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Lead Tetraacetate in Organic Synthesis

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Abstract

Lead tetraacetate (LTA),a versatile oxidizing agent for different functional groups, has been widely used for oxidative decarboxylation of carboxylic acid, cleavage of 1,2-diol, formation of the cyclic ether, acetoxylation, methylation, dehydrogenation etc. The present micro review describes the utility of LTA in 1,2-glycol-cleavage and decarboxylation of carboxylic acid.

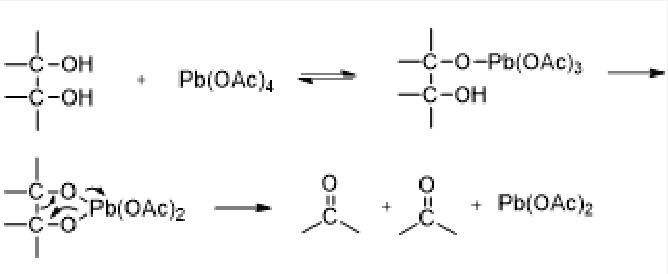
Keywords: Lead tetraacetate (LTA); Oxidative decarboxylation; Glycol cleavage; Bromination

Introduction

The commercially available LTA is hygroscopic and turns brown due to the formation of lead oxide. Therefore, LTA should be stored in absence of moisture, kept tightly sealed and stored under 10°C in the dark and in the presence of about 5% glacial acetic acid. LTA is very toxic and may be absorbed through the skin. Due to the high toxicity the reagent should be handled with care in chemical fume hood. It is soluble in hot acetic acid, benzene, cyclohexane, chloroform, and carbon tetrachloride.

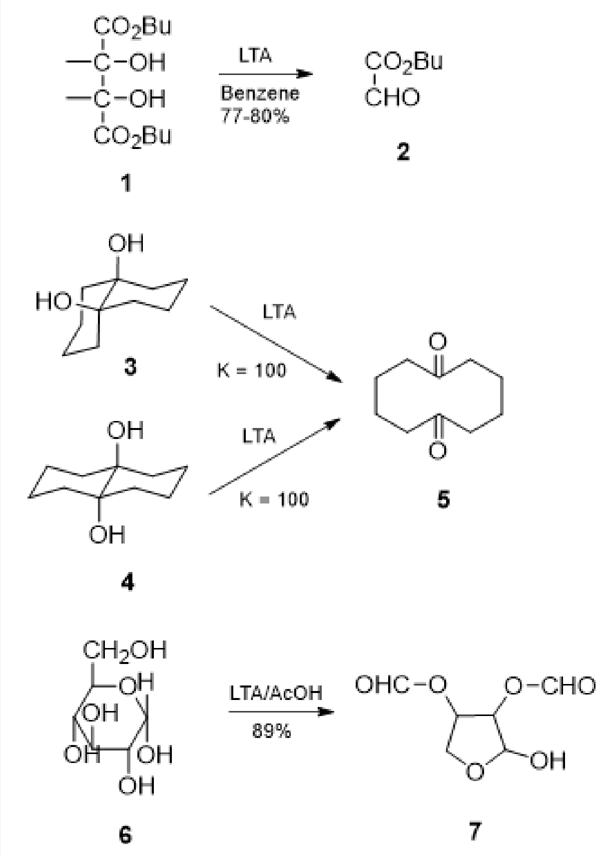
Use of LTA in Organic Synthesis

1,2-glycol-cleavage



Scheme 1: Cleavage of diols.

LTA is one of the most frequently used reagents for the cleavage of glycols and for the preparation's carbonyl compounds. The reactions are performed either in aprotic solvents (benzene, nitrobenzene,1,2-dichloroethane) or in protic solvents such as acetic acid [1]. The role of LTA in glycol cleavage is highly dependent on the structure and stereochemistry of the substrate. The cleavage of diols proceeds via a cyclic intermediate [2]. as shown in Scheme 1. The cleavage of *cis* diol occurs more easily than the trans-diol which does not permit the easy formation of the cyclic intermediate. Some examples are given in Scheme 2.



Scheme 2: Cleavage of diols 1, 3, 4 and 6 with LTA.

The diol 1 on treatment [3] with LTA in benzene affords aldehyde 2 but the diols 3 and 4 with LTA suffer4 cleavage and yield ketone 5. 1,2-Glycol cleavage [4] by LTA has been widely applied for the oxidation of carbohydrates and sugars [5]. The diol 6 on oxidation with LTA in acetic acid yields the aldehyde 7. The reactivity of individual glycol units in sugar molecules is often different and thus the LTA reaction is helpful tool for structural determination and for degradation studies in carbohydrate chemistry [6]. It has been observed that trans-1,2-diols which are cleaved slowly with LTA in acetic acid are readily cleaved if pyridine is used as reaction solvent [7].

The cyclopropene ester 9, prepared from the bromo derivative of *cis*-1,2-hydrocatechol 8, on treatment with LTA produces [8] the cyclopropane aldehyde 10 which is a potential intermediate for the *cis*-pyrethroid class of insecticides. The trans-diol 12, obtained from D-mannitol 11, with LTA affords ketone [9] 13 in unspecified yield. Reduction of 13 with sodium borohydride produces the alcohol 14 which is utilized for the synthesis of mixed-acid phospholipids polyunsaturated fatty acid as shown in Scheme 3.

Decarboxylation of carboxylic acid

Oxidative decarboxylation of carboxylic acids by LTA has been frequently used in the synthesis of terpenoid compounds. Oxidative decarboxylation by LTA depends on the conditions of reaction, core agents and structure of acids and hence a variety of products such as acetate esters, alkanes, alkenes, and alkyl halides can be obtained [10]. The reactions are performed [10] in nonpolar solvents (benzene, carbon tetrachloride) or polar solvents (acetic acid, pyridine, HMPA). Decarboxylation of primary and secondary carboxylic acids usually affords acetate esters as major products. If a mixture of acetate and olefin is formed, it is recommended to perform the reaction in presence of potassium acetate [10]. The cyclohexane carboxylic acid 15 if heated under reflux with LTA in benzene furnishes a mixture of acetate 16 and the olefin 17 but only the acetate 16 is produced in high yield when heated with potassium acetate in acetic acid (Scheme 4).

The monocarboxylic acid on oxidation with LTA in presence of copper (II) salts gives mainly alkenes (Scheme 5). The free radical mechanism is generally accepted [11]. Rosefuran 19 has been obtained in crude form (70%) by the oxidative decarboxylation of 3-methyl-2-furoic acid 18 with LTA in boiling benzene in the presence of copper acetate [12]. Bisdecarboxylation [13] of compounds containing carboxyl groups on adjacent carbons can be achieved with LTA in the presence of oxygen and pyridine. Thus, the dicarboxylic acid [14] 20 on decarboxylation affords the tetrahydrobenzene 21. Similarly, the acid [15] 22 if subjected

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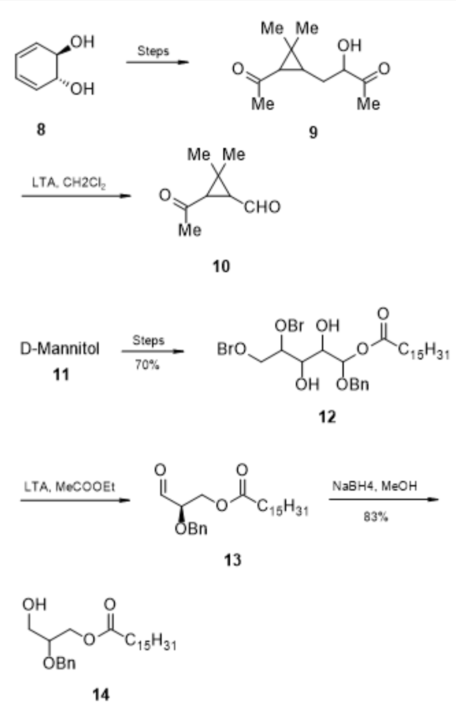
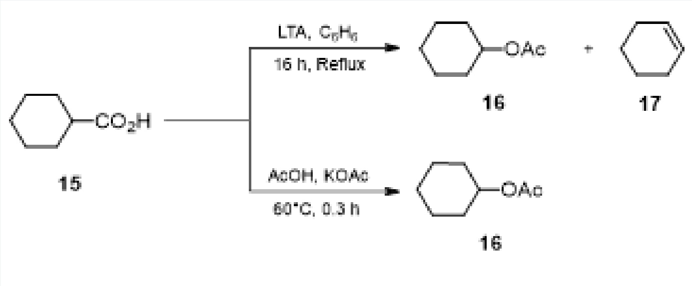
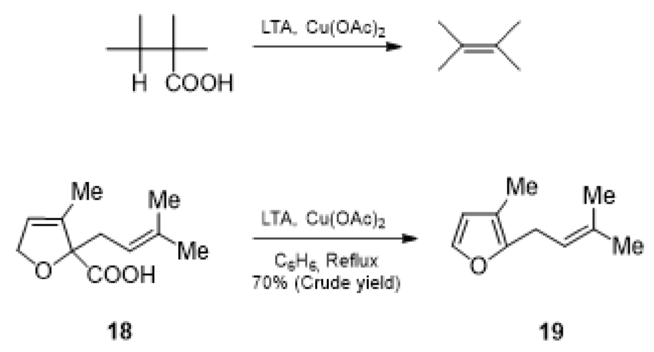
to bisdecarboxylation can yield compound 23 (Scheme 6). The compounds containing germinal carboxyl groups (malonic acid derivatives) 24 are decarboxylated with LTA to give *gem* diacetate which can easily be hydrolyzed to ketone [16] 25.



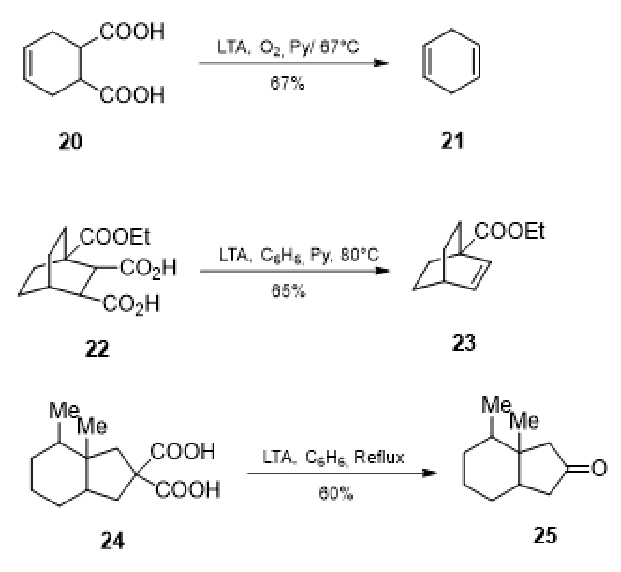
Scheme 3: Obtention of 10 and 13 by treatment of 8 and 11 with LTA, respectively.



Scheme 4: Decarboxylation of 15 with LTA.

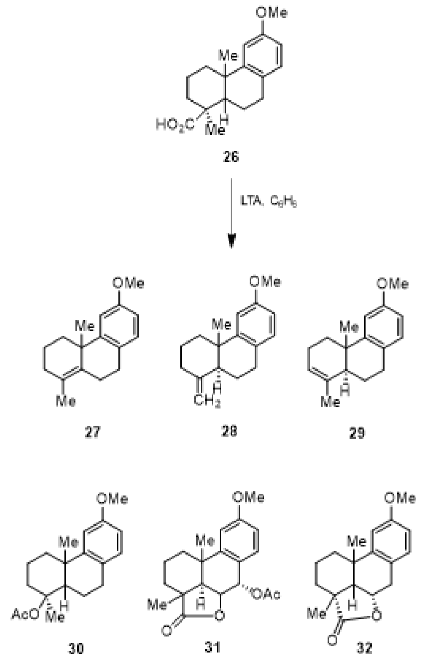


Scheme 5: Decarboxylation of 18 with LTA in boiling benzene in the presence of copper acetate.



Scheme 6: The compounds 21, 23 and 25 are obtained respectively by treatment of 20, 22 and 24 with LTA.

The LTA decarboxylation of tertiary carboxylic acids gives a mixture of alkenes and acetate esters. O-methylpodocarpic acid 26 on heating with LTA yields a mixture of olefins [17] 27, 28, 29 and acetates 30 and 31. In addition a lactone 32 is obtained (Scheme 7). Banerjee and collaborators [18] have observed that the decarboxylation of the acid 34, prepared from the cyclic ether 33, with LTA, pyridine and DMF [19] affords a mixture of olefins 35 (scheme 8). The transformation of 35 into the ketone 36 is affected in two steps: (a) demethoxylation [19] with sodium iodide, boron tribromide, 15-crown ether-5, (b) oxidation [20] with Jones Reagent. Bromination of 36 followed by dehydrobromination and aromatization respectively yield tetraol 37 in 60% Yield. The tetraol 37 is a potential intermediate [21] for the synthesis of diterpenoid quinones cryptotanshinone and tanshinone IIA.



Scheme 7: Decarboxylation of tertiary carboxylic acid 26 with LTA.

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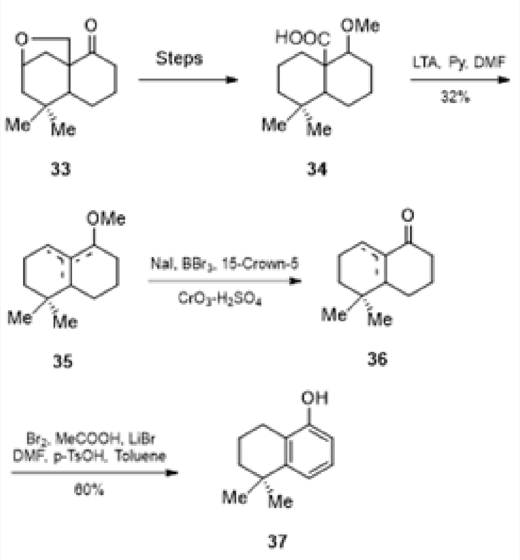
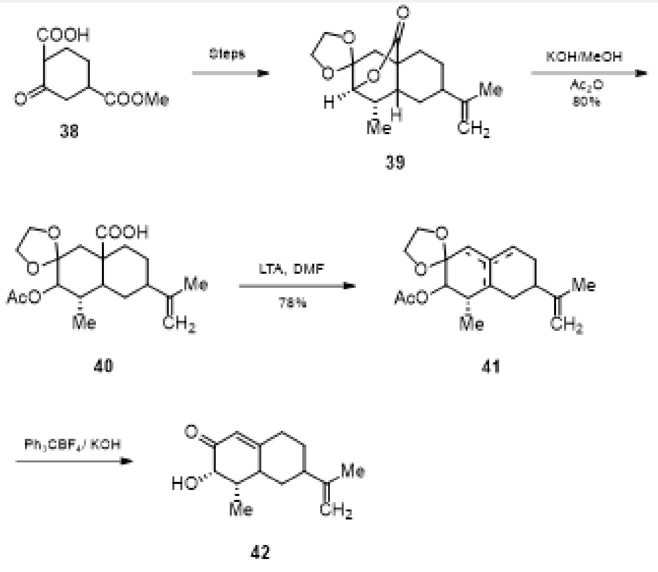


Scheme 8: Decarboxylation of tertiary carboxylic acid 34 with LTA, to obtain 37.

Masamune and collaborators [19] have also studied the decarboxylation of tertiary carboxylic acid with LTA in relation of the studies on the synthesis of the terpene glutinosone. The lactone 39, prepared from the ketoester 38, on alkaline hydrolysis and acetylation respectively is converted to the acid 40 (Scheme 9). The acid 40 on being heated with LTA and DMF undergoes decarboxylation and produces a mixture of olefins 41. Treatment of 41 with methanolic potassium hydroxide (5%) followed by the addition of triphenyl methyl fluoborite afford glutinosone 42.



Scheme 9: Decarboxylation of tertiary carboxylic acid 40 with LTA.

Oxidative decarboxylation reaction has proved usefull in the synthesis [22] of sesquiterpene furoventalene 46 as depicted in the scheme 10. m-Anisic ester 43 is converted into the ester 44 in three steps (reductive alkylation, metalation, and alkylation). Acidic hydrolysis and cyclization of the ester 44 yield dihydro benzofuran 45. Alkaline hydrolysis and oxidative decarboxylation with LTA lead the formation of furoventalene 46. Banerjee and collaborators [23] have utilized oxidative decarboxylation for the synthesis of sesquiterpene (±) frullanalide the details are described in scheme 11.

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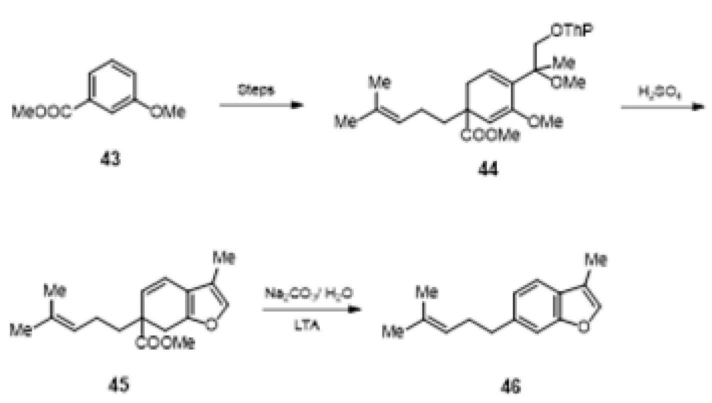
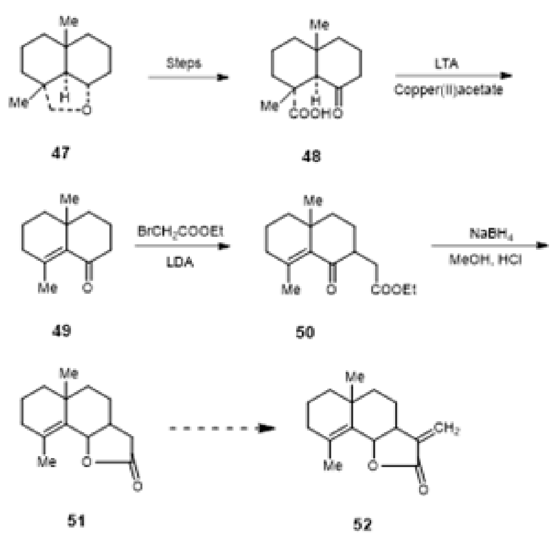
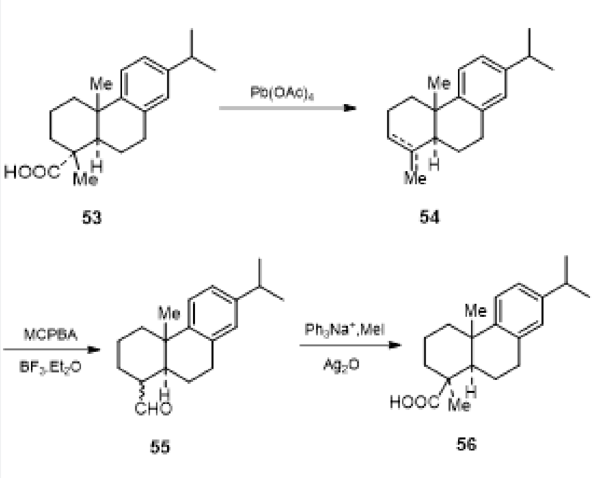


Scheme 10: Decarboxylation of 45 with LTA to obtain 46.



Scheme 11: Decarboxylation of 48 with LTA to obtain 52.



Scheme 12: Oxidative decarboxilation of 53 with LTA and synthesis of Callitrisic acid 56.

The ketone acid 48, prepared from the cyclic ether 47, on heating with LTA and copper (II) acetate undergoes oxidative decarboxylation yielding enone 49. Alkylation of 49 with ethyl bromoacetate produces ketoester 50 which on reduction with sodium borohydride in methanol followed by stirring with hydrochloric acid afford the lactone 51. As the lactone 51, has already converted [24] into (±) frullanalide 52 the present synthesis of 51 constitutes a formal total synthesis [25] of frullanalide 52.

Another interesting use of oxidative decarboxylation [26] with LTA is shown in scheme 12. The acid 53 on decarboxylation with LTA gives a mixture of olefins 54. Epoxidation followed by hydrolysis with Lewis acid produces aldehyde 55 which on methylation and oxidation respectively afford Callitrisic acid 56. The above-mentioned examples exhibit the importance of LTA in the synthesis of terpenoid compounds.

Other Applications

LTA has also been utilized for acetoxylation [27,28] of ketones in enol form, nuclear methylation [29], oxidation [30] of phenols. Alkyl sulfides [31], alkyl hydroperoxides [32] and organometallic compounds are also oxidized33 by LTA. Several cyclic ethers have been synthesized by LTA oxidation [34].

Conclusion

The present review describes application of LTA in cleavage of diols and decarboxylation of carboxylic acids. In near future we expect to see more new applications of LTA in organic synthesis.

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