Encyclopedia of Reagents for Organic Synthesis

Editor-in-Chief
Leo A. Paquette

Volume 5

L - M

ENCYCLOPEDIA

of

Reagents

for

Organic Synthesis

Editor-in-Chief

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Volume 5

L – M

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Editorial Board

Preface

The extent to which organic synthetic methodology has developed and flourished during the past several decades has placed unusually heavy demands on the broad range of scientists who utilize chemical reagents. There exists the vital need to know which reagent will perform a specific transformation. Since a number of reagents are often amenable to similar objectives, a researcher's ability to access readily a comparative summary of those features that distinguish one reagent from another can result in a considerable economy of time. The purpose of the *Encyclopedia of Reagents for Organic Synthesis* is to incorporate into a single work a genuinely authoritative and systematic description of the utility of all reagents used in organic chemistry. Its comprehensiveness is further served by an unrivaled ease to locate any specific entry or topic.

These objectives have been met by inviting practicing chemists from throughout the world to provide specific contributions in their area of expertise. Furthermore, the masthead for each of the 3000 reagents provides valuable information concerning physical data, solubility, form supplied in, purification, and, where relevant, preparative methods. The CAS registry number, handling/storing information, and precautions will further serve potential users. The first literature reference in each entry provides reviews, if available, dealing with the subject reagent. The critical coverage of all relevant literature is extensive.

The goal of the *Encyclopedia of Reagents for Organic Synthesis* is to serve as a reference work where the retrievability of useful information concerning any specific reagent is made facile. For this reason there is a detailed subject index and, in addition, a formula index of all the reagents, and also two further indexes that list the reagents by structural class and by function.

In any undertaking of this type, it is important that the term 'reagent' be clearly defined. The guideline that has dominated the thinking of the members of the Editorial Board is that a reagent be an agent or a combination of agents which with some generality effects the transformation of a substrate into a product. In addition, many useful building blocks have been included. As a consequence, we anticipate that a work has been produced that will serve biochemists, material scientists, pharmacologists, and chemical engineers, in addition to chemists from all disciplines, in that manner most conducive to accelerating progress in their respective fields of research.

The entries highlight the various uses characteristic of each reagent, with specific examples illustrative of these chemical reactions. The contributions are organized alphabetically and the cross-referencing to other reagents is liberal. Thus, a concerted effort has been made to bring together in one place a detailed compilation of the uses of those reagents that will serve both the beginning and experienced investigator. The wealth of facts contained within the *Encyclopedia of Reagents for Organic Synthesis* has been assimilated in a manner which will cause all scientists to want this source of information kept in close proximity to their laboratory.

A work of this magnitude could not have been brought to realization without the input of a great deal of time, effort, and dedication on the part of a large number of highly responsible individuals. I am especially indebted to the editors – Steven Burke, Robert Coates, Rick Danheiser, Scott Denmark, David Hart, Lanny Liebeskind, Dennis Liotta, Anthony Pearson, Hans Reich, James Rigby, and William Roush – for their tremendously valuable enthusiasm, intensive work, and unstinting persistence. A most critical role has been played by Colin Drayton, not only in conceiving the project but also as a consequence of his range of knowledge of the publishing business in steering us continually in the proper direction and in overseeing the massive editing operation. James Edwards and Mark Volmer are also to be thanked for their central role as assistant section editors. The body of this encyclopedia was composed by over 1000 authors from 40 countries around the world. The knowledge and expertise contributed by these experienced investigators in the form of authoritative treatises dealing with reagents with which they are thoroughly familiar constitutes the scientific underpinning of the entire undertaking. The enlightening end product of their contributions will have a major impact on the conduct of research in organic chemistry and I thank each of these individuals for their insightful entries.

The large contingent of organic chemists alluded to above, directly and indirectly, expects the *Encyclopedia of Reagents for Organic Synthesis* to play a vital role in stimulating creative research in organic chemistry in the years immediately ahead. All of us hope that you will share in this excitement by perusing its many pages and creatively adapting the valuable information contained therein.

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Foreword

This Encyclopedia covers comprehensively over 3000 reagents, alphabetically arranged using IUPAC nomenclature. The articles are self-contained but ***Bold Italics*** are used within each article to indicate other reagents that have their own entries in the Encyclopedia. A list of related reagents is given at the end of articles.

Although most articles are devoted to a single reagent, in some cases closely related reagents are covered under one heading, e.g. Methyl Trimethylsilylacetate is discussed in the article on Ethyl Trimethylsilylacetate, and Lithium Trimethoxyaluminum Hydride in the article on Lithium Tri-*t*-butoxyaluminum Hydride.

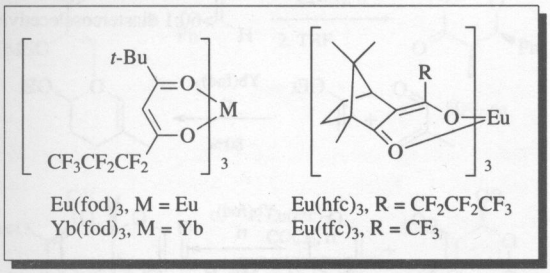
A particular reagent can be found either directly, by going to the appropriate place in the Encyclopedia, or from the Subject Index in Volume 8. Numerous other topics, such as types of reaction, named reactions, named reagents, general substrates or products, and specific substrates or products, are included in this index.

Volume 8 also contains a Formula Index, listing all reagents covered in the Encyclopedia.

In addition, there are two further compilations of all the reagents in Volume 8, a Reagent Structural Class Index and a Reagent Function Index. The former groups the reagents under headings such as Dienes, Hydrides, and Titanium Reagents, while the latter has headings such as Alkylating Agents, Desilylation Reagents, and Ring Expansion Agents.

The abbreviations used for journals in the references are on the front endpapers of all volumes, while the back endpapers list other abbreviations used throughout the Encyclopedia.

Lanthanide Shift Reagents



Eu(fod)$_3$, M = Eu
Yb(fod)$_3$, M = Yb

Eu(hfc)$_3$, R = $CF_2CF_2CF_3$
Eu(tfc)$_3$, R = CF_3

(Eu(fod)$_3$)
[17631-68-4] $C_{30}H_{30}EuF_{21}O_6$ (MW 1037.50)
(Yb(fod)$_3$)
[18323-96-1] $C_{30}H_{30}F_{21}O_6Yb$ (MW 1058.58)
(Eu(hfc)$_3$)
[34788-82-4] $C_{42}H_{42}EuF_{21}O_6$ (MW 1193.73)
(Eu(tfc)$_3$)
[34830-11-1] $C_{36}H_{42}EuF_9O_6$ (MW 893.72)

(mild Lewis acids capable of catalyzing a variety of synthetic transformations)

Alternate Names: Eu(fod)$_3$ = tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)europium; Yb(fod)$_3$ = tris(6,6,-7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)ytterbium; Eu(hfc)$_3$ = tris[3-(heptafluoropropylhydroxymethylene)-(+ or –)-camphorato]europium; Eu(tfc)$_3$ = tris[3-(trifluoromethylhydroxymethylene)-(+ or –)-camphorato]europium.

Physical Data: Eu(fod)$_3$: mp 203–207 °C; Yb(fod)$_3$: mp 108–111 °C; Eu(hfc)$_2$: mp 156–158 °C; Eu(tfc)$_3$: mp 195–198 °C.

Solubility: generally sol in a wide variety of organic solvents; commonly used in chlorinated solvents such as CH_2Cl_2 and $CHCl_3$.

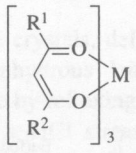
Form Supplied in: hygroscopic solids; commercially available.

Drying: if necessary, they can be dried and stored over P_2O_5.

Purification: can generally be used directly without purification. Occasionally contain insoluble material which can be removed by filtration of a solution of the reagent through a millipore filter or a plug of cotton or glass wool. Insoluble material can also be separated and removed by centrifugation.

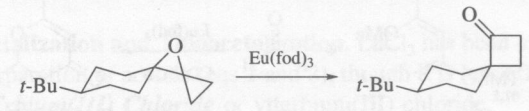
Handling, Storage, and Precautions: though hygroscopic, they can be handled for short periods of time in the presence of air without deleterious effect. In general, the use of glove bags or dry boxes is not required.

Fluorinated lanthanide dionato complexes are commonly employed as NMR shift reagents.[1] The Lewis acidity of these reagents has allowed them to be exploited as catalysts for a variety of synthetic transformations. In general, they are easy to use and handle and are mild enough to tolerate a variety of acid labile functionality. A wide array of these complexes is commercially available. They have an octahedral geometry with the general structure (**1**) but are capable of expanding their coordination environment in order to accommodate additional Lewis bases. Generally they are believed to function by coordination at a single site, though chelation to two sites has also been suggested to occur.[2–4] Achiral versions generally employ the heptafluorooctanedionato (fod) ligand while complexes of optically active camphor derived ligands, 3-(trifluoromethylhydroxymethylene)camphorato (tfc) or 3-(heptafluoropropylhydroxymethylene)camphorato (hfc), have been investigated in connection with enantioselective synthesis. Both the (+)- and (–)-isomers of Eu(hfc)$_3$ and Eu(tfc)$_3$ are commercially available. Most commonly employed is the europium derivative, Eu(fod)$_3$. In several cases, Yb(fod)$_3$ has been reported to be a stronger Lewis acid than Eu(fod)$_3$ and a more effective catalyst for certain transformations.



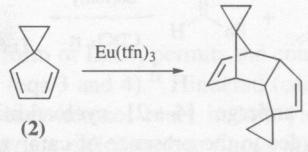
(**1**)

The first report of their use as catalysts involved the Eu(fod)$_3$ induced rearrangement of oxaspiropentanes to cyclobutanones (eq 1).[5] The lanthanide complex is more effective at catalyzing this reaction than other more conventional Lewis acid catalysts.

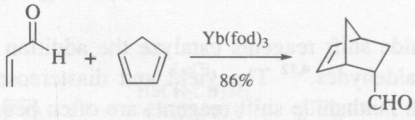


(1)

During a study of its shift reagent properties, Eu(tfn)$_3$ (tris(1,1,1,2,2,3,3,7,7,8,8,9,9,9-tetradecafluoro-4,6-nonanedionato)europium) was found to smoothly catalyze the Diels–Alder dimerization of (**2**) (eq 2).[6] More recently, it has been demonstrated that Yb(fod)$_3$ will catalyze the cycloaddition of a variety of dienes with acrolein (eqs 3–5).[7] Several of these reactions cannot be readily accomplished with other catalysts or reaction conditions because of problems associated with the polymerization of acrolein.

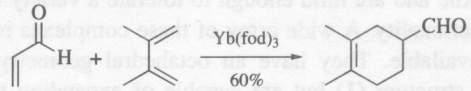


(**2**) (2)

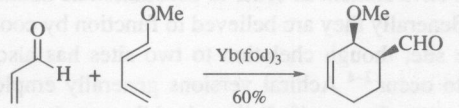


(3)

The lanthanide shift reagent catalyzed Diels–Alder cycloaddition reaction of oxygenated dienes with aldehydes has been ex-

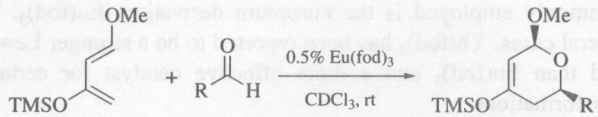


(4)



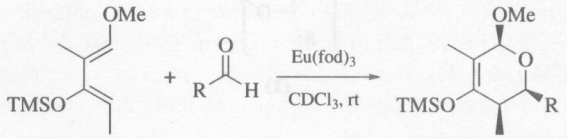
(5)

tensively investigated. Eu(fod)$_3$ effectively catalyzes this reaction at room temperature and, in many cases, allows the relatively unstable silyl enol ether intermediates to be isolated (eqs 6–11).[3,8–10]



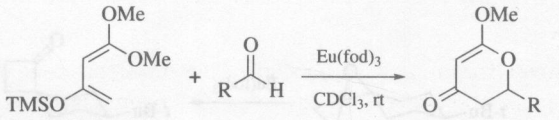
(6)

R = Ph, 82%
R = 2-furyl, 86%
R = CH=CHPh, 94%



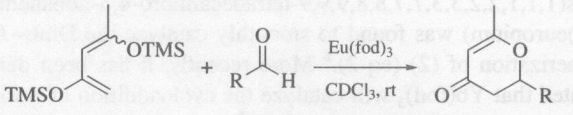
(7)

R = Ph, 66%
R = Me, 66%
R = C_6H_{13}, 49%



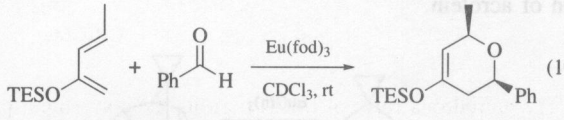
(8)

R = Ph, 85%
R = C_6H_{13}, 73%



(9)

R = Ph, 62%
R = C_6H_{13}, 47%

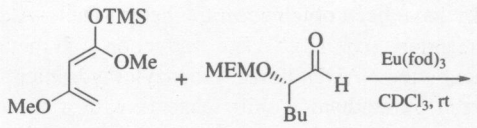


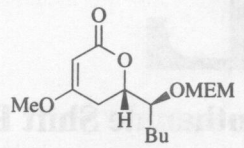
(10)

Enol ethers undergo [4 + 2] cycloaddition with α,β-unsaturated aldehydes in the presence of catalytic amounts of lanthanide shift reagents to give dihydropyran derivatives (eqs 12 and 13).[11]

Lanthanide shift reagents catalyze the addition of silyl enol ethers to aldehydes.[4,12] The yield and diastereoselectivity obtained with lanthanide shift reagents are often better than those observed with more conventional catalysts (eq 14).

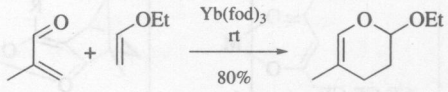
Shift reagents also catalyze the [2 + 2] cycloaddition of ketenimines with aldehydes to produce 2-iminooxetanes (eq 15).[13] Again, the acid labile product is not stable to other catalysts.



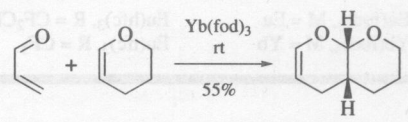


(11)

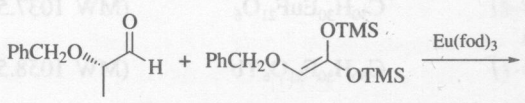
>60:1 diastereoselecetivity

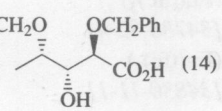


(12)



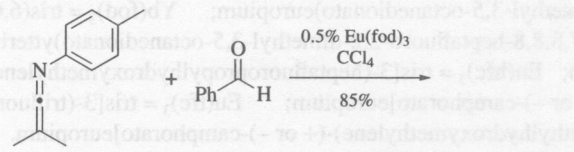
(13)





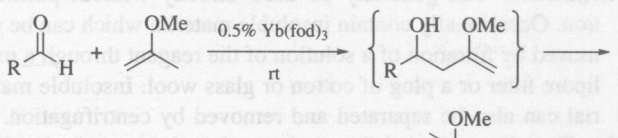
(14)

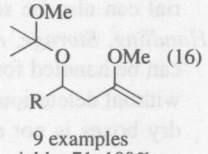
major diastereomer



(15)

The ene reaction of aldehydes with alkyl enol ethers is effectively catalyzed by Yb(fod)$_3$ (eq 16).[14]



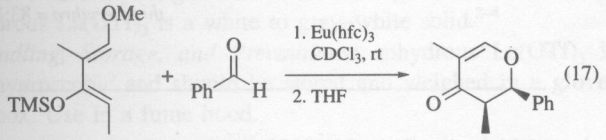


(16)

9 examples
yield = 71–100%

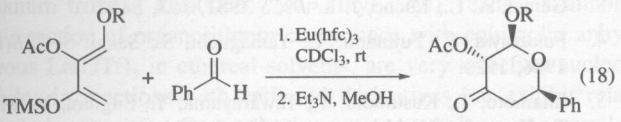
The optically active camphor derivative Eu(hfc)$_3$ has been used as an enantioselective catalyst. Though the enantioselectivity with this catalyst alone is often modest (eq 17),[8,15] when used in concert with additional chiral auxiliaries, high levels of

enantioselectivity have been obtained in the hetero-Diels–Alder cycloaddition reaction (eq 18).[15] The reduction of methyl phenylglyoxylate by the NADH mimic *N*-benzyldihydronicotinamide is catalyzed by lanthanide shift reagents with a modest level of asymmetric induction (eq 19).[16]



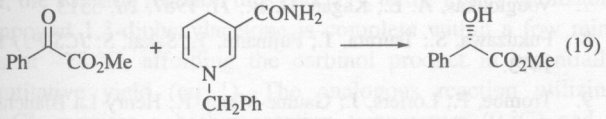
(17)

50% ee



(18)

R = 1-menthyl, 86% de



(19)

Eu(tfc)$_3$, CH_2Cl_2, rt 28%, 55% ee
Eu(tfc)$_3$, MeCN, 70 °C 98%, 25% ee

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16. Zekhani, S.; Gelbard, G. *CC* **1985**, 1162.

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University of California, San Diego, CA, USA

Lanthanum(III) Chloride[1]

$LaCl_3 \cdot 7H_2O$

(anhydrous)
[10099-58-8] Cl_3La (MW 245.26)
(heptahydrate)
[17272-45-6] $Cl_3H_{14}LaO_7$ (MW 371.40)

(mild Lewis acid for acetalization;[2] selective reducing agent in association with $NaBH_4$[3] or $LiAlH_4$;[4] preparation of organolanthanum reagents;[5] catalyst for various acid mediated reactions[6–8])

Physical Data: triclinic crystals; mp (hydrate) 91 °C (dec); mp (anhyd) 852 °C; bp 1750 °C; density (anhyd) 3.8 g cm^{-3}.

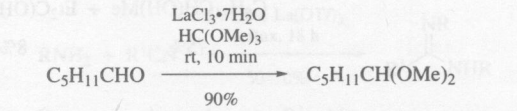
Solubility: 3.89 g L^{-1} in H_2O; sol methanol, ethanol; anhydrous form sol pyridine.

Form Supplied in: white crystals, deliquescent.

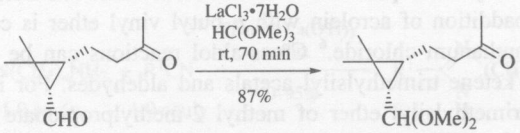
Preparative Methods: anhydrous lanthanum chloride is obtained from the hydrate by refluxing in thionyl chloride, or by heating to 400 °C in a HCl stream (see also ***Cerium(III) Chloride***). The reagent can also be prepared by treatment of a lanthanum benzoate suspension with dry ethereal HCl solution.[9]

Handling, Storage, and Precautions: anhydrous $LaCl_3$ should be freshly prepared and used without delay. Oral toxicity: LD_{50} 4.2 g kg^{-1} in rats.

Acetalization and Thioacetalization. $LaCl_3$ has been used in the preparation of acetals (eqs 1 and 2), though it is less efficient than ***Erbium(III) Chloride*** or ytterbium(III) chloride.[2,10]

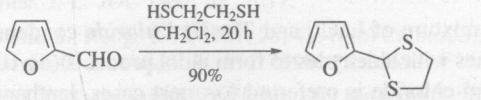


(1)

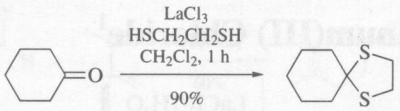


(2)

The anhydrous form of $LaCl_3$ permits the convenient production of thioacetals (eqs 3 and 4).[11] Hindered (camphor) and aromatic (benzophenone) ketones react in low yield. Lanthanum trichloride is much less efficient than ***Samarium(III) Chloride*** for acetal cleavage.[12]

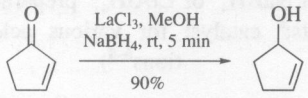


(3)



(4)

Regioselective Reduction of α,β-Unsaturated Carbonyl Compounds. In the presence of ***Sodium Borohydride***, α,β-unsaturated ketones are reduced to allylic alcohols in high yield (eq 5).[3] In THF, ***Lithium Aluminum Hydride*** shows the same selectivity with both ketones and aldehydes (eq 6).[4]



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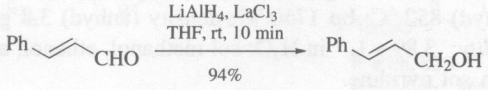
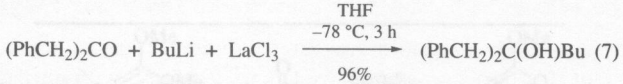


(6)

Organolanthanum Reagents. Upon treatment with 1 equiv of ***n-Butyllithium***, anhydrous $LaCl_3$ yields a reagent of reduced basicity and good nucleophilicity, similar to the analogous cerium reagent (eq 7).[5] With ***Methyllithium***, the reagent exhibits a good selectivity for additions to aldehydes in the presence of a ketone (eq 8). Lanthanum gives the highest selectivity of all the lanthanides tested.[13]



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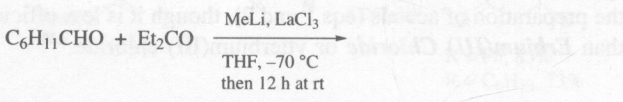
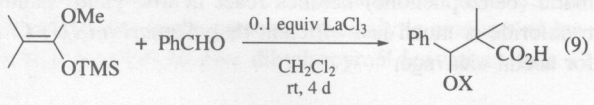


(8)

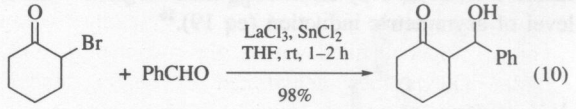
Catalytic Properties in Various Reactions. The Diels–Alder cycloaddition of acrolein with *n*-butyl vinyl ether is catalyzed by lanthanum chloride.[6] Cross-aldol reactions can be effected with ketene trimethylsilyl acetals and aldehydes. For instance, the trimethylsilyl ether of methyl 2-methylpropionate couples with benzaldehyde in the presence of catalytic amounts of $LaCl_3$; a mixture of the protected and unprotected hydroxy esters is obtained (eq 9).[7]



(9)

X = TMS, 21%; H, 42%

A mixture of $LaCl_3$ and ***Tin(II) Chloride*** condenses α-bromo ketones with aldehydes to form aldol products (eq 10). Although cerium chloride is preferred for most cases, lanthanum chloride offers a combination of the highest yield and satisfactory selectivity.[8] With α,α′-dibromo ketones, the same reagent mixture leads to oxyallyl cations which add to furan under mild conditions (see ***Cerium(III) Chloride***).[14]



(10)

threo:*erythro* = 83:17

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Lanthanum(III) Triflate[1]

$La(CF_3SO_3)_3$

[52093-26-2] $C_3F_9LaS_3O_9$ (MW 586.10)

(Lewis acid catalyst useful for aldol, Michael, Diels–Alder, and other C–C bond forming reactions; also useful for preparing organolanthanum reagents, which react with hindered tertiary amides to afford ketones)

Alternate Name: lanthanum trifluoromethanesulfonate.
Physical Data: mp >360 °C.
Solubility: sol H_2O; partially sol THF, CH_2Cl_2; sparingly sol Et_2O; insol hexane.
Preparative Methods: to an aqueous solution of triflic acid (50% v/v), a slight excess of lanthanum oxide (La_2O_3) is ad-

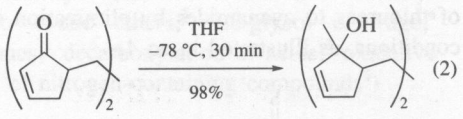
ded; the resulting mixture is stirred for 15 min at rt and then filtered to remove the unreacted oxide; the filtrate is concentrated in vacuo at about 60 °C; residual water is removed by azeotropic distillation with toluene in vacuo to dryness; the resulting hydrate is placed in a flask equipped with a stirring bar, a stopcock filled with a glass wool plug, and a NaOH trap, and is then dehydrated by heating under vacuum (140 °C/0.1 mmHg or 180 °C/1.0 mmHg) for 16 h. The anhydrous $La(OTf)_3$ is a white to gray–white solid.[2–4]

Handling, Storage, and Precautions: anhydrous $La(OTf)_3$ is hygroscopic and should be stored and weighed in a glovebox. Use in a fume hood.

Preparation of Organolanthanum Reagents.[1,4] Organolanthanum triflates $RLa(OTf)_2$ (R = alkyl, aryl), readily available by reaction of organolithium compounds with equimolar anhydrous $La(OTf)_3$ in ethereal solvents, are very effective nucleophiles in reactions with carbonyl derivatives but exhibit relatively low basicity. Generally these reagents behave in a parallel manner to their organocerium chloride counterparts,[5] but are soluble in ethereal solvents and thus are more reactive. In particular, the addition reaction of $RLa(OTf)_2$ to the highly enolizable compound 1,3-diphenylacetone is complete within a few minutes at –78 °C, affording the carbinol product in essentially quantitative yield (eq 1). The analogous reaction utilizing $RCeCl_2$ requires a higher reaction temperature (0 °C) and a longer reaction time (1.5 h).[5] One application of $MeLa(OTf)_2$ in organic synthesis is depicted in eq 2 in which efficient 1,2-addition is achieved.[6] In this case, the use of MeLi or MeMgBr reagents gives a mixture of the starting material and mono- and di-1,2- and 1,4-addition products.

$$MeLi + La(OTf)_3 \xrightarrow[-78 \text{ to } 0\ ^\circ C]{THF} MeLa(OTf)_2 \xrightarrow[-78\ ^\circ C,\ 30\ min]{(PhCH_2)_2CO} (PhCH_2)_2C(OH)Me \quad (1)$$

98%



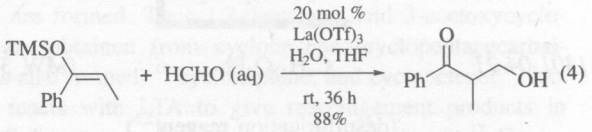
(2)

A unique characteristic of organolanthanum triflate reagents is that they smoothly react with sterically hindered aliphatic, aromatic, and heterocyclic tertiary amides to provide the corresponding ketones in excellent yields (eq 3); unsatisfactory results are obtained when employing organocerium or conventional RLi or RMgX reagents.[4] If amides possess additional donor functionality (i.e. MeO), an excess of the $RLa(OTf)_2$ reagent is needed to ensure complete conversion. Even so, further addition to the ketone product is not usually observed due to the formation of stable tetrahedral adducts prior to aqueous workup.

$$MeLa(OTf)_2 + PhCONEt_2 \xrightarrow[-78\ ^\circ C,\ 30\ min]{THF} PhCOMe \quad (3)$$

95%

Lewis Acid Catalyst for Aldol, Michael, and Diels–Alder Reactions. $La(OTf)_3$ has been used as a Lewis acid catalyst to promote aldol condensations between silyl enol ethers and formaldehyde under aqueous conditions (eq 4).[7] $La(OTf)_3$ can catalyze the Michael addition of silyl enol ethers to α,β-unsaturated ketones at rt in CH_2Cl_2 to afford the expected products in high yields (eq 5). In some of the cases studied, as little as 1 mol % of $La(OTf)_3$ is sufficient, and other lanthanide triflates are also effective. Enol silanes derived from ketones, thioesters, and esters are suitable, and no 1,2-addition products are obtained.[8] $La(OTf)_3$ is also an effective catalyst for the Diels–Alder cycloaddition of carbonyl-containing dienophiles with cyclopentadiene.[8] For all three catalytic processes mentioned here, $La(OTf)_3$ can be almost quantitatively recovered upon aqueous workup and can be reused.[7,8]



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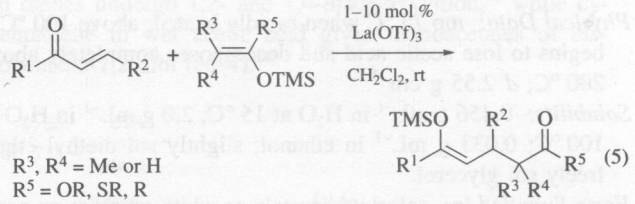
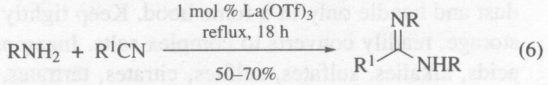


(5)

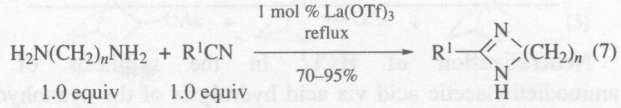
R^3, R^4 = Me or H
R^5 = OR, SR, R

Synthesis of Amidines. In the presence of 1 mol % of $La(OTf)_3$, reaction of primary amines (2 equiv) with nitriles results in the formation of *N,N′*-disubstituted amidines in good yields (eq 6);[3] when primary diamines (1 equiv) are employed, cyclic amidines are obtained in good to excellent yields (eq 7).[3]



(6)

R = primary, secondary, Ar; R^1 = Me



(7)

n = 2, 3, 4

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Lead(II) Acetate

$Pb(OAc)_2 \cdot 3H_2O$

[301-04-2] $C_4H_{12}O_7Pb$ (MW 379.33)

(desulfurization reagent[2,3])

Physical Data: mp 75 °C when rapidly heated; above 100 °C it begins to lose acetic acid and decomposes completely above 200 °C; *d* 2.55 g cm^{-3}.

Solubility: 0.456 g mL^{-1} in H_2O at 15 °C; 2.0 g mL^{-1} in H_2O at 100 °C; 0.033 g mL^{-1} in ethanol; slightly sol diethyl ether; freely sol glycerol.

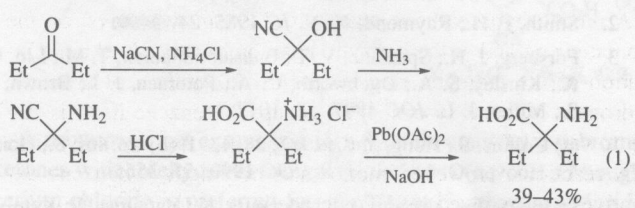
Form Supplied in: colorless crystals or white granules or powder; slowly effloresces; widely available; may contain insoluble lead carbonate resulting from exposure to air.

Drying: dry at rt because of facile dehydration. Drying over H_2SO_4 at rt leads to formation of the anhydride.

Purification: recrystallize from water containing 2–3% acetic acid.

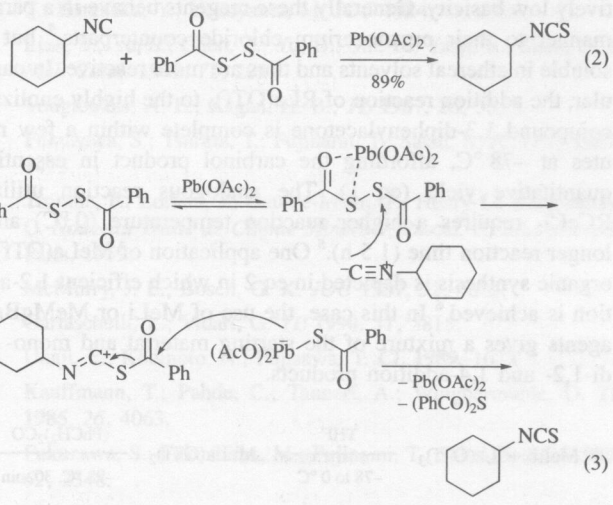
Handling, Storage, and Precautions: poisonous; carcinogen; LD_{50} 200 mg kg^{-1} (intraperitoneal in rats); avoid breathing dust and handle only in a fume hood. Keep tightly closed for storage; readily converts to complex salts. Incompatible with acids, alkalies, sulfates, sulfites, citrates, tartrates, chlorides, carbonates, tannin, phosphates, resorcinol, salicylic acid, and phenol.

Neutralization of HCl.[1] In the synthesis of α-aminodiethylacetic acid via acid hydrolysis of the cyanohydrin of diethyl ketone, the crude amino acid hydrochloride is neutralized by lead hydroxide (prepared by hydrolysis of this reagent with sodium hydroxide) to yield the amino acid in liberated form (eq 1). This procedure appears to be superior to that using ***Lead(IV) Oxide*** for this neutralization.

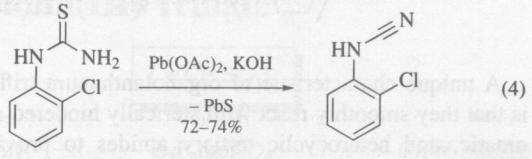


Removal of Selenium and Selenious Acid.[2] ***Selenium(IV) Oxide*** and selenious acid are good reagents for the oxidation of the α-methylene carbon of carbonyl compounds to give 1,2-dicarbonyl compounds. However, it is difficult to remove the resulting colloidal selenium and excess of the oxidant from the desired product in this method. A procedure for the oxidation of paraldehyde to glyoxal and the isolation of the product as the bis-bisulfite addition compound specifies the use of lead(II) acetate. Thus the addition of aqueous solution of this reagent to the reaction mixture gives insoluble lead selenite as a precipitate which is removed readily by filtration.

Conversion of Isocyanides into Isothiocyanates.[3] Reactions of isocyanides with dibenzoyl disulfide occur smoothly in the presence of this reagent to give isothiocyanates in high yield (eq 2). The activity of this reagent is almost identical with that of ***Thallium(I) Acetate***. In this reaction, a complex of the reagent with dibenzoyl disulfide is believed to be the key intermediate in the sulfurization of the isocyanide (eq 3).

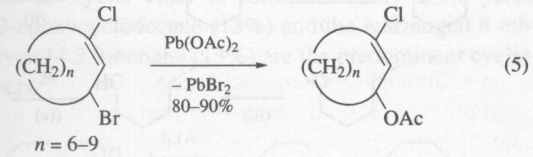


Elimination of H_2S.[4] This reagent is used for the conversion of thioureas to cyanamides by elimination of H_2S under mild conditions, as illustrated in eq 4.



Acetoxylation of Allylic Bromide.[5] This reagent is used for the preferential replacement of a bromine atom by an acetoxy group in 1-chloro-3-bromocycloalkenes (eq 5). Lead(II) acetate is superior to ***Silver(I) Acetate*** for this transformation.

Preparation of Cyclic Disulfides.[6] Reactions of dithiols with an aqueous solution of this reagent give lead dithiolates in nearly quantitative yield. The dithiolates react with sulfur in benzene at rt to give the cyclic disulfides in high yields without the formation of polymeric disulfides (eq 6).



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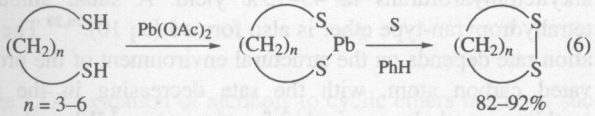

(6)

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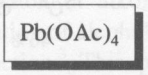
Lead(IV) Acetate[1]



[546-67-8] $C_8H_{12}O_8Pb$ (MW 443.37)

(oxidizing agent for different functional groups;[1] oxidation of unsaturated and aromatic hydrocarbons;[2] oxidation of monohydroxylic alcohols to cyclic ethers;[3] 1,2-glycol cleavage;[4] acetoxylation of ketones;[1] decarboxylation of acids;[5] oxidative transformations of nitrogen-containing compounds[6])

Alternate Name: lead tetraacetate; LTA.

Physical Data: mp 175–180 °C; *d* 2.228 g cm^{-3}.

Solubility: sol hot acetic acid, benzene, cyclohexane, chloroform, carbon tetrachloride, methylene chloride; reacts rapidly with water.

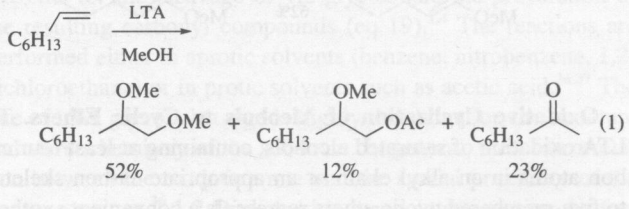
Form Supplied in: colorless crystals (moistened with acetic acid and acetic anhydride); widely available, 95–97%.

Analysis of Reagent Purity: iodometrical titration.

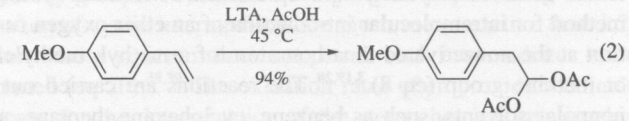
Drying: in some cases, acetic acid must be completely removed by drying the reagent in a vacuum desiccator over potassium hydroxide and phosphorus pentoxide for several days.

Handling, Storage, and Precautions: the solid reagent is very hygroscopic and must be stored in the absence of moisture. Bottles of lead tetraacetate should be kept tightly sealed and stored under 10 °C in the dark and in the presence of about 5% of glacial acetic acid.

Oxidations of Alkenic and Aromatic Hydrocarbons. Lead tetraacetate reacts with alkenes in two ways: addition of an oxygen functional group on the double bond and substitution for hydrogen at the allylic position.[2] In addition to these two general reactions, depending on the structure of the alkene, other reactions such as skeletal rearrangement, double bond migration, and C–C bond cleavage can occur, leading to complex mixtures of products, and these reactions therefore have little synthetic value (eq 1).[1a,b,2,7] Styrenes afford 1,1-diacetoxy derivatives when the LTA reaction is performed in acetic acid (eq 2), while in benzene solution products resulting from the addition of both the methyl and an acetoxy group to the alkenic double bond are formed.[7,8] Other nucleophiles, such as azide ion, carbanions, etc. can be introduced onto the alkenic bond in a similar fashion.[9] In the LTA oxidation of cyclic alkenes, depending on ring size, structure, solvent, and reaction conditions, several types of products are formed. Thus 1,2-diacetates and 3-acetoxycycloalkenes are obtained from cyclohexene (cyclopentanecarbaldehyde is also formed),[10] cycloheptene, and cyclooctene.[11] Norbornene reacts with LTA to give rearrangement products in which 2,7-diacetoxynorbornane predominates (eq 3).[12] Conjugated dienes undergo 1,2- and 1,4-diacetoxylation,[13] while cyclopentadiene in wet acetic acid gives monoacetates of *cis*-cyclopentene-1,2-diol (eq 4).[14]



(1)



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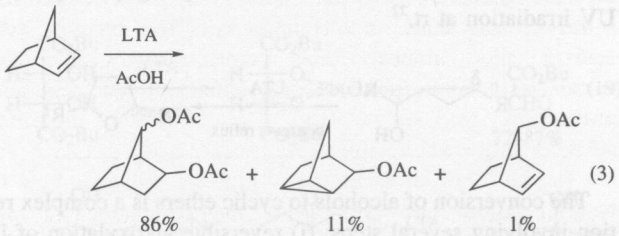

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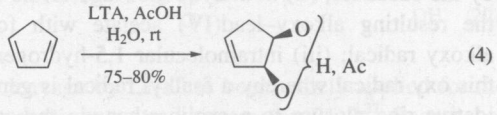
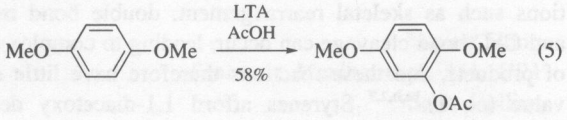


(4)

Aromatic hydrocarbons react with LTA in two ways: on the aromatic ring and at the benzylic position of the side chain. Oxidation of the aromatic ring results in substitution of aromatic hydrogens by acetoxy or methyl groups.[1c] Benzene itself is stable towards LTA at reflux and is frequently used as solvent in LTA reactions. However, mono- and polymethoxybenzene derivatives are oxidized by LTA in acetic acid to give acetoxylation products (eq 5).[15] Oxidation of anthracene in benzene gives

9,10-diacetoxy-9,10-dihydroanthracene, whereas in AcOH a mixture of 10-acetoxy-9-oxo-9,10-dihydroanthracene and anthraquinone is obtained.[16] The LTA oxidation of furan affords 2,5-diacetoxy-2,5-dihydrofuran (eq 6).[17]



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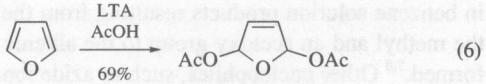
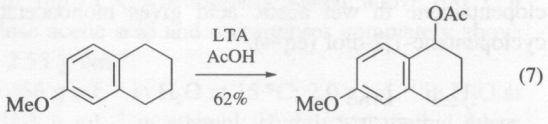


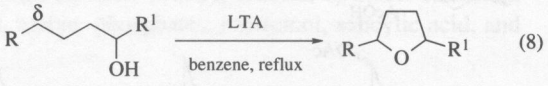
(6)

Aromatic compounds possessing a C–H group at the benzylic position are readily oxidized by LTA to the corresponding benzyl acetates. Benzylic acetoxylation is preferably performed in refluxing acetic acid (eq 7).[18] Acetoxylation at the benzylic position can be accompanied by methylation of the aromatic ring, followed sometimes by acetoxylation of the newly introduced methyl group.[18]



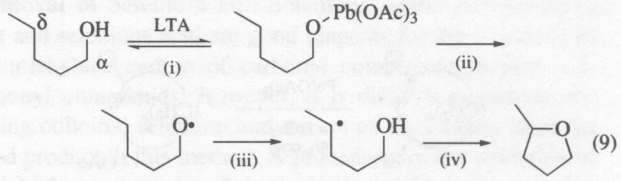
(7)

Oxidative Cyclization of Alcohols to Cyclic Ethers. The LTA oxidation of saturated alcohols, containing at least four carbon atoms in an alkyl chain or an appropriate carbon skeleton, to five-membered cyclic ethers represents a convenient synthetic method for intramolecular introduction of an ether oxygen function at the nonactivated δ-carbon atom of a methyl, methylene, or methine group (eq 8).[3,19,20] The reactions are carried out in nonpolar solvents, such as benzene, cyclohexane, heptane, and carbon tetrachloride, either at reflux temperature[1a,d,3,20,21] or by UV irradiation at rt.[22]



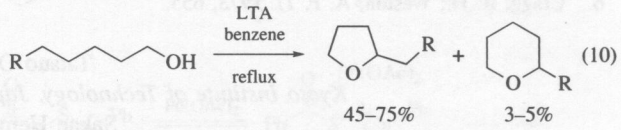
(8)

The conversion of alcohols to cyclic ethers is a complex reaction involving several steps: (i) reversible alkoxylation of LTA by the substrate; (ii) homolytic cleavage of the RO–Pb bond in the resulting alkoxy–lead(IV) acetate with formation of an alkoxy radical; (iii) intramolecular 1,5-hydrogen abstraction in this oxy radical whereby a δ-alkyl radical is generated; (iv) oxidative ring closure to a cyclic ether via the corresponding δ-alkyl cation (eq 9).[3,20] The crucial step is the formation of the δ-alkyl radical by way of 1,5-hydrogen migration. This type of rearrangement is a general reaction of alkoxy radicals, and, independently of the radical precursor, involves a transition state in which the δ-CH group must be conformationally suitably oriented with respect to the attacking oxygen radical.[1,3,23,24] Regioselective hydrogen abstraction proceeds preferentially from the δ-carbon atom, since in that case an energetically favorable quasi-six-membered transition state is involved.[3,23,24]



(9)

The LTA oxidation of primary aliphatic alcohols affords 2-alkyltetrahydrofurans in 45–75% yield. A small amount of tetrahydropyran-type ether is also formed (eq 10).[3a,20] The oxidation rate depends on the structural environment of the pro-activated carbon atom, with the rate decreasing in the order: methine > methylene > methyl δ-carbon atom.[3] When the δ-carbon atom is adjacent to an ether oxygen function, the reaction rate and the yield of cyclic ethers increases.[25] An ether oxygen attached to the δ-carbon atom increases considerably the yield of six-membered cyclic ethers (eq 11). An aromatic ring adjacent to a δ-methylene group does not noticeably affect the yield of tetrahydrofuran ethers, but when the phenyl group is attached to an ε-methylene group, the yield of six-membered cyclic ethers are enhanced.[26]



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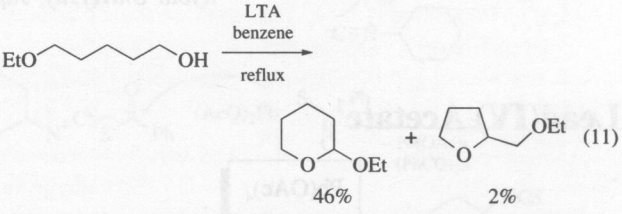
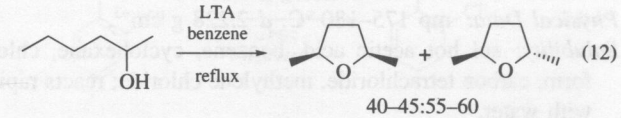


(11)

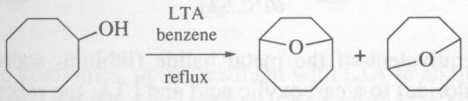
Secondary aliphatic alcohols containing a δ-methylene group afford a *cis/trans* mixture of 2,5-dialkyltetrahydrofurans in about 33–70% yield (eq 12).[20,22] The LTA oxidation of secondary alcohols is much slower than that of primary alcohols and isomeric six-membered cyclic ethers are not formed.[20,21] Tertiary aliphatic alcohols, because of unfavorable steric and electronic factors, are less suitable for the preparation of tetrahydrofurans by LTA oxidation.[22,27]



(12)

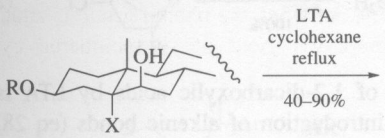
In the cycloalkanol series, the ease of intramolecular formation of cyclic ether products strongly depends on ring size. Cyclohexanol, upon treatment with LTA, affords only 1% of 1,4-cyclic ether, whereas cycloalkanols with a larger ring, such as cycloheptanol and cyclooctanol, can adopt appropriate conformations necessary for transannular reaction, affording bicyclic ethers in moderate yields (eq 13).[28] Large-ring cycloalkanols, such as cyclododecanol, cyclopentadecanol, and cyclohexadecanol, also give the corresponding 1,4-epoxy compounds as major cyclization products.[3a,28] However, the special

geometry of cyclodecanol is not favorable for the 'normal' reaction and the 1,4-cyclic ether is formed in only 2.5% yield, whereas 1,2-epoxycyclodecane (13%) and the rearranged 8-ethyl-7-oxabicyclo[4.3.0]nonane (13%) are the predominant cyclization products.[29]

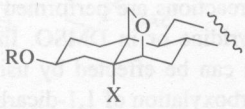


35% 1% (13)

The LTA oxidation of alcohols to cyclic ethers has been successfully applied as a synthetic method for activation of the angular 18- and 19-methyl groups in steroidal alcohols containing a β-oriented hydroxy group at C-2, C-4, C-6, and C-11 (eq 14).[3c,30,31] Hydroxy terpenoids with suitable stereochemistry can also undergo transannular cyclic ether formation (eq 15).[32]



X = H, Cl, Br, OH



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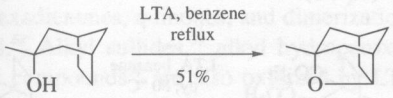
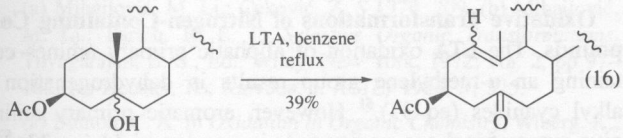


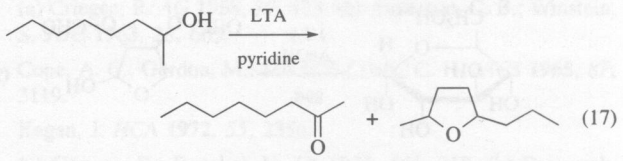
(15)

Another possible reaction of alkoxy radical intermediates, formed in the LTA oxidation of alcohols in nonpolar solvents, is the β-fragmentation reaction.[3] This process, which competes with intramolecular 1,5-hydrogen abstraction, consists of cleavage of a bond between the carbinol (α) and β-carbon atoms, thus affording a carbonyl-containing fragment and products derived from an alkyl radical fragment (usually acetates and/or alkenes).[1a,3,22] Interesting synthetic applications of the LTA β-fragmentation reaction are the formation of 19-norsteroids from their 19-hydroxy precursors and the preparation of 5,10-secosteroids (containing a ten-membered ring) from 5-hydroxy steroids (eq 16).[32]



(16)

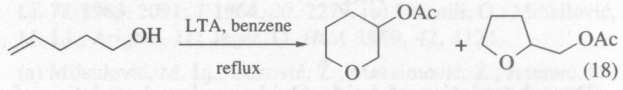
In the LTA oxidations of primary and secondary alcohols in nonpolar solvents, the corresponding aldehydes or ketones are usually obtained as minor byproducts (up to 10%).[3,20,21] However, in the presence of excess pyridine or in pyridine alone, either with heating or at rt, the cyclization and β-fragmentation processes are suppressed and good preparative yields of aldehydes or ketones are obtained (eq 17).[20,21,33] Carbonyl compounds are also obtained when the LTA oxidation of alcohols is carried out in benzene solution in the presence of manganese(II) acetate.[33]



58% 2% (17)

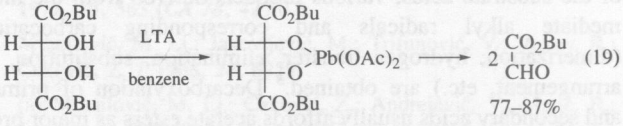
In addition to cyclic ethers, β-fragmentation products, and carbonyl compounds, acetates of starting alcohols are also usually formed in the LTA oxidation, in yields up to 20%.[20]

Unsaturated alcohols, possessing an alkenic double bond at the δ or more remote positions, react with LTA in nonpolar solvents to give acetoxylated cyclic ethers in good yield (eq 18),[34,35] while 5-, 6- and 7-alkenols undergo in great predominance an *exo*-type cyclization, affording six-, seven- and eight-membered acetoxymethyl cyclic ethers, respectively.[35]

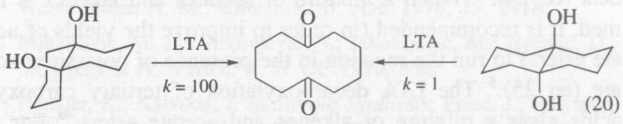


26% 14% (18)

1,2-Glycol Cleavage. LTA is one of the most frequently used reagents for the cleavage of 1,2-glycols and the preparation of the resulting carbonyl compounds (eq 19).[1,4] The reactions are performed either in aprotic solvents (benzene, nitrobenzene, 1,2-dichloroethane) or in protic solvents such as acetic acid.[36,37] The rate of LTA glycol cleavage is highly dependent on the structure and stereochemistry of the substrate. In general, there is correlation between the oxidation rate and the spatial proximity of the hydroxy groups.[36] 1,2-Diols having a geometry favoring the formation of cyclic intermediates are much more reactive than 1,2-diols whose structure does not permit such intermediates to be formed (eq 20).[38,39] The oxidation rates often provide a reliable means for the determination of the stereochemical relationship of the hydroxy groups.[39,40]



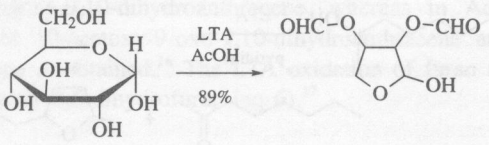
77–87% (19)



(20)

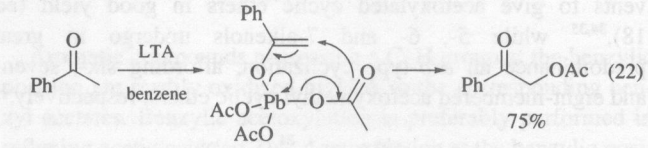
1,2-Glycol cleavage by LTA has been widely applied for the oxidation of carbohydrates and sugars (eq 21).[4,37] Because of structural and stereochemical differences, the reactivity of individual glycol units in sugar molecules is often different, thus rendering the LTA reaction a valuable tool for structural determination and for degradation studies in carbohydrate chemistry.[41]

α-Acetoxylation of Ketones. The reaction of enolizable ketones with LTA is a standard method for α-acetoxylation (eq 22).[1,3,42] The reactions are usually carried out in hot acetic acid



(21)

or in benzene solution at reflux. The reaction proceeds via an enol–lead(IV) acetate intermediate, which undergoes rearrangement to give the α-acetoxylated ketone. Acetoxylation of ketones is catalyzed by ***Boron Trifluoride***.[43] Enol ethers, enol esters, enamines,[1] β-dicarbonyl compounds, β-keto esters, and malonic esters are also acetoxylated by LTA.[42]

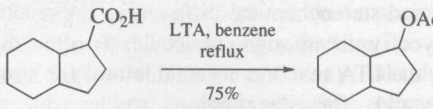


(22)

Decarboxylation of Acids. Oxidative decarboxylation of carboxylic acids by LTA depends on the reaction conditions, coreagents, and structure of acids, and hence a variety of products such as acetate esters, alkanes, alkenes, and alkyl halides can be obtained.[1,5] The reactions are performed in nonpolar solvents (benzene, carbon tetrachloride) or polar solvents (acetic acid, pyridine, HMPA).[5] Mixed lead(IV) carboxylates are involved as intermediates, and by their thermal or photolytic decomposition decarboxylation occurs and alkyl radicals are formed (eq 23).[5,44,45]

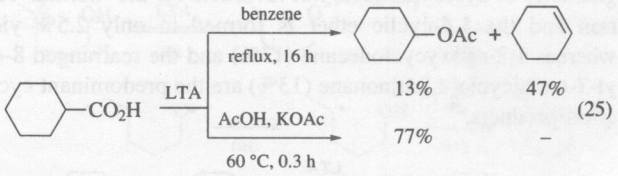
$$n\,R\text{–}CO_2H + Pb(OAc)_4 \rightleftharpoons (RCO_2)_nPb(OAc)_{4-n} \xrightarrow[(\text{or } h\nu)]{\Delta} n\,R^{\bullet} + CO_2 + Pb(OAc)_2 \quad (23)$$

Oxidation of alkyl radicals by lead(IV) species give carbocations and, depending on the reaction conditions and structure of the substrate acids, various products derived from the intermediate alkyl radicals and corresponding carbocations (dimerization, hydrogen transfer, elimination, substitution, rearrangement, etc.) are obtained.[5] Decarboxylation of primary and secondary acids usually affords acetate esters as major products (eq 24).[44] When a mixture of acetates and alkenes is formed, it is recommended (in order to improve the yields of acetate esters) to run the reaction in the presence of potassium acetate (eq 25).[5] The LTA decarboxylation of tertiary carboxylic acids gives a mixture of alkenes and acetate esters.[46] For the preparative oxidative decarboxylation of acids to alkenes, see ***Lead(IV) Acetate–Copper(II) Acetate***.



(24)

A useful modification of the LTA reaction with carboxylic acids is the oxidation in the presence of halide ions, whereby the corresponding alkyl halides are obtained (eqs 26 and 27).[47] Halodecarboxylations of acids are performed by addition of a molar equivalent of the metal halide (lithium, sodium, potassium chloride) to a carboxylic acid and LTA, the reactions being performed in boiling benzene solution.[5,47] For the iododecarboxylation of acids, see ***Lead(IV) Acetate–Iodine***.



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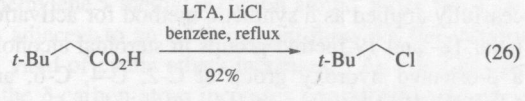

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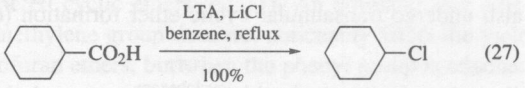
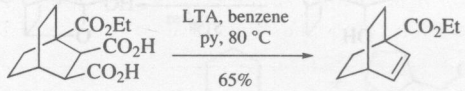


(27)

Bis-decarboxylation of 1,2-dicarboxylic acids by LTA is a useful method for the introduction of alkenic bonds (eq 28).[48] The reactions are performed in boiling benzene in the presence of pyridine or in DMSO. In some cases, LTA bis-decarboxylation can be effected by using acid anhydrides (eq 29).[49] Bis-decarboxylation of 1,1-dicarboxylic acids yields the corresponding ketones (eq 30).[50]



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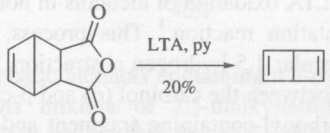

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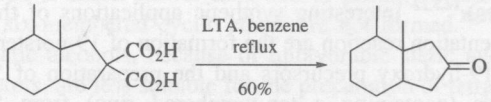
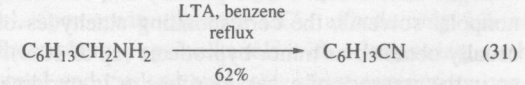


(30)

Oxidative Transformations of Nitrogen-Containing Compounds. The LTA oxidation of aliphatic primary amines containing an α-methylene group results in dehydrogenation to alkyl cyanides (eq 31).[51] However, aromatic primary amines give symmetrical azo compounds in varying yield (eq 32).[52]



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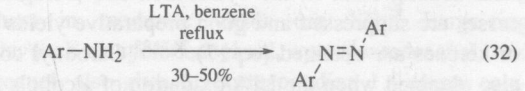
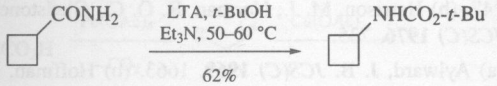


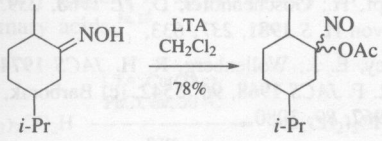
(32)

Primary amides react with LTA in the presence of alcohols to give the corresponding carbamates (eq 33), but in the absence of alcohol, isocyanates are formed.[53]

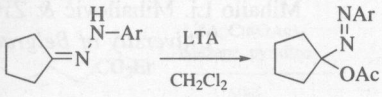


(33)

Aliphatic ketoximes, upon treatment with LTA in an inert solvent, undergo acetoxylation at the α-carbon producing 1-nitroso-1-acetoxyalkanes (eq 34),[54] whereas hydrazones afford azoacetates (eq 35) or, when the reactions are performed in alcohol solvent, azo ethers.[55] Arylhydrazines, *N,N′*-disubstituted hydrazines,[56] and *N*-amino compounds[57] are oxidized by LTA to different products.



(34)



(35)

Other Applications. By LTA oxidation of phenols, acetoxycyclohexadienones, quinones, and dimerization products can be formed.[58] Alkyl sulfides,[59] alkyl hydroperoxides,[60] and organometallic compounds[61] are also oxidized by LTA.

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