

IN THE NAME OF GOD

11137



Faculty of Science

M.Sc. Thesis in Organic Chemistry

NEW APPLICATION OF ALUMINUM TRIS (DODECYLSULFATE)
TRIHYDRATE AS A LEWIS ACID-SURFACTANT-COMBINED
CATALYST IN WATER

By

Asma Riazi

Supervised by

Professor Habib Firouzabadi

۱۳۸۸/۲/۱۸

September 2008

دکتر احسانتاج محمدی
رئیس هیئت مدیره

۱۱۸۳۳۷



دانشکده علوم

پایان نامه کارشناسی ارشد در رشته شیمی آلی

کاربردهای جدید آلومینیوم تریس دودسیل سولفات سه آبه به
عنوان یک کاتالیست ترکیبی لوئیس اسید و سورفکتانت در آب

بوسیله ی:

اسماء ریاضی

استاد راهنما:

دکتر سید حبیب فیروز آبادی ۱۸ / ۷ / ۱۳۸۸

کتابخانه مرکزی علمی شاهرود
شهر شاهرود

شهریور ماه ۱۳۸۷

۱۱۸۳۳۶

IN THE NAME OF GOD

**NEW APPLICATIONS OF ALUMINUM TRIS
(DODECYLSULFATE) TRIHYDRATE AS A LEWIS ACID-
SURFACTANT-COMBINED CATALYST IN WATER**

BY:

Asma Riazi

THESIS

SUBMITTED TO THE SCHOOL OF GRADUATE STUDIES IN PARTIAL
FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCE (M.Sc.)

IN

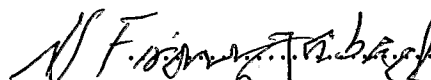
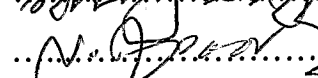
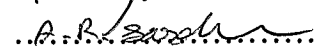
ORGANIC CHEMISTRY

SHIRAZ UNIVERSITY

SHIRAZ

ISLAMIC REPUBLIC OF IRAN

EVALUATED AND APPROVED BY THE THESIS COMMITTEE AS: Excellent

 H. Firouzabadi, Ph.D., Prof. of Chemistry (Chairman)
 N. Iranpoor, Ph.D., Prof. of Chemistry
 A. R. Sardarian., Ph.D., Associated prof. of Chemistry

September 2008

Dedicated to:

My Parents and my brother, Dr.

Ehsan Riazi

ACKNOWLEDGEMENTS

I am greatly indebted to Professor H. Firouzabadi, my major supervisor, for his instructions towards the fulfillment of this thesis, which were undoubtedly very helpful. I am also grateful to Professor N. Iranpoor for his unreserved advice and guidance through the course of this study. I would like to express my gratitude to the honorable members of the thesis committee for suggestions and evaluation of my studies. Finally, my deep acknowledgement is offered to my best advisor, Dr. A. R. Sardarian.

A. Riazi

September 2008

Abstract

**New applications of aluminum tris(dodecylsulfate) trihydrate as a
Lewis acid-surfactant- combined catalyst in water**

By:

Asma Riazi

In this thesis we have focused our attention on three important transformations in organic synthesis in water in the presence of aluminum tris(dodecylsulfate) trihydrate as a potential Lewis acid surfactant combined catalyst (LASC). We have studied the ring opening of epoxides with different nucleophils, the three component Biginelli reaction and Michael reaction with carbon nucleophiles such as α -nitro ethyl acetate, malononitrile and etc. Reactions proceeded with excellent yields in mild conditions.

TABLE OF CONTENT

CONTENT.....	PAGE
CHAPTER ONE: INTRODUCTION AND LITERATURE	
REVIEW	1
1.1.Introduction.....	2
1.2. A brief literature review on organic chemistry in water.....	3
1.2.1.Oxidations.....	4
1.2.1.1.Oxidation of alcohols in water.....	5
1.2.1.2.Oxidation of sulfides to sulfoxides.....	6
1.2.1.3. Dehydrogenation of amines to nitriles in aqueous micelles....	7
1.2.2. Reduction.....	7
1.2.2.1. Reduction of ketones to alcohols.....	7
1.2.2.2.Reduction of carbon-carbon double bonds and aryl halides with nano-palladium particles (ARP-Pd).....	9
1.2.2.3. Reductive coupling	10
1.2.2.3.1. Ullmann-type coupling.....	10
1.2.2.4. Reduction of aromatic rings.....	11
1.2.3. Reactions of radicals and carbenes in aqueous media.....	12
1.2.3.1. Synthesis of lactones.....	12
1.2.4. Carbene reactions.....	13
1.2.4.1. The reaction of carbenes with alkenes in aqueous media.....	14
1.2.5. Pericyclic reactions.....	15
1.2.5.1. Diels-Alder cyclo addition.....	16
1.2.5.1.1. Aza- cycloaddition reactions.....	18

1.2.5.2. $2\sigma + 2\sigma + 2\pi$ Cycloaddition reaction.....	19
1.2.5.3. Claisen rearrangement reactions.....	21
1.2.6. Reaction of carbanion equivalents.....	22
1.2.6.1. Wittig reaction in water.....	22
1.2.6.2. Barbier- type reactions.....	23
1.2.6.2.1. Allylation of carbonyl compounds.....	24
1.2.6.2.2. Aldol reaction in water.....	26
1.2.6.2.3. Reformatsky-type reactions.....	28
1.2.7. Reactions of carbocation equivalents.....	29
1.2.7.1. Michael reaction.....	29
1.2.7.1.1. Addition of thiols to α,β -unsaturated carbonyl compounds in water.....	31
1.2.7.1.2. Addition of amines to α,β -unsaturated carbonyl compounds in water.....	31
1.2.7.2. Mannich-type reaction in water.....	32
1.2.7.3. Strecker reaction in water.....	33
1.2.7.4. Biginelli reaction in water.....	34
1.2.7.5. Three component, regioselective, one-pot synthesis of β - hydroxytriazoles from epoxides.....	35
1.2.8. Transition-metal catalysis.....	35
1.2.8.1. Heck reaction.....	36
1.2.8.2. Suzuki reaction.....	37
1.2.8.3. Stille coupling in water.....	38
1.3. Micellar catalysis.....	39
1.3.1. Anionic surfactants.....	39
1.3.1.1. Reactions conducted in water catalyzed by sodium dodecyl sulfate (SDS).....	40
1.3.1.1.1. Michael addition of amines and thiols to α,β -unsaturated ketones in water catalyzed by micellar solution of (SDS).....	40

1.3.1.1.2. Ring opening of epoxides with various nucleophile catalyzed by SDS in water.....	40
1.3.1.1.3. Iodination of arenes with Ce (IV) catalyzed by SDS in water.....	41
1.3.1.1.4. Aldol reactions using Lewis acids and SDS	42
1.3.1.1.5. Synthesis of homoallylic amines using allyltributylstannane in water.....	43
1.3.1.1.6. Three-component Mannich-type reaction.....	43
1.3.1.1.7. Heck reactions.....	43
1.3.1.2. Lewis acid- surfactant- combined catalysts (LASCs).....	45
1.3.1.2.1. Scandium tris(dodecyl sulfate) [Sc(DS) ₃].....	45
1.3.1.2.1.1. Mukayama aldol condensation.....	45
1.3.1.2.1.2. Three-component Mannich-type reaction.....	45
1.3.1.2.1.3. Michael reactions in water.....	46
1.3.1.2.1.4. Synthesis of α -amino phosphonate.....	47
1.3.1.2.1.5. Asymmetric ring opening of meso-epoxides with aromatic amines in water.....	48
1.3.1.2.1.6. Aldol and allylation reactions catalyzed with LASCs and Brønsted acids.....	49
1.3.1.2.2. Zirconium tetrakis(dodecyl sulfate).....	50
1.3.1.2.2.1. Synthesis of quinoline from <i>o</i> -aminoaryl ketones and ketones or β -diketones.....	50
1.3.1.2.3. Copper dodecyl sulfate Cu(DS) ₂	50
1.3.1.2.3.1. Asymmetric aldol reaction.....	50
1.3.1.2.3.2. Diels-Alder reaction with Cu(DS) ₂	51
1.3.1.2.4. Aluminum dodecyl sulfate Al(DS) ₃	51
1.3.1.2.4.1. Michael addition of indoles and pyrroles to α,β -unsaturated compounds.....	52

1.3.1.2.4.2. Efficient conversion of epoxides to thiiranes and to amino alcohols at room temperature.....	52
1.4. The objective of this study.....	52
CHAPTER TWO: EXPERIMENTAL.....	55
2.1. General Information.....	56
2.2. Preparation of $\text{Al}(\text{DS})_3 \cdot 3\text{H}_2\text{O}$ from AlCl_3 and sodium dodecyl sulfate.....	56
2.3. General procedure for the reaction of CN^- with epoxides catalyzed by $\text{Al}(\text{DS})_3 \cdot 3\text{H}_2\text{O}$ to produce β -hydroxy nitriles in water.....	57
2.4. Typical procedure for the reaction of phenylglycidyl ether with KCN catalyze by $\text{Al}(\text{DS})_3 \cdot 3\text{H}_2\text{O}$ to produce corresponding β -hydroxy nitrile in water.....	57
2.5. General procedure for the reaction of N_3^- with epoxides catalyzed by $\text{Al}(\text{DS})_3 \cdot 3\text{H}_2\text{O}$ to produce β -azidoalcohols in water.....	59
2.6. Typical procedure for the reaction of phenylglycidyl ether with NaN_3 catalyzed by $\text{Al}(\text{DS})_3 \cdot 3\text{H}_2\text{O}$ to produce corresponding β -azido alcohol in water.....	60
2.7. General procedure for the reaction of NO_2^- with epoxides catalyzed by $\text{Al}(\text{DS})_3 \cdot 3\text{H}_2\text{O}$ to produce β -nitro alcohols in water.....	61
2.8. Typical procedure for the reaction of cyclohexene oxide with NaNO_2 catalyzed by $\text{Al}(\text{DS})_3 \cdot 3\text{H}_2\text{O}$ to produce corresponding β -nitro alcohol in water.....	62
2.9. General procedure for the reaction of NO_3^- with epoxides catalyzed by $\text{Al}(\text{DS})_3 \cdot 3\text{H}_2\text{O}$ to produce β -nitrate alcohols in water.....	63
2.10. Typical procedure for the reaction of cyclohexene oxide with NaNO_3 catalyzed by $\text{Al}(\text{DS})_3 \cdot 3\text{H}_2\text{O}$ to produce corresponding β -nitrate alcohol in water.....	63

2.11. General procedure for the three component Biginelli reaction of aldehyde, urea and ethyl acetoacetate catalyzed by Al (DS) ₃ .3H ₂ O to produce substituted 3,4-dihydropyrimidin-2(1H)-ones in water.....	64
2.12. Typical procedure for the three component Biginelli reaction of benzaldehyde, urea and ethyl acetoacetate catalyzed by Al (DS) ₃ .3H ₂ O and a Brønsted acid to produce 3,4-dihydropyrimidin-2(1H)-ones in water.....	65
2.13. General procedure for the Michael addition reaction of α-nitro ethyl acetate to ketones catalyzed by Al (DS) ₃ .3H ₂ O in water.....	67
2.14. Typical procedure for the Michael addition reaction of α-nitro ethyl acetate to methyl vinyl ketone catalyzed by Al (DS) ₃ .3H ₂ O in water.....	68
2.15. General procedure for the Michael addition reaction of malononitrile to ketones catalyzed by Al (DS) ₃ .3H ₂ O in water.....	69
2.16. Typical procedure for the Michael addition reaction of malononitrile to methyl vinyl ketone catalyzed by Al (DS) ₃ .3H ₂ O in water.....	70
2.17. Typical procedure for the Michael addition reaction of malononitrile to cyclohexenone catalyzed by Al (DS) ₃ .3H ₂ O in water....	70
CHAPTER THREE: RESULT AND DISCUSSION.....	72
3.1. Efficient and highly regioselective ring opening of epoxides with CN ⁻ , N ₃ ⁻ , NO ₂ ⁻ and NO ₃ ⁻ nucleophiles in water.....	73
3.2. Preparation of β-hydroxy nitriles from epoxide.....	75
3.3. Preparation of β-azido alcohols.....	78
3.4. Preparation of β-nitro and β-nitrato alcohols.....	80
3.5. Aluminum tris(dodecyl sulfate) trihydrate and Brønsted acid - catalyzed three component Biginelli reactions of aldehydes, urea and ethyl acetoacetate in aqueous solutions.....	83

3.6. Michael addition reaction of α -nitro ethyl acetate and malononitrile to α,β -unsaturated carbonyl compounds in water catalyzed by aluminum tris(dodecyl sulfate) trihydrate as a Lewis acid-surfactant combined catalys.....	90
SPECTRA OF PRODUCTS.....	97
REFERENCES.....	124
ABSTRACT AND TITLE PAGE IN PERSION.....	

LIST OF TABLES

TABLE.....	PAGE
Table 1.1. The effect of different salting out agents upon the enantioselectivity of the Reduction of ketones to alcohols.....	8
Table 1.2. Comparison of different catalysts for Diels-Alder reaction.....	17
Table 1.3. Comparison of organic solvent and water for Strecker-type Reaction from different aldehydes with diphenyl methyl amine and tributyltin cyanide.....	33
Table 3.1. Reaction of KCN with epoxides catalyzed with $\text{Al}(\text{DS})_3 \cdot 3\text{H}_2\text{O}$ in water at room temperature.....	76
Table 3.2. The effect of different acid catalysts at different pHs upon the reaction of KCN with styrene oxide in neat water.....	78
Table 3.3. Reaction of NaN_3 with epoxides catalyzed with $\text{Al}(\text{DS})_3 \cdot 3\text{H}_2\text{O}$ in water at room temperature.....	79
Table 3.4. Reaction of NaNO_2 and NaNO_3 with epoxides catalyzed by $\text{Al}(\text{DS})_3 \cdot 3\text{H}_2\text{O}$ in water.....	80
Table 3.5. The three component Biginelli condensation of aldehydes, urea and ethyl acetoacetate in the presence of $\text{Al}(\text{DS})_3 \cdot 3\text{H}_2\text{O}$ in water.....	86
Table 3.6. Biginelli reaction of benzaldehyde, ethyl acetoacetate and urea catalyzed by $\text{Al}(\text{DS})_3 \cdot 3\text{H}_2\text{O}$ and Brønsted acids in water at 80°C	88

Table 3.7: Biginelli reaction of benzaldehyde, ethyl acetoacetate and urea catalyzed by Brønsted acids in the absence of $\text{Al}(\text{DS})_3 \cdot 3\text{H}_2\text{O}$ in water at 80 °C.....	88
Table 3.8. The three component Biginelli condensation of aldehydes, urea and ethyl acetoacetate in the presence of $\text{Al}(\text{DS})_3 \cdot 3\text{H}_2\text{O}$ and $\text{CF}_3\text{CO}_2\text{H}$ in water.....	89
Table 3.9. The Michael addition reaction of α -nitro ethylacetate and malononitrile with several α, β -unsaturated ketones in the presence of $\text{Al}(\text{DS})_3 \cdot 3\text{H}_2\text{O}$ in neat water.....	92

CHAPTER ONE
INTRODUCTION AND LITERATURE REVIEW

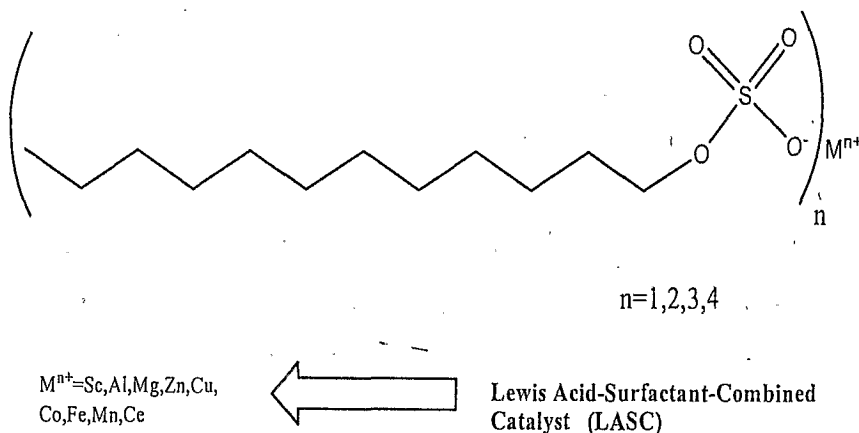
CHAPTER ONE

INTRODUCTION AND LITERATURE REVIEW

1.1. Introduction:

Although today's environmental consciousness imposes the use of water as a solvent on both industrial and academic chemists but organic solvents are still used instead of water for mainly two reasons. First, most organic substances are insoluble in water, and as a result, water does not function as a reaction medium. Second, many reactive substrates, reagents, and catalysts are decomposed or deactivated by water. Our goal is to develop a novel catalytic system which enables the use of water as a solvent for a wide range of reactions of organic materials.¹ The first drawback in the use of water (the solubility problem) may be overcome by using surfactants, which solubilize organic materials or form colloidal dispersions with them in water.² Indeed, surfactants have been occasionally used in organic synthesis. One very successful example is emulsion polymerization.³ Some late transition metal-catalyzed reactions in water have been also conducted in the presence of surfactants or surfactant-like ligands.⁴ In many other cases, however, large quantities of surfactant molecules in compare to the reaction substrates are needed for the desired reactions to proceed efficiently, and thus, the systems are impractical even if water can be used as a solvent.⁵ From the viewpoints of practicability and applicability, the surfactant-aided organic synthesis is still at the preliminary stage. In the course of investigations to circumvent the second drawback in the use of water (the decomposition problem), Kobayashi and co-workers studied Lewis acids that work in aqueous media. To avoid the use of cosolvents, which are often required for best efficiency, the effect of anionic surfactants such as SDS on Lewis-acid-catalyzed aldol reactions and allylation reactions in water was investigated. These reactions, too, benefited greatly

from the addition of surfactants. Taking this concept one step further, Kobayashi and co-workers developed a new type of Lewis acids in which the active metal cation carries long anionic hydrocarbon sulfate or sulfonate ligands (Figure 1) that gave them ability of micellar aggregates in water. These so-called Lewis acid- surfactant combined catalysts (LASCs) have been successfully employed in aqueous Diels-Alder reactions, aldol reactions, Mannich-type reactions, and allylation reactions.⁷ Recently, in our laboratory, Firouzabadi et. al have also introduced aluminum tris(dodecyl sulfate) trihydrate [Al(DS)₃.3H₂O] as another Lewis acid-surfactant- combined catalyst (LASC) for Michael addition of indoles and pyrroles to α , β -unsaturated electron-deficient compounds,⁸ ring opening of epoxides with aromatic amines and synthesis of thiiranes from epoxides in water.⁹



(Figure 1)

1.2. A Brief literature review on organic chemistry in water:

Water plays an essential role in life processes, however its use as a solvent has been limited in organic synthesis. Despite the fact that it is the cheapest, safest and most non-toxic solvent in the world, its presence is generally avoided through the

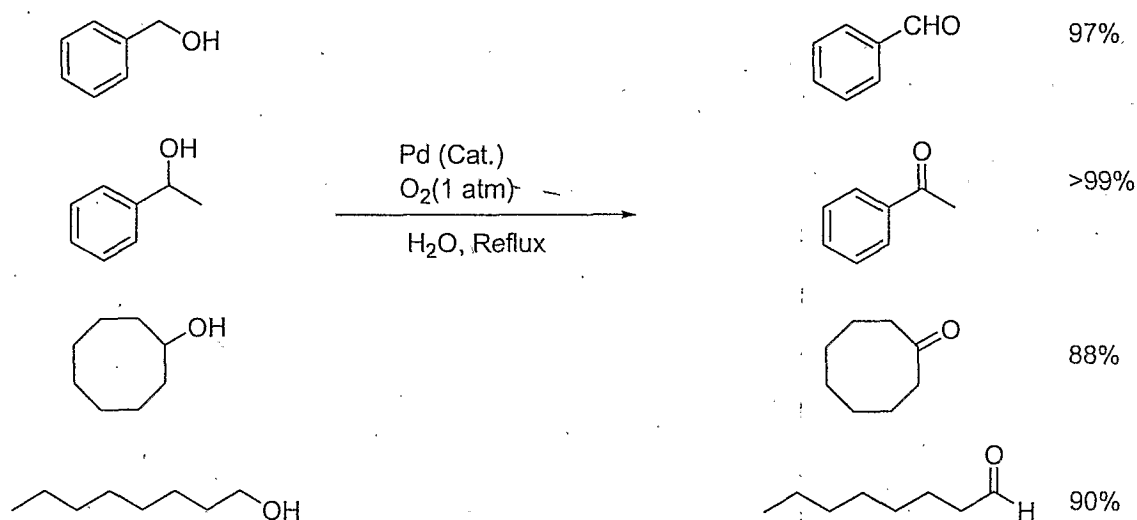
dehydrative drying of substrates and solvents. The use of water as a medium for organic reactions is therefore one of the latest challenges for modern organic chemists.¹⁰ The types of organic reactions in water are broad including pericyclic reactions, reactions of carbanion equivalent, reactions of carbocation equivalents, reactions of radicals and carbenes, transition-metal catalysis, oxidations-reductions. Aqueous organic reactions have broad applications such as synthesis of biological compounds from carbohydrates and chemical modification of biomolecules.

1.2.1. Oxidations

Oxidative transformations of functional groups are fundamental processes in organic chemistry, being used in both laboratory synthesis and in the manufacturing of bulk chemicals.¹¹ The search for new, modified, and improved procedures is intensifying, driven mostly by the need for cleaner selectivity and higher efficiency, and by economic and environmental constraints. In the last few years, there has been a strong emphasis on the use of so-called "Green Chemistry" in an effort to protect the environment from pollutants.^{12,13} Stoichiometric oxidation with metal oxidants, such as silver oxide, manganese oxide, nickel peroxide, and chromium and copper compounds, are generally used for the selective transformation of functional groups.¹⁴ These reagents however are corrosive and contain toxic heavy metals in their reduced form. The disposal of these metal oxidants is undesirable from both an economic and environmental point of view. Therefore, research has been directed towards finding ways to use these metals in catalytic amounts. As a result, great effort has been made to develop new and improved catalytic processes. An ideal catalytic oxidation reaction should take place at room temperature in an environmentally friendly solvent system, for example, in water with a green co-oxidant such as oxygen (air) or the extensively studied hydrogen peroxide.¹⁵

1.2.1.1. Oxidation of alcohols in water

Transition-metal-catalyzed aerobic oxidation of alcohols¹⁶ is one of the typical examples. Although many highly efficient aerobic alcohol oxidation systems either catalyzed by transition-metal catalysts (mainly copper,¹⁷ palladium,^{18,19} or ruthenium²⁰) alone or in combination with nitroxyl radical 2,2,6,6-tetramethyl-piperidyl-1-oxy (TEMPO)^{21,22} have been developed, only a few examples of catalytic aerobic oxidations of alcohols in water have been reported to date. For example, catalytic oxidation of alcohols can be achieved in water by molecular oxygen by using a novel amphiphilic resin-dispersion of palladium nanoparticles (ARP-Pd). In the presence of the nano-palladium catalyst, primary alcohols give the corresponding aldehyde products and secondary alcohols give the corresponding ketones in water (Scheme 1.1). ARP-Pd can be reused with negligible loss of catalytic activity after several runs.²³



(Scheme 1.1)