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Oxallyl Complexes in Organic Synthesis

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The review is devoted to new methods of synthesis of carbonyl and other oxygen-containing compounds involving oxallyl complexes of transition metals.
The bibliography includes 180 references.

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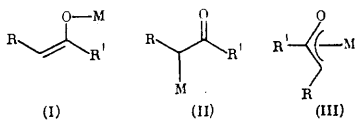
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I. INTRODUCTION

The allyl compounds of metals constitute one of the most thoroughly investigated classes of organometallic compounds. Numerous reviews and monographs have been devoted to the use of the allyl complexes in synthesis. The metal oxallyl complexes, in which one of the carbon atoms of the allyl system has been replaced by oxygen and which have a similar structure, have been investigated to a much lesser extent. At the same time the continuous growth of interest during the last 5–10 years in the use of oxallyl complexes in organic synthesis and metal complex catalysis makes it essential to survey the scattered literature data available in this field. The present review is the first survey of the employment of oxallyl complexes of transition metals in organic synthesis.

II. GENERAL CHARACTERISTICS OF OXALLYL COMPLEXES AND METHODS OF THEIR SYNTHESIS

Oxallyl complexes can exist in three forms: (a) as enolates having an oxygen–metal σ-bond (I); (b) as 2-oxoalkyl derivatives of metals having a carbon–metal σ-bond (II); (c) as π-oxallyl complexes (III):



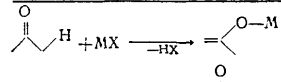
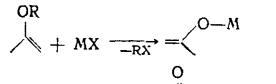
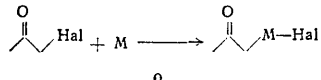
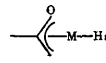
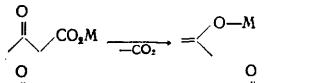
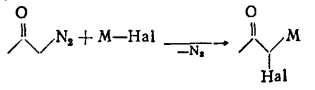
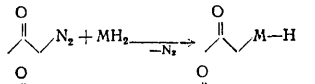
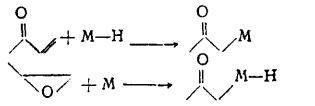
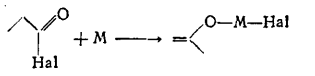
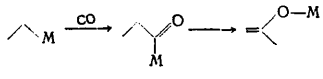
(I) (II) (III)

The existence of oxallyl complexes in a particular form depends on the nature of the metal itself and on the ligands linked to it. In solution there may be equilibrium between the above forms analogous to the equilibrium between the σ- and π-allyl structures of allyl complexes.[1] For example, the transition of the σ-oxallyl complex (II) of iron to the π-oxallyl form (III) under mild conditions has been described.[2] Since many oxallyl complexes are active intermediates in chemical reactions, they cannot be always isolated or identified in solution by spectroscopic methods. In this case their intermediate formation can be inferred from the structure of the reaction products or on the basis of kinetic data.

Metal oxallyl complexes can be obtained (usually *in situ*) by various methods which are summarised in Table 1.

Enol ethers and α-halogeno-, α-diazo, and β-carboxy-substituted and αβ-unsaturated carbonyl compounds are most often used to obtain oxallyl complexes. In addition, they can be obtained from epoxides, acid chlorides, and acyl or

Table 1. Methods of synthesis of oxallyl complexes.

Reaction	Refs.
	M=Fe [9*], Ti [10]
	M=Pd [3*, 4*, 5*], Pt [7, 8*], Au [11]
	M=Pd [6*]
	M=Pd [13], Fe [14*], Cu [14*], Sn [18], Ag [15*], Ti [16*]
	M=Pd [13], Sn [17, 18], Au [19]
	M=Pd [12]
R = $SiMe_3$, Ac, All	
	M=Fe [20, 21]
	M=Fe [2]
	M=Cu [22], Pd [23*]
	M=Os [25]
	M=Pd [24]
	M=Os [25]
	M=Fe [26, 27], Os [25], Mo [28, 29], W [29, 30*], Co [31–38]
	M=Ir [39, 40], Rh [80], Pd [40], Pt [40]
	M=Ta [41], Nb [41], Ti [42]
	M=Zr [43, 44, 47, 48], U [45], Th [45], Ta [46]

*The oxallyl complexes were detected by spectroscopic methods or their intermediate formation has been postulated.

Note. Here and in the other Tables the numerals in square brackets denote references (Ed. of Translation).

alkyl complexes of metals. The references quoted in Table 1 apply mainly to communications in which the isolation of oxallyl complexes has been reported and which contain data on their structure.

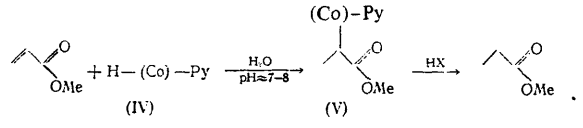
III. REACTIONS WITH PARTICIPATION OF OXALLYL COMPLEXES

1. Reactions Without the Formation of New C–C Bonds

(a) Hydrogenation

The hydride and other complexes of molybdenum,[28] iron,[49] cobalt,[32,50,51] ruthenium,[52] rhodium,[53] osmium,[25] and iridium[54] have been used as reagents or catalysts for the reduction of the double bond in αβ-unsaturated carbonyl compounds. As a rule, the reduction takes place under mild conditions (20–65°) at normal hydrogen pressure with a high yield of the saturated carbonyl compound.

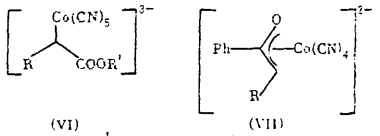
Metal oxallyl complexes are formed as intermediates in the hydrogenation reaction, which has been demonstrated, for example, in the reaction of Cp_2MOH_2 with esters of maleic, fumaric, and acrylic acids[28] and also in the reaction of the hydride derivative of cobaloxime (IV) with methyl acrylate:[51]



(IV) (V)

The cobalt complex (V) has been isolated and its thermal stability and chemical properties have been investigated.[51] Metal oxallyl complexes of this type are models of the active intermediates in enzyme reactions with participation of coenzyme B_{12}.[35]

In the presence of hydrogen the hydrogenation of αβ-unsaturated carbonyl compounds proceeds as a catalytic reaction. Cobalt carbonyls[55] or $Na_2Co(CN)_5$[31,51,56,57] are more often used as catalysts. The intermediate complexes (VI)[31] and (VII)[51] have been detected spectroscopically in these reactions:

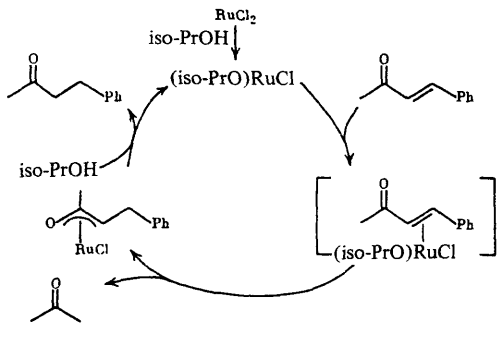


(VI) (VII)
R = H, Me; R' = H, Et R = Me, Et

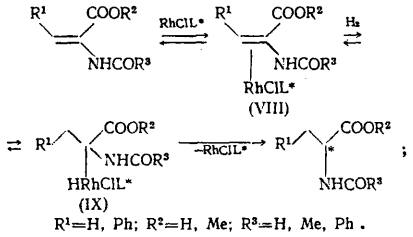
Ruthenium catalysts, for example $RuCl_2(PPh_3)_3$ at 180 °C in a primary or secondary alcohol, have also been used for the catalytic reduction of αβ-unsaturated carbonyl compounds (Scheme 1, the phosphine ligands are not shown). The catalytic yield of the hydrogenation products was 10^4–10^5%.[52]

The reduction of αβ-unsaturated ketones in the presence of the complexes $IrXL_n$ (X = Cl, I, ClO_4; L = o-phenanthroline, bipyridyl, or substituted bipyridyls) and KOH in ethanol proceeds analogously with a high catalytic yield.[54]

Scheme 1

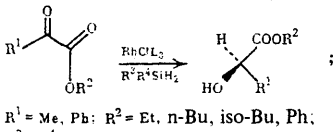


The reduction of prochiral olefins catalysed by rhodium complexes with chiral phosphine ligands takes place stereoselectively and leads to the formation of (*R*)- or (*S*)-substituted α-aminoacid esters with an optical purity of 85–89%.[53,58,59] The intermediate complexes (VIII) and (IX) have been isolated and characterised:[59]



R¹=H, Ph; R²=H, Me; R³=H, Me, Ph.

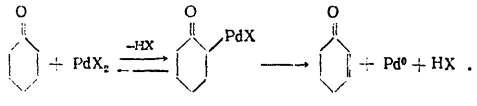
The reduction of α-ketoacids esters by silanes, catalysed by rhodium complexes with chiral ligands, for example, (*R*)-(+)-benzylmethylphenylphosphine, makes it possible to obtain (*R*)-lactates with an optical purity of 30–85%.[60] The mechanism of this reaction is probably similar to that quoted above:



R¹ = Me, Ph; R² = Et, n-Bu, iso-Bu, Ph;
R³ = R⁴ = Me, Et, Ph.

(b) Dehydrogenation

With the aid of the metal complexes, it is possible to achieve the αβ-dehydrogenation of carbonyl compounds. Palladium(II) compounds are as a rule used for this purpose: $PdCl_2$,[3,4,12] $PdCl_2(MeCN)_2$,[61] $PdCl_2(PhCN)_2$,[4,5,12] $PdCl_2$·$(PhCN)_2$–AgOTf,[62] $PdCl_2(PPh_3)_2$,[23] $Pd(OAC)_2$,[12,63,64] and $Pd(OAc)_2$–dppe.[65,67]† The dehydrogenation proceeds via a stage involving the formation of oxallyl complexes of palladium(II), which have been in many instances isolated and characterised:[12]

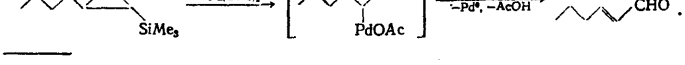


The reactivity of aliphatic and alicyclic ketones in the dehydrogenation reaction catalysed by $PdCl_2(PhCN)_2$ decreases in the sequence cyclohexanone > cyclopentanone > cyclo-octanone > 2-heptanone ≅ 4-heptanone, i.e. cyclic ketones are more reactive than aliphatic ones.[4] Dicyclic ketones are dehydrogenated less effectively than monocyclic ones.

The oxidative decarboxylation of salts of carboxylic β-keto-acids when these interact with $PdCl_2(PPh_3)_2$ also leads to αβ-unsaturated ketones.[23]

αβ-Unsaturated β-aminoketones have been synthesised by dehydrogenating β-aminoketones with the aid of $PdCl_2L_2$ (L = MeCN) in the presence of triethylamine in 50–95% yield.[61]

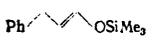
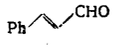
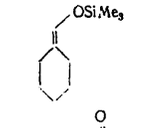
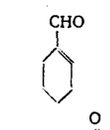
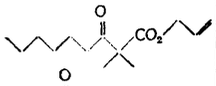
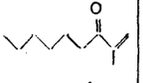
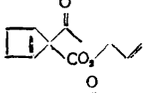
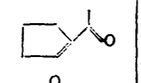
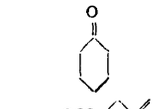
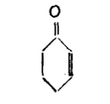
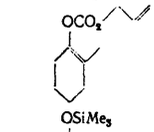
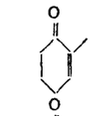
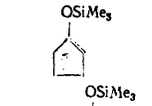
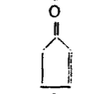
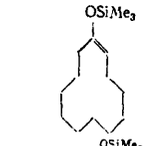
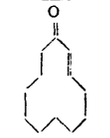
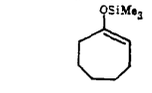
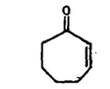
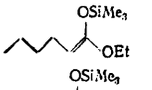
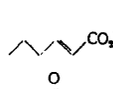
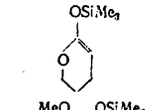
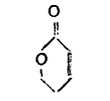
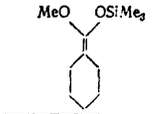
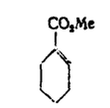
A somewhat unusual method of synthesis of αβ-unsaturated aldehydes and ketones from αβ-epoxysilanes has been proposed:[63]



†Tf = CF_3SO_2 and dppe = diphenylphosphinoethane.

Apart from the dehydrogenation of carbonyl compounds and their derivatives by a stoichiometric amount of palladium(II), catalytic versions of this reaction have been developed in recent years (Table 2). The simplest of these is the catalytic dehydrogenation of ketones with the aid of $Pd(OCOCF_3)_2/Cu(OCOCF_3)_2/O_2$ system.[6] The reaction can be carried out catalytically also in the presence of methylallyl carbonate, which behaves as an oxidant in relation to zerovalent palladium (Scheme 2).[67,68] Methylallyl carbonate is consumed in the course of this reaction with formation of CO_2 and propene. The silyl ethers of enols are usually employed in this catalytic system.[67]

Table 2. Catalytic dehydrogenation of carbonyl compounds and their derivatives in the presence of palladium complexes.*

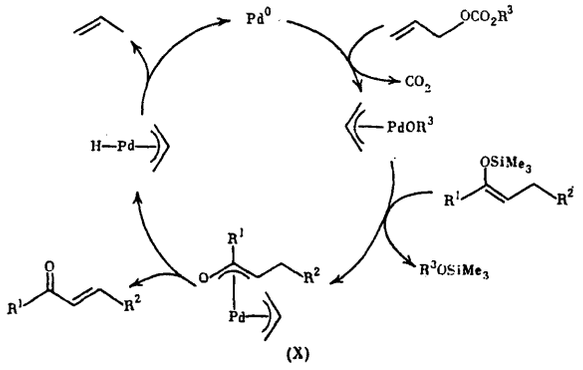
Initial compound	Catalytic system**	Solvent, temperature, °C	Reaction product	Yield w.r.t. initial compound, %	Refs.
	$Pd(OAc)_2$, dppe, AMC	MeCN, 80		80	[67]
	»	»		74	[67]
	$Pd(OAc)_2$, dppe	»		76	[66]
	»	dioxan, 100		57	[66]
	$Pd(OOCCF_3)_2$, $Cu(OOCCF_3)_2$, O_2	—, 20—25		85	[6]
	$Pd(OAc)_2$, dppe	MeCN, 80		98	[65]
	$Pd(OAc)_2$, dppe, AMC	PhCN, 190		69	[67]
	»	MeCN 80		78	[67]
	$Pd(OAc)_2$, dppe, AMC, $MeOSnBu_3$	»		70	[67]
	$Pd(OAc)_2$, AMC	»		79	[64]
	»	»		70	[64]
	»	PhCN, 190		75	[64]

*[substrate]/[Pd] = 10—100.
**AMC = allyl methyl carbonate.

Note. Numbers in square brackets denote references (Ed. of Translation).

The αβ-unsaturated ketones are formed via an analogous mechanism from enol acetates in the presence of methylallyl carbonate[69] and also from allylenol carbonates[67] and the allyl esters of carboxylic β-ketoacids.[66] In all these catalytic reactions the common key intermediates are mixed allyloxallyl complexes of palladium (X) (see Scheme 2).

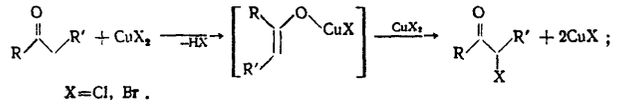
Scheme 2



(X)

(c) Halogenation

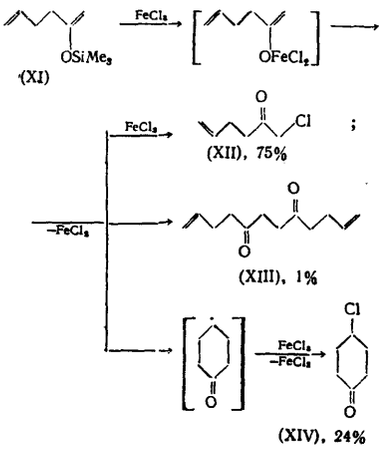
Copper(II) and iron(III) salts are used as a rule for the halogenation of carbonyl compounds (aldehydes, ketones, and esters). The α-halogenocarbonyl compound is formed on halogenation by copper salts probably as a result of the concerted reduction of two copper(II) ions to copper(I):[70]



X=Cl, Br.

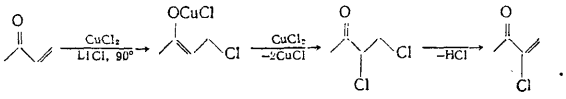
The relative reactivity of aliphatic ketones in the reaction with $CuCl_2$ varies in the sequence 2,2-dimethyl-3-pentanone (0.05) < 3-methyl-2-butanone (0.25) < 2-butanone (0.5) ≅ 2-hexanone (0.5) < acetone (1.0). The following sequence has been obtained for cycloalkanones: cyclobutanone (0.01) ≪ cyclopentanone (0.38) < 2-methylcyclohexanone (0.53) < 4-t-butylcyclohexanone (0.94) < cyclohexanone (1.0).[71]

α-Halogenoketones have also been obtained by the interaction of the silyl ethers of enols with $CuCl_2$ or $FeCl_3$ at 20 °C in dimethylformamide (DMF) or MeCN respectively (Table 3). In the presence of $FeCl_3$, the diketone (XIII) and chlorocyclohexanone (XIV) are also formed from the ether (XI) in addition to the main product (XII), which may indicate a cryptoradical mechanism of the chlorination reaction:[14]



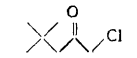
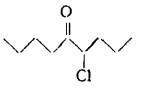
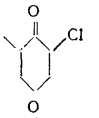
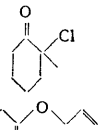
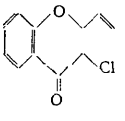
(XIV), 24%

The halogenation of αβ-unsaturated carbonyl compounds also proceeds with retention of the double bond in accordance with the following postulated scheme:[70]



The halogenation of acetylenecarboxylic acid esters with copper chloride or bromide leads to esters of αβ-dihalogeno-substituted αβ-unsaturated acids.[72]

Table 3. The synthesis of α-chloroketones from the corresponding silyl ethers.[14]*

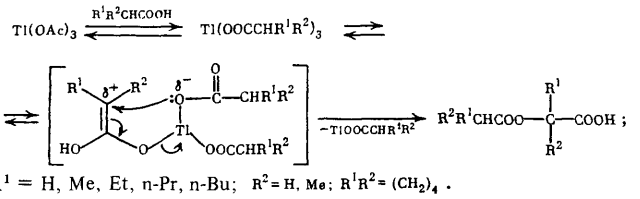
Metal chloride	α-Chloroketone	Yield, %
$CuCl_2$		65
$CuCl_2$		70
$CuCl_2$		58
$CuCl_2$		58
$FeCl_3$		76
$CuCl_2$		61

*Solvent—DMF ($CuCl_2$) or MeCN ($FeCl_3$); molar ratio ether/salt = 1:(2–3) for $CuCl_2$ and 1:(4–5) for $FeCl_3$; reaction temperature 20 °C.

(d) Oxidation

The oxidation of carbonyl compounds by metal salts can also proceed via two pathways: with formation of compounds having a functional group in the α-position or oxidative cleavage products.

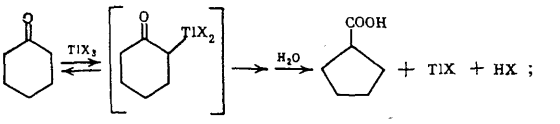
When thallium(III) carboxylates are heated in an excess of carboxylic acid (120–160 °C), α-acetoxyacids are formed[73] in 65–96% yield, thallium(III) being reduced under these conditions to thallium(I). A reaction mechanism involving the formation of an enolate complex has been proposed:



R^1 = H, Me, Et, n-Pr, n-Bu; R^2 = H, Me; $R^1R^2 = (CH_2)_4$.

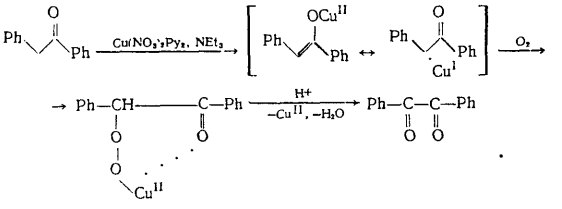
Branched carboxylic acids are oxidised by thallium(III) acetate less effectively than acids having the straight-chain structure. The reactions involving the use of mercury[74] and lead[74] carboxylates proceed analogously.

The oxidation of cyclohexanone by thallium(III) ions leads to the formation of cyclopentanecarboxylic acid:[75]

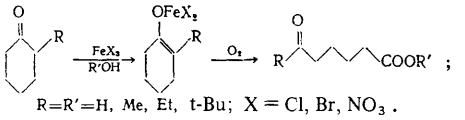


X = OAc.

When certain ketones and esters are oxidised by oxygen in the presence of catalysts (pyridinecopper complexes), α-diketones or α-ketoacid esters are formed in 40–70% yield:[76–78]



The alkyl esters of carboxylic 6-ketoacids have been obtained in 65–95% yield by oxidising 2-alkylcyclohexanones or the acetates of the corresponding enols with oxygen in an alcohol–benzene medium at 60 °C, the reaction being catalysed by iron(III) salts [ketone/Fe(III) = 20–50]. The reaction also probably takes place via the intermediate formation of the oxallyliron(III) complex:[79]

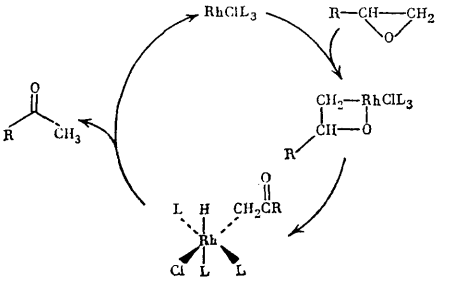


R=R′=H, Me, Et, t-Bu; X = Cl, Br, NO_3.

(e) Isomerisation of Epoxides and Other Compounds

1,2-Epoxides are isomerised to carbonyl compounds in the presence of palladium, rhodium, or ruthenium catalysts (Table 4). The mechanism of the isomerisation reaction (Scheme 3) has been investigated in relation to catalysis by rhodium complexes.[80,81] The oxallyl complex (XV; R = Me or Ph; L = PMe_3), formed as an intermediate as a result of the oxidative addition of the epoxide to $ClRhL_3$ and subsequent transfer of the β-hydrogen atom, has been isolated and characterised.[80] The rate of isomerisation of *trans*-stilbene oxide to benzyl phenyl ketone, catalysed by the complexes $(p\text{-}XC_6H_4P)_3RhCl$, increases in the following sequence of substituents X: Cl < H < Me < OMe.

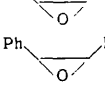
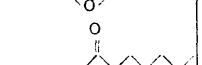
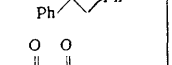
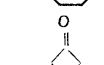
Scheme 3



The phosphine complexes of ruthenium[82] are less effective isomerisation catalysts than the rhodium complexes.

The isomerisation of α-ketoepoxides catalysed by $Pd(PPh_3)_4$ leads to 1,3-diketones,[83] while the isomerisation of the monoepoxides of 1,2-dienes using the same catalysts affords either substituted allyl alcohols or βγ-unsaturated carbonyl compound, depending on the structure of the epoxide.[84]

Table 4. The synthesis of carbonyl compounds and alcohols by the catalytic isomerisation of epoxides.*

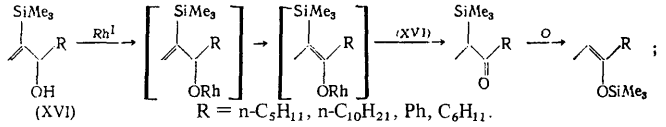
Epoxide	Catalyst	Solvent, temperature, °C	Product	Yield of product, moles per mole of complex	Refs.
	$RhCl(PMe_3)_2$	—, 70		85	[80]
	»	—, 25		12	[80]
	$RhCl(PPh_3)_3$	1-methylnaphthalene, 210		43	[81]
	$Pd(PPh_3)_4$	toluene, 140		16	[83]
	»	toluene, 80		30	[83]
	»	toluene, 140		10,4	[83]
	»	Et_2O, 0		150	[84]
	»	benzene, 110		135	[84]
	»	Et_2O, 60		800	[84]
	»	THF, 50		180	[84]

*In the examples quoted, the degree of conversion of the epoxide was ~85–95% and the yield of product with respect to the epoxide which has reacted was ~100%.

Note. Numbers in square brackets denote references (Ed. of Translation).

The isomerisation of phenyl-substituted epoxides in the presence of $Fe(CO)_5$ is a stoichiometric reaction and takes place only under the influence of UV irradiation.[85]

The isomerisation of trimethylsilyl-substituted allyl alcohols (XVI), catalysed by $HRh(CO)(PPh_3)_3$ in the presence of a small amount of α-trimethylsilylketone (1 mole per mole of the complex) at 105 °C in benzene, leads to trimethylsilyl enol ethers:[86]



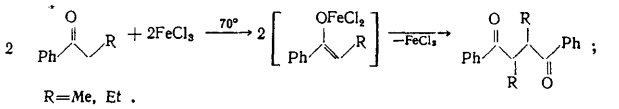
(XVI)

R = n-C_5H_{11}, n-$C_{10}H_{21}$, Ph, C_6H_{11}.

2. Reactions with Formation of New C=C Bonds

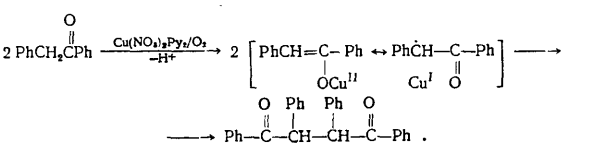
(a) Dimerisation of Carbonyl Compounds and Their Derivatives

One-electron oxidants, namely iron(III) and copper(II) salts, $TiCl_4$, or Ag_2O, are used for the dehydrodimerisation of carbonyl compounds. Thus the dehydrodimerisation of alkyl aryl ketones in the presence of $FeCl_3$ leads to substituted 1,4-diketones in 50–85% yield relative to the oxidant:[87]

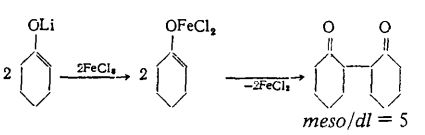


R=Me, Et .

1,4-Diketones are formed analogously from 2-butanone and 2-methyl-4-pentanone, but in a smaller yield (25–35%), when acted upon by the pyridine complex of copper(II) in the presence of PPh_3 in methanol at 40 °C.[77] The dehydrodimerisation of deoxybenzoin in the presence of pyridine-copper complex and oxygen proceeds as a catalytic reaction:[76]



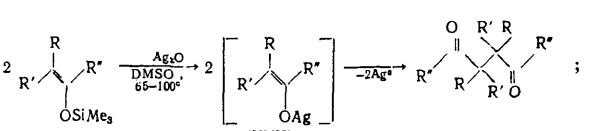
Lithium enolates[88,90] and silyl ethers of enols[91] have also been used as the starting compounds for the synthesis of 1,4-diketones. For example, the oxidative dimerisation of the lithium enolate derived from cyclohexanone, catalysed by $FeCl_3$, leads to a mixture of diastereoisomeric diketones with the *meso*-isomer predominating:[88]



meso/*dl* = 5

The yield of the 1,4-diketone obtained from the lithium t-butyl methyl ketone enolate is also influenced by the nature of the anion in the copper salt:[89] $CuCl_2$ (92) > $CuBr_2$ (64) > $Cu(acac)_2$ (60) > $Cu(OAc)_2$ (24).

It is believed that the reaction of silyl ethers of enols with Ag_2O proceeds with the intermediate formation of the silver enolate (XVII):[15]



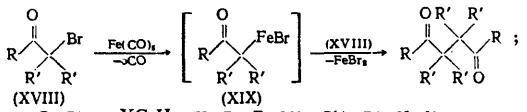
(XVII)

R=R′=H, Me; R″=Me, Et, iso-Pr, Ph; R, R′=$(-CH_2-)_n$; n=3, 10 .

The yield of the 1,4-diketone (mixture of *meso*- and *dl*-diastereoisomers) is 40–80% and diminishes with increase of the number and bulk of the substituents at the double bond of the silyl enol ether.

The mechanism of the reaction of the enolate (XVII) has not been considered, but it has been shown[92] that n-$C_4H_9Ag(PPh_3)$ decomposes with formation of n-octane probably via a homolytic mechanism in the coordination sphere of silver ions (via an intermediate dinuclear complex).

1,4-Diketones can be obtained by the reductive dimerisation of α-halogenoketones. When α-bromoketones (XVIII) were allowed to interact with $Fe(CO)_5$ in dimethoxyethane at 95–100 °C, 1,4-diketones were synthesised in 30–65% yield, depending on the structure of the substituents:[2]

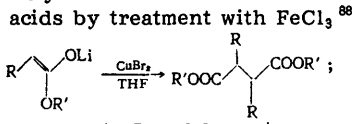


(XVIII) (XIX)

R=Ph, p-XC_6H_4 (X=Br, F, OMe, Ph); R′=H, Me.

The intermediate oxallyl iron complex (XIX, $R = p$-PhC_6H_4, $R' = H$) has been isolated and characterised.

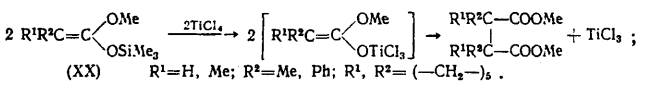
The esters of substituted succinic acids have been obtained in 50–85% yield from the lithium enolates derived from carboxylic acids by treatment with $FeCl_3$ [88] and $CuBr_2$: [93]



R=H, Me, Ph, iso-Pr, n-C_5H_{11}; R′ = Et, t-Bu.

The mechanism of this reaction is apparently analogous to that of the dimerisation of ketones and their derivatives.

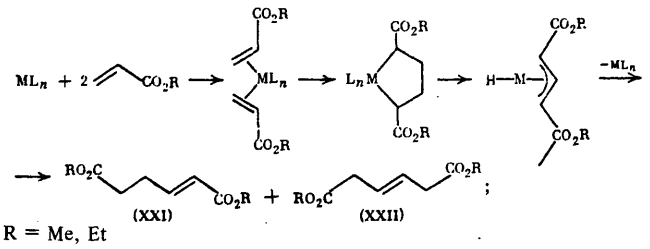
Carboxylic acid derivatives, namely the silyl esters (XX), are also converted into dimeric products—substituted succinic esters (mixture of *meso*- and *dl*-diastereoisomers)—on interaction with $TiCl_4$. The yield is 75–80%.[16] These esters are obtained in a low yield in reactions with copper(II) and iron(III) halides:[16]



(XX) R¹=H, Me; R²=Me, Ph; R¹, R²=$(-CH_2-)_5$.

The "tail to tail" dimerisation of αβ-unsaturated carbonyl compounds is catalysed by palladium and rhodium complexes.[94,95] The main product of the dimerisation of methyl acrylate in the presence of $[(C_2H_4)_2RhCl]_2$ or $PdCl_2(PhCN)_2$ catalysts and Lewis acids ($FeCl_3$, $AgBF_4$, and $AgPF_6$) is the unsaturated ester (XXI) containing 90% of the *trans*-isomer [(XXI)/(XXII) = 9] (Scheme 5).

Scheme 5



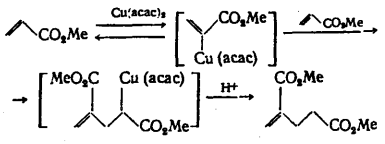
(XXI) (XXII)

R = Me, Et

The number of catalytic cycles in the presence of the rhodium catalyst at 75 °C reaches 280.

Copper(II) acetylacetonate and CuO catalyse the "head to tail" dimerisation of methyl acrylate in the presence of t-butyl isocyanide in t-butyl alcohol (olefin/Cu = 50). The catalytic yield of the dimerisation product is 50–550% (Scheme 6).[96]

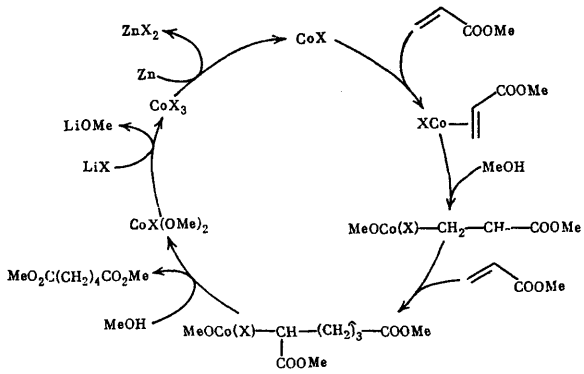
Scheme 6



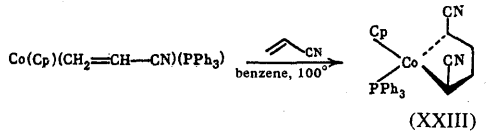
Saturated "tail to tail" dimers have been obtained (2–11 moles per mole of the catalyst) by the hydrodimerisation of methyl vinyl ketone and acrylate esters in methanol on treatment with metallic zinc in the presence of $[Co(bipy)_3]ClO_4$ or $CoBr(PPh_3)_3$.[97,98] The hydrodimerisation of methyl acrylate catalysed by cobalt complexes leads to the dimethyl ester of adipic acid in 25–90% yield relative to the initial acrylate and 50–700% yield relative to the catalyst,[99] the yield of the ester depending on the nature of the anion in the complex $CoX(PPh_3)_3$ and increasing in the following sequence of substituents X: Cl < Br < I.

The proposed reaction mechanism is presented in Scheme 7.[99]

Scheme 7



In the given instance one probably cannot rule out also a mechanism similar to that discussed above for the dimerisation of acrylates in the presence of palladium and rhodium catalysts (see Scheme 5).[95] This is indicated, in particular, by the fact that the intermediate complex (XXIII) (in the form of two geometrical isomers) was isolated in the presence of cobalt catalysts:[100]

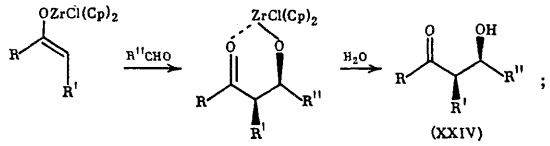


(XXIII)

(b) The Aldol and Crotonic Condensations and Similar Reactions

The use of transition metal complexes makes it possible to achieve the stereo-selective synthesis of aldols from carbonyl compounds and their derivatives.

The zirconium enolates derived from ketones and acid esters and amides, obtained from $ZrCl_2(Cp)_2$ and the corresponding lithium enolates, react with aliphatic and aromatic aldehydes at −78 °C in tetrahydrofuran (THF)[101,102] with formation of more than 90% of the *erythro*-aldol (XXIV):



(XXIV)

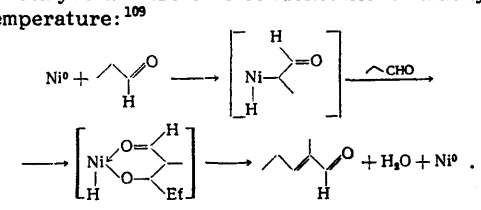
R = OMe, O-t-Bu, S-t-Bu, $N(CH_2)_4$, N(iso-Pr)$_2$, Et,
R′ = Me; R, R′ = $(-CH_2-)_3$, $(-CH_2-)_4$; R″ = n-Pr, n-Bu, Ph.

The greatest stereoselectivity (95–99%) has been observed for the reaction of zirconium enolates obtained from acid amides with aldehydes having nitrogen-containing heterocyclic substituents.[103] The hydrolysis of the amides yielded the corresponding carboxylic *erythro*-β-hydroxy acids.

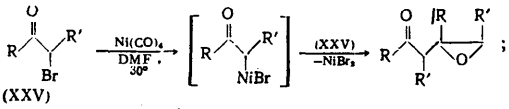
Titanium(IV),[42,104] mercury,[105] and tin[106] enolates react analogously in the presence of $BF_3.OEt_2$ with aliphatic and aromatic aldehydes, forming 70–90% of the *erythro*-aldol. The reaction can also be carried out catalytically using the silyl ethers of enols, for example, when the latter interact with α-alkoxyaldehydes in the presence of $TiCl_4$.[107] The

reaction of silyl ethers of enols with optically active α-keto-acid esters in the presence of $TiCl_4$ leads to the formation of aldols with two optically active centres.[108] The extent of the asymmetric induction (35–70%) is in this case much higher than in the case where organomagnesium compounds are employed.

Complexes of zerovalent nickel, for example (bipy)Ni.$(PPh_3)_2$, catalyse the crotonic condensation of aldehydes at room temperature:[109]



The aldol condensation of α-bromoketones in the presence of $Ni(CO)_4$ leads to substituted βγ-epoxyketones in 50–85% yield:[110]



(XXV)

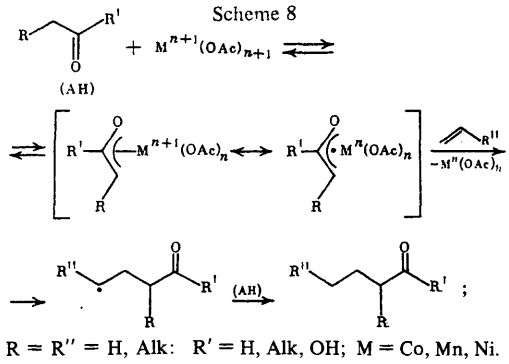
R = Me, Et, t-Bu; R′ = H, Me.

This is the simplest and most effective of the existing methods of synthesis of βγ-epoxyketones.

(c) Alkylation of Carbonyl Compounds

The α-alkylation of aldehydes, ketones, and carboxylic acids by olefins has been achieved on treatment with $Mn(OAc)_3$[111,112] or the redox systems $Mn(OAc)_2/O_2$[113] and $Co(OAc)_2/O_2$[113] (Table 5). The study of the characteristics and kinetics of the alkylation of aldehydes led to a catalytic mechanism of the reaction involving the intermediate formation of oxallyl complexes in which the oxallyl ligand has a radical character (scheme 8):[114]

Scheme 8

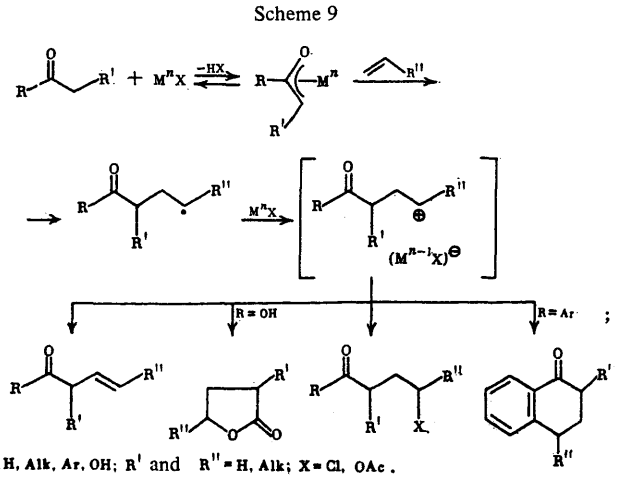


R = R″ = H, Alk: R′ = H, Alk, OH; M = Co, Mn, Ni.

In terms of their selectivity in the α-alkylation reaction, the catalysts can be arranged in the following sequence:[113] Co(II) > Mn(II) ≅ Ni(II) > Ce(III) > Cr(III).

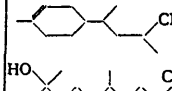
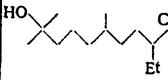
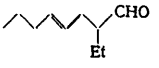
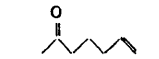
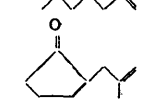
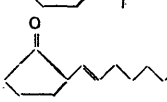
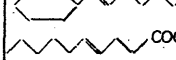
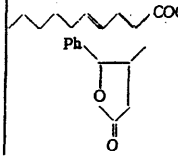
The reaction involving the homolytic *oxidative addition* of aldehydes, ketones, and carboxylic acids to multiple bonds is important for synthetic purposes. Its difference from the alkylation reaction considered above consists in the oxidation of the intermediate adduct-radical to a carbonium ion intermediate. Depending on its structure and the reaction conditions, the latter is capable of reacting via different pathways, for example, β-elimination with formation of an ethylenic bond, of cyclising to a substituted lactone,[118–121] tetralone, and similar compounds,[122] or of interacting with external nucleophiles to form products substituted by functional groups in the γ-position[111,115,119,123] (Scheme 9):

Scheme 9



R = H, Alk, Ar, OH; R′ and R″ = H, Alk; X = Cl, OAc.

Table 5. The synthesis of α-alkyl-substituted carbonyl compounds.

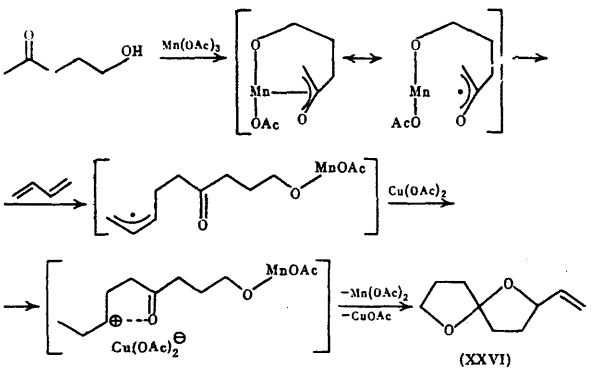
Carbonyl compound	Unsaturated compound	Initiating system*	t, °C	α-Alkylation product	Yield %	Refs.
EtCHO	dipentene	$Co(II)/O_2$	50		67	[113]
PrCHO	7-hydroxy-3,7-dimethyl-oct-1-ene	»	70		53	[113]
PrCHO	hex-1-ene	Mn(III)/Cu(II)	60		40	[111]
Acetone	ethylene	»	80–100		70	[115]
Cyclo-pentanone	isobutene	»	40		70	[112]
»	hept-1-yne	Mn(III)	80		52	[112]
AcOH	oct-1-ene	Mn(III)/Cu(II)	120		63	[116]
»	*trans*-β-methyl-styrene	Mn(III)	135		79	[117]

*Metal acetates were used.

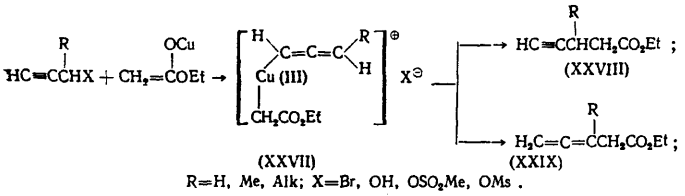
Note. Numbers in square brackets denote references (Ed. of Translation).

Other pathways are also possible in this reaction. Thus the vinyl-substituted spiroketal (XXVI)—the direct precursor of chalcogran, which is a pheromone of the conifer bark beetle,[124] has been obtained by the reaction of acetylpropyl alcohol with butadiene catalysed by the $Mn(OAc)_3/Cu.(OAc)_2$ system (Scheme 10). Vinyl-substituted 2,8-dioxa-*cis*-bicyclo[3.3.0]octane is formed together with the spiroketal (XXVI) in this reaction.[124] The reaction of acetone with butadiene proceeds analogously:[124]

Scheme 10



(XXVI)



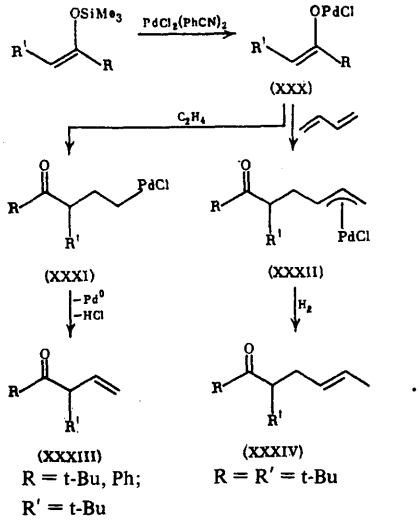
(XXVII) (XXIX)

R=H, Me, Alk; X=Br, OH, OSO_2Me, OMs .

The reactions of the oxallyl complexes of copper(I), obtained from the corresponding lithium enolates, with propargyl alcohol and its derivatives result in the formation of the substituted allenes (XXIX) in 45–70% yield. The acetylenic compound (XXVIII) is formed as a side product in this reaction with the ratio (XXIX)/(XXVIII) = 10–20 : 1. The use of lithium enolate in the above reaction leads to only the acetylenic compound (XXVIII). The authors explain the difference by the fact that, in the case where copper enolates are used, the unstable complex (XXVII) is formed as an intermediate.[125]

Palladium(II) complexes have been used in another group of reactions of carbonyl compounds with olefins and dienes. In the presence of $PdCl_2(PhCN)_2$, the silyl ethers of enols react with ethylene and butadiene.[13] The reaction proceeds via the intermediate formation of the palladium enolate (XXX). The complexes (XXX) are isolated in a dimeric form. The reaction of the complex (XXX) with ethylene at 50 °C and a pressure of 50 atm leads to the βγ-unsaturated ketone (XXIII) in 60–75% yield, while the reaction with butadiene leads to the allyl complex (XXXII), whose reduction with hydrogen afforded the γδ-unsaturated ketone (XXXIV) in 65-90% yield (Scheme 11):

Scheme 11



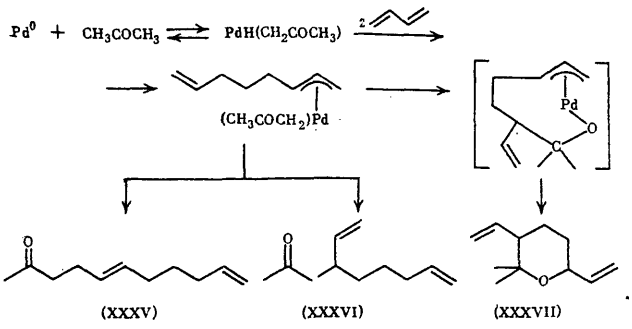
(XXXIII) (XXXIV)

R = t-Bu, Ph; R = R′ = t-Bu

R′ = t-Bu

Palladium complexes, for example $Pd(PEt_3)_4$, also catalyse the addition of two butadiene molecules to acetone[126] (Scheme 12).

Scheme 12



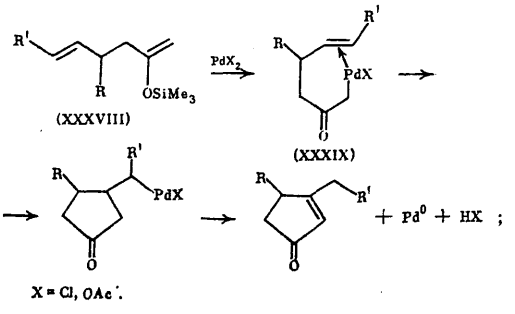
(XXXV) (XXXVI) (XXXVII)

The reaction results in the formation of the isomeric unsaturated ketones (XXXV) (*trans* : *cis* = 10) and (XXXVI) in proportions of 10 : 1 in 11% yield and also 2,2-dimethyl-3,6-divinyltetrahydropyran (XXXVII) (*cis* : *trans* = 3) in 20% yield. The comparatively low yields of the products (XXXV)–(XXXVII) are associated with the side reaction involving the catalytic dimerisation of butadiene to octa-1,3,7-triene. When the trimethylphosphine ligand is replaced by the triphenylphosphine ligand in the initial palladium complex, only the dimerisation of butadiene takes place.

The reaction of cycloalkanones with butadiene in the presence of a palladium catalyst[127] leads to 2-alkadienylcycloalkanones, whose structure is analogous to that of the ketones (XXXV) and (XXXVI) (the ketone with the unbranched substituent predominates). In terms of their reactivity, the cycloalkanones can be arranged in the following sequence: $C_5 > C_8 \cong C_6 > C_7$. The yield of the addition products is 5–30% relative to the initial compound and (3–25) × 10^3% relative to the catalyst.

The αβ-unsaturated cycloalkanones have been obtained by cyclising the unsaturated silyl enol ethers (XXXVIII) in the presence of palladium(II) compounds[128,129] (Scheme 12a).

Scheme 12a



(XXXVIII) (XXXIX)

X = Cl, OAc.

The intermediate oxallyl complexes (XXXIX, R = Ph, R′ = H; RR′ = $(-CH_2-)_{3-5}$] have a dimeric structure. They have been isolated and characterised by physicochemical methods.[129]

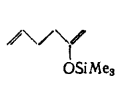
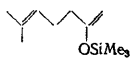
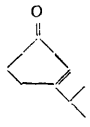
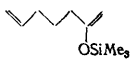
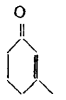
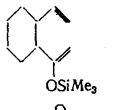
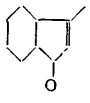
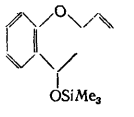
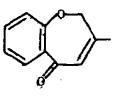
Table 6 presents the known examples of the cyclisation of unsaturated silyl enol ethers catalysed by $Pd(OAc)_2$ in acetonitrile.

(d) Arylation of Carbonyl Compounds

The reactions of acetone with aromatic and heteroaromatic compounds catalysed by $Mn(OAc)_3$ make it possible to introduce the acetonyl group into the aromatic ring under comparatively mild conditions (50–80 °C).[130,131] The reactions

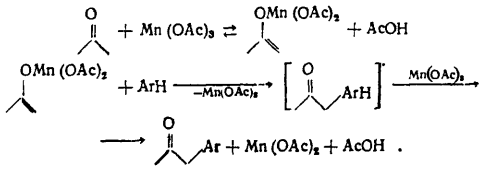
with naphthalene, furan, and thiophen proceed exclusively at the α-carbon atom of the aromatic ring. The yield of 3-aryl-2-propanones is 40–95% with respect to the oxidant.

Table 6. The synthesis of αβ-unsaturated cyclic ketones.[129]*

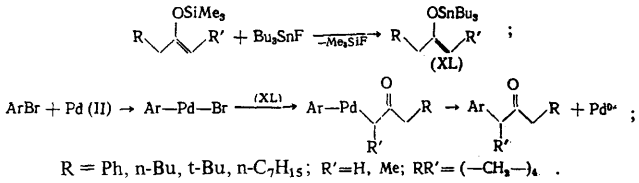
Silyl enol ether	Ketone	Yield, %
		87
		40**
		36
		99
		25

*$Pd(OAc)_2$/(silyl enol ether) = 1:1, MeCN, 20 °C.
**Oxidant—$PdCl_2(PhCN)_2$.

In monosubstituted benzenes substitution takes place predominantly in the *ortho*-position in the benzene ring, electron-donating substituents in the ring facilitating the reaction.[131] The reactivities of aromatic compounds in the reactions with acetone decrease in the following sequence: sylvan [α-methyfuran] > furan ≅ naphthalene > thiophen > anisole > benzene ≅ chlorobenzene > benzonitrile.[132] The following reaction mechanism has been proposed:

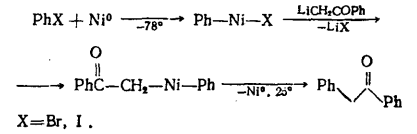


The α-arylation of aliphatic and cyclic ketones is achieved by the interaction of trimethylsilyl ethers of enols or enol acetates with ArBr (Ar = Ph or substituted phenyl) in the presence of Bu_3SnF [133] or Bu_3SnOMe [134] and $PdCl_2[P(o\text{-}MeC_6H_4)_3]_2$ (ArBr/Pd = 30–100) as the catalyst at 80–100 °C in benzene or toluene. The yield of α-aryl-substituted ketones is 30–100%:



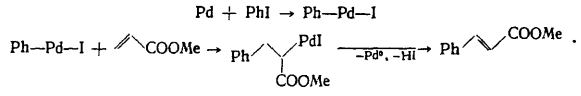
R = Ph, n-Bu, t-Bu, $n\text{-}C_7H_{15}$; R′=H, Me; RR′=$(-CH_2-)_4$.

α-Aryl-substituted carbonyl compounds have also been obtained by the reaction of phenyl halides with $LiCH_2COPh$ in the presence of $Ni(PPh_3)_4$ [PhX/Ni(0) = 4].[135] The mechanism of this reaction is similar to that quoted above:



X=Br, I.

β-Aryl substituted carbonyl compounds can be obtained by the reaction of aryl halides with αβ-unsaturated carbonyl compounds. Thus the reaction of iodobenzene with methyl acrylate (PhI/Pd = 30), catalysed by metallic palladium (palladium black), at 125 °C in acetic acid in the presence of sodium acetate leads to the formation of methyl cinnamate in accordance with the following suggested mechanism:[136]



When $Pd(PPh_3)_4$ is used as the catalyst, bromobenzene and substituted aryl bromide also enter into this reaction.[137]

The reactions of benzene with α-substituted chalcones in the presence of $Pd(OAc)_2$ (chalcone/Pd = 1–15) in acetic acid lead to saturated or unsaturated ββ-diphenyl-substituted ketones, depending on the structure of the chalcones[138] (Table 7):

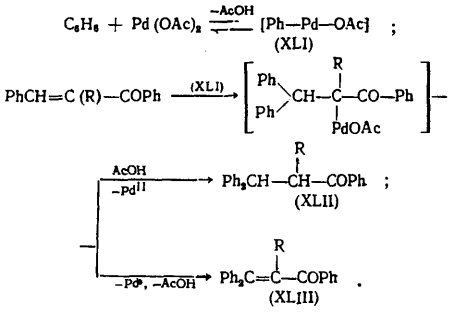


Table 7. The yields (%) of the products of the reactions of benzene with chalcones in the presence of $Pd(OAc)_2$*[138]

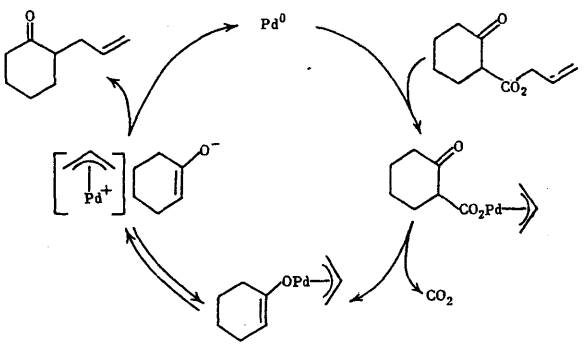
Product	R					
	H	Ph	COPh	NO_2	CO_2Et	CH_2Ph
(XLII)	25	—	52	20	12	—
(XLIII)	75	46	8	—	56	66

*[chalcone]/[Pd] = 1:1.

(e) α-Allylation of Carbonyl Compounds

A convenient method for the introduction of alkenyl groups into the α-position in carbonyl compounds is based on the use of mixed allyloxallyl complexes of palladium(II) (XLIV) which are formed, for example, from allyl β-ketocarboxylates (Scheme 13).[23]

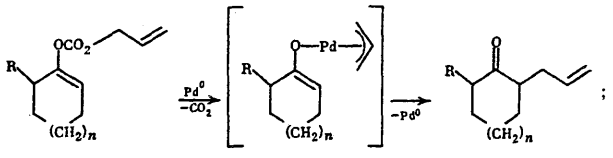
Scheme 13



(XLIV)

In the presence of $Pd(PPh_3)_4$ (ester/Pd = 20), α-allyl-substituted alkanones and cycloalkanones were obtained at room temperature in 60–95% yield.

α-Allyl-substituted carbonyl compounds are also synthesised from allyl carbonates at 0 °C in dimethoxyethane:[139]

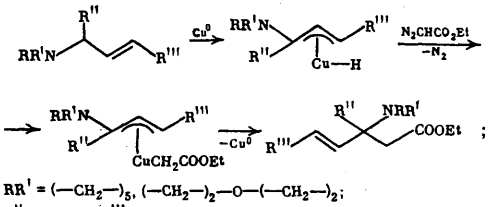


R = H, Me; $n = 0, 1$.

The complexes $Ni[P(OEt)_3]_4$, $RhH(PPh_3)_4$, and $Mo(CO)_6$ can be used as catalysts of this reaction in addition to $Pd(PPh_3)_4$.[140] However, more severe conditions are required (60–110 °C).

Apart from the two reactions examined above, the syntheses of α-allylalkanones and α-allylcycloalkanones by the reaction of silyl enol ethers[64,141] or enol acetates[142] with allyl methyl carbonate in the presence of $Pd(dppe)_2$ and also by the reaction of allyl acetates with tributyltin enolate in the presence of $Pd(PPh_3)_4$ [143] at 20–80 °C in dioxan or THF have been described.

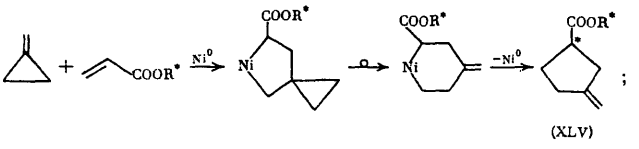
The reactions of ethyl diazoacetate with allylamines (allylamine/metal = 40), catalysed by the $Cu(acac)_2/AlEt_3$ and $Rh_2(OAc)_4/AlEt_3$ systems in the presence of PEt_3, PBu_3, or pyridine in benzene at 20 °C, lead to esters of β-amino-β-vinyl-substituted carboxylic acids in 20–60% yield.[144] The reaction probably proceeds via the following mechanism:



$RR' = (-CH_2-)_5$, $(-CH_2-)_2-O-(-CH_2-)_2$;
$R'' = H$, Me; $R''' = H$, Me, C_5H_9 .

(f) Cycloaddition to αβ-Unsaturated Carbonyl Compounds

Zerovalent nickel complexes catalyse the cycloaddition of strained molecules, for example, methylenecyclopropane and its derivatives [initial compound/Ni(0) = 30] to αβ-unsaturated ketones and acrylates with formation of substituted methylene-cyclopentanes in 60–90% yield.[145] The reaction is stereoselective. Thus esters of 3-methylenecyclopentanecarboxylic acid (XLV) having two chiral centres have been obtained from methylenecyclopropane and optically active acrylate esters in the presence of Ni(cyclo-octadiene)$_2$ (ester/Ni = 100) at −20–+40 °C. The degree of the asymmetric induction for the second chiral centre is 25–65%.[146]

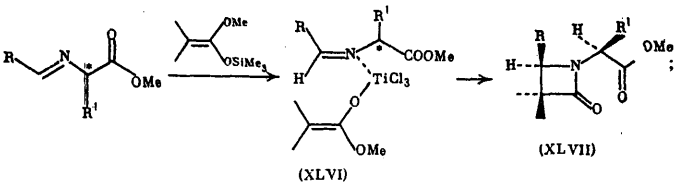


(XLV)

R* = (−)-bornyl, (−)-menthyl, (−)-8-phenylmenthyl.

The cycloaddition of bicyclo[2.1.0]pentane in methyl acrylate, dimethyl maleate, and dimethyl fumarate, catalysed by $Ni(CH_2{=}CHCN)_2$, probably proceeds via a similar mechanism.[147,148]

The reaction of the *O*-trimethylsilyl derivatives obtained from methyl isobutyrate with the Schiff bases obtained from aldehydes and chiral α-aminoethers in the presence of $TiCl_4$ leads to the formation of β-lactams with high regio- and stereo-selectivities.[149,150] Its mechanism involves the formation of the titanium(IV) enolate (XLVI) (detected by spectroscopic methods), which undergoes intramolecular cyclisation with formation of the β-lactam (XLVII), having the (*S*,*R*)-configuration to the extent of 60–99%:

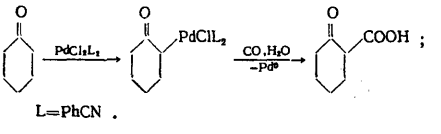


(XLVI) (XLVII)

R = Et, iso-Pr, iso-Bu; R′ = Me, iso-Pr, CH_2Ph, CH_2COOMe.

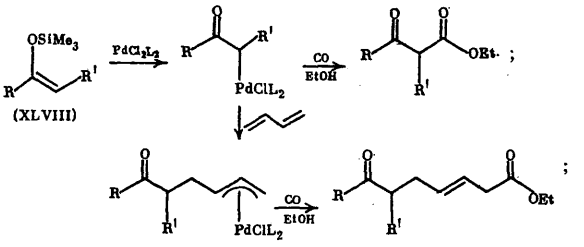
(g) Reactions with Participation of Carbon Monoxide

When the oxallyl complexes of palladium are acted upon by carbon monoxide, carboxylic β-ketoacids are formed in 40–75% yield:[4]



L=PhCN .

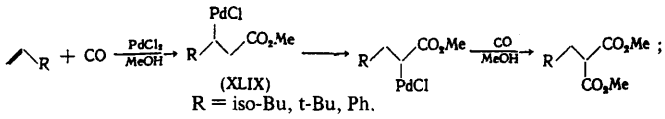
The esters of carboxylic β-ketoacids have been synthesised in 85–100% yield by carbonylating in an alcoholic medium the palladium complexes obtained from silyl enol ethers (XLVIII) (50 °C, 50 atm CO pressure); in the presence of butadiene, the above reaction leads to esters of unsaturated ketoacids:[13]



(XLVIII)

L = PhCN; R = t-Bu, Ph; R′ = t-Bu.

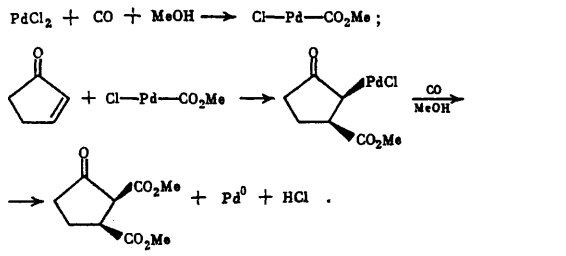
The esters of alkylmalonic acids can be obtained by the carbonylation of alkenes, catalysed by $PdCl_2$, in the presence of an excess of $CuCl_2$,[151] probably via a medium involving the rearrangement of the organopalladium intermediate (XLIX):



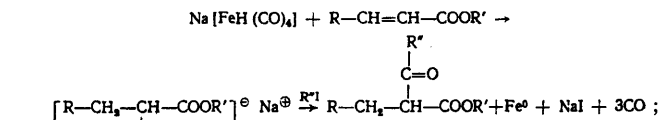
(XLIX)

R = iso-Bu, t-Bu, Ph.

The carbonylation of αβ-unsaturated ketones, catalysed by the $PdCl_2/CuCl_2$ system (ketone/Pd = 10–50, 20 °C, 3 atm CO pressure), leads to esters of substituted succinic acids.[152] The reaction with cyclopentenone results in the 99% yield of the ester of *cis*-3-oxocyclopentane-1,2-dicarboxylic acid:



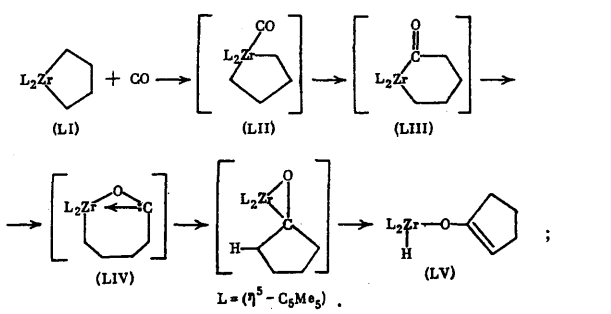
The hydroacylation of esters of αβ-unsaturated carboxylic acids takes place in THF at 20–50 °C with participation of $Na[FeH(CO)_4]$ (stoichiometric amount) and allyl iodide; the yield of β-ketoacid esters is 50–80%.[153] The intermediate oxallyl complex (L, R = H, R′ = Me) was isolated and characterised:



(L)

R=H, Me; R′=R″=Me, Et .

The carbonylation of alkylzirconium complexes leads to the formation of derivatives of carbonyl compounds in high yields (80–95%).[43,154,155] Thus the zirconium complex (LI) readily combines with CO at 25 °C to form the white crystalline enolate (LV), which is quantitatively converted into cyclopentanone on treatment with HCl.[43] The reaction probably proceeds via the successive formation of the carbonyl intermediates (LII), the acyl intermediate (LIII), and the carbenoid intermediates (LIV):

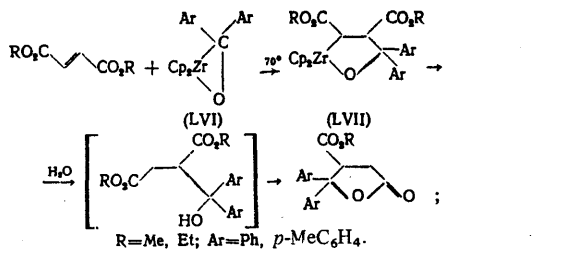


(LI) (LII) (LIII) (LIV) (LV)

L = (η^5-C_5Me_5) .

(h) Other Reactions

γγ-Diarylbutyrolactones have been synthesised in 80–85% yield by the reaction of maleate and fumarate esters with organozirconium compounds (LVI):

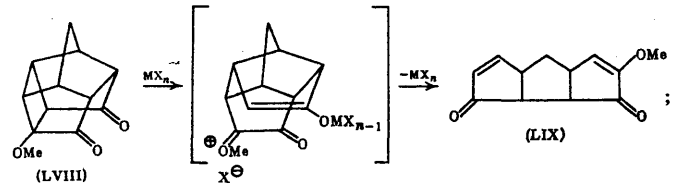


(LVI) (LVII)

R=Me, Et; Ar=Ph, *p*-MeC_6H_4.

The intermediate oxallyl complexes (LVII) have been detected by ^1H NMR.

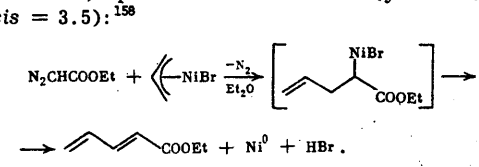
The unsaturated diketone (LIX) has been obtained in 65–70% yield as a result of the catalytic decyclisation of the polycyclic ketone (LVIII) at 40 °C in benzene or $CHCl_3$ (ketone/MX_n = 10):[157]



(LVIII) (LIX)

$MX_n = TiCl_4, PdCl_2$.

The reaction of ethyl diazoacetate with (π-allyl)NiBr at 0 °C leads to 2,4-pentadienoic acid ester (yield 90%, *trans*/*cis* = 3.5):[158]



Thus examination of the data presented shows that the oxallyl complexes of transition metals plays an important role in the reactions of carbonyl compounds and their derivatives such as hydrogenation, oxidation, halogenation, dimerisation, alkylation, etc. Many of these reactions are catalytic and involve the formation and further reaction of oxallyl intermediates. The use of oxallylmetal complexes in stoichiometric and catalytic reactions makes it possible to synthesise various carbonyl compounds under mild conditions with a high regioselectivity and, in a number of instances, also high stereoselectivity.

The chemistry of oxallyl complexes of transition metals constitutes a branch of metal complex catalysis which has been rapidly developing since the middle 1970's. There is every reason to suppose that further studies on these lines will lead to the creation of new highly selective catalytic methods for the synthesis of carbonyl and other oxygen-containing compounds.

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During the preparation of the review for the press, additional data were published in the literature. In particular, the oxallyl complexes of molybdenum, tungsten, and rhenium were synthesised from α-chloroketones.[159] Titanium(IV) enolates have been obtained by treating aliphatic ketones, aldehydes, and carboxylic acid esters or amides with $Cp_2Ti{=}CH_2$.[160] The isomerisation of an acyl complex of iron in a primary aliphatic alcohol in the presence of $HOSO_2CF_3$ resulted in the synthesis of the corresponding oxallyl complex.[161] The oxallyl complexes of rhodium(III) have been

obtained by the reaction of aliphatic alkanones with octaethylporphyrin complexes of rhodium.[162,163] The oxallyl complexes of ruthenium(II) (mixture of two stereoisomers) have been synthesised by the reaction of $HRuCl(CO)(PPh_3)_3$ with dimethyl fumarate.[164]

A review has been devoted[165] to the isomerisation of 1,2-epoxides in the presence of phosphine complexes of rhodium(I) and iridium(I).

Cerium enolates, obtained from the corresponding lithium enolates derived from ketones, react with alicyclic ketones or aromatic aldehydes at −78 °C, forming a *threo*-aldol in more than 90% yield[166] (when zirconium enolates are used, mainly the *erythro*-aldol is obtained[101,102]). The aldol condensation of vinyl ketones with aldehydes at 40–110 °C in the presence of $HRh(PPh_3)_4$ affords β-hydroxy-α-methyleneketones in 30–460% yield relative to the catalyst.[167]

The interaction of lithium or rhodium enolates derived from ketones or carboxylic acids with esters of αβ-unsaturated acids or with vinylketones in the presence of iron carbonyls leads to carboxylic acid esters substituted by a functional group in the β-position.[168–170]

A convenient method of synthesis of heterocyclic compounds involves the intramolecular alkylation of unsaturated esters or amides of α-halogeno-substituted carboxylic acids, catalysed by zerovalent palladium or nickel complexes.[171–173] The palladium complexes are more effective in this reaction than the nickel complexes.

Another example of the intramolecular alkylation is provided by the synthesis of bicyclic ketones from the trimethylsilyl ethers of the enols of α-allylcyclohexanones catalysed by $Pd(OAc)_2$.[174]

The reaction of PPh_3 with CO and acetone, catalysed by $[RhCl(CO)_2]_2$ led to the synthesis of α-benzylacetone in a yield of 2.2–11 moles per mole of the catalyst.[175]

Depending on the conditions, the stoichiometric reaction of 1,1-dibromocyclopropanes with $Ni(CO)_4$ leads to cyclopropanecarboxylic acid esters or amides or the corresponding γδ-unsaturated derivative.[176–178]

αβ-Unsaturated bicyclic ketones have been obtained by the intramolecular cyclisation of alkeneacetylenic [vinyl ethynyl?] ethers with participation of $Co_2(CO)_8$ and CO.[179]

The reaction of vinyl triflates with acrylic monomers, which results in the formation of β-cyclohexenyl-substituted αβ-unsaturated carboxylic acid aldehydes, esters, or amides, proceeds via a stage involving the formation of intermediate oxallyl complexes.[180]

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