

OXIDATION OF 1-METHYLCYCLOBUTANOL BY Pb(IV) AND Mn(III) COMPOUNDS

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The main product of the reaction of 1-methylcyclobutanol with Pb(OAc)₄ in benzene is 1-phenyl-4-pentanone; the use of Mn(OAc)₃ in acetic acid gives a mixture of 2,9-decanedione and methyl propyl ketone; 1-(chloro-, bromo-, thiocyano-, or cyano)-4-pentanone is formed in the presence of the systems Pb(OAc)₄-metal halide or Mn(OAc)₃-metal halide.

Keywords: oxidation, 1-methylcyclobutanol, lead tetraacetate, manganese triacetate, β -cleavage.

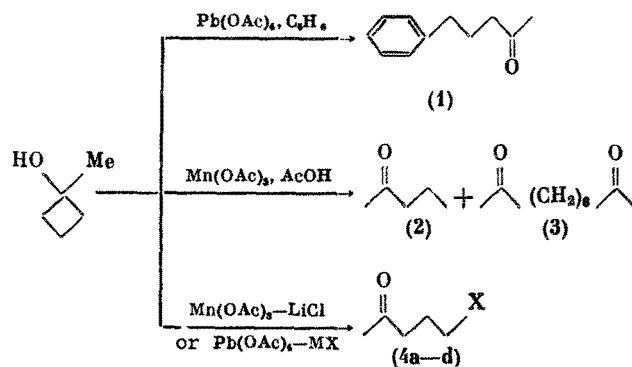
The oxidation of cyclobutanol (CB) by salts of Ce(IV), Ru(VI), Ru(VII), Cr(IV), Cr(VI), V(V), Mn(III), and Pb(IV) occurs in two directions: with ring cleavage and formation of linear aldehydes and without ring cleavage, with formation of cyclobutanone. The ratio of these directions depends on the nature of the oxidizing agent. The solvent also affects the composition of the products. Thus, in the reaction of CB with cerium ammonium nitrate (CAN) in water the main product is superaldehyde, in acetonitrile mainly 4-nitratobutanal is obtained, and saturation of the reaction mixture with oxygen results in the formation of succinic acid [1]. Chromic acid and sodium ruthenate (Na₂RuO₄) oxidize CB to cyclobutanone by a two-electron transfer mechanism; Cr(IV) and sodium perruthenate (NaRuO₄) behave as single-electron oxidizing agents, converting CB to 4-hydroxybutanal and 3-butenal. Here cyclobutanone is obtained in an insignificant amount [2, 3]. Compounds of V(V) and Mn(III) oxidize CB only to 4-hydroxybutanal [1]. When lead tetraacetate (LTA) is used, cyclobutanone and 3- and 4-acetoxybutanals are formed [4].

Information on the oxidation of tertiary cyclobutanols is limited to several examples. The reaction of CAN with 1-methylcyclobutanol (MCB) results in a mixture of aliphatic ketones, i.e., 2,9-decanedione, 2-pentanone, and 4-penten-2-one [1]. Cerium(IV) sulfate selectively oxidizes MCB to 2-pentanone [5], and the system LTA-Cu(OAc)₂ oxidizes it to 4-penten-2-one [6].

Continuing our investigations of the oxidation of cycloalkanols [6, 7], in the present paper we studied the reaction of 1-methylcyclobutanol with manganese triacetate (MTA), MnO₂, LTA, and the systems MTA-LiCl and LTA-MX (M = Li, K; X = Cl, Br, SCN, CN). The reaction with MTA, MnO₂, and MTA-LiCl was carried out in AcOH at 100°C, and the oxidation by LTA and systems based on it was carried out in benzene at 80°C. The reaction of the alcohol with LTA in benzene gave mainly 1-phenyl-4-pentanone (1). The main products in the case of the use of MTA were methyl propyl ketone (2) and 2,9-decanedione (3) in a 1:1 ratio, and 1-(chloro-, bromo-, thiocyano-, or cyano)-4-pentanone (4) was formed selectively during oxidation by the systems MTA-LiCl and LTA-MX (4) (see scheme on top of following page) (Table 1). The process of oxidation of 1-methylcyclobutanol by LTA and MTA can be represented as follows. The 1-methylcyclobutoxy radicals (A) obtained in the first step isomerize to 4-oxopentyl radicals (B) (the formation was confirmed in [8]), which can further undergo addition to benzene, abstract a hydrogen atom, recombine, or oxidize. The reaction with benzene is the first example of alkylation of an aromatic compound by oxoalkyl radicals generated from cycloalkanols. It probably occurs similarly to the reaction of benzene with 2-oxopropyl radicals obtained from acetone in the presence of MTA [9].

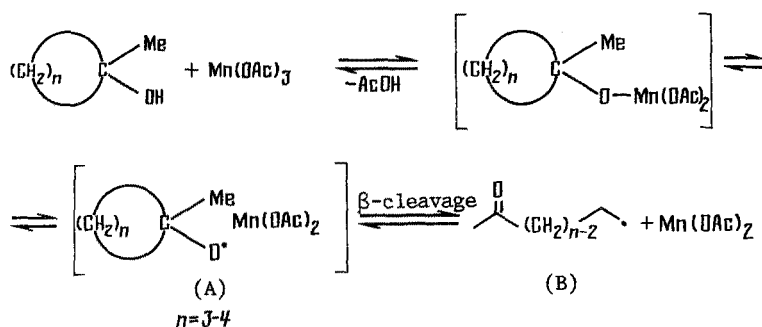
A mixture of methyl propyl ketone, 2,9-decanedione, and 3-acetopropyl acetate is formed in the reaction of MCB with manganese dioxide in acetic acid. Methyl propyl ketone is the main product.

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X = Cl(a), Br(b), SCN(c), CN(d).

It should be noted that 1-methylcyclobutanol differs significantly from its five-membered analog, 1-methylcyclopentanol, in its behavior with respect to MTA. Manganese triacetate does not oxidize 1-methylcyclopentanol. Such a difference in the reaction of MTA with these alcohols suggests that the steps of formation of the manganese alcoholate, its cleavage with formation of cycloalkoxy radical A and $\text{Mn}(\text{OAc})_2$, and isomerization of radical A to C-centered radical B are reversible.



For 1-methylcyclopentoxy radicals, the rate of the reaction with $\text{Mn}(\text{OAc})_2$ is probably significantly higher than the rate of β -cleavage; therefore, oxidation of 1-methylcyclopentanol does not occur. On the other hand, for 1-methylcyclobutoxy radicals the rate of β -cleavage is significantly greater than the rate of reaction with $\text{Mn}(\text{OAc})_2$, because of which aliphatic ketones 2 and 3 are formed. Another confirmation of the above-presented scheme is the data of [10], according to which 5-formylpentyl radicals can cyclize with formation of cyclohexanol.

TABLE 1. Oxidation of 1-Methylcyclobutanol

Oxidizing system	Alcohol conversion, %	Products, yield, %	
$\text{Pb}(\text{OAc})_4\text{-C}_6\text{H}_5$ *	69	5	Ph 17
$\text{Mn}(\text{OAc})_3\text{-AcOH}$ †	87	36	$\text{CH}_3\text{CO}(\text{CH}_2)_3$ 41
$\text{MnO}_2\text{-AcOH}$ †	95	47	$\text{CH}_3\text{CO}(\text{CH}_2)_3$ 5
$\text{Pb}(\text{OAc})_4\text{-LiCl}$	86	+	Cl 75
$\text{Pb}(\text{OAc})_4\text{-KBr}$ ‡	72	6	Br 62
$\text{Pb}(\text{OAc})_4\text{-KBr}$ ‡	100	3	Br 75
$\text{Pb}(\text{OAc})_4\text{-KSCN}$	65	+	SCN 58
$\text{Pb}(\text{OAc})_4\text{-KCN}$	40	+	CN 38
$\text{Mn}(\text{OAc})_3\text{-LiCl}$	60	+	Cl 35

Note. The yield is given on the basis of the starting alcohol: the mole ratio of MCB to $\text{Pb}(\text{IV})$ or $\text{Mn}(\text{III})$ is 1:1, the mole ratio of $\text{Pb}(\text{IV})$ or $\text{Mn}(\text{III})$ to the metal halide is 1:5 (1:2 for KCN); the reaction time is 5-10 min and 5 h (for MnO_2).

*Also, 2-3% 2,9-decanedione is formed.

†Also, 5-7% 3-acetopropyl acetate is formed.

‡The MCB: $\text{Pb}(\text{IV})$: KBr mole ratio is 1:1.5:5, and the reaction time is 1 h.

Oxidizing systems based on LTA in combination with a metal halide or pseudohalide quantitatively oxidize oxoalkyl radicals B by a ligand-transfer mechanism to 1-(chloro-, bromo-, thiocyano-, or cyano)-4-pentanone (4a-d). The system $\text{Mn}(\text{OAc})_3\text{-LiCl}$ oxidizes 4-oxopentyl radicals similarly to $\text{Pb}(\text{OAc})_4\text{-LiCl}$.

EXPERIMENTAL

The GLC analysis was carried out with an LKhM-80 chromatograph in a nitrogen stream (30 ml/min) using a flame-ionization detector and 3-m \times 3-mm glass columns with 5% XE-60, 5% tris(cyanoethoxy)propane, and 5% polyethylene glycol monolaurate 600 on Inerton-Super (0.20-0.25 mm). The ^1H and ^{13}C NMR spectra were recorded with Bruker WM-250 and Bruker AM-300 instruments in CDCl_3 . The IR spectra were recorded with a Specord-M80 instrument in a thin layer. Lead tetraacetate, a pure-grade reagent, was washed with glacial acetic acid and dried under vacuum over KOH. Manganese triacetate was obtained by the method of [11]. The starting 1-methylcyclobutanol was distilled before the reaction.

Oxidation of 1-Methylcyclobutanol by Lead Tetraacetate in Benzene. A mixture of 0.01 mole of MCB and 0.01 mole of LTA in 20 ml of benzene was vigorously stirred at 80°C until complete conversion of the oxidizing agent (sample for KI). After cooling, the mixture was analyzed by GLC, and the reaction product, 1-phenyl-4-pentanone, was recovered chromatographically on a column with silica gel (L 40/100); a 1:1.5 ethyl acetate/hexane mixture was used as the eluent. IR spectrum (ν , cm^{-1}): 750, 1600, and 3000 (C_6H_5), 1720 ($\text{C}=\text{O}$). PMR spectrum (δ , ppm): 1.90 m (2H, CH_2), 2.13 s (3H, CH_3), 2.45 t (2H, $\text{CH}_2\text{-C}_6\text{H}_5$), 2.75 t (2H, CH_2CO), 7.15-7.35 m (5H, C_6H_5). Found, %: C 80.96; H 8.71. $\text{C}_{11}\text{H}_{14}\text{O}$. Calculated, %: C 81.48; H 8.64.

Oxidation of 1-Methylcyclobutanol by Manganese Triacetate. A mixture of 0.05 mole of MCB and 0.05 mole of MTA in 30 ml of AcOH was vigorously stirred for 3 min at 100°C (until change of the dark-brown color of manganese triacetate to the white color of manganese diacetate). After cooling, the reaction mixture was analyzed by GLC using an internal standard. The reaction products (methyl propyl ketone and 3-acetopropyl acetate) were identified chromatographically, and 2,9-decanedione (3) was recovered by distillation. Its bp was 132°C (10 mm), and its mp was 64°C. Found, %: C 70.40; H 10.56. $\text{C}_{10}\text{H}_{18}\text{O}_2$. Calculated, %: C 70.59; H 10.59. PMR spectrum (δ , ppm): 1.25 m (4H, CH_2), 1.53 m (4H, CH_2), 2.09 s (6H, CH_3CO), 2.38 t (4H, CH_2CO).

Oxidation of 1-Methylcyclobutanol by Systems $\text{Pb}(\text{OAc})_4\text{-MX}$ and $\text{Mn}(\text{OAc})_3\text{-LiCl}$. A mixture of 0.01 mole of MCB, 0.01 mole of the oxidizing agent ($\text{Pb}(\text{OAc})_4$ or $\text{Mn}(\text{OAc})_3$), and 0.05 mole of MX was heated with stirring in benzene at 80°C (for LTA) or in acetic acid at 100°C (for MTA) until complete conversion of the oxidizing agent. After cooling, the mixture was analyzed chromatographically, and the reaction products were recovered by distillation.

By oxidation of MCB by the systems $\text{Pb}(\text{OAc})_4\text{-LiCl}$ and $\text{Mn}(\text{OAc})_3\text{-LiCl}$, 1-chloro-4-pentanone (4a), with bp 72°C (20 mm), was obtained. PMR spectrum (δ , ppm): 1.90-2.08 m (2H, CH_2), 2.10 s (3H, CH_3CO), 2.60 t (2H, CH_2CO), 3.50 t (2H, CH_2Cl).

By oxidation of MCB by the system $\text{Pb}(\text{OAc})_4\text{-KBr}$, 1-bromo-4-pentanone (4b), with bp 68°C (10 mm), was obtained. PMR spectrum (δ , ppm): 1.86-2.10 m (2H, CH_2), 2.13 s (3H, CH_3CO), 2.60 t (2H, CH_2CO), 3.45 t (2H, CH_2Br).

By oxidation of MCB by the system $\text{Pb}(\text{OAc})_4\text{-KSCN}$, 1-thiocyano-4-pentanone (4c) was obtained. IR spectrum (ν , cm^{-1}): 1720 ($\text{C}=\text{O}$), 2160 ($-\text{SCN}$). PMR spectrum (δ , ppm): 1.90-2.10 m (2H, CH_2), 2.17 s (3H, CH_3CO), 2.63 t (2H, CH_2CO), 3.00 t (2H, CH_2SCN).

By oxidation of MCB by the system $\text{Pb}(\text{OAc})_4\text{-KCN}$, 1-cyano-4-pentanone (4d) was obtained; it was recovered chromatographically on a column with silica gel (L 40/100), and the solvent was 1:0.5 hexane/ethyl acetate. IR spectrum (ν , cm^{-1}): 1720 ($\text{C}=\text{O}$), 2240 ($\text{C}\equiv\text{N}$). PMR spectrum (δ , ppm): 1.80 m (2H, CH_2), 2.12 s (3H, CH_3CO), 2.60 t (2H, CH_2CO), 2.32 t (2H, CH_2CN). ^{13}C NMR spectrum (δ , ppm): 15.70 (CH_2), 18.81 ($\underline{\text{C}}\text{H}_2\text{CN}$), 29.34 ($\underline{\text{C}}\text{H}_3\text{CO}$), 40.68 ($\underline{\text{C}}\text{H}_2\text{CO}$), 118.98 ($\text{C}\equiv\text{N}$), 208.39 ($\text{C}=\text{O}$). Found, %: C 65.03; H 8.29; N 13.21. $\text{C}_6\text{H}_9\text{ON}$. Calculated, %: C 64.86; H 8.11; N 12.61.

Oxidation of 1-Methylcyclobutanol by Manganese Dioxide. A mixture of 0.01 mole of MCB and 0.01 mole of MnO_2 in 20 ml of AcOH was vigorously stirred for 5 h at 120°C (until conversion of the black color to light-brown). After cooling, the reaction mixture was analyzed by GLC.

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