CONCLUSIONS

1. We investigated the thermal transformations of n-hexane, ethylene and a mixture of n-hexane—ethylene-^{14}C at 800°C and partial pressures of the starting hydrocarbons not more than 55 torr. We established that the conversion of ethylene in the presence of n-hexane is substantially increased.

2. The data obtained make it possible to assume that in the pyrolysis of n-hexane the ethylene being formed is involved in the formation of aromatic hydrocarbons, by interacting with radicals or with molecules capable of reacting, in particular with 1,3-butadiene.

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OXIDATIVE SPLITTING OF SECONDARY CYCLOALKANOLS BY $Pb(OAc)_4$—LiCl AND $Pb(OAc)_4$—$Cu(OAc)_2$ SYSTEMS

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In the reaction of tertiary cyclic alcohols with oxidizing systems based on lead tetraacetate (LTA), oxoalkyl radicals $RCO(CH_2)_2\dot{C}H_2$ (n =2-5) are formed, which in a LTA—$Cu(OAc)_2$ system quantitatively transform into ω-unsaturated ketones as the result of oxidative deprotonation [1], while in the LTA—metal halide system they become oxidized to ω-haloalkanones [2].

Information on the reaction of secondary cyclic alcohols with LTA proceeding with ring opening is limited. It is known that for cyclobutanol, the contribution of the decyclization reaction (β-fragmentation) of cyclobutoxyl radicals formed at the first stage to the overall transformation process is ∿15%. During oxidation with LTA, secondary cycloalkanols with C_5-C_{16} ring size convert mainly into cyclic ketones; the amount of β-fragmentation products does not exceed ∿1.5-4%. If due to structural features of the cycloalkoxyl radicals, their rearrangement with 1,5- or 1,6-migration of the hydrogen atom is possible, then epoxycycloalkanes, products of intramolecular oxidative cyclization, are formed [3].

To prepare ω-formylalkyl radicals $\dot{C}H_2(CH_2)_{n+1}CHO$ (n =2, 3) and to study their oxidative transformations, in the present work we oxidized cyclopentanol and cyclohexanol by LTA—LiCl and LTA—$Cu(OAc)_2$ system. The reactions were carried out at 65-80°C in benzene in the presence of pyridine (∿1 mole per mole of LTA) to complete conversion of LTA.

Table 1 lists the oxidation products of cyclopentanol and cyclohexanol by the LTA—LiCl system, and Table 2 the oxidation products of these alcohols by the LTA—$Cu(OAc)_2$ system. Their formation can be represented by the following scheme:

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TABLE 1. Oxidation of Cycloalkanols by LTA—LiCl System*

Cycloalkanol	Conversion of cycloalkanol, %	Yield of oxiation products, %					B/B†
		(I)	(II)	(IV)	(V)	(VII)	
Cyclopentanol	95	8	80	2	3	3	11,0
Cyclohexanol	92	43	40	2	4	2	1,1

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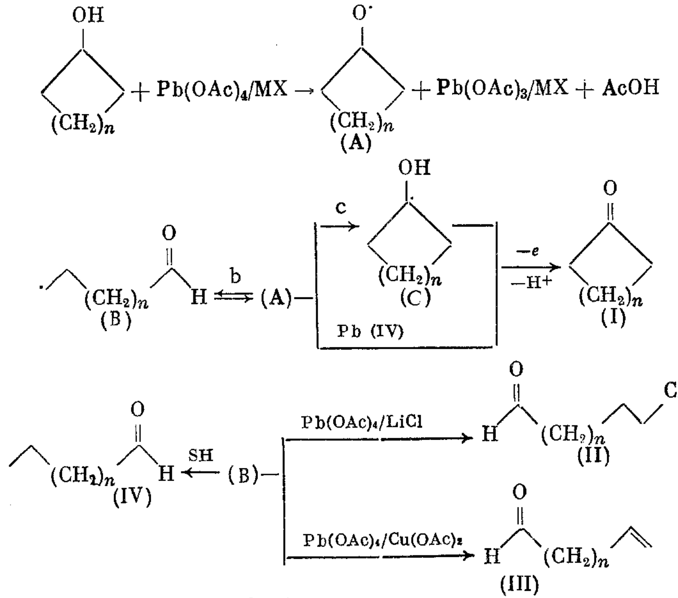
*65-70°C, 10-15 min, alcohol — 0.01 mole, pyridine — 0.01 mole, benzene — 25 ml, alcohol:LTA:LiCl =1:2:5; conversion of LTA — 100%. Yield of products is given per converted alcohol.

†Molar ratio of products derived from B (Σ(II), (IV), (VII)) and C(I).



MX = LiCl, Cu(OAc)$_2$; n = 2 (a), 3 (b).

Cycloalkoxyl radicals A generated at the first stage transform at two directions (b and c) simultaneously: They dissociate to form ω-formylalkyl radicals B and convert into α-hydroxycycloalkyl radicals C, which become oxidized into cycloalkanone (I). The oxidation of radicals A into cycloalkanone by LTA by a synchronous mechanism is also possible. The ω-formylalkyl radicals B are oxidized quantitatively by LTA—Cu(OAc)$_2$ system into ω-alkenals (III), while the action of LTA—LiCl leads to the formation of ω-haloalkanals (II) from them. The hydrogen splitting reaction by these radicals with the formation of alkanals (IV) proceeds to an inappreciable extent, and its contribution to the overall oxidation process of cycloalkanol is ∿2-4%.

The rate of decyclization (stage b) of the cyclo-$C_5H_9O^{\bullet}$ radicals is one order of magnitude higher than that of the cyclo-$C_6H_{11}O^{\bullet}$ radicals (the calculation was carried out from the difference and from the ratio of the products, Tables 1 and 2), which agrees with [4].

In the oxidation of cyclopentanol, aldehydes (II) and (III) are mainly formed, while from cyclohexanol, besides (II) and (III), considerable amounts of cyclohexanone are also formed. By the action of LTA the alcohols become partially acetoxylated at the OH group.

The decyclization stage of radicals B is reversible, A $\rightleftharpoons$ B. This conclusion follows from the existence of a dependence of the molar ratio of products obtained from B and C (see Table 2, B/C, n =3) on the amount of Cu(II) acetate used. In the oxidation of cyclohexanol by the LTA—Cu(OAc)$_2$ system, the contribution of the decyclization reaction (evaluated from the sum of products obtained from B) increases proportionally to the increase in the content of Cu(II) acetate in the system. In the absence of the copper salt, which effectively

TABLE 2. Oxidation of Cycloalkanols by LTA—$Cu(OAc)_2$ System[a]

Cycloal-kanol	Ratio of cycloalkanol Pb(IV):Cu(II)	Conversion of cycloal-kanol, %	Yield of cycloal-kanol, %	Yield of oxidation products, %					B/C[b]
				(I)	(III)	(IV)	(VI)	(VIII)	
Cyclo-pentano	1:1:0,1	72	2	15	65	3	5	2	5,0
As above	1:2:0,1	98	8	10	59	2	5	2	6,8
Cyclo-hexxano	1:1:0[c]	48	21	63	+[d]	3	–	–	0,05
As above	1:1:0,05[e]	51	9	67	14	4	+	+	0,3
»	1:1:0,1	60	12	50	20	+	3	2	0,5
»	1:1:0,3	78	10	41	30	+	4	2	0,9
»	1:2:0,1	91	18	37	25	3	6	3	1,0

[a] 80°C, 30-60 min, alcohol – 0.01 mole, pyridine – 0.01 mole, benzene – 25 ml, conversion of LTA – 100%. Yield of products is given per converted alcohol.

[b] Molar ratio of products derived from radicals B (Σ(III), (IV), (VI), (VIII)) and C (I).

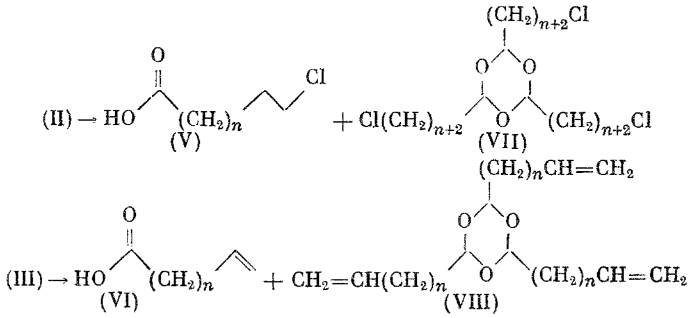
[c] Time of reaction 4 h.

[d] Detected in trace amounts.

[e] Time of reaction 1.5 h.

oxidizes radicals B, and thus plays the role of an interceptor, ω-alkenals are not formed. It should be stressed that under these conditions other ring cleavage products are practically not formed (see Table 2). Lead tetraacetate converts cyclohexanol preferentially into cyclohexanone, i.e., it oxidizes radicals C and does not react with radicals B, which because of this cyclize into A. The latter rearrange into C, and then cyclohexanone is formed from C. These results correspond to the data in [5], according to which 5-formylpentyl radicals can cyclize according to scheme B → A.

Under the reaction conditions, the oxidation of aldehydes (II) and (III) formed to the corresponding acids (V), (VI) and the trimerization of (II) and (III) into 1,3,5-trioxane (VII), (VIII) are inappreciable



$n = 2$ (a), 3 (b).

EXPERIMENTAL

The GLC analysis was carried out on the LKhM-8MD chromatograph in a nitrogen current, at a flow rate of 25 ml/min, using a flame-ionization detector and columns 2 m long and 3 mm in diameter with 15% FFAP and with 15% 1,2,3-tris[(β-cyanoethoxy)]propane on Chromatone N-AW-HMDS (0.16-0.20 mm). The yield of the products was determined by the internal standard method, taking into account the experimentally found correction coefficients. For preparative GLC, a copper column 2 m long and 10 mm in diameter was used with 15% 1,2,3-tris[(β-cyanoethoxy)]propane on Chromatone N-AW (0.20-0.25 mm), with carrier gas helium. The PMR spectra were run on the "Bruker WM-250" spectrometer, using $CDCl_3$ as solvent; the IR spectra were run on the UR-20 spectrophotometer in a thin layer or in a CCl_4 solution.

Lead tetraacetate (LTA) was obtained from Pb_3O_4 by the method in [6]. The content of Pb(IV) in the product obtained and its conversion in the oxidation reaction of alcohols was controlled iodometrically [7]. LTA with ≥ 97% of Pb(IV) was used. The initial cyclopentanol and cyclohexanol (grade "pure" preparations) were purified from admixture of cyclic ketones by treatment with $NaBH_4$, followed by flash distillation. $Cu(OAc)_2 \cdot H_2O$ and $LiCl \cdot H_2O$ (grade "pure" reagents) were calcined to remove water of crystallization. Benzene and pyridine were dried and distilled.

Oxidation of Secondary Cycloalkanols by LTA—LiCl System (general procedure). A mixture of 0.01 mole of the alcohol, 0.02 mole of LTA, 0.05 mole of LiCl and 0.01 mole of pyridine in 25 ml of benzene was stirred for 10-15 min at 65-70°C, and then it was cooled and filtered. The filtrate and ether extracts after the precipitate were washed and combined, and the yield of the reaction products and the conversion of the alcohol were determined by the GLC method. The experimental results are listed in Table 1. The conversion of LTA, controlled iodometrically, was 100% in all experiments. To isolate the ω-chloroalkanals (II), the combined filtrate was acidified by 10% HCl, washed with $NaHCO_3$ solution and water, dried over $MgSO_4$, and distilled. Cyclic ketone (I), saturated aliphatic aldehyde (IV), the ω-chlorocarboxylic acid (V), and substituted 1,3,5-trioxane (VII) were also identified in the reaction mixture by GLC, IR, and PMR spectroscopy methods. The overall yield of (IV), (V), and (VII) is $\sim$8%.

Oxidation of Cyclopentanol. The following compounds were obtained in the oxidation of cyclopentanol: a) 5-chloropentanal (IIa), bp 66-68°C (30 mm). Found: C 49.10; H 7.30; Cl 28.57%. C_5H_9OCl. Calculated: C 50.00; H 7.50; Cl 29.17%. IR spectrum (ν, cm^{-1}): 655 and 730 (CCl), 1715 (C=O), 2730 (CHO). PMR spectrum (δ, ppm): 1.75 m (4H, CH_2), 2.45 m (2H, $C\underline{H}_2$—CHO), 3.50 t (2H, CH_2Cl), 9.70 t (H, CHO); b) 5-chloropentanoic acid (Va), IR spectrum (ν, cm^{-1}): 1735 (C=O), 3300 (OH). PMR spectrum (δ, ppm): 1.75 m (4H, CH_2), 2.35 m (2H, $C\underline{H}_2$—COOH), 3.50 t (2H, CH_2Cl), 10.95 s (H, COOH); c) 2,4,6-tris(4-chlorobutyl)-1,3,5-trioxane (VIIa), PMR spectrum (δ, ppm): 1.55 m (6H, CH_2—C—O), 1.75 m (12H, CH_2), 3.50 t (6H, CH_2Cl), 4.85 t (3H, H—C—O).

Oxidation of Cyclohexanol. The following compounds were isolated as the result of the oxidation of cyclohexanol: a) 6-chlorohexanal (IIb), bp 75-80°C (10 mm). IR spectrum (ν, cm^{-1}): 650 and 725 (CCl), 1720 (C=O), 2730 (CHO). PMR spectrum (δ, ppm): 1.80 m (6H, CH_2), 2.40 m (2H, $C\underline{H}_2$—CHO), 3.50 t (2H, CH_2Cl), 9.75 t (H, CHO); b) 6-chlorohexanoic acid (Vb), IR spectrum (ν, cm^{-1}): 1735 (C=O), 3350 (OH). PMR spectrum (δ, ppm): 1.80 m (6H, CH_2), 2.30 m (2H, $C\underline{H}_2$—COOH), 3.50 t (2H, CH_2Cl), 10.90 s (H, COOH); c) 2,4,6-tris(5-chloroamyl)-1,3,5-trioxane (VIIb), PMR spectrum (δ, ppm): 1.60 m (6H, CH_2—C—O), 1.80 m (18H, CH_2), 3.50 t (6H, CH_2Cl), 4.80 t (3H, H—C—O).

Oxidation of Secondary Cycloalkanols by LTA—$Cu(OAc)_2$ System (general procedure). A mixture of alcohol, LTA, $Cu(OAc)_2$ and pyridine in benzene was vigorously stirred for 30-60 min at 80°C. The mixture was then cooled and filtered. The precipitate was washed with ether and analyzed iodometrically for its content of Pb(IV) [7]. The conversion of LTA was quantitative in all the experiments. The filtrate and the ether extracts were combined, and the amount of the reaction products and the conversion of the alcohol were determined by GLC. The results of the analysis are listed in Table 2. After the usual treatment of the reaction mixture (see the above procedure), the solvent was distilled, and the reaction products were isolated from the residue by either distillation or preparative GLC.

Oxidation of Cyclopentanol. The following compounds were obtained as the result of the oxidation of cyclopentanol: a) 4-pentenal (IIIa), IR spectrum (ν, cm^{-1}): 920, 1000 and 1642 (CH_2=CH), 1724, 2722 and 2822 (CHO). PMR spectrum (δ, ppm): 2.45 m (4H, CH_2), 5.00 m (2H, CH_2=C), 5.75 m (H, C=CH), 9.70 t (H, CHO), 2,4-DNPH, mp 112-114°C (alcohol). Found: C 49.10; H 4.61; N 20.95%. $C_{11}H_{12}N_4O_4$. Calculated: C 50.00; H 4.55; N 21.21%; b) 4-pentenoic acid (VIa), IR spectrum (ν, cm^{-1}): 1640 (C=C), 1740 (C=O), 3345 (COOH). PMR spectrum (δ, ppm): 2.40 m (4H, CH_2), 4.95 m (2H, CH_2=C), 5.70 m (H, C=CH), 11.05 s (H, COOH); c) 2,4,6-tris(but-3-enyl)-1,3,5-trioxane (VIIIa), PMR spectrum (δ, ppm): 1.60 m (6H, CH_2—C—O), 2.40 m (6H, CH_2), 4.60 t (3H, H—C—O), 4.95 m (6H, CH_2=C), 5.70 m (3H, C=CH).

Oxidation of Cyclohexanol. The following compounds were obtained in the oxidation of cyclohexanol: a) 5-hexenal (IIIb), IR spectrum (ν, cm^{-1}): 915, 1005 and 1640 (CH_2=CH), 1720, 2725 and 2830 (CHO). PMR spectrum (δ, ppm): 2.00 m (2H, CH_2), 2.40 m (4H, CH_2), 5.15 m (2H, CH_2=C), 5.90 m (H, C=CH), 9.25 t (H, COH); b) 5-hexenoic acid (VIb), IR spectrum (ν, cm^{-1}): 1635 (C=C), 1735 (C=O), 3300 (COOH). PMR spectrum (δ, ppm): 2.00 m (2H, CH_2), 2.30 m (4H, CH_2), 5.15 m (2H, CH_2=C), 5.90 m (H, C=CH), 11.00 s (H, COOH); c) 2,4,6-tris-(pent-4-enyl)-1,3,5-trioxane (VIIIb), PMR spectrum (δ, ppm): 1.65 m (6H, CH_2—C—O), 2.00 m (6H, CH_2), 2.35 m (6H, CH_2), 4.85 t (3H, H—C—O), 5.00 m (6H, CH_2=C), 5.95 m (3H, C=CH).

CONCLUSIONS

As the result of the reaction of cyclopentanol and cyclohexanol with the $Pb(OAc)_4$—LiCl and $Pb(OAc)_4$—$Cu(OAc)_2$ systems, ω-formylalkyl radicals $\dot{C}H_2(CH_2)_{n+1}CHO$ (n = 2, 3) are formed, which are oxidized by these systems into ω-chloroalkanals and ω-alkenals, respectively.

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α-KETO DERIVATIVES OF N-NITRAMIDES AND N-NITRAMINES

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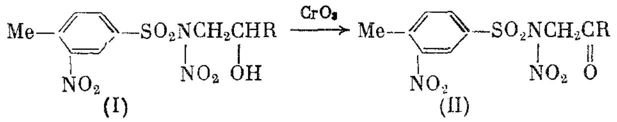
To synthesize and to investigate the properties of the previously unknown α-keto derivatives of N-nitramines and N-nitramides, we studied the oxidation of N-(β-hydroxyalkyl)-N-nitramine compounds [1] and the alkylation of salts of N-nitramides by halomethyl ketones.

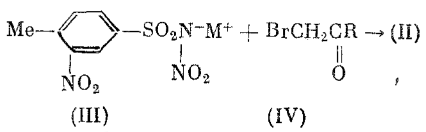
The oxidation of N-(β-hydroxyalkyl)-N-nitrosulfonamides by chromic anhydride in H_2SO_4 or AcOH leads to the formation of α-carboxyl or α-keto derivatives of N-nitramides (IIa-c), depending on whether in the initial compounds the hydroxyl group is attached to the primary or secondary carbon atom



R = H (Ia); OH (IIa); Me (Ib), (IIb), CH_2Cl (Ic), (IIc).

The yields of (II) are 78-98%, and thus the above reaction may serve as a convenient method for their synthesis.

For this purpose we can also use the reactions of salts of nitramides with bromomethyl ketones, as shown on the example of a reaction of potassium, silver and triethylammonium salts of m-nitro-p-toluenesulfonic acid N-nitramide (IIIa-c) with bromoacetone (IVa) or bromoacetophenone (IVb); however, the yields of (II) thus decrease to 25-35%, which is possibly explained by the formation of alkylation products at the oxygen atom of the nitramine group



R = Me (IIb), (IVa); Ph (IId); (IVb); M = K (IIIa), Ag (IIIb); $HNEt_3$ (IIIc).

The structure of (II) is confirmed by elemental analysis, IR and PMR spectra.

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