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Oxidative methods in the synthesis of vicinal di- and polycarbonyl compounds

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Abstract. The review systematises and summarises the oxidative methods for the synthesis of compounds with vicinal carbonyl functions. The oxidative reagents used for this purpose, their scope and limitations are discussed. The bibliography includes 307 references.

I. Introduction

Alicyclic and cyclic 1,2-dicarbonyl and vicinal polycarbonyl compounds have been known for over 150 years. The properties of many of them have been well studied, and some have found practical use as biologically active compounds, intermediates in the synthesis of various heterocyclic compounds, analytical reagents, photopolymerisation initiators *etc*. Bis-1,2-diketones find use as monomers for the preparation of thermostable polyphenylquinoxalines.

Some representatives of this class (*e.g*., 'oxocarbons' and 'pseudooxocarbons') are rather exotic compounds but present considerable interest for theoretical organic chemistry.[1–3] To date, vicinal polycarbonyl compounds with five carbonyls have been obtained. Activity in this field of research does not cease.

Methods for the synthesis of 1,2-, bis-1,2- and polycarbonyl compounds[1,4] and cyclic oxocarbons and pseudooxocarbons[2] have been reviewed.

The present review systematises and summarises the literature data on the oxidative methods for the synthesis of di- and polycarbonyl compounds with preservation of the carbon skeleton of the starting substrates. The existing methods for the synthesis of these compounds are divided into the following main groups: (1) introduction of a carbonyl group at the α-position with respect to the existing one in aldehydes, ketones, carboxylic acids and their α-substituted (hydroxy-, halogeno-, *etc*.) derivatives; (2) oxidative transformations of epoxides and vicinal compounds containing the CHX-CHY moiety; (3) oxidation of the alkyl groups and compounds with multiple bonds. The reagents used for oxidation are described for each of the above substrate types. Generally, we refer to studies not included in the reviews mentioned above.[1,2,4] However, in some instances we mention them in order to give a full picture of the existing reagents and the most reliable methods.

One should bear in mind that vicinal di- and polycarbonyl compounds tend to undergo hydration, and their mono- or dihydrates, *i.e*., *gem*-diols, are commonly obtained as the final products. It is also typical of vicinal di- and polycarbonyl compounds to exist as various types of enols; the ratio of the carbonyl and enol forms has not been always determined with certainty.

II. Oxidation of carbonyl compounds and their derivatives

Syntheses of vicinal di- and polycarbonyl compounds are most commonly based on substrates already containing at least one carbonyl group.

1. Oxidation of the α-methyl and α-methylene groups of aldehydes, ketones and carboxylic acids

The reagents known for the preparative oxidation of the α-methyl and α-methylene groups of aldehydes and ketones are listed in Table 1. Nitrogen oxides and aromatic nitrosamines were the first reagents used for the oxidation of ketones (more seldom, aldehydes). They had been used rather widely in the synthesis of 1,2-dicarbonyl compounds before such reagents as selenium dioxide and DMSO appeared.[1,2,4,5]

Since the turn of the century, treatment of 1,3-diarylpropan-2-ones with 'nitrous gas', which is generated from nitric acid and arsenic oxide at −30 °C, has been known to give 'isonitrosodimers'. The latter decomposed on heating to give nitrogen and aromatic vicinal triketone hydrates.[6] This reaction was used in the synthesis of diethyl oxomalonate from diethyl malonate and N_2O_3 (yield 75%).[7] It was pointed out that the oxidation of diethyl malonate is more convenient if NO_2 is used.[1] Later, diaryl triketones were obtained in high yields using an equimolar mixture of NO and NO_2.[8]

In 1901, the oxidising effect of *p*-nitrosodimethylaniline on the methylene group of certain β-diketones and/or β-oxo esters, which resulted in contiguous tricarbonyl derivatives, was discovered. Examples of such reactions have been presented in reviews.[1,5] Despite the high toxicity of the reagent, the method is sometimes used even now. For example, the following scheme for the preparation of dioxo esters (**1a–c**) from esters has been implemented.[9]

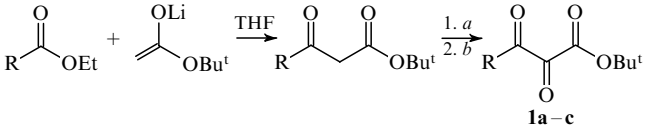
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Table 1. Reagents used for the oxidation of carbonyl compounds and their derivatives into vicinal di- and polycarbonyl compounds.

Substrate	Reagent	Product
RCOMe	AlkONO, $NaNO_2-H^+$, HalNO, HSO_4NO, NH_4CrO_3Cl, nitrosonium salts, SeO_2, H_2SeO_3, PhSeSePh – $(NH)_4S_2O_8$ – MeOH, HBr – DMSO	RCOCHO
$RCOCH_2R$ and cyclic ketones	$KMnO_4-Al_2O_3$, NH_4CrO_3Cl, $O_2-V_2O_5$ or V_2O_5, nitrosonium salts, SeO_2, H_2SeO_3, HBr – DMSO, NBS – DMSO	RCOCOR
β-Diketones	$NO-NO_2$, 4-$Me_2NC_6H_4NO$, $^1O_2-h\nu-Bu_4NF$, PhIO, SeO_2, H_2SeO_3, HBr – DMSO, NBS – DMSO	Vic. triketones
β-Oxo esters	$NO-NO_2$, 4-$Me_2NC_6H_4NO$, $KMnO_4-Al_2O_3$, $Bu^tOOH-V_2O_5-SiO_2$, CrO_3, $O_2-Co(OBz)_2$, PhSeSePh – $(NH)_4S_2O_8$ – MeOH	$R^1COCOCOOR^2$
$R(Me_3SiO)C=CR(OSiMe_3)$	Br_2-CHCl_3	RCOCOR

Note. NBS is *N*-bromosuccinimide.



1a–c

R = 1-allyl-3-indolyl (**a**), 4-$Me_2NC_6H_4$ (**b**), 1-methyl-2-pyrrolyl (**c**); (*a*) 4-$Me_2NC_6H_4NO$, KOH, EtOH; (*b*) HCl, CH_2Cl_2.

It was noted that compounds **1a–c** could not be obtained by the photooxidation of the phosphorylides of intermediate β-diketones.[9]

Certain ketones react with pentyl nitrite to give α-nitroso derivatives (oximes); this reaction with an excess of the reagent under mild conditions gives α-diketones.[10] This procedure made it possible to synthesise 1-phenylpropane-1,2-dione from propiophenone and camphorquinone from camphor. Alkyl nitrites react with ketones as sources of the nitrosonium ion (NO^+). Ketones are also successfully oxidised with other reagents that generate NO^+ *in situ*, for example, inorganic nitrites in the presence of acids, nitrosyl halides and nitrososulfates. Some of aryl methyl ketones were oxidised with these reagents under mild conditions into arylglyoxals or their acetals.[11] Acetals are formed in 50%–70% yields in the reaction of acetophenones with MeONO in a mixture of MeOH with HCl at 0–5 °C in 4 h. Heating of aryl methyl ketones with $NaNO_2$ in HCl at 60 °C gives the corresponding arylglyoxals directly in yields higher than 60%.[11]

The oxidative properties of organic nitrosonium salts are similar to those of nitrosodimethylaniline and alkyl nitrites. Their use as oxidants of alcohols, amines and ketones is covered in a review,[12] and we shall not dwell on this topic.

Such a popular oxidant as potassium permanganate generally cleaves ketones to carboxylic acids or (in basic media) transforms them to oxocarboxylic acids.[5] However, $KMnO_4$ immobilised on alumina can selectively oxidise the α-methylene groups of ketones. Oxidation of cyclohexanone in dichloromethane at room temperature for 120 h results in cyclohexane-1,2-dione in 58% yield.[13] The same reagent oxidises ethyl phenylacetate in 161 h to give ethyl phenylglyoxylate in an almost quantitative yield. However, phenylacetic acid undergoes decarboxylation under these conditions to give benzaldehyde.[13]

Ferrocenyl diketones (**2a–c**) were first obtained[14] in 50%–65% yields upon the oxidation of the corresponding ferrocenyl ketones with MnO_2 in boiling dichloromethane.

$$FcCOCH_2R \xrightarrow[CH_2Cl_2]{MnO_2} FcCOCOR$$

2a–c

Fc is ferrocenyl; R = Ph (**a**), 4-C_6H_4Ph (**b**), Fc (**c**).

Yet another example of a fundamental change in the properties of an oxidant after its immobilisation on a support was demonstrated for V_2O_5 adsorbed on montmorillonite or SiO_2, which is an efficient catalyst for the oxidation of the methylene group of methyl phenylacetates with *tert*-butylhydroperoxide to give alkyl arylglyoxylates (**3a–j**).[15]

$$RC_6H_4CH_2COOMe \xrightarrow[PhH,\ 70\ ^\circ C]{Bu^tOOH,\ V_2O_5,\ N_2} RC_6H_4COCOOMe$$

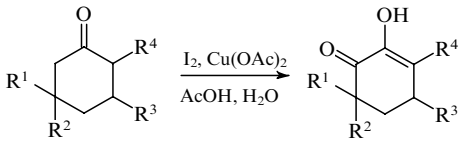
3a–j

R = H(**a**), 2-MeO(**b**), 4-MeO(**c**), 4-Me(**d**), 4-NH_2(**e**), 4-NO_2(**f**), 2-Cl(**g**), 4-Cl(**h**), 2-$PhCH_2$(**i**), 4-$PhCH_2$(**j**).

Choudary *et al.*[15] claimed that they were the first to oxidise the α-methylene group in arylacetic esters to the carbonyl group. However, as early as in 1957 phenylacetic acid was transformed to the acid **3a** in 86% yield upon treatment with air in the presence of cobalt benzoate at 110–115 °C.[16] Diethyl malonate is oxidised with N_2O_3 as discussed above.

Butan-2-one is oxidised on V_2O_5 under aerobic and anaerobic conditions at 250–350 °C to butane-2,3-dione.[17,18] Experiments involving $^{18}O_2$ showed that the resulting diketone did not contain this isotope. Acetic acid and acetaldehyde are the main side products, which are formed mainly due to the decomposition of butanedione. To a smaller extent, these products result from the oxidation of the original ketone in the enol form.

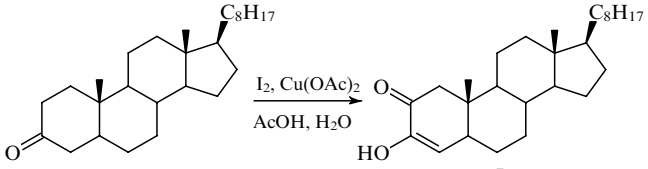
Copper acetate has been long used for the synthesis of 1,2-dicarbonyl compounds from α-hydroxy ketones (see Section III). An equimolar mixture of I_2 and $Cu(OAc)_2$ oxidises the α-methylene group in cyclohexanone and its derivatives on boiling in aqueous acetic acid for 15 h to give the corresponding cyclohexane-1,2-diones (**4a–h**) in up to 70% yields.[19]



4a–h

$R^1=R^2=R^3=H$, R^4 = (**a**), Me (**b**), Et (**c**), cyclo-C_6H_{11} (**d**), Ph (**e**); $R^1=R^2=H$, $R^3=R^4=Me$ (**f**); $R^1=R^4=H$, $R^2=R^3=Me$ (**g**); $R^1=R^2=R^3=Me$, $R^4=H$ (**h**).

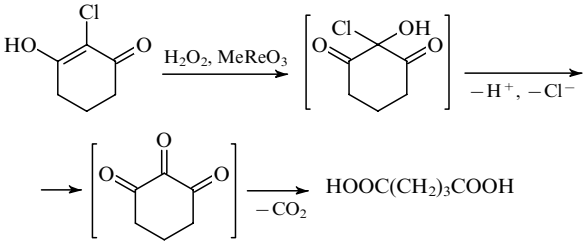
The same procedure made it possible to obtain cholestane-2,3-dione (**5**) from cholestan-3-one in 40% yield.[19]



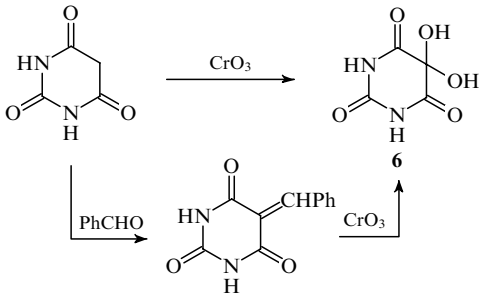
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According to IR, ^1H and ^{13}C NMR spectral data, compounds **4a–h** and **5** exist in the enol form.[19]

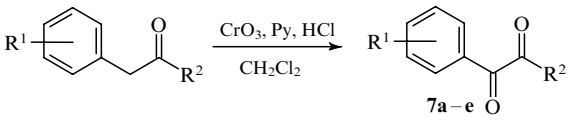
Oxidation of cyclic α-chloro β-diketones with hydrogen peroxide in the presence of $MeReO_3$ resulted in their decomposition to dicarboxylic acids *via* intermediate contiguous tricarbonyl compounds, which were detected in some instances by NMR spectroscopy.[20]



The methylene group in barbituric acid can be oxidised with CrO_3 to give alloxan (**6**). The same result was obtained in the oxidation of benzylidenebarbituric acid (yield 75%–84%).[21,22]



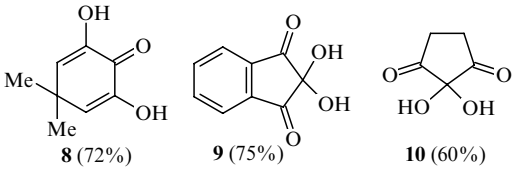
The other known reagent based on CrO_3, namely, pyridinium chlorochromate introduced in practical organic synthesis in 1977 by Corey, oxidises successfully various benzyl ketones (but not aliphatic ketones) in boiling CH_2Cl_2.[23]



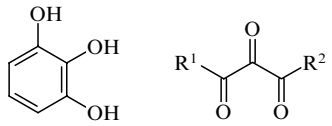
Compound	R^1	R^2	Yield (%)
7a	H	Ph	80
7b	H	Me	85
7c	H	Et	80
7d	4-MeO	Me	60
7e	2-Me	Me	65

A similar reagent, ammonium chlorochromate (NH_4CrO_3Cl), transforms acetophenone to phenylglyoxal rather easily (DMF, 75 °C, 6 h) in 80% yield.[24] The same authors[25] used this reagent to oxidise butan-2-one to a mixture of ethylglyoxal and butane-2,3-dione and to oxidise 3-methylbutan-2-one to isopropylglyoxal.

A new method for the photooxidation of the methylene group of acyclic and cyclic β-diketones by singlet oxygen was suggested in 1985.[26,27] The reaction occurs successfully only in the presence of tetrabutylammonium fluoride. Presumably, the fluoride anion enhances the nucleophilic properties of the enol forms, thus activating the electrophilic attack by singlet oxygen. This method gave high yields (60%–97%) of tricarbonyl compounds (**8**–**11**, **12a**–**c**).



8 (72%) **9** (75%) **10** (60%)



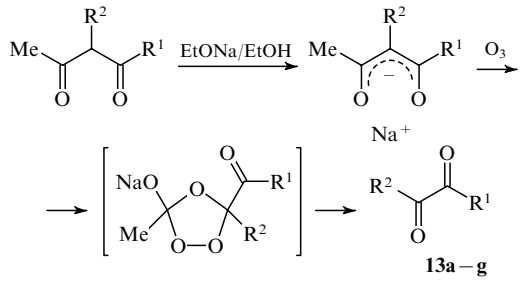
11 (70%) **12a**–**c**

$R^1 = R^2 = Ph$ (**12a**); $R^1 = Ph$, $R^2 = Me$ (**12b**); $R^1 = R^2 = Me$ (**12å**).

It should be noted that the similar photooxidation of five- and six-membered cyclic α-diketones results in ring opening to give aldehydo or oxo carboxylic acids, probably *via* intermediate *endo*-peroxides.[26–29]

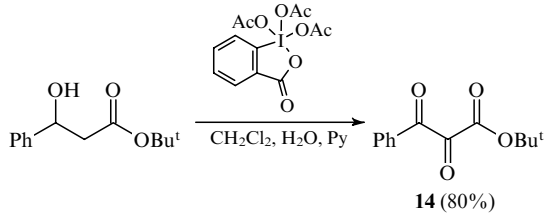
It is well known that the oxidation of acyclic ketones with oxygen in the presence of bases serves as a method for the synthesis of carboxylic acids. Oxidation of 3-methyl- and 3-ethylpentane-2,4-diones gives a mixture of acetic acid and the corresponding 3-hydroxy 2-ketones and 2,3-diketones.[30] This process is not a preparative method for the synthesis of diketones. However, it was found that cyclohexanone and cyclopentanone dissolved in dimethoxyethane undergo oxidation with atmospheric oxygen in the presence of Bu^tOK at −20 °C to give the diketone **4a** and cyclopentane-1,2-dione, respectively.[31] The yields of cyclopentanedione and especially diketone **4a** are low due to ring opening resulting in dicarboxylic acids. The similar reactions with cycloheptanone and cyclooctanone also give the corresponding diketones, but only as intermediates, which undergo subsequent aldol condensation. The stability of the diketone **4a** and cyclopentane-1,2-dione under these conditions is explained[31] by the predominance of the enol forms.

1,2-Diketones and α-oxo esters (**13a**–**g**) are obtained in moderate to high yields (21%–83%) by the ozonolysis of Na-salts of β-diketones and β-oxo esters followed by treatment of the intermediate ozonides with hydrogen peroxide or dimethyl sulfide.[32]



$R^1 = OEt$: $R^2 = Bu$ (**a**), $PhCH_2$ (**b**), $4\text{-}EtOCH_2C_6H_4CH_2$ (**c**), $(EtO)_2P(O)CH_2CH_2$ (**d**); $R^1 = Me$: $R^2 = Bu^t$ (**e**), $PhCH_2$ (**f**), $4\text{-}EtOCH_2C_6H_4CH_2$ (**g**).

Compounds of hypervalent iodine are used very widely in organic synthesis, particularly as oxidising reagents for the α-hydroxylation of carbonyl compounds (see *e.g.*, the reviews[33–36]). Much less is known about direct oxidation of ketones with these reagents to α-dicarbonyl compounds. The use of 1,1,1-triacetoxy-1-λ^5-benzo-1,2-iodoxol-3-one ('periodinane' or the Dess–Martin reagent) in moist CH_2Cl_2 in the presence of pyridine for the oxidation of *tert*-butyl 2-hydroxy-2-phenylpropionate to the corresponding dioxo ester **14** was reported.[37]



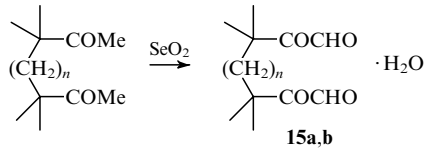
14 (80%)

Diacetoxy-λ^3-iodanylbenzene oxidises 1,3-indanedione in alcohols in the presence of H_2SO_4 to the corresponding 2,2-dialkoxyindanediones.[38]

The kinetics and mechanism of the oxidation of cyclopentanone and cyclohexanone to the corresponding 1,2-diketones with bromoamine-T (4-$MeC_6H_4SO_2NNaBr$) in acidic media was studied.[39] Enolisation of the starting ketones was found to be the limiting step of the oxidation.

Selenium dioxide is a much more versatile reagent for the synthesis of vicinal polycarbonyl compounds. Its extensive use in practical organic synthesis started in the early 30's, and this reagent is still important today. Both SeO_2 and selenious acid (H_2SeO_3), which is prepared by concentrating aqueous solutions of selenium dioxide, are used in syntheses of dicarbonyl compounds. Both reagents selectively oxidise the α-methyl groups of aliphatic and aromatic ketones and acetaldehyde as well as the α-methylene groups of cyclic ketones. Oxidation can be carried out by heating the reagent and substrates in the absence of solvents. However, the reaction is more commonly performed in such solvents as water, ethanol, acetic acid and dioxane; sometimes, xylene, acetic anhydride and pyridine are used. A wide range of aryl methyl ketones with various donor and acceptor substituents in the ring are oxidised with SeO_2 to the corresponding arylglyoxals in yields usually exceeding 70%.[4, 5, 40] However, *ortho*-acetylacetophenone, unlike the *para*-isomer,[4] gives 2-hydroxy-1,4-naphthoquinone rather than bisglyoxal.[41] It is reported in patent literature that the oxidation of acetophenone with SeO_2 in C_{1-9} aliphatic alcohols at 100 °C gives the corresponding phenylglyoxal acetals.[42] Acetaldehyde is oxidised with H_2SeO_3 to glyoxal (isolated as a bisulfite derivative in 72%–74% yield[43]). It can be noted that glyoxal is also formed from acetone by refluxing the latter with SeO_2 in xylene in the presence of water.[40] Selenious acid in aqueous dioxane readily oxidises cyclohexanone at room temperature to give cyclohexane-1,2-dione (yield 60%).[44] The use of SeO_2 in this reaction gives nearly the same yield but requires more drastic conditions (refluxing for 6–8 h).[45]

Selenium dioxide has also been used to oxidise many β-diketones (acetylacetone, benzoylmesitoylmethane, dimesitoylmethane, 5-hydroxy-4-phenylcyclopent-4-ene-1,3-dione, *etc*.) to the corresponding 1,2,3-triones.[1] Bisglyoxals (**15a**,**b**) used in the synthesis of cyclic vicinal tetraketones were also obtained with this reagent.[46]



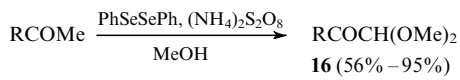
15a,**b**

n = 6 (**a**), 8 (**b**).

The possible mechanisms of oxidation with selenium dioxide have been discussed in reviews.[4, 40]

Despite the high efficiency and selectivity combined with mild conditions of the reaction, SeO_2 has a serious drawback noted in many works, namely, the difficulty of purification of the final products from selenium that is formed. Black selenium that is evolved can be filtered off, but a small amount of colloidal selenium ('red selenium') remains in solution and cannot be removed even by distillation. This necessitates an additional work-up of the products, *viz*., shaking with mercury or inactive Raney nickel or treatment with potassium cyanide, SO_2, potassium hydrogensulfite in acidic media or thiourea.[5, 40]

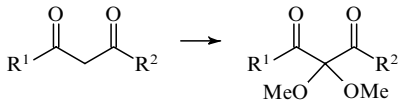
Yet another selenium-based oxidant, diphenyl diselenide, has been suggested recently.[47] It proved to be very efficient (in catalytic or stoichiometric quantities) for the preparation of α-oxo acetals **16** from the corresponding methyl ketones in the presence of ammonium peroxodisulfate $(NH_4)_2S_2O_8$.



16 (56%–95%)

The reaction is carried out in boiling methanol and is applicable to a broad range of aromatic and heterocyclic methyl ketones (except for acetylpyridine) as well as to unsaturated, cycloaliphatic and, in certain cases, aliphatic methyl ketones. It is assumed that the process occurs through electrophilic attack of $PhSe^+$ on the enol form of the ketone.[47]

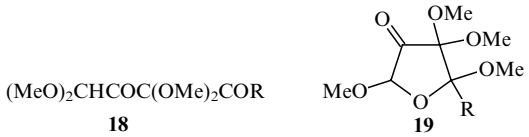
The same group of authors[48] expanded this oxidation method to β-diketones and β-oxo esters.



17

R^1 = Alk, Ph; R^2 = Alk, Ph, OAlk, OCH_2Ph.

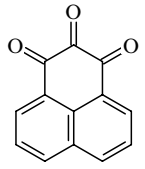
In this case, only a catalytic amount of PhSeSePh was used, and the yields of oxo acetals **17** were considerably lower (10%–75%), especially for the diketones containing the acetyl fragment, which also undergoes partial oxidation. This reaction affords side products **18** and **19**.[48]



18 **19**

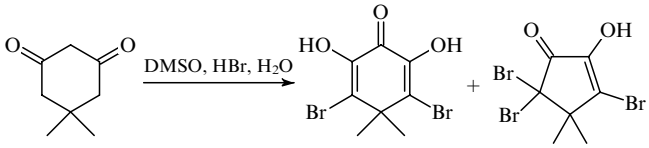
Since the discovery of a very simple method for the oxidation of activated alkyl halides, including phenacetyl bromides, with DMSO in the presence of bases (the Kornblum reaction),[49] a large number of studies have appeared in which DMSO is used as a convenient oxidant (for the relevant reviews, see Refs 5, 50–52). No wonder that DMSO plays an important role in the synthesis of α-dicarbonyl compounds as well.

For example, DMSO in the presence of dry HBr oxidises the methylene groups in cyclic β-diketones to produce 1,2,3-triones **9** and **20** in 80% and 30% yields, respectively.[53, 54]



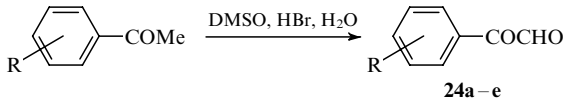
20

It was found later that the oxidation of another cyclic diketone, dimedone (**21**), with DMSO in the presence of hydrogen bromide brings about not only oxidation of the methylene group but also ring bromination to give dibromotriketone **22**. In addition, a product of ring contraction, *viz*., tribromocyclopentanedione **23**, is formed.[55]



21 **22** (46%) **23** (17%)

The DMSO–aqueous HBr system turned out to be very efficient in the transformation of acetylarenes to arylglyoxals **24a**–**e**.[56]



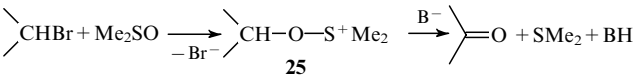
24a–**e**

R = 4-Ph (**a**), 4-MeO (**b**), 4-NO_2 (**c**), 4-Br (**d**), 2-Ph (**e**).

This is probably the most convenient reagent presently available for this transformation. The reaction is carried out at 55 °C for 1–24 h to give the corresponding arylglyoxals in high yields (42%–94%). Side processes have been noted in two cases only.

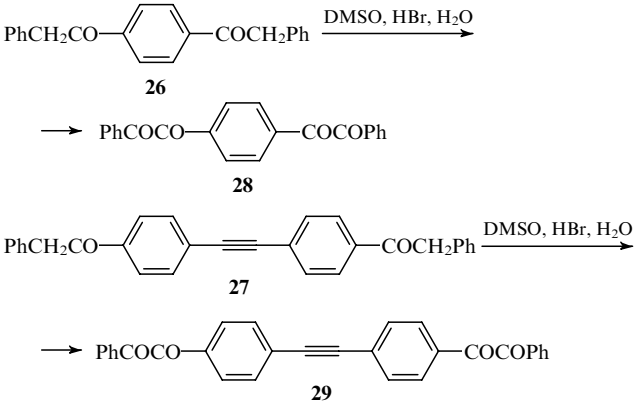
For example, the oxidation of 2-acetylbiphenyl results in oxidative cyclisation to give phenanthrenequinone in 47% yield. In the case of 4-acetyldiphenylamine, oxidation is accompanied by bromination of the unsubstituted phenyl ring to afford 4-(4-bromoanilino)phenylglyoxal (90%). Under the same conditions, 1,2-diphenylethanone affords quantitatively diphenylethanedione **7a** in 24 h, while 1,3-diphenylpropane-1,3-dione gives diphenyltriketone hydrate **12a**.[56]

The following point related to the mechanism of this reaction is worthy of note. It is generally accepted that the Kornblum reaction occurs through the following pathway (without details of the decomposition step of the dimethylsulfoxonium intermediate **25**):[50–52]



25

However, comparison of the results of oxidation of aryl methyl ketones in the DMSO – HBr – H_2O system and oxidation of α-bromoacetophenone in dry DMSO made it possible to suggest a different mechanism for oxidation with aqueous DMSO.[56] It was assumed that in this case the role of DMSO is reduced to the oxidative generation of a small amount of bromine followed by bromination and debromination of ketones with subsequent hydrolysis to arylglyoxal hydrates. Whatever the actual mechanism of this reaction, the DMSO – HBr – H_2O system is the most convenient for the preparative oxidation of acyclic ketones to α-dicarbonyl compounds and of acyclic β-diketones to triketones, provided that the substrates subject to oxidation are insensitive to bromine. A method has been patented for the synthesis of benzil **7a** using a concentrated HBr – DMSO system.[57] Other examples of smooth oxidation of methylene groups in bisdeoxybenzoins **26**, **27** to bis-α-diketones (**28**, **29**) are also known.[58, 59]



26 → **28**

27 → **29**

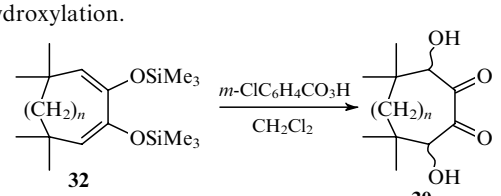
The latter reaction, which serves as one of the steps in the synthesis of an aromatic tris-α-diketone[59] (see Section IV), demonstrates the high regioselectivity of the DMSO – HBr oxidising system with respect to the methyl groups in the acetylenic diketone **27**, since the triple bond remains unaffected. It is difficult or impossible to reach such a selectivity with other oxidants, *e.g.*, SeO_2.

The methylene groups in 1,2-diphenylethanone and 1,3-diphenylpropane-1,3-dione are smoothly oxidised with a mixture of DMSO with concentrated H_2SO_4 in the presence of a catalytic amount of iodine.[60] However, the use of the same oxidative system for 1-phenylpropan-2-one and cyclohexanone gives very low yields of the diketones **7b** and **4a**. In this case, acetophenone gives a mixture of *Z*- and *E*-isomers of the enol form of 2-methylthio-1,4-diphenylbutane-1,4-dione, which are formed as products of phenylglyoxal transformation.[60]

On prolonged action, *N*-bromosuccinimide in dry DMSO oxidises 1,2-diarylethanones at room temperature to give the corresponding diarylethanediones and oxidises indan-1-one, indan-2-one and indane-1,2-dione to indane-1,2,3-trione (**9**). The reaction with 1,3-diphenylpropane-1,3-dione under the same conditions affords diphenyl triketone **12a**.[61, 62] It is assumed[62] that *N*-bromosuccinimide acts as a brominating agent to give the intermediate 3-bromoindan-1-one, which is then oxidised with DMSO according to the Kornblum reaction.

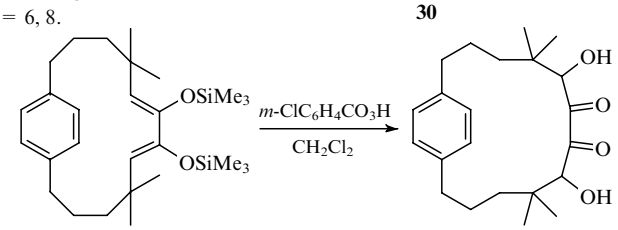
The methyl groups of aryl methyl ketones are oxidised on treatment with DMSO and benzoyl chloride at room temperature. However, instead of arylglyoxals, the reaction gives acetals of their fully hydrated forms with formaldehyde, *i.e.* 1-aryl-2,4,6,8-tetraoxabicyclo[3.3.0]octanes.[63]

The vast variety of methods and reagents for the synthesis of α-hydroxycarbonyl compounds by hydroxylation of stable enol forms, *e.g.*, of vinyl ethers/esters and thioethers/thioesters, enol silyl ethers and ketene silylacetals (for reviews, see Refs 5, 35, 64, 65) contrasts with the surprisingly small number of reagents known for their direct transformation to α-dicarbonyl derivatives. In fact, even the formation of α-dicarbonyl structures **30** and **31** in the oxidation of bissilyl ethers **32** and **33** with *m*-chloroperbenzoic acid (the Rubbotom method)[46, 66, 67] actually occurs due to hydroxylation.



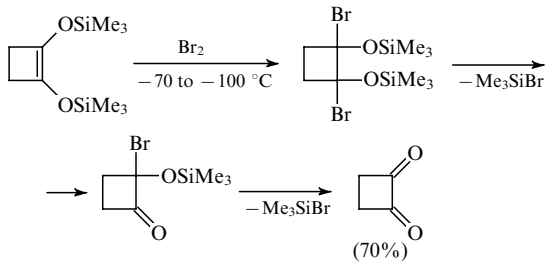
32 → **30**

n = 6, 8.

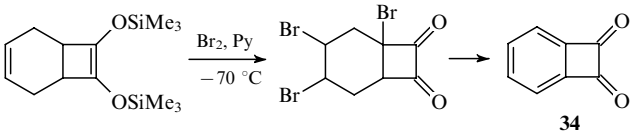


33 → **31**

It is known that 1,2-bis(trimethylsilyloxy)alkenes, which are stable under non-hydrolytic conditions, can be oxidised with bromine in chloroform or CCl_4 to the corresponding cyclic diketones. This reaction occurs most successfully if it results in cyclobutanedione or non-enolizing diketones.[68–71] In other cases, Me_3SiBr that is formed reacts with the enol forms of the resulting diketones, giving new silyl ethers of enols and, subsequently, various halogen-containing compounds.[70]



A similar approach afforded 3,3,7,7-tetramethylcycloheptane-1,2-dione[72, 73] and adamantylcyclobutanedione.[74] Likewise, the reaction of bromine with the bissilyl ether of bicyclo[4.2.0]octa-2,6-diene gives benzocyclobutanedione (**34**) through bromination and dehydrobromination.[73]



34

2. Oxidation of α-hydroxycarbonyl compounds

Transformations of α-hydroxycarbonyl compounds to α-dicarbonyl compounds are well studied. Undoubtedly, the largest number of reagents for this kind of transformations have been

approved using the oxidation of benzoin as a very convenient model. Even 150 years ago, Laurent[75] and Zinin[76] showed that benzoin can be oxidised to benzil **7a** on treatment with chlorine or nitric acid. However, these reactions, unlike those developed later, did not become preparative methods.

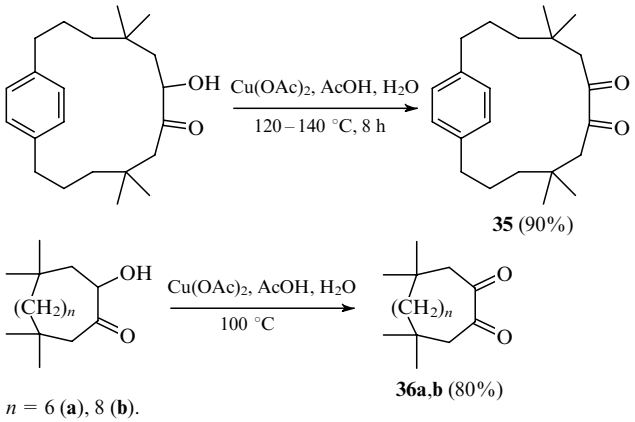
Treatment of a solution of benzoin in pyridine with air in the presence of copper(II) sulfate at 100 °C for 2 h oxidises it to diketone **7a** in 86% yield.[77] Compound **7a** is obtained in quantitative yield by refluxing a solution of benzoin in acetic acid in the presence of a catalytic amount of copper acetate and ammonium nitrate.[78] Similar results are obtained if a catalytic amount of cobalt,[78,79] iron or nickel salts[78] or complexes of Fe(II) with certain cysteine-containing peptides[80] are used. Complexes of Fe(II) with α,α′-xylenedithiolates catalyse the oxidation of benzoin to benzil **7a** in DMF at room temperature both by the atmospheric oxygen and *p*-benzoquinone; the latter oxidant was found to be more efficient in this reaction.[81] It was suggested[82] to prepare 4,4′-bis(carboxyphenyl)ethanedione ethers by oxidation of the appropriate benzoins with air in ethanol in the absence of catalysts at 60 °C for 13 h. 2-Hydroxy-1-phenyl-2-(2-quinolyl)ethanone (α-quinaldoin) is readily oxidised on passing air through its boiling solution in dioxane to give phenyl(2-quinolyl)ethanedione.[5]

The most commonly used oxidants are listed in Table 2 together with the relevant reaction conditions. These data make it possible to compare the reactivities of different reagents with respect to the oxidation of α-hydroxy ketones. Quinolinium fluorochromate, $Bi(MnO_4)_2$, $AgBrO_3$, $AlCl_3$, and *o*-iodylbenzoic acid can be regarded as the most efficient reagents.

In several studies,[87–92] benzoin and other alcohols were oxidised with the same reagents under similar conditions. It turned out that such alcohols as benzyl alcohol, diphenylmethanol, and 1-phenylethanol were comparable with each other and with benzoin with respect to the time required for their oxidation and the yields of the monoketones in the preparative experiments, *i.e.* the activity of these substrates is quite similar. However, oxidation of 4- and 4′-chloro-, bromo-, and methoxy-substituted benzoins with sodium or silver bromates in the presence of $AlCl_3$[90] or barium permanganate[88] is accompanied by an insignificant decrease in the yields of the corresponding diarylethanediones and an approximately twofold increase in the reaction time. The oxidation of 2-furoin with barium permanganate occurs much more slowly (4 h, yield 80%). These results of preparative experiments provide no more than a qualitative picture of the effect of the nature of α-hydroxy ketones and oxidants on the oxidation to 1,2-diketones. In order to reveal distinct regularities, one has to determine the rates of oxidation of different substrates under similar conditions. However, to our knowledge, there are no comparable kinetic experiments of this kind, although both the kinetics and the oxidation mechanism of α-hydroxy ketones have been studied rather thoroughly. For example, it follows from kinetic studies on the oxidation of benzoin with quinolinium dichromate to compound **7a** that the oxidation is 6 times slower than the substrate enolisation. Oxidation occurs through the initial coordination of the chromium atom with the carbonyl group of the substrate.[97]

Many other reagents are known that oxidise benzoin to the diketone **7a**. For example, anhydrous $Fe(NO_3)_3$, which is normally unstable, is rather stable if impregnated in acidic montmorillonite. It affords benzil **7a** in a higher yield (85%–95%) than ytterbium nitrate.[98] On the other hand, K_2FeO_4 immobilised on the same support gives the diketone **7a** in only 36% yield, since this reagent cleaves the C–C bond of benzoin, producing benzaldehyde.[99] It was reported,[100] without specifying the conditions and yields of the reaction products, that catalytic amounts of tris(2,4-dibromophenyl)aminium hexachloroantimonate oxidise benzoins to the corresponding diarylethanediones. Benzoin can be oxidised with titanium isopropoxide,[101] benzyltriethylammonium tribromide,[102] triphenylstibine dibromide (Ph_3SbBr_2),[103] Ph_3PBr_2,[104] and $PhMe_3N^+Br_3^- \cdot NBS$[105] to benzil **7a** in almost quantitative yield. Cobalt(III) acetate in acetic acid oxidises deoxybenzoins to benzoins and further to diphenylethanedione derivatives.[106]

Copper sulfate and acetate have long been widely used for the oxidation of various benzoin structures. For instance, stoichiometric amounts of $CuSO_4 \cdot 5H_2O$ oxidise 1,2-difuryl-2-hydroxyethanone (2-furoin) and 2-phenyl-1-(2-pyrrolyl)-2-hydroxyethanone in aqueous pyridine at 100 °C in 2 h to give difurylethanedione (furil)[107] and phenyl(2-pyrrolyl)ethanedione[108] in 63% and 95% yields, respectively. Probably, copper acetate has an even higher oxidising activity. It oxidises 3-hydroxy-1,4-diphenylbutan-2-one to 1,4-diphenylbutane-2,3-dione in almost quantitative yield on refluxing for 7 min in 70% AcOH[109] and 2-hydroxycyclodecanone (sebacoin), also in aqueous AcOH,[110] to cyclodecane-1,2-dione (sebacil) in 1 min. Copper acetate in AcOH was successfully used in the synthesis of cyclic diketones **35** and **36a**,**b**.[46,65]



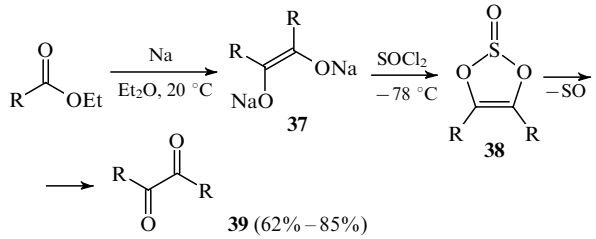
n = 6 (**a**), 8 (**b**).

Table 2. Reagents and reaction conditions for the oxidation of 2-hydroxy-1,2-diphenylethanone (benzoin) to diphenylethanedione (benzil).

Reagent	Solvent	Temperature /°C	Time /h	Yield (%)	Ref.
O_2, $CuSO_4$	C_5H_5N	100	2.0	86	77
$Cu(OAc)_2$, NH_4NO_3	AcOH	reflux	1.5	90–100	78
PhSe(O)Se(O)Ph	THF	"	3.0	92	83
Quinolinium fluorochromate	CH_2Cl_2	20	2.0	98	84
Trichloromelamine	CH_2Cl_2	20	125.0	98	85
DMSO, HBr, H_2O	–	55	24.0	95	56
Bi_2O_3	AcOH, $EtO(CH_2)_2OH$	104	1.0	95	86
$Zn(BiO_3)_2$	Xylene	reflux	0.7	97	88
$Ba(MnO_4)_2$	MeCN	"	0.25	96	88
$BaFeO_4 \cdot H_2O$	MeCN	"	6.0	95	89
$AgBrO_3$, $AlCl_3$	MeCN	"	0.5	97	90
$NaBrO_3$, $AlCl_3$	MeCN	"	0.75	97	90
Chromium bipyridylperoxide	MeCN	"	3.0	90	91
$Bu_4N^+IO_4^-$	$CHCl_3$	"	2.5	85	92
$FeCl_3 \cdot 6H_2O$	AcOH, H_2O	"	0.8	90–95	93
o-Iodylbenzoic acid	THF, DMSO	20	6.0	>90	94
	THF, DMSO	reflux	0.2	92	94
$NaBrO_3$, NaOH	H_2O	100	5–6	84–95[a]	95
N-Chlorosuccinimide, Me_2Se, base	MeC_6H_5	0	2.0	93	96

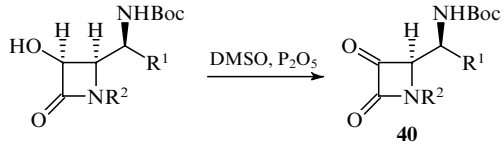
[a] Benzylic acid is formed as a product of benzylic rearrangement of diphenylethanedione.

Sodium salts of enolic forms of hydroxy ketones that are formed in the acyloin condensation of esters (enedioxides **37**) are oxidised with thionyl chloride *in situ* at low temperature to symmetric α-diketones **39** *via* intermediate sulfites **38**.[111]



R = Me, Et, Bu^t, cyclo-C_3H_5, adamantyl, Ph.

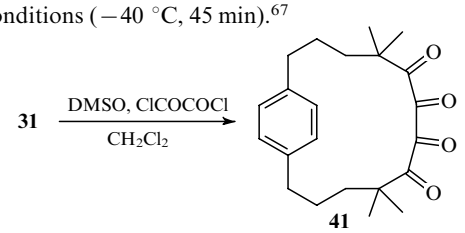
Reagents based on DMSO were successfully used for the oxidation of α-hydroxycarbonyl compounds. An aqueous solution of HBr in DMSO readily oxidises benzoin to benzil **7a** in high yield.[56] It is interesting that the same reagent also oxidises *o*-methylbenzoin to compound **7a**.[112] The reactivity of deoxybenzoin and its α-substituted derivatives in the oxidation to benzil **7a** was studied.[113] The series of reactivities, benzoin > 2-bromo-1,2-diphenylethanone > 1,2-diphenylethanone, is a good confirmation of the suggested scheme of the oxidation of ketones with HBr in DMSO.[56] A combination of DMSO with P_2O_5 was used in the synthesis of azetidine-2,3-diones **40**, which were then oxidised to α-amino acid *N*-carboxyanhydrides according to Baeyer–Villiger.[114]



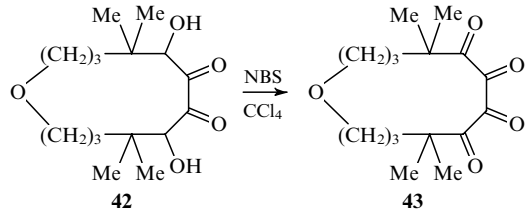
R^1 = Me, Bu, Pr^i, Bu^t; R^2 = Ph, Ar, CH_2Ph.

Such reagents as *N*-chlorosuccinimide with Me_2S and Et_3N, pyridinium chromate, pyridinium chlorochromate, the Jones reagent (CrO_3, H_2SO_4, H_2O), trifluoroacetic anhydride in DMSO, tetra-n-propylammonium perruthenate, RuO_4, and $NaIO_4$ proved to be unsuitable for this purpose. The Corey reagent (Me_2SBr_2, Et_3N) was also inefficient,[114] although it has been used successfully in the synthesis of various azetidine-2,3-diones from α-hydroxy-β-lactams.[115] Treatment of hydroxy-β-lactams with sodium hypochlorite also leads to their oxidation according to Baeyer–Villiger.[116]

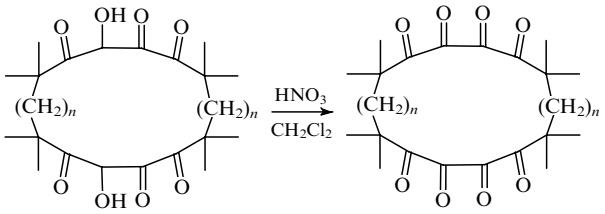
The Swern reagent (DMSO–ClCOCOCl) oxidises dihydroxy[12]paracyclophanedione **31** to the tetraketone **41** under mild conditions (−40 °C, 45 min).[67]



Oxidation of cyclotridecanedione **42** to the tetraketone **43** has been performed successfully by the same authors[68] with such a well-known reagent for the oxidation of alcohols as *N*-bromosuccinimide in CCl_4.



However, bistetraketones **44** were obtained using nitric acid.[46]



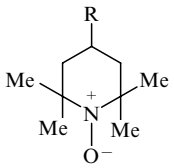
n = 4, 6.

As a rule, aromatic derivatives of α-hydroxy ketones are readily oxidised with DMSO–Ac_2O, but the yields of α-diketones from aliphatic derivatives are low.[117]

α-Oxocarboxylic acids are important biologically active compounds and are of considerable interest for organic synthesis. It is not surprising that the development of methods for their synthesis draws much attention. Many reagents for the oxidation of alkyl α-hydroxycarboxylates to the corresponding oxo derivatives are known. These include $Pb(OAc)_4$, Ph_3SbBr_2, tertiaty amine oxides, sodium peroxodisulfate, 2-fluoro-1-methylpyridinium tosylate, DMSO with hexamethylenetetramine, PhSOCl, a complex of dimethyl selenide with *N*-chlorosuccinimide, sodium hypochlorite, diacetoxy-λ^3-iodanylbenzene, Co(II) compounds, bis(tetrabutylammonium) dichromate, $KMnO_4$–$CuSO_4$, ammonium vanadate, manganese pyrophosphate, immobilised chromic acid, chromyl chloride, vanadium(V) derivatives, periodinane (see *e.g.* Ref 118 and the references cited therein). A review published recently[119] deals with the use of tetrapropylammonium perruthenate ($Pr_4N^+RuO_4^-$) as a mild catalytic reagent, particularly for the synthesis of α-keto acids. It was suggested to obtain esters of β,γ-unsaturated α-oxocarboxylic acids by the oxidation of the corresponding α-hydroxy derivatives according to the Swern procedure (DMSO, ClCOCOCl, CH_2Cl_2, −50 °C).[120]

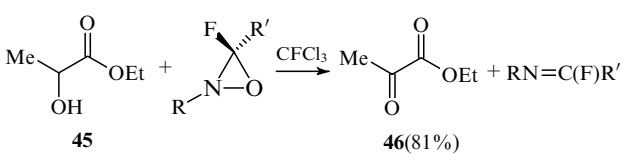
In view of the abundance of studies in this field, the detailed discussion of oxidative methods for the synthesis of α-oxocarboxylic acids is beyond the scope of our review. Therefore, we shall discuss here only relatively new and, in our opinion, versatile reagents applicable for the synthesis of other α-dicarbonyl compounds as well.

For example, the importance of tetramethyl-1-piperidinyloxyls (TEMPO) has increased in recent years.

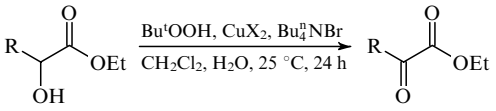


In particular, it was shown that various linear and cyclic primary and secondary alcohols are oxidised in high yields to high-purity aldehydes or ketones under mild conditions on treatment with 4-acetylamino-TEMPO (R = AcNH) in dichloromethane in the presence of *p*-TsOH.[121] The reagent is readily generated in the reaction mixture. Phenylglyoxylic acid is formed under these conditions in 91% yield from phenylglycolic acid.[121]

Oxaziridines, particularly various 2-sulfonyloxaziridines, are powerful oxidants due to the high electrophilicity of the ring oxygen atom. They are used most widely for the α-hydroxylation of carbonyl compounds.[64, 122] It was found that perfluoro-*cis*-2,3-dialkyloxaziridines also oxidise secondary alcohols to ketones at room temperature. In particular, they oxidise ethyl lactate (**45**) to ethyl pyruvate (**46**).[123]



Finally, let us note a recently observed example of the oxidation of alkyl hydroxycarboxylates to α-oxo esters **46** and **47** on treatment with *tert*-butyl hydroperoxide in the presence of copper(I) and (II) salts and even metallic copper under phase-transfer catalysis conditions.[124]



46, **47** (60% – 96%)

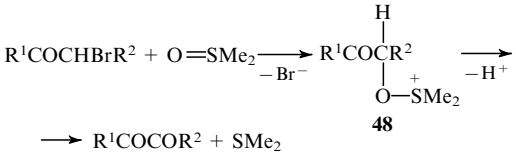
R = Me (**46**), Ph (**47**).

Dibismuth trioxide oxidises 12-hydroxy-11-ketosteroids to 11,12-diketosteroids in up to 70% yields.[125] This reagent can also be used for the synthesis of vicinal vinyl diketones from the corresponding vinyl α-hydroxy ketones.[126] Iodine combined with AcOH and MeOH oxidises D-(−)-ascorbic acid to D-(−)-dehydroascorbic acid in low yield.[127] Aliphatic α-hydroxy ketones are transformed to the corresponding α-diketones on treatment with *N*-bromosuccinimide in dry CCl_4 or aqueous dioxane.[128] Basic copper(II) carbonate [$CuCO_3 \cdot Cu(OH)_2$] acts in a similar way.[129] Acyloins of dioxepane structure were successfully oxidised to the corresponding α-diketones upon boiling with SeO_2 in a mixture of toluene and acetic acid.[130] The action of a solution of ferric chloride in HCl on 2-hydroxycyclohexanone results in a high yield of cyclohexanedione **4a**.[131]

3. Oxidation of α-halocarbonyl compounds

Oxidation of α-halocarbonyl compounds is one of the most convenient and popular methods for the synthesis of diketones.[132]

A very simple and convenient method is the oxidation of halo ketones according to Kornblum with DMSO in the presence of bases.[49 – 52, 133] In this case, α-bromocarbonyl compounds are oxidised more readily than alkyl or even benzyl bromides. The oxidation of α-bromo ketones with DMSO is commonly carried out at room temperature. This is explained by easier elimination of the proton from the intermediate dimethylsulfoxonium salt **48** due to the adjacent carbonyl group (see also Section II.1).[134, 135]



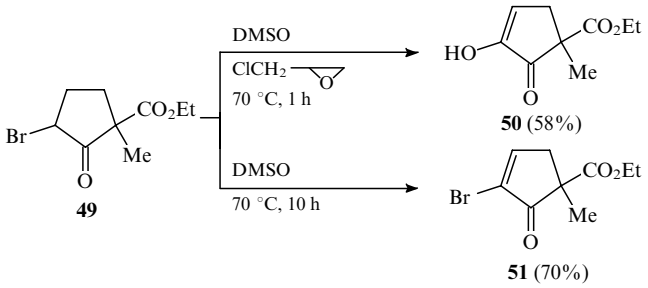
48

The method is particularly convenient for the oxidation of acyclic α-bromocarbonyl compounds. For example, phenylglyoxal (yield 71%) and diketone **7a** (yield 95%) were obtained by the oxidation of 2-bromo-1-phenylethanone and diphenylbromoethanone in dry DMSO at 25 and 45 °C, respectively.[49] The addition of sodium carbonate accelerates the process. However, the oxidation of *e.g.* ethyl bromoacetate with DMSO was also carried out without a base, using 2-phenoxymethyloxirane to bind the HBr evolved (the yield of ethyl glyoxylate was 70%).[136] However, it was noted[137] that *tert*-butyl bromoacetate could not be oxidised with DMSO. It was also shown that the addition of potassium iodide to a mixture of DMSO and Na_2CO_3 accelerates the oxidation of bromo ketones.[138]

In the first studies by Kornblum and co-workers and in many subsequent studies, dry DMSO was used. Thorough dehydration of such a hygroscopic compound as DMSO is a difficult procedure. It was shown[56] that it is easier to oxidise aryl methyl ketones, α-hydroxy- and α-bromoacetophenone with aqueous HBr in DMSO. In this case, the oxidation mechanism differs considerably from that of the classical Kornblum reaction. The role of DMSO in an aqueous medium is reduced to the generation of Br_2 from HBr, while the dimethylsulfoxonium ion **48**, which is the key intermediate in the Kornblum reaction, is not formed in aqueous HBr (see Section II.1).

3-Bromocamphor is oxidised to camphoroquinone upon passing air through a solution of the substrate and NaI in DMSO.[139] However, despite the apparent similarity with the Kornblum reaction, its mechanism is different: DMSO serves as a solvent, while the process goes *via* free-radical intermediates.[139]

Complications are observed in the oxidation of cyclic α-bromo ketones with DMSO. In this case, oxidation often competes with elimination of the DMSO molecule from the intermediate **48**. Instead of diketones, or along with them, this process produces α,β-unsaturated ketones and α-hydroxy ketones. This reaction pathway is particularly typical of steroid derivatives.[140] Heating of 2-bromocyclohexanone and 2-bromocyclopentanone in DMSO at 100 °C gives 3-bromocyclohexane-1,2-dione and 3-bromocyclopentane-1,2-dione rather than the corresponding diketones.[141, 142] Under these conditions, the bromo ketone **49** gives the diketone **50**, which exists in the enol form, only in the presence of epichlorohydrin to bind the HBr that evolves. The reaction in the absence of epichlorohydrin results in the compound **51** as the main product.[142, 143]

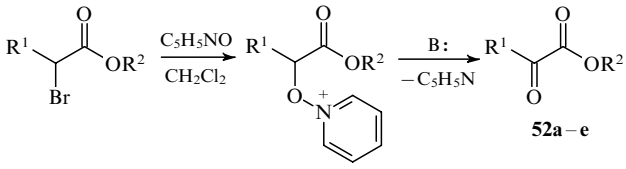


It was suggested[142, 143] that this effect is due to the oxidation of the hydrogen bromide, which is formed in the primary oxidation act, with dimethyl sulfoxide to bromine, which brominates the intermediate diketone.

Nitrates formed in the reaction of α-bromo ketones and α-bromo acids with $AgNO_3$ undergo smooth transformations on treatment with a catalytic amount of sodium acetate in DMSO at room temperature to give high yields of α-dicarbonyl compounds or α-oxo acids.[144 – 146]

The Kröhnke method (treatment of α-bromo ketones with pyridine and 4-nitrosodimethylaniline followed by hydrolysis) is of very limited use in the synthesis of 1,2-dicarbonyl compounds.[132]

The oxidation of α-bromo acids and their esters with pyridine *N*-oxide is an efficient method for the synthesis of α-oxo acids and their esters.[147]



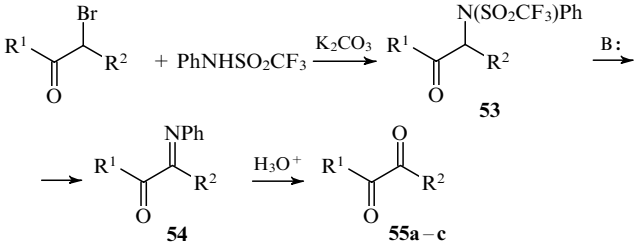
52a – e

Compound **52**	R^1	R^2	Yield (%)
a	H	H	37
b	H	Bu^t	97
c	H	CH_2Ph	89
d	Ph	H	70
e	Ph	Me	95

The addition of silver nitrate facilitates the formation of alkoxypyridinium salts. Their subsequent decomposition is carried out by heating in methanol or acetonitrile in the presence of Et_3N or in aqueous NaOH at room temperature.[147] A stronger nucleophile, 4-dimethylaminopyridine *N*-oxide, was also used in an oxidative transformation of this kind. However, in this case the intermediate salt was decomposed with the use of 1,8-diazabicyclo[5.4.0]undec-7-ene.[148]

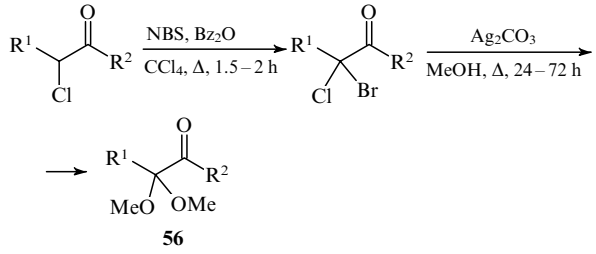
Similar oxidative properties are manifested by *N*,*N*-diethylhydroxylamine, which oxidises, readily and in high yields, various aromatic bromomethyl ketones to arylglyoxals in boiling methanol in the absence of bases.[149] The method is attractive due to its simplicity and serves as a rare example in which α-oxo aldehydes are formed more easily than aromatic α-diketones. The method is not applicable to 2-bromo-1,2-diphenylethanone, 2-chlorocyclohexanone and 2-bromo-1-phenylpropanone.

α-Bromocarbonyl compounds (as well as other activated alkyl halides) react with *N*-phenyltrifluoromethanesulfonamides under mild conditions. The resulting products **53** are readily decomposed with bases to anils **54**, which are, in turn, hydrolysed to α-dicarbonyl compounds **55**.[150]



$R^1 = C_8H_{17}$, R^2 = Me (79%); R^1 = OEt: R^2 = Pr (67%), C_6H_{13} (62%).

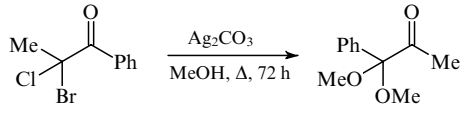
Monoketals of aliphatic diketones **56** were obtained in 43%–87% yields in two stages according to the following scheme:[151]



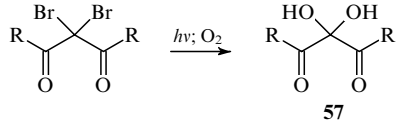
$R^1 = R^2$ = Me; R^1 = Et, R^2 = Me; R^1 = Me, R^2 = Et.

The method has the advantage that it provides the possibility of direct regiospecific synthesis of dimethyl ketals with involvement of only one carbonyl group of α-diketones that are difficult to obtain directly from the corresponding dicarbonyl compounds. The method is a good supplement to the synthesis of α-oxo acetals by the oxidation of methyl ketones with diphenyl diselenide as discussed in Section II.1.[47]

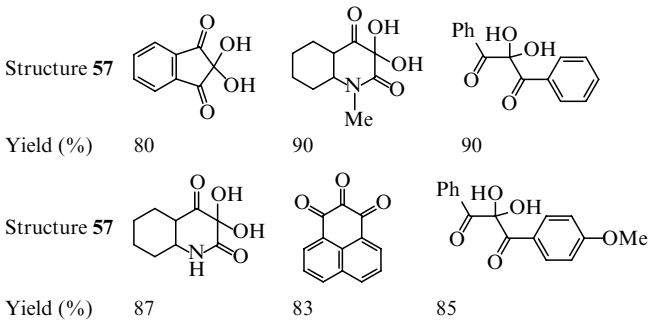
It is interesting that the formation of an acetal from an aromatic bromo chloro ketone, namely, 2-bromo-2-chloro-1-phenylpropan-2-one, is accompanied by a rearrangement[151] that gives 1,1-dimethoxy-1-phenylpropan-2-one.



Cyclic and acyclic geminal dibromo diketones are transformed under conditions of photochemical oxidation at room temperature to hydrates of the corresponding vicinal triketones **57** in good yields.[152]



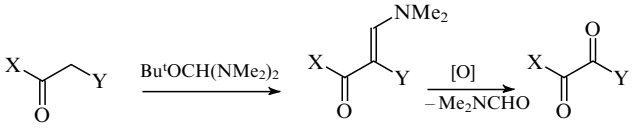
57



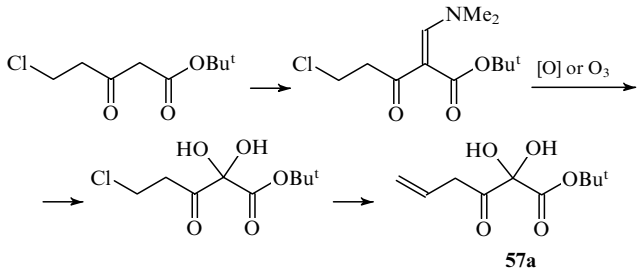
4. Oxidation of other classes of compounds with the CX–C=O function and oxidative rearrangements

In certain cases, carbonyl compounds containing nitrogen, sulfur or phosphorus in the α-position are rather accessible and can serve as good precursors in the synthesis of 1,2-dicarbonyl compounds.

A general method for the insertion of an α-oxo group in ketones, esters, amides and lactams has been elaborated. This method is based on photooxidation of α-oxo enamines obtained from the corresponding carbonyl compounds according to the general scheme:

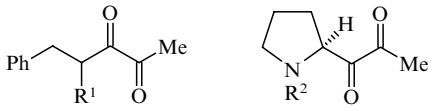


Dicarbonyl compounds obtained by this method are presented in Table 3. The photooxidation is carried out at −78 °C with subsequent heating of the reaction mixture to 25 °C. The method shows high selectivity. Using the same approach, the allylic vicinal tricarbonyl compound hydrate **57a**, which is a versatile di- and trielectrophilic synthon, was synthesised.[154]



57a

The same method was used to obtain polyfunctional α-diketones **58** and **59** from carboxylic acids.[155]



58 **59**

R^1 = H, COOH, CH_2COOBu^t (**58**); R^2 = H, $COOBu^t$ (**59**).

It was shown that treatment of α-hydroxyimino ketones with N_2O_4 in THF or acetonitrile at −20 °C gives diketones **7a**,**e** and triketone **12a** in over 60% yields.[156] Cyclohexane-1,2,3-trione hydrate was synthesised in an analogous way.[156] The reaction is assumed to occur *via* the intermediates **60**, since isotope-labelling experiments have shown[157] that the oxidation of oximes to ketones with NO^+ occurs *via* oxaziridine intermediates.

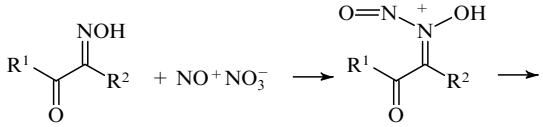
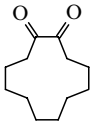
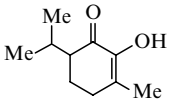
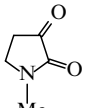
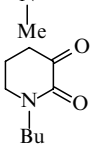
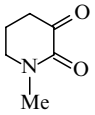
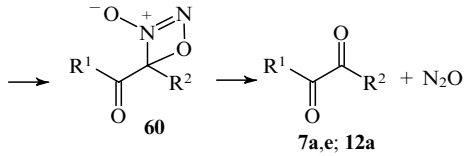


Table 3. Dicarbonyl compounds obtained by photooxidation of α-oxo enamines.[153]

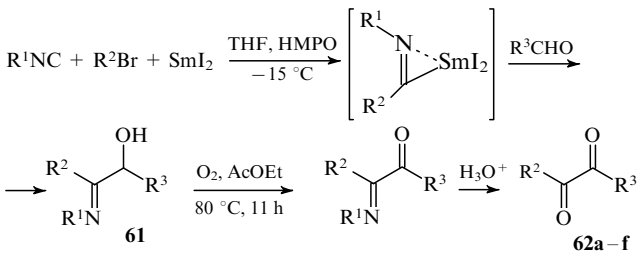
Compound	Yield (%)	Compound	Yield (%)
PhCOCOMe	68	PhCOCOPh	89
PrCOCOEt	74		82
	81	Cholestanedione (**5**)	87
PhCOCOOEt	91	4-$MeOC_6H_4COCOOEt$	92
EtCOCOOEt	81		74
$Me(CH_2)_3COCOOEt$	75		58
	78		



60 **7a**,**e**; **12a**

R^1 = Ph: R^2 = Ph (**7a**), CH_2Ph (**7e**), COPh (**12a**).

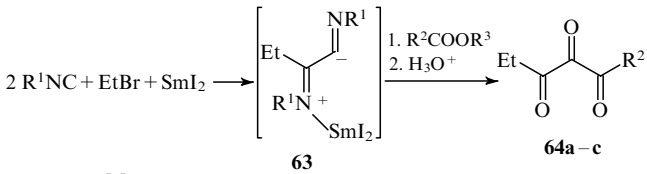
Autooxidation of α-hydroxy imines **61** to diketones is rather a general method. Compounds **61** are obtained by the SmI_2-induced coupling of alkyl halides with xylyl isocyanide and aldehydes.[158] The yields of diketones **62a**–**f** are higher than 90%.



61 **62a**–**f**

R^1 =  ; R^2 = CH_2CH_2Ph: R^3 = Et (**a**), Pr^i (**b**);
R^2 = Pr^i, R^3 = CH_2CH_2Ph (**c**); R^2 = Et, R^3 = Ph (**d**);
R^2 = $(CH_2)_4OBu$, R^3 = 2-furyl (**e**);
R^2 = cyclo-C_6H_{11}, R^3 = 2-pyridyl (**f**).

Organosamarium intermediates **63** obtained similarly are so nucleophilic that they readily react with esters and carbonates, thus providing a general way to vicinal triketones **64a**–**c**.[159]

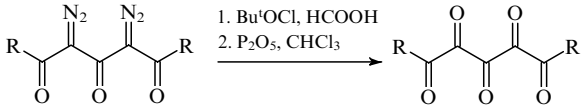


63 **64a**–**c**

R^1 =  : R^2 = Me (**a**), Et (**b**), OMe (**c**).

Aroylation of α-chloro imines in the presence of 1,3-dimethylimidazolinium iodide is rather a general method for the synthesis of aromatic 1,2-diketones. The oxo imines that are formed readily undergo hydrolysis to give the diketones ArCOCOPh (Ar = Ph, 3-ClC_6H_4, 4-ClC_6H_4, 4-$MeOC_6H_4$, 4-$NO_2C_6H_4$) in excellent yields.[160] The method was found to be applicable to the synthesis of heterocyclic diketones ArCOCOR (R = thienyl).[160]

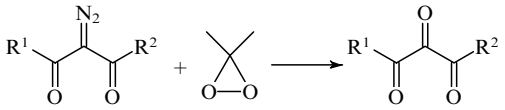
Examples of the oxidation of α-diazo ketones and diazo diketones are known.[161,162] For instance, treatment of α-diazo ketones with triphenylphosphine gave phosphoranes, which were converted to α-oxo aldehydes with nitric acid. Phenylglyoxal was obtained by this method in 70% yield with respect to the starting benzoyl chloride.[161] At present, there are reliable methods for direct oxidation of diazo ketones. For example, *tert*-butyl hypochlorite was used in one stage of the synthesis of pentaketones **65a**,**b**.[162]



65a,b

R = Bu^t (**a**), Ph (**b**).

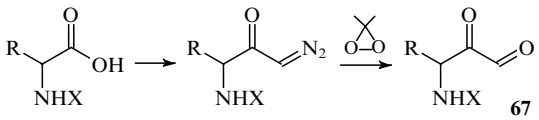
Vicinal triketones **66** (in the form of mohohydrates) were obtained in nearly quantitative yields by prolonged oxidation (10–30 h) of diazo diketones with dimethyldioxiranes (DMO, 'oxone') in acetone at room temperature.[163]



66

R^1 = R^2 = Me, Ph, OEt; R^1 = Me, R^2 = Ph, OEt; R^1 = Ph, R^2 = OEt; R^1, R^2 = $(CH_2)_3$, $CH_2CMe_2CH_2$, *o*-phenylene.

Oxidation of diazo ketones, that are obtained from substituted α-amino acids and dipeptides, with DMSO provides a general route for the synthesis of homochiral amino oxo aldehydes **67**, which exist as hydrates.[164]

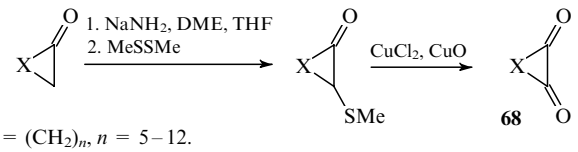


67

It was shown that phenylglycine undergoes oxidation with atmospheric oxygen in ethanol in the presence of an equimolar amount of $VO(OEt)Cl_2$ to give ethyl phenylglyoxylate.[165] The preparative value of this method is diminished by the side reaction of decarboxylation leading to the formation of a considerable amount of ethyl benzoate.

It is well known that the oxidation of bishydrazones of 1,2-diketones with mercury(II) oxide is one of general methods to synthesise disubstituted alkynes. In the case of diphenylethanedione (benzil) monohydrazone, oxidation with Ag_2O results in benzil **7a**.[166] The use of some other oxidants mostly gives α-diazo ketones or ketazines, whereas diketones are only formed as by-products (see, *e.g.*, Ref. 167 and the references cited therein).

It was shown that cyclic ketones can be transformed to the corresponding α-diketones **68** by oxidation of their methylthio derivatives under mild conditions (acetone, 25–35 °C).[168] The overall yield of diketones over two stages is 42%–76%. Methylglyoxal was obtained in a similar way.[169]

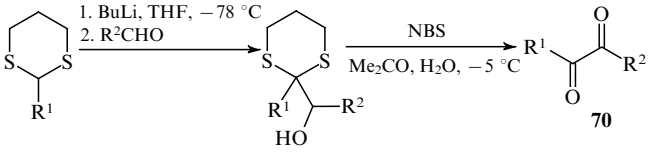


68

X = $(CH_2)_n$, *n* = 5–12.

(Biphenyl)phenylethanedione was isolated in ~90% yield after heating of ketone sulfur-containing derivatives 4-$PhC_6H_4COCH(X)Ph$ (X = SMe, $S^+Me_2Br^-$) with aqueous HBr in DMSO at 55 °C.[56]

It is known that derivatives of dithiane **69**, which are readily formed from aldehydes and 1,3-dithianyllithium, give α-hydroxy ketones in the presence of mercury(II) salts.[170] In another study,[171] 1,3-dithiane was used as an acylic synthon, but the intermediate product **69** was then oxidised with an excess of *N*-bromosuccinimide to give a series of α-diketones **70**, including fluorine-containing ones, in 54% – 87% yields.



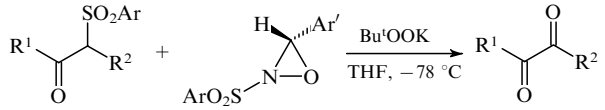
69 **70**

R^1 = Ph, R^2 = 2-FC_6H_4, 3-FC_6H_4, 4-FC_6H_4;
R^1 = 2-FC_6H_4, R^2 = 3-FC_6H_4, 4-FC_6H_4.

The oxidation of α-hydroxyalkyl-1,3-dithianes with $NaNO_2$ in trifluoroacetic acid to ketones was used[172] for the synthesis of certain alkaloid analogues containing an α-diketone fragment.

Iodine is yet another reagent for desulfurisation of α-oxo thioacetals. For instance, azetidine-2,3-diones were synthesised by refluxing diethyl dithioacetals of 2-oxo β-lactams with iodine in aqueous acetonitrile for 35 – 45 min.[114]

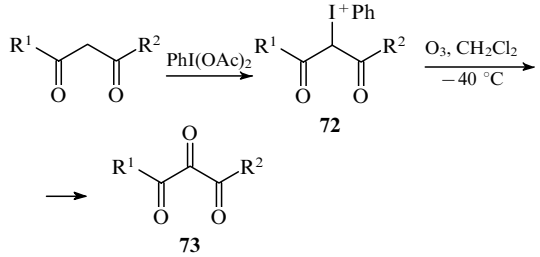
Very mild oxidative desulfonylation of α-sulfonyl ketones is carried out with oxaziridine **71**.[173]



71

The method is unique due to its selectivity, as it makes it possible to obtain a wide range of complex cyclic and acyclic α-diketones containing such reactive functional groups as the azide, allenyl, acetal, furyl and other groups. Unfortunately, the more readily accessible (+)- and (−)-(camphorsulfonyl)oxaziridines turned out to be unsuitable for this reaction.[173]

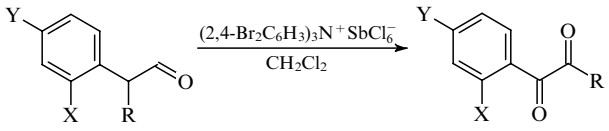
Various phosphorus and iodine ylides readily formed from β-diketones can serve as convenient precursors of vicinal tricarbonyl compounds.[164, 174, 175] For example, oxidation of phosphorus ylides with singlet oxygen or ozone was used in the synthesis of allylic tricarbonyl compounds **57** and dioxo diester $Bu^tOCOCOCOCH_2CH_2CO_2Et$.[164, 175] Potassium permanganate oxidises β-oxo(triphenylphosphoranylidenes) in a two-phase system to give substituted benzils or 1-arylpropane-1,2-diones in high yields.[176] Ozonolysis of α,α′-dioxoalkyl phenyliodonium **72** at low temperature made it possible to synthesise more than 20 cyclic and acyclic triketones **73** containing various fragments (alkyl, aryl, acetal, carbamido and other groups).[174]



72 **73**

The important advantage of this method over the majority of others is that compounds **73** are formed and isolated on a preparative scale in the ketone rather than hydrate form.[174]

A rearrangement of diarylacetaldehydes that can be used for the synthesis of substituted benzils occurs at room temperature in the presence of tris(2,4-dibromophenyl)aminium hexachloroantimonate as the oxidant.[99]

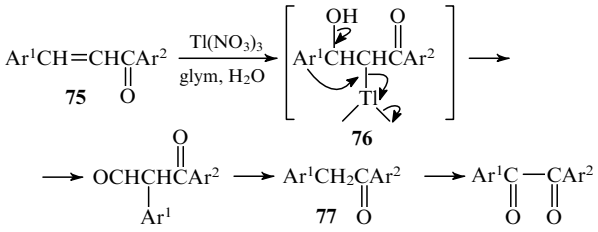


74

X = H: Y = Me, R = 4-MeC_6H_4;
Y = OMe, R = 4-$MeOC_6H_4$;
X = H, Y = Cl, R = 4-ClC_6H_4; X = Cl, Y = Me, R = 4-ClC_6H_4.

However, diphenylacetaldehyde and D,L-2-phenylpropionaldehyde do not enter into this reaction.[99]

Oxidation of chalcones with thallium(III) nitrate[177] or PhIO[178] also results in benzils. For example, treatment of chalcones **75** with $Tl(NO_3)_3$ in aqueous solutions of glym in the presence of acids is a convenient way to synthesise benzils. The reaction scheme involves hydroxythallation of the double carbon – carbon bond, oxidative migration of an Ar group in the intermediate **76**, retro-Claisen condensation to give benzoins **77** and subsequent oxidation to diketones.



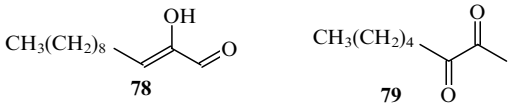
75 **76** **77**

III. Oxidation of 1,2-diols, epoxides and other vicinally substituted compounds

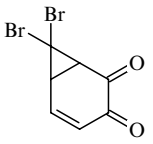
The oxidation of glycols to α-dicarbonyl compounds can serve as a versatile method for the synthesis of the latter. However, these methods have been developed rather little, except for the industrial synthesis of glyoxal by gas-phase oxidation of ethylene glycol on copper or silver contacts. Various reactions leading to *o*-quinones are also known; these will not be considered in the present review. Much more commonly, syntheses of carbonyl compounds or carboxylic acids utilise the oxidative cleavage of the carbon – carbon bond in vicinal diols. The classic reagents of this type include lead tetraacetate, periodic acid and its salts (of which sodium periodate is particularly popular) (see, *e.g.*, the reviews[179, 180]). In addition, cleavage of glycols occurs on treatment with $KMnO_4$, MnO_2, $NaBO_3$, $NaBiO_3$ and organobismuth salts (Ph_3BiCO_3), Ce(IV) and Co(II) salts, hypochlorites, pyridinium chlorochromate, I_2 with AgOAc or iodine triacetate (ICl_3, AgOAc), *N*-iodosuccinimide in THF, $VO(acac)_2$, H_2O_2 in the presence of metal salts, *tert*-butyl peroxide with $Al(OBut)_3$, upon anodic oxidation, *etc.*[180 – 182] Considerable interest of researchers is attracted to the selective monooxidation of 1,2-diols aimed at the synthesis of chiral α-hydroxy ketones.

Probably, the most general reagents used for the oxidation of glycols to dicarbonyl compounds include DMSO, the H_2O_2 – peroxytungstate system, *o*-iodylbenzoic acid and TEMPO-based reagents.

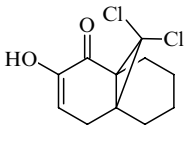
Dry DMSO in the presence of $(CF_3CO)_2O$ and triethylamine oxidises acyclic and cyclic 1,2-diols to 1,2-diones at −60 °C.[183] Benzil **7a** and 1,2-dicarbonyl compounds **78** – **81** (some of these, in the enol form) were obtained by this method in 54% – 98% yields with conservation of the carbon skeleton of the original diols.



78 **79**

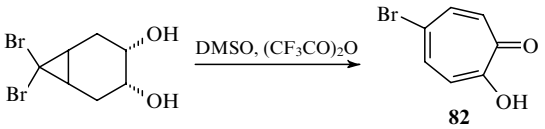


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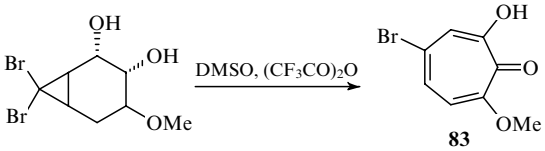


81

Treatment of diols containing the bicyclo[4.1.0]heptane skeleton with DMSO in trifluoroacetic acid results in tropolones **82** and **83**. It is assumed that the reaction occurs through ring expansion of the originally formed bicyclic diketones.

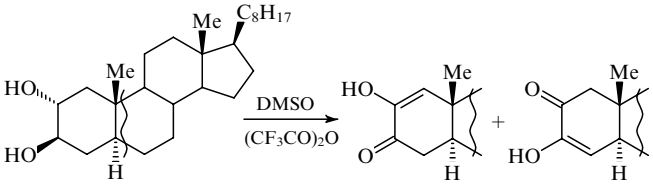


82



83

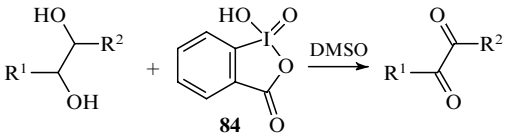
The oxidation of 5α-cholestane-2α,3β-diol affords a mixture of 2-hydroxy-5α-cholest-1-en-3-one and 3-hydroxy-5α-cholest-3-en-2-one in 84% overall yield.[183] The use of the Swern reagent in this reaction gives poorer results.[183]



DMSO oxidises cyclohexane-1,2-diol and a number of acyclic vicinal diols to the corresponding 1,2-diketones at room temperature in the presence of dicyclohexylcarbodiimide in 60% – 75% yields.[184]

Diketone **7a** and its 4,4′-dibromo derivative are obtained smoothly and in high yields by oxidation of the corresponding 1,2-diarylethane-1,2-diols with DMSO in aqueous HBr at 110 – 115 °C.[59,112]

It was found that *o*-iodylbenzoic acid **84** is a very mild oxidant for alcohols in DMSO at room temperature. It can also oxidise glycols without cleavage of the C – C bond giving the corresponding 1,2-diketones at room temperature in almost quantitative yields.[185]



84

R^1, R^2 = Me, Ph, $(CH_2)_4$.

A method for the oxidation of primary and secondary alcohols and 1,2-diols with the reagent **84** has been patented.[186]

Hydrogen peroxide usually cleaves glycols. However, it has recently been shown that acyclic vicinal diols are oxidised by H_2O_2 in a two-phase system in the presence of a catalytic amount of the $[\pi\text{-}C_5H_5N(CH_2)_{15}Me]_3\{PO_4[W(O)(O_2)_2]_4\}$ complex to give diketones in 70% – 93% yields.[187] The reaction occurs in a stepwise manner *via* intermediate α-hydroxy ketones. The results of the oxidation of cyclic diols are noticeably poorer: cyclooctane-1,2-dione was obtained in yields as low as 48% – 58%, while cyclohexane-1,2-diol gives adipic acid rather than the diketone **4a**.[187]

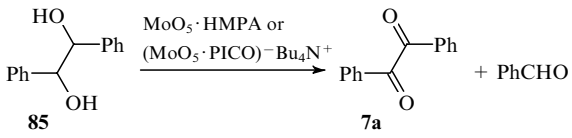
It is well known that such efficient oxidants as TEMPO transform vicinal diols to α-hydroxycarbonyl compounds (see, *e.g.*, Refs 188 and 189) and oxidise 1,2-diphenylethane-1,2-diol **85** to benzil **7a**.[190] It was shown that the readily accessible 4-acetamido-TEMPO in combination with toluene-*p*-sulfonic acid in chloroform or CH_2Cl_2 can serve as a general reagent for the mild oxidation of linear and cyclic vicinal diols to α-diones.[191]

At present, the majority of other reagents for the oxidation of glycols are used less commonly. For example, it was shown that *cis*-cyclododecane-1,2-diol is oxidised to cyclododecane-1,2-dione on treatment with tris(triphenylphosphine)ruthenium dichloride $[(Ph_3P)_3RuCl_2]$ in 53% yield.[192] Later, an almost identical result was obtained using *tert*-butyl hydroperoxide in benzene in the presence of a phase-transfer catalyst, namely, $PhCH_2N^+Me_3\ ^-OMoBr_4$.[193] Cyclohexane-1,2-diol undergoes oxidation to cyclohexane-1,2-dione **4a** in 51% yield at room temperature on treatment with a ruthenium complex $(LPh_4)(RuO_2Cl_3)$, where L = P or As.[194]

It was shown that $KMnO_4$ in the presence of nonionic tris[2-(2-methoxyethoxy)ethyl]amine, unlike other phase-transfer catalysts, oxidises phenylethane-1,2-diol and the diol **85** to phenylglyoxal and diketone **7a** in high yields.[195] Hydrogen peroxide applied onto the TS-1 zeolite converts one or both of the hydroxy groups in 1,2-diols to carbonyls, while cleavage of the C – C bond occurs only if an excess of the reagent is used.[196] Solvents affect strongly the reaction selectivity. For example, butane-2,3-diol is converted into 3-hydroxybutan-2-one in methanol and to butane-2,3-dione in acetone.

Unlike other periodates, tetrabutylammonium periodate in the presence of $AlCl_3$ in boiling chloroform oxidises the diol **85** to give mostly the diketone **7a** (yield 70%), and glycol cleavage occurs to a small extent (20% of benzaldehyde).[87] PhSe(O)Se(O)Ph is another reagent that enables the selective oxidation of the diol **85** to benzil **7a** (refluxing in THF for 3 h, yield 77%).[83] Quantitative yield of the compound **7a** in the oxidation of the diol **85** under very mild conditions is also provided by the system *N*-chlorosuccinimide – Me_2Se.[96] The catalytic system $RuO_4^- - BrO_3^-$ cleaves the diol **85** to benzoic acid, whereas *trans*-$RuO_3(OH)_2^{2-} - S_2O_8^-$ affords benzil **7a** in 65% yield.[197]

The mechanism of oxidation of *meso*- and *d,l*-diol **85** with peroxomolybdenum complexes, *viz.*, neutral $MoO_5 \cdot HMPA$ and anionic $(MoO_5 \cdot PICO)^-Bu_4N^+$ (PICO is picoline *N*-oxide) was studied.[198]



85 **7a**

In all cases, the oxidation of the diol **85** results in benzil **7a** and benzaldehyde. The latter is formed due to glycol cleavage of the diol **85**. The ratio of the reaction products is strongly affected by the nature of the substrates and oxidants. For example, the action of $MoO_5 \cdot HMPA$ on both *meso*- and *d,l*-diol **85** results almost exclusively in benzaldehyde. However, the $(MoO_5 \cdot PICO)^-Bu_4N^+$ oxidant mostly converts the *meso*-form of the diol **85** to the diketone **7a**, while the *d,l*-diol **85** is converted to benzaldehyde. Benzil **7a** is formed from a complex of the substrate with the oxidant in which the glycol is coordinated as a monodentate ligand, while benzaldehyde is formed from a complex in which the substrate plays the role of a chelating ligand. If the reaction is carried out in air, autooxidation takes place. There is evidence that the reaction occurs in the coordination sphere of the metal according to a homolytic mechanism.[198]

A biochemical method was suggested for the transformation of ethylene glycol to glyoxal by treatment with oxidoreductase or microorganisms containing oxidoreductase, at 30 °C in aqueous solutions.[199]

Ethylene glycol can also be oxidised to glyoxylic acid. Accessible oxidants based on nitric acid, namely, $HNO_3 - H_2SO_4 -$

V_2O_5 [200] and HNO_3 with Co, Al and Cu acetylacetonates,[201] have recently been suggested for this purpose.

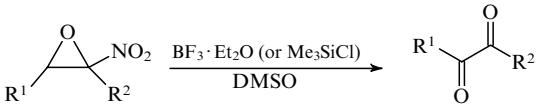
Such an efficient reagent as dimethyldioxirane can oxidise 1,2-diols without cleavage of the C–C bond of the glycol. However, the reaction stops at the step of the formation of hydroxy ketones, while diketones are found in the reaction mixture only as traces, since the carbonyl group that is formed deactivates the methine group as regards further oxidation.[202]

Glycol cleavage can be used for the synthesis of α-dicarbonyl compounds. Cleavage of methyl and ethyl D-tartrates in dry ether to the corresponding alkyl glyoxylates in 80%–85% yields on treatment with periodic acid [203] can serve as an example.

Oxidation of epoxides usually results in α-hydroxy ketones. This was found for the first time in the treatment of epoxides with DMSO in the presence of a catalytic amount of BF_3 etherate.[204] The same result was obtained on passing air through solutions of epoxides in DMSO. It was assumed [205] that the oxidation follows a radical mechanism. It was shown subsequently that the reaction follows an ionic mechanism with epoxide ring opening on treatment with DMSO in the presence of various protic acids (CF_3COOH, H_2SO_4, $MeSO_3H$, HBF_4, HNO_3) resulting in the formation of an α-hydroxysulfoxonium salt. In turn, the latter decomposes to α-hydroxy ketones according to Kornblum.[206, 207] Hydroxy ketones are also formed on treatment of epoxides with DMSO in the presence of molecular sieves [208] or clay with microwave heating.[209] Epoxysilanes are also oxidised in DMSO in the presence of triflates and tertiary amines to give α-hydroxyacylsilanes.[210]

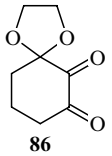
Unlike the reagents indicated above, the aqueous HBr–DMSO system smoothly converts diphenyloxirane to benzil **7a** in 71% yield; however, bis(α-diketone) **28** is formed from the corresponding bis(epoxide) in 31% yield only.[211]

1,2-Diones are formed upon oxidation of α-nitro epoxides.[212–214] This process occurs in the presence of tetrakis(triphenylphosphine)palladium and triethylamine in boiling benzene and gives satisfactory yields of α-diketones.[212, 214] The oxidation of nitro epoxides with the $BF_3 \cdot Et_2O$ (or Me_3SiCl)–DMSO system in CH_2Cl_2 at 0 °C followed by the addition of triethylamine gives the corresponding diketones in somewhat higher yields (54%–87%).[213, 214]



R^1, R^2 = Ph, Pr, Me, $(CH_2)_4Me$, $(CH_2)_3$, $(CH_2)_4$.

The same method afforded the triketone ketal **86**.[213, 214]

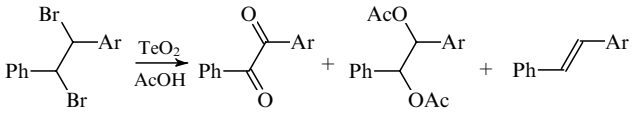


86

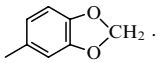
The reaction of α-nitro epoxides with $BF_3 \cdot Et_2O$ in acetonitrile in the presence of NaI gave good yields of α-iodo ketones.[213, 214]

Transformations of vicinal dihalides (or halohydrins) to α-dicarbonyl compounds are not typical in organic synthesis, although dibromination of alkanes or bromination of alkenes followed by transformation to α-diketones can serve as an alternative to hydrocarbon oxidation. These transformations can be performed efficiently with a number of reagents that have appeared in the last few years.

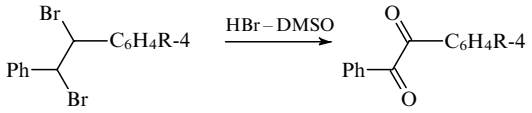
Refluxing of 2-aryl-1,2-dibromo-1-phenylethanes in acetic acid in the presence of tellurium dioxide gives benzil **7a** and its derivatives (yields 19%–82%) as well as the diacetates of the corresponding 1,2-diols and stilbenes.[215] The diacetates and stilbenes predominate among the products in the case of substrates with electron-withdrawing substituents.



Ar = Ph, 4-$MeOC_6H_4$, 4-MeC_6H_4, 2,3,4-MeC_6H_2, 4-ClC_6H_4, 4-$NO_2C_6H_4$, 4-NCC_6H_4,



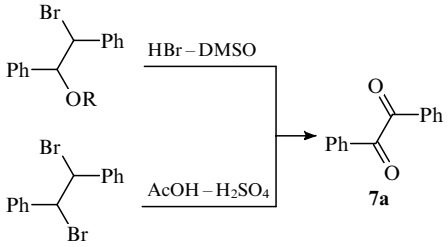
DMSO is a more convenient and accessible reagent for this kind of transformation.[216] For example, it was found that heating of *meso*- and *d*,*l*-2-aryl-1,2-dibromo-1-phenylethanes in the aqueous HBr–DMSO system at 110 °C for 4–8 h readily gives benzil **7a** and its derivatives in 70%–80% yields.



R = H, Me, MeO, Cl, NO_2.

This transformation occurs also without HBr but requires a longer time.[112] Later, this reaction was carried out with many acyclic and cyclic vicinal dibromides under microwave irradiation and gave α-diketones in 51%–75% yields.[217]

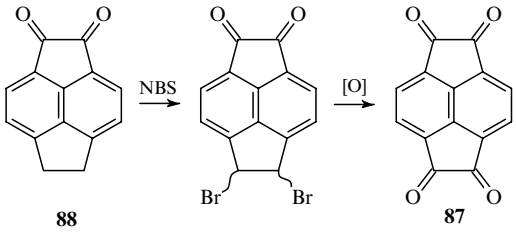
2-Bromo-1,2-diphenylethanol and even its methyl ether and formate undergo oxidation to diphenylethanedione in aqueous HBr–DMSO even more readily than 1,2-dibromo-1,2-diphenylethane.[112] If the oxidation is carried out without HBr, it follows the same direction but occurs more slowly.[112]



R = H, Me, CHO.

The cheapest way to oxidise 1,2-dibromo-1,2-diphenylethane to benzil (yield 80%) is heating the substrate in acetic acid in the presence of sulfuric acid.[218] It was found later that the addition of such compounds as iodine, potassium iodide or sodium sulfite to the reaction mixture accelerates considerably the oxidation of vicinal dibromides.[219]

The possibility of the synthesis of 1,2,5,6-tetraketopyracene (**87**), a structural element of buckminsterfullerene, according to the following scheme was studied:[220, 221]

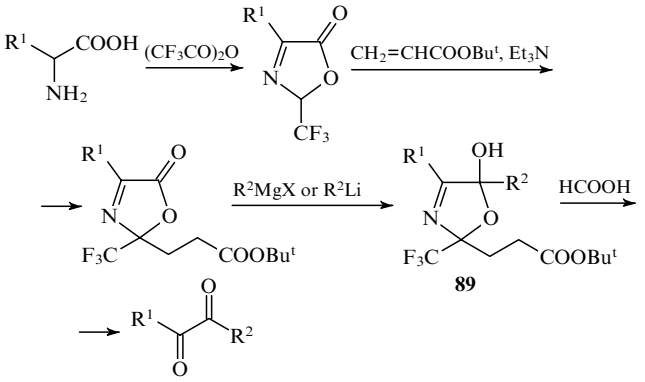


88 **87**

Oxidation of the starting 1,2-dioxopyracene (**88**) with sodium dichromate resulted in the cleavage of the diketone carbon–carbon bond. However, the target tetraketone **87** could be obtained by the oxidation of the dibromide prepared by bromination of the diketone **88** with *N*-bromosuccinimide according to the reported procedure.[222] The oxidation of the dibromide was carried out by treatment with the $AgNO_3$–MeCN system and then with $NaOAc \cdot 3H_2O$–DMSO.[220] The yield of the tetraketone **87** reached 80% but was irreproducible. Later, the same research

group found that the dioxopyracene **88** could be directly oxidised to the tetraketone **87** by treatment with benzeneseleninic anhydride[221] (see Section IV).

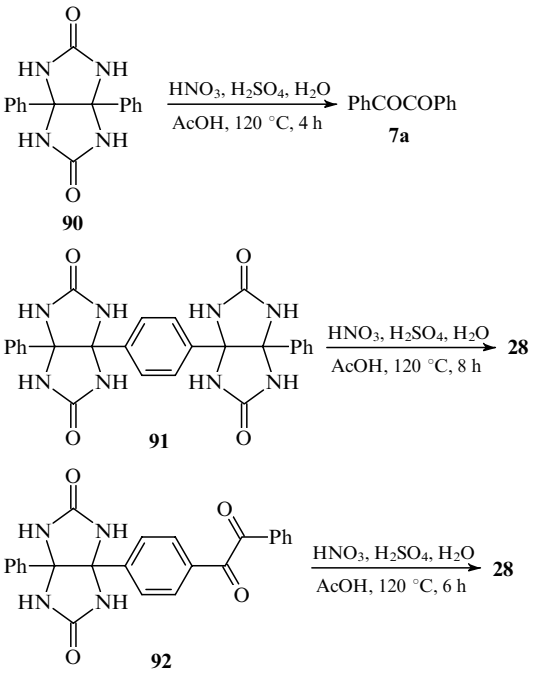
Methods are known for the transformation of five-membered heterocycles to α-diones. Certain 5-hydroxyoxazolines of the type **89** decompose in formic acid at room temperature to give the corresponding α-diketones in good yields. A method based on this reaction was elaborated for the synthesis of α-diketones from α-amino acids, as shown below.[223]



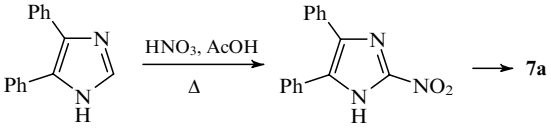
R^1 = Pr^i; R^2 = Ph, C≡CPh; R^1 = Bu^s, R^2 = Bu^n; R^1 = Ph, R^2 = Bu^n; R^1 = CH_2CH_2SMe, R^2 = Me; R^1 = $(CH_2)_3NHCOCF_3$: R^2 = Bu^n, Ph.

A number of acetylenic α-diketones used in the synthesis of tetrasubstituted furans were obtained according to the same scheme.[224]

Diaryl-substituted glycolurils **90**–**92** are oxidised to benzil **7a** and diketone **28** (yield 80%–90%) on heating with nitric acid in aqueous acetic acid in the presence of H_2SO_4.[225]



The oxidation of 4,5-diphenylimidazole to the benzil **7a** occurs at milder conditions than that for glycolurils. It does not require the presence of sulfuric acid and water and affords the products in 80%–85% yield. The reaction involves the intermediate formation of 2-nitro-4,5-diphenylimidazole.[225]



IV. Oxidation of alkanes, alkenes, alkynes and their derivatives

Of the classes of compounds listed above, alkynes can be converted to α-dicarbonyl compounds most easily (followed by alkenes and finally alkanes). Table 4 lists the reagents used for the preparative oxidation.

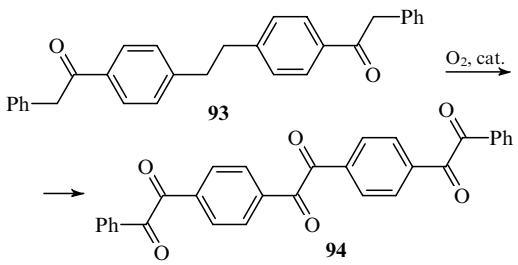
Table 4. Reagents used for the preparative oxidation of alkanes, alkenes, alkynes and their derivatives to α-dicarbonyl compounds R^1COCOR^2.

Substrate	Reagent
$R^1CH_2CH_2R^2$	$Na_2Cr_2O_7$–AcOH–$Ce(OAc)_3$, $(PhSeO)_2O$, O_2–($Co(OAc)_2$, $Mn(OAc)_2$, NaBr); Gif-system: $Fe(NO_3)_3 \cdot 9H_2O$–Bu^tOOH–$MeCOCH=CH_2$
$R^1CH=CHR^2$	SeO_2, $KMnO_4$, CrO_3–AcOH, O_2–($Co(OAc)_2$, $Mn(OAc)_2$, NaBr), OsO_4, HBr–DMSO, I_2–DMSO, NaBr–HCl–DMSO, Bu_4NBr–HCl–DMSO, Br_2–H_2SO_4, I_2–H_2SO_4, HBr–H_2SO_4, NaBr–H_2SO_4
$R^1-C\equiv C-R^2$	O_3, $KMnO_4$, NH_4MnO_4, $Zn(MnO_4)_2$, RuO_4, OsO_4, $Tl(NO_3)_3$, SeO_2, O_2, PhSeSePh–$(NH_4)_2S_2O_8$–MeOH, $MoO(O_2)_2$–$Hg(OAc)_2$, H_2O_2–$H_3PMo_{12}O_{40}$, H_2O_2–$H_3PW_{12}O_{40}$, H_2O_2–$MeReO_3$, CF_3COOOH, HNO_3–$NaNO_2$–$PdCl_2$, Cr(V)–*N*,*N*′-ethylenebissalicylydene iminate, H_3PO_5, dialkyldioxiranes, PhIO–$RuCl_2(PPh_3)_3$, $PhI(OCOCF_3)_2$, H_5IO_6, I_2O_5, HgO–I_2, NBS–DMSO, I_2–DMSO, anodic oxidation

For many reasons, direct oxidation of alkanes to α-dicarbonyl compounds is a difficult technical problem, and only a few examples of this kind of oxidation are known.

For example, in view of the great practical importance of acenaphthenequinone, processes for its synthesis by direct oxidation of acenaphthene were studied. Such oxidants as H_2O_2, HNO_3, permanganates and oxygen under pressure or in the presence of various catalysts were used.[226] None of these methods gave good yields of acenaphthenequinone. The oxidation of acenaphthene with $Na_2Cr_2O_7$ in AcOH with addition of cerium acetate at 40 °C does not provide high yield of acenaphthenequinone either (38%–60%). On the other hand, as noted above, sodium dichromate does not oxidise dioxopyracene **88** to the tetraketone **87**. However, this was performed with the use of benzeneseleninic anhydride $(PhSeO)_2O$, which oxidises compound **88** to the tetraketone **87** in 82% yield on heating in chlorobenzene at 125 °C.[221]

1,2-Diphenylethane and its derivatives undergo oxidation with oxygen in the liquid phase in the presence of Co–Mn–MBr catalysts to give the corresponding diphenylethanediones.[228–230] If oxygen is passed through a solution of compound **93** in glacial acetic acid containing the tetrahydrates of manganese and cobalt acetates and NaBr, not only the α-ketomethylene groups but also the ethane fragment are oxidised at 110 °C, leading to the formation of the hexaketone **94** in 70% yield.[228]

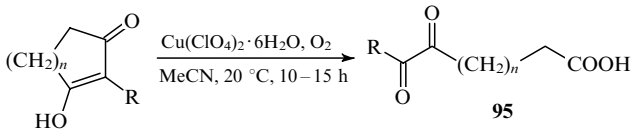


A study of the oxidation of 1,2-diphenylethane with oxygen in the presence of Co – Mn – MBr catalysts showed that this process follows the radical mechanism. In the first step, it gives 1,2-diphenylethane-1,2-diol, which is then oxidised to 1,2-diphenylethanone. The latter is transformed to benzil **7a**. The overall selectivity reaches 80%.[229,230] The selectivity of oxidation is affected only by the reaction temperature and the concentration of $Mn(OAc)_2 \cdot 4H_2O$.[230]

Oxidation of pentane and hexane with the $Ph_3Bi - Bu^tOOH$ system at room temperature initially gives α-diketones, which are then oxidised to carboxylic acid anhydrides.[231] In this case, it is the oxygen formed from the hydroperoxide in the coordination sphere of the metal that serves as the actual oxidant.[231]

Dicarbonyl compounds are also obtained upon oxidative formation or cleavage of the C – C bonds. Oxidation of cyclohexane, cyclooctane and cyclododecane in Gif-systems under the action of $Fe(NO_3)_3 \cdot 9H_2O - Bu^tOOH$ in the presence of methyl vinyl ketone results in the corresponding 1-cycloalkylbutane-2,3-diones as the main products.[232] The reaction occurs through the Michael-type addition of the cycloalkane to methyl vinyl ketone followed by the insertion of the *tert*-butylperoxy group at the α-position to the carbonyl group of the adduct, which then slowly eliminates Bu^tOH to give α-diketones.[232]

Oxidative cleavage of the C – C bonds can also result in dioxo carboxylic acids. For instance, the oxidation of the enol forms of cyclic 1,3-diketones with copper(II) salts and oxygen results in acids **95**.[233]



95

$n = 0$, R = Me; $n = 1$: R = Me, $CH{=}CH_2$, $CH_2CH{=}CH_2$, Ph.

Over ten years ago, Haines[234] noted that there are probably few reliable methods for the transformation of alkenes to 1,2-dicarbonyl compounds. This statement is no longer wholly true since the late 80's when new oxidising DMSO-based reagents appeared.

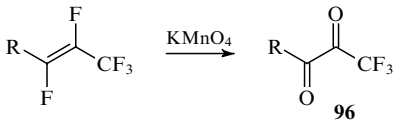
Selenium dioxide was among the first reagents that oxidise alkenes to α-dicarbonyl compounds. It oxidises alkenes containing no allylic hydrogen atoms rather successfully on heating them in acetic acid, trichlorobenzene or without a solvent. For example, ethylene and stilbene are oxidised to glyoxal and benzil **7a** in up to 70% yields;[35,234] styrene is converted to phenylglyoxal along with hydroxylation products,[235] while propene, a representative of allylic alkenes, gives methylglyoxal in only 19% yield.[234]

The direction of the oxidation of alkenes with potassium permanganate strongly depends on the reaction conditions. In alkaline media, internal alkenes mostly form 1,2-diols, while in nearly neutral or weakly alkaline media (pH 9 – 9.5) α-hydroxy ketones are formed.[234] Symmetric cyclic and acyclic alkenes are oxidised with potassium permanganate in cold acetic anhydride (not above 10 °C) to give the corresponding α-diketones in moderate yields.[236,237] The selectivity of the process is not high as noticeable amounts of 2-acetoxy ketones and dicarboxylic acids are formed. It was noted that the reaction may be hazardous.[237] In addition, attempts to synthesise diketones from cyclohexene and norbornene failed.[234] The oxidation of *E*-alkenes gives somewhat higher yields of diketones than the oxidation of the *Z*-isomers.[234,236] Styrene can be converted to phenylglyoxylic acid by oxidation with potassium permanganate under alkaline conditions.[238]

Oxidation of nonterminal alkenes with permanganate under conditions of phase-transfer catalysis gives α-diols, α-diketones and α-hydroxy ketones along with carboxylic acids. The ratio of the oxidation products can be controlled by varying the conditions.[234] For example, cyclododecane-1,2-dione and decane-5,6-dione were obtained in 69% and 53% yields from the corresponding alkenes in the $KMnO_4 - CH_2Cl_2 - H_2O$ system containing acetic acid and Adogen 464.[239]

Such a heterogeneous reagent as $KMnO_4 - CuSO_4 \cdot 5H_2O - Cu(OAc)_2 \cdot H_2O$ in CH_2Cl_2 oxidises cyclooctene and cyclododecene to the corresponding diketones in moderate yields.[240] In the absence of copper acetate, the reaction stops in the step of formation of α-hydroxy ketones.[240]

Oxidation of nonterminal fluoroalkenes with permanganate under strictly controlled conditions (the ratio alkene : $KMnO_4$ = 1 : 0.3 – 0.7, acetone : water = 24 : 1; – 30 to – 20 °C) affords diketones **96** in 30% – 80% yields.[241,242]



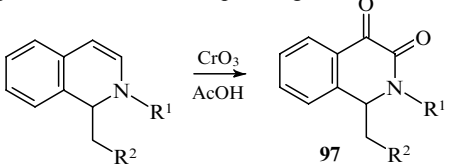
96

R = CF_3, Ph.

It is assumed that this reaction occurs *via* an intermediate product of hydroxylation of the C = C bond, which undergoes dehydrofluorination to give the target products. Although satisfactory yields are obtained, cleavage of the C – C bond cannot be avoided completely, even at 50% conversion of the starting olefin.[242]

Perfluoroalkenes can also be converted to dicarbonyl compounds by catalytic or stoichiometric oxidation with osmium tetroxide. In this case, tetrafluoroethylene is converted to glyoxylic acid in good yield, while perfluorocyclohexene gives perfluorocyclohexane-1,2-dione.[243,244]

Chromium(VI) compounds are mostly known as oxidants that cleave the C = C bonds. However, a few cases have been reported in which dicarbonyl compounds were obtained upon oxidation of the double bonds with chromium trioxide. For example, CrO_3 in acetic acid was used for the oxidation of a series of 1,2-dihydroisoquinolines to the corresponding 3,4-dioxo derivatives **97**.[245]



97

R^1 = 2,4,6-$(NO_2)_3C_6H_2CH_2$, R^2 = PhCO;
R^1 = 2,4-$(NO_2)_2C_6H_3CH_2$: R^2 = $PhSO_2$, 4-$NO_2C_6H_4CO$.

Both stilbene isomers are converted on treatment with a catalytic amount of CrO_3 and an excess of aqueous *tert*-butyl hydroperoxide to give mixtures of oxidation products, *trans*-stilbene oxide being the major component. In this case, approximately equal amounts of benzil **7a**, benzophenone and benzoin benzoate are formed.[246] Norbornene was found to be inert under these conditions.[246]

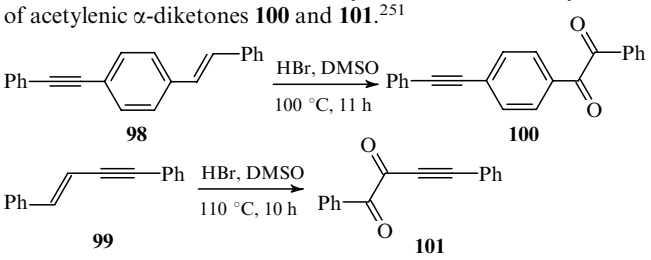
A study of the liquid-phase oxidation of (*E*)-stilbene with oxygen in acetic acid at 105 °C in the presence of a Co – Mn – bromide catalyst showed that rapid and total conversion of the substrate results in a complex mixture of products [PhCOOH, Ph_2CO, Ph_2CHCHO, PhCOCOPh, $PhCH_2COPh$, PhCH(OAc)COPh, PhCH(OAc)CH(OAc)Ph, *etc*.] with up to 46% content of benzil **7a**.[247] These products are formed from the primary oxidation product, *i.e*. 1,2-diphenyloxirane.[247]

Peracetic acid oxidises *trans*-1-acetoxy-2-iodo-1,2-diphenylethylene to diketone **7a** in low yield.[248]

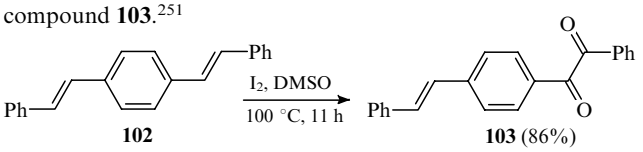
DMSO-based oxidants are much more versatile and convenient reagents for the synthesis of α-dicarbonyl compounds from alkenes. This was first discovered in 1989 for stilbene, which was oxidised readily and in high yield to benzil **7a** in the $HBr - H_2O_2 -$ DMSO system.[249] It was found subsequently that hydrogen peroxide accelerates the reaction but does not act as an oxidant. A solution of aqueous HBr in DMSO successfully oxidises stilbenes with both donor and acceptor substituents to

give the corresponding diarylethanediones in 56% – 86% yields. It turned out that the first act of the process involves the electrophilic addition of bromine, which is formed *in situ* from HBr and DMSO, to the double bond, but it is the intermediate 1,2-diaryl-1,2-dibromoethanes that undergo oxidation. In this case, DMSO plays a dual role, specifically, it generates a microscopic amount of bromine from HBr (it is this reaction that is accelerated by hydrogen peroxide) and oxidises dibromides by a mechanism resembling that of the Kornblum reaction.[112, 157] Since the first act of the reaction is the electrophilic addition of bromine to the double bond, it becomes clear why the oxidation of 4-nitrostilbene requires much longer time than that of stilbene, while 4,4′-dinitrostilbene does not undergo oxidation at all.[112] Compounds other than hydrogen bromide can be successfully utilised as the bromine sources. For instance, good results were achieved in the $NaBr-H_2SO_4-DMSO$, $NaBr-HCl-DMSO$, and $Bu_4NBr-HCl-DMSO$ systems.[114] In some cases, passage of air through a solution of HBr in DMSO increases the oxidation efficiency.[250]

Triple bonds are practically inert with respect to HBr in DMSO. This fact was successfully used to perform selective oxidation of double bonds in the enynes **98** and **99** in the synthesis of acetylenic α-diketones **100** and **101**.[251]

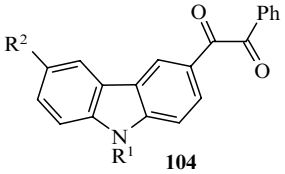


Iodine in DMSO can also oxidise alkenes to dicarbonyl compounds, but it is much less reactive than HBr–DMSO.[251–254] This reagent oxidises only stilbene and its derivatives containing electron-donating or weak electron-withdrawing substituents (Me, OMe, Cl) at position 4.[252, 253] The decrease in the reaction rate caused by electron-withdrawing substituents made it possible for the first time to perform selective oxidation of only one bond in 1,4-(*E*,*E*)-distyrylbenzene (**102**) to give compound **103**.[251]



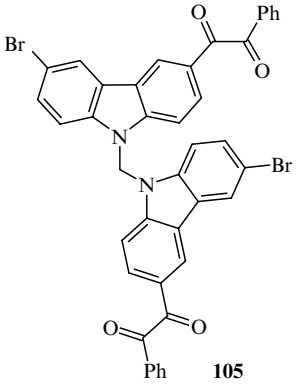
Styrene, being an alkene with a terminal double bond, is oxidised both with bromine and HBr in DMSO to give phenylglyoxal. This results in a much larger amount of side products than in the oxidation of stilbenes.[255]

In the oxidation of 3-styryl- and 3,6-distyrylcarbazoles with the HBr–DMSO system, oxidation of the double bonds is accompanied by side processes such as bromination of the carbazole moiety and methylenation of the free NH groups to give dioxo- and tetraoxocarbazole derivatives **104** and **105**.[256]



104

R^1 = H, Me; R^2 = H, Br.

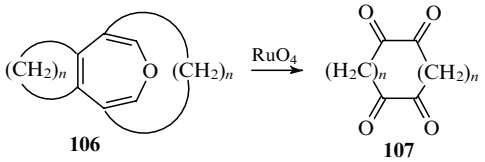


105

These side processes that are beneficial in this case occur due to the reaction of the carbazole moiety with bromine and formaldehyde generated upon the reaction of HBr with DMSO at 120 °C.[256]

The most efficient method for the oxidation of stilbenes to diketones (yields 50% – 81%) is probably refluxing the substrates in acetic acid in the presence of H_2SO_4 containing admixtures of bromine, iodine, HBr, NaBr or sodium sulfite.[218, 219] As mentioned above, the reaction involves intermediate electrophilic halogenation of double bonds if halogens, hydrogen halides or their salts are used.[218, 219]

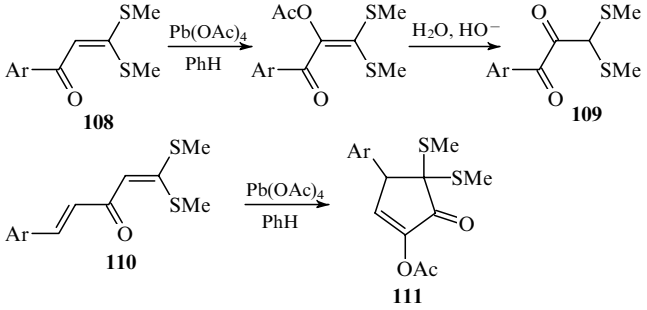
In addition, examples of the specific oxidation of double bonds with the formation of specific types of dicarbonyl compounds are worth noting. Oxidation of compounds **106** with RuO_4 (formed from $RuCl_3 \cdot 3H_2O$ and $NaIO_4$) in a mixture of CCl_4 and aqueous MeCN affords macrocyclic bis-α-diketones **107** in yields up to 40%.[257]



106 **107**

n = 6, 10.

Aroylketene dithioacetals **108** are oxidised with $Pb(OAc)_4$ in boiling benzene to give acetoxy dithioacetals, which are hydrolysed under mild conditions to compounds **109**. Under similar conditions, their vinylogues **110** undergo oxidative cyclisation according to Nazarov, giving 2-acetoxycyclopentenone derivatives **111**, which are precursors of di- and tri-ketones.[258]



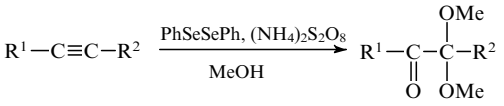
Oxidation of alkynes to α-dicarbonyl compounds, unlike that of alkanes and alkenes, is one of reliable methods to obtain compounds of this class. Numerous reagents are known to perform this type of transformation successfully, although there is always a danger of cleavage of the carbon – carbon bond both in substrates and in products. The oxidation of alkynes has been covered in reviews and books rather thoroughly,[4, 5, 40, 234] and in most cases we are going to refer to the newer studies or those not included in these sources.

Alkynes are comparatively resistant against oxygen, and only few examples of their oxidation with oxygen to diketones are known. Passage of air through a solution of diphenylacetylene in acetic acid containing a Co – Mn – MBr catalyst for 3 h at 110 °C gives benzil **7a** in up to 90% yield.[259] Oxidation of cyclooctyne with air at low temperatures to give the corresponding α-dione was also reported.[260]

Ozonisation of both terminal and internal alkynes in alcohols at low temperatures serves as a method for the synthesis of oxo aldehydes and α-diketones. The ozonisation of 1-ethoxypent-1-yne in hexane gave ethyl 2-oxopentanoate.[234]

Oxidation of alkynes that do not contain methylene groups adjacent to the triple bond to α-dicarbonyl compounds is carried out with selenium dioxide.[40, 234] The oxidation is facilitated upon addition of catalytic amounts of sulfuric acid. For example, refluxing diphenylacetylene with SeO_2 in AcOH containing sulfuric acid gives diketone **7a**. The reaction with phenylacetylene

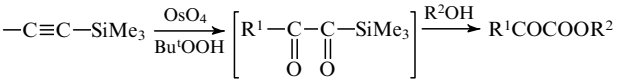
under the same conditions gives phenylglyoxylic acid.[234] Diphenyl diselenide is another selenium-containing reagent that oxidises the triple bond. It converts alkynes to diketone and oxo aldehyde monoacetals in high yields in boiling methanol in the presence of ammonium peroxodisulfate.[261]



R^1 = Ph: R^2 = H, Ph, 3-Bu^{t}C$_6$H$_4$, 4-FC$_6$H$_4$, 2-BrC$_6$H$_4$;
R^2 = H: R^1 = PhCH$_2$, Bu^n, C$_6$H$_{13}$, HOOCCH$_2$; R^1 = R^2 = Pr^n.

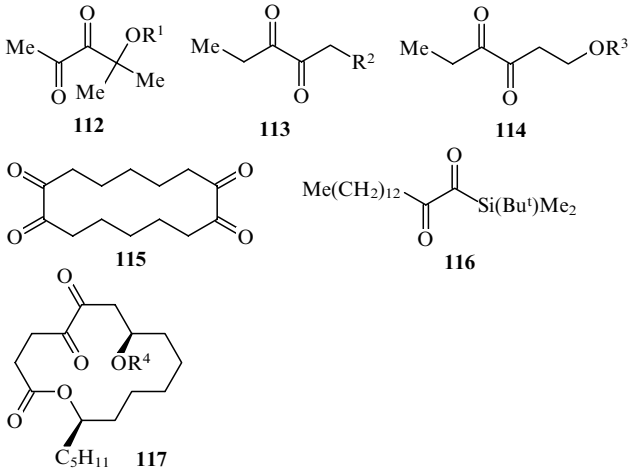
Potassium, zinc and ammonium permanganates are widely used to oxidise alkynes (for the reviews, see Refs 4, 234, 262). To our knowledge, in these reactions terminal alkynes undergo only oxidative cleavage with the formation of carboxylic acids and loss of one carbon atom, whereas α-diketones can be obtained only from internal alkynes. A particularly efficient general method for the synthesis of α-dicarbonyl compounds from alkynes involves the oxidation of the latter with potassium permanganate in aqueous acetone or dioxane under nearly neutral conditions provided by the addition of sodium hydrogen carbonate and magnesium sulfate.[234] Of potassium, magnesium and zinc permanganates, the latter is the most efficient reagent for the oxidation of alkynes in dichloromethane.[263] Potassium permanganate in aqueous acetone proved to be a convenient oxidant of 3,6-di(phenylethynyl)carbazoles to the corresponding 3,6-bis(phenylglyoxylyl)carbazoles.[264, 265] The mechanism of the oxidation of alkynes with $KMnO_4$ and the effect of the substrate structure on the process were studied.[266] It was shown that the oxidation rate depends on electronic rather than on steric factors.

Certain similarity is observed between the oxidation of alkynes with osmium and ruthenium tetroxides. Terminal alkynes are oxidised with OsO_4 to carboxylic acids. On the other hand, alkynes with an internal triple bond can be oxidised to α-diketones using this reagent.[234, 267] It was found that OsO_4 forms complexes with alkynes in the presence of pyridine or isoquinoline, $2OsO_4L_4R^1C{\equiv}CR^2$ (where L is pyridine or isoquinoline); these complexes are hydrolysed in the presence of sodium sulfite to the corresponding diketones, R^1COCOR^2. However, phenylacetylene is converted to benzoic acid under these conditions.[268] There are methods for the transformation of alkynes to dicarbonyl derivatives with a catalytic amount of OsO_4 in the presence of co-oxidants, such as potassium chlorate, hydrogen peroxide, *tert*-butyl hydroperoxide and morpholine *N*-oxide.[234] It is believed that OsO_4 is the actual oxidant, while a co-oxidant, for example, potassium chlorate, regenerates OsO_4 from the osmium dioxide formed in the first step.[269] Acetylene is oxidised with the OsO_4-KClO_3 system to give glyoxylic acid,[267] and alkoxyalkynes form α-oxo esters in high yields under similar conditions.[269] Trimethylsilylalkynes are oxidised to methyl or butyl phenyl(alkyl)glyoxylates on treatment with a catalytic amount of OsO_4 in the presence of ButOOH in methanol or *tert*-butyl alcohol at 0 °C.[270] It is believed that α-oxo esters are formed from the primary oxidation products, *i.e.* silylated diketones, on decomposition with an alcohol.[270]



R^1 = Ph, C_5H_{11}, C_6H_{13}; R^2 = Me, Bu^t.

Ruthenium tetroxide, which is generated *in situ* from RuO_2 dihydrate, $RuCl_3$ or tris(triphenylphosphine)ruthenium dichloride and such oxidants as $NaIO_4$, NaOCl or PhIO or by electrochemical oxidation, serves as an efficient reagent for the transformation of internal alkynes to α-diketones under mild conditions.[234, 271] Probably, the main advantage of RuO_4 is that its reacts under mild conditions (often at, or below, room temperature) and its high selectivity. For example, benzil **7a** and α-diketones **112**–**117** with various functional groups are obtained in 27%–95% yields from the corresponding internal alkynes and ruthenium dichloride with $NaIO_4$.[272]



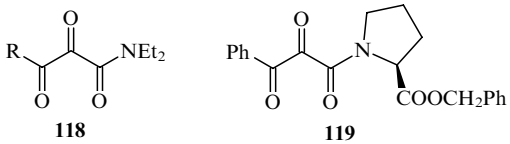
112 **113** **114**

115 **116**

117

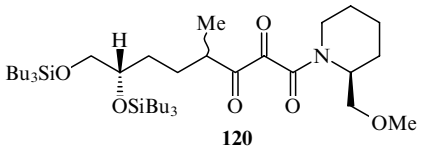
R^1 = Ac, tetrahydropyran-2-yl; R^2 = COOMe, OCOBu^t;
R^3 = CH_2Ph, tetrahydropyran-2-yl; R^4 = Si(Bu^t)Me$_2$.

The same method was used in the synthesis of dioxo amides **118**–**120** from the corresponding acetylenic carboxamides.[273]



118 **119**

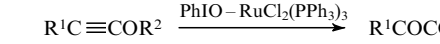
R = Ph, Bu, BuO(CH$_2$)$_4$.



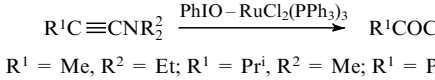
120

Terminal alkynes are converted to carboxylic acids upon oxidation with a catalytic amount of ruthenium tetroxide generated electrochemically from ruthenium dioxide.[271] On the other hand, dialkyl- and phenylalkylalkynes are oxidised with RuO_4 to give α-diketones in high yields in a two-phase system CCl_4–saturated aqueous NaCl.[271]

Iodosylbenzene combined with $RuCl_2(PPh_3)_3$ in CCl_4 readily oxidises internal alkynes to the corresponding α-diketones.[274] The same reagent oxidises alkoxy- and aminoalkynes to α-oxo esters and α-oxo carboxamides in 44%–84% yields.[275]



R^1 = Me, R^2 = Et; R^1 = Pr^i, R^2 = Me; R^1 = *n*-C_6H_{13}, R^2 = Me;
R^1 = Bu, R^2 = Pr^i; R^1 = Ph, R^2 = Et.



R^1 = Me, R^2 = Et; R^1 = Pr^i, R^2 = Me; R^1 = Ph, R^2 = Me, Et.

Thallium nitrate is one more reagent that readily oxidises triple bonds. However, its use in the synthesis of α-dicarbonyl compounds is rather limited. Symmetric dialkylalkynes are converted with $Tl(NO_3)_3$ in acidic methanolic medium to give α-hydroxy or α-methoxy ketones, whereas alkylarylalkynes undergo oxidation with 1,2-alkyl shift to give α-branched carboxylic acids.[5] It is only diphenylacetylene and its substituted derivatives that undergo oxidation on refluxing with $Tl(NO_3)_3$ in glym containing $HClO_4$ to give benzils in 45%–97% yields.[276]

In recent years, molybdenum and tungsten peroxocomplexes have been extensively studied as oxidants of alkynes.[277–282] It was

shown that both terminal and internal alkynes undergo oxidation to the corresponding α-oxo aldehydes and α-diketones in rather good yields (55%–90%) on treatment with a $MoO(O_2)_2$–hexamethylphosphoramide complex in the presence of mercuric acetate in a dichloroethane–methanol mixture.[277]

$$R^1C{\equiv}CR^2 \xrightarrow[C_2H_4Cl_2]{(HMPA)MoO(O_2)_2,\ Hg(OAc)_2} R^1COCOR^2$$

R^1 = Ph, R^2 = H, Ph; $R^1 = R^2 = C_6H_{13}$; R^1 = Bu, R^2 = H, Ph.

No oxidation occurs in the absence of $Hg(OAc)_2$. It is known that the action of hydrogen peroxide on Na_2MO_4 salts [wherein M = Mo(VI) or W(VI)] results in oxodiperoxo complexes with the composition $MoO(O_2)_2$, which possess strong oxidative properties. It turned out that dilute H_2O_2 oxidises phenylacetylene and hex-1-yne rather readily in the presence of a catalytic amount of molybdates or tungstates (Na_2MO_4), phase-transfer catalysts, and mercuric acetate. However, the yields of the resulting oxo aldehydes are low, while carboxylic acids are the main products.[278] Diphenylacetylene was inert under these conditions. Heteropolyacids, such as $H_3PMo_{12}O_{40}$ and $H_3PW_{12}O_{40}$, manifest higher catalytic activity in the oxidation of alkynes with hydrogen peroxide;[280–282] these catalysts convert acetylene to glyoxal (yields up to 63%).[280] However, phenylacetylene and certain dialkyl- and alkylphenylalkynes are oxidised under these conditions mostly to give carboxylic acids, unsaturated ketones and α-oxo epoxides.[279,281,282] Generally, this type of catalytic oxidation of the triple bond to α-dicarbonyl compounds is no more selective than the oxidation with hydrogen peroxide or peroxy acids. For instance, it is known that trifluoroperacetic acid oxidises diphenylacetylene to afford a mixture of benzil **7a** and benzoic acid.[283] Mixtures of products are also formed upon oxidation of alkynes with hydrogen peroxide in the presence of methylrhenium trioxide $MeReO_3$.[284] The reaction in the two-phase system CH_2Cl_2–H_2O converts diphenyl-, dipropyl-, and *tert*-butyl(methyl)alkynes to the corresponding α-diketones (yields 38%–67%), and terminal alkynes (phenylacetylene and non-1-yne) are oxidised to phenyl- and heptylglyoxalic acids (yields 68% and 47%).[284]

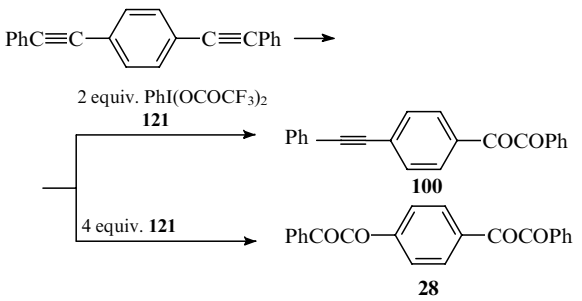
Nitrogen oxides catalyse the oxidation of acetylene to glyoxal at temperatures from 170 to 250 °C,[285] and Pd(II) catalyses its oxidation in 30%–60% HNO_3 to oxalic acid.[286] It was shown that acetylene is not oxidised in HNO_3 at 25 °C or in the HNO_3–$NaNO_2$ system, but $PdCl_2$–$NaNO_2$ in nitric acid at 15 °C favours the formation of glyoxal in 40%–50% yield with respect to the acetylene consumed.[287] $Hg(NO_3)_2$ is less reactive. Methylacetylene was found to be more reactive than acetylene with respect to oxidation, while phenylacetylene gives stable organopalladium compounds that do not undergo further oxidation under the reaction conditions.[287]

Diphenylacetylene is oxidised in high yield to benzil **7a** under the action of complexes of Cr(V) with *N*,*N*′-ethylenebissalicylideneiminate (salen-complexes). However, phenylacetylene is mostly converted to benzoic acid under these conditions, while only a small amount of phenylglyoxal is formed.[288,289]

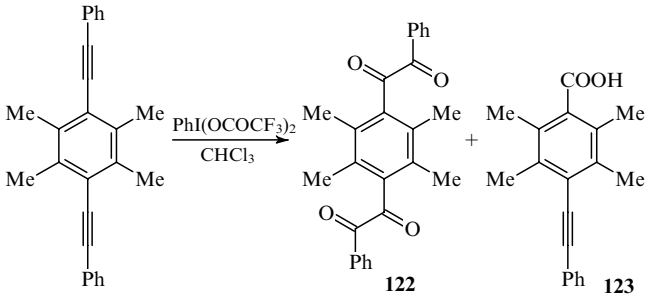
Phenylacetylene and certain internal alkynes are efficiently oxidised with monoperoxyphosphoric acid (H_3PO_5). However, this reaction produces mixtures of the corresponding α-dicarbonyl compounds with benzoic acid and rearrangement products. The reaction involves α-oxo carbenes as intermediates.[290]

The oxidation of alkynes with dimethyl- and methyl(trifluoromethyl)dioxiranes also occurs *via* α-oxo carbene intermediates. The reaction results in mixtures of oxidation products, including α-diketones and α-oxo acids.[291,292]

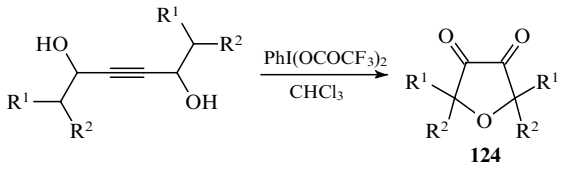
Bis(trifluoroacetoxy)-λ^3-iodanylbenzene **121** smoothly oxidises internal alkynes to α-diketones and terminal alkynes to α-hydroxy ketones.[293–296] Two equivalents of the reagent **121** selectively oxidise one triple bond in bisphenylethynylbenzene to give acetylenic diketone **100**, while four equivalents of the reagent oxidise the substrate completely, converting it to the tetraketone **28**.[293]



Compound **121** oxidises only one triple bond in diphenylbutadiyne to produce a mixture of diphenyl-1,4-dioxobutyne (40%) and acetylenic diketone **101** (30%).[296] Compound **121** oxidises diphenylacetylene and its derivatives with electron-donating or moderate electron-withdrawing groups to the corresponding benzils in yields above 70%. However, (4-nitrophenyl)phenylacetylene is converted to 4-nitrobenzil in only 28% yield.[294] Despite the high selectivity of the reagent **121** as the oxidant, cleavage of the triple bond cannot be avoided completely. For example, the oxidation of bisphenylethynyldurene gives the acid **123** in addition to the tetraketone **122**.[294]



The action of compound **121** on 1,4-dihydroxybutynes results, as expected, in the oxidation of the triple bond along with the intramolecular dehydration to give substituted tetrahydrofurandiones **124** in one step and in high yields.[297]



R^1 = R^2 = Me, R^1, R^2 = $(CH_2)_4$.

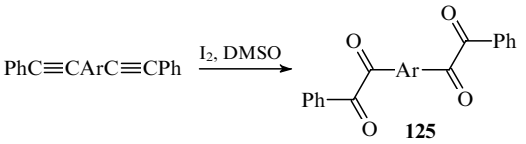
Like compound **121**, iodosylbenzene oxidises diphenylacetylene to benzil **7a**. The mechanism of its action is somewhat analogous to the mechanism of oxidation of alkynes with ozone.[298]

Periodic acid (H_5IO_6) is yet another iodine-based oxidant, which converts diphenylacetylene to benzil **7a** in almost quantitative yield on heating in acetic acid.[299] Like I_2O_5, this oxidant has the advantage that treatment of diphenylacetylene in boiling methanol or ethylene glycol affords mono- and diketals of benzil **7a**, which are difficult to obtain by other methods.[299] It is believed that I^+ rather than I^{7+} or I^{5+} is the actual oxidising particle in this case. This opinion is supported by the conversion of diphenylacetylene to mono- and dimethyl ketals of benzil **7a** on heating in methanol with HgO–I_2.[299]

N-Bromosuccinimide in dry DMSO is an efficient oxidant of triple bonds in phenylacetylene, diphenyl-, dimethyl- and methylphenylacetylene.[300] The reaction can occur even at room temperature. The yield of benzil **7a** reaches 98%, but other alkynes mentioned above form α-dicarbonyl derivatives in lower yields. Diphenylbutadiyne is oxidised to diphenyl tetraketone (PhCO–COCOCOPh) isolated as the dioxime.[300] A certain drawback of

this oxidising system is that DMSO has to be dried thoroughly, as the oxidation of diphenylacetylene does not occur even in the presence of 0.5% water.[300] Oxidative reagents based on commercial, non-dried DMSO, *viz*., HBr, I_2 or $PdCl_2$ in DMSO,[253, 254] do not have this drawback. Heating of diarylalkynes in DMSO containing iodine at 115–155 °C provides high yields of benzils.[253, 254] High reactivity and selectivity of the reagent are confirmed by the fact that it oxidises (4-nitrophenyl)phenylacetylene in 90% yield and does not affect the formyl group in (4-formylphenyl)phenylacetylene, which is very reactive and liable to oxidation.

Various bisphenylethynylarenes are oxidised to the tetraketone **28**, as well as tetraketones **125**, on heating in DMSO with an equimolar amount of iodine (yields 71%–90%).[253, 254]



Ar = 1,4-C_6H_4, 4,4′-$C_6H_4C_6H_4$, 4,4′-$C_6H_4OC_6H_4$, dibenzofuran-3,8-diyl, 4,4′-$C_6H_4CH_2C_6H_4$, 4,4′-$C_6H_4COC_6H_4$, fluorene-2,7-diyl, fluorenone-2,7-diyl.

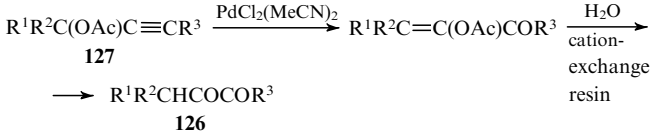
The same reagent was successfully used in the synthesis of 4,4′-bis(arylglyoxylyl)benzophenones from 4,4′-bis(arylethynyl)benzophenones[301] and a series of fluoro-derivatives of bis-α-diketones, $FC_6H_5COCOC_6H_5XC_6H_5COCOC_6H_5F$ (X = CO, COCO, Het).[302]

By decreasing the quantity of iodine to a catalytic amount, it was possible to oxidise only one triple bond in bis(phenylethynyl)benzene and to obtain the diketone **100**.[252] It was noted above that the reactivity of iodine in DMSO as an oxidant of the double bonds in stilbenes is low. This enables selective oxidation of only the triple bond in compound **98** giving (*E*)-styrylbenzil **103**.[251] The acetylene-containing tetraketone **29** is readily converted on treatment with the I_2–DMSO system to the hexaketone **94** in 90% yield.[59] Thus, the use of a combination of two oxidants, HBr–DMSO and I_2–DMSO, opens for the first time the possibility of the selective oxidation of either triple or double bonds in enynes.

The reactivity of iodine in DMSO decreases abruptly in the oxidation of a sterically hindered acetylenic substrate, *viz*., mesitylacetylene, although the direction of the oxidation does not change.[253, 254] A new oxidative process has been discovered recently.[303] Prolonged heating of sterically hindered bis(phenylethynyl)durene with iodine in DMSO gave duroquinone, 2,3,5,6-tetramethyl-4-hydroxybenzil and benzoic acid as the main products, instead of the expected tetraketone **122**. This reaction is a rare example in which iodine in DMSO causes the cleavage of the carbon–carbon bonds. A similar process was observed in the oxidation of the enyne **99**, which resulted in benzil **7a** and benzoic acid instead of the expected diphenylbutenedione.[251] The I_2–DMSO system also proved to be inefficient in the oxidation of a terminal alkyne, *viz*., phenylacetylene. In this case, a complex mixture of oxidation products with a content of phenylglyoxal no more than 20% is formed even if the conversion of the substrate is incomplete.[255]

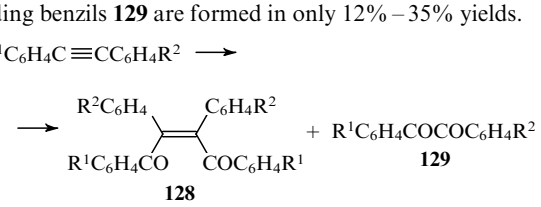
It was shown [251, 253, 254, 304] that internal alkynes [diarylalkynes and bis(phenylethynyl)benzenes] are readily oxidised to benzil **7a** and tetraketones **28** and **125** on heating in DMSO in the presence of a catalytic amount of $PdCl_2$. This reagent proved to be even more selective with respect to the triple bonds than I_2–DMSO. It is totally inert to alkenes. This enables its efficient use in the oxidation of acetylenic compounds containing double bonds.[251] On the other hand, $PdCl_2$–DMSO is more sensitive to steric factors in substrates than I_2–DMSO.[253, 254]

A method for the synthesis of α-diketones **126** from α-acetoxyalkynes **127** in high yields was suggested.[305] In the first step, substrates **127** are oxidised with complexes of $PdCl_2$ with acetonitrile or benzonitrile under very mild conditions at room temperature. The resulting enol acetates are readily hydrolysed to diketones **126** in the presence of cation-exchange resins.



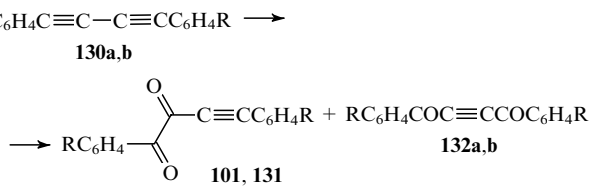
R^1, R^2, R^3 = H, Alk, cyclo-Alk, Ar.

Anodic oxidation of diarylalkynes in acetonitrile on a graphite electrode gives mixtures of products, of which 1,2,3,4-tetraarylbut-2-ene-1,4-diones **128** are the main components.[306] The corresponding benzils **129** are formed in only 12%–35% yields.



R^1, R^2 = H, OMe.

Anodic oxidation of diarylbutadiynes **130a**,**b** under similar conditions results in the respective 1,2-diketones **101** (5%) and **131** (28%) and butyne-1,4-diones **132a**,**b** (60% and 12%).[306]



R = H (**101**, **130a**, **132a**), OMe (**130b**, **131**, **132b**).

As shown previously, a mixture of the same products, *viz*., **101** and **132a**, results from the oxidation of diphenylbutadiyne with bis(trifluoroacetoxy)-λ³-iodanylbenzene **121**.[296]

V. Conclusion

Despite the great diversity of oxidative methods for the synthesis of vicinal di- and polycarbonyl compounds (most often, α-diketones), extensive studies in this field are being continued. In our opinion, several most topical problems can be distinguished.

For example, now there are many reliable and general reagents for the oxidation of such substrates as ketones, their α-hydroxy and α-halogeno derivatives and β-diketones. On the other hand, methods for the oxidation of alkenes, vicinal dihalides and especially alkanes have been developed insufficiently. There are almost no versatile reagents for the oxidation of these classes of compounds, except for the recently suggested DMSO-based oxidants suitable for the oxidation of alkenes and substituted 1,2-dibromoethanes. Only after such reagents as HBr–DMSO, I_2–DMSO and $PdCl_2$–DMSO had appeared, did selective oxidation of either the triple or the double bond in enynes become possible. The results presented in Section IV show convincingly that alkynes rather than alkenes, and even more so alkanes, are the most suitable as substrates in the synthesis of α-dicarbonyl compounds. Thus, the traditional belief that 'alkynes are more difficult to oxidise than alkenes' has to be reconsidered.[307]

Yet another problem is the obvious lack of reliably proven mechanisms for the oxidation reactions presented in this review. Although a great deal of studies have been carried out, the mechanisms of action of even such well-studied oxidants as SeO_2 and $KMnO_4$ remain debatable. There are relatively few systematic studies on the quantitative estimation of the effect of the structure of substrates and oxidants on the reactivity. Because of the insufficiency of the theoretical basis, new reagents in this branch

of synthetic chemistry mostly appear incidentally, and the majority of publications are of preparative character.

Finally, it is to be noted that general approaches to the synthesis of compounds with more than three contiguous carbonyl groups have not been developed so far, and only a few syntheses of acyclic pentaketones have been reported. On the other hand, recent non-empirical quantum-chemical calculations show that hypothetical polyketones $R(CO)_nR$ ($n = 6-11$) can be rather stable.[3] Synthesis of such compounds is one of the urgent problems of organic synthesis.

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