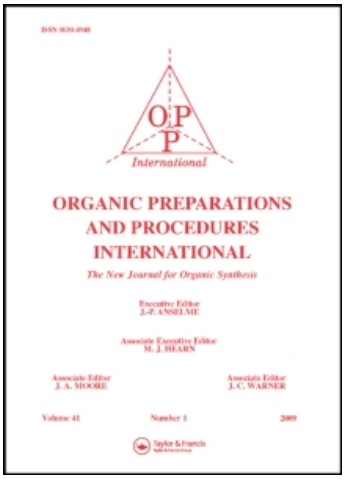

Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

RECENT APPLICATIONS OF OXOCHROMIUMAMINE COMPLEXES AS OXIDANTS IN ORGANIC SYNTHESIS. A REVIEW

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To cite this Article Luzzio, Frederick A. and Guziec Jr., Frank S.(1988) 'RECENT APPLICATIONS OF OXOCHROMIUMAMINE COMPLEXES AS OXIDANTS IN ORGANIC SYNTHESIS. A REVIEW', Organic Preparations and Procedures International, 20: 6, 533 — 584
To link to this Article: DOI: 10.1080/00304948809356301
URL: http://dx.doi.org/10.1080/00304948809356301

ORGANIC PREPARATIONS AND PROCEDURES INT. 20(6), 533-584 (1988)

RECENT APPLICATIONS OF OXOCHROMIUMAMINE COMPLEXES AS OXIDANTS IN ORGANIC SYNTHESIS. A REVIEW‡

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‡ Dedicated to the memory of Professor James W. Wilt, Loyola University of Chicago

RECENT APPLICATIONS OF OXOCHROMIUM-AMINE COMPLEXES AS OXIDANTS IN ORGANIC SYNTHESIS. A REVIEW‡

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INTRODUCTION

Continuing interest in the development of new methods for the mild, selective oxidation of alcohols to aldehydes and ketones has prompted reports of many new reagents which are effective in accomplishing these transformations. The majority of these reagents are oxidation systems based on oxochromium-amine complexes and their use has found wide applicability in many types of oxidative reactions in addition to the typical conversions of alcohols to carbonyl compounds. In this report, we review recent applications of oxochromium-amine derived reagents in complex organic synthesis, concentrating on the period of January 1980 to March 1987. A number of excellent reviews cover earlier work in this area.[1,2]

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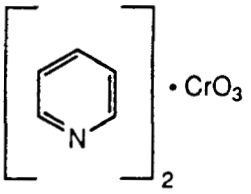
I. CHROMIUM TRIOXIDE-AMINE COMPLEXES

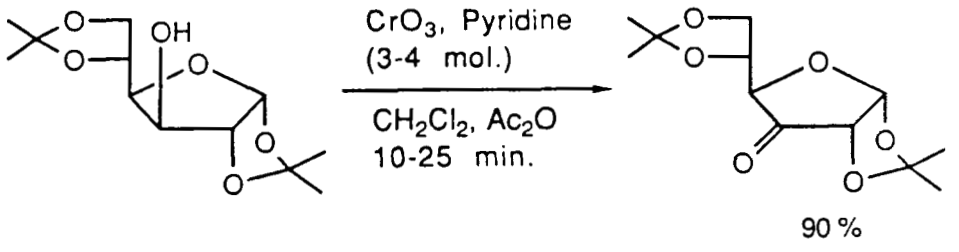
Prior to 1975 the principal oxochromium-amine reagent used for the conversion of alcohols to carbonyl compounds was the Collins reagent[3] **1** and

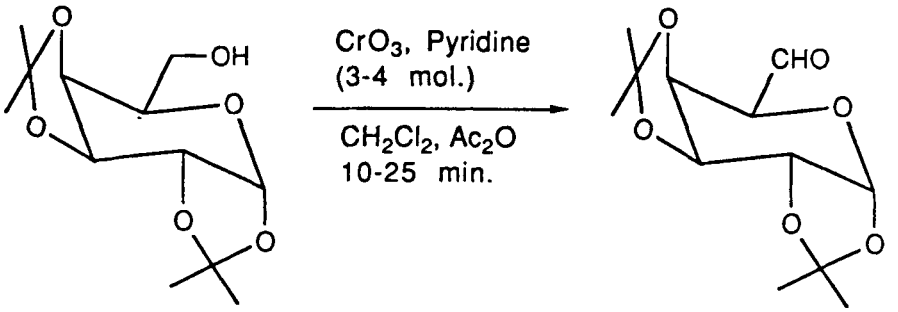


1

related systems based on the chromium trioxide-pyridine complex first described by Sarett.[4] This reagent provided an especially convenient method for the oxidation of primary alcohols to aldehydes without significant over-oxidation to the corresponding carboxylic acids. Despite some significant shortcomings -- especially the necessity to use large excesses of the complex and difficulties in workup due to formation of large amounts of gummy chromium-containing by-products -- these reagents are still widely used in the oxidation of acid sensitive substrates. For example, an acetic anhydride-activated Collins reagent has recently been used for the oxidations of partially protected carbohydrates to the corresponding carbonyl compounds in excellent yield (**Scheme 1**).[5]

Scheme 1

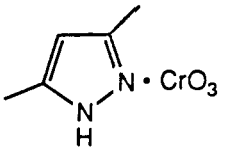




93 %

In 1973 Corey and Fleet reported an oxochromium-amine complex **2** prepared in situ from 3,5-dimethylpyrazole and chromium trioxide in dichloromethane.[6] This reagent was reported to oxidize a wide range of alcohols to carbonyl compounds in good yields (70-100%) using a ca. 2.5 molar excess of oxidant to substrate over a reaction period of 30-40 minutes.

Later, the chromium trioxide-bipyridine complex **3** was prepared and shown to be significantly less reactive than the Collins reagent.[7] Clearly, varying the heterocyclic amine moiety of the oxochromium-amine complex could change the properties and selectivity of these oxidation reagents.



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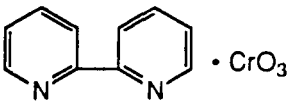


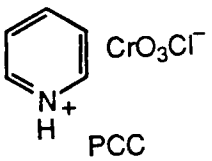
3

II. AMINE CHLOROCHROMATE REAGENTS IN ALCOHOL OXIDATIONS

A. Pyridinium Chlorochromate (PCC)

While investigating the preparation and use of chromium (V) reagents as mild oxidants for alcohols,[8] Corey and Suggs discovered that pyridinium

chlorochromate (PCC) **4** a compound long known in the literature, was a mild and



PCC

4

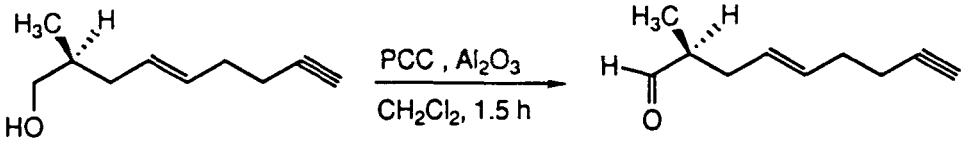
efficient chromium (VI)-amine oxidant for the conversion of alcohols to carbonyl compounds.[9] For routine small and large scale oxidations, PCC has proved to be superior to the Collins reagents in terms of oxidation efficiency (equivalents of oxidant per mole of substrate), ease and safety of preparation, ready availability and shelf stability. This commercially available compound has proved to be the reagent of choice for oxidations of primary alcohols to aldehydes and it is extensively used in oxidations of secondary alcohols to ketones. Still there are a number of deficiencies associated with PCC oxidations. This reagent is generally considered on acidic oxidant and should be used with buffers when oxidizing acid-sensitive compounds. In addition, work-up and removal of chromium-containing by-products is often difficult with this reagent.

Piancatelli has extensively reviewed the versatility of the pyridinium chlorochromate reagent,[2] including the following applications: oxidation of carbohydrates; selective oxidation of steroidal allylic alcohols; oxidation of organoboranes, organoborates and organoboroximes to aldehydes and ketones; oxidative rearrangement of tertiary allylic alcohols to enones and α, β-unsaturated aldehydes; oxidative rearrangements of tertiary cyclopropyl carbinols to β, γ-unsaturated ketones; oxidative cationic cyclizations; oxidation of 1,4-dienes to

1,4-dienones; oxidation of enol ethers to esters and lactones; cleavage of oximes to carbonyl compounds; oxidation of various substituted furan ring systems to pyrones, butenolides, and β-unsaturated-γ-dicarbonyl compounds (2-ene-1,4-diones) and applications of the polymer-supported chlorochromates including poly(vinylpyridinium) chlorochromate.

Since the Piancatelli review, however, many new applications of PCC have been reported. Pyridinium chlorochromate adsorbed on alumina as a pre-prepared material, has been demonstrated to be a very useful reagent for the oxidation of acid-sensitive alcohols to the corresponding carbonyl compounds.[10] Corey and Tramontano have shown that a good yield of aldehyde **6** may be obtained from alcohol **5** by using pyridinium chlorochromate in the presence of neutral alumina (**Scheme 2**).[11] A comparison with the pre-prepared reagent was not made in this case.

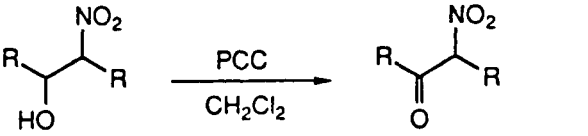
Scheme 2



5 **6**

Rosini and Ballini have discovered that pyridinium chlorochromate is effective in oxidizing 2-nitroalkanols **7** to the corresponding α-nitroketones **8** in yields of 61-87% using a modest excess of oxidant (2.25 equivalents) for a reaction duration of ~36 hours (**Scheme 3**).[12] Usually these oxidations are accomplished

Scheme 3

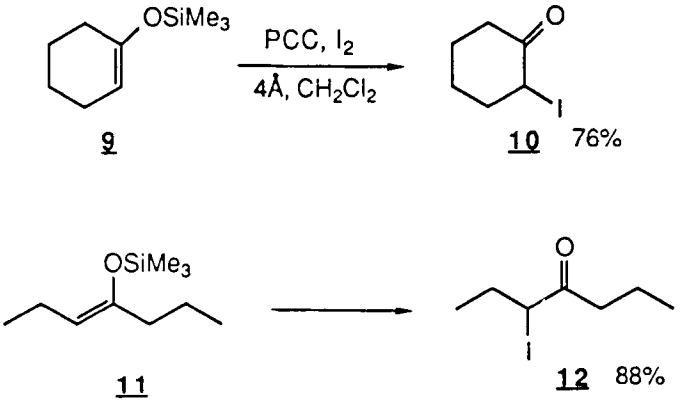


7 **8** 61-87%

using strongly acidic chromium (VI) conditions where the yields of α-nitroketones are compromised due to side reactions involving retro-aldol pathways or dehydration which due to β-elimination lead to nitroalkenes.

Enol silyl ethers **9** and **11** may be converted to α-iodocarbonyl compounds **10** and **12** by treatment with pyridinium chlorochromate/iodine in

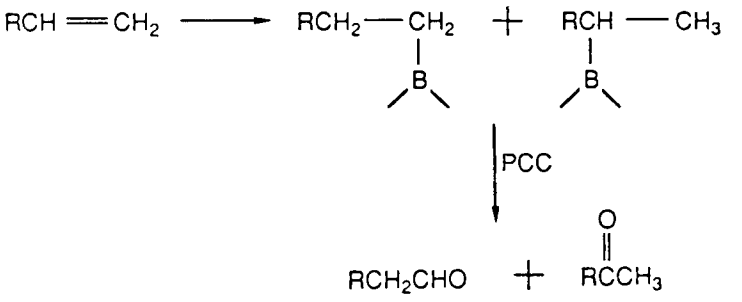
Scheme 4



dichloromethane **(Scheme 4)**.[13] The yields range from 76% to quantitative for this conversion. The yields of α-iodocarbonyl compounds starting from enol methyl ethers and dihydropyrans under the same conditions were lower (19-53%).

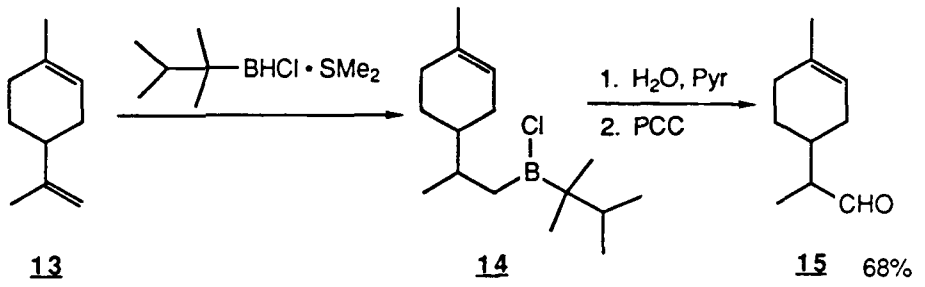
Brown has reported several improvements in the preparation of aldehydes **12** through hydroboration of terminal alkenes and pyridinium chlorochromate oxidation of the resulting organoboranes **(Scheme 5)**.

Scheme 5



For example, treatment of d-limonene (13) with thexyl chloroborane selectively afforded mixed dialkylchloroborane 14. Oxidation of 14 with PCC afforded p-menth-1-ene-9-al (15) in 68% yield (Scheme 6).[14]

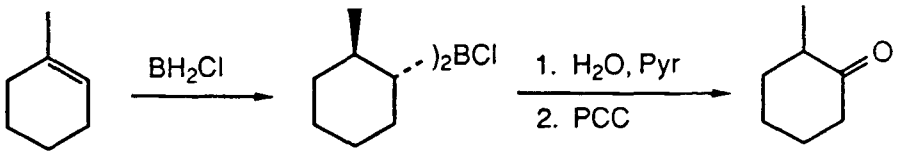
Scheme 6



13 14 15 68%

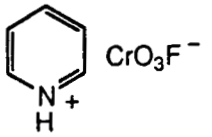
Similarly, Brown reported that dialkylchloroboranes derived from cyclic alkenes afforded excellent yields of cyclic ketones upon oxidation with pyridinium chlorochromate (Scheme 7). Chlorohydroboration - PCC oxidation of a variety of representative cyclic alkanes was also described in this study.[14]

Scheme 7



B. Pyridinium Fluorochromate (PFC)

Pyridinium fluorochromate (PFC) 16 is an oxidation reagent which is prepared in the same manner as pyridinium chlorochromate but is reported to be less acidic.

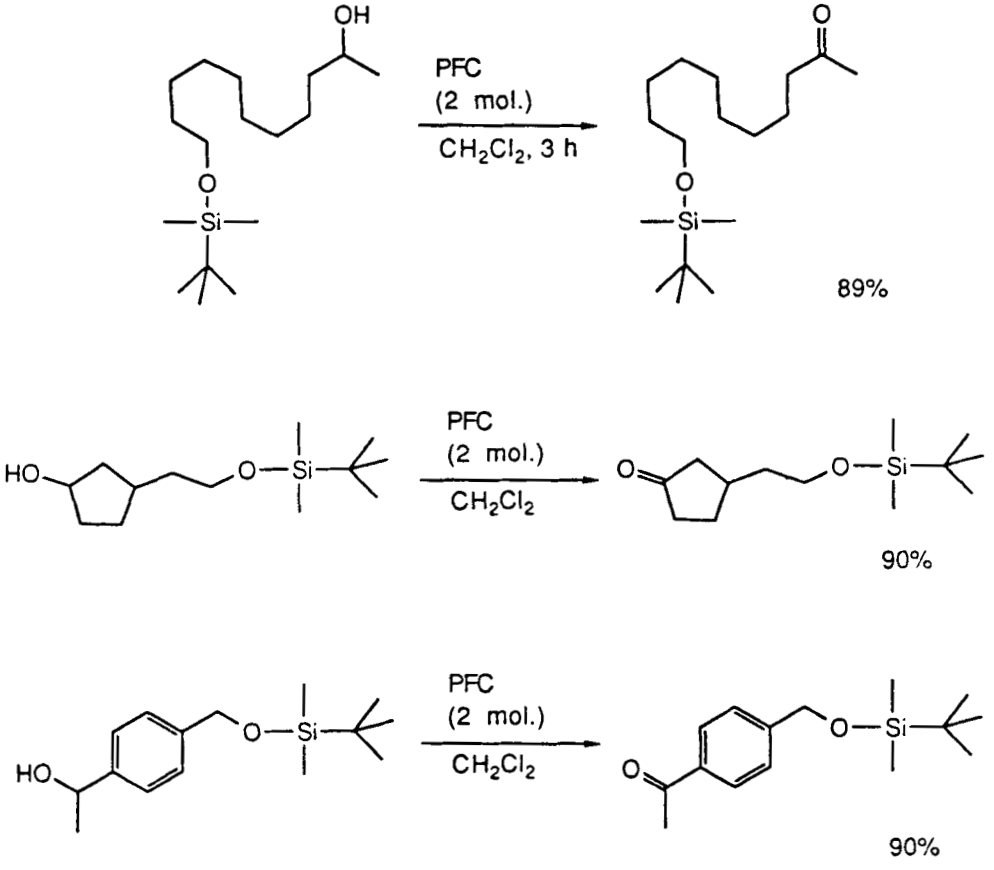


PFC

16

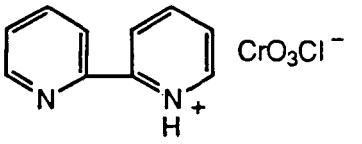
Chaudhari reports that this reagent is effective in oxidizing a wide range of alcohols to carbonyl compounds.[15,16] PFC is also reported to have been successfully used in the oxidation of a secondary alcohol function in the presence of a silyl-ether protected primary alcohol **(Scheme 8)**.[17]

Scheme 8



C. Bipyridinium chlorochromate (BPCC) and Related Complexes

Bipyridinium chlorochromate (BPCC) **17** was introduced as a reagent which affords aldehydes or ketones from the corresponding alcohols in high yields with purification steps greatly simplified due to the granular nature of the chromium

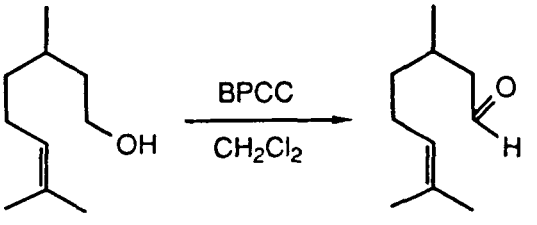


BPCC

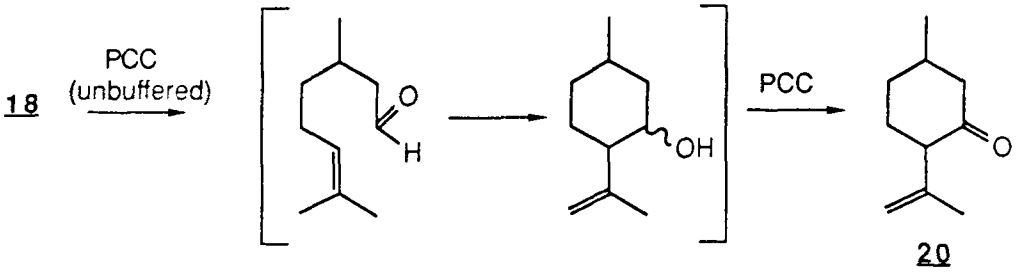
17

containing by-products.[7] The compound is easily prepared analogously to PCC. It is non-hygroscopic and shelf stable, and is commercially available. Acid-sensitive moieties of many compounds survive oxidations using BPCC possibly due to the "internal buffering" of the 2,2'-bipyridyl system. For example, treatment of citronellol **18** with BPCC yielded citronellal **19** in 89% isolated yield. No isopulegone **20**, arising from acid-promoted cationic cyclization and further oxidation (See Section VII) as in the case of unbuffered pyridinium chlorochromate (Scheme 9),[18] was observed.

Scheme 9



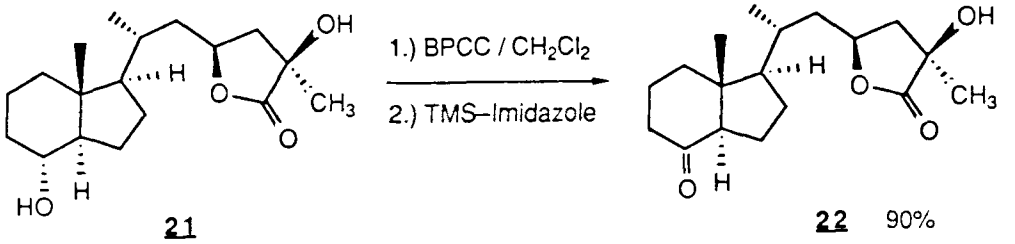
18 **19** 89%



20

In a total synthesis of calcitriol lactone, a metabolite of vitamin D_3, bipyridinium chlorochromate was used in the high yield conversion of diol **21** to ketone **22** **(Scheme 10)**.[19]

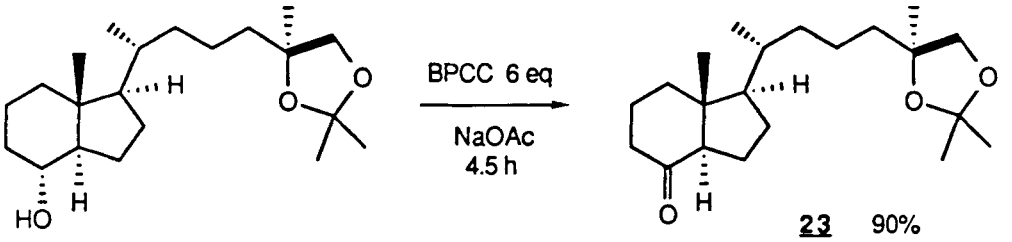
Scheme 10



21 **22** 90%

Similarly ketone **23** could be efficiently prepared using the buffered oxidant **(Scheme 11)**.[20] No significant epimerization at the ring junction was reported under these conditions. It should be noted that this type of vitamin D_3 ring system is rather prone to such epimerization. Significant isomerization was observed in similar cases when unbuffered pyridinium chlorochromate was used as an oxidant.[21]

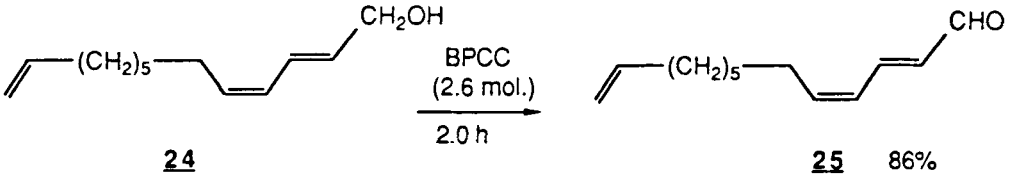
Scheme 11



23 90%

For the last step of their total synthesis of (2E, 4Z)-2,4,11- dodecatrien-1-al **25**, a degradation product of linolenic acid, Bohlmann and Rotard used BPCC to oxidize alcohol **24** in 86% isolated yield **(Scheme 12)**.[22]

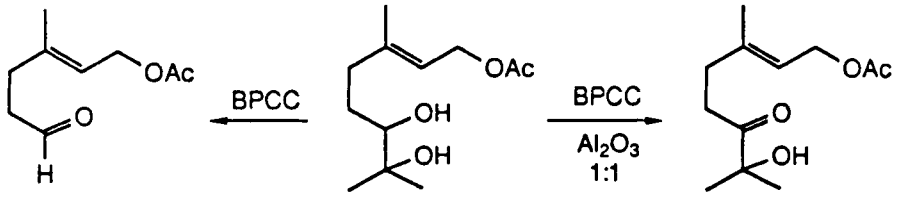
Scheme 12



24 25 86%

While conducting their synthesis of 1,2-epoxycarotinoids, Pfander and Kamber found a mixture of bipyridinium chlorochromate and alumina (activity III, 1:1 by weight) to be the most effective reagent system for the conversion of diol **26** to keto-alcohol **27 (Scheme 13)**.[23]

Scheme 13

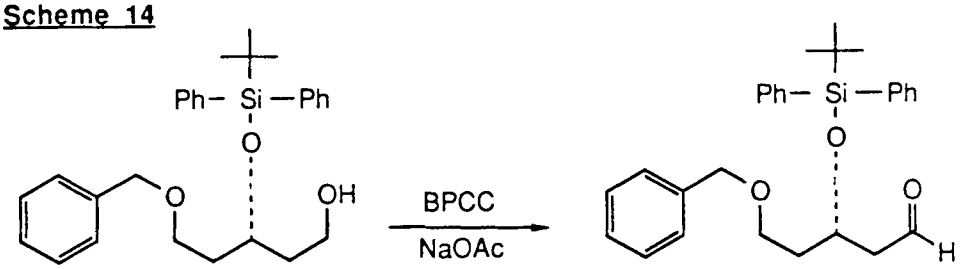


28 major product 26 27 32%

Walba reported that treatment of the same diol with bipyridinium chlorochromate alone afforded aldehyde **28** via oxidative cleavage as the major product.[24]

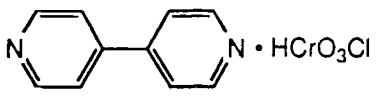
Bipyridinium chlorochromate has also recently been used to oxidize the silyl-protected chiral alcohol **29** to aldehyde **30** (**Scheme 14**).[25] This procedure utilized BPCC in conjunction with sodium acetate as a buffering agent. Aldehyde **30** was of sufficient purity for direct use in further synthetic steps.

Scheme 14

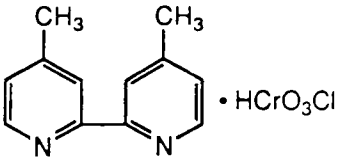


29 **30**

A number of related chlorochromate-derived reagents have also been evaluated.[26] 4,4'-Bipyridinium chlorochromate **31** and 4,4-dimethyl-2,2'-bipyridinium chlorochromate **32** each proved to be less reactive than the unsubstituted 2,2'-derivative; however, near quantitative conversions of cinnamyl

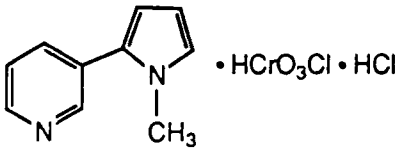


31



32

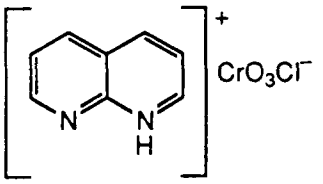
alcohol and 4-isopropylcyclohexanol to the corresponding carbonyl compounds were obtained using three-fold excesses of these reagents in refluxing dichloromethane. The chlorochromate salt of (-)-nicotine hydrochloride **33** proved to be an effective oxidant for the conversion of (±) benzoin to benzil; however no kinetic resolution of benzoin was observed when 0.6 equivalent of the reagent was used in an attempted oxidation of the racemic material.



33

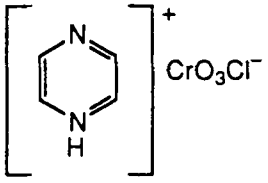
D. Napthyridinium Chlorochromate (NapCC) and Pyrazinium Chlorochromate (PzCC):

Napthyridinium chlorochromate (NapCC) **34** and pyrazinium chlorochromate (PzCC) **35** are prepared in the same manner as pyridinium chlorochromate or bipyridinium chlorochromate.



NapCC

34

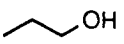
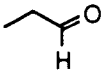
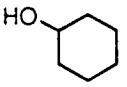
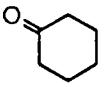
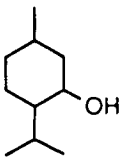
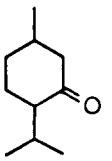
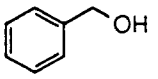
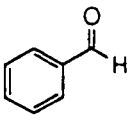
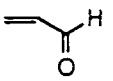


PzCC

35

Both of these reagents are reported to be crystalline, non-hygroscopic and stable for three months when stored in the dark. A study was made which compared **34**, **35**, and pyridinium chlorochromate in the course of oxidation of simple alcohols.[27] The results of this study are listed in **Table 1.**

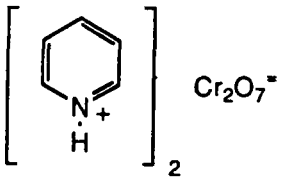
Table 1: **Comparison of Chlorochromate Oxidants** [Conv./Time (hr)]

Reactant	Product	NapCC	PzCC	PCC
		84/23.5	100/5.3	86/0.08
		38/6.0	96.6/7.6	97/0.67
		67/7.3	82/6.7	90/0.23
		81/6.25	91.5/2.8	100/0.17
		71/4.7	97/5.6	57/0.08

III. AMINE DICHROMATE REAGENTS IN ALCOHOL OXIDATIONS

A. Pyridinium Dichromate (PDC)

Corey and Schmidt developed pyridinium dichromate (PDC) **36** in an effort to find a chromium (VI) oxidation reagent which was less acidic than pyridinium chlorochromate, thus having the more neutral characteristics of the Collins reagent, and also exhibiting greater oxidation efficiency than the Collins reagent.



PDC

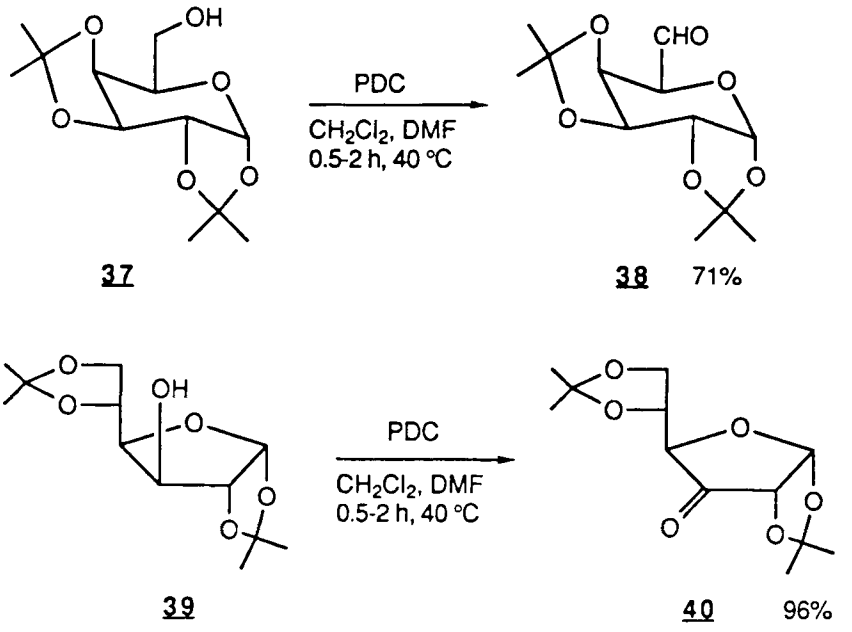
36

PDC is easily prepared by the addition of pyridine to an aqueous solution of chromium trioxide and collecting the resulting bright orange precipitate. PDC is commercially available, can be stored for long periods of time, and is soluble in a wide variety of polar solvents such as dimethylformamide, dimethylsulfoxide, water or dimethylacetamide.[28]

The solvents commonly used with this reagent are dimethylformamide and dichloromethane. The wide applicability of pyridinium dichromate has been reviewed with respect to the following transformations: oxidation of primary and secondary allylic alcohols to α,β-unsaturated aldehydes and ketones (PDC/DMF), oxidation of primary saturated alcohols to the corresponding carboxylic acids (PDC/DMF), and oxidation of primary and secondary alcohols to the corresponding aldehydes and ketones (PDC/dichloromethane).[29]

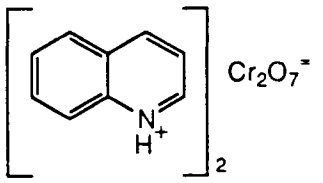
The addition of acetic anhydride to pyridinium dichromate (PDC) in dichloromethane or dichloromethane/dimethylformamide forms a highly efficient reagent which is reported to be very useful for the oxidation of primary and secondary carbohydrate alcohols **37** and **39** to the corresponding carbonyl compounds **38** and **40 (Scheme 15)**.[30]

Scheme 15



B. Quinolinium Dichromate (QDC)

Quinolinium dichromate **41** can be prepared by adding quinoline to an aqueous solution of chromium trioxide. Using refluxing dichloromethane as a reaction medium for a duration of 4 hours aldehydes are obtained from the corresponding alcohols in yields of 45-70%.[31]

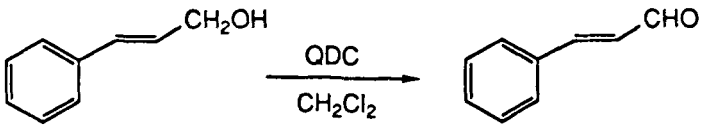


QDC

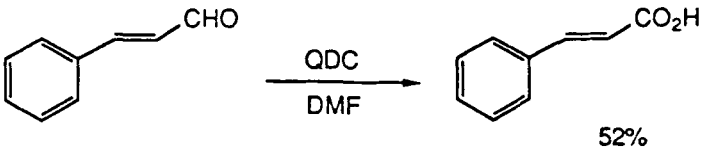
41

In contrast to pyridinium dichromate/DMF which is reported to oxidize primary alcohols to the corresponding carboxylic acids QDC/DMF is more selective, oxidizing primary alcohols to the corresponding aldehydes. The treatment of allylic or benzylic aldehydes with QDC/DMF (4 hr/RT) however, results in the formation of carboxylic acids **(Scheme 16)**.

Scheme 16



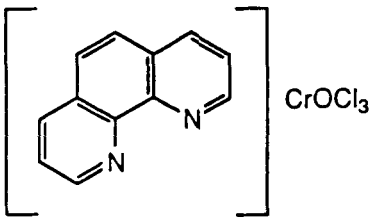
70%



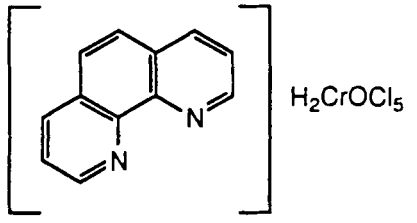
52%

IV. CHROMIUM (V) REAGENTS IN THE OXIDATION OF ALCOHOLS AND ALDEHYDES

Since chromium (V) is postulated as an intermediate in oxidations using chromium (VI), Chandrasekaran undertook a study of the preparation and use of four chromium (V) complexes as oxidants. Phenanthroline-derived reagents (Phen)$CrOCl_3$ **42** and (Phen)H_2CrOCl_5 **43** were reported to be useful for the oxidation of a wide range of alcohols to the corresponding carbonyl compounds in yields ranging from 92-96%.[32]



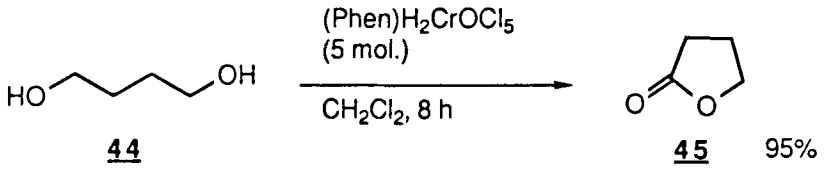
42



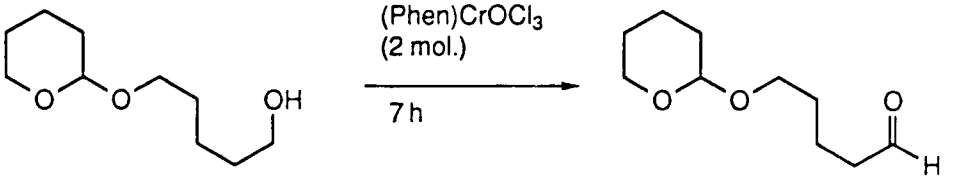
43

Most notable is the oxidation of 1,4-butanediol **44** to γ-butyrolactone **45** and the oxidation of THP-protected alcohol **46** to the corresponding aldehyde **47** **(Scheme 17)**.

Scheme 17

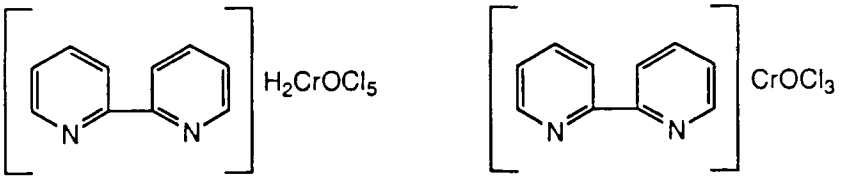


44 **45** 95%



46 **47** 85%

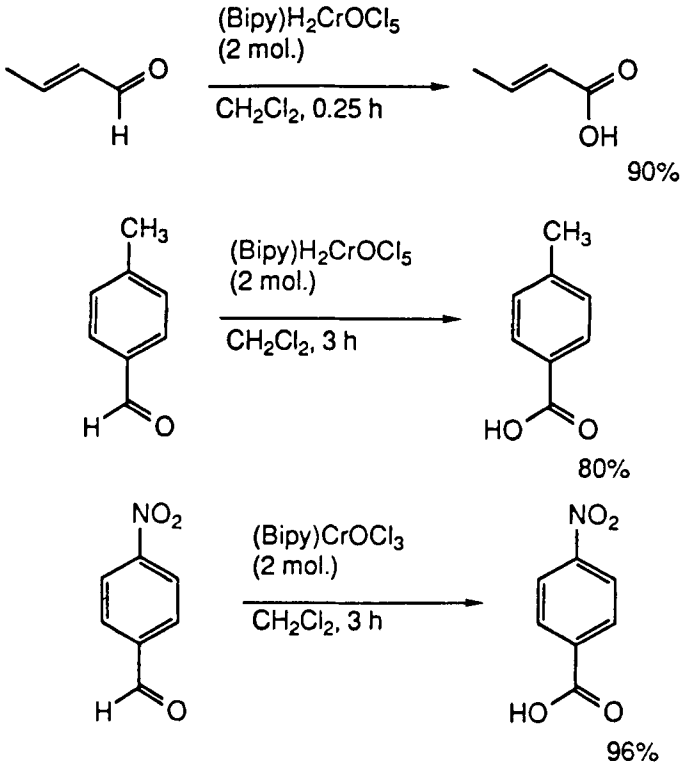
Chandrasekaran also prepared the chromium (V) complexes (bipy) H_2CrOCl_5 **48** and (bipy) $CrOCl_3$ **49**.[33]



48 **49**

These reagents are effective in oxidizing aldehydes to the corresponding carboxylic acids in high yield. Some examples of oxidations using **48** and **49** are shown in **Scheme 18**.

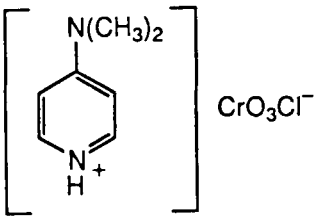
Scheme 18



V. REAGENTS FOR THE SELECTIVE OXIDATION OF BENZYLIC AND ALLYLIC ALCOHOLS

A. 4-(Dimethylamino)pyridinium Chlorochromate

The results encountered in the development of bipyridinium chlorochromate (BPCC) clearly demonstrated that synthetically useful changes could be brought about by altering the amine ligand associated with the oxochromium species. The use of 4-(dimethylamino)pyridinium chlorochromate (DMAPCC) **50** as an effective oxidant for the selective conversion of allylic and benzylic alcohols to the corresponding carbonyl compounds reinforces this concept.[34]

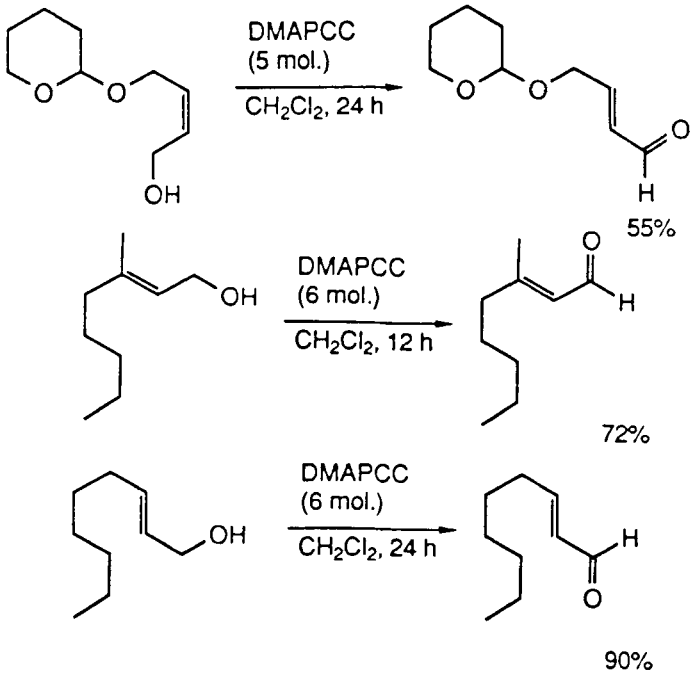


DMAPCC

50

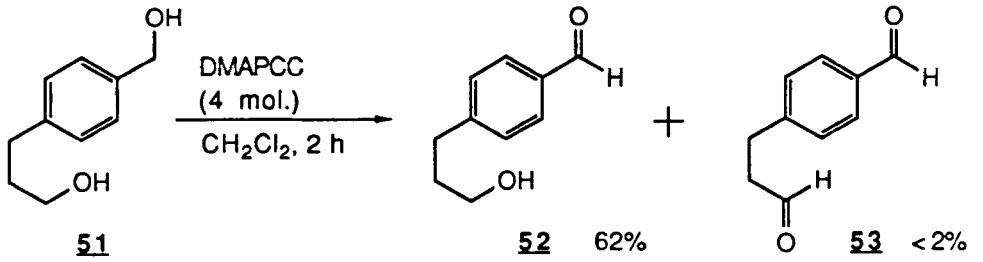
Dimethylaminopyridinium chlorochromate offers two distinct advantages when compared with both the widely used "active" manganese dioxide (MnO_2)[35] and pyridinium chlorochromate (PCC) allylic oxidants. DMAPCC is more easily prepared, is shelf-stable and requires less reaction time than MnO_2. The chromium reduction products from DMAPCC oxidation are easily separable granular precipitates in contrast to the intractable gummy tars encountered when working up PCC oxidations. Some selected examples which outline the use of DMAPCC in the oxidation of allylic and benzylic alcohols are given in **(Scheme 19)**.

Scheme 19



The selectivity of DMAPCC in oxidizing benzylic versus primary alcohol functions is indicated In the oxidation of diol **51**. DMAPCC was found to oxidize diol **51** to hydroxyaldehyde **52** with less than 2% formation of dialdehyde **53** **(Scheme 20)**. In comparison, when **51** was treated with pyridinium

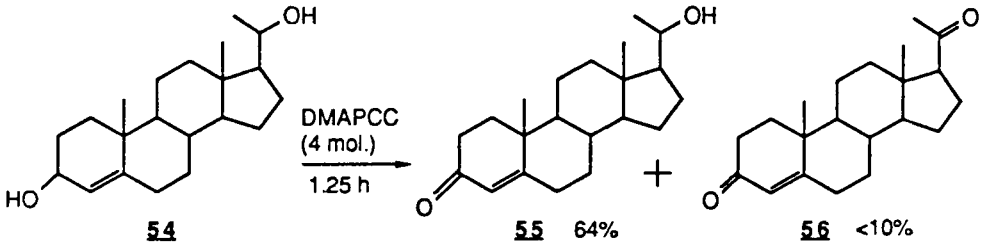
Scheme 20



51 **52** 62% **53** <2%

chlorochromate (PCC), under normal reaction conditions (1.5 equiv., 20 min), hydroxyaldehyde **52** and dialdehyde **53** were obtained in yields of 45% and 32% respectively.[34] Similarly, treatment of pregenenediol **54** with DMAPCC in chloroform (4.0 equiv., 1.25 hr) afforded hydroxyketone **55** in 64% isolated yield accompanied by less than 10% dione **56** **(Scheme 21)**.

Scheme 21



54 **55** 64% **56** <10%

In comparison, treatment of **54** with PCC/CH_2Cl_2 (1.5 equiv., 0.5 hr) afforded **55** in 34% yield and dione **56** in 38% yield.[36]

B. Bis-Tetrabutylammonium Dichromate (TBADC), Tetrabutylammonium Chlorochromate (TBACC)

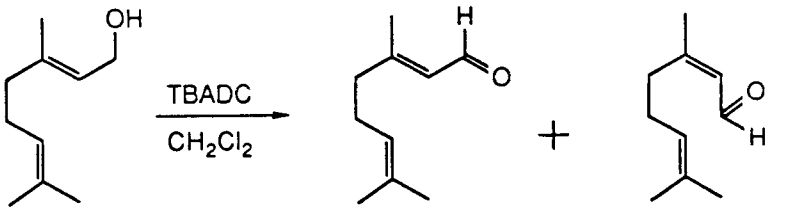
Santaniello and co-workers have developed two related chromium (VI) oxidants which are selective for the oxidation of allylic and benzylic alcohols to the corresponding carbonyl compounds.[37,38] Both reagents bear the tetrabutylammonium cation which allows for good solubility in many types of organic media. These reagents are designated as bis-tetrabutylammonium dichromate (TBADC) **57** and tetrabutylammonium chlorochromate (TBACC) **58**.

$[(n\text{-}C_4H_9)_4N^+]_2\ Cr_2O_7^=$ TBADC **57**

$(n\text{-}C_4H_9)_4N^+\ CrO_3Cl^-$ TBACC **58**

TBADC **57** was reported to oxidize geraniol **59** to a mixture of geranial **60** and neral **61** (9:1) in 90% yield using 1.0 equivalent of the reagent in refluxing dichloromethane for 1 hr (Scheme 22).

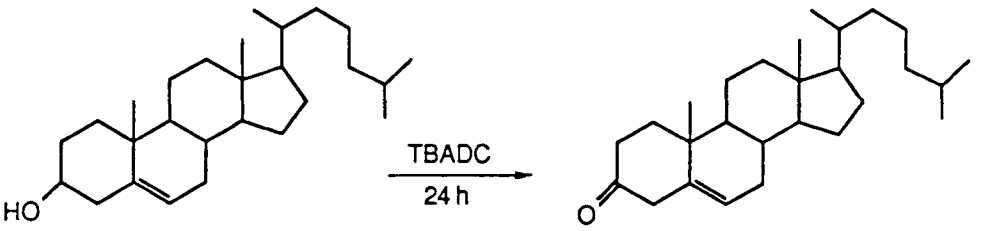
Scheme 22

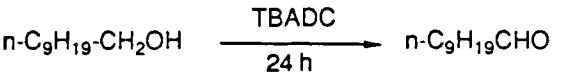


59 **60** 9 : 1 **61**

Even under prolonged reaction conditions TBADC only oxidizes 1-decanol and cholesterol to the extent of 10-20% **(Scheme 23)**.[37]

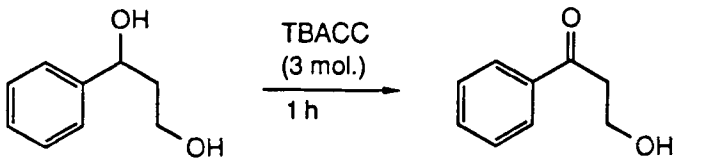
Scheme 23





TBACC **58** may be also used to selectively oxidize a wide range of allylic and benzylic alcohols to corresponding carbonyl compounds. For example, 1-phenyl-1,3-propanediol **62** was oxidized to 3-hydroxy-1-phenyl-1-propanone **63** in 52% yield using TBACC **(Scheme 24)**. The yields of carbonyl compounds from the corresponding mono-hydroxylic substrates using TBACC range from 65-78%.[38]

Scheme 24



62 **63** 52%

C. Tetrabutylammonium Chromate (TBAC)

During the course of developing an oxidation reagent which operates under homogenous conditions as well as exhibiting reasonable reactivity and selectivity, Misiti, Cacchi and Latorre reported the preparation and use of the dichloromethane and chloroform soluble tetra-n-butylammonium chromate **64**. This reagent is

$$(n\text{-}C_4H_9)_4N^+\ HCrO_4^-$$

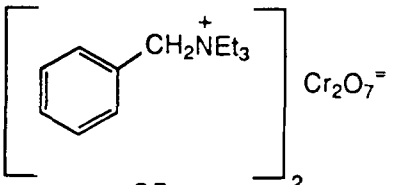
TBAC

64

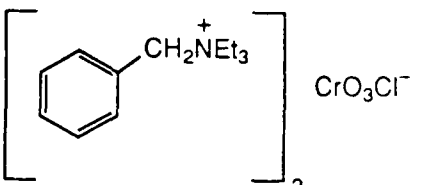
easily prepared by the addition of an aqueous solution of tetra-n-butylammonium chloride to an aqueous solution of an equimolar amount of chromium trioxide. The resulting orange-yellow crystalline quaternary ammonium chromate is collected by filtration and dried. Dichloromethane or chloroform solutions of TBAC can be used to oxidize benzylic or allylic alcohols to the corresponding carbonyl compounds in yields of 43-29% over a reaction time of 1-12 hours.[39]

D. Benzyltriethylammonium Chlorochromate

Huang and Chan reported that bis[benzyltriethyl]ammonium dichromate **65** may be prepared by adding a solution of chromium trioxide and hydrochloric acid to an aqueous solution of benzyltriethylammonium chloride.[40] Rao subsequently showed that the compound in fact obtained under these conditions is actually benzyltriethylammonium chlorochromate **66** rather than **65**. This has been



65



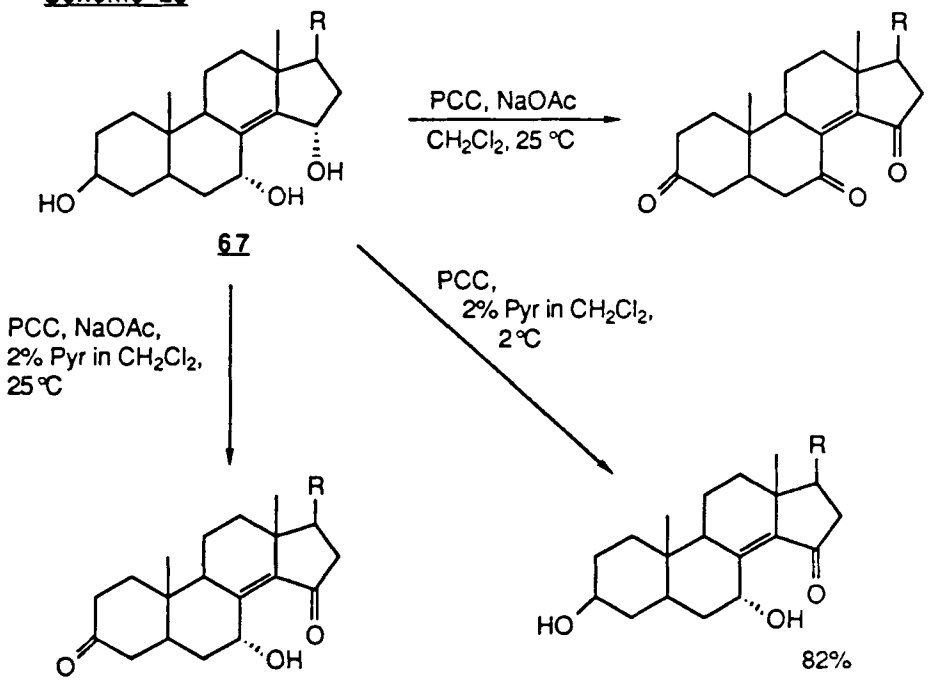
66

confirmed by preparation of **66** by two other methods as well as by combustion analysis.[41] Both reports disclose that this reagent is selective for oxidizing benzylic alcohols to the corresponding carbonyl compounds in either HMPT (hexamethylphosphoric triamide), chloroform, or under phase transfer (PTC) conditions (yields 75-99%).

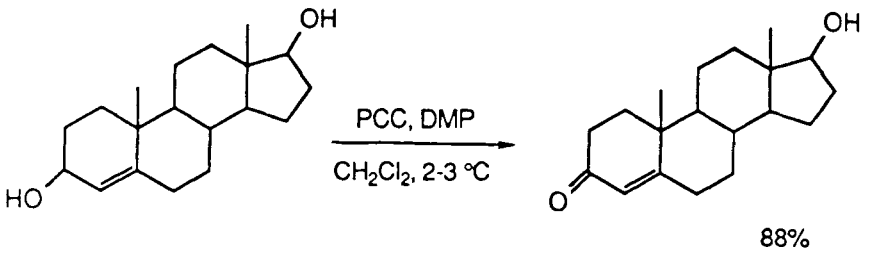
E. PCC-Pyridine; PCC-Dimethylpyrazole

Schroepfer and Parish showed that the selectivity of PCC could be significantly increased in steroidal oxidations by the addition of 2% pyridine to the reagent in dichloromethane at 2-3°C. For example, selective allylic mono-oxidation of 5α-cholest-8(14)- ene-3β, 7α, 15α-triol **67** could be achieved using this reagent **(Scheme 25)**.[42] Similar results could be achieved using added excess 3,5-dimethylpyrazole (PCC/DMP) **(Scheme 26)**.[43,44]

Scheme 25

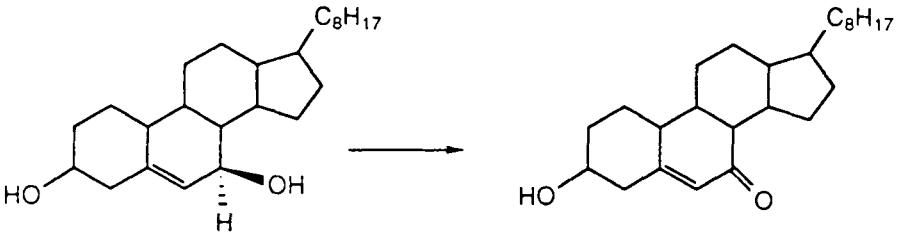


Scheme 26



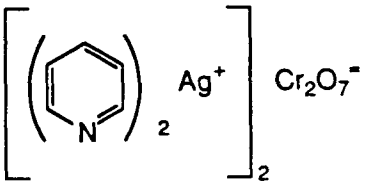
Parish has also reported remarkable selectivity in allylic steroidal oxidations using PCC-pyrazole or PCC-benzotriazole **(Scheme 27)**.[45,46] These oxidations were carried out using 3-3.5 equivalents of pyridinium chlorochromate in the presence of 2% pyrazole or benzotriazole affording the enone in 95% yield.

Scheme 27



F. Tetrakis(Pyridine)silver Dichromate (TPSD)

Firouzabadi has reported that tetrakis(pyridine)silver dichromate **68** will selectively oxidize benzylic and allylic alcohols to the corresponding carbonyl compounds.[47] TPSD is prepared by adding an aqueous solution of potassium dichromate to an aqueous solution of silver nitrate and pyridine and then collecting the resulting yellow-orange precipitate by filtration. Typically the oxidations are

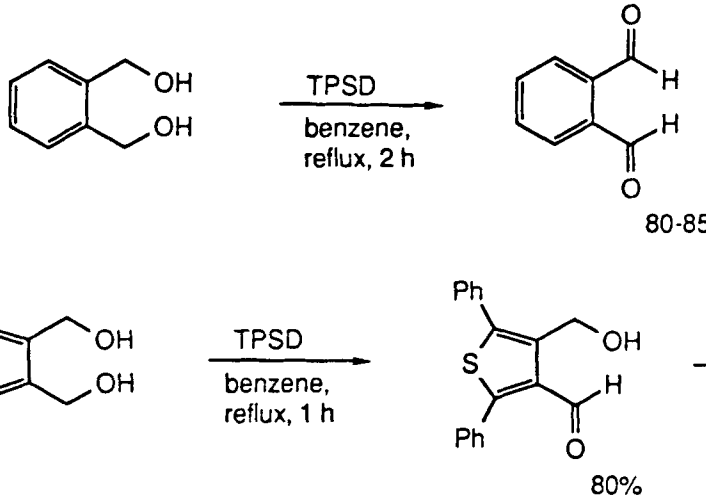


TPSD

68

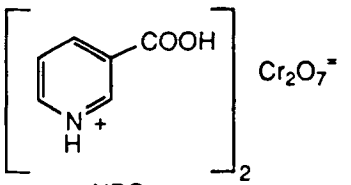
done in refluxing benzene (0.5-6 hr) using one to four equivalents of TPSD (Scheme 28).

Scheme 28

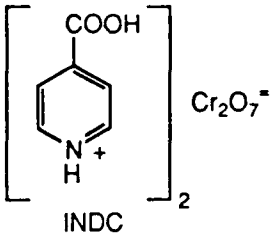


G. Nicotinium Dichromate (NDC); Isonicotinium Dichromate (INDC)

Palomo and co-workers prepared nicotinium dichromate (NDC) **69** and isonicotinium dichromate (INDC) **70** and reported that these reagents in conjunction with pyridine and dichlormethane are useful for oxidizing allylic and benzylic alcohols to the corresponding carbonyl compounds.[48] These workers report that addition of pyridine to NDC facilitated the oxidation of β-lactam



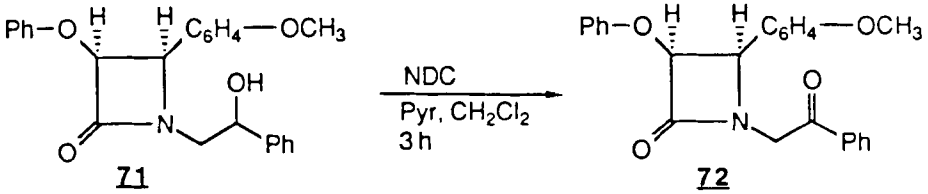
NDC
69



INDC
70

71 into the corresponding carbonyl compound 72 in 95% yield (**Scheme 29**). These results are an improvement over the PDC/pyridine reagent which gave only a 60% yield of compound 72. Optimum conditions necessary for the selective oxidations of a variety of alcohols using pyridine-NDC, including other β-lactam derivatives have also been recently reported.[48]

Scheme 29



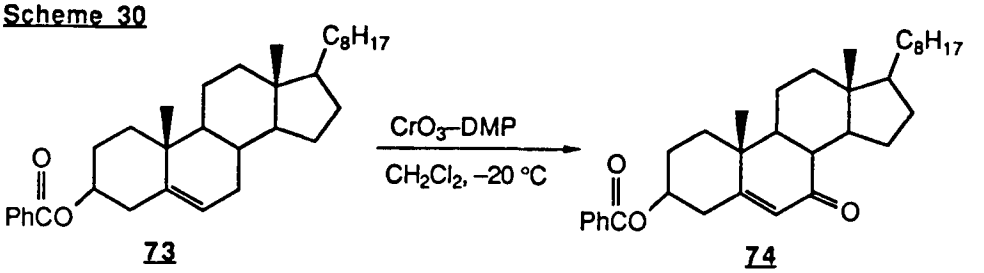
71 72

VI. OXIDATIONS OF ACTIVE METHYLENE GROUPS AND FURANS

The oxidation of allylic methylene groups to afford α,β-unsaturated carbonyl compounds using chromium trioxide-pyridine complex was initially reported by Dauben and coworkers.[49] Subsequently a variety of other oxo-chromium amine reagents have been used with considerable success in this type of oxidation.

Salmond and coworkers described the oxidation of a variety of Δ^5-steroids to the corresponding α,β-unsaturated ketones using chromium trioxide-3,5-dimethylpyrazole (CrO_3-DMP).[50] For example, treatment of cholesteryl benzoate 73 with this reagent afforded the 7-ketone 74 in 74% yield (**Scheme 30**).

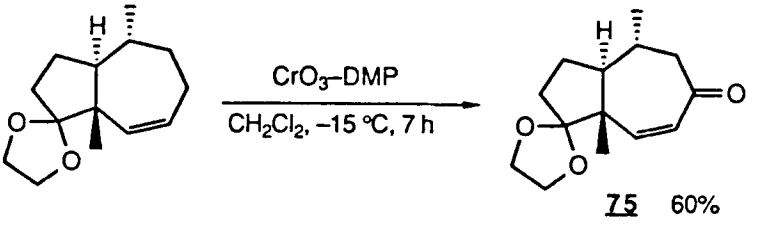
Scheme 30



73 74

This reagent has also been used in the preparation of a key intermediate in the synthesis of (±) carpesiolin **75 (Scheme 31)**.[51]

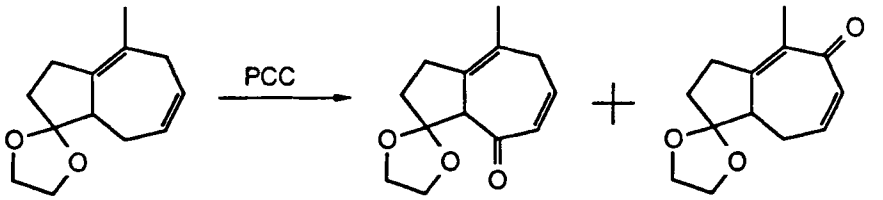
Scheme 31



75 60%

While pyridinium chlorochromate oxidations of alcohols can be carried out selectively in the presence of isolated double bonds, this reagent has found significant use in the oxidation of activated methylene groups. For example it has been used in the oxidation of 1,4-dienes such as **76** to the corresponding carbonyl compounds **(Scheme 32)**.[52]

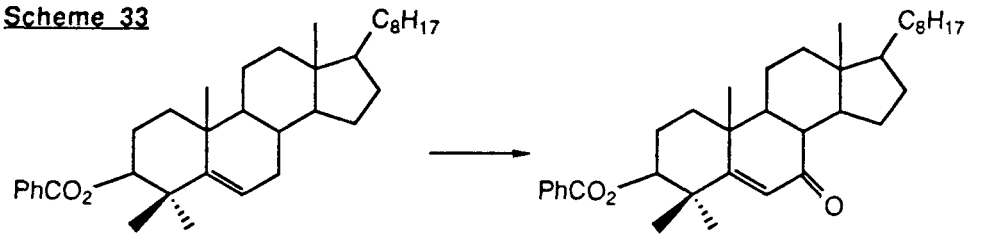
Scheme 32



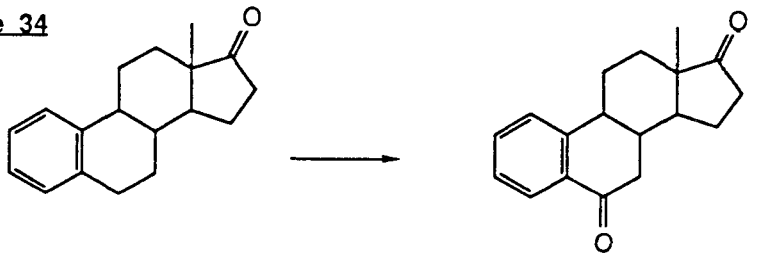
76 63% 7%

Parish and co-workers were able to effect the previously described transformation **73** to **74** **(Scheme 30)** using pyridinium chlorochromate (87% yield) or chromium trioxide-benzotriazole (71% yield).[53] Further studies by this group investigated the effect of solvent on PCC and PDC oxidations of related active methylene compounds **(Schemes 33, 34)**.[54,55]

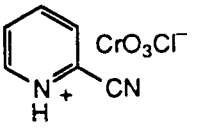
Scheme 33



Scheme 34



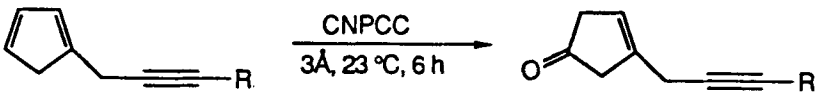
During the course of work involving the total synthesis of the clavulone family of marine eicosanoids, Corey and Mehrotra found that 2-cyanopyridinium chlorochromate (CNPCC) **77** was more effective than pyridinium chlorochromate in converting the substituted cyclopentadiene **78** to cyclopentenone **79** **(Scheme 35)**.[56] The mechanism for this reaction presumably involves the 1,4-addition



CNPCC

77

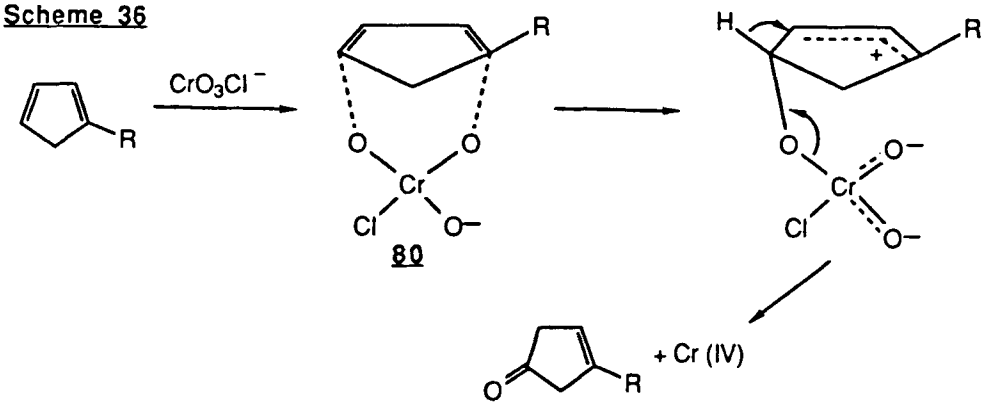
Scheme 35



78 R = n-C_5H_{11} **79** 82%

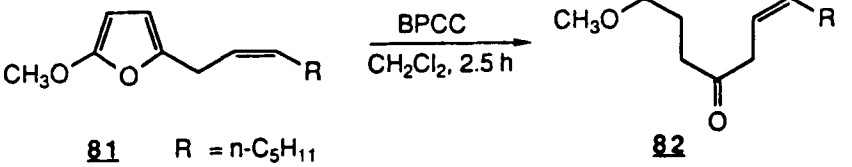
of chlorochromate anion which forms the bicyclic chromate ester **80** **(Scheme 36)**. This intermediate then rearranges to afford the β, γ-unsaturated ketone. Similar 1,4-additions have been noted in the reactions of PCC with furan derivatives.[57]

Scheme 36



An Abbott group reported that treatment of substituted furan **81** with bipyridinium chlorochromate afforded the sensitive cis-substituted keto ester **82** in good yield **(Scheme 37)**.

Scheme 37

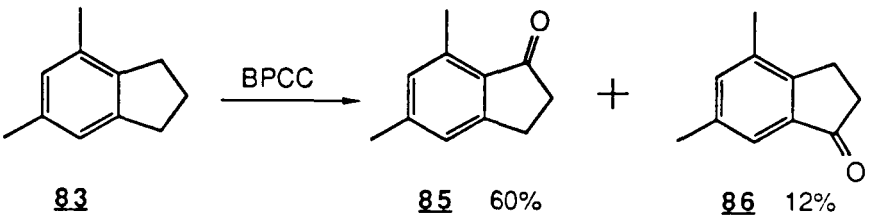


81 R = n-C_5H_{11} **82**

These workers noted that the treatment of **81** with pyridinium chlorochromate gave complex mixtures and a poor yield of **82**. Keto-ester **82** was a key intermediate in the total synthesis of (±)-12-hydroxy-5(Z), 8(Z), 10(E), 14(Z)-eicosatrienoic acid (12-HETE).[58]

Eisenbraun and Ranganathan have found pyridinium chlorochromate to be unreactive in the benzylic oxidation of indanes and tetralins to 1-indanones and tetralones using the original procedure published by Corey and Suggs. Indane and tetralin derivatives **83** and **84** may be oxidized to 1-indanones **85** and **86** and 1-tetralone **87** using bipyridinium chlorochromate in acetone (16 equiv. of BPCC to 1 equiv. substrate) for a reaction duration of 24-28 hours **(Scheme 38)**.[59] The yields for these benzylic oxidations range from 50 to 72%.

Scheme 38

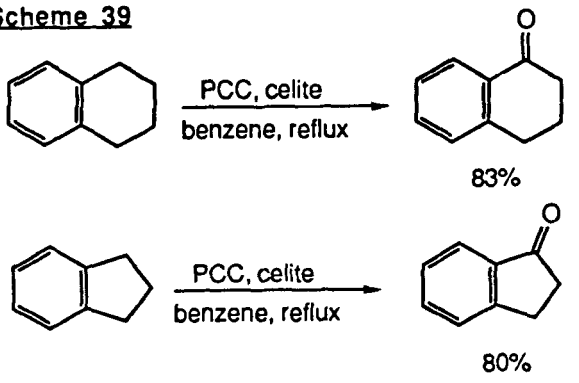


83 **85** 60% **86** 12%

84 **87** 63%

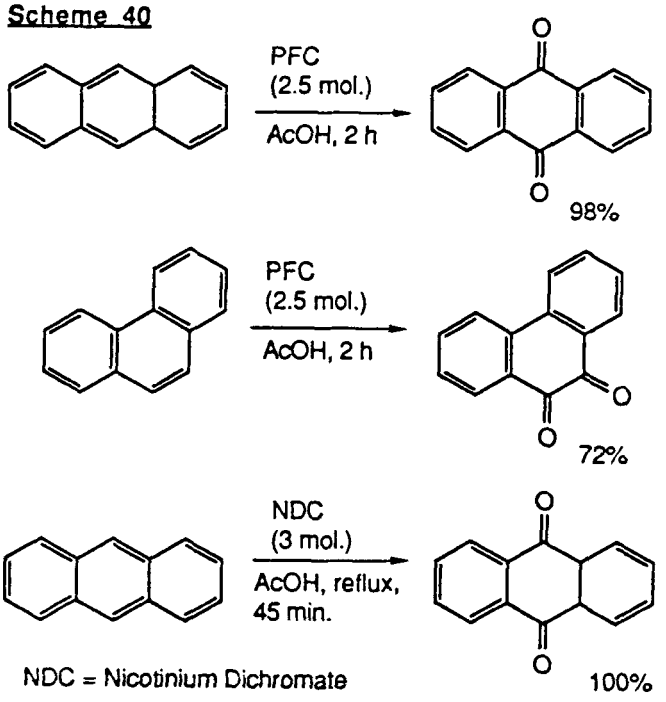
Chandresekaran later reported that pyridinium chlorochromate is effective in these types of benzylic oxidations by using the reagent (5 equivalents) with Celite in refluxing benzene for 8-15 hours. Yields for this conversion are 54-89% **(Scheme39)**.[60]

Scheme 39



Pyridinium fluorochromate (PFC) is reported to oxidize anthracene and phenanthrene to the corresponding quinones. Similar results have been reported for nicotinium dichromate (NDC) (Scheme 40).[48]

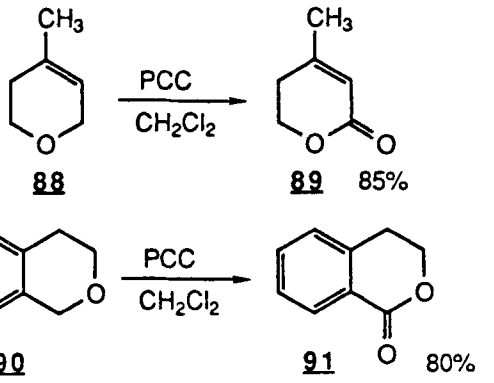
Scheme 40



NDC = Nicotinium Dichromate

Cyclic ethers such as **88** and **90** can be converted to the corresponding lactones **89** and **91** by treatment with pyridinium chlorochromate **(Scheme 41)**.[61]

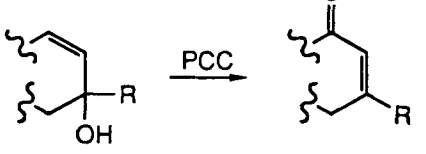
Scheme 41



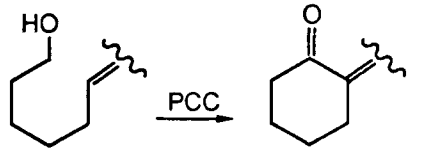
VII. OXIDATIVE CATIONIC CYCLIZATIONS AND OXYGEN TRANSPOSITIONS

There have been a large number of examples of the use of pyridinium chlorochromate in oxidative transformations of the types outlined in **Schemes 42** and **43**.[62-64] The reactions presumably occur via cationic or [3.3] sigmatropic rearrangements catalyzed by the slightly acidic PCC.

Scheme 42

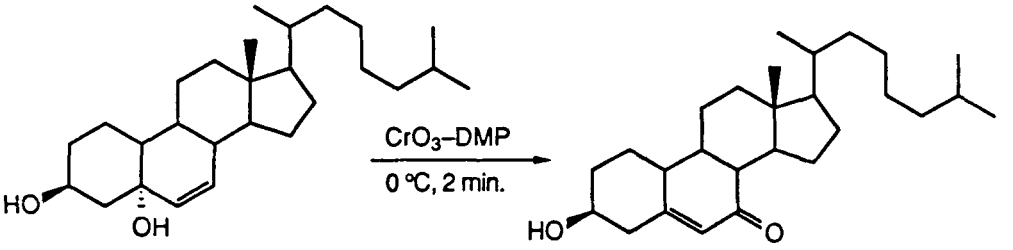


Scheme 43



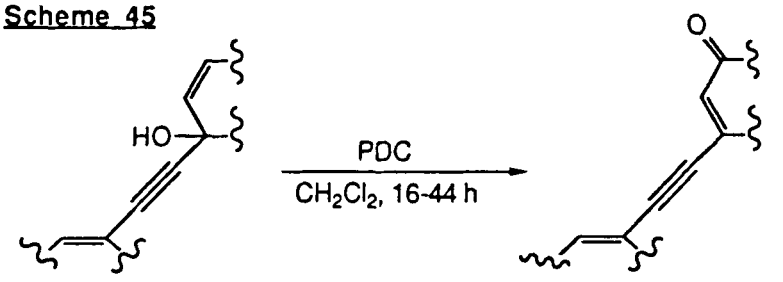
A similar transformation has been noted by Salmond and coworkers using chromium trioxide-dimethylpyrazole (CrO_3-DMP) **(Scheme 44)**.[50]

Scheme 44



Liotta and co-workers have reported that treatment of 1-ene-4-yne-3-ols of general structure **92** with pyridinium dichromate (PDC) in dichloromethane at room temperature affords the oxidatively transposed enynones **93** in yields of 62-90% **(Scheme 45)**. These oxidative rearrangements are completely regiospecific and are synthetically useful in cases where the 1,2 double bond is in the Z-configuration. Liotta surmises that the reaction proceeds through a [3.3]-sigmatropic rearrangement due to the lack of products resulting from oxygenation at the acetylenic site.[65]

Scheme 45

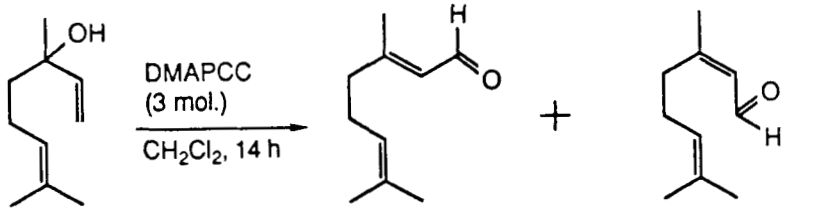


92 **93**

Treatment of linalool **94** with dimethylaminopyridinium chlorochromate (DMAPCC) in dichloromethane afforded only small amounts of geranial **95** and neral **96** as products of oxidative transposition **(Scheme 46)**. The remainder of

the material isolated was unreacted starting linalool, indicating that the less acidic DMAPCC is less prone to promote such transposition reactions.[66]

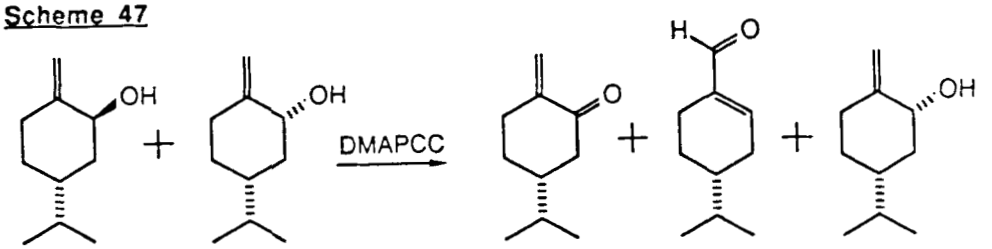
Scheme 46



94 95 13% 96 8%

During their search for a suitable oxidation reagent for the conversion of the epimeric mixture of alcohols **97** and **98** to ketone **99**, Pietra and co-workers treated the mixture with DMAPCC under standard oxidation conditions and obtained a mixture of desired **99** and transposed aldehyde **100** in a 1:1 ratio along with unreacted **98** (Scheme 47).[67]

Scheme 47



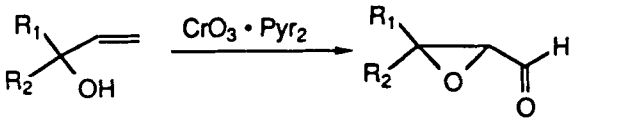
97 98 99 100 recovered

Since **98** was recovered unchanged, Pietra explained that only alcohol **97** with an axial hydroxyl group was oxidized to enone **99** by DMAPCC. Treatment of the same mixture with pyridinium chlorochromate (PCC) gave mainly aldehyde **100**. The yield of **99** could be increased somewhat by buffering the PCC oxidation with sodium acetate.

VIII. OXIDATIVE TRANSPOSITION - EPOXIDATION REACTIONS

It has been shown that the Collins reagent was useful for the conversion of tertiary allylic alcohols **101** to α,β-epoxy aldehydes **102 (Scheme 48)**. Smaller

Scheme 48

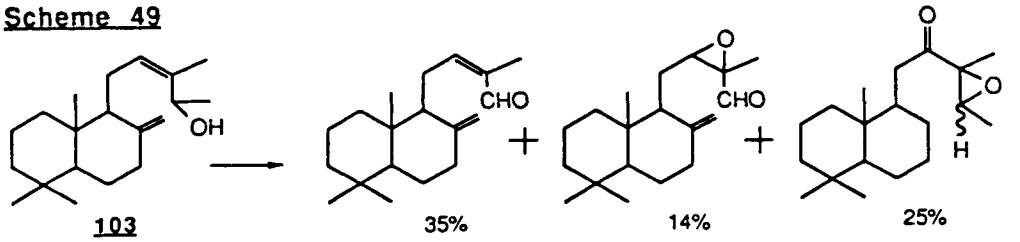


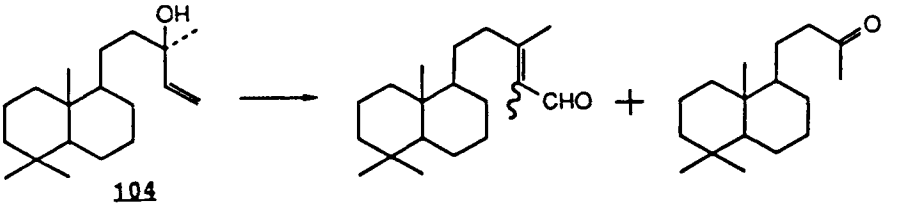
101 **102** 51-81%

amounts of α,β-unsaturated aldehydes also accompanied the epoxy-aldehydes. Compounds such as **101** are easily prepared by the addition of vinyl lithium to a ketone. The product of the overall oxidative transformation is the equivalent of the epoxidation of the product of a directed aldol condensation between acetaldehyde and the ketone.

The allylic transposition-epoxidation properties of CrO_3/dimethyl-pyrazole were also studied by Herz; for example, in the oxidation of labda-8-(20)-12-diene-14-ol **(103)** and manool **(104) (Scheme 49)**.[68]

Scheme 49

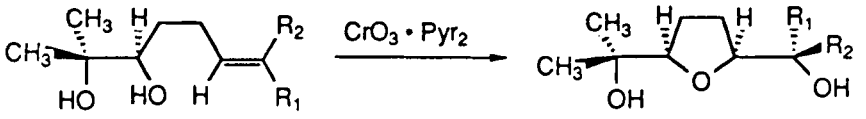




IX. OXIDATIVE ETHER AND ESTER FORMATION

The Collins reagent was found to promote oxidative transformations affording cis-disubstituted tetrahydrofuran derivatives **107** from neryl/geranyl acetate-derived diols **105** and **106** **(Scheme 50)**.[24] Such transformations may prove useful in preparing cis-substituted tetrahydrofuran-type natural products such as monensin.

Scheme 50



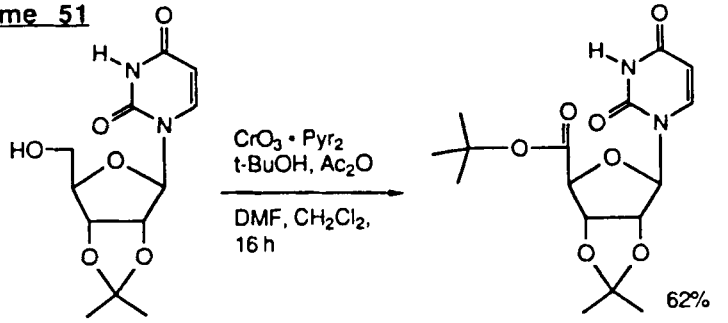
104

105 $R_1 = CH_2OAc$, $R_2 = H$

106 $R_1 = H$, $R_2 = CH_2OAc$

Corey and Samuelsson report that carbohydrate-derived tert-butyl esters may be prepared from the corresponding carbohydrate primary alcohols.[69] This is achieved by first treating the primary alcohol with four equivalents of chromium trioxide-pyridine complex in dichloromethane-dimethylformamide (4:1) followed by adding acetic anhydride/tert-butyl alcohol to the reaction mixture. Thus the intermediate aldehyde is converted to the tert-butyl hemiacetal, which is itself then further oxidized to the ester **(Scheme 51)**.

Scheme 51

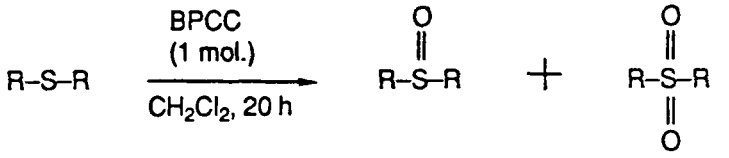


The direct oxochromium-amine mediated oxidation of cyclic ethers to lactones has been previously described **(Scheme 41)**.

X. OXIDATIONS OF SULFUR-CONTAINING MOLECULES

2,2'-Bipyridinium chlorochromate (BPCC) may be used to oxidize dialkyl sulfides **108** to the corresponding sulfoxides **109** and sulfones **110**. Dialkyl sulfoxides are the predominant products **(Scheme 52)**.[70]

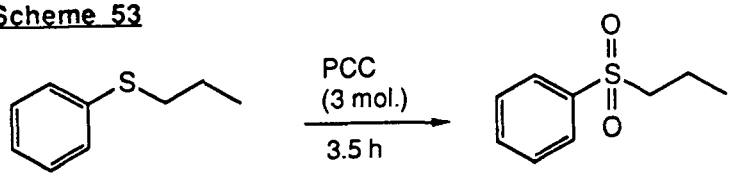
Scheme 52



	108	**109**	**110**
a.	R = n-propyl	80%	19%
b.	n-butyl	87%	2.8%
c.	tert-butyl	68%	0%

In comparison, Suggs reported that treatment of phenyl propyl sulfide **111** with pyridinium chlorochromate (PCC) gave the corresponding sulfone **112** in 60% yield **(Scheme 53)**.[71]

Scheme 53

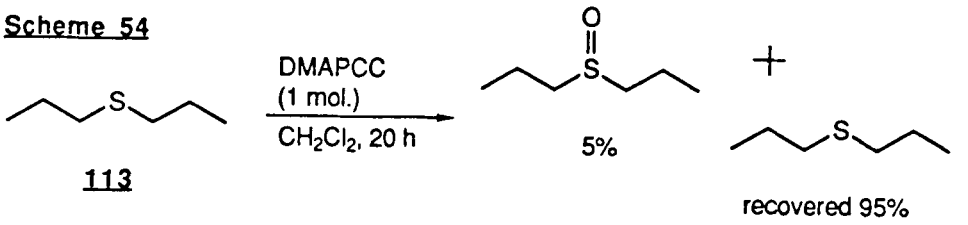


111 **112** 60%

It is worth noting that the attempted oxidation of di-n-propyl sulfide **113** with 1.0 equivalent of dimethylaminopyridinium chlorochromate (DMPCC) for 20 hr. in dichloromethane led to 95% recovery of the starting sulfide and only 5% oxidation

to the sulfoxide, suggesting that this reagent might prove to be a selective oxidant in the oxidation of sulfur containing molecules **(Scheme 54)**. Continued research in this area is currently in progress.

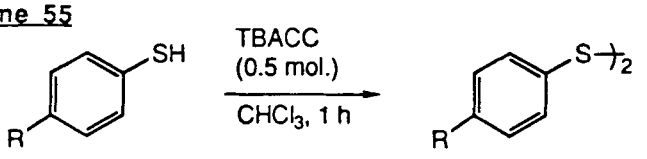
Scheme 54



113

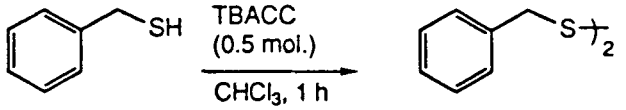
The previously described tetrabutylammonium chlorochromate (TBACC),[38] nicotinium dichromate (NDC)[48] and isonicotinium dichromate (INDC)[48] have all been used as effective reagents in the oxidation of thiols **114-116** to the corresponding disulfides **117-119**. Some examples of these transformations are listed in **Scheme 55**.

Scheme 55



114 R = H
115 R = CH_3

117 R = H 87%
118 R = CH_3 84%



116 → **119** 80%

114 → (NDC (0.5 mol.), Pyr; CH_2Cl_2, 1 h) → **117** 90%

115 → (NDC (0.5 mol.), Pyr; CH_2Cl_2, 1 h) → **118** 80%

XI. THE OXIDATION OF ALCOHOLS WHICH CONTAIN BASIC HETEROCYCLIC AMINE MOIETIES

One significant limitation of chromium (VI)-amine complexes is in the attempted oxidation of basic nitrogen-containing molecules. A critical comparison of oxidation reagents for the conversion of isoxazole alcohol **120** to the corresponding aldehyde **121** was reported by Natale **(Scheme 56)**.[72] Several of the methods investigated involved the use of oxochromium (VI) complexes under standard conditions. The results are given in **Table 2**. The optimum oxidation conditions observed in this study utilized Swern conditions [DMSO-/$(COCl)_2$-Et_3N] affording **121** in 84% yield.

Scheme 56

120 121

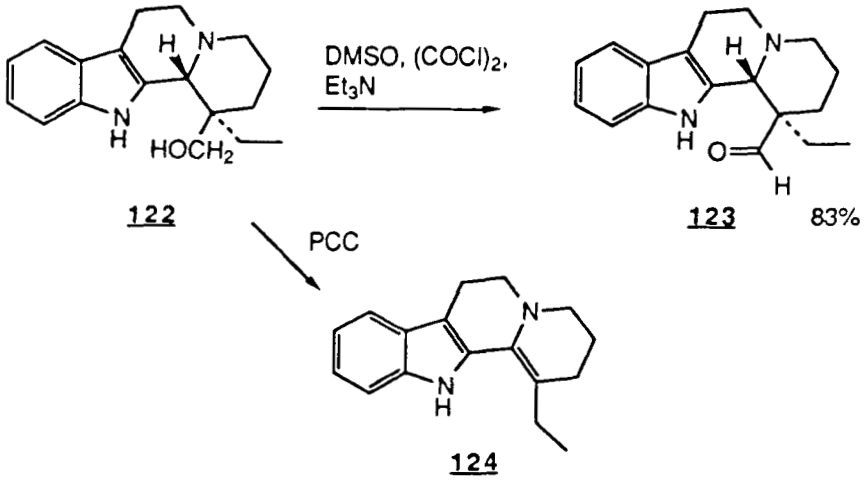
Table 2: Yields for the Conversion of 120 to 121 Using Oxochromium-Amine Complexes Under Standard Conditions

Reagent	Yield
Pyridinium Chlorochromate (PCC)	80%
Bipyridinium Chlorochromate (BPCC)	77%
Chromium Trioxide/Pyridine (CrO_3 • 2Pyr)	44%
Pyridinium Dichromate (PDC)	47%
Poly(vinylpyridinium dichromate) (PVPDC)	29%

During the course of investigations involving the total synthesis of eburnane alkaloids, Danieli reports that treatment of alcohol **122** with pyridinium

chlorochromate (PCC) did not afford the expected aldehyde **123** but yielded instead the enamine **124**. Presumably **124** arises through the metal-assisted retro-aldol cleavage of **122** as suggested by these workers.[73] Under Swern conditions, which appear to be the method of choice for the oxidation of basic nitrogen-containing molecules, aldehyde **123** was obtained in 83% yield **(Scheme 57)**. Conditions for the formation of the enamine by the PCC route were not disclosed.

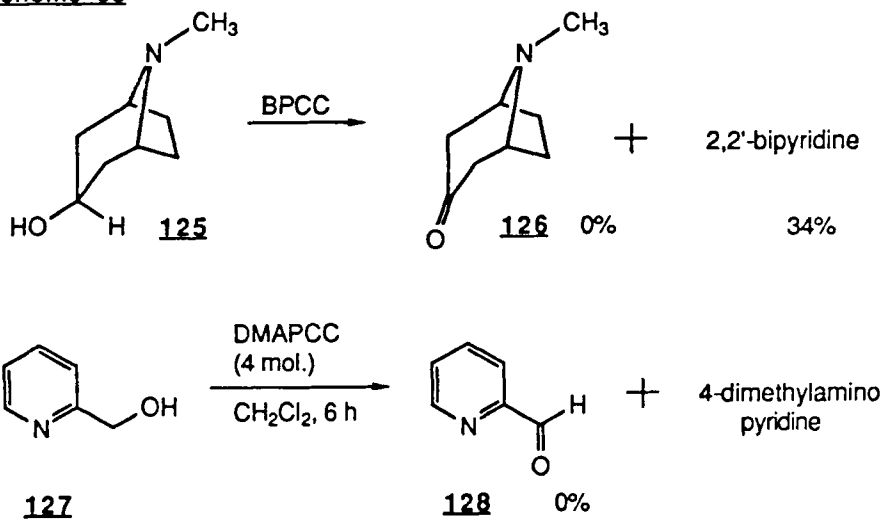
Scheme 57



Treatment of tropine **125** with bipyridinium chlorochromate (BPCC) in dichloromethane yielded only 2,2'-bipyridine (34%) and none of the expected product tropinone **126 (Scheme 58)**. Similar results were obtained when 2-pyridyl carbinol **127** was treated with 4-(dimethylamino)pyridinium chlorochromate (DMAPCC). Attempted oxidation of **127** with DMAPCC under standard conditions resulted in a vigorous exotheremic reaction affording 4-dimethylaminopyridine as the only characterizable product. Starting alcohols **125** and **127** could not be recovered from either reaction **(Scheme 58)**.[74] This and the isolation of the

amine ligand after these oxidations suggested that the amine ligand had exchanged with the substrate, the substrate being strongly bound to the chromium species. Oxidation of pyridyl carbinol **127** under the Swern conditions afforded the desired aldehyde **128** in 70% G.C. yield which could be isolated as its 2,4-dinitrophenylhydrazone derivative.[75]

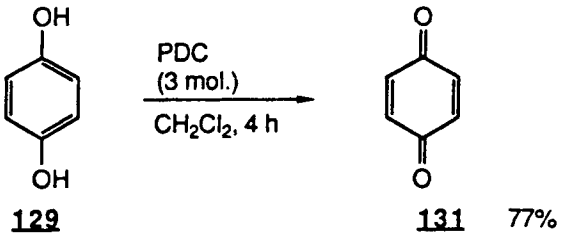
Scheme 58

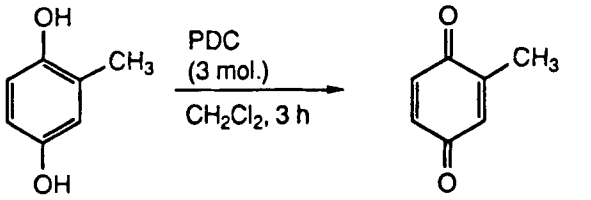


XII. HYDROQUINONE OXIDATIONS

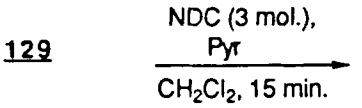
Pyridinium dichromate (PDC) and nicotinium dichromate (NDC) both can be used for the conversion of hydroquinones **129** and **130** to quinones **131** and **132** (**Scheme 59**).[48] Hydroquinone silyl ethers may be oxidized to quinones using PCC (**Scheme 60**).[76]

Scheme 59

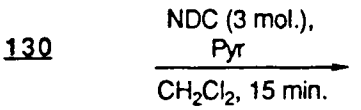




130 → 132 64%

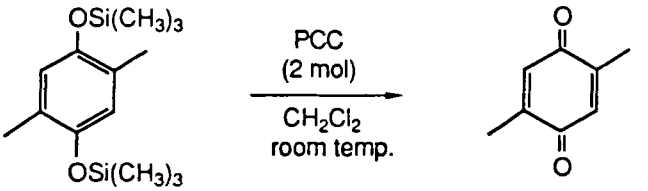


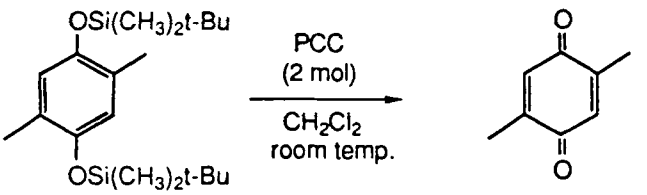
129 → 131 90%



130 → 132 85%

Scheme 60





XIII. STEREOCHEMICAL CONSIDERATIONS IN CHROMIUM-AMINE OXIDATIONS

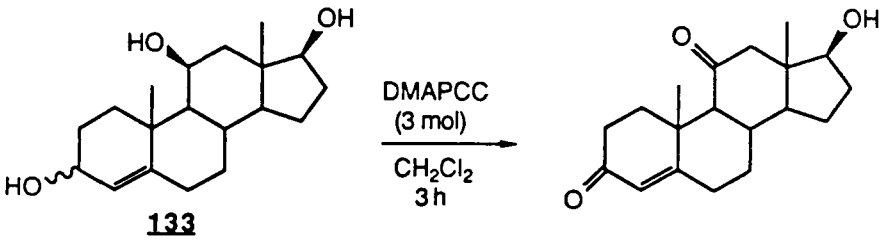
The pioneering mechanistic studies by Westheimer on the mechanism of

chromium (VI) oxidations showed that this reaction involves rapid reversible formation of a chromate ester followed by its rate-determining decomposition. It was subsequently established that in cyclohexane systems the more hindered axial alcohol function is more rapidly oxidized than a corresponding equatorial substituent. This rate enhancement has been explained by relief of strain in the transition state of the oxidation.[77]

Similar results were obtained by Suggs who studied the relative rates of oxidation of cis- and trans-4-tert-butylcyclohexanol with pyridinium chlorochromate.[78] In a competition experiment he treated an isomeric mixture of alcohols with PCC and found that the axial hydroxyl of the cis-isomer was oxidized more quickly than the equatorial hydroxyl of the trans compound. The rate ratio (k_{cis}/k_{trans}) was found to be 3.3, very close to that obtained in studies of the same alcohols using chromic acid and chromium trioxide as an oxidants.[79,80]

As previously mentioned, 4-(dimethylamino)pyridinium chlorochromate, DMAPCC, is a remarkably selective reagent for the oxidation of allylic and benzylic alcohols (**Section V-A**). It also exhibits axial selectivity in oxidation of non-allylic alcohols. When triol **133** was treated with this reagent, the axial 11-hydroxyl group as well as the allylic hydroxyl were oxidized at comparable rates (**Scheme 61**).[34] There are significant 1,3-diaxial interactions of the 11-hydroxyl function with the

Scheme 61



133

flanking methyl groups, increasing steric strain. Relief of this strain probably accounts for the increased reactivity of the 11-hydroxy moiety.

XIV. OVERVIEW

While oxochromium amine complexes have proved to be valuable reagents in organic synthesis, many limitations in this area are apparent. Oxidation yields of even simple substrates are rarely near quantitative. In only a few cases has a comparison of oxochromium-amine reagents and other oxidants in a given synthetic step been reported. Removal of chromium-containing by-products is still in most cases difficult. Finally, the deleterious effects of even common functionality on oxidation yields have for the most part been ignored in reports on new reagents, often leaving such discoveries to be made with severe consequences in a total synthesis. Much systematic chemistry remains to be carried out in this area before the optimal oxochromium reagent required for a given transformation can be scientifically chosen.

Acknowledgement.- We gratefully acknowledge the helpful suggestions and comments of Dr. Lynn SanFilippo and Dr. Loide Wasmund and also for their preparation of structures used in the text. We also thank Ann Marie Luzzio for assistance in preparing this manuscript.

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(Received October 16, 1987; in revised form October 3, 1988)