The problem

The diols, such as ethane-1,2-diol, which are the products of the reaction with cold dilute potassium manganate(VII), are themselves quite easily oxidised by manganate(VII) ions. That means that the reaction won't stop at this point unless the potassium manganate(VII) solution is *very* dilute, very cold, and preferably not under acidic conditions.

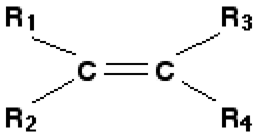
If you are using hot concentrated acidified potassium manganate(VII) solution, what you finally end up with depends on the arrangement of groups around the carbon-carbon double bond.

Writing a structural formula to represent any alkene

The formula below represents a general alkene. In organic chemistry, the symbol **R** is used to represent hydrocarbon groups or hydrogen in a formula when you don't want to talk about specific compounds. If you use the symbol more than once in a formula (as here), the various groups are written as R_1, R_2, etc.

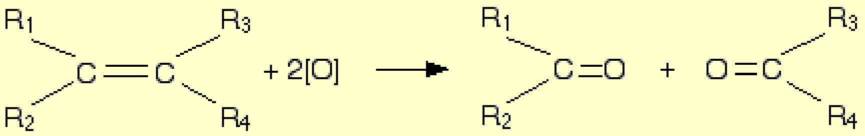
In this particular case, the double bond is surrounded by four such groups, and these can be any combination of same or different - so they could be 2 hydrogens, a methyl and an ethyl, or 1 hydrogen and 3 methyls, or 1 hydrogen and 1 methyl and 1 ethyl and 1 propyl, or any other combination you can think of.

In other words, this formula represents every possible simple alkene:



The first stage of the extended oxidation

The acidified potassium manganate(VII) solution oxidises the alkene by breaking the carbon-carbon double bond and replacing it with two carbon-oxygen double bonds.



The products are known as ***carbonyl compounds*** because they contain the carbonyl group, C=O. Carbonyl compounds can also react with potassium manganate(VII), but how they react depends on what is attached to the carbon-oxygen double bond. So we need to work through all the possible combinations.

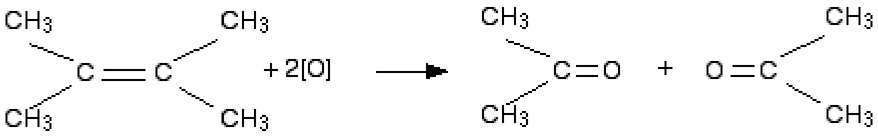
What happens next?

If both attached R groups in the products are alkyl groups

Carbonyl compounds which have two hydrocarbon groups attached to the carbonyl group are called ketones. Ketones aren't that easy to oxidise, and so there is no further action. (But see note in red below.)

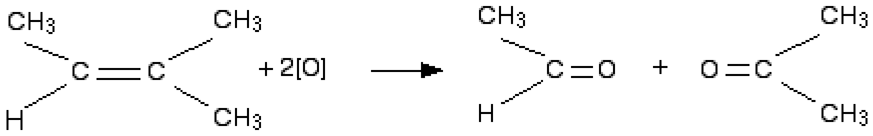
If the groups attached either side of the original carbon-carbon double bond were the same, then you would end up with a single ketone. If they were different, then you would end up with a mixture of two.

For example:



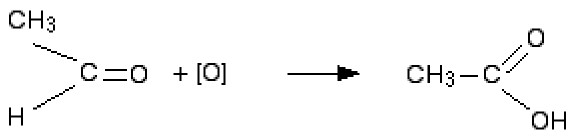
In this case, you would end up with two identical molecules called propanone. On the other hand, if one of the methyl groups in the original molecule was replaced by an ethyl group, you would get a mixture of two different ketones - propanone and butanone.

What would you get if there was a methyl and an ethyl group on both sides of the original carbon-carbon double bond? Again, you would get a single ketone formed - in this case, butanone. If you aren't sure about this, draw the structures and see.



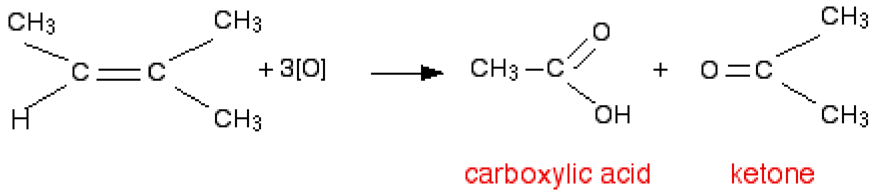
In this case, the first product molecule has a methyl group and a hydrogen attached to the carbonyl group. This is a different sort of compound known as an aldehyde.

Aldehydes are readily oxidised to give carboxylic acids, containing the -COOH group. So this time, the reaction will go on a further step to give ethanoic acid, CH_3COOH.



The acid structure has been turned around slightly to make it look more like the way we normally draw acids, but the net effect is that an oxygen has been slotted in between the carbon and hydrogen.

The overall effect of the potassium manganate(VII) on this kind of alkene is therefore:



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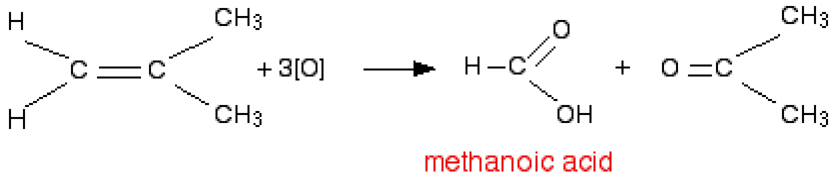
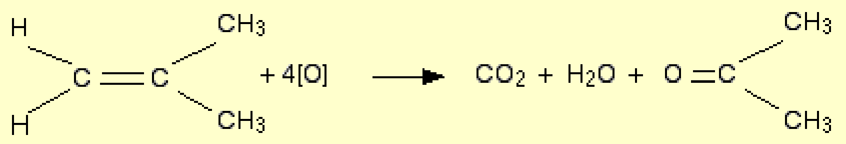


But it doesn't! That's because methanoic acid is also easily oxidised by potassium manganate(VII) solution. In fact, it oxidises it all the way to carbon dioxide and water.

So the equation in a case like this might be, for example

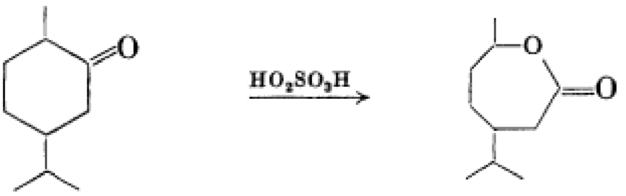


The exact nature of the other product (in this example, propanone) will vary depending on what was attached to the right-hand carbon in the carbon-carbon double bond.

If there were two hydrogens at both ends of the double bond (in other words, if you had ethene), then all you would get would be carbon dioxide and water.

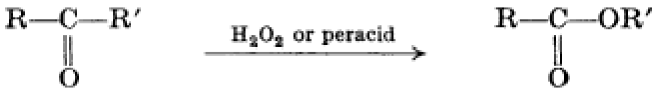
Oxidation by Perbenzoic acid

In 1899, Baeyer and Villiger(**1**) showed that the oxidation of the alicyclic ketones menthone, tetrahydrocarvone (I), and camphor with permonosulfuric acid led to the formation of lactones.



I

Further studies, using a variety of ketones or aldehydes and hydrogen peroxide or peracids in various media, have established that the oxidation represented by the following equation is of wide applicability.



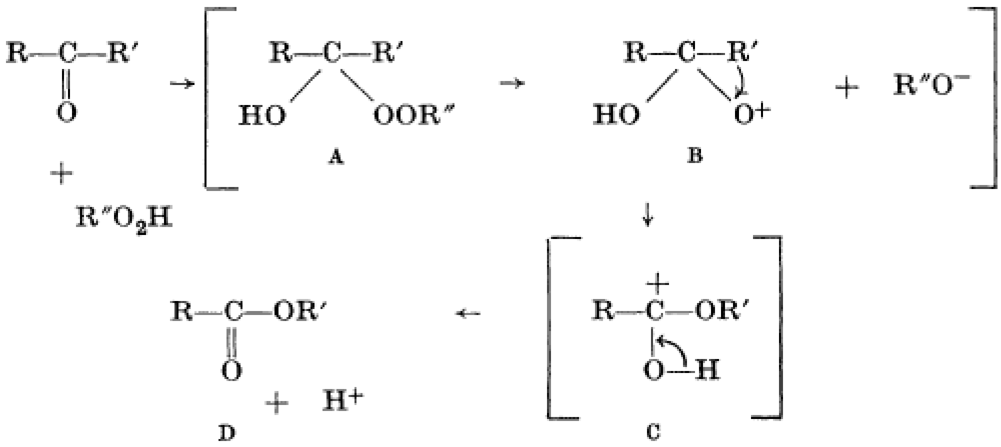
$$\underset{\underset{\displaystyle O}{\|}}{R-C-R'} \xrightarrow{H_2O_2 \text{ or peracid}} \underset{\underset{\displaystyle O}{\|}}{R-C-OR'}$$

This oxidation, the Baeyer ‐ Villiger reaction, is the subject of this review. As the oxidation normally employs mild conditions, gives reasonable yields, and shows a high degree of selectivity, it has proved useful in a variety of both synthetic and degradative studies. Recent investigations have led to a better definition of favorable experimental conditions and have extended appreciably the scope of the reaction.

Mechanism of the Reaction

It is now generally agreed that the Baeyer - Villiger reaction is ionic in character. The favored reaction pattern was first outlined by Criegee in 1948. It assumes that in the first instance addition of the peroxide to the carbonyl group yields a hydroxyperoxide (A). This dissociates to give an electron - deficient ion (B), which rearranges to C with cleavage of a carbon - carbon bond. The postulated carbonium ion C decomposes to the ester D in a normal way.

This mechanism has recently been the subject of detailed discussion by a number of authors. The scheme accounts for the observation that in the oxidation of substituted acetophenones with perbenzoic acid the rate - determining step is the acid - catalyzed addition of perbenzoic acid to the carbonyl group. It recognizes that in certain cases hydroxyhydro - peroxides have been isolated and converted to rearrangement products by heating alone. It explains the fact that the migratory aptitude of aryl groups R, R′ is normally proportional to their capacity for electron release. There is a general similarity of the mechanism to those postulated, inter alia, for the Beckmann, pinacol - pinacolone, Hofmann, Curtius, Wagner - Meerwein, and acid catalyzed hydroperoxide rearrangements.



Scope of the Reaction

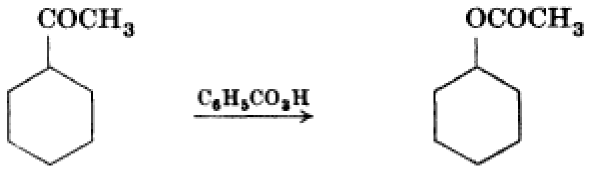
Saturated Aliphatic Ketones

There is only one example of the Baeyer - Villiger oxidation of a simple ketone of the type RCH_2COCH_2R' to an ester. Methyl - hexyl ketone gives - hexyl acetate (VI) and its hydrolysis products on treatment with hydrogen peroxide in hydrofluoric acid.

$$CH_3(CH_2)_5COCH_3 \xrightarrow[HF]{H_2O_2} \underset{\text{VI}}{CH_3(CH_2)_5OCOCH_3} + CH_3CO_2H + CH_3(CH_2)_5OH$$

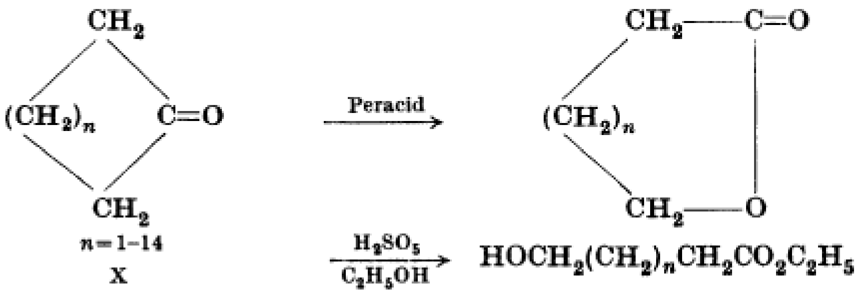
It has been shown that hydrogen peroxide in the presence of sulfuric acid may oxidize such ketones to ketone peroxides and α-ketols. Perbenzoic acid is said to have no significant action. However, as peracids have not yet been used under the most favorable conditions there is no decisive evidence that they will not react with these simple ketones.

When ketones with the carbonyl group attached to at least one secondary carbon atom are treated with peracids, esters are formed. The secondary grouping rearranges in preference to a primary one. In the series of alicyclic methyl ketones from methyl cyclobutyl ketone to methyl cycloheptyl ketone, oxidation with perbenzoic acid gives yields of acetates ranging from 58 to 78%.



Alicyclic Ketones

Alicyclic ketones ranging from cyclobutanone to cycloheptadecanone have been oxidized under Baeyer-Villiger conditions. The reaction provides a convenient method for determining structure and for preparing relatively inaccessible lactones and hydroxy acids. When persulfuric acid or hydrogen peroxide-hydrofluoric acid is used for the oxidation, polyesters of the hydroxy acids are obtained. The ethyl esters of the simple hydroxy acids are formed when ethanol is present. Organic peracids give excellent yields of lactones. The oxidation has also been carried out under alkaline conditions but the yields recorded are low.

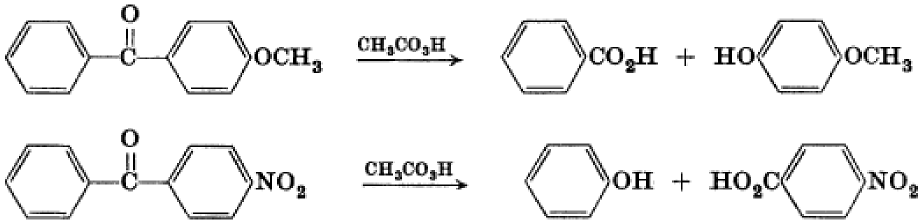


X

Aromatic Ketones

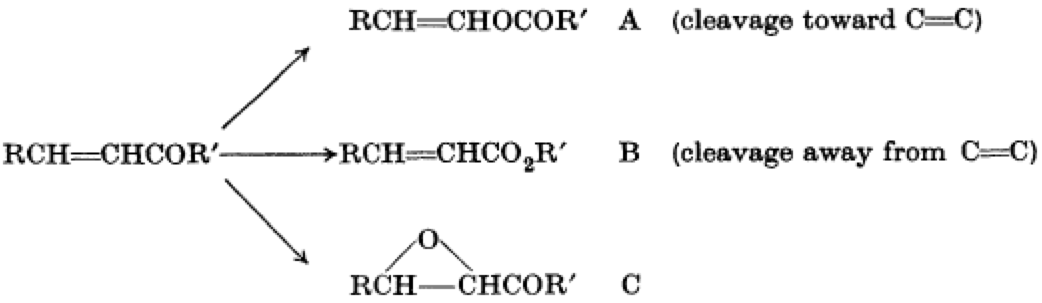
The oxidation of diaryl ketones with peracids regularly leads to the formation of esters or their hydrolysis products. Although this reaction is of little value as a preparative procedure, it does provide a convenient means of establishing the structures of polysubstituted benzophenones and alkyl aryl ketones. The method is less drastic and more specific than the degradation procedures involving alkali fusion or acid hydrolysis that have been applied to natural products.

In the cleavage of unsymmetrical ketones the migrating group is normally the more electron - releasing one. Substituents in the aromatic nuclei influence the course of reaction in a manner similar to that observed in normal nucleophilic aromatic substitution. Thus treatment of *p* - methoxybenzophenone with peracetic acid gives benzoic acid and hydroquinone monomethyl ether, while cleavage of *p* - nitrobenzophenone gives *p* - nitrobenzoic acid and phenol exclusively.



α,β - Unsaturated Ketones

The application of the Baeyer - Villiger reaction to this group of compounds should lead to reaction according to either A or B. Another possibility is preferential attack at the olefinic linkage leading to an α, β - epoxyketone (C).

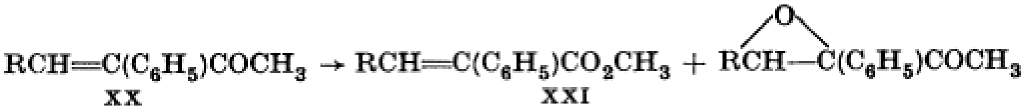


Although only a limited number of cases have been studied, examples of the formation of all three types of compound are available. The oxidation of benzalacetone (XVIII) with peracetic acid leads exclusively to the ester XIX.

An α - phenyl - α, β - unsaturated ketone (XX) gives a mixture of epoxyketone and the ester XXI.

$$\underset{\text{XVIII}}{C_6H_5CH{=}CHCOCH_3} \rightarrow \underset{\text{XIX}}{C_6H_5CH{=}CHOCOCH_3}$$

An α - phenyl - α, β - unsaturated ketone (XX) gives a mixture of epoxyketone and the ester XXI.



$$\underset{\text{XX}}{RCH{=}C(C_6H_5)COCH_3} \rightarrow \underset{\text{XXI}}{RCH{=}C(C_6H_5)CO_2CH_3} + RCH{-}\overset{O}{\ }{-}C(C_6H_5)COCH_3$$

Oxidation of Δ^{16} - 20 - ketosteroids with perbenzoic acid leads to preferential attack at the olefinic linkage. Pregna - 5,6 - dien - 3β - ol - 20 - one acetate has been converted in this way to 16,17 - epoxypregna - 5 - en - 3β - ol - 20 - one acetate, a useful intermediate in the preparation of 17α - hydroxyprogesterone.(**55**)

When α, β - unsaturated ketones are treated with hydrogen peroxide in alkaline solution, epoxyketones are formed.(**56**-**58**) There is no evidence of the Baeyer - Villiger reaction occurring under these conditions.

Reactive intermediates

In chemistry, a reactive intermediate or an intermediate is a short-lived, high-energy, highly reactive molecule. When generated in a chemical reaction, it will quickly convert into a more stable molecule. Only in exceptional cases can these compounds be isolated and stored, e.g. low temperatures, matrix isolation. When their existence is indicated, reactive intermediates can help explain how a chemical reaction takes place.

Most chemical reactions take more than one elementary step to complete, and a reactive intermediate is a high-energy, yet stable, product that exists only in one of the intermediate steps. The series of steps together make a reaction mechanism. A reactive intermediate differs from a reactant or product or a simple reaction intermediate only in that it cannot usually be isolated but is sometimes observable only through fast spectroscopic methods. It is stable in the sense that an elementary reaction forms the reactive intermediate and the elementary reaction in the next step is needed to destroy it.

When a reactive intermediate is not observable, its existence must be inferred through experimentation. This usually involves changing reaction conditions such as temperature or concentration and applying the techniques of chemical kinetics, chemical thermodynamics, or spectroscopy. We will often refer to certain reactive intermediates based on carbon, viz., carbocations, radicals, carbanions and carbenes.

Common features

Reactive intermediates have several features in common:

- low concentration with respect to reaction substrate and final reaction product
- often generated on chemical decomposition of a chemical compound
- it is often possible to prove the existence of this species by spectroscopic means
- cage effects have to be taken into account
- often stabilization by conjugation or resonance
- often difficult to distinguish from a transition state
- prove existence by means of chemical trapping

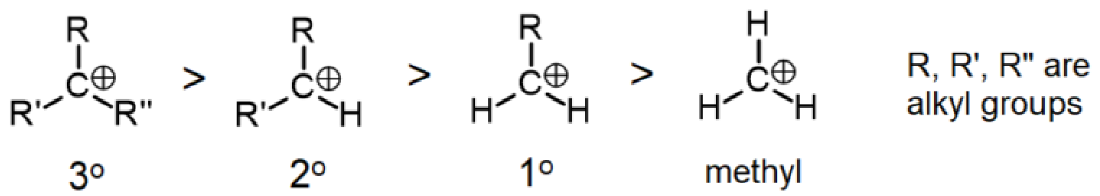
Carbocations (R+)

A **carbocation** is an ion with a positively-charged carbon **atom**. Among the simplest examples are methenium CH_3^+, methanium CH_5^+, and ethanium $C_2H_7^+$. Until the early 1970s, all carbocations were called carbonium ions.[1] In present-day chemistry, a carbocation is any positively charged carbon atom, classified in two main categories according to the valence of the charged carbon:

- +3 in carbenium ions (protonated carbenes),
- +5 or +6 in the carbonium ions (protonated alkanes, named by analogy to ammonium). These are much less common.

Structure and properties

The charged carbon atom in a carbocation is a “sextet”, i.e. it has only six electrons in its outer valence shell instead of the eight valence electrons that ensures maximum stability (octet rule). Therefore, carbocations are often reactive, seeking to fill the octet of valence electrons as well as regain a neutral charge. One could reasonably assume a carbocation to have sp3sp3 hybridization with an empty sp3sp3 orbital giving positive charge. However, the reactivity of a carbocation more closely resembles sp2sp2 hybridization with atrigonal planar molecular geometry. An example is the methyl cation, CH+3CH3+.



Order of stability of examples of tertiary (3^{o}), secondary (2^{o}), and primary (1^{o}) alkyl **carbenium ions**, as well as the methyl cation (far right). The methyl group is so unstable it is only observed in the gas phase.

Carbocations are often the target of nucleophilic attack by **nucleophiles** such as water or halide ions.

Carbocations typically undergo **rearrangement reactions** from less stable structures to equally stable or more stable ones with **rate constants** in excess of 10/sec. This fact complicates synthetic pathways to many compounds. For example, when 3-pentanol is heated with aqueous HCl, the initially formed 3-pentyl carbocation rearranges to a statistical mixture of the 3-pentyl and 2-pentyl. These cations react with chloride ion to produce about 1/3 3-chloropentane and 2/3 2-chloropentane.

A carbocation may be stabilized by **resonance** by a carbon-carbon double bond next to the ionized carbon. Such cations as ***allyl*** cation $CH_2{=}CH{-}CH_2^+$ and ***benzyl*** cation $C_6H_5{-}CH_2^+$ are more stable than most other carbocations. Molecules that can form allyl or benzyl carbocations are especially reactive. These carbocations where the C+ is adjacent to another carbon atom that has a double or triple bond have extra stability because of the overlap of the empty p orbital of the carbocation with the p orbitals of the π bond. This overlap of the orbitals allows the charge to be shared between multiple atoms – delocalization of the charge – and, therefore, stabilizes the carbocation.