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Reactions of Unsaturated Systems with Hexavalent Chromium

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The literature data on the interaction of unsaturated compounds with hexavalent chromium reagents are surveyed. Attention is concentrated on reactions with coordination complexes of hexavalent chromium and also methods suitable for the chemospecific, regiospecific, and stereospecific oxidative generation of functional groups in highly unsaturated systems. The advances in the application of chromium(VI) in the synthesis of natural structures are described.
The bibliography includes 389 references.

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I. INTRODUCTION

The oxo-derivatives of manganese, chromium, ruthenium, and osmium have been applied to an increasing extent in recent times for the generation of functional groups in organic molecules. Among the selectively acting oxo-derivatives of variable-valence metals, chromium compounds play the most important role, because the oxidative reactions based on them can be readily carried out and the reagents themselves are readily available and cheap. The oxidation of carbon–carbon multiple bonds by chromium(VI)–containing reagents leads to the formation of epoxides, glycols, aldehydes, ketones, and carboxylic acids.[1-9] Furthermore, if we add to this that coordination complexes of chromium can be used successfully for the conversion of hydroxy into the carbonyl groups in unsaturated systems, the prospects for their application in the chemistry of unsaturated compounds become evident.[10-19] For these purposes, one uses chromic acid (in water or in acetic or sulphuric acids), the dichromate ion (in water or in acetic acid), chromyl acetate (in acetic anhydride or in its mixture with acetic acid), t-butyl chromate, chromyl nitrate, coordination complexes of chromium dioxide, and chromyl chloride (in inert solvents).

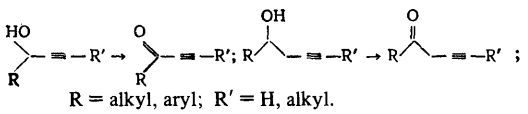
The literature data on the application of chromium compounds as oxidising agents for organic substrates available in foreign literature have been partly considered and surveyed.[20-27] Despite the enormous importance of the above reagents, there have been no Soviet reviews, which led us to compile and arrange systematically the data on the interaction of hexavalent chromium compounds with unsaturated compounds. The reactions of chromium derivatives with unsaturated systems can be arbitrarily divided into the following groups: (1) oxidation of hydroxy-groups and other functional groups; (2) oxidation of multiple bonds; (3) allylic oxidation.

II. REACTIONS OF UNSATURATED ALCOHOLS

The search for readily available and selectively active reagents for the oxidation of alcohols to carbonyl compounds has been for a long time the object of numerous investigations. An enormous number of reagents containing chromium(VI) were tested but the majority of them did not exhibit an adequate activity and selectivity and as a result proved to be unsuitable for use in modern organic synthesis.[28] However, the series of reagents considered in this review had been used successfully in reactions with unsaturated alcohols.

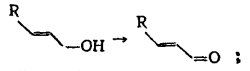
1. Oxidation by Chromic Acid, the Dichromate Ion, and t-Butyl Chromate

Chromic acid (H_2CrO_4) was first used as an oxidant in the conversion of derivatives of cyclopentenol into cyclopentenones and it was recommended that the reaction be carried out in acetic acid (Fieser's reagent) or in sulphuric acid.[29,30] A major advance in the oxidation of the hydroxy-group to the carbonyl group in unsaturated alcohols and in particular in acetylenic systems by chromium trioxide in sulphuric acid has been the successful employment of acetone as the solvent (Jones' reagent), which ensured high yields of carbonyl compounds:[31-38]



R = alkyl, aryl; R′ = H, alkyl.

It has been reported that various primary allyl alcohols give rise to aldehydes in moderate yields on oxidation by the chromate ion in sulphuric acid:[39-43]

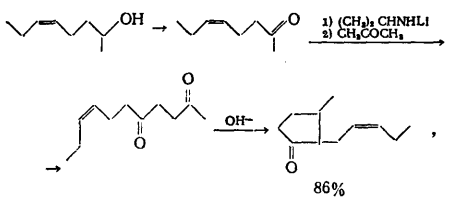


R = alkyl, alkenyl.

According to the results of a number of investigators,[30,31,44-48] when concentrated sulphuric acid is used, reactions with unsaturated primary alcohols do not stop at the aldehyde formation stage but continue until the formation of the corresponding acid. This fact has been used in the synthesis of the pheromone of the black carpet beetle—megatomoic acid.[47]

Other literature data exists concerning the oxidation of unsaturated alcohols to aldehydes with the aid of the Jones reagent.[49-51] Among them the use of chromic acid in the

synthesis of *cis*-jasmone, in accordance with the scheme[52]



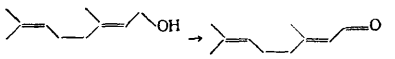
is of great interest.

The synthesis of a series of α-acetylenic carbonyl compounds is also of interest.[53-60]

The above methods have been used successfully in the conversion of polycyclic unsaturated carbinols into ketones.[61-64]

The dichromate ion $[Cr_2O_7]^{2-}$ in acetic or sulphuric acid has been used to oxidise various allyl alcohols.[65] The above reagent has been used successfully also to convert cholesterol into cholestanone[66] and also for the oxidation of propargyl alcohols.[67]

t-Butyl chromate ($t\text{-}Bu_2CrO_4$) has been used on a comparatively wide scale for the oxidation of the hydroxy-group in unsaturated systems, which demonstrates its advantage over other reagents. Studies in this field have been examined and surveyed by Matsuura and Suga.[68] Chromium trioxide in t-butyl alcohol was first used as the reagent for the oxidation of hydroxy-groups in unsaturated alcohols in the conversion of geraniol into geranial in 85% yield:[69]



Subsequently this reagent was applied successfully for the conversion of various allyl alcohols into unsaturated carbonyl compounds[70-72] and also for the oxidation of octa-3,5-diene-2,7-diol into the corresponding diketone.[73]

In the 1970's oxidising agents based on chromium trioxide began to be used in the presence of carriers. When chromium trioxide is added to a solution of an alcohol in a 1:3 mixture of diethyl ether with dichloromethane in the presence of celite, carbonyl compounds are formed.[74] There are data concerning the oxidation of unsaturated alcohols by chromic acid deposited on a polymeric carrier[75] and adsorbed on silica gel,[76] by the graphite chelate of chromium trioxide,[77] by chromium trioxide in hexamethylphosphoramide[78-80] deposited on wood charcoal[81] or on a polymer,[82] and by the dichromate of polyvinylpyridine.[83]

The mechanism of the oxidation of alcohols on polymers of saturated compounds has been the subject of investigations by many workers. It follows from these studies that the rate of oxidation depends on the concentration of the acid ester of chromic acid;[84-97] this dependence and the isotope effect[98] show that the slow stage involves the rupture of a C–H bond at the carbon atom linked to the hydroxy-group. The fact that the reaction is faster in deuterium oxide than in water is no less important.[99] These data agree with the hypotheses of both one- and two-electron transfer in the rate-limiting stage. According to Watanabe and Westheimer,[100] these two alternatives can be distinguished by employing the unusual ability of manganese(II) ions to induce the reaction. Thus, in the oxidation of isopropyl alcohol in the presence of a large excess of manganese(II) ions, half a mole of manganese dioxide is formed for each mole of acetone in accordance with the equations

$$(CH_3)_2CHOH + Cr^{VI} \rightarrow (CH_3)_2C{=}O + Cr^{IV} \ ;$$
$$2Cr^{IV} + Mn^{II} \rightarrow MnO_2 + 2Cr^{III} \ .$$

In the absence of the alcohol, the reaction between hexavalent chromium and bivalent manganese does not take place. In the presence of a large excess of the alcohol, manganese(II) ions decrease the rate of oxidation by a factor of two:

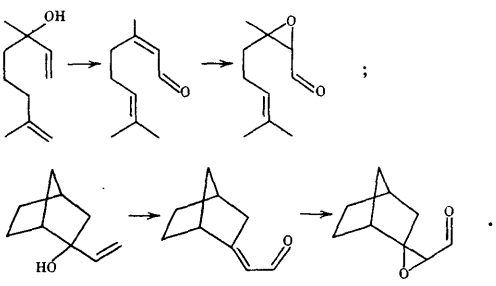
$$(CH_3)_2CHOH + Cr^{VI} \rightarrow (CH_3)_2C{=}O + Cr^{IV} \ ;$$
$$Cr^{VI} + Cr^{VI} \rightarrow 2Cr^{V} \ ;$$
$$2[Cr^{V} + (CH_3)_2CHOH \rightarrow (CH_3)_2C{=}O + Cr^{III}] \ .$$

It is seen from the equations presented that the oxidation is only one-third induced by hexavalent chromium and is two-thirds induced by quinquevalent chromium. The above examples of the induced oxidation demonstrate that chromium(IV) and chromium(V) complexes are formed as intermediates in the oxidation by chromium(VI). We may note that the latter are in fact effective oxidants which convert unsaturated alcohols into the corresponding carbonyl compounds.[101] In the rate-limiting stage, the intermediate chromic acid esters of primary and secondary alcohols are decomposed.[102,103] It has been suggested that the reaction proceeds via the formation of acid chromates,[104,105] which agrees best not only with the observed kinetics and the isotope effect but also with the presence of acid esters in the reaction medium.[106] Some workers assume that the reaction proceeds via the direct elimination of the hydride ion,[87,107,108] while others claim that chromic acid esters are formed initially.[103,109] However, despite the numerous data available,[82-86,105,110-123] it is difficult to make a final choice between the proposed mechanisms. Furthermore, since the rate of oxidation is independent of the oxidant concentration and corresponds to the rate of the acid-catalysed dehydration of alcohols to alkenes, some investigators have concluded that the initial stage involves the formation of an alkene, which is then oxidised by chromic acid.[124-126]

2. Oxidation by Coordination Complexes of Chromium Trioxide

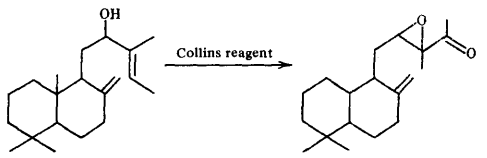
First Sarett and co-workers[127] and then Collins et al.[128] demonstrated that the complex of chromium trioxide with pyridine[129] can be used successfully for the oxidation of alcohols to carbonyl compounds. Subsequently pyridine chromate (PC) ($C_5H_5.CrO_3$), the reagent of Sarett and Collins, was used to oxidise allyl and benzyl alcohols[130-131] — geraniol, nerol, citronellol, and cinnamyl alcohol[131] and bicyclic and tricyclic unsaturated carbinols,[132,133] including cholesterol[134] and cholesteryl acetate,[135] also in the synthesis of prostaglandins.[136]

The oxidation of tertiary and secondary allyl alcohols by the Collins reagent involves an oxidative rearrangement with formation of αβ-unsaturated aldehydes.[16] Under the reaction conditions, the latter are mainly converted into epoxy-derivatives:



There have been several communications in the literature about the formation of epoxy-derivatives as a result of oxidation by other chromium reagents,[137-146] but none has been synthetically useful. In this sense the example presented

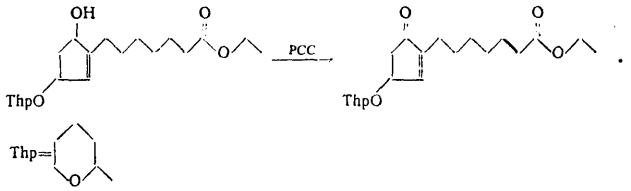
below is valuable in biogenetic syntheses:[16]



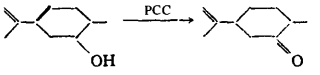
However, following the publication of the interesting report by Corey and Suggs,[10] who proposed pyridinium chlorochromate (PCC) $\{C_5H_5\overset{+}{N}H[CrO_3Cl]^-\}$ as a safe and readily available reagent, PC began to be used to a lesser extent.

In contrast to the Sarett and Collins oxidant, the Corey complex is non-hygroscopic, is safe, and there is no need to employ it in a fivefold and sixfold excess.[10,147] Hitherto, the Corey reagent has been used in somewhat modified forms; it is employed in a buffer mixture,[10] and in the forms where it is deposited on celite,[148] alumina,[149] poly(vinyl alcohol),[150] and molecular sieves.[151]

The Corey reagent is an effective oxidant for the conversion of many allyl[10,149,150] and homoallyl[151,152] alcohols into the corresponding carbonyl compound. With its aid, citronellal can be obtained in satisfactory yields from citronellol.[10,149] The reaction of a hydroxyacid ester presented below is of interest:[153]

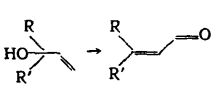


Isopulegone can be obtained in a quantitative yield in accordance with the following scheme:[149]



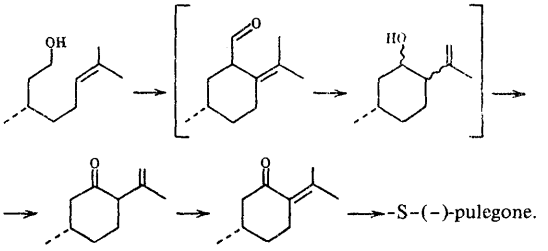
When alkenyl alcohols with a specific configuration of the double bond are oxidised, *cis–trans* isomerisation is observed.[10] In steroids containing several hydroxy-groups, including some of the allyl type, it is possible to oxidise the required hydroxy-group by varying the conditions.[154–157]

On interaction with PCC, tertiary and certain secondary allyl alcohols undergo an oxidative rearrangement, forming exclusively an unsaturated aldehyde and ketones in almost quantitative yields:[15,16,158]



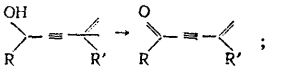
Such oxidation with a rearrangement is caused, according to the authors, by the weakly acid character of PCC, under the influence of which tertiary alcohols rearrange to primary alcohols and the oxidation of the latter leads to unsaturated aldehydes.[16,158]

Another promising synthetic application of the Corey reagent is in the oxidative cyclisation of unsaturated alcohols. Thus (-)-citronellol can be readily converted into (-)-pulegol by treatment with PCC:[13]



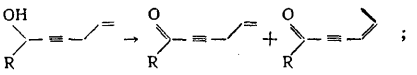
The acid properties of PCC, which induces the annelation of a number of other linear and cyclic unsaturated alcohols or aldehydes to form cyclohexanone derivatives, also promote this course of the reaction.[14] The above reaction is suitable for the asymmetric synthesis of prostaglandins.[159,160]

Pyridine chlorochromate has been used successfully also for the oxidation of certain propargyl alcohols;[10,161,162] it is exceptionally suitable for the synthesis of vinylacetylenic aldehydes and ketones:[163–165]



R = H, alkyl, aryl; R′ = H, CH_3.

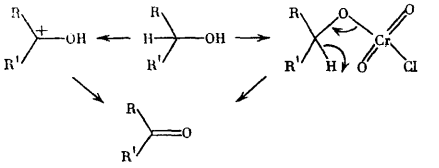
It is noteworthy that reactions of primary and secondary allylacetylenic carbinols with PCC are accompanied by a prototropic rearrangement with formation of mixtures of allyl- and propenyl-propargyl aldehydes and ketones:[166]



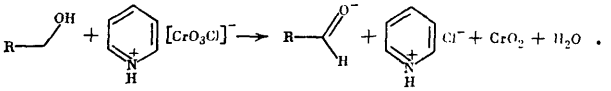
R = H, alkyl.

This reagent has also been used successfully for the oxidation of propenyl-acetylenic[166] and vinylallenic alcohols,[166] for the synthesis of *cis*-tagetone[167] and ocimenone,[168] and for reactions in the series of gibberellins.[51] The oxidation of unsaturated alcohols to butanolide derivatives is also of interest.[169]

The mechanism of the oxidation of alcohols by pyridinium chlorochromate has been investigated by a number of workers.[170–177] Two main pathways whereby alcohols are converted into carbonyl compounds have been suggested: via the intermediate formation of the carbonium ion or via a chromic acid ester chloride:[170–172]

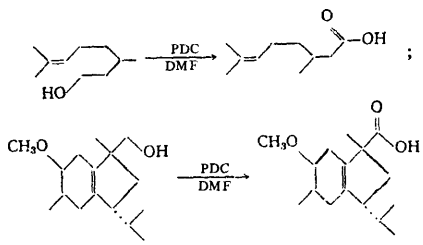


The authors believe that in both cases three electrons are transferred and that the oxidation state of chromium changes from +6 to +3 during the reaction. However, it has been noted that[177] two electrons are transferred in the above reaction in accordance with the mechanism

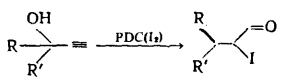


Pyridinium dichromate (PDC) $(C_5H_5\overset{+}{N}H)_2Cr_2O_7^{2-}$ in dimethylformamide (DMF) was suggested in 1979 as the oxidant for the selective conversion of the hydroxy-group into the

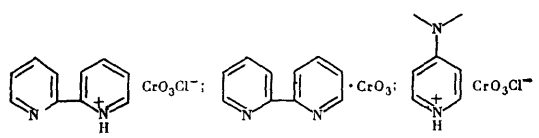
carbonyl group.[12] The reagent oxidises rapidly 2-cyclohexanol, cinnamyl alcohol, and geraniol to 2-cyclohexenone, cinnamaldehyde, and geranial respectively in quantitative yields. In many instances the formation of the corresponding acids from the alcohols has been observed, for example:



PDC in methylene chloride proved to be an even milder oxidant.[12] Regardless of the nature of the substrate, the reaction proceeds in this instance only as far as the formation of aldehydes. For example, citronellol gives rise to citronellal in 92% yield. It has also been noted that allyl alcohols are oxidised faster than their saturated analogues (2-cyclohexenol 10 times faster than cyclohexanol). Pyridinium dichromate in methylene chloride has been used to synthesise a series of αβ-unsaturated carbonyl compounds containing both double and triple bonds. Here it is noteworthy that the oxidation of geraniol to geranial involves partial inversion (9%). This *E*/*Z* isomerisation takes place before oxidation to geranial in the stage involving the formation of the intermediate chromate ester as a consequence of a reversible allyl rearrangement. PDC has been used successfully in the syntheses of pheromones.[178,179] In the presence of iodine in methylene chloride, this reagent converts smoothly tertiary acetylenic carbinols into αβ-unsaturated α-iodoaldehydes:[180]

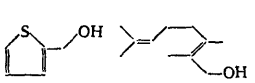


2,2′-Bipyridyl chlorochromate (BPCC) and the corresponding chromate (BPC)[181-183] as well as 4-(dimethylamino)-pyridinium chlorochromate (DMAPCC),[184,185] have been proposed as oxidants for the oxidation of the hydroxy-group to the carbonyl group:

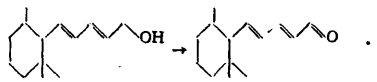


BPCC BPC DMAPCC

2,2′-Bipyridyl chlorochromate containing an internal buffer (the 2,2′-bipyridyl system) has been recommended for the oxidation of alcohols containing acid-sensitive groups, of the type presented below:



As regards BPC, one should note, on the one hand, certain difficulties in its use, which are also characteristic of the Collins reagent (increase of the reaction time and the necessity to use an appreciable excess of the reagent and, on the other hand, the special selectivity in the oxidation of allyl and benzyl alcohols). The authors note that DMAPCC combines the selectivity of BPC and the advantages of BPCC. DMAPCC has been used successfully for the selective oxidation of polyols.[184] This reagent converts geraniol into geranial in a quantitative yield. The oxidation of the exceptionally sensitive vitamin A synthone into the corresponding aldehyde also proceeds smoothly:[184]



However, when DMAPCC is used in certain cases, the complete inversion of the configuration of the initial *Z*-alcohols is observed together with oxidation, and *E*-aldehydes are obtained.[184] Despite its limited applicability compared with its chlorine analogue, pyridinium fluorochromate has a less pronounced acidity and is an effective agent for the oxidation of a number of polycyclic organic substrates.[186-188]

Ammonium dichromate $(NH_4)_2Cr_2O_7$, which has been used to convert primary allyl alcohols, including geraniol and nerol, into aldehydes, manifested oxidising properties.[131] Among nitrogen complexes of chromium trioxide, mention should also be made of naphthyridinium chlorochromate ($C_8H_6\overset{+}{N}_2H.CrO_3Cl^-$),[189] pyrazinium chlorochromate ($C_4H_4.\overset{+}{N}_2H.CrO_3Cl^-$),[189] tetrabutylammonium chlorochromate ($Bu_4\overset{+}{N}.CrO_3Cl^-$),[190] dimethylpyrazole chromate ($C_5H_8\overset{+}{N}_2.CrO_3$),[16,191,192] tetrabutylammonium dichromate ($Bu_4\overset{+}{N}_2Cr_2O_7^{2-}$),[193] the pyridine complex of oxodiperoxochromium ($C_5H_5N.CrO_5$),[194] and the dipyridine complex of chromium trioxide ($2C_5H_5N.CrO_3$) in acetic acid.[195] Poly(4-vinylpyridinium dichromate) (PVPDC) P–C=CHCH=NH$(Cr_2O_7)_{0.5}$CH=CH_2—the polymeric analogue of pyridinium chlorochromate—has been proposed recently.[196] It has been noted that the main advantage of the polymeric reagent is the ease of the purification of the final product, because both the initial polymer, used in excess to complete the reaction, and the reaction product are insoluble in the reaction medium and can be removed by simple filtration.

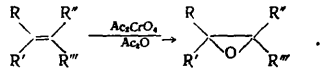
III. REACTIONS OF CARBON–CARBON MULTIPLE BONDS

There are literature data on the oxidation of double bonds both with decomposition of the unsaturated systems and without change in the carbon chain. The latter are of great interest and will be the subject of further discussion.

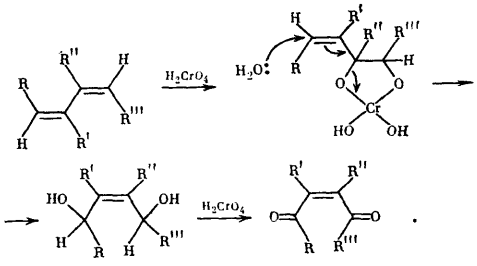
1. Oxidation by Chromic Acid, Chromyl Acetate, and Chromyl Nitrate

The oxidation of tetraphenylethylene by chromium trioxide (CrO_3) in acetic acid leads to an epoxide.[9,197,198] Alkenes of various types have been introduced into the reaction but mainly allylic oxidation was observed under these conditions.[199-213] The reactions of alkenes in aqueous acid media usually lead to products of the rearrangement of the epoxides formed initially.[2,5,6,214-218] Furthermore, on treatment with acid, camphene oxide affords camphenaldehyde, while the reaction of camphene with chromic acid leads to camphor and not to camphenic acid.[7] Assuming that the acid-catalysed rearrangement of camphene hydrate to isoborneol is faster than the oxidation of camphene, the authors conclude that camphor is obtained by the oxidation of isoborneol. In contrast to this, the reaction of 1,1-diarylethylenes with chromic acid affords only the cleavage product but not the epoxides, which were shown to be unreactive under the conditions used.[219,220] It has therefore been suggested that epoxides cannot be intermediates in the oxidation of the multiple bonds by chromic acid. It is also of interest that the very electrophilic addition of chromic acid is disproved by the fact that the carbonium ion formed in this process should have given rise to a large amount of a rearranged product.[221,222]

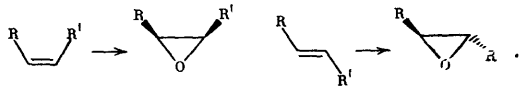
The reactions of alkenes with chromyl acetate (Ac_2CrO_4) proceed more successfully. They have been studied in detail in a number of investigations.[1,3,4,192,219,220] Here the main products of the interaction are epoxides, whose yield is higher the greater the degree of substitution at the double bond:



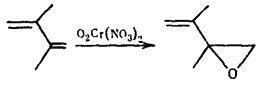
It is noteworthy that both the products of the rearrangement of the postulated epoxides[3,4,6,223-225] and acetates[226] and pinacol carbonates[8] are then isolated. Conjugated dienes also react successfully with chromic acid, which leads to the formation of enediones:[206-208,227]



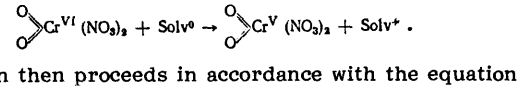
Chromyl nitrate $O_2Cr(NO_3)_2$ has been proposed recently as a reagent for the epoxidation of olefins.[228] It has been shown that different alkenes react stereospecifically at −78 °C in aprotic media (pyridine, DMF, or methylene chloride) with chromyl nitrate to form epoxides:



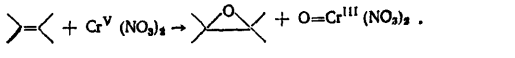
A high degree of retention of configuration has also been observed in the oxidation of olefins by chromyl acetate.[229,230] The products of the oxidation in acetone were ketals.[228] 2,3-Dimethylbutadiene enters smoothly into this reaction:



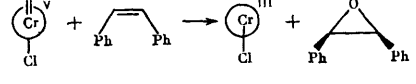
The authors believe that oxochromium(V), formed from chromium(VI) as a result of the preliminary one-electron oxidation of the solvent (Solv), is the active species in epoxidation by chromyl nitrate:[228]



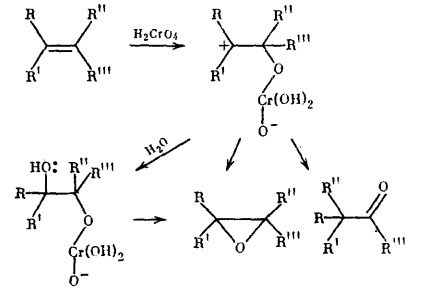
The reaction then proceeds in accordance with the equation



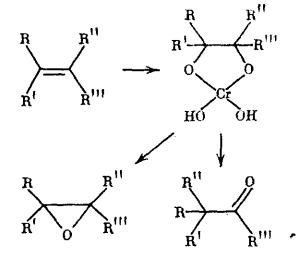
The active involvement of the intermediate chromium(V) has been confirmed by comparison with the ability of "macrocyclic oxochromium(V)" to convert alkenes effectively with a high degree of stereospecificity:[231]



The corresponding intermediates have been detected by EPR.[229] Despite the inadequacy of data concerning the role of chromium(IV) and chromium(V), the influence of substituents and stoichiometry, etc., it is believed that electrophilic attack on the double bond takes place:[219,220,232,233]



Cycloaddition, by analogy with oxidation by permanganate, is not ruled out either:[221,222]



The non-stereospecific epoxidation of tetraarylethylenes by chromyl acetate indicates indirectly that the reaction proceeds via a carbonium ion, in contrast to the oxidation of alkenes by permanganate,[234-236] where process stereospecificity is observed. The hypothesis of the intermediate formation of carbonium ions in the oxidation of alkenes by chromium trioxide in acetic anhydride to oxirans has been developed in other investigations.[219,220,237,238] These conditions ensure satisfactory yields of oxirans, while in the presence of hydrogen in the allyl position, the competing allylic oxidation is observed.[239]

Kinetic data have shown that the rate of oxidation by chromic acid increases with increase of the degree of branching of the olefin chain. It has been established that the rate depends on the number of alkyl substituents to a greater extent than on the configuration of the olefin.[240] The acceleration of the reaction by the substituent at the double bond has also been noted in the oxidation of chalcones (phenyl styryl ketones); it was shown that electron-donating groups in the *para*-position in the benzene ring increase the rate, while electron-accepting groups diminish it.[241] In terms of their influence on the activity, the groups can be arranged in a sequence indicating the electrophilic character of the process:

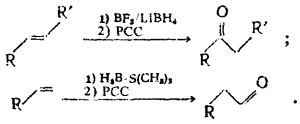
$$4\text{-}OCH_3 > 3\text{-}OCH_3 > 2\text{-}OCH_3 > 4\text{-}Cl > 3\text{-}Cl > H > 3\text{-}NO_2 > 4\text{-}NO_2 .$$

The reaction is thought to proceed via a three-membered cyclic activated complex.[241,242] Analogous complexes have been postulated in the oxidation of alkenes by chromyl chloride.[243,244]

2. Oxidation by Coordination Complexes of Chromium Trioxide

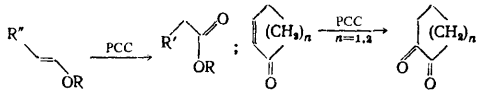
The oxidation of multiple bonds by chromium trioxide complexes proceeds via the preliminary conversion of alkenes into organoelemental derivatives.[245-247] A promising variant involves their interaction with hydroborating agents and

subsequent oxidation with PCC:[248,249]

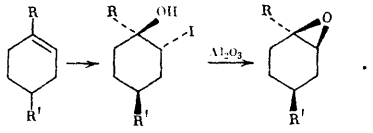


Numerous alkenes, including some with functional-group substituents, have been converted into aldehydes and ketones by this method.[250–252] A series of unsaturated carbonyl compounds have been synthesised in an analogous way via the dissociation of the C–Sn bond in organotin compounds by the pyridine complex of chromium trioxide.[253]

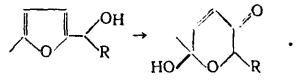
As already mentioned, direct oxidation of multiple bonds by pyridinium chlorochromate is difficult and, furthermore, its inertness with respect to double[10] and triple[10,254] bonds has been reported. Nevertheless, it has been established that vinyl ethers interact smoothly with PCC:[255]



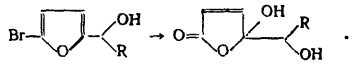
In the presence of iodine, trisubstituted olefins are converted by PDC regiospecifically and stereospecifically into iodohydrins and epoxides.[256] Certain natural polyenes, subjected to an analogous treatment, have been converted selectively into iodohydrins and then into epoxides:[256]



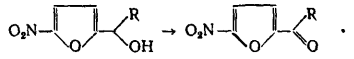
Substituted furans are also fairly sensitive to PCC:[257–261]



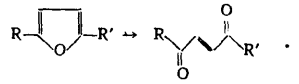
In the case of bromofurylcarbinol, ring expansion is not observed and the reaction leads to the formation of γ-hydroxybutenolides:[262–268]



Under analogous conditions, nitrofurylcarbinol is converted into a ketone:[269]

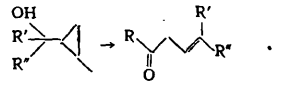


Among these reactions, the oxidative opening of the rings of arylfurans to form linear diketones is no less important:[270]



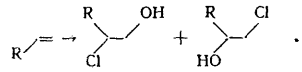
It is believed that the mechanism of the oxidation of furans by PCC includes the initial electrophilic 1,4-addition with subsequent ring opening.[270,272,273]

Ring opening has been observed also in the conversion of cyclopropylcarbinols into unsaturated ketones:[271]

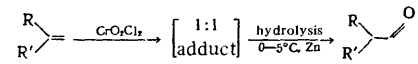


3. Oxidation by Chromyl Chloride

The oxidation of alkenes by chromyl chloride was already known at the beginning of the century.[274–281] However, the products thus obtained were first identified only in 1950.[282] It was found that the oxidation entails the preferential formation of chlorohydrins with a primary-hydroxy-group:[282,283]

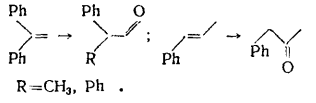


When cycyoalkenes are used in this reaction, mixtures of *cis*- and *trans*-chlorohydrins are formed. It is remarkable that the *trans*- and *cis*-isomers predominate respectively for cyclohexene and cyclopentene.[283] The formation of carbonyl compounds has also been noted under these conditions.[282,283] Other workers obtained mainly aldehydes from disubstituted terminal olefins;[279] the reaction involving phenylmethylethylene produces benzyl methyl ketone.[284] However, a more detailed study of the reaction[279, 282,283,285] showed that the reductive hydrolytic stage is mainly responsible for the reaction pathway and the yields of products. When zinc dust was used as the reductant instead of sulphur dioxide,[286] it was possible to obtain carbonyl compounds in high yields:[285]



This reaction is of practical interest and has been used in the synthesis of chrysomelidial and gastrolactone.[287]

Among substituted olefins used in the reaction with chromyl chloride, styrenes are of great interest. A particular reason for this is that the familiar Etard reaction (oxidation of arylalkanes) proceeds according to many investigators via the intermediate formation of arylalkenes.[283, 286, 288–290] The interaction of chromyl chloride with *trans*-1-phenylpropene yielded at least seven compounds, including 1-phenyl-2-propanol.[288] However, other workers isolated only 1-phenyl-2-propanol.[284,291] Satisfactory results have been achieved in the oxidation of both 1,1- and 1,2-disubstituted styrenes (1-methyl-1-phenylethylene, 1,2-diphenylethylene, *trans*-1-phenyl-1-propene) by chromyl chloride at a low temperature where the reductive hydrolysis of the intermediate was carried out with the aid of zinc dust:[291]



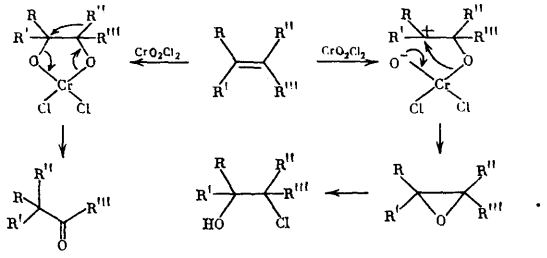
The oxidation of alkenes,[282,285,292] cycloalkenes,[284,293] and styrenes[291,293] by chromyl chloride has been the subject of controversy. It has been reported that treatment with an excess of chromyl chloride results in the formation of chlorohydrins in low yields,[282,292] while the reaction involving the use of equimolar ratios of the reactants produces carbonyl compounds.[243,285]

It has been established quite recently that various enynes interact selectively with chromyl chloride via the double bond with formation of alkyne chlorohydrins:[294]



A whole series of different enyne ethers, esters, and ketones have been introduced into this reaction.[294]

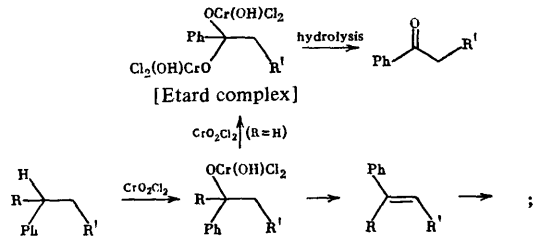
The interaction of chromyl chloride with multiple bonds is usually represented as proceeding via cyclic intermediates[282,283,291,295,296] in accordance with the scheme[243,285]

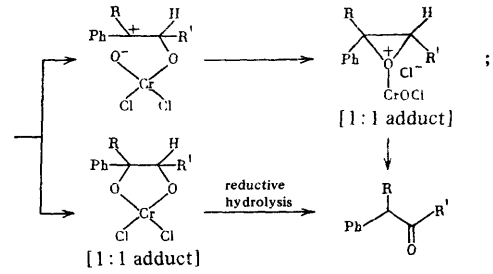


However, this hypothesis required confirmation with the aid of kinetic studies. Freeman and Yamachika[297] attempted to investigate the kinetics of the oxidation of cyclopentene, cyclohexene, and norbornene by chromyl chloride.[297]

The influence of ring size on the nature of the activated complex and on the rate of epoxidation,[298] oxidation with chromic acid,[240] and the addition of dibromocarbene and phenyl and picryl azides[299–301] had been investigated earlier. For example, in 1,3-dipolar cycloaddition reactions (via a five-membered cyclic activated complex), norbornene reacts 10^3—10^4 times faster than cyclohexene,[297] while the difference between the rates of epoxidation, addition of dibromocarbene to cyclopentene and cyclohexene or their epoxidation (which proceed via a three-membered ring) is very small.[299–301] Measurements of the rate constants for the oxidation of the above compounds by chromyl chloride and of the thermodynamic parameters under the conditions of a large excess of the cycloalkene and their comparison led the authors to the conclusion that the activated complexes in the case of cyclopentene and cyclohexene may be three- and five-membered cyclic compounds,[297] while in the case of norbornene only a five-membered transition state is produced. The same workers believe that, in the interaction of norbornene with chromyl chloride, an intermediate should be formed with a structure such that it can be converted into a *cis*-glycol or an epoxide rearrangement product.[242] However, it was soon established that, in the oxidation of norbornene and many of its substituted analogues at −80 °C, 74% of the isolated products are due to the initial formation of an *exo-cis*-chlorohydrin[302] and only 5% correspond to those predicted by Freeman. In contrast to the reaction of chromyl chloride with alkenes,[283] a mixture of *cis*- and *trans*-isomers is not formed in this instance—the interaction is stereospecific in the *exo*-position.[302]

In the early communications on the oxidation of styrene and its derivatives with chromyl chloride,[283,285,291,297,303,307] kinetic data were not quoted. However, styrenes[283] and cycloalkenes[296] were postulated as intermediates in the oxidation of cycloalkanes and arylalkanes respectively,[291,303,308] so that the overall process mechanism was represented as follows:





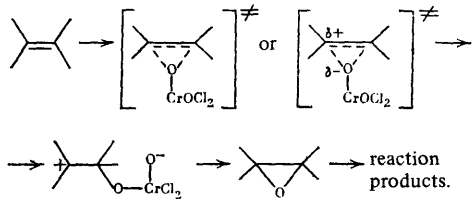
Subsequently, in the study of the kinetics of the reaction of chromyl chloride with styrenes, it was concluded[244] that it is of first order (first order with respect to each reactant) and that there is a correlation between the σ^+ constants of the substituents and the rate constants. These data as well as the thermodynamic parameters of the reaction agree with the mechanism involving electrophilic attack by chromyl chloride on the multiple bond with formation of resonance-stabilised partially bridged five-membered or three-membered activated complexes. From the value $\rho^+ = 1.99$, it was assumed in other investigations[309–312] that these complexes are hardly likely to be products of *cis*-addition, although this type of mechanism with an unbalanced charge in the transition state in cycloaddition has in fact been postulated.[313,314] However, since values of ρ^+ ranging from −3 to −5 were noted in reactions with a high degree of carbonium ion character of the transition state, the relatively low value $\rho^+ = -1.99$ conflicts with the idea that there is a full positive charge on the benzyl carbon.[244] Spectrophotometric data for the interaction of alkenes with chromyl chloride agree best with the idea that a three-membered cyclic intermediate complex is formed in the rate-determining stage.[243,291] The data obtained in the oxidation of bicyclic systems suggested that here too three-membered cyclic transition states are produced.[291] Next, the study of the kinetics of the addition of chromyl chloride to substituted styrenes showed that the rate of reaction increases after the introduction of electron-donating substituents. α-Methylstyrene is more reactive than *cis*-β-methylstyrene. The latter is oxidised at a lower rate than *trans*-β-methylstyrene, while *cis*-stilbene reacts twice as fast as *trans*-stilbene and 1,1-diphenylethylene is almost twice as reactive as α-methylstyrene and is superior to styrene by a factor of 13.[242] However, the question of the relative reactivities of the *cis*- and *trans*-isomers is not always susceptible to interpretations; for example, the higher reactivity of *cis*-stilbene compared with *trans*-stilbene has been observed in bromination reactions[315–317] and in oxidation with peracetic acid.[318,319] In contrast to this, *trans*-stilbene reacts faster than the *cis*-isomer in oxidation with chromic acid[240] and in *cis*-1,3-dipolar cycloaddition.[320] It is also essential to emphasise that neither *cis*- nor *trans*-stilbene afforded the expected carbonyl product on oxidation with chromyl chloride under the experimental conditions employed[285,291,321,322] and that they were successfully oxidised by chromyl chloride to carbonyl compounds only by varying the conditions.[323]

In the study of the kinetics of the oxidation of a number of alkenes, the first order of the reaction with respect to each reactant was observed.[243] The reaction is little influenced by steric factors and is characterised by low enthalpies of activation ($\Delta H^{\neq} = 5.4$–7.2 kcal mol^{-1}) and high negative entropies of activation ($\Delta S^{\neq} = -27.4$–-40.7). Excellent correlations have been obtained between the rate constants and Taft σ^+ constants as well as a good correlation based on the Hammett equation.[243] Comparison of the relative reactivities in the oxidation with chromyl chloride and in other

electrophilic reactions of alkenes (the addition of bromine and chlorine, oxidation with chromic acid, and epoxidation) suggested that the rate limiting stage involves a partially positively charged three-membered activated complex like the activated complex in the epoxidation of alkenes by peracids[324] or in the oxidation of alkenes with chromic acid.[240] From these data, the authors rule out the concerted *cis*-1,3-dipolar addition of chromyl chloride to the multiple bond in the rate determining stage, since this does not agree with kinetic data obtained for ring- or chain-substituted styrenes.[244,282] On this basis,[243] using the principle of the relative reactivities in solvolytic reactions,[325] oxidation with chromic acid,[239] epoxidation,[298,324] chlorination,[326] bromination,[327] and the addition of carbenes,[290,328] Freeman et al.[243] elucidated the nature of the activated complex in the oxidation of alkenes with chromyl chloride. The relative reactivities of alkenes in relation to chromyl chloride were obtained:[243]

pent-1-ene	1.22	2,3,3-trimethylbut-1-ene	10.5
hex-1-ene	1.00	2,4,4-trimethylpent-1-ene	23.6
oct-1-ene	0.77	*cis*-pent-2-ene	14.8
dec-1-ene	0.88	*trans*-pent-2-ene	15.1
2-methylpent-1-ene	8.00	2-methylbut-2-ene	202.0
3,3-dimethylbut-1-ene	5.36	2,3-dimethylbut-2-ene	3910
4,4-dimethyl-2-neopentylpent-1-ene	7.54	2,4,4-trimethylpent-2-ene	1380
cyclopentene	4.9	norbornene	312
cyclohexene	1.0	styrene	366

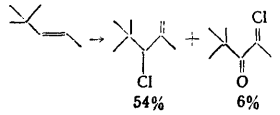
It is noteworthy that the mechanism of the oxidation of single and multiple carbon–carbon bonds with chromyl chloride still remains controversial.[292,293,304,305,329–335] Nevertheless, for the intermediate complex the rate of formation of which determines the rate of the entire reaction, a three-membered structure was adopted in the case of alkenes[282,293,296,297,329] and three- and five-membered asymmetric structures in the case of styrenes.[242,244,335] In an attempt to elucidate further the nature of the oxidation of cycloalkenes by chromyl chloride,[335] the kinetic data and thermodynamic parameters obtained were compared with data for the rearrangement of the epoxides;[218,219,242,334,336,337] the authors concluded that the process proceeds via the formation of epoxides, but the possibility of the intermediate formation of a carbonium ion was not ruled out:



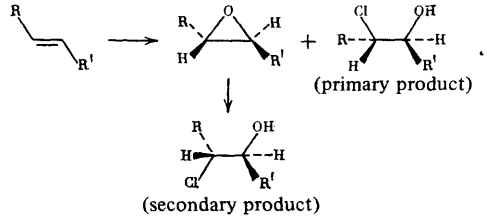
In their view, the fact that the rate of oxidation increases with increase of the number of methyl groups at the double bond agrees with the hypothesis. The involvement of a positively charged asymmetric three-membered activated complex in the rate limiting stage is indicated also by the fact that almost identical mixtures of final products are obtained from the following pairs of compounds in their reactions with chromyl chloride: 1-methylcyclopentene and methylenecyclopentane, 1-methylcyclohexene and methylene cyclohexane, and 1-methylenecycloheptene and methylenecycloheptane.[335]

The mechanism of the oxidation of multiple bonds has been formulated in a different way by Sharpless et al.,[230] who believe that reactions involving oxidation by metal oxo-compounds in general and by chromyl chloride in particular, begin with attack by the organic reductant on the metallic centre.[293] They believe that the mechanism proposed in a number of studies,[242,243,282,283,291,292,335,338,339] involving the formation of a three-membered intermediate, obtained by the electrophilic interaction of $[CrO_2Cl]^+$ with the olefin, followed by the attack on the latter from the rear by a chloride ion, is based on data showing that cyclohexene gives rise to *trans*-chlorohydrin, while the terminal olefins are products of the addition of the elements of the addend contrary to the Markovnikov rule. However, the authors note that this picture disagrees with the result of a study[283] where both *cis*- and *trans*-chlorohydrins were obtained from cyclohexene and cyclopentene. It was therefore necessary to assume that the reaction proceeds via a carbonium ion intermediate and that the latter is responsible for the formation of the *cis*- and *trans*-products.

It has been shown that the oxidation of *E*-t-butylmethylethylene with chromyl chloride in acetone results in the formation of mainly a ketone and the product of the Wagner–Meerwein rearrangement:[340]



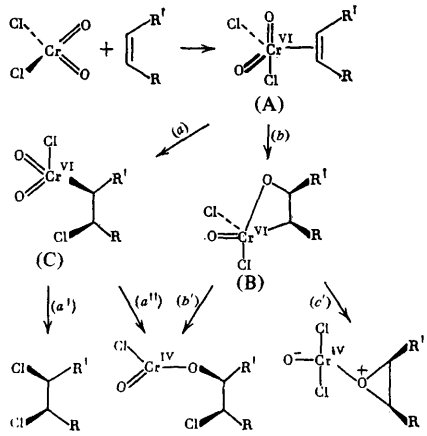
The authors believe that this result conflicts with the possibility of the existence of the intermediate structures presented above. On the other hand, it is known that the oxidation of olefins with chromyl chloride leads mainly to complex mixtures of compounds.[282,283,339] However, it has been reported recently[341,342] that epoxides are formed at a low temperature, although it has in fact been stated[302] that *exo-cis*-chlorohydrin is the main product in the reaction of chromyl chloride with norbornene. Sharpless et al. established unexpectedly that *cis*-addition is a common feature of the reactions of chromyl chloride with olefins.[230] On comparing the results of the oxidation of different alkenes with chromyl chloride at low temperatures and of the addition of the elements of HOCl to the same olefin, the authors concluded that the epoxides and chlorohydrin are the results of *cis*-addition and are the primary oxidation products, while the isomeric chlorohydrin (the product of *trans*-addition) is a secondary product obtained as a consequence of the opening of the epoxide ring:



It has been found that, analogously to other chromium reagents,[343] chromyl chloride is stereospecific and that epoxides with the geometry of the initial olefin are formed when it is used.

It has been shown[230] that the oxidation yields also a certain amount of dichloro-derivatives, which are likewise formed as a result of *cis*-addition. In their view, this can be in no way accounted for by the mechanisms proposed previously. On the basis of these data and also the fact that carbonyl compounds (aldehydes and ketones) give rise to nucleophilic reactions involving exclusively the carbon of the carbonyl group despite being less polarised than metal oxides, the authors assume that the oxidation of alkenes

with chromyl chloride proceeds via the formation of organometallic intermediates:[230]



It has been suggested that the complex (A) is formed initially from the olefin and chromyl chloride. In the case of ligands more basic than olefins, stable type (A) complexes are known (chromium trioxide–bipyridyl, osmium tetroxide–pyridine). In a transition metal complex of type (A), the displacement of the coordinated olefin with formation of a metal-ligand either π- or σ-bond is a likely process. For this reason, the authors proposed two reaction pathways, (*a*) and (*b*), for chromyl chloride, which lead to organometallic intermediate complexes of chromium(VI). Via pathway (*a*), the olefin is inserted in the chromium–carbon bond (*cis*-chlorometallation), forming the alkylchromium intermediate complex (C), which is converted into the dichloride, pathway (*a'*), involves reductive elimination or [conversion?]† into the chromium derivative of chlorohydrin, and pathway (*a''*) involves migration of the alkyl group from chromium to oxygen. Both these processes take place with retention of the configuration of the carbon centre and result in *cis*-addition. Reductive elimination with formation of a chlorine–carbon bond (pathway *a'*) is well known in organic chemistry and takes place with retention of the configuration at the carbon atom.[344–346] The migration of 1,2-shift via pathway (*b'*) can take place, by analogy with the Stevens rearrangement, only with retention of the configuration at the carbon atom.[347] The earlier hypothesis of high-valence organometallic compounds such as the compounds (A), (B), and (C) would seem to be unrealistic. However, the literature, starting from as early as 1970's has been saturated by examples of organometallic derivatives of vanadium,[348,349] tantalum,[350] chromium,[351,352] tungsten,[353] and rhenium.[354,355] A tungsten complex (CH_3WO_2Cl), whose structure is very similar to that of organometallic type (C) intermediates, has been isolated and characterised.[353]

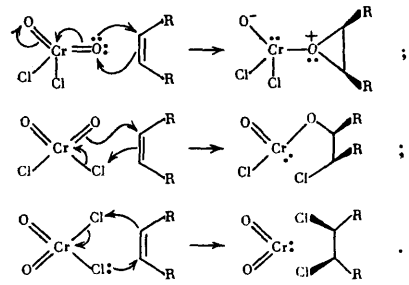
The mechanism presented actually involves [2 + 2] addition. The competing pathways (*a*) and (*b*) are especially sensitive to the nature of the medium, as expected. When the reaction is carried out in acetone or in the presence of a nucleophile (the chloride ion), the yield of chlorides increases.[341,356] Next it was established that, in oxidation with chromyl chloride in the presence of lithium bromide, only bromohydrins and bromoketones are obtained, because the bromide ion is more nucleophilic than the chloride ion:

$$CrO_2Cl_2 \xrightarrow{2Br^-} CrO_2Br_2 + 2Cl^- .$$

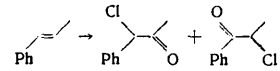
†Word(s) missing in Russian text. (Editor of Translation).

The *cis*-addition of chromyl bromide leads to the final product.[230]

Sharpless and co-workers also did not rule out a mechanism involving direct attack on the heteroatom in accordance with the following schemes:



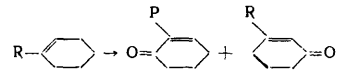
They had already established that different internal olefins can be converted into α-chlorohydrins by oxidation with chromyl chloride in acetone.[340] *cis*-Olefins react more slowly and with lower yields;[357] when the reaction mixture is treated with zinc dust, ketones are isolated.[340] In certain cases, for example with *E*-methylphenylethylene, a mixture of isomeric chloroketones in proportions of 3 : 1 is produced:



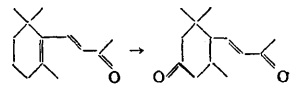
Thus new aspects of the oxidation of alkenes with chromyl chloride (via the initial formation of a high valence complex of the transition metal with a chromium–carbon σ-bond) have been examined and it has been shown that the primary oxidation products are epoxides and chlorohydrins.

IV. ALLYLIC OXIDATION

Treibs and Schmidt[358] showed for the first time that chromium trioxide in acetic anhydride is able to oxidise cyclohexene, α-pinene, tetralin, and other unsaturated compounds with formation of unsaturated ketones. It was later established[359] that this entails allylic oxidation:

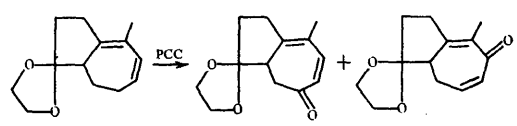


It was subsequently demonstrated that a more convenient reagent for allylic oxidation is di(t-butyl) chromate:[77]

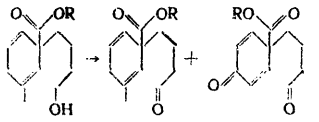


Cholesteryl acetate also gives rise to quantitative yields of the ketone;[77] the reaction was carried out in a non-polar solvent with added acetic anhydride. The latter reagent has been used successfully for the oxidation of various terpenoids in the allyl position.[360–373] Cyclohexadiene and cyclopropene also react with hexavalent chromium at the allyl carbon–hydrogen bond.[374]

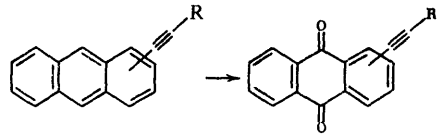
The reaction of dienes with PCC is of interest:[375]



The 1,4-diene ester shown below is oxidised analogously in the allyl position:[376]

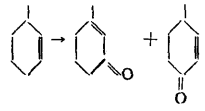


The oxidation of polynuclear aromatic hydrocarbons to quinones by chromium trioxide in acetic acid merits attention.[377] Alkylethynyl-substituted aromatic hydrocarbons are converted into quinones under similar conditions:[378]

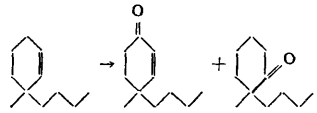


It is noteworthy that, in contrast to the manganese compounds which react rapidly with alkenes and alkynes[379,380] to form 1,2-diols and 1,2-diketones, chromium compounds (chromyl acetate,[358] chromic acid,[359] t-butyl chromate,[69] and the pyridine complex of chromium trioxide[381]), which are readily available and cheap oxidants,[382-385] interact slowly to form α-oxidation products.

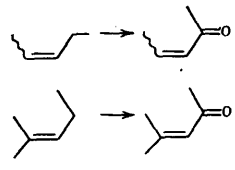
When substituted cyclohexenes and steroids interact with the dipyridine complex of chromium trioxide in methylene chloride, the allyllic methylene groups are oxidised slowly.[381] If there is more than one methylene group in the conformationally flexible molecule, then enones are obtained as a result of attack directed to a series of possible positions, while in a conformationally rigid system a rigorous selectivity of the oxidation reaction is observed; attack at the methine position (wherever this is possible) leads to the formation of the isomeric enone:



An analogous picture has been observed also in a sterically shielded methylene system, for example:[381]



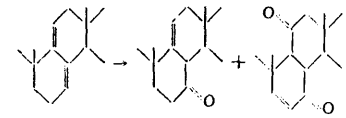
These reactions are characteristic also of substituted cyclopentenones.[386] The hexavalent chromium ion has been used also for the allylic oxidation of acyclic alkenes:[205]



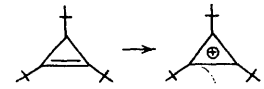
The allylic oxidation of alkynes has been demonstrated in two investigations.[254,387] Various internal alkynes react with chromium(VI) compounds to form α-diketones and allylic oxidation products, high yields of the latter being attained in the presence of the bipyridyl complex of chromium trioxide.[387]

When α-steryl acetate is made to react with chromic acid in acetic acid, allylic oxidation takes place together with epoxidation.[200] α-Cholestenyl acetate,[388] α-spinosterol,[202,203] and other polycyclic alkenes[204,205] react analogously.

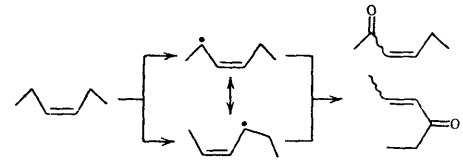
The reaction of steroid dienes, where allylic oxidation takes place with formation of diketones, is of special interest.[206-209]



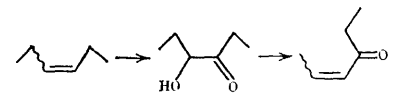
On the other hand, it has been estaalished that in the oxidation of a multiple bond in steroids the formation of ketols is also observed.[210-212] Cyclohexadiene reacts at room temperature with chromium trioxide in acetic acid with formation of benzene.[365] Under analogous conditions, tri-(t-butyl)cyclopropene affords the tri(t-butyl)cyclopropenylium cation:[389]



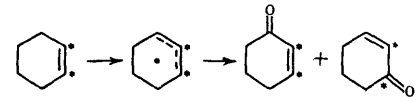
It has been suggested that allylic oxidation does not involve the initial attack on the multiple bond and proceeds either via the allyl radical or via a carbonium ion, which may lead to the isomerisation of the double bond, as is in fact observed in reality:[199]



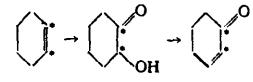
The initial oxidation of the multiple bond via epoxides to the corresponding hydroxyketones, which subsequently afford αβ-unsaturated ketones after eliminating water, has been suggested as an alternative:[210]



Since isomeric products are formed on oxidation, it has been postulated that the process proceeds via the first of the mechanisms postulated. Indeed, it has been established by the tracer atom method (at the multiple bonds) that both the methylene and methylidyne groups are oxidised in the reaction of cyclohexene with chromic acid:[199]



If the reaction proceeded via a hydroxyketone, then only one isomer would have been formed:



It is believed that an intermediate in which chromium is in the +4 oxidation state is obtained in allylic oxidation.[337,364]

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The data presented in this review demonstrate the extensive synthetic possibilities of the application of hexavalent chromium compounds as reagents in the chemistry of unsaturated compounds. Many oxidants, which are quite usual in

organic chemistry, are unsuitable for alkenes, alkynes, alkadienes, enynes, etc. with functional groups as substituents. As regards chromium reagents, the most promising proved to be the coordination complexes of hexavalent chromium, in particular, the pyridine complexes. Pyridinium chlorochromate, which is irreplaceable in the generation of functional groups in highly unsaturated carbinols and polyols, is comparatively universal. However, one should note the impossibility of using it in the synthesis of compounds which are exceptionally sensitive to increased acidity and which can readily undergo prototropic transformations. The growing interest in chromium(VI) coordination complexes has led to the discovery of reagents with a less pronounced acidity: pyridinium dichromate, 2,2'-bipyridyl chlorochromate, and 4-(dimethylamino)pyridinium chlorochromate, as well as reagents on carriers and polymeric supports. For example, the possibility of the selective oxidation of diene carbinols by 4-dimethylaminopyridinium chlorochromate has been demonstrated. Chromyl nitrate proved to be irreplaceable in the stereospecific epoxidation of dienes. An interesting approach to the formation of acetylenic epoxides involving the chemoselective oxidation of enynes by chromyl chloride has been discovered.

The main bulk of studies on the oxidation of unsaturated systems having functional groups as substituents by chromium reagents are not only of theoretical but also of practical importance and can find further applications in the construction of natural structures and in the synthesis of hormones, pheromones, prostaglandins, and their synthones. In the future, the studies in this field will in all probability be directed to finding new oxidising systems, which will permit smooth regiospecific, chemospecific, and stereospecific syntheses.

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