LITERATURE CITED

1. É. I. Troyanskii, I. V. Svitan'ko, and G. I. Nikishin, Izv. Akad. Nauk SSSR, Ser. Khim., 2318 (1982).
2. É. I. Troyanskii, I. V. Svitan'ko, and G. I. Nikishin, Izv. Akad. Nauk SSSR, Ser. Khim., 2751 (1982).
3. J. C. Little, A. R. Sexton, Yu-Lan Chang Tong, and T. E. Zurawic, J. Am. Chem. Soc., 91, 7098 (1969).
4. R. Kh. Freidlina and A. B. Terent'ev, in: Advances in Free-Radical Chemistry, Vol. 6, Heyden, London (1980), p. 1.
5. B. E. Nadin, Zh. Anal. Khim., 33, 836 (1978).
6. É. D. Venus-Danilova and V. F. Kazimirova, Zh. Obshch. Khim., 7, 2639 (1937).
7. Th. J. De Boer and H. J. Backer, Rec. Trav. Chim. Pays-Bas, 73, 229 (1954).
8. J. C. Little, Yu-Lan Chang Tong, and J. P. Heeschen, J. Am. Chem. Soc., 90, 7090 (1969).

OXIDATIVE CLEAVAGE OF TERTIARY CYCLOALKANOLS BY THE LEAD TETRAACETATE – METAL HALIDE SYSTEM*

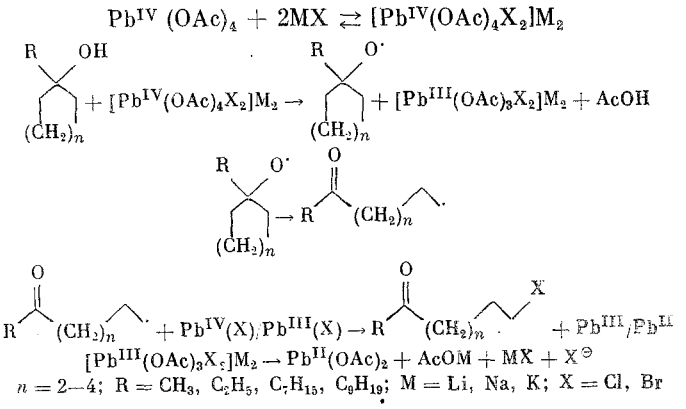
B. I. Kapustina, S. S. Spektor, and G. I. Nikishin

UDC 542.92:542.943.7:547.514.46

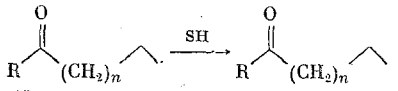
Reaction of tertiary cyclic alcohols with lead tetraacetate (LTA) affords oxoalkyl radicals $RCO(CH_2)_{n+1}\text{-}\dot{C}H_2$ (n = 1 – 4) [2-4]. These radicals are oxidized by the LTA–$Cu(OAc)_2$ system to ω-unsaturated ketones [2], by the LTA–KSCN system to ω-oxoalkyl thiocyanates [3], and on treatment with the LTA–AgOAc system these radicals recombine to give diketones [4].

We here examine the oxidation of tertiary cyclic alcohols with the LTA–group I metal halide (MX, where M = Li, Na, or K, and X = Cl or Br) system. The reaction is carried out in benzene with the addition of pyridine, which accelerates the oxidative reaction. In the first step, a complex of LTA with MX is probably formed, and this then reacts with the alcohol. Similar complexes $[K_2[Pb(OAc)_6]$ and $K_2[Pb(OAc)_4Cl_2]]$ have been prepared [5, 6].

The mechanism of the oxidative cleavage may be represented as follows



Initially, oxidation of the alcohol with the lead complex salt gives cyclic alkoxyl radicals. Reduction of Pb^{IV} to Pb^{III} may occur according to the equation shown in the Scheme, and also probably, to $[Pb^{III}(OAc)_4X]M_2$. The alkoxyl radicals then isomerize to oxoalkyl radicals. The latter are, for the most part, oxidized by Pb^{IV} or Pb^{III} to 1-haloalkanones, and to a very small extent they mediate removal of hydrogen from the H-donor (~ 1-2%)



* For the previous communication, see [1].

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Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 7, pp. 1541-1545, July, 1983. Original article submitted November 16, 1982.

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TABLE 1. Oxidation of 1-Ethylcyclopentanol with the LTA–MX System*

Ratio alcohol: LTA:MX	MX	Extent of reaction of alcohol, %	Yield of C_2H_5CO-$(CH_2)_4X$, % on alcohol reacted	Ratio alcohol: LTA:MX	MX	Extent of reaction of alcohol, %	Yiel of C_2H_5CO-$(CH_2)_4X$, % on alcohol reacted
1:2:5	LiCl	99	99	1:1:5	NaBr	69	99
1:2:5	NaCl	30	94	1:1:10		73	99
1:2:5	KCl	76	95	1:1.5:5		81	99
1:1:0.5	$CuCl_2$ †	75	52	1:2:5		98	98
1:1:5	LiBr	63	98	1:1:5	KBr	65	99
1:1:1	NaBr	21	95	1:2:5		97	99

* 80°C, 3-6 h, 0.01 mole of alcohol, 0.01 mole of pyridine, 25 ml of benzene; extent of reaction of LTA, 100%.

† 1-Heptene-5-one (34% on original alcohol) also identified.

TABLE 2. Oxidation of 1-Alkylcyclopentanols with the System LTA–LiCl*

Alkyl (R)	Extent of reaction of alcohol, %	Yield of RCO-$(CH_2)_4Cl$, % on alcohol reacted
CH_3	71	99
C_2H_5	68	98
C_7H_{15}	56	96
C_9H_{19}	50	90

* 80°C, 5 h, alcohol:LTA:LiCl: C_5H_5N = 1:1:5:1, benzene 25 ml; extent of reaction of LTA, 100%.

In Table 1 are given data on the cleavage of 1-ethylcyclopentanol by LTA–metal chloride (or bromide). The most efficient chloride in this reaction is LiCl. One reason for the high efficiency of LiCl as a component of the oxidative system is its higher solubility in benzene, as compared with NaCl and KCl. Lithium, sodium, and potassium bromides are equally reactive in the oxidation of alcohols by the system LTA–MBr; using a ratio of alcohol:LTA:MBr of 1:2:5, the yield of 1-bromoheptan-5-one was nearly quantitative with all of these bromides, and with a ratio of 1:1:5 it was 60-70%.

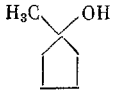
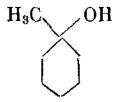
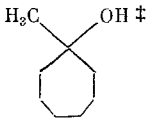
When the oxidant pair LTA–$CuCl_2$ was employed, from 1-ethylcyclopentanol there was obtained, in addition to 1-chloropentan-5-one, hept-1-ene-5-one, i.e., the 5-oxoheptyl radical reacted in two ways, by a substitution mechanism and by a deprotonation mechanism. It appears that $CuCl_2$ or its complex with LTA oxidizes the 5-oxoheptyl radical to the corresponding chloride. The Cu(I) which is formed in the reaction is converted by LTA into Cu(OAc)Cl, and perhaps partially to Cu(II) acetate, which oxidize the 5-oxoheptyl radical to the unsaturated ketone.

These findings are in accordance with the results of decarboxylation of valeric acid by the LTA–$CuCl_2$ pair, which affords a mixture of butyl chloride and 1-butene [7].

In the reaction of 1-alkylcycloalkanols with LTA–MX, the alkyl group exerts a screening effect, shown by the reduction in the extent of reaction of the alcohol in the homologous series from 1-methyl- to 1-nonylcyclopentanol with LTA–LiCl (Table 2).

The most reactive of the 1-methylcycloalkanols examined was 1-methylcyclopentanol (Table 3). As is the case with the oxidative systems LTA–$Cu(OAc)_2$ [2] and LTA–KSCN [3], the reactivities of tertiary cyclic alcohols in oxidative decyclization with LTA–metal halide decrease in the sequence $C_5 > C_7 > C_6$, β-fragmentation of the alkoxyl radical being virtually the sole route of oxidation. Only in the case of 1-methylcyclopentanol is 1-methyl-1,4-epoxycyclopentane also formed.

TABLE 3. Oxidation of 1-Methylcycloalkanols by LTA–MX*

Alcohol	MX	Extent of reaction of alcohol, %	Yield of CH_3CO-$(CH_2)_{n+1}CH_2X$, % †	
	LiCl	71	70	$n=2$
	LiBr	67	65	
	NaBr	71	70	
	KBr	66	65	
	LiCl	60	57	$n=3$
	LiBr	48	47	
	NaBr	63	62	
	KBr	57	55	
	LiCl	65	48	$n=4$
	LiBr	55	39	
	NaBr	68	51	
	KBr	60	43	

* 80°C, 3 h (for MBr) or 5 h (for LiCl), alcohol: LTA:MX:C_5H_5N = 1:1:5:1, benzene 25 ml, extent of reaction of LTA 100%.

† On alcohol taken.

‡ In addition, 10-15% of 1-methyl-1,4-epoxycyclopentane was formed.

TABLE 4. Properties of 1-Haloalkanes

Ketone	Bp, °C (mm Hg)	n_D^{20}	Molecular formula	Found/calculated, %		
				C	H	Hal
$CH_3CO(CH_2)_4Cl$	78(10)	1,4476	$C_6H_{11}OCl$	53,84 / 53,70	8,18 / 8,21	25,82 / 26,20
$CH_3CO(CH_2)_5Cl$	108(20)	1,4479	$C_7H_{13}OCl$	56,57 / 56,74	8,81 / 8,78	23,67 / 23,70
$CH_3CO(CH_2)_6Cl$	50(0,6)	1,4504	$C_8H_{15}OCl$	59,00 / 59,10	8,93 / 9,25	22,30 / 21,90
$C_2H_5CO(CH_2)_4Cl$	89(15)	1,4463	$C_7H_{13}OCl$	56,71 / 56,74	8,60 / 8,78	23,62 / 23,70
$C_7H_{15}CO(CH_2)_4Cl$	89(0,5)	1,4549	$C_{12}H_{23}OCl$	66,00 / 66,10	11,00 / 10,50	15,98 / 16,00
$C_9H_{19}CO(CH_2)_4Cl$	176(10)	–	$C_{14}H_{27}OCl$	67,94 / 68,40	10,85 / 10,98	14,58 / 14,20
$CH_3CO(CH_2)_4Br$	83(6)	1,4700	$C_6H_{11}OBr$	40,31 / 40,22	6,27 / 6,14	44,67 / 44,92
$CH_3CO(CH_2)_5Br$	70–72(1)	1,4707	$C_7H_{13}OBr$	43,30 / 43,60	7,07 / 6,74	41,49 / 41,50
$CH_3CO(CH_2)_6Br$	79–80(1)	1,4768	$C_8H_{15}OBr$	46,00 / 46,40	7,13 / 7,25	39,24 / 38,70
$C_2H_5CO(CH_2)_4Br$	91–92(6)	1,4702	$C_7H_{13}OBr$	43,96 / 43,60	6,85 / 6,74	41,00 / 41,50

To judge from the amounts of the products (A) and (B), which do not undergo further reactions, the ratio of the rate constants for the β-breakdown of the alkoxyl radical and its rearrangement with 1,5-migration of the H atom, is $K_E/K_R = 4$.

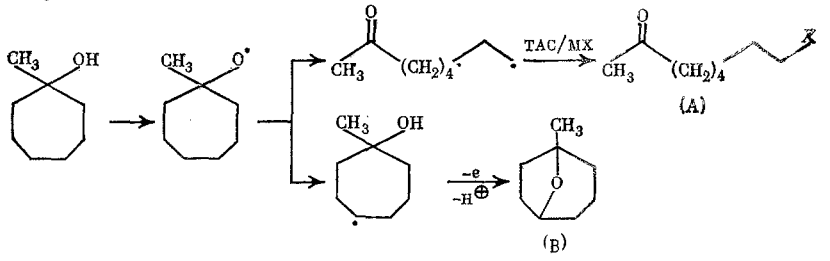


TABLE 5. IR and Mass Spectra of 1-Haloalkanes

Ketone	IR spectrum, cm^{-1}	Mass spectrum, m/z
$CH_3CO(CH_2)_4Cl$	1720(C=O), 653 and 730(CCl)	134(M)+, 119(M−CH_3)+, 98(M−HCl)+, 91(M−CH_3CO)+, 85($CH_3CO(CH_2)_3$)+, 71($CH_3CO(CH_2)_2$)+, 57(CH_3COCH_2)+, 43(CH_3CO)+
$CH_3CO(CH_2)_5Cl$	1715(C=O), 658 and 725(CCl)	–
$CH_3CO(CH_2)_6Cl$	1715(C=O), 650 and 730(CCl)	162(M)+, 147(M−CH_3)+, 139(M−CH_3CO)+, 126(M−HCl)+, 57(CH_3COCH_2)+, 43(CH_3CO)+
$C_2H_5CO(CH_2)_4Cl$	1715(C=O), 658 and 730(CCl)	148(M)+, 119(M−C_2H_5)+, 112(M−HCl)+, 91(C_4H_8Cl)+, 57(C_2H_5CO)+, 29(C_2H_5)+
$C_7H_{15}CO(CH_2)_4Cl$	1720(C=O), 655 and 730(CCl)	–
$C_9H_{19}CO(CH_2)_4Cl$	1720(C=O), 655 and 725(CCl)	246(M+), 210(M−CH_3)+, 161($C_9H_{15}COCH_2$)+, 127(C_9H_{19})+, 119(M−C_9H_{19})+
$CH_3CO(CH_2)_4Br$	1710(C=O), 563 and 647(CBr)	178(M)+, 163(M−CH_3)+, 135(M−CH_3CO)+, 121(C_3H_7Br)+, 107(C_2H_5Br)+, 71($CH_3CO(CH_2)_2$)+, 43(CH_3CO)+
$CH_3CO(CH_2)_5Br$	1710(C=O), 566 and 650(CBr)	–
$CH_3CO(CH_2)_6Br$	1720(C=O), 560 and 655(CBr)	206(M)+, 191(M−CH_3)+, 163(M−CH_3CO)+, 149($C_5H_{11}Br$)+, 121(C_3H_7Br)+, 71($CH_3CO(CH_2)_2$)+, 43(CH_3CO)+
$C_2H_5CO(CH_2)_4Br$	1715(C=O), 570 and 650(CBr)	192(M)+, 163(M−C_2H_5)+, 135(M−C_2H_5CO)+, 121(C_3H_7Br)+, 71($C_2H_5COCH_2$)+, 57(C_2H_5CO)+

The 1-haloalkanones obtained were isolated preparatively. Their structures were confirmed by IR spectroscopy, and PMR and mass spectrometry.

EXPERIMENTAL

GLC analyses were carried out on an LKhM-8MD chromatograph in a stream of nitrogen (24 ml/min), using a flame ionization detector and a column of length 1-2 m and diameter 15 mm, with 15% FFAP and 15% Tween-85 on Chromosorb W (60-80 mesh). Yields of products were determined using an internal standard with allowance for experimentally determined correcting factors. PMR spectra were obtained on Tesla BS-497 (100 MHz) and Bruker WM-250 (250 MHz) spectrometers, internal standard HMDS, and mass spectra on a Varian MAT-CH-6 instrument. IR spectra were obtained on a UR-20 spectrophotometer in thin layers or in solution in CCl_4. The initial 1-alkylcycloalkanones were obtained from the cycloalkanones and alkylmagnesium halides. Lead tetraacetate (LTA) was obtained from red lead (Pb_3O_4) as described in [8]. The purity of the LTA and the extent of its reaction in the oxidation of the alcohols were determined iodometrically [9]. NaCl, KCl, $LiCl \cdot H_2O$, $CuCl_2$, NaBr, KBr, LiBr were commercial materials, chemically pure grade. Lithium chloride was ignited to drive off water of crystallization. Benzene and pyridine were dried over Na and caustic alkali, and redistilled.

Oxidation of Tertiary Cycloalkanols with the LTA–Metal Halide System (General Method). A mixture of the alcohol, LTA, metal halide, and pyridine in benzene was stirred vigorously at 80°C until all the Pb^{IV} had been converted into Pb^{II}, when the reddish-brown color changed to yellow (3-6 h, depending on the salt used). The mixture was then cooled and filtered. The solid was washed with ether, and analyzed iodometrically for its Pb^{IV} content [9]. The filtrate and ethereal extracts were washed with a 10% solution of HCl, $NaHCO_3$ solution, and water, dried over $MgSO_4$, and the solvent distilled off. The extent of reaction of the alcohol and the yields of products were determined by GLC on the residue. The main product was the 1-chloro (or bromo)-ketone. In addition, in all the experiments, the saturated aliphatic ketone (1-2%) was identified by GLC (using a marker), IR and GC-MS. The experimental results are shown in Tables 1-5.

CONCLUSIONS

The oxoalkyl radicals $RCO(CH_2)_{n+1}\dot{C}H_2$ (n = 2-4) generated from five-, six-, and seven-membered 1-alkylcycloalkanols by treatment with an oxidizing system (lead tetraacetate–metal halide) are quantitatively oxidized to 1-haloalkanones.

LITERATURE CITED

1. G. I. Nikishin, N. I. Kapustina, S. S. Spektor, and E. P. Kaplan, Izv. Akad. Nauk SSSR, Ser. Khim., 2383 (1979).
2. G. I. Nikishin, N. I. Kapustina, S. S. Spektor, and E. P. Kaplan, Izv. Akad. Nauk SSSR, Ser. Khim., 1548 (1979).
3. S. S. Spektor, N. I. Kapustina, E. P. Kaplan, and G. I. Nikishin, Izv. Akad. Nauk SSSR, Ser. Khim., 1140 (1979).
4. G. I. Nikishin, S. S. Spektor, and N. I. Kapustina, Izv. Akad. Nauk SSSR, Ser. Khim., 1172 (1981).
5. K. C. Malhorta and D. S. Katoch, Indian J. Chem., A14, 528 (1976).
6. N. W. Alcock, V. M. Tracy, and T. C. Waddington, J. Chem. Soc., Dalton Trans., 2238, 2243 (1976).
7. J. K. Kochi, J. Am. Chem. Soc., 87, 2500 (1965).
8. L. Fieser, Reagents for Organic Synthesis, Vol. 3, (Wiley).
9. M. S. Kharasch, M. N. Friedlander, and W. Urry, J. Org. Chem., 16, 533 (1951).

TELOMERIZATION OF 1-HEXENE WITH METHYL CHLOROACETATE AND METHYL PROPIONATE

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UDC 66.095.2:547.313.6

The telomerization of 1-hexene with esters of monocarboxylic acids, and the identification of the resulting telomers, has not been described in the literature. Comparison of the results obtained for the telomerization of ethylene and propylene with esters of monocarboxylic acids shows that only with propylene does 1,3-migration of hydrogen occur in the first growing radical [1]

$$R\dot{C}HCH_2CHXCO_2CH_3 \xrightarrow{1,3\text{-H}} RCH_2CH_2\dot{C}XCO_2HC_3$$
$$R = CH_3;\ X = H,\ Cl,\ CH_3.$$

The use of 1-hexene as the monomer enables the influence of the monomer, and in particular the length of the alkyl substituent R, on the course of the telomerization to be assessed. The reaction takes the following course

$$XCH_2CO_2CH_3(DH) \xrightarrow{TBP} X\dot{C}HCO_2CH_3$$
$$X\dot{C}HCO_2CH_3 + RCH{=}CH_2 \rightarrow \underset{(A)}{R\dot{C}HCH_2CHXCO_2CH_3}$$
$$(A) \xrightarrow{DH} \underset{(T_1),\ (P_1)}{RCH_2CH_2CHXCO_2CH_3}$$
$$(A) + RCH{=}CH_2 \xrightarrow{DH} \underset{(T_2),\ (P_2)}{RCH_2CH_2\underset{\underset{R}{|}}{C}HCH_2CHXCO_2CH_3}$$
$$(A) \xrightarrow{1,3\text{-H}} \underset{(B)}{RCH_2CH_2\dot{C}XCO_2CH_3}$$
$$(B) + RCH{=}CH_2 \rightarrow R\dot{C}HCH_2\underset{\underset{RCH_2CH_2}{|}}{C}XCO_2CH_3 \xrightarrow{DH} \underset{(T_2'),\ (P_2')}{(RCH_2CH_2)_2CXCO_2CH_3}$$
$$X = CH_3(T),\ Cl\ (\Pi);\ R = C_4H_9;\ TBP\ \text{—tert-butyl peroxide.}$$

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Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 7, pp. 1546-1551, July, 1983. Original article submitted October 26, 1982.

0568-5230/83/3207-1398 $07.50

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