Pb(OAc)₄-Cu(OAc)₂-MEDIATED OXIDATION OF 1-ALKYLCYCLOHEXANOLS; β -DECOMPOSITION OF 1-ALKYLCYCLOALKOXY RADICALS

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The lead tetraacetate (LTA)-copper diacetate-mediated oxidation of l-methylcycloalkanols produces l-methylcycloalkoxy radicals which, as a result of β -decomposition along the C¹-C² bond, are converted into oxoalkyl radicals CH₃CO(CH₂)_nCH₂. The latter are quantitatively oxidized by Cu(II) to give ω -unsaturated ketones [1].

The present paper describes the influence of the size and structure of the alkyl group on the oxidation of 1-alkylcyclopentanols and cyclohexanols and the utilization of this reaction for the synthesis of ω -unsaturated ketones. The oxidations were carried out at 80°C in benzene in the presence of pyridine with a mole ratio of Pb(IV):Cu(II) = 10:1.

Generally, the oxidation of tertiary cycloalkanols produces cycloalkoxy radicals which may decompose via two pathways — ring opening and generation of oxoalkyl radicals (reaction α), or elimination of an alkyl radical and formation of a cycloalkanone (reaction b). The formation of cycloalkoxy radicals was confirmed by ESR. The oxidation of 1-methylcyclohexanol with Pb(OAc), in benzene at 20°C in the presence of the spin trapping agent C₆H₅CH = N(O)C• (CH₃)₃ (FBN) gave an ESR spectrum consisting of a triplet of doublets ($\alpha_{\rm N}$ = 14.0, $\alpha_{\rm H}\beta$ = 1.90e), corresponding to the structure of the adduct of the alkoxy radical with FBN [2]:



n=4;5.

Since the radicals $RCO(CH_2)_{\Pi-1}CH_2$ are transformed quantitatively into unsaturated ketones (A), and, furthermore, since the two products, both cyclic and unsaturated ketones, do not undergo any further reactions, their amounts may be used to determine the rate ratios for pathways α and b (see Tables 1 and 3).

The direction of β -decomposition of the cycloalkoxy radicals is affected primarily by the structural characteristics of the alcohol. 1-Alkylcyclohexanols which do not possess α branching in the alkyl groups are transformed predominantly into unsaturated ketones according to pathway α , i.e., β -fragmentation of the alkoxy radical occurs with ring opening. β -Fragmentation with elimination of an alkyl group (R·) and formation of cyclohexanone (pathwayb) occurs with less frequency. In the case of 1-methylcyclohexanol the contribution due to this pathway is negligible; the A/B product ratio is 25 (Table 1). In the oxidation of 1-ethylcyclohexanol decomposition of the intermediate alkoxy radical according to pathway b occurs to the extent of \sim 15%; the A/B ratio is 7. An A/B ratio = 7 is also found for the thermal decomposition of 1-ethylcyclohexyl hypochlorite [3]. An increase in the length of the nalkyl substituent up to C₈ increases the A/B ratio to 14.

Table 2 presents the relative rates (k_{rel}) for the elimination of alkyl radicals (R[•]) in the decomposition of tertiary cycloalkoxy radicals. These results agree qualitatively with the relative rates for the elimination of primary alkyl radicals in the decomposition of R¹R²R³CO[•] $(k_{rel}$ in parentheses): CH₃ (0.003), C₂H₅(1), C₃H₇ (0.65), C₄H₉(0.43) [4]. The markedly smaller rate difference for the elimination of CH₃ and C₂H₅ in our study compared with that in [4] may apparently be attributed to the fact that the direction of β -decomposition of alkoxy radicals depends upon the conditions of their generation. Thus, in the decomposition

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Puparia		Conversion of	Reaction produ	icts, yield, † %	
ment number	R	alcohol, mole/ mole LTA	unsaturated ketone (A)	cyclohexanone (B)	A /B
1 2 3	CH ₃ C ₂ H ₅ C ₃ H ₇	0,40 0,40 0,38	87,5 87,5 89,5	3,5 12,5 9,0	25 7 10
4 5 6	$\begin{array}{c} C_4H_9\\ C_6H_{13}\\ C_8H_{17} \end{array}$	0,36 0,32 0,28	50,0 53,0 50,0	5,5 4,5 3,5	9 12 14
7 8 9	(CH ₃) 2CH (CH ₃) 3C Цикло-C6H ₁₁	0,34 0,32 0,44	17,5 1,5 32,0	79,5 94,0 61,5	0,2 0,02 0,5
10 11 12	C_6H_5 $C_6H_5CH_2$ $CH_2=CHCH_2$	0,20 0,22 0.88	75	5 95,5 95,5	15
13 14	CH = C CH ₃ COO(CH ₂) ₃	0,04 0,26	81,0	98 11,5	7

TABLE 1. LTA-Cu(OAc)_2-Mediated Oxidation of 1-R-Cyclohexanols*

*80°C, 2 h, 0.02 moles of alcohol, 0.01 moles LTA, 0.01 moles pyridine, 0.001 moles $Cu(OAc)_2$, 25 ml benzene; conversion of LTA = 100%.

[†]Based on reacted alcohol.

[‡]2-Alky1-5-pentamethylenetetrahydrofuran is also formed: experiment 4, 40%; experiment 5, 40.5%; experiment 6, 43%.

TABLE 2. Relative Rates for the Elimination of Alkyl Radicals

 $(\ensuremath{\mathbb{R}}^{\,\boldsymbol{\cdot}})$ in the Decomposition of Cycloalkoxy Radicals

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R'	CH3	C_2H_5	C3H7	C4H9	C_6H_{13}	C ₈ H ₁₇	(CH ₃) ₂ CH	(CH₃) 3C
^k rel	0,3	1	0,7	0,8	0,6	0,5	~35	~350

of tert-butyl hydroperoxide at 25°C in the presence of metal salts of variable valence, either tert-butyl alcohol (H atom abstraction) or acetone and a methyl radical (β -fragmentation) is formed; the ratio of these products varies with the salt used: $[(CH_3)_3COH]/[(CH_3)_2CO]$ for TiCl₃ is 0.59; for FeSO₄, 1; for CrCl₂, 4.3; and for K₄Fe(CN)₆, 10 [3, 5].

When a primary alkyl group in a 1-alkylcyclohexanol is replaced with a secondary or tertiary group, β -fragmentation of the intermediate alkoxy radical occurs without ring opening, i.e., according to pathway b. Alkoxy radicals obtained from isopropyl- or tert-butylcyclohexanol decompose primarily with formation of cyclohexanone; for isopropylcyclohexanol the A/B ratio is 0.2, and for tert-butylcyclohexanol the A/B ratio is 0.02 (see Table 1). A comparison of the relative rates for elimination of CH₃CH₂, (CH₃)₂CH, and (CH₃)₃C radicals reveals that β -decomposition according to pathway b occurs with increasing frequency as the stability of the departing radical increases (cf. Table 2).

In the oxidation of 1-alkylcyclohexanols containing n-alkyl groups longer than three C atoms the initially formed alkoxy radical can react along a third pathway — rearrangement with 1,5-hydrogen migration from the alkyl group. Thus, in the oxidation of 1-buty1-, 1-hexy1-, and 1-octylcyclohexanols, 2-alky1-5-pentamethylenetetrahydrofurans are formed along with the unsaturated ketones.



TABLE 3. LTA-Cu(OAc)₂-Mediated Oxidation of 1-Alkylcyclopentanols*

Fyneria		Conversion	Reaction prod	ucts, yield,† %	
ment number	R	of alcohol, mole/mole of LTA	unsaturated ketone (A)	cyclopenta- none (B)	A /B
15 16 17 18 19 20 21	$\begin{array}{c} CH_{3} \\ C_{2}H_{5} \\ C_{7}H_{15} \\ (CH_{3})_{2}CH \\ CH_{2} = CHCH_{2} \\ C_{6}H_{13}C = C \\ CH = C \end{array}$	0,80 0,82 0,72 0,70 0,94 0,42 0,40	91,0 94,0 97,0 85,5 - 71,5 -	0,25 0,60 0,30 8,5 94,0 19,0 85,0	>350 >150 >300 10 - 3,8 -

*80°C, 2 h, 0.02 moles of alcohol, 0.01 moles LTA, 0.01 moles 0.01 moles pyridine Cu(OAc)₂, 25 ml benzene; conversion of LTA, 100%. [†]Based on reacted alcohol.

In the present study ring cleavage of the alkoxy radical and its rearrangement occurred at about the same rate. 1,5-Hydrogen migration does not take place from the primary C atom in the oxidation of 1-propylcyclohexanol, since this would result in the formation of a primary alkyl radical.

Aromatic substituents in the 1-position of cyclohexanols exert varying effects on the β decomposition of cycloalkoxy radicals. If as a result of β -fragmentation a relatively stable benzylic radical is generated, then pathway b predominates. In the oxidation of 1-benzylcyclohexanol it was not possible to detect the ring cleavage product; the only products formed were cyclohexanone, benzyl acetate, and, in very low yield, dibenzyl. In the case of 1-phenylcyclohexanol oxidation only the unsaturated ketone was obtained, and elimination of the phenyl radical for all practical purposes did not occur.

An allylic substituent exerts a very strong influence on both the rate and direction of oxidation; 1-allylcycloalkanols react with LTA-Cu(OAc)₂ at a markedly greater rate than 1- alkylcycloalkanols (see Tables 1 and 3). At 20°C the reaction is complete within a few minutes; under the same conditions 1-alkylcycloalkanols are practically inert toward oxidation. The products of the oxidation are cycloalkanone and allyl acetate. It is apparent that in the case of 1-allylcycloalkanols oxidation of the alcohol occurs via a synchronous two-electron transfer mechanism without the formation of intermediate radicals.



Another factor which governs the oxidative stability of cycloalkanols is the ring size of the substrate. In the present study 1-alkylcyclohexanols were oxidized ca. two times more slowly than 1-alkylcyclopentanols. This conclusion is derived from data for both the degree of conversion of the alcohols and the yields of oxidation products obtained under standard conditions. The analytical results were obtained as a result of a competitive reaction study (experiment 22).

In the case of 1-alkylcyclopentanol oxidation only one direction of β -decomposition, namely ring opening, is almost always observed, regardless of the size or structure of the alkyl substituent. Thus, in the oxidation of 1-heptylcyclopentanol the cyclic ether, which is observed in the reaction of tertiary cyclohexanols with a long-chain n-alkyl group, is not formed. Furthermore, cyclopentanone appears in significant yield only in the reaction of 1isopropylcyclopentanol with LTA-Cu(OAc)₂. The relative rate of ring opening vs oxidation to cyclopentanone in this case is 10:1 (see Table 3). A similar relative rate (14:1) was obtained in the thermal decomposition of 1-isopropylcyclopentyl hypochlorite [3].

1-Ethynylcyclopentanol and 1-ethynylcyclohexanol are practically inert to oxidation by Pb(IV), apparently due to complex formation between the alcohols and Cu(II) ions [6]. Earlier we had shown that tertiary cycloalkanols are not significantly oxidized (5-10% conversion) by LTA in the absence of copper salts [1]. Evidence for the formation of complexes between 1-ethynylcycloalkanols and Cu(II) comes from the fact that acetylenic alcohols containing non-

xperiment		ر • •		2	und, %		Calcu	lated. %
number	Unsaturated ketone	(b, mm Hg)	8 ² 0	σ	Н	Molecular formula	υ	H
Ŧ	CH ₃ CO (CH ₂) ₃ CH=CH ₂	40(10)	1,4344	. 74,69	10,80	C ₇ H ₁₂ O	75,00	10,70
ଷ	C ₂ H ₅ CO (CH ₂) ₃ CH=CH ₂	37-38(9)	1,4360	75,95	11,08	C ₈ H ₁₄ O	76,30	11,10
ന	$C_{3}H_{7}CO(CH_{2})_{3}CH=CH_{2}$	60(8)	1,4372	77,25	11,36	$C_{9}H_{10}O$	77,80	11,40
10	$C_6H_5CO(CH_2)_3CH=CH_2*$		ł	1	ł	1	1	ſ
15	$CH_{s}CO(CH_{2})_{2}CH=CH_{2}$	130	1,4211	72,99	10,10	C6H100	73,60	10,20
16	C ₂ H ₅ CO (CH ₂) ₂ CH=CH ₂	88-89(10)	1,4265	74,37	10,51	C7H120	75,00	10,70
17	$C_{7}H_{15}CO(CH_{2})_{2}CH = CH_{2}$	105 - 108(7)	1,4430	80,48	12,23	C12H22O	79,50	12,06

Ketones
w-Unsaturated
of
Characteristics
4.
TABLE

٦ • ·/~ 177/ ر *Isolated as the dinitrophenylhydrazone derivative, mp 166° N 15.58. C18H18N4O. Calculated: C 61.00; H 5.10; N 15.82.

	Mass spectrum, m/z	2 M+; 69 [M-CH ₃ CO]+; 57 CH ₃ COCH ₂]+; 43 [CH ₃ CO]+	3 M+; 69 [M-C ₂ H ₅ CO]+, 57 [C ₂ H ₅ CO]+	0 M+; 85 [C ₈ H,COCH ₈]+; 71 [C ₈ H,CO]+; 99 [M-C ₃ H,CO]+; 43 [C ₈ H ₇]+	$ \begin{array}{l} M + : 125 \left[M - C_{9}H_{8} \right] + : 112 \left[M - C_{6}H_{6} \right] + : \\ 37 \left[M - C_{4}H_{9} \right] + : 85 \left[C_{4}H_{6}CO \right] + : \\ 39 \left[M - C_{4}H_{6}CO \right] + : 57 \left[C_{4}H_{6} \right] + : \\ 51 \left[C_{4}H_{7} \right] + : 43 \left[C_{6}H_{7} \right] + : 41 \left[C_{6}H_{5} \right] + \\ \end{array} $	2 M+; 113 [C ₆ H ₁₃ CO]+; 97 [M-C ₆ H ₁₃]+; 55 [C ₆ H ₁₃]+; 69 [M-C ₆ H ₁₃ CO] ⁺	I	0 M+; 97 [M-C ₃ H ₇]+; 71 [C ₃ H ₇ C0]+; 9 [M-C ₃ H ₇ C0]+; 43 [C ₃ H ₇]+
ed Ketones	PMR spectrum, 5, ppm	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	- 126	$ \begin{array}{cccc} 0.90 \ t & (3H, CH_3), 2, 30 \ m (6H, \\ CH_2 COCH_3, CH_2 C=C), 4, 95 \ m \\ (2H, C=CH_3), 5, 75m (H, CH=C) \end{array} $	1	$\begin{array}{cccc} 0.95 \ t & (3H, CH_3), 2,35 \ m & (6H, \\ CH_2 COCH_3, CH_2 C=C), 4,85 \ m \\ (2H, C=CH_3), 5,60 \ m(H, CH=C) \end{array} \right \begin{array}{c} 182 \\ 82 \\ 82 \\ 182 \\ $	0.90 t (3H, CH ₃), 2,40 m (6H, CH ₂ COCH ₂ , CH ₂ C=C), 4,85 m (2H, C=CH ₂), 5,60 m (H, CH=C)	14(
w-Unsaturat	$ \begin{array}{c} \mathbb{R} \text{ spectrum} \\ \nu \text{ c=0} \\ \nu \text{ c=C} \\ \nu \text{ cm}^{-1} \end{array} $	1720 1645 and 3090	1710 1640 and 3080	1715 1650 and 3080	1705 1645 and 3075	1715 1645 and 3080	1710 1640 and 3075	1720 1645 and 3080
. IR, PMR, and Mass Spectra of	Unsaturated ketone	CH ₃ COCH ₂ CH ₂ CH ₂ CH=CH ₂	$CH_{3}CH_{2}COCH_{2}CH_{2}CH_{2}CH = CH_{2}$	CH ₃ CH ₂ CH ₂ COCH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂	CH ₃ (CH ₂) ² CH ₂ COCH ₂ CH ₂ CH ₂ CH=CH ₂	CH ₃ (CH ₂),CH ₂ COCH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂	CH ₃ (CH ₂) 6CH ₂ COCH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂	(CH ₃) ₂ CHCOCH ₂ CH ₂ CH ₂ CH ₂ CH=CH ₂
TABLE 5	Experi- ment number	4	62	r.	7	ۍ. ۲	G	2

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8	(CH ₃) 3CCOCH ₂ CH ₂ CH ₂ CH ₂ CH=CH ₂	1710 1645 m 3080	I	154 M ⁺ ; 97 [M-C ₄ H ₉] ⁺ ; 85 [C ₄ H ₉ CO] ⁺ ; 57 [C ₄ H ₉] ⁺
6	Cyclo C ₆ H ₁₁ COCH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂	1720 1645 and 3075	2,30 m (4H, COCH ₃ , CH ₂ C=C), 4,90 m (2H, C=CH ₂), 5,65 m (H, CH=C)	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
10	C ₆ H ₅ COCH ₂ CH ₂ CH=CH ₂	1695 1650 and 3080 700 and 745 (C ₆ H ₅)	$\begin{array}{c} 2,35 \mbox{m} (4H, \mbox{COCH}_3, \mbox{CH}_2 \mbox{CH}_2 \mbox{C}), \\ 5,00 \mbox{m} (2H, \mbox{C} \mbox{C} \mbox{H}_3), \\ 5,95 \mbox{m} \mbox{m}, \\ (H, \mbox{CH} \mbox{C} \mbox{C}), \\ 7,90 \mbox{m}, \mbox{(5H} \mbox{C}_8 \mbox{H}_3) \end{array}$	174 M+; 105 [C ₆ H ₅ CO]+; 77 [C ₆ H ₅]+; 51 [C ₆ H ₃]+; 39 [C ₃ H ₃] ⁺
14	CH ₃ COO(CH ₂) ₂ CH ₂ COCH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂	1710 1645 and 3080 1740 (0-C=0)	ł	198 M+; 138 [M-CH ₃ COOH]+; 112 [M-CH ₃ COO (CH ₂) ₂ CH]+; 97 [CH ₂ =CH (CH ₂) ₃ CO]+; 69 [C ₅ H ₉]+; 55 [C ₄ H ₇] ⁺ ; 43 [CH ₃ CO]+; 41 [C ₃ H ₅]+
15	CH ₃ COCH ₂ CH ₂ CH=CH ₂	1720 1645 and 3080	2,00 \$ (3H, CH ₃ CO), 2,30 m (4H, COCH ₂ , CH ₂ C=C), 5,00m (2H, C=CH ₂), 5,70 m (H, CH=C)	98 M+; 55 [M-CH ₃ CO]+; 43 [CH ₃ CO]+
16	CH ₃ CH ₂ COCH ₂ CH ₂ CH=CH ₂	1710 1640 and 3080	1,00 t $(3H, CH_3)$, 2,30 m $(6H, CH_2COCH_2CH_2C=C)$, 4,95 m $(2H, C=CH_2)$, 5,70 m $(H, CH=C)$	112 M+; 71 [C ₂ H ₅ COCH ₂]+; 57 [C ₂ H ₅ CO]+; 55 [M-C ₂ H ₅ CO]+
17	$CH_{3}(CH_{2})_{5}CH_{2}COCH_{2}CH_{2}CH=CH_{2}$	1720 1645 and 3085	0;90 t (3H, CH ₃), 2,40m (6H, CH ₂ COCH ₂ CH ₂ C=C), 5,00 m(2H, C=CH ₂), 5,60 m (H, CH=C)	182 M ⁺ ; 127 [C ₇ H ₁₈ C0] ⁺ ; 99 [C ₇ H ₁₈] ⁺ ; 88 [M-C ₇ H ₁₈] ⁺ ; 55 [M-C ₇ H ₁₅ C0] ⁺
18	(CH ₃) ₂ CHCOCH ₂ CH ₂ CH ₂ CH=CH ₂	1710 1645 and 3085	I	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
20	$CH_3(CH_2)_5C=CCOCH_2CH_2CH=CH_2$	1680 1645 and 3085 2215 (C=C)	0.95 t (3H, CH ₃), $2,45 \text{ m}$ (4H, COCH ₂ CH ₂ C=C), 4,90 m (2H, C=CH ₂), 5,70 m (H, CH=C)	1

terminal (internal) C≡C triple bonds undergo LTA—Cu(OAc)₂-mediated oxidation in a manner analogous to 1-aklylcycloalkanols.

The oxidation products were separated on a preparative scale. Their structures were determined by physicochemical methods of analysis. The characteristics of the ω -unsaturated ketones are presented in Tables 4 and 5.

The oxidative ring cleavage of tertiary cyclic alcohols described herein by us constitutes a new method for the synthesis of ω -unsaturated ketones, which may be obtained in 50-95% yield.

EXPERIMENTAL

GLC analyses were performed on a LKhM-8MD chromatograph (N₂ carrier gas, 24 m1/min) equipped with a flame ionization detector; the column (2-3 m long and 3-mm diameter) contained 15% FFAP and 15% TVIN 85 on Chromosorb W (60-80 mesh). Yields of products were determined using the internal standard method with experimentally determined coefficients. IR spectra were taken on a UR-20 spectrophotometer on CC14 solutions or neat phases. PMR spectra were recorded on Varian DA-60-IL (60 MHz) and Tesla BS-497 (100 MHz) spectrophotometers with HMDS as internal standard. Mass spectra were obtained on Varian MAT-111 (GN OM) and Varian MAT CH-6 spectrometers. Starting alcohols (bp, °C/p, mm Hg given in parentheses): 1-methy1- (53/15); 1-ethy1- (156-158); 1-hepty1- (112/5); 1-isopropy1- (70-72/10); 1-ally1 cyclopentanol (173-175) and 1-methyl- (67-68/20); 1-ethyl- (77-78/25); 1-propyl- (71-72/10); 1-buty1- (89/10); 1-hexy1- (89-90/1); 1-octy1- (91-96/4); 1-isopropy1- (175-178); 1-tertbuty1- (63-64/13); 1-cyclohexy1- (78-79/2); 1-pheny1- (98-100/0.5); 1-benzy1- (94/1); 1-ally1cyclohexanol (183-186) were obtained by treatment of the corresponding cycloalkanones with the appropriate Grignard reagents. 1-(1'-Octyny1)cyclopentanol was synthesized according to [7]. 1-Ethynylcyclopentanol was prepared from cyclopentanone, acetylene, and NaNH₂ [8]. 1-(3'-Acetoxypropyl)cyclohexanol was obtained by the free radical addition reaction of cyclohexanol with allyl acetate in the presence of di-tert-butyl peroxide at 150°C. The purity of the alcohols was determined by means of GLC and elemental analyses and, in some cases, by means of their IR and PMR spectra. 1-Ethynylcyclohexanol and reagent grade Pb(OAc)4 were obtained according to [9]. The purity of the starting LTA and its conversion during the course of the oxidation reactions were determined iodometrically. Cu(OAc)₂·H₂O (reagent grade) was oven dried to remove the water of crystallization. Benzene and pyridine were dried and distilled prior to use.

LTA-Cu(OAc)₂-Mediated Oxidation of 1-R-Cycloalkanols. (General method, experiments 1-11, 13-18, 20, and 21). A mixture of 0.02 moles of alcohol, 0.01 moles LTA, 0.01 moles pyridine, 0.001 moles Cu(OAc)₂, and 25 ml of benzene was stirred vigorously at 80°C for 2 h, cooled, and filtered. The precipitate was washed with two 20-ml portions of ether, dried in vacuo, and then analyzed for Pb(IV) content. The analysis was carried out by dissolving the precipitate in AcOH, adding a solution containing 150 g KI, 250 g NaOAc, and 100 g Na₂CO₃ in 1 liter H₂O, and titrated with Na₂S₂O₃ in the presence of starch. The filtrate and ether washes were combined, the solvent was evaporated, and the residue was analyzed by GLC for conversion of alcohol and yields of reaction products. The results are presented in Tables 1 and 3. The conversion of LTA in all of the experiments was 100%. In addition to unsaturated ketone . and cycloalkanone a minor amount (ca. 1%) of a saturated aliphatic ketone was identified in all cases by means of GLC, IR, PMR, and chromatography-mass spectroscopy.

In order to isolate the ω -unsaturated ketones the reaction mixture was heated at 80°C with 15-20% H₂SO₄ to dehydrate any unreacted alcohol. The product was then extracted with three 20-ml portions of ether, dried over MgSO₄, and the ketone was isolated (the isolated yield constitutes \sim 80-90% of the yield as determined by GLC). The properties of the ω -unsaturated ketones are given in Tables 4 and 5.

Experiment 4. In the oxidation of 1-butylcyclohexanol, in addition to 1-decen-6-one and cyclohexanone (cf. Table 1), the reaction product contained 39% 2-methyl-5-pentamethylenetetrahydrofuran (yield based on reacted alcohol). IR spectrum (ν , cm⁻¹): 1075 (CQC). PMR spectrum (δ , ppm): 3.75 m (H, CH). MS (m/z): 154 M⁺, 139 [M - CH₃]⁺; 125 [M - C₂H₅]⁺; 112 [M - C₃H₆]⁺; 111 [M - CH₃CO and C₃H₇]⁺; 97 [M - C₄H₉]⁺; 81 [C₆H₉]⁺; 57 [C₄H₉]⁺; 43 [CH₃CO and C₃H₇]⁺; 41 [C₃H₅]⁺.

Experiment 5. In the oxidation of 1-hexylcyclohexanol, in addition to 1-dodecen-6-one and cyclohexanone (cf. Table 1), 2-propyl-5-pentamethylenetetrahydrofuran was obtained in 40.5% yield. IR spectrum (ν , cm⁻¹): 1080 (COC). PMR spectrum (δ , ppm): 3.70 m (H, CH). MS (m/z): 128 M⁺; 139 [M - C₃H₇]⁺; 125 [M - C₄H₉]⁺; 57 [C₄H₉]⁺; 43 [CH₃CO and C₃H₇]⁺.

Experiment 6. The oxidation of 1-octylcyclohexanol gave 1-tetradecen-6-one, cyclohexanone (Table 1), and 43% 2-pentyl-5-pentamethylenetetrahydrofuran. IR spectrum (ν , cm⁻¹): 1070 (COC). PMR spectrum (δ , ppm): 3.80 m (H, CH). MS (m/z): 210 M⁺; 181 [M - C₂H₅]⁺; 167 [M - CH₃CO and C₃H₇]⁺; 153 [M - C₄H₉]⁺; 139 [M - C₅H₁₁]⁺; 71 [C₅H₁₁]⁺; 57 [C₄H₉]⁺; 43 [CH₃CO and C₃H₇]⁺.

Experiment 10. Oxidation of 1-phenylcyclohexanol gave unsaturated ketone and cyclohexanone (cf. Table 1), and a small amount of biphenyl (2.5%). IR spectrum (ν , cm⁻¹): 700 and 750 (C₆H₅). PMR spectrum (δ , ppm): 7.25 m (10H, C₆H₅).

 $\begin{array}{c} \underline{\text{Experiment 11.}} & \text{Oxidation of 1-benzylcyclohexanol gave cyclohexanone (cf. Table 1), and} \\ 82\% & \underline{\text{benzyl acetate.}} & \text{IR spectrum } (\nu, \text{cm}^{-1}): 1750 \ (\text{OC=O}); \text{ mass spectrum } (m/z): 150 \ \text{M}^+; 107 \\ [\text{M} - \text{CH}_3\text{CO}]^+; 91 \ [\text{C}_6\text{H}_5\text{CH}_2]^+; 90 \ [\text{M} - \text{CH}_3\text{CO}_2\text{H}]^+; 79 \ [\text{C}_6\text{H}_7]^+; 77 \ [\text{C}_6\text{H}_5]^+; 65 \\ [\text{Dibenzyl } (5\%) \ \text{was also obtained, Mass spectrum } (m/e): 182 \ \text{M}^+; 91 \ [\text{C}_6\text{H}_5\text{CH}_2]^+; 77 \ [\text{C}_6\text{H}_5]^+; 65 \\ [\text{C}_5\text{H}_5]^+. \end{array}$

LTA-Cu(OAc)₂-Mediated Oxidation of 1-Allylcycloalkanols. (General method, experiments 12 and 19). A mixture containing 0.02 moles of alcohol, 0.01 moles LTA, 0.01 moles pyridine, and 0.001 moles Cu(OAc)₂ in 25 ml benzene was stirred at 20°C for 20-30 min. The reaction mixture was worked up according to the method described above. In addition to cycloalkanone (cf. Tables 1 and 3), allyl acetate is formed in 70-75% yield. IR spectrum (v, cm⁻¹): 1745 (0C=0).

Experiment 22. Competitive oxidation of 1-methylcyclopentanol (I) and 1-methylcyclohexanol (II) with LTA-Cu(OAc)₂. A mixture containing 0.01 moles of I, 0.01 moles II, 0.01 moles LTA, 0.01 moles of pyridine, and 0.001 moles Cu $(OAc)_2$ in 25 ml benzene was heated at 80°C for 2 h, cooled, and filtered. The conversions of alcohols and yields of reaction products were determined by GLC. Results: the ratio of I/II was 1.8, and the ratio of 1-hexene-5-one to 1-heptene-6-one was 2.0.

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CONCLUSIONS

1. The LTA-Cu(OAc)₂-mediated oxidation of tertiary cyclic alcohols produces cycloalkoxy

radicals $\dot{CH}_2(CH_2)_{n-1}C(R)O^*$ (R = alkyl; n = 4-5), which undergo β -fragmentation along two pathways: a) with ring opening to generate oxoalkyl radicals $RCO(CH_2)_{n-1}CH_2$, which are oxidized quantitatively to ω -unsaturated ketones, and b) with elimination of alkyl radicals (R^{*}) and the formation of cycloalkanones. This reaction forms the basis for the synthesis of ω -unsaturated ketones.

2. The relative rates for the two pathways of β -decomposition depend upon the structure of the alkyl substituent. The frequency of β -fragmentation via ring cleavage increases as the stability of the departing radical (R[•]) decreases:

$$\dot{\mathrm{CH}}_{2} < \mathrm{RCH}_{2}\dot{\mathrm{CH}}_{2} < \mathrm{CH}_{3}\mathrm{CH}_{2} < (\mathrm{CH}_{3})_{2}\dot{\mathrm{CH}} < (\mathrm{CH}_{3})_{3}\dot{\mathrm{C}} < \mathrm{C}_{6}\mathrm{H}_{5}\mathrm{CH}_{2}$$

3. The oxidation of 1-alkylcyclohexanols in which the alkyl groups exceed four carbon atoms results in the formation of alkoxy radicals which undergo oxidative cyclization and are converted into 2-alkyl-5-pentamethylenetetrahydrofurans.

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