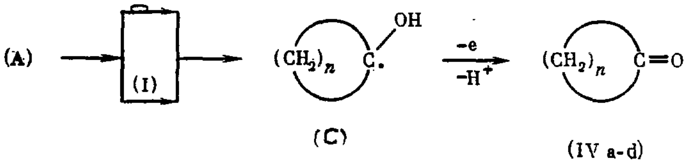


Cu(II) = $Cu(OAc)_2$, $CuSO_4$, CuO, n = 4 (a), 5 (b), 6 (c), 7 (d).

The regeneration of copper Cu(I) → Cu(II) in the catalytic cycle can probably occur because of reaction both with (II) and with LTA.

The maximum yield of the unsaturated aldehyde was observed when the LTA–$Cu(OAc)_2$ system was used, apparently because $Cu(OAc)_2$ has better solubility in benzene than do $CuSO_4$ and CuO (Table 1).

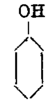
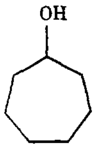
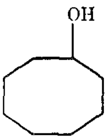
Cycloalkanones (IV) were also formed during the reaction. In the case of cyclohexanol, an equal amount of 5-hexenal and cyclohexanone was obtained, and in the oxidation of cyclopentanol the main product was the unsaturated aldehyde. A significant amount of the cyclic ketone (25-30%) was also obtained in the reaction of cycloheptanol and cyclooctanol with LTA–$Cu(OAc)_2$. The formation of cycloalkanone (IV) can occur by two routes:



n = 4 (a), 5 (b), 6 (c), 7 (d).

The formation of radicals of type (A), (B), and (C) was proven by an EPR method (Table 2). In the reaction of cyclopentanol and cyclohexanol with LTA in the presence of C-phenyl-N-tert-butylnitrone (PBN), the EPR spectrum contained a triplet and a triplet of doublets. The triplet (a_N = 7.8 Oe) characterized the radicals $C_6H_5C(O)N(\dot{O})C(CH_3)_3$ the formation of which was described in [7]. On the basis of [8], the triplet of doublets was assigned to spin adducts of radicals of type (A) with PBN. The spin adducts of radicals of type (A) were

TABLE 1. Oxidation of Cycloalkanols by the $Pb(OAc)_4$–Cu(II)* System

Alcohol	Cu(II)	Conversion of alcohol, %	Yield† % based on converted alcohol		
			(III)	(IV)	(V)
	$Cu(OAc)_2$	91	81 (IIIa)	7 (IVa)	–
	$CuSO_4$	92	72 (IIIa)	11 (IVa)	–
	CuO	86	65 (IIIa)	12 (IVa)	–
	$CuSO_4$	40	48 (IIIb)	45 (IVb)	–
	$Cu(OAc)_2$	79	35 (IIIc)	24 (IVc)	37 (Vc)
	$CuSO_4$	65	23 (IIIc)	23 (IVc)	51 (Vc)
	$Cu(OAc)_2$	72	8 (IIId)	31 (IVd)	46 (Vd)

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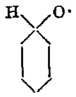
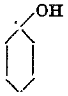
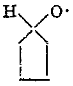
*80°C, 0.5-3.5 h, alcohol:Pb(IV):Cu(II) = 1:1:0.1; 0.01 mole of alcohol and 20 ml of benzene; $Pb(OAc)_4$ conversion 100%.

†In all runs the yield of the acetate of the starting alcohol was 2-10%.

TABLE 2. Parameters of the EPR Spectra of Radical Adducts Formed in the Oxidation of Cyclohexanol and Cyclopentanol by LTA in the Presence of a Spin Trap*

Radical	Spin trap	a_N, Oe	a_β^H, Oe
	PBN ND	13,6 26,7	1,9 –
	MNP ND	15,2 13,3	– –
$H(O)C(CH_2)_4\dot{C}H_2$	ND	13.8	10,4
$(O)\dot{C}(CH_2)_4CH_3$	ND	7,3	–
Ditto	MNP	7.8	–
$H(O)C\dot{C}H(CH_2)_3CH_3$	ND	13,7	6.8
Ditto	MNP	13.5	1,3
	PBN	13,6	1,9
$H(O)C(CH_2)_3\dot{C}H_2$	ND	13.8	10.4
$(O)\dot{C}(CH_2)_3CH_3$	ND	7,3	–

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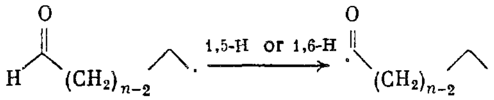
*Spin traps: $C_6H_5CHN(O)C(CH_3)_3$, PBN; 2,3,5,6-$(CH_3)_4C_6HNO$, ND; and $(CH_3)_3CNO$, MNP.

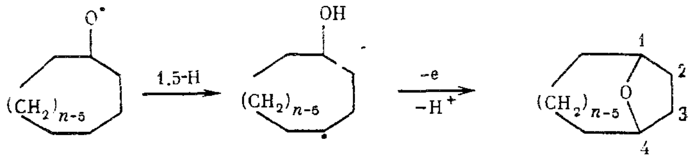
also identified by the EPR method using nitrosodurene (ND) in the reaction of cyclohexanol with LTA. In addition to the signals of spin adducts of these radicals, we recorded signals from the spin adducts of carbon-centered primary (B) and tertiary (C) radicals with ND and, in addition, from secondary and acyl radicals. The formation of acyl radicals probably occurred because of 1,5 and 1,6 migration of the H atom in the 4-formylbutyl and 5-formylpentyl radicals, respectively,



The secondary alkyl radicals observed only in the oxidation of cyclohexanol can be assigned to the $H(O)C\dot{C}H(CH_2)_3CH_3$ radicals formed because of 1,5 H migration in the 5-formylpentyl radical.

Radicals of type (C) were also identified in the reaction of cyclohexanol with LTA in the presence of 2-methyl-2-nitrosopropane (MNP), and the spectrum of the spin adducts of these radicals consisted of a triplet due to splitting at the nitrogen atom of the nitroso group. The generation of primary radicals (B) in the oxidation of cyclopentanol in the presence of LTA was confirmed by the signals of their spin adducts with ND. The EPR spectra showed hyperfine splitting at the nitrogen atom and the β protons of the captured radical.

Cyclic alcohols with C^7 and C^8 ring sizes (Ic and Id) were also oxidized by the investigated system in a third direction with the formation of 1,4-epoxycycloalkanes (V). The contribution of this direction to the overall oxidation process was significant, 35-50% based on the converted alcohol. The formation of the cyclic ethers occurred as a result of 1,5 migration of the H atom in the ring



(Vc, d)

n = 6 (c), 7 (d).

Only 1,4-epoxycyclooctane, the structure of which was confirmed by ^{13}C NMR spectra, was obtained in the oxidation of cyclooctanol. The formation of 1,5-epoxycyclooctane, possible in the case of oxidation of this alcohol, was not observed.

According to the data presented in Table 1, cyclopentanol is oxidized most facilely with ring cleavage. Cyclohexanol and cyclopentanol tended to undergo this reaction to a lesser degree. Cyclooctanol reacted with the LTA–$Cu(OAc)_2$ system predominantly without ring cleavage, and the contribution of the decyclization reaction to the overall alcohol-conversion process did not exceed 10%. Such behavior of this alcohol was probably due to the fact that the mobility of the CH_2 groups in the ring increased with increasing number of carbon atoms in the ring, and thus the conformational stability of the six-membered transition state, leading to the bicyclic ether 1,4-epoxycyclooctane, increased sharply.

EXPERIMENTAL

A GLC analysis was carried out on an LKhM-80 chromatograph in a 30-ml/min nitrogen stream using a flame-ionization detector and 3 × 0.003-m glass columns with 5% XE-60 and 10% TCEP (tris(cyanoethoxy)propane) on Chromosorb W (60-80 mesh). The yield of the products was determined by the internal-standard method taking into account experimentally determined correction coefficients. The proton NMR spectra were recorded on a Bruker WM-250 instrument with a $CDCl_3$ solvent, the ^{13}C NMR spectra were recorded on a Bruker WM-250 instrument, and the IR spectra were recorded on UR-20 and Specord M-80 spectrometers in a thin layer. The EPR spectra were recorded on an RÉ-1306 spectrometer. Pure-grade lead tetraacetate was washed with glacial AcOH and dried with KOH. The starting alcohols were prepared by reduction of the corresponding ketones. The $Cu(OAc)_2 \cdot H_2O$ and $CuSO_4 \cdot H_2O$ were dried in vacuo over P_2O_5 at 120°C, and analytical-grade CuO was used without preliminary treatment. Benzene was dried over sodium and distilled.

The EPR Spectra. The EPR spectra were obtained with oxidation of cyclohexanol and cyclopentanol by LTA in the absence of Cu(II). When PBN was used, its benzene solution ([PBN] = 0.033146 M) contained 0.003 M LTA and 0.2 M alcohol. The LTA (~0.012 M) and the nitroso compounds (ND and MNP) (~0.01-0.001 M) were placed in glass cylindrical ampuls. A solution of the alcohol (~0.5-1.0 M) in C_6H_6 or C_6F_6 with a volume of 0.2 ml was poured into the ampuls. The solutions in the ampuls were degassed by freezing, vacuum treatment, and thawing. The ampuls, sealed under vacuum, were placed in the resonator of a spectrometer. The spectra were recorded at 20°C.

Oxidation of Secondary Cycloalkanols by the $Pb(OAc)_4$–Cu(II) System (General Procedure). A mixture of 0.01 mole of the alcohol, 0.01 mole of LTA, and 0.001 mole of the Cu(II) compound in 20 ml of absolute benzene was stirred vigorously at 80°C for 0.5-3.5 h until complete conversion of Pb(IV) (iodometric sample). Then the conversion of the starting alcohol and the yield of the products were determined by GLC (Table 1). The obtained unsaturated aldehydes were identified in the form of acids, for which air was passed through the reaction mixture for 10 h, then the reaction mixture was treated with a sodium hydroxide solution, and the aqueous layer was separated and acidified to pH 2. Then it was extracted with ether, and the extract was dried with $MgSO_4$ and distilled.

4-Pentenal (IIIa). The IR and proton NMR spectra corresponded to those given in [6]. In addition, 4-pentenal was identified in the form of 4-pentenoic acid. IR spectrum (ν, cm^{-1}): 1640 and 3080 ($CH_2{=}CH$), 1720 (C=O), 2930 (OH). Proton NMR spectrum (δ, ppm): 1.6 multiplet (2H, CH_2), 2.3 triplet (2H, CH_2COOH), 5.0 multiplet (2H, $CH_2{=}$), 5.8 multiplet (1H, =CH), 9.8 singlet (1H, OH).

5-Hexenal (IIIb). The IR and proton NMR spectra corresponded to those given in [6]. In addition, 5-hexenal was identified in the form of 5-hexenoic acid. IR spectrum (ν, cm^{-1}): 1640 and 3080 ($CH_2{=}CH$), 1715 (C=O), 2930 (OH). Proton NMR spectrum (δ, ppm): 1.2-1.5 multiplet (4H, CH_2), 2.3 triplet (2H, CH_2COOH), 5.0 multiplet (2H, $CH_2{=}$), 5.8 multiplet (1H, =CH), 10.3 singlet (1H, OH).

6-Heptenal (IIIc). This compound was identified in the form of 6-heptanoic acid. Found: C 65.57; H 9.22%. $C_7H_{12}O_2$. Calculated: C 65.58; H 9.22%. IR spectrum (ν, cm^{-1}): 1640 and 3080 ($CH_2{=}CH$), 1720 (C=O), 2930 (OH). Proton NMR spectrum (δ, ppm): 1.3-1.8 multiplet (4H, CH_2), 2.1 multiplet (2H, CH_2), 2.4 triplet (2H, CH_2COOH), 5.0 multiplet (2H, $CH_2{=}$), 5.8 multiplet (1H, =CH), 9.0 multiplet (1H, OH).

7-Octenal (IIId). Proton NMR spectrum (δ, ppm): 1.2-2.0 multiplet (6H, CH_2), 2.2 triplet (2H, CH_2COOH), 4.9 multiplet (2H, $CH_2=$), 5.6 multiplet (1H, =CH), 9.5 triplet (1H, CHO).

1,4-Epoxycycloheptane (Vc). IR spectrum (ν, cm^{-1}): 1060 (C—O—C). Proton NMR spectrum (δ, ppm): 1.3-2.1 multiplet (10H, CH_2), 4.4 multiplet (2H, CH—O—CH).

1,4-Epoxycyclooctane (Vd). IR spectrum (ν, cm^{-1}): 1060 (C—O—C). Proton NMR spectrum (δ, ppm): 1.3-2.1 multiplet (12H, CH_2), 4.5 multiplet (2H, CH—O—CH). Carbon-13 NMR spectrum (δ, ppm): 24.4 (C^6, C^7), 31.5 (C^2, C^3), 36.1 (C^5, C^8), 77.8 (C^1, C^4).

CONCLUSIONS

1. The formation of cycloalkoxy, α-hydroxycycloalkyl, and ω-formylalkyl radicals in the oxidation of secondary cycloalkanols by $Pb(OAc)_4$ was recorded by an EPR method in the presence of spin traps.

2. In the presence of the $Pb(OAc)_4$—Cu(II) system, the ability of secondary cyclic alcohols to undergo oxidative decyclization with the formation of ω-alkenals decreases in the series cyclopentanol > cycloheptanol > cyclohexanol > cyclooctanol.

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EFFECTIVE REDUCTION OF HALOGEN-CONTAINING HYDROCARBONS BY DIISOBUTYL ALUMINUM HYDRIDE IN THE PRESENCE OF TRANSITION METAL HYDRIDES

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Organometallic compounds: $i\text{-}PrMgCl/MnCl_2$ [1], $i\text{-}PrMgBr/Cp_2TiCl_2$ [2], and $i\text{-}Bu_2AlH{\cdot}BuLi$ [3] have earlier been proposed as reagents for use in the reduction of halohydrocarbons; however, these reagents are not readily available and are distinguished by low activity with respect to secondary and tertiary alkyl and aryl halides.

We studied the reduction of aryl and alkyl halides using the available $i\text{-}Bu_2AlH$ in the presence of transition metal complexes of: Ti, V, Mn, Fe, Co, Ni, Zr, Mo, Ru, Rh, Pd, Nd, Hf, W. To find the optimal reaction conditions we studied in detail the reduction of bromobenzene with $i\text{-}Bu_2AlH$.

The nature of the ethereal solvent (Et_2O, THF, dioxane) in the presence of metal chlorides ($NiCl_2$, $CoCl_2$, $MnCl_2$, WCl_6, $HfCl_4$, VCl_3, $MoCl_5$, $PdCl_2$, $FeCl_3$, $TiCl_4$), taken in a ratio relative to the other reagents of $MCl_n:PhBr:i\text{-}Bu_2AlH = 1:20:30$ little influences the yield of benzene (40-60%). In aromatic solvents (toluene, xylene) the formation of traces of benzene is observed. In the absence of a catalyst, the initial bromobenzene is recovered from the reaction mixture entirely unchanged.

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