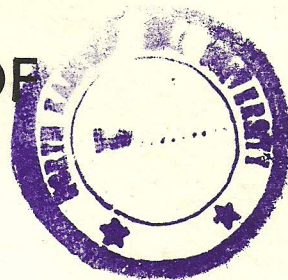


# KINETICS OF OXIDATION OF AMINO ACIDS



**ENAMUL KARIM, M. Sc.**  
DEPARTMENT OF CHEMISTRY  
SCHOOL OF PHYSICAL SCIENCES

A THESIS  
SUBMITTED  
IN  
FULFILMENT OF THE REQUIREMENT OF THE DEGREE OF  
**DOCTOR OF PHILOSOPHY**

To



**THE NORTH-EASTERN HILL UNIVERSITY**

**SHILLONG - 793 001**

**INDIA**

**JULY 1992**



DEPARTMENT OF CHEMISTRY,  
**North-Eastern Hill University**  
Shillong-793003 (Meghalaya),  
INDIA

**Dr. Mahendra K. Mahanti**  
PROFESSOR

I certify that the thesis entitled "KINETICS OF OXIDATION OF AMINO ACIDS" submitted by Mr. Enamul Karim for the Degree of Doctor of Philosophy of the North-Eastern Hill University, Shillong, embodies the record of original investigation carried out by him under my supervision. He has been duly registered, and the thesis presented is worthy of being considered for the Award of the Ph.D. Degree. This work has not been submitted for any Degree of any other University.

*Mahendra K. Mahanti*

SHILLONG  
the 22nd July 1992

PROFESSOR MAHENDRA K. MAHANTI  
Supervisor

*Professor*  
*Department of Chemistry*  
*North-Eastern Hill University*  
*Shillong — 793 003.*

Dedicated  
to  
My Parents

## ACKNOWLEDGEMENT

At the outset, I express my sincere gratitude to Dr. Mahendra K. Mahanti, Professor in the Department of Chemistry, NEHU, Shillong, for suggestion of the problem and for his able guidance and supervision throughout the course of this investigation.

I am grateful to the Dean, School of Physical Sciences and the Head of the Department of Chemistry, NEHU, for providing me the facility to carry out this work. I am thankful to all the faculty members for their good wishes. My special thanks are due to Head and staff of RSIC, NEHU, Shillong, for allowing me to avail various instrumental facilities needed during the course of my work.

I place on record my heartfelt gratitude to Principal, St. Anthony's College, Shillong, for allowing me to carry out part-time research work in NEHU. My special thanks are also due to my colleagues of Chemistry Department of St. Anthony's College, Sri B.K. Roy Choudhury, Sri S.C. Sinha, Dr. B. Das, Dr. M. Das Gupta, Dr. J.N. Viswakarma, Dr. B.L. Marwein and Fr. J. Nalanett for the cooperation they extended during this period.

It is my pleasure to acknowledge the help and generous co-operation extended by my fellow workers in the laboratory, Dr. G.C. Sarma, Mr. Abhijit Deb Roy, Mrs. S. Das Gupta and Ms. Irona Nongkynrih. My thanks are also due to Mr. C.R. Bhattacharjee, Mr. Pradip C. Paul, Mr. P. Srinivasan and Mr. S.K. Chetry for the help they rendered on various occasions during the course of my work.

I will be failing in my duty if I do not convey my thanks to the non-teaching staff of the Department of Chemistry, NEHU, and the staff of library, for their co-operation.

My grateful thanks to Mr. N.K. Paul Choudhury for the pain and trouble he has taken in efficiently and neatly typing out this thesis. I wish to thank Mr. Sebastian Hunmona for xeroxing the thesis.

Last but not the least, I express my deepest sense of gratitude to my parents for the sacrifice they did to mould my career and who were always a source of inspiration to me. I am indebted to my wife for the constant encouragement and inspiration she extended to me for achieving this goal. I am thankful to all my brothers and sisters, my brothers and sisters-in-law, my father and mother-in-law for their good wishes.

*Enamul Karim*

ENAMUL KARIM

## CONTENTS

	<u>Page</u>
INTRODUCTION	1
SCOPE OF THE PRESENT INVESTIGATION	20
EXPERIMENTAL	23
DISCUSSION	
CHAPTER 1	
KINETICS OF OXIDATION OF GLYCINE, ALANINE, VALINE, LEUCINE AND PHENYLALANINE	41
CHAPTER 2	
KINETICS OF OXIDATION OF SERINE, THREONINE AND TYROSINE	79
CHAPTER 3	
KINETICS OF OXIDATION OF METHIONINE AND CYSTEINE	102
CHAPTER 4	
KINETICS OF OXIDATION OF GLUTAMIC ACID AND ASPARTIC ACID	125
CHAPTER 5	
KINETICS OF OXIDATION OF LYSINE, ARGININE AND HISTIDINE	144
SUMMARY	167
LIST OF PUBLICATIONS	

## INTRODUCTION

Oxidation is an essential operation in organic syntheses and several reagents have been developed for a wide variety of transformations(1,2). Hexavalent chromium compounds have been widely used as oxidizing agents reacting with diverse kinds of organic substrates. In the course of these reactions, the Cr(VI) compounds are reduced to the Cr(III) species.

The earliest known Cr(VI) oxidants are chromium trioxide and chromyl chloride. Chromium trioxide has been used in various kinds of reaction media such as water, sulphuric acid, acetic anhydride, t-butyl alcohol and pyridine. Chromyl chloride has been generally used in carbon tetrachloride and carbon disulphide.

In the recent past, a large number of novel Cr(VI) oxidizing agents have been introduced, mostly in response to the needs of mildness and selectivity. The usefulness of "Jones reagent"(3) for the oxidation of organic compounds has been well established.

One of the earliest and most widely employed Cr(VI) oxidants was "Collins reagent" - dipyridinium-Cr(VI)

oxide in dichloromethane(4). The use of dichloromethane as the reaction medium constituted a major breakthrough in oxidation with dipyridinium-Cr(VI) oxide.

For oxidation purposes, the most widely used Cr(VI) complex with pyridine has been pyridinium chlorochromate(PCC) popularly known as "Corey's reagent"(5). Its principal advantage is that this reagent is not air or moisture sensitive, and oxidation with it does not involve handling a large volume of solvent. Studies on the kinetics of oxidation of primary alcohols by PCC have provided important information on the mechanism of the process(6). Involvement of protonated chromium species in the rate determining step was indicated by the catalysis of the reaction by acid, the acid catalysed reaction being first order. PCC does not polymerise acrylonitrile, and a hydrogen transfer hypothesis was thus not tenable. A substantial kinetic isotope effect,  $k_H/k_D=5.71$ , at 303K suggested a hydride transfer in the rate determining step. The transfer could occur directly between the alcohol and the protonated species or intramolecularly after the initial formation of a chromate ester. A few representative examples of oxidation of primary and secondary alcohols by PCC are given in Table 1.

Table 1. Oxidation of Primary and Secondary Alcohols by PCC (ref.5).

Alcohol	Product	% yield
1-Heptanol	Heptanal	78
1-Decanol	Decanal	92
1,6-Hexane diol	Hexandial	68
Oct-2-yn-1-ol	Oct-2-ynal	84
Citronellol	Citronellal	82
Benzhydrol	Benzophenone	100

The difficulties in handling Collins reagent and the problem arising out of the acidic nature of Corey's reagent were overcome by the use of pyridinium dichromate,  $\text{PyCr}_2\text{O}_7$  (PDC), which was recognised as a mild and selective oxidizing agent(7). This reagent is soluble in a number of solvents, though an aprotic medium is necessary for getting satisfactory results. PDC is generally used either in solution in DMF or as a suspension in dichloromethane. Anhydrous conditions were used during oxidation with PDC, and when the oxidation was performed in DMF, the carbonyl compounds were isolated by ether extraction after pouring the reaction mixture in water. PDC shows remarkable selectivity as an oxidizing agent. When dissolved in DMF, it clearly oxidizes allylic alcohols to the corresponding  $\alpha,\beta$ -unsaturated aldehydes in excellent yields.

PDC in dichloromethane oxidized primary and secondary alcohols efficiently. The aldehydes obtained as products from primary alcohols do not undergo further oxidation.

Cr(VI) oxide-3,5-dimethyl pyrazole(8) is a Cr(VI) complex which has been used as an oxidant with mixed success. The reagent is presumed to form a cyclic chromate ester that generates the carbonyl compound through intramolecular elimination. Despite the high yields of some simple aldehydes and ketones from the corresponding alcohols and near quantitative oxidation of geraniol, this reagent proved to be unsatisfactory in a number of cases(9,10).

Pyridine oxodiperoxy chromium,  $C_5H_5N:CrO_5$ , a complex of chromium pentoxide with pyridine, has also been used for the oxidation of primary and secondary alcohols(11).

In order to protect acid sensitive functional groups during oxidation of alcohols with Cr(VI)oxide, various polar aprotic solvents have been used. At least three such solvents, namely DMF(12), hexamethyl phosphoramide or HMPT(13-15) and dimethyl sulphoxide(16), have been used with some success. A solution of Cr(VI) oxide in DMF containing a trace of concentrated sulfuric acid

was able to oxidize alcohols containing acid sensitive protecting groups. The presence of catalytic amounts of sulfuric acid was essential, accompanied by the presence of an ice bath and an inert nitrogen atmosphere. Oxidation with Cr(VI) oxide in HMPT showed excellent selectivity. When a solution of Cr(VI) oxide was added to an equal volume of the substrate dissolved in HMPT, simple axial and equatorial hydroxyl functions were oxidized, the latter at a much faster rate(13). Under the same experimental conditions, Cr(VI)oxide in HMPT was found to oxidize allylic hydroxyl functions in preference to other alcoholic groups(13). A series of primary and secondary alcohols were oxidized in 80-90% yields by a solution of sodium dichromate dihydrate in concentrated sulfuric acid in DMSO at 70°C. DMSO acts as a solvent in these oxidations and not as an oxidant, as shown by the negligible oxidation of the substrate in the absence of dichromate.

The technique of using reagents intercalated in, or adsorbed on, a solid support(17) has also been exploited in oxidations with Cr(VI) oxidizing agents. The solid supports used have included graphite, silica, alumina, silica gel, celite and various reagents. As in the case of other Cr(VI) reagents, attempts were made to achieve

mild reaction conditions, better selectivity and convenient isolation of the oxidation products. On heating with graphite under reduced pressure, Cr(VI)oxide was claimed to be uniformly intercalated and the resulting substance was found to oxidize primary alcohols to aldehydes in high yields(18). Later work showed that the oxidizing agent was a surface deposit of Cr(VI) oxide on graphite (19-20).

Chromyl chloride adsorbed on silica-alumina was found to be an effective oxidizing agent for primary and secondary alcohols under neutral non-aqueous conditions (21). It has been reported that chromic acid adsorbed on silica gel was able to bring about the instantaneous oxidation of primary and secondary alcohols(22). Collins reagent adsorbed on celite has been used to oxidize allylic alcohols to the corresponding aldehydes(23-24). Chromic acid supported on an ion-exchange resin has been used to oxidize primary and secondary alcohols(25). This polymer supported reagent is prepared by adding the chloride form of the resin to an aqueous solution of Cr(VI)oxide under stirring. PCC, adsorbed on alumina, has been claimed (26) to be a better oxidizing agent than in dichloromethane suspension. Better efficiency has also been claimed(27)

for the oxidation of primary and secondary alcohols using PCC supported on polymer. The reagent, poly[Vinyl(pyridinium chlorochromate)], (PVPCC), is prepared by adding Cr(VI) oxide and concentrated hydrochloric acid to polyvinyl pyridine suspended in water.

Several facile oxidations of secondary alcohols with chromic acid in a two-phase system of ether and water have been reported (28-30). This method has proved particularly suitable for the synthesis of ketones, which are susceptible to epimerization under oxidizing conditions(28).

Cr(VI)oxide in a mixture of ether and dichloromethane oxidizes several secondary alcohols in the presence of celite(31).

There have been several reports on the oxidation of primary and secondary alcohols by Cr(VI) oxidants under phase transfer catalysis(32-36).

Allylic and benzylic alcohols were efficiently oxidized to the corresponding aldehydes with bis-tetrabutyl ammonium dichromate (TBADC) in refluxing dichloromethane(37).

The 2,2'-bipyridine complex of chlorochromic acid is a useful oxidizing agent and the use of this reagent had resulted in simplified procedures for the purification of the resulting carbonyl compounds(38). The 2,2'-bipyridinium chloro chromate and the 2,2'-bipyridine-chromium trioxide complex have both proved to be specially useful in oxidations of compounds with acid-sensitive protecting groups, due to the internal buffering of the 2,2'-bipyridyl system. These results indicated that synthetically useful changes in the properties and reactivity of Cr(VI) reagents could be brought about by varying the amine ligand associated with chromium trioxides. Another Cr(VI) reagent which has proved useful as a mild selective reagent for the oxidation of complex allylic and benzylic alcohols to the corresponding carbonyl compounds was 4-(dimethylamino)pyridinium chlorochromate(39). Secondary alcohols proved to be more reactive towards this reagent than primary alcohols. The ready preparation of this oxidizing agent, its selectivity, and the ease of using this reagent indicated that it may prove to be a useful alternative to other reagents in the oxidation of complex allylic and benzylic alcohols.

Since the process of oxidation in organic chemistry is of great value as a fundamental process in a wide

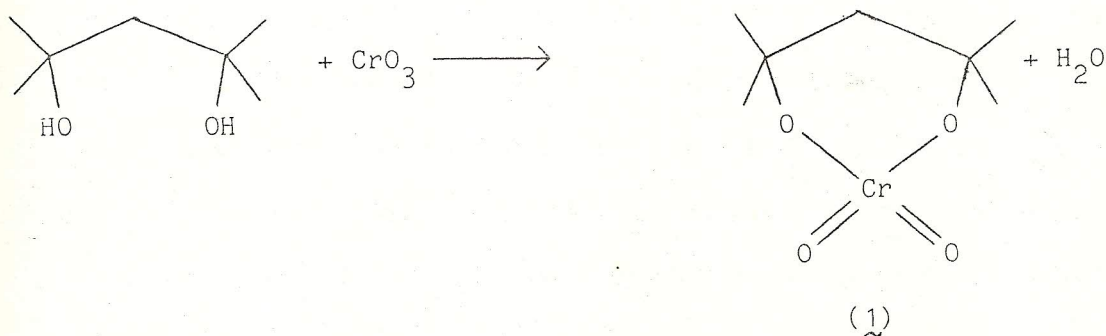
scope of chemical conversions, there has been considerable interest in the development of newer Cr(VI) reagents for the oxidation reactions. Since the appearance of pyridinium chlorochromate(5,40), other similar oxidizing agents have been developed varying the amine ligand associated with the chlorochromate anion.

A Cr(VI) reagent which was found to have certain advantages over similar oxidizing agents in terms of amounts of oxidant and solvent required, short reaction times, and high yield was pyridinium fluorochromate, PFC(41). In dichloromethane as solvent, PFC was found to oxidize primary and secondary alcohols to the corresponding aldehydes or ketones, and was also found to oxidize benzoin to benzil, as also anthracene and phenanthrene to their corresponding quinones(41).

A new class of Cr(VI) reagents derived from chromium trioxide and halosilanes has been developed(42). These reagents are highly efficient for the oxidation of alcohols to carbonyl compounds, for the oxidative coupling of mercaptans into disulphides and for a mild cleavage of oximes to carbonyl compounds. Chlorotrimethylsilane-chromium trioxide has been shown to be an efficient oxidizing

agent for the conversion of arylmethanes to benzaldehyde, and for the oxidative cleavage of some benzyl esters(42).

The oxidation of primary and secondary alcohols to the corresponding carbonyl compounds is most frequently accomplished in synthetic practice by the use of Cr(VI) reagents in amounts ranging from stoichiometric to large excess over stoichiometric(43). A new and highly effective reagent combination for the catalytic oxidation of secondary alcohols to ketones has been used(44). The reagent consisted of peroxy acetic acid as the stoichiometric oxidant and the Cr(VI) ester(1) as the catalyst with carbon tetrachloride-methylene chloride mixture as solvent. A solution of Cr(VI) ester(1) was prepared from 2-4 dimethylpentan-2,4-diol and  $\text{CrO}_3$  in dry  $\text{CCl}_4$ .



The efficient oxidation of alcohols to carbonyl compounds under mild conditions has been a necessary theme in organic syntheses. An improved procedure was described for the extremely rapid and efficient oxidation of alcohols, by the addition of a small quantity of anhydrous acetic acid to pyridinium dichromate(PDC) and freshly activated molecular sieve powder in dichloromethane at room temperature(45).

Chromium peroxide complexes have been used as general oxidants in organic syntheses. 2,2'-bipyridyl chromium peroxide has been used to convert different classes of alcohols to the carbonyl compounds, for C-C bond cleavages in 1,2-diols, for the quantitative decarboxylation of  $\alpha$ -hydroxy acids, for the conversion of oximes to their carbonyl compounds, thiols to disulphides, dihydroxy phenolic compounds to quinones, benzylamine to benzaldehyde, aromatic amines to their azo compounds, and for the conversion of anthracene and phenanthrene to their quinones(46). Pyridine chromium peroxide has been used to convert different classes of alcohols to the carbonyl compounds, thiols to disulphides, anthracene to anthraquinone, and for the decarboxylation of mandelic and benzylic acids(46). Chromium peroxide etherate has also been used as an effective reagent for the oxidation

of different classes of alcohols to their carbonyl compounds(46).

Imidazolinium dichromate(IDC) has been shown to be very useful and reliable for the oxidation of allylic and benzylic alcohols to the corresponding carbonyl compounds in high yields under mild conditions(47).

The phase transfer catalysed oxidation of benzylic alcohols using benzyltriethylammonium chlorochromate has been reported(48).

Pyridinium bromochromate has been reported as an efficient oxidant for the oxidation of benzyl alcohols, fluorenols and benzoin, all these reactions being performed in chloroform(49).

The biphosphonium dichromate reagent,  $(C_6H_5)_3 P^+CH_2P^+(C_6H_5)_3 Cr_2O_7^{2-}$ , was a particularly mild and selective reagent for the oxidation of primary and secondary alcohols(50). The oxidation of primary alcohols to aldehydes occurs without further oxidation to acid, and without double bond isomerisation or migration for such alcohols as geraniol(50).

The oxidation kinetics of alcohols by pyridinium fluorochromate (PFC) indicated that PFC was an efficient two-electron oxidant which was capable of participating in oxygen-transfer oxidations(51).

3-Carboxy pyridinium dichromate(NDC), readily prepared from nicotinic acid and chromium trioxide, is an efficient reagent for the oxidation of alcohols to carbonyl compounds in the presence of pyridine(52). The optimum molar ratio of substrate:oxidant:pyridine to ensure complete oxidation of starting material in a short reaction time was found to be 1:2.5 : 20 respectively.

The Cr(VI)oxide diperoxide oxidation of organic sulphides(53) and of tertiary amines(54) have been reported. The rate law observed suggested a mechanism involving a preliminary coordination of the amine to the metal. The oxidation rate of the amines and organic sulphides indicated a mechanism having some single-electron-transfer (SET) character.

Quinolinium dichromate(QDC) having the structure,  $(C_9H_7NH^+)_2Cr_2O_7^{2-}$ , has been used for the oxidation of alcohols and aldehydes(55). QDC is a stable orange solid,

which has been prepared by dissolving  $\text{CrO}_3$  in water, adding quinoline and collecting the product. It has been shown that quinolinium dichromate(QDC) works as efficiently as Collins' reagent(4) and activated manganese dioxide(56). The data in Table 2 shows the details of the oxidation of some alcohols and aldehydes by QDC in dichloromethane and dimethyl formamide solvents.

Table 2. Oxidation of alcohols and aldehydes by QDC (ref.55)

Compound	Product	Yield (%)	
		In $\text{CH}_2\text{Cl}_2$	In DMF
n-Butanol	n-Butanal	69	74
Benzyl alcohol	Benzaldehyde	45	45
Benzhydrol	Benzophenone	55	48
Benzaldehyde	Benzoic acid		55
Cinnamaldehyde	Cinnamic acid		52
Crotonaldehyde	Crotonic acid		85

Quinolinium dichromate (QDC) has emerged as a very useful and versatile oxidant, which is clearly deserving of widespread application. QDC in dimethyl formamide-water mixtures, in the presence of acid, has been used for the oxidation of a variety of organic substrates. Some of the organic substrates which have been oxidized by QDC,

in acid medium, have included benzyl alcohols(57), aryl-  
alkanes(58), toluene and substituted toluenes(59,60),  
fluorene(61), polynuclear aromatic hydrocarbons(59,62),  
and diphenylamines(63).



## REFERENCES

1. K.B. Wiberg, "Oxidation in Organic Chemistry", Part A, Academic Press, New York (1965).
2. H.O. House, "Modern Synthetic Reactions", W.A. Benjamin, Ed., 2nd Ed., p.257, London (1972).
3. K. Bowden, I.M. Heilbron, E.R.H. Jones and B.C.L. Weeden, J. Chem. Soc., 39(1949).
4. J.C. Collins, W.W. Hess and F.J. Frank, Tet. Lett., 3363(1968).
5. E.J. Corey and J.W. Suggs, Tet. Lett., 2647(1975).
6. K.K. Banerji, Bull. Chem. Soc. Japan, 51, 2732(1978).
7. E.J. Corey and G. Schmidt, Tet. Lett., 399(1979).
8. E.J. Corey and G.W.J. Fleet, Tet. Lett., 4499(1973).
9. J.C. Grandguillot and F. Rouessac, Synthesis, 607(1979).
10. D.N. Kirk and C.J. Slade, J. Chem. Soc. Perkin Trans. 1, 2591(1980).
11. G.W.J. Fleet and W. Little, Tet. Lett., 3749(1977).
12. G. Snatzke, Chem. Ber., 94, 729(1961).
13. R. Beugelmans and M. Legoff, Bull. Soc. Chim. France, 335(1969).
14. G. Cardillo, M. Orena and S. Sandri, Synthesis, 394(1976).
15. A.K. Banerji, H.H. Hurtado and M.C. Carrasco, Synth. Comm., 10, 261(1980).
16. Y.S. Rao and R. Filler, J. Org. Chem. 39, 3304(1974).
17. A. Mckillop and D.W. Young, Synthesis, 415(1974).
18. J.M. Lalancette, G. Rollin and P. Dumas, Can. J. Chem., 50, 3058 (1972).
19. H.B. Kagan, Chem. Tech., 510(1978).

20. L.B. Ebert, R.A. Huggins and J.I. Brauman, *Carbon*, 12, 199(1974).
21. J.S. Fillipo and C.I. Chern, *J. Org. Chem.*, 42, 2182(1977).
22. E. Santaniello, F. Ponti and A. Manzocchi, *Synthesis*, 534(1978).
23. N.H. Anderson and H.S. Uh, *Synth. Commun.*, 3, 115(1973).
24. N.H. Anderson and H.S. Uh, *Tet. Lett.* 2079(1973).
25. G. Cainelli, G. Cardillo, M. Orena and S. Sandri, *J. Amer. Chem. Soc.*, 98, 6737(1976).
26. Y.S. Cheng, W.L. Liu and S.H. Chen., *Synthesis*, 223(1980).
27. J.M.J. Frechet, J. Warnock and M.J. Farrall, *J. Org. Chem.*, 43, 2618(1978).
28. H.C. Brown and C.P. Garg, *J. Amer. Chem. Soc.*, 83, 2952(1961).
29. A.E. Vanstone and J.S. Whitehurst, *J. Chem. Soc. (C)*, 1972(1966).
30. W.E. Fristad, T.R. Bailey and L.A. Paquette, *J. Org. Chem.*, 43, 1620(1978).
31. S.J. Flatt, G.W.J. Fleet and B.J. Taylor, *Synthesis*, 815(1979).
32. R.O. Hutchins, N.R. Natale, W.J. Cook and J. Ohr, *Tet. Lett.*, 4167(1977).
33. D. Pletcher and S.J.D. Tait, *Tet. Lett.*, 1601(1978).
34. D. Landini, F. Montanari and F. Rolla, *Synthesis*, 134(1979).
35. S. Cacchi, F. La Torre and D. Misti, *Synthesis*, 356(1979).
36. G. Gelbord, T. Brunulet and C. Jouitteau, *Tet. Lett.*, 465(1980).
37. E. Santaniello and P. Ferrobaschi, *Synth. Commun.*, 10, 75(1980).
38. F.S. Guziec, Jr., and F.A. Luggio, *Synthesis*, 691(1980).
39. F. Guziec, Jr. and F.A. Luzzio, *J. Org. Chem.*, 47, 1787(1982).

40. G. Piancatelli, A. Scettri, and M.D'Auria, *Synthesis*, 245(1982).
41. M.N. Bhattacharjee, M.K. Chaudhuri, H.S. Dasgupta, N. Roy and D.T. Khathing, *Synthesis*, 588(1982).
42. J.M. Azipurna, M. Juaristi, B. Lecea and C. Palomo, *Tetrahedron*, 41, 2903(1985).
43. G. Cainelli and G. Cardillo, "Chromium Oxidations in Organic Chemistry", Springer-Verlag, Berlin (1984).
44. E.J. Corey, E. Paul Barette and P.A. Magriotis, *Tet. Lett.*, 5855 (1985).
45. S. Czernecki, C. Geargoulis, C.L. Stevens and K. Vijayakumaran, *Tet. Lett.*, 1699(1985).
46. H. Firouzabadi, N. Iranpoor, F. Kiaeezadeh and J. Toofan, *Tetrahedron*, 42, 719(1986).
47. S. Kim and D.C. Lhim, *Bull. Chem. Soc. Japan*, 59, 3297(1986).
48. C.S. Rao, A.A. Deshmukh, M.R. Thakor and P.S. Srinivasan, *Ind. J. Chem.*, 25B, 324(1986).
49. N. Narayanan and T.R. Balasubramanian, *Ind. J. Chem.*, 25B, 228 (1986).
50. H.J. Cristau, E. Torreilles, P. Morand and H. Christol, *Tet. Lett.*, 1775(1986).
51. M.N. Bhattacharjee, M.K. Chaudhuri and S. Purkayastha, *Tetrahedron*, 43, 5389(1987).
52. F.P. Cossio, M.C. Lopez and C. Palomo, *Tetrahedron*, 43, 3963(1987).
53. R. Curci, S. Giannattasio, O. Sciacovelli and L. Troisi, *Tetrahedron*, 40, 2763(1984).

54. F. Ciminale, M. Camporeale, R. Mello, L. Troisi and R. Curci, J. Chem. Soc. Perkin Trans. II, 417(1989).
55. K. Balasubramanian and V. Prathiba, Ind. J. Chem., 25B, 326(1986).
56. A.J. Fatiadi, Synthesis, 65, 133(1976).
57. D. Dey and M.K. Mahanti, J. Org. Chem., 55, 5848(1990).
58. G.C. Sarma and M.K. Mahanti, Oxidation Commun., 13, 62(1990).
59. G.C. Sarma and M.K. Mahanti, J. Phys. Org. Chem., 4, 217(1991).
60. J. Raha, G.C. Sarma and M.K. Mahanti, Bull. Soc. Chim. France, 128, 487(1991).
61. G.C. Sarma and M.K. Mahanti, Bull. Soc. Chim. France, 128, 449 (1991).
62. G.C. Sarma and M.K. Mahanti, Oxidation Commun., 13, 224(1990).
63. A. Gupta and M.K. Mahanti, Oxidation Commun., 13, 70(1990).