

OXIDATION IN ORGANIC CHEMISTRY

Edited by **WALTER S. TRAHANOVSKY**

DEPARTMENT OF CHEMISTRY
IOWA STATE UNIVERSITY
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PART D

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Part D

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Preface

Some of the most important and common reactions in organic chemistry involve oxidation and reduction. Because of the importance of this class of reactions, numerous reagents have been developed that will bring about certain oxidations or reductions selectively. This treatise is devoted to detailed discussions of specific oxidants or topics involving oxidation of organic compounds.

In this volume, the first chapter covers oxidations with lead tetraacetate, an oxidant that has been used widely for the selective oxidation of a variety of functional groups. The second chapter is concerned with an oxidant that has a long and extensive history—permanganate—but concentrates primarily on the recently studied phase transfer assisted permanganate oxidations. The third chapter discusses the intramolecular oxidative coupling of aromatic substrates and focuses on the utility of recently developed methods, such as vanadium oxytrifluoride oxidations, in the syntheses of complex natural products. The subject of the fourth chapter is the oxidation of coal with emphasis on the selective oxidative degradation procedures as tools for characterization of coal structure. Each chapter was written by an active researcher or researchers who have made important contributions in the area of chemistry being reviewed.

The level of all chapters is such that experts in these areas of research and students and researchers who wish a thorough and rigorous discussion of these topics should find them useful. In general, emphasis is on the scope and preparative use as well as the mechanistic aspects of the various oxidations.

WALTER S. TRAHANOVSKY

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I. Introduction

Lead tetraacetate [(LTA), mp 175°C] was first isolated in 1851¹ and has been used extensively as an oxidant by organic chemists since 1920. Although LTA can be produced in the laboratory by the reaction of red lead oxide (Pb₃O₄) with acetic acid in the presence of acetic anhydride,² the reagent is commercially available at moderate cost. The commercial LTA contains 10% acetic acid to retard decomposition due to reaction with water. This acetic acid is readily removed either by washing the LTA with anhydrous

¹ A. Jacquelin, *J. Prakt. Chem.* **53**, 151 (1851).

² J. C. Bailar, *Inorg. Synth.* **1**, 47 (1939).

ether or by azeotropic distillation with benzene just prior to use. LTA is compatible with a number of common solvents including acetic acid, benzene, methylene chloride, chloroform, nitrobenzene, pyridine, DMF, and DMSO.

LTA exists as a monomer in the solid state and in both benzene and acetic acid solution.³ A distorted cubic geometry has been proposed with both oxygen atoms of each acyloxy group coordinated with lead.⁴ Infrared measurements support this arrangement.⁵ The solubility and conductance properties of LTA suggest that the compound is covalent,⁴ but in acetic acid or carboxylic acid solvents, in general, rapid ligand exchange occurs between LTA and the solvent.⁶

Oxidation of inorganic compounds by LTA is facilitated by the high redox potential, 1.6 V in perchloric acid, of the reagent.⁷ With organic compounds LTA is normally reduced to lead(II) acetate in reactions involving both homolytic and heterolytic mechanisms. Photolysis of LTA affords lead(II) acetate and acetoxy radicals as primary products.⁸

The basic properties of LTA as an oxidizing agent have been reviewed⁷ and several excellent general reviews on the reactions of LTA with organic substrates are extant.⁹⁻¹² Reviews concerning the behavior of LTA toward specific functional groups are cited where appropriate in the text. The primary literature included in this chapter covers mainly the period of 1970 through January, 1980.

II. LTA Reactions with Hydroxyl Groups

A. ALCOHOLS

The treatment of alcohols with LTA leads to the formation of acetates, oxidation to the corresponding aldehyde or ketone, fragmentation, and

³ G. Rudakoff, *Z. Naturforsch. B. Anorg. Chem., Org. Chem.* **17**, 623 (1962).

⁴ R. Partch and J. Monthony, *Tetrahedron Lett.*, 4427 (1967).

⁵ K. Huesler and H. Loeliger, *Helv. Chim. Acta* **52**, 1495 (1969).

⁶ E. A. Evans, J. L. Huston, and T. H. Norris, *J. Am. Chem. Soc.* **74**, 4985 (1952).

⁷ J. Zýka, *Pure Appl. Chem.* **13**, 569 (1966).

V. Franzen and R. Edems, *Angew. Chem.* **73**, 579 (1961).

⁹ R. N. Butler, in "Synthetic Reagents" (J. S. Pizey, ed.), p. 277, Ellis Horwood, Chichester, England, 1977.

¹⁰ L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," p. 537; Vol. 2, p. 234; Vol. 3, p. 168; Vol. 4, p. 278; Vol. 5, p. 365; Vol. 6, p. 313; Vol. 7, p. 185. Wiley, New York, 1967.

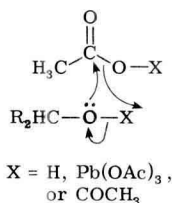
^{10a} G. W. Rothermund, in "Houben-Weyl, Methoden der Organischen Chemie" (E. Müller, ed.), 4th ed., Vol. IV/1b, p. 167. Thieme, Stuttgart, 1975.

¹¹ H. O. House, "Modern Synthetic Reactions," 2nd ed., p. 359. Benjamin, California, 1972.

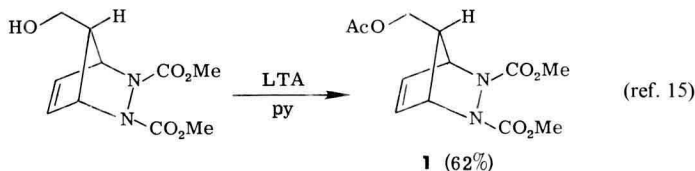
¹² R. Criegee, in "Oxidation in Organic Chemistry" (K. B. Wiberg, ed.), Part A, p. 277. Academic Press, New York, 1965.

cyclization. The parameters leading to each mode of behavior have been thoroughly discussed with respect to substrate structure and solvent effects. Comprehensive lists of examples have also been tabulated.^{13,14}

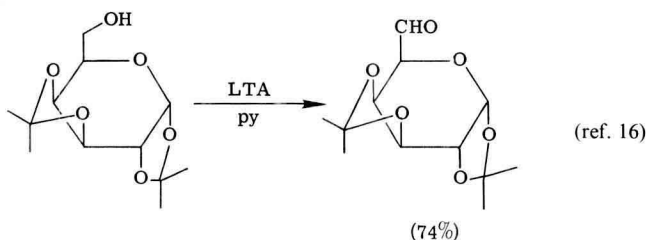
The formation of acetates is a process that accompanies most LTA oxidations. The retention of configuration encountered in the acetate has led to postulation of the generalized attack of the alcohol on the acetate carbonyl of a lead(IV) species and/or acetic acid (or anhydride) attack on an alkoxy lead(IV) intermediate.¹³ Although the use of benzene seems to maximize acetate production (when cyclization is not possible) whereas



pyridine minimizes it, generalizations are dangerous as shown by the production of **1**.¹⁵



The LTA oxidation of primary and secondary alcohols to the corresponding aldehyde or ketone can be a moderately high yield process.¹⁶⁻¹⁸ With the

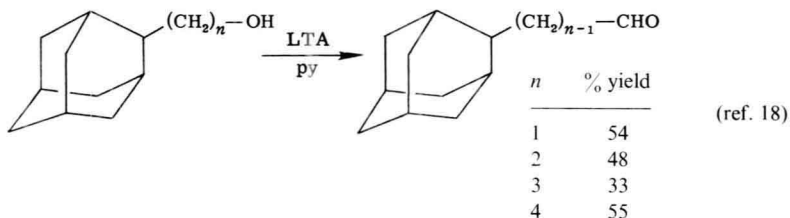
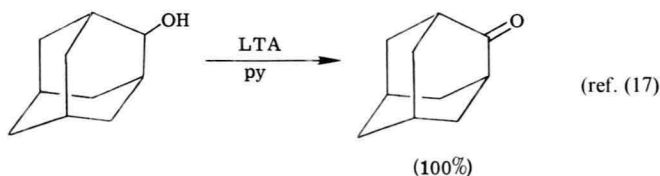


¹³ M. Lj. Mihailović and R. E. Partch, in "Selective Organic Transformations" (B. S. Thyagarajan, ed.), Vol. II, p. 97. Wiley (Interscience), New York, 1972.

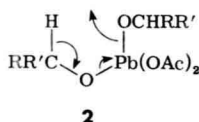
¹⁴ M. Lj. Mihailović and Ž. Čeković, *Synthesis*, 209 (1970).

¹⁵ B. M. Trost, R. M. Cory, P. H. Scudder, and H. B. Neubold, *J. Am. Chem. Soc.* **95**, 7813 (1973).

¹⁶ D. J. Ward, W. A. Szarek, and J. K. N. Jones, *Carbohydr. Res.* **21**, 305 (1972).



ω -(2-adamantyl)alkan-1-ols, the production of aldehyde was accompanied by acetate formation as well.¹⁸ As noted by the examples, the use of pyridine gives maximum yields of carbonyl derivatives. This is in sharp contrast to the role of acidic or apolar solvents such as acetic acid or benzene wherein products of substitution, fragmentation, and cyclization become paramount.¹⁷ This dramatic shift in reaction pathway can be attributed to the occurrence of a heterolytic mechanism in pyridine while homolytic routes prevail in both acetic acid and benzene.^{13,14} It has been suggested that the carbonyl formation that does occur in the absence of pyridine arises from heterolytic disproportionation of the dialkoxylead(IV) derivative **2**^{14,19-21}



in line, for instance, with studies on the oxidation of benzyl alcohol and 1-phenylethanol in which the reaction is first order with respect to LTA and second order with respect to alcohol.²⁰ The role of pyridine is generally believed to involve $[\text{ROPb}(\text{OAc})_3 \cdot \text{py}]$ formation,^{14,20} and the suggestion has been made that Pb—N bond formation increases the electrophilicity of

¹⁷ J. Burkhard, J. Janků, V. Kubelka, J. Mitera, and S. Landa, *Collect. Czech. Chem. Commun.* **39**, 1083 (1974).

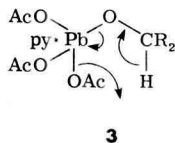
¹⁸ J. Burkhard, J. Janků, and S. Landa, *Collect. Czech. Chem. Commun.* **39**, 1072 (1974).

¹⁹ Y. Pocker and B. C. Davis, *J. Chem. Soc. Chem. Commun.*, 803 (1974).

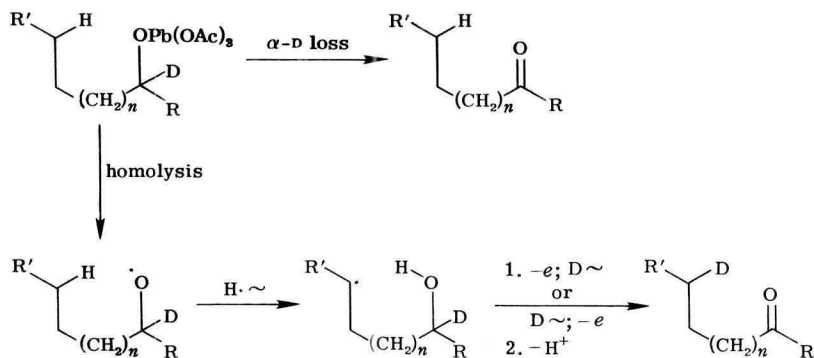
²⁰ K. K. Banerji, S. K. Banerjee, and R. Shanker, *Indian J. Chem. Sect. A* **15**, 702 (1977).

²¹ K. K. Banerji, S. K. Banerjee, and R. Shanker, *Bull. Chem. Soc. Jpn.* **51**, 2153 (1978).

the complex and thus favors α -hydrogen removal over the homolysis which occurs when neutral or acidic conditions pertain.²⁰ The rate-determining nature of the proton removal step has been shown by isotope studies,^{14,20,21} and transition state **3** has been proposed for the carbonyl forming oxidation of both benzyl alcohol and 1-phenylethanol.²⁰



In cases where either 1,4- or 1,5-hydrogen transfer is possible, another mode of carbonyl formation becomes important when benzene (homolytic conditions) is used as solvent.^{22,23}

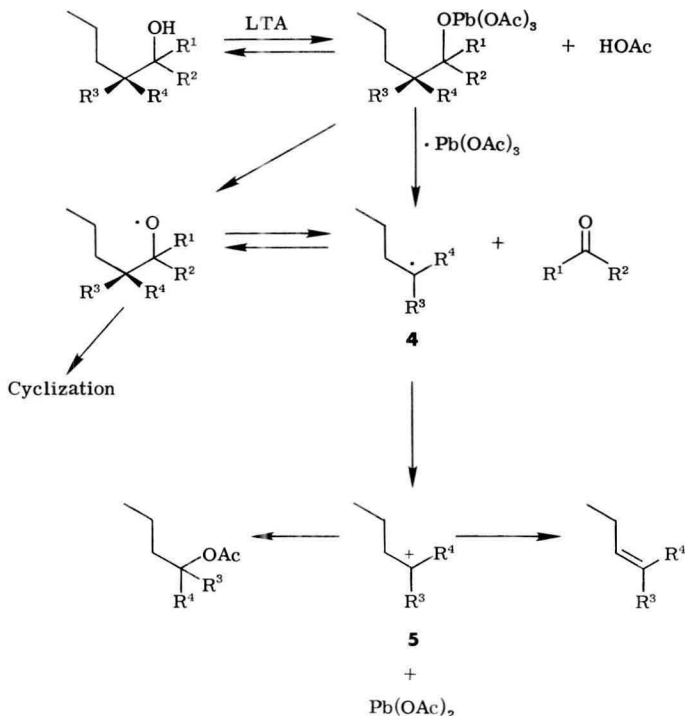


As noted above, although the reactions of alcohols with LTA to form esters and to undergo heterolysis in pyridine have received attention, a great deal more work has been devoted to the study of homolytic fragmentation and cyclization of alcohols by LTA in neutral and/or acidic media.^{13,14} Scheme 1 indicates the generally accepted pathway leading to both cyclization and fragmentation.^{14,23a} Fragmentation occurs best when substituents favor the stabilization of **4** and when ring strain can be released. Radical **4** then is oxidized to the corresponding carbocation **5** that undergoes typical

²² D. Jeremić, S. Milosavljević, V. Andrejević, M. Jakovljević-Marinković, Ž. Čeković, and M. Lj. Mihailović, *J. Chem. Soc. Chem. Commun.*, 1612 (1971).

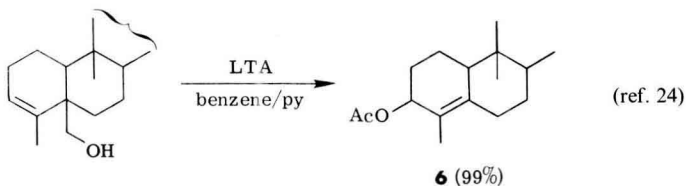
²³ S. Milosavljević, D. Jeremić, and M. Lj. Mihailović, *Tetrahedron* **29**, 3547 (1973).

^{23a} W. S. Trahanovsky, in "Methods in Free-Radical Chemistry" (E. S. Huyser, ed.), Vol. 4, p. 133. M. Dekker, New York, 1973.



SCHEME 1

carbonium ion reactions.^{14,23a} Production of **6**,²⁴ **7**,²⁵ and **8**^{25a} reflects the importance of radical stabilization as does the increased amount of fragmentation noted from *trans*-2-methylcyclohexanol as opposed to cyclohexanol.²⁶ The preparative cleavage of both α - and β -amyrin to give the corresponding seco aldehyde is another case in point.^{26a}



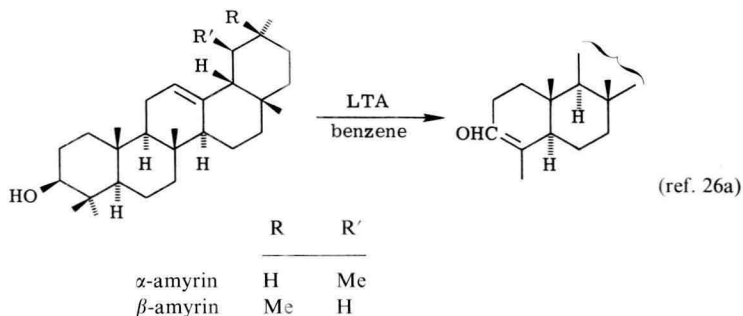
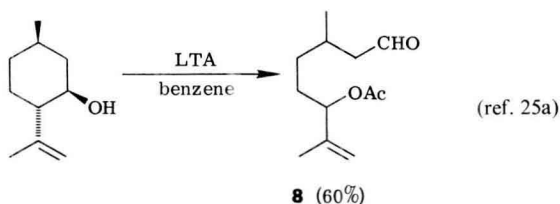
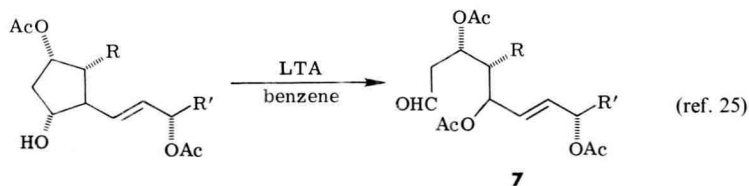
²⁴ H. Kakisawa, T. Horie, and T. Kusumi, *Bull. Chem. Soc. Jpn.* **48**, 727 (1975).

²⁵ W. P. Schneider and R. A. Morge, *Tetrahedron Lett.*, 3283 (1976).

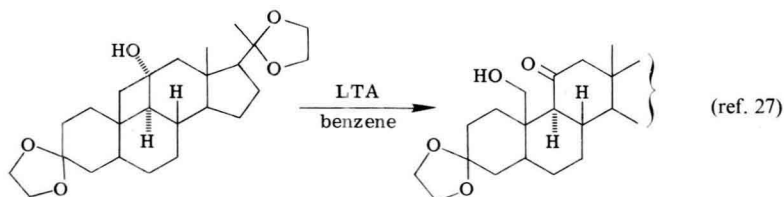
^{25a} K. Shankaran and A. S. Rao, *Indian J. Chem. Sect. B* **18**, 507 (1979).

²⁶ J. Bošnjak, V. Andrejević, Ž. Čeković, and M. Lj. Mahailović, *Tetrahedron* **28**, 6031 (1972).

^{26a} A. K. Devi, G. K. Trivedi, and S. C. Bhattacharyya, *Indian J. Chem. Sect. B* **16**, 8 (1978).



The effect of relieving ring strain can be seen in the oxidation of a series of steroidal and triterpenoidal cyclobutanols to give either the corresponding hydroxyketones or hemiacetals.²⁷⁻²⁹ Arguments involving substituent steric interactions have been advanced to explain the predominance of both types of product.²⁹ Patchouli alcohol fragments when treated with LTA in



²⁷ H. Wehrli, M. S. Heller, K. Schaffner, and O. Jeger, *Helv. Chim. Acta* **44**, 2162 (1961).

²⁸ R. Imhof, W. Graf, H. Wehrli, and K. Schaffner, *J. Chem. Soc. Chem. Commun.*, 852 (1969).

²⁹ W. Herz and D. H. White *J. Org. Chem.* **39**, 1 (1974).