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Carbonylation of Polyunsaturated Hydrocarbons and of Saturated and Unsaturated Alcohols and Halogeno-derivatives

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A survey is made of the catalytic carbonylation of various di- and poly-unsaturated hydrocarbons, alcohols and halogeno-derivatives by carbon monoxide in the presence of complexes of Group VIII metals and acid catalysts. A list of 200 references is included.

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I. INTRODUCTION

Active investigations of carbonylation with carbon monoxide have been made not only on unsaturated hydrocarbons containing one multiple bond [1] but also on polyunsaturated hydrocarbons together with various alcohols and halogeno-derivatives. These reactions take place under conditions of homogeneous catalysis in the presence of catalysts based on Group VIII metals (predominantly complexes). The carbonylation of saturated alcohols and of polyenes with well separated double bonds occurs under conditions of acid catalysis. The survey covers these reactions except for those involving hydroformylation, which has been widely discussed in the literature.

II. CARBONYLATION OF DI- AND POLY-UNSATURATED HYDROCARBONS

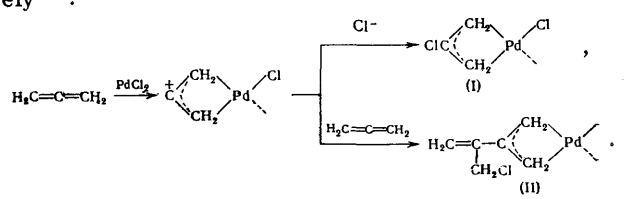
1. Reactions of the presence of Catalysts based on Group VIII Metals

(*a*) Enynes and Diynes

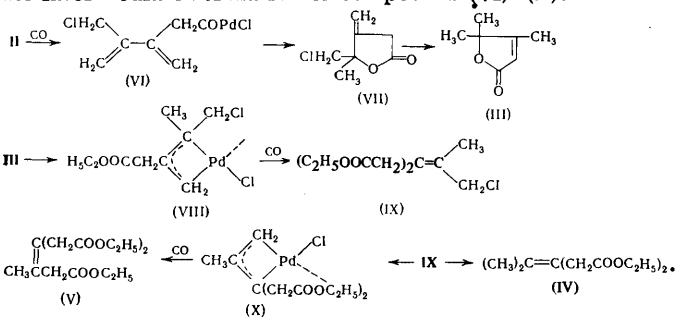
Butenyne is more difficult to carbonylate by means of tetracarbonylnickel than are hydrocarbons containing only a triple bond. The chief product is the cyclic dimer of 2-methylenebut-3-enoic acid [2]. The reaction is accelerated by the addition of pyridine [3,4]. It has not proved possible to carbonylate butadiyne [5].

(*b*) Dienes and polyenes

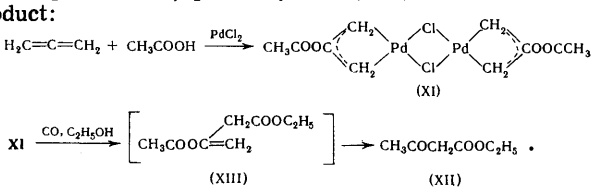
With palladium dichloride allene forms the complexes (I) and (II) in benzene and methanolic solution respectively [6-8]:



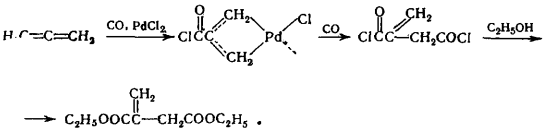
The formation of derivatives of $\beta\gamma$-unsaturated acids from π-allyl complexes of palladium has been investigated [9-12]. Complex (I) in an alcoholic medium at 100°C under carbon monoxide pressures of 100–110 atm yields the 3-chlorobut-3-enoic ester [13]; and complex (II) forms the γ-lactone of 4-hydroxy-3,4-dimethylpent-2-enoic acid (III), the β-isopropylideneglutaric diester (IV), and a triester (V), with the intermediate formation of compounds (VI)–(X):



The carbonylation of allene in the presence of palladium dichloride and the carboxylate ion (in a solution of sodium chloropalladate and acetate in acetic acid) at room temperature gives the di-μ-chlorobis-(2-acetoxy-π-allylpalladium) complex (XI); and the latter in benzene at 100°C and a carbon monoxide pressure of 100 atm forms the compound (XII), probably with (XIII) as intermediate product:



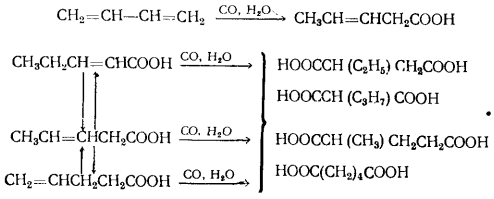
Carbon monoxide acts on allene in ethanol to give a low yield of itaconic ester [13]:



In the presence of small quantities of ruthenium nonacarbonyl or trichloride in methanol at 150°C and a carbon monoxide pressure of 900 atm allene is converted into methyl methacrylate (18%) and dimethyl $\alpha\alpha$-dimethyl-α'-methyleneglutarate (23%), but on the addition of pyridine the products are methyl methacrylate and methyl 1,3,4-trimethylcyclohex-3-enecarboxylate. In an aqueous medium methacrylic acid or the lactones of 3- and

4-hydroxy-1,3,4-trimethylcyclohexanecarboxylic acids are formed (at 700–1000 atm) [14].

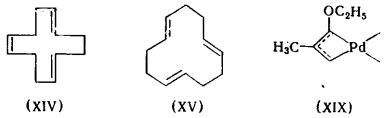
The carbonylation of butadiene gives a mixture of dicarboxylic acids, with the intermediate formation of vinylcyclohexene [15]. Rudkovskii and his coworkers [16–21] obtained from butadiene, carbon monoxide, and water in the presence of bistetracarbonylcobalt at 160–200 °C and 250 atm pent-3-enoic acid and products of the carbonylation of this acid (and its isomers)—unsaturated C_6 dicarboxylic acids—contaminated with valeric acid:



This process is accomplished by the addition of pyridine, which reacts with unsaturated acyl carbonyls, thereby preventing side-reactions [22,23]. The yield of reaction products was raised by using 4,4′-bipyridyl instead of 2,2′-bipyridyl as solvent [24,25].

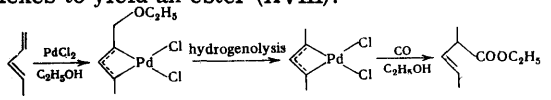
Cobalt carbonyl is the best catalyst for the reaction in pyridine solution. Rhodium and iridium carbonyls are less active and less selective. Iron carbonyl has little activity, and nickel carbonyl is completely inactive. The selectivity (with respect to pent-3-enoic acid) falls in the sequence cobalt > rhodium > iridium [20]. Addition of the elements of formic acid H–COOH can occur also at the 1,2-positions with the formation of pent-4-enoic and 2-methylbut-3-enoic acids. The latter isomerises to 2-methylbut-2-enoic and α-methylenebutyric acids [16]. The rates of formation of pent-3-enoic acid (yield up to 95%) and C_6 tricarboxylic acids (up to 65%) are directly proportional to the concentrations of catalyst and butadiene, decrease with increase in the concentration of water, and pass through a maximum with increase in the pyridine concentration and the carbon monoxide pressure [21]. The reactivity of dienes diminishes in the sequence—buta-1,3-diene, isoprene > hexa-1,5-diene > penta-1,3-diene, hexa-2,4-diene > 2,3-dimethylbuta-1,3-diene. The diene undergoes rapid *cis–trans* isomerisation under the reaction conditions, but its geometrical configuration has no significant effect on the reaction velocity. Penta-1,3-diene undergoes secondary hydrogenation to pentane [17]. In the presence of a palladium catalyst, e.g. $[Pd((C_6H_5)_3P)_2]\cdot Cl_2/HCl$, the carbonylation of butadiene takes place at ~120 °C with the formation of pent-2-enoic acid [26–28]. In the absence of pyridine, rhodium catalysts promote the formation of unsaturated esters from conjugated dienes [29].

Carbon monoxide acts on the *cis–trans–trans* and *trans–trans–trans* forms of cyclododeca-1,5,9-triene (XIV and XV) in the presence of a finely dispersed metal, salt, or carbonyl (nickel or cobalt) to give cyclododecanecarboxylic acid or (in methanol) its ester in 60% yield, together with cyclododecadiene, cyclododecene, and cyclododecylmethanol [30].



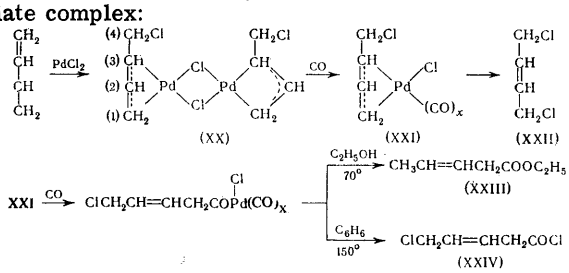
(XIV) (XV) (XIX)

The carbonylation of penta-1,3-diene in ethanolic solution in the presence of small quantities of palladium dichloride at 110 °C and 120 atm depends on intermediate formation of ethoxy-π-allyl (XVI) and symmetrical (XVII) complexes to yield an ester (XVIII):[31]



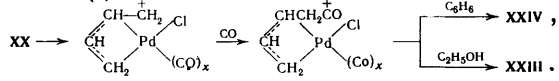
(XVI) (XVII) (XVIII)

Intermediate formation of the complex (XVI) is based on results [32] indicating that the carbonylation of butadiene and isoprene involves intermediate formation of the complex (XIX), which undergoes hydrogenolysis, as is indicated by the production of pent-3-enoic and 4-methylpent-3-enoic esters. In the presence of palladium dichloride various derivatives of unsaturated acids are formed depending on the reaction conditions, in conformity with two modes of attack by carbon monoxide on the intermediate complex:

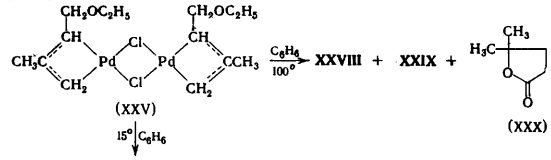


(XX) (XXI) (XXII) (XXIII) (XXIV)

The relative yields of (XXII) and (XXIV) are 3 : 2 in benzene and 1 : 2 in ethanol. Compound (XXIII) is formed by the attack of carbon monoxide on the $C_{(1)}$ atom followed by hydrogenolysis and detachment of chlorine from $C_{(4)}$. Attack by carbon monoxide on $C_{(4)}$ with hydrogenolysis at $C_{(1)}$ is also possible. Product (XXIV) can be produced by the attack of carbon monoxide on $C_{(4)}$ with the appearance of an intermediate carbonium ion and by the attack of chlorine on $C_{(1)}$:[32]

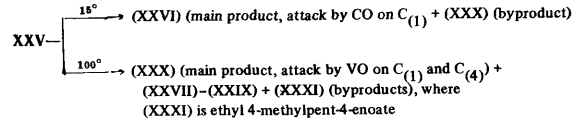


In the reaction with isoprene, attack by carbon monoxide at $C_{(1)}$ and $C_{(4)}$ atoms leads to the formation of different products:

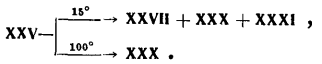


(XXV) (XXVI) (XXVII) (XXVIII) (XXIX) (XXX)

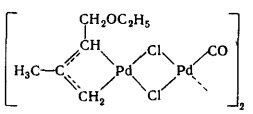
The 4-ethoxyl in the complex (XXV) is readily eliminated, as is chlorine from (XX), to form a carbonium ion. In benzene a mixture of acid chlorides and esters is formed, mainly as a result of attack by carbon monoxide on $C_{(1)}$ at room temperature and on this atom and $C_{(4)}$ at higher temperatures. At room temperature (XXVI) is the main product, while (XXVII) and (XXVIII) are side-products; at 100 °C the main product is (XXVIII), with (XXIX) and (XXX) (γγ-dimethylbutyrolactone) as secondary products. In ethanol the reaction is



When hydrogen chloride is introduced into the reaction mixture at room temperature, attack by carbon monoxide on $C_{(4)}$ is accompanied by hydrogenolysis:



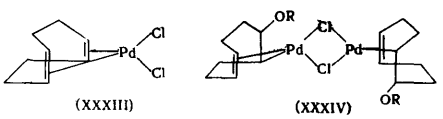
In benzene and alcohol at room temperature a new complex



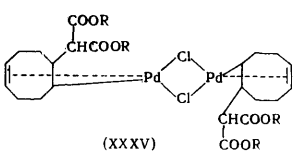
(XXXII)

is formed[33].

Metallic palladium is active only in the presence of hydrogen chloride. The reaction of cyclo-octa-1,5-diene involves intermediate formation of the complex (XXXIII), which could be isolated. The products were a monoester and a mixture of diesters, with the possibility of selective formation of the monoester. Carbonylation of (XXXIII) yields cyclo-oct-4-enecarboxylic and cyclo-octane-1,4- and -1,5-dicarboxylic esters. The bridged dinuclear complex (XXXIV), obtained by the action of sodium carbonate on (XXXIII) in alcohol[34], is converted by carbon monoxide in benzene at 60°C into 8-methoxycyclo-oct-4-enecarboxylic ester[35]. Cyclo-octa-1,3-diene gives a low yield of cyclo-oct-2-enecarboxylic ester. When (XXXIII) is treated with excess of ethyl malonate in the presence of sodium carbonate, the complex (XXXV) is obtained[36]. Cyclododeca-1,5,9-triene forms mono- and di-esters without ring-opening. Triesters have not been detected[37].



(XXXIII) (XXXIV)

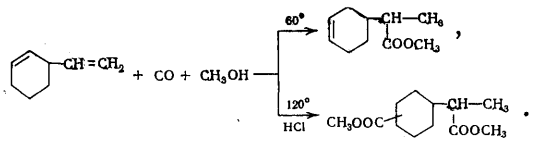


(XXXV)

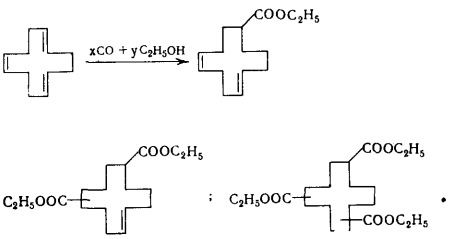
Cyclic ketones are obtained in the presence of bistetracarbonylcobalt at 165°C and a carbon monoxide pressure of 70 atm: hexa-1,5-diene yields 2,5-dimethylcyclopentanone (35%) and 2,5-dimethylcyclopent-2-enone (6%), penta-1,4-diene gives 2-methylcyclopentanone, and hepta-1,6-diene forms 2-ethyl-5-methylcyclopentanone[38].

Halides and chelate compounds of Group VIII metals, in particular ruthenium(III) acetylacetonate, catalyse the reactions of dienes with carbon monoxide and water in pyridine to form saturated monohydric alcohols. Butadiene yields pentanol and isopentanol, and hexa-1,5-diene gives heptan-1-ol, heptan-1-al, and dihexenyl ketone[39,40].

Complex compounds of palladium, platinum, and nickel with such ligands as chlorine, bromine, iodine, tertiary amines, arsines, phosphines, organic sulphides, sulphones, or phosphates in excess of alcohol are active catalysts for the carbonylation of conjugated dienes in alcoholic or phenolic medium at 200°C and carbon monoxide pressures up to 2000 atm to form esters[41]. Unstable polyenes are carbonylated in the presence of complexes of general formula PdL_mX_n, where L is a ligand (e.g. phosphine, nitryl, amine, alkene), X is an acid radical, and $m + n = 3-4$. The greatest catalytic activity is observed when $X = Cl^-$ and Br^-. These complexes exhibit catalytic activity even at concentrations of 0.05% and below at 50–140°C and 300–700 atm[42]. The reaction of vinylcyclohexene catalysed by palladium complexes is represented by the scheme[42]



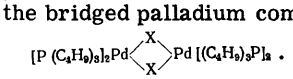
The carbonylation of several polyenes has been accomplished almost without side-reactions. Cyclododeca-1,5,9-triene forms mono-, di-, and tri-esters in up to 90% yield based on the triene that has reacted[37,42]:



The reaction is used for the industrial synthesis of trideca-1,3-lactam[42,43]. The di-μ-chlorodi-π-but-2-enyldipalladium complex is converted by carbonylation into pent-3-enoic acid[44].

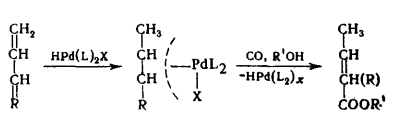
Carbon monoxide acts on butadiene in the presence of rhodium carbonyls and hydrogen chloride to give low yields of α-methylbutyrolactone and 1,3-dichlorobutane[45], but in the presence of rhodium carbonyls[46] or palladium dichloride[32,47] in an alcoholic medium pent-3-enoic esters are obtained. Alkenes react readily with palladium dichloride to form π-complexes or π-allyl complexes[48]. Buta-1,3-diene and palladium dichloride give 1-chloromethyl-π-allyl-palladium chloride[33]. The complex of palladium dichloride with butadiene is converted by carbon monoxide in benzene at 20°C and 50 atm into 5-chloropent-3-enoyl chloride and 1,4-dichlorobut-2-ene, but in an alcoholic medium at the same pressure and 70°C the products are ethyl pent-3-enoate and 1,4-dichlorobut-2-ene[47].

Complexes of palladium vary in their catalytic activity[49]. Sodium chloro- and bromo-palladates give only 1–2% yields of pent-3-enoic esters from butadiene at 70°C and 1000 atm, but with sodium iodopalladates yields of 35–40% are obtained. Modifying the catalyst by adding tributylphosphine enhances the catalytic activity and makes the catalyst thermally stable up to 150°C. In the case of palladium di-iodide the yield of esters is increased to 68%, but with the dichloride to 20%. The most active was the bridged palladium complex



(XXXVI)

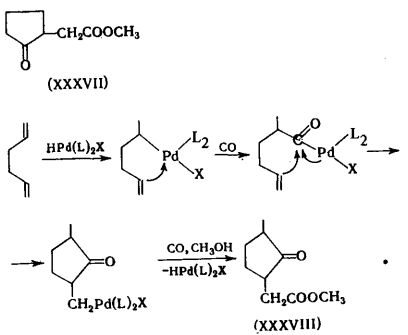
Esters of $\beta\gamma$-unsaturated acids are obtained from conjugated dienes by the general scheme



(L = ligand; X = Cl, Br, I)

Penta-1,3-diene gives methyl 2-methylpent-3-enoate (yield 34%), cyclopentadiene the cyclopent-2-enecarboxylate (70%), 2,3-dimethylbuta-1,3-diene the 3,4-dimethylpent-3-enoate (50%), and isoprene the 3-methylpent-3-enoate (15%), 4-methylpent-3-enoate (38%), and 4-methylpent-4-enoate (10%). Unconjugated dienes react more rapidly than conjugated dienes with carbon monoxide and methanol in the presence of bistributylphosphinepalladium di-iodide at 150°C and 1000 atm, to form unsaturated monoesters and saturated diesters [50]. Cyclo-octa-1,5-diene is converted into methyl cyclo-oct-5-enecarboxylate (45%) and the dimethyl ester of a saturated dicarboxylic acid (30%); cyclo-octa-1,3-diene gives a monoester (14%) and a diester (3%).

$\alpha\omega$-Dienes form not only unsaturated monoesters and saturated diesters but also compounds containing a ketonic group—the cyclic γ-keto-ester (XXXVII) (10%) from penta-1,4-diene, and the compound (XXXVIII) (50%) from hexa-1,5-diene:

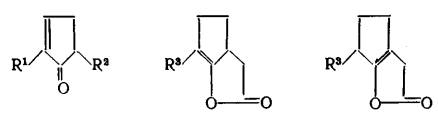


(XXXVII)

(XXXVIII)

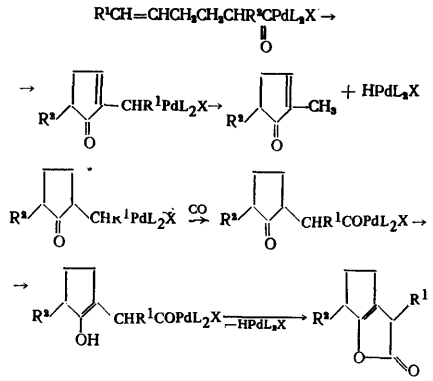
Hepta-1,6-diene gives only traces of ketonic products.

The addition of toluene-*p*-sulphonic acid to the palladium complex enables the pressure to be lowered from 1000 to 250 atm, while the reaction velocity is raised, but addition of a base, e.g. calcium acetate, lowers the rate of the reaction [50]. In the presence of 1% of bistributylphosphinepalladium di-iodide cyclo-octa-1,5-diene is converted in oxolan solution (at 150°C and 1000 atm) into bicyclo[3,3,1]non-2-en-9-one [51], but in the presence of palladium dichloride at 100°C and 100 atm the products are cyclo-oct-4-enecarboxylic and cyclo-octanedicarboxylic esters [35, 52].



(XXXIX) (XL) (XLI)

In the presence of bistributylphosphinepalladium di-iodide in oxolan at 200°C and 1000 atm $\alpha\omega$-dienes are converted into unsaturated ketones and lactones: penta-1,4-diene into 2-methylcyclopent-2-enone (XXXIX: R^1 = CH_3; R^2 = H) and a mixture of unsaturated lactones (XL, XLI: R^3 = H); hexa-1,5-diene into 2,5-dimethylcyclopent-2-enone (XXXIX: $R^1 = R^2 = CH_3$) and enelactones (XL, XLI: $R^3 = CH_3$); and hepta-1,6-diene into 5-ethyl-2-methylcyclopent-2-enone (XXXIX: $R^1 = C_2H_5$; $R^2 = CH_3$). Hepta-1,6-diene probably isomerises into hepta-1,5-diene before carbonylation. The addition of one carbon monoxide molecule to 1,4- and 1,5-dienes yields unsaturated cyclic ketones, but two carbon monoxide molecules give unsaturated lactones [53]:



In the presence of hydrogen iodide and nickel acetate at 270°C and a carbon monoxide pressure of 300 atm cyclo-octa-1,5-diene gives a good yield of cyclo-octanecarboxylic acid [54].

2. Reactions in the presence of Acid Catalysts

The lower dienes polymerise rapidly under the influence of strong mineral acids, and therefore are not used for the preparation of dicarboxylic acids. The latter are formed only from branched dienes in which the double bonds are separated by at least 5–8 carbon atoms. 2,5-Dimethylhexa-1,5-diene in the presence of sulphuric acid with formic acid as carbonylating agent at room temperature and atmospheric pressures gives $\alpha\alpha\alpha'\alpha'$-tetramethyladipic acid in 2–3% yield together with monocarboxylic acids (20–40%) such as 2,2,5-trimethylhexanoic acid, a dimeric C_{17} acid, and 1,2,4-trimethylcyclopentanecarboxylic acid, as well as neutral products such as esters, lactones, hydrocarbons, and 2,2,5,5-tetramethyloxolan. 2,11-Dimethyldodeca-1,11-diene forms 2,11-dimethyldodecanedicarboxylic acid (30%). [55] Cyclic polyenes—cyclododeca-1,5-diene and cyclododeca-1,5,9-triene—yield the expected di- and tri-carboxylic acids. A transannular reaction takes place with hydride migration, resulting in tricyclic systems, which combine with carbon monoxide to form acids having a carboxyl attached to the bridge carbon atom. Cyclododeca-1,5-diene forms a mixture of *cis*- and *trans*-decahydronaphthoic acids; a mixture of isomeric perhydroacenaphthenecarboxylic acids is obtained from cyclododeca-1,5,9-triene. Dienes in which the double bonds are isolated are carboxylated in the presence of the same catalyst under similar conditions to form low yields of dicarboxylic acid, and only if the double bonds are separated by 7–9 carbon atoms [56].

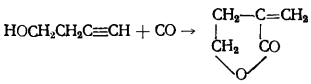
III. CARBONYLATION OF ALCOHOLS

1. Reactions in the presence of Catalysts based on Group VIII Metals

(*a*) Acetylenic alcohols

When acetylenic compounds undergo carbonylation, the carboxyl appears on a carbon atom attached to a substituent (A)—e.g. Alk, Ar, CH_2OH, CH_2CH_2OH, $CH_2CH_2CH_2OH$, $CH_3COOCHR$, $CH_2CH_2O\underline{CHO[CH_2]_3CH_2}$—that "attracts" carbon monoxide. Substituents of type B, which "repel"

carbon monoxide—e.g. H, CHROH, CR_2OH, COOH, $COOCH_3$, $COOC_2H_5$, $COCH_3$, $CH_2C(CH_3)_2OH$—promote its addition at the other carbon atom forming the triple bond. If in any compound XC : CY the substituents X and Y are both of type A, carbonylation will be rapid. When X is of type A, and Y of type B, the reaction is still quite rapid, the compound XC(COOH) : CHY being formed. If X and Y are both of type B, reaction is slow, and only after prolonged heating are unsaturated carboxylic acids formed in low yield. An exception is unsubstituted acetylene, which is carbonylated easily and smoothly [1]. Acetylenic compounds containing a primary or secondary hydroxyl give unsaturated hydroxy-acids, which under the reaction conditions often polymarise or form lactones. This route has been used to synthesise the natural antibiotic α-methylenebutyrolactone [4,5,57]:



Prop-2-ynyl alcohol reacts with carbon monoxide in ethanol in the presence of stoichiometric quantities of tetracarbonylnickel at 55°C and atmospheric pressure to give $CH_2 : C(CH_2OH)COOC_2H_5$ (58%) and $HOCH_2CH : CHCOOC_2H_5$ (11%). The methyl, n-butyl, and isobutyl esters have been prepared similarly. With catalytic quantities of the carbonyl reaction takes place at 85 to 145°C and 1.4–14 atm. A maximum pressure corresponds to a fixed reaction temperature, and exceeding this pressure by 10% brings the reaction to a halt [58]. Secondary $\alpha\beta$-acetylenic carbinols react readily with tetracarbonylnickel to form unsaturated acids:

$$CH_3CH(OH)C \equiv CCH_3 \rightleftarrows CH_3CH(OH)CH{=}C(CH_3)COOH .$$

Under similar conditions tertiary $\alpha\beta$-acetylenic carbinols, e.g. 1,1-dimethylprop-2-ynol, hardly react with stoichiometric quantities of tetracarbonylnickel [57], but in anhydrous butanol containing hydrogen chloride this carbinol gives at room temperature and atmospheric pressure a product containing $(CH_3)_2C(OH)CH : CHCOOC_4H_9$. [59]
1-Ethynylbutyl acetate in a mixture of ethanol and acetic acid reacts readily with tetracarbonylnickel at 70°C to form $CH_3CH_2CH_2CH(OCOCH_3)C(COOH) : CH_2$ (40%). [59]

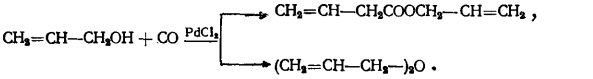
Acetylenic alcohols and glycols are carbonylated also in the presence of bistetracarbonylcobalt. In the intermediate complexes the triple bond is perpendicular to the cobalt–cobalt bond [60].

Prop-2-ynyl alcohol in methanolic hydrogen chloride, in the presence of small quantities of palladium on carbon at 100°C and a carbon monoxide pressure of 100 atm gives methyl itaconate (63%) and aconitate (10%) contaminated with methyl α-methoxymethylacrylate. Substituted prop-2-ynols react similarly [61].

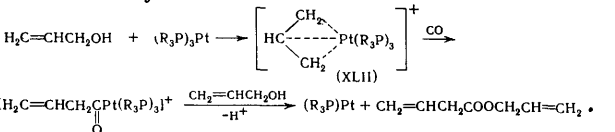
(*b*) Olefinic alcohols

Aliphatic 2,3- and 3,4-unsaturated alcohols and their alkylated derivatives react with carbon monoxide in the presence of bistetracarbonylcobalt or rhodium trichloride in benzene at 200–250°C and 300 atm to form γ- or δ-lactones. 2,2-Disubstituted primary alcohols give the highest yield of lactones. Primary and secondary 2,3- and 3,4-unsaturated alcohols isomerise under the reaction conditions into carbonyl compounds, the aldehydes condensing by the Tishchenko reaction. The carbonylation of tertiary 2,3- and 3,4-unsaturated alcohols is a slow reaction accompanied by dehydration. The reaction is slower in the presence of hydrogen tetracarbonylcobaltate than with bistetracarbonylcobalt [62]. Allyl alcohol gives a 60% yield of γ-butyrolactone with the latter catalyst at carbon monoxide pressures of 100–300 atm in the presence of 6–10% of hydrogen at 100–170°C. The addition of pyridine accelerates the reaction, and the use of acetonitrile and its derivatives as solvents tends to increase the rate and enhance the selectivity [63–65].

A feature of the use of palladium catalysts in the carbonylation of allyl alcohols is that the double bond may be preserved with the formation of an ester of a β-unsaturated acid [42,66]. Ethyl esters of $\beta\gamma$-unsaturated carboxylic acids are obtained from allyl alcohols in ethanol in the presence of palladium dichloride at 80–120°C and 100 atm. In the absence of a solvent the reaction is



Under the same conditions substituted allyl alcohols, e.g. but-2-enol and but-3-enol, are converted into the same product, ethyl pent-3-enoate [67]. Allyl alcohol reacts with carbon monoxide in the presence of tristri-*p*-fluorophenylphosphineplatinum to form mainly allyl crotonate, into which the initially formed but-3-enoic ester isomerises:



The π-allyl complex (XLII) is formed at 1000 atm and 200°C from allyl alcohol and a catalyst [68].

The interaction of allylic alcohols with carbon monoxide in the presence of acetylene, alcohol, tetracarbonylnickel, and hydrogen chloride yields dienoic acids with intermediate formation of allyl halides [69,70].

(*c*) Saturated alcohols

The earlier investigations on the carbonylation of saturated alcohols using catalysts based on Group VIII metals have been reviewed previously [71]. The carbonylation of methanol to acetic acid $CH_3OH + CO \rightarrow CH_3COOH$ has now acquired great practical importance, the most effective catalyst being cobalt acetate modified with potassium iodide. The reaction is conducted with the addition of 0.1% of the catalyst at temperatures of 220–260°C and pressures above 300 atm with 30–70 mole % of water in the methanol [72,73]. The conversion of methanol into acid is 50–80% with a constant of 40–60% of acetic acid in the reaction products. Methyl acetate is formed as an intermediate [72], the rate constant is proportional to $[CO]^2$, and its (Arrhenius) temperature dependence is non-linear [74]. The reaction has also been conducted as a continuous process at 200°C and 400 atm with an initial mixture comprising (mole %) 47.5 CH_3OH + 50.0 H_2O + 2.5 CH_3COOH and a conversion of methanol of 60.5% [75] The activity of the catalyst is adversely affected by replacing potassium iodide by iodine [76]. It has been shown spectroscopically that, in the presence of excess of iodide ions, most of the cobalt(II) forms the tetrahedral complex ion $[CoI_n(OCOCH_3)_{4-n}]^{2-}$ ($n = 1-4$) instead of carbonyls. The content of this ion increases during the reaction. The course of the reaction is affected by the addition of potassium acetate. With the proportions $CH_3COOK : Co^{II} = 1-2$ the reaction velocity is a maximum, and the formation of acetone is inhibited; if, however, this ratio is 4, reaction

does not take place. The formation of cobalt carbonyl is accelerated by the addition of potassium acetate [77]. Similar effects are exerted by lithium, sodium, magnesium, and manganese acetates, potassium propionate, and sodium benzoate [78]. The productivity of the catalyst is 0.1–0.2 kg litre^{-1} h^{-1}. [77] When sufficient water is present, the methyl acetate and acetone formed as byproducts are hydrolysed to methanol [79]. Another selective catalyst is nickel acetate modified with iodine [80]. The following scheme has been suggested for the reaction

$$2CoI_2 \xrightarrow[-(HI+CO_2)]{CO+H_2O} Co_2(CO)_8 \xrightarrow[-CO_2]{CO+H_2O} 2HCo(CO)_4;$$

$$CH_3OH \xrightarrow[-H_2O]{HI} CH_3I;\ HCo(CO)_4 \underset{HI}{\overset{CH_3I}{\rightleftarrows}} CH_3Co(CO)_4 \rightarrow CH_3COCo(CO)_3 .$$

Acetic acid may then be formed in two ways:

$$\underset{CO\downarrow\uparrow -CO}{CH_3COCo(CO)_3} \xrightarrow{+H_2O} CH_3COOH + \underset{CO\downarrow\uparrow -CO}{HCo(CO)_3},$$

$$CH_3COCo(CO)_4 \xrightarrow{+H_2O} CH_3COOH + HCo(CO)_4 .$$

In 1964 an installation producing 1000 metric tons of acetic acid per month was started up in West Germany [79]. Several large works are operating this process in the U.S.A. and West Germany [81–83]. Acetic acid is obtained in 90% yield based on methanol and 70% based on carbon monoxide with the use of cobalt(II) iodide at 250–260°C and 650–700 atm. In the presence of cobalt diacetate and sodium, potassium, lithium, and calcium iodides with a catalyst concentration of 1–20 mole % at 180–220°C and 300–500 atm the reaction of methanol with a mixture of carbon monoxide and hydrogen (1.5 : 1) is used to obtain acetic esters (40–60%), acetaldehyde, and the hydrogenation product of the latter—ethanol [84].

Rhodium and iridium catalysts are employed for the carbonylation of methanol under homogeneous reaction conditions—e.g. $RhCl_3.3H_2O$, $Rh_2O_3.5H_2O$, $RhCl(CO).(P(C_6H_5)_3)_2$, $(RhCl(CO)_2)_2$, $IrCl_3.3H_2O$, $Ir_4(CO)_2$, $IrCl(CO)(P(C_6H_5)_3)_2$—modified with halides and halogens (iodine, hydrogen iodide, calcium iodide dissolved in benzene, water, methanol, nitrobenzene, acetic acid) [85]. These catalysts are active at 175–250°C and low pressures, even subatmospheric, when the selectivity reaches 99%.

In the presence of a rhodium sesquioxide–carbon catalyst modified with methyl iodide or hydrogen iodide, under conditions of heterogeneous catalysis at 1–15 atm, the conversion of methanol into acetic acid and methyl acetate is 93%. [86]

The carbonylation of alcohols in the presence of α-oxides and carbonyls of cobalt, rhodium, and iridium at ~300 atm and 120–250°C has been used to prepare [87] hydroxy-carboxylic esters in yields up to 97%.

2. Reactions in the presence of Acid and Basic Catalysts

The early results on the carbonylation of alcohols in the presence of catalysts of acidic and basic character have been discussed in a previous review [71].

The carbonylation of saturated alcohols at carbon monoxide pressures of 50–90 atm and 15–70°C occurs in two stages in the presence of 96–98% sulphuric acid [88]. The first stage involves interaction of the initial alcohol, carbon monoxide, and sulphuric acid, with the assumed formation of acylsulphuric acids in equilibrium with acylium and hydrogen sulphate ions. In the second stage water or alcohol is added to the reaction mixture, which results in the formation of carboxylic acids or their esters mixed with small quantities of the free acids:

$$ROH + H_2SO_4 \xrightarrow[-H_2O]{} R^+ + \bar{O}SO_2OH \xrightarrow{CO} R'\overset{+}{C}O + \bar{O}SO_2OH \rightleftarrows$$

$$\rightleftarrows R'\underset{\underset{O}{\|}}{C}OSO_2OH \xrightarrow[-H_2SO_4]{HX} R'\underset{\underset{O}{\|}}{C}-X$$

where R′ is a radical isomeric with R but more branched, and X = OH, OR″. With C_{3-5} aliphatic alcohols the yield of acids and esters increases with the molecular weight of the alcohol and on passing from a straight-chain alcohol to a branched-chain isomer. The main reaction products are carboxylic acids (or their esters) containing one more carbon atom than in the initial alcohol, with a quaternary or more rarely a tertiary carbon atom in the α-position. Propyl and isopropyl alcohols give isobutyric acid, n-butanol yields α-methylbutyric acid, isobutanol forms αα-dimethylpropionic acid, n-pentanol yields a mixture of αα-dimethyl- and α-ethyl-butyric acids (1.7 : 1), and isopentanol gives αα-dimethylbutyric acid. The total yield of acids and esters from C_{6-10} alcohols is 70–95%, and varies little with the molecular weight of the alcohol [89]. Cyclohexanol yields 1-methylcyclopentanecarboxylic and cyclohexanecarboxylic acids (2 : 1), cyclopentanol gives cyclopentanecarboxylic and *cis*-decahydronaphthalene-9-carboxylic acids (20 : 1), and *p*-menthol forms methane-*p*-carboxylic acid [90]. Raising the carbon monoxide pressure from 5 yo 75 atm increases the total yield of esters on methoxycarbonylation. In the case of isobutyl alcohol the content of the αα-dimethylpropionic ester is independent of the carbon monoxide pressure at ~80%; [91] but in the case of n-pentanol the content of the α-ethylbutyric ester increases at the expense of the αα-dimethylbutyric ester, the total yield of esters at 70 atm being 82–86%. [92] The composition of the products of the methoxycarbonylation of n-pentanol is almost independent of the molar ratio of sulphuric acid to alcohol in the range 4–10. The optimum temperature in the first stage of the reaction is ~60°C. [93]

Carboxylic acids are synthesised from alcohols with formic acid as carbonylating reagent in the presence of sulphuric acid at atmospheric pressure and room temperature. Alcohols of the neopentyl type, which cannot be directly dehydrated to alkenes, also undergo the above reaction [94]. This shows that alcohols may not be dehydrated to alkenes under the influence of an acid catalyst, but may form carbonium ions directly, which then react with carbon monoxide.

Neopentyl alcohol gives αα-dimethylbutyric acid, 2,2-dimethylbutanol yields a mixture of αα-dimethylvaleric and α-ethyl-α-methylbutyric acids (1 : 2), and 1′-methylcyclopentylmethanol forms 1-methylcyclohexanecarboxylic acid. In the case of 1′-methylcyclohexylmethanol and its homologues the hydroxymethyl carbon enters an alkyl side-chain. Bicyclo[3,3,0]oct-1′-ylmethanol gives bicyclo[3,3,1]nonane-1-carboxylic acid, hexahydroindan-8′-ylmethanol yields a mixture of *cis*- and *trans*-decahydro-9-naphthoic acids, decahydronaphth-9′-ylmethanol a mixture of decahydro-1- and -2-methylnaphthoic acids contaminated with bicyclo[5,4,0]undecane-1-carboxylic acid [95,96], and adamantan-1-ol is converted into adamantanecarboxylic acid [97].

Diprimary diols give on carbonylation mainly unsaturated monocarboxylic acids and lactones contaminated with dicarboxylic acids. Nonane-1,9-diol and decane-1,10-diol yield respectively αα′α′-tetramethylpimelic acid (33%) and αα′α′-tetramethylsuberic acid (7%). [55]

The course of carbonylation of ditertiary diols of general formula $HO.CR_2.[CH_2]n.CR_2.OH$ ($n = 4-8$; $R = CH_3$, C_2H_5, $n\text{-}C_4H_9$) is not affected by increase in the size of the alkyl groups provided that the distance between the hydroxyls is maintained. 2,7-Dimethyloctane-2,7-diol ($n = 4$) forms a mixture of four isomeric C_{11} cyclic monocarboxylic acids in ~70% yield. 3,8-Diethyldecane-3,8-diol and 5,10-di-n-butyltetradecane-5,10-diol ($n = 4$) give only cyclic monocarboxylic acids (~70%), and 2,8-dimethylnonane-2,8-diol ($n = 5$) yields a mixture of monocarboxylic (40%) and dicarboxylic (42%) acids. The products from 2,9-dimethyldecane-2,9-diol ($n = 6$) and 2,10-dimethylundecane-2,10-diol ($n = 7$) are dicarboxylic acids (61–63%); the total yield of mixtures of carboxylic acids is 87%, consisting mainly of $\alpha\alpha\alpha'\alpha'$-tetramethylsebacic and $\alpha\alpha\alpha'\alpha'$-tetramethylbrassylic acids respectively, together with 16 to 24% of cyclic monocarboxylic acids. 2,11-Dimethyldodecane-2,11-diol ($n = 8$) yields a mixture of carboxylic acids (69%) containing 34% of dicarboxylic acids, mainly 2,2,11,11-tetramethyldodecanedioic acid, and monocarboxylic acids (15%) together with polymeric acids (20%), a neutral oil (15%), and polymers (10%).[55]

Carboxylic esters are obtained in two stages from alcohols and formic acid in the presence of a large excess of sulphuric acid at atmospheric pressure; in the second stage water is replaced by alcohol. This method has been used to prepare methyl $\alpha\alpha$-dimethyl- and α-ethyl-alkanoates from C_4-C_7 saturated alcohols and cyclohexanol using methanol in the second stage. The free acids are formed together with the esters. The total yield of esters and acids increases with the molecular weight of the initial alcohol and the degree of branching of its molecule[98]. 1-Methyl-, 1-ethyl-, and 1-propyl-cyclohexanols are methoxycarbonylated to form the corresponding methyl 1-alkylcyclohexanecarboxylates in yields up to 40%, cyclohexylmethanol to form methyl 1-methylcyclohexanecarboxylate, cyclopentanol to give methyl cyclopentanecarboxylate (45%) and *cis*-decahydro-9-naphthoate (2%), and 1-methyl- and 1-ethyl-cyclopentanols to yield methyl 1-methylcyclopentanecarboxylate (1%) and 1-methylcyclohexanecarboxylate (4%) respectively[99].

Concentrated orthophosphoric acid is also used as catalyst for the carbonylation of saturated alcohols by carbon monoxide. The optimum temperature for the reaction lies between 125° and 175°C, i.e. 100 deg higher than in the presence of sulphuric acid. The optimum pressure of carbon monoxide is 70–80 atm. Variation in the molar ratio of orthophosphoric acid to alcohol in the range 10–2.5 : 1 has no significant effect on the course of the reaction. The acid can be used repeatedly[100]. The main products of the carbonylation of saturated C_4-C_7 alcohols are their $\alpha\alpha$-dimethyl-, α-ethyl-α-methyl-, and α-ethyl-alkanoates together with the alkanoic acids themselves—derivatives of monomeric, dimeric, and trimeric forms of the initial alcohol—as well as products of the disproportionation of carbonium ions formed from the initial alcohol. Cyclopentanol and cyclohexanol yield only the corresponding free acids, predominantly derivatives of the dimeric form: cyclopentanol gives a mixture of *cis*- and *trans*-decahydro-9-naphthoic acids; cyclohexanol produces not only derivatives of the dimeric form but also small quantities of 1-methylcyclopentanecarboxylic and cyclohexanecarboxylic acids[101-103].

Hydrates of boron trifluoride are active catalysts for the carbonylation of alcohols. In the presence of the dihydrate at 100°C and a carbon monoxide pressure of 100 atm 2-methylpropan-1-ol gives up to 76% yields of $\alpha\alpha$-dimethylpropionic acid or up to ~90% of its isobutyl ester[104]. In the presence of the monohydrate pentan-1-ol and 3-methylbutan-1-ol form a mixture of carboxylic acids containing mainly $\alpha\alpha$-dimethylbutyric acid; the former alcohol produces also α-methylvaleric and α-ethylbutyric acids. In the presence of other hydrates of boron trifluoride, containing 1.5–3.0 H_2O, pentyl $\alpha\alpha$-dimethylbutyrate is obtained from pentan-1-ol, and the isopentyl ester from 3-methylbutan-1-ol; the yield of these esters passes through a maximum at the dihydrate as the water content is decreased[105]. Hexan-1-ol gives hexyl $\alpha\alpha$-dimethylvalerate and α-ethyl-α-methylbutyrate with maximum yields of 76% and 30% respectively, the reaction occurring only in the presence of the sesquihydrate[106]. Heptan-1-ol forms heptyl α-ethyl-α-methylvalerate and 2,2-dimethylhexanoate with respective maximum yields of 46% and 42%; if the hydrate contains more than 1.5 H_2O, hardly any reaction occurs with heptan-1-ol[106]. With pentanol and 3-methylbutanol in the presence of boron trifluoride monohydrate the reaction mixture separates into two layers—carboxylic acids and catalysts—at the end of the reaction only after water has been added. With a catalyst having a higher water content the reaction is accompanied by a sharp separation of reaction products from the catalyst phase without the addition of water, probably because of the presence of a sufficient quantity of water in the catalyst itself[107]. The reaction is represented by the scheme

$$RCH_2CH_2OH + [BF_3 \cdot (n-1)H_2O \cdot OH]^-H^+ \rightarrow R\overset{+}{C}HCH_3 + BF_3 \cdot nH_2O,$$

$$R\overset{+}{C}HCH_3 \xrightarrow{CO} R'\overset{+}{C}O \xrightarrow[-H+]{ROH} R'COOR.$$

Mixtures of oxiran, methyloxiran, or phenyloxiran with salts (sodium, potassium, or calcium formate, acetate, or benzoate), amines, arsines, or phosphines may serve as catalysts for the carbonylation of methanol with carbon monoxide at 200 atm and 170°C. Methyl formate is obtained in yields up to 64% when the ratio by weight of salt to alkene oxide is 1 : 10. The catalytic activity is ascribed to an alkoxide ion formed, e.g. when the catalyst system comprises oxiran and triphenylphosphine, by the scheme

$$RCOO^- + CH_2\text{—}CH_2 \rightarrow RCOOCH_2CH_2O^- \xrightarrow{CH_3OH} RCOOCH_2CH_2OH + CH_3O^-,$$

$$(C_6H_5)_3P + CH_2\text{—}CH_2 \rightarrow (C_6H_5)_3P\overset{+}{C}H_2CH_2O^- \xrightarrow{CH_3OH} (C_6H_5)_3P\overset{+}{C}H_2CH_2OH + CH_3O^-.$$

The true catalyst of the latter reaction is regarded[108] as the compound

$$(C_6H_5)_3\overset{+}{P}CH_2CH_2OCH_2\overline{O}CH_3$$
(XLIII)

formed from the alcohol, oxiran, and the base.

IV. CARBONYLATION OF HALOGENO-DERIVATIVES

1. Acetylenic Halogeno-derivatives

In the presence of tetracarbonylnickel α-iodoacetylenes are reduced to acetylenic hydrocarbons, which are not carbonylated[4,57,109]. α-Chloroacetylenes form allenic acids mixed with substituted malonic acids and ketones. The carbonylation of β- and γ-halogenated acetylenes occurs more easily the more remote is the halogen from the triple bond[110-112]. Prop-2-ynyl chloride, carbon monoxide, and water in the presence of tetracarbonylnickel give a 70% yield of a mixture of butadienoic and itaconic acids[112]:

$$CH_2{=}C(COOH)CH_2COOH \xleftarrow[-HCl]{2CO+2H_2O} CH{\equiv}CCH_2Cl \xrightarrow[-HCl]{CO+H_2O} H_2C{=}C{=}CHCOOH.$$

In the presence of small quantities of water itaconic acid is the main product [111]. Prop-2-ynyl bromide reacts with tetracarbonylnickel in alcoholic solution at atmospheric pressure and 70°C to form ethyl 3-bromobut-3-enoate in ~20% yield. Reaction is less vigorous under carbon monoxide pressure, probably because in the first stage the complex of the acetylenic compound with the carbonyl is formed with the evolution of carbon monoxide [113]. It is preferable to prepare allenic acids in an aqueous–alcoholic buffer by the reaction

$$R^1C{\equiv}CCR^2R^3Cl \xrightarrow[-HCl]{Ni(CO)_4,\ H_2O} HOOCCR^1{=}C{=}CR^2R^3$$

than by means of Grignard reagents and carbon dioxide. The possibility of initial rearrangement of the α-chloroacetylene into a chloroallene is eliminated, since chloroallene does not react under these conditions [114].

In the presence of palladium dichloride at ~20°C and 100 atm carbon monoxide pressure prop-2-ynyl chloride in methanolic solution reacts with carbon monoxide to form methyl itaconate in 66% yield together with small quantities of methyl 3-chlorobut-3-enoate [61].

2. Ethylenic Halogeno-derivatives

Unsaturated acids or their esters are obtained by the carbonylation of alkenyl halides in aqueous or alcoholic solution in the presence of tetracarbonylnickel under carbon monoxide pressure. With unbranched 1-halogenoalkenes the reaction is

$$RCH{=}CHCH_2Cl + CO + R^1OH \xrightarrow{Ni(CO)_4} RCH{=}CHCH_2COOR^1 + HCl$$

accompanied by the side-reaction

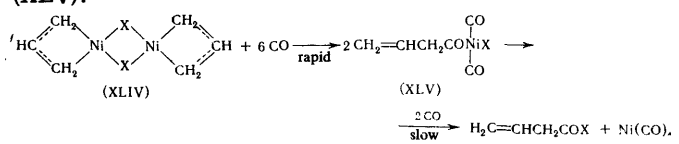
$$2\,RCH{=}CHCH_2Cl + Ni(CO)_4 \rightarrow (RCH{=}CHCH_2)_2 + 4CO + NiCl_2\ .$$

Allyl chloride yields crotonic acid by isomerisation of the initially formed but-3-enoic acid [112], but-2-enyl chloride gives pent-3-enoic acid, and 5-chloropent-3-enonitrile forms the mononitrile of dihydromuconic acid, which on hydrogenation is converted into caprolactam.

The catalytic activity of tetracarbonylnickel is explained by the intermediate formation of a complex carbonyl-π-allylnickel chloride $[Ni(CO)_3CH_2CH{:}CHR]^+Cl^-$, which breaks down under the influence of carbon monoxide and alcohol [112,114–118]. Five-coordinated nickel complexes of the type $[NiHalCO\pi\text{-allyl}.(C_6H_5)_3P]$ are assumed to be formed as intermediates in the carbonylation of allyl compounds. These complexes are obtained by the reaction of allyl halides with tricarbonyltriphenylphosphinenickel in a mixture of methanol and benzene [119]. The carbonylation of bis-π-allylnickel halide complexes (Hal = Br or I) in the presence of tetracarbonylnickel yields methyl methacrylate (50–70%) contaminated with methyl crotonate [120,121]. The main product of the carbonylation of allyl halides with carbon monoxide at 50 atm and 100°C is methyl but-3-enoate, which is also obtained by the carbonylation of bis-π-allylnickel bromide [122]. The reaction is represented by the scheme [123]

$$RCH{=}CHCH_2Br + 2\,Ni(CO)_4 \rightarrow [RCH{=}CHCH_2\cdot Ni(CO)_3]^+Br^- \rightarrow$$
$$\rightarrow RCH{=}CHCH_2COOR^1 + Ni(CO)_4 + HCl\ .$$

The carbonylation of allyl halides is conducted under milder conditions. In the reaction of π-allylnickel iodide with carbon monoxide in ether at 0°C, infrared spectroscopy has detected nickel carbonyl and butenoyl iodide. An unstable intermediate dimeric halogeno-π-allylnickel complex (XLIV) has been isolated, which can exist in ethereal solution at 0°C, and reacts rapidly with carbon monoxide to form a carbonylbutenoylnickel halide (XLV):[124]



(XLIV) (XLV)

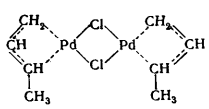
Compounds of noble metals are active catalysts for the carbonylation of unsaturated halogeno-derivatives by carbon monoxide. In the presence of palladium dichloride dehalogenation occurs at the same time, and rise in temperature favours the formation of derivatives of unsaturated acids. Vinyl chloride in benzene solution yields $\beta\beta$-dichloropropionyl chloride, but in alcoholic solution saturated with hydrogen chloride at 130°C and 600 atm the ethyl ester is obtained, and at 80°C and 100 atm a mixture of ethyl β-chloropropionate and propionate. Allyl chloride in benzene solution at room temperature and 100 atm forms 3,4-dichlorobutyryl chloride, and at 130°C but-3-enoyl chloride; in alcoholic solution at 120–170°C the products are ethyl but-3-enoate together with the but-2-enoic and isobutyric esters, and at 80°C and 100 atm a mixture of ethyl butyrate, isobutyrate, and β-chloro-α-methylpropionate. These reactions are catalysed also by metallic palladium alone and on carbon, alumina, or a zeolite.

Heating the complex of palladium dichloride with allyl chloride yields but-3-enoyl chloride [9,42,67,125–127]. This complex catalyses the carbonylation by carbon monoxide of allyl chlorides to form chlorides or esters of alk-3-enoic acids [11]. In the presence of bistriphenylphosphinepalladium dichloride the carbonylation of allyl chlorides also takes place with maintenance of the double bond:

$$CH_2{=}CHCH_2X + CO + ROH \rightarrow CH_2{=}CHCH_2COOR + HX$$

where X = Hal and R = Alk or Ar. [66] Pyridine, benzonitrile, and other compounds may also serve as ligands in palladium dichloride.

1-Chlorobut-2-ene and 3-chlorobut-1-ene react with carbon monoxide in the presence of di-π-allylchloropalladium at 100°C and 150–180 atm via the intermediate complex



(XLVI)

to form pent-3-enoyl chloride in 80% yield. 3-Methylbut-3- and -2-enoyl chlorides are obtained from 3-chloro-2-methylpropene [11]. The carbonylation of allyl chlorides in the presence of metallic palladium and rhodium, their complexes or salts, to give acid halides is accelerated by additions of acetylene, cycloheptadiene and cyclopentadiene hydrocarbons, indene, and fluorene [128].

3. Allyl Halides in the presence of Acetylene

Acetylene may enter into the reaction of allyl halides with carbon monoxide, water, or alcohol in the presence of metal carbonyls and their salts, generally tetracarbonylnickel, in hydroxylated solvents at 20–60°C to form unbranched dienoic acids or their esters. When 20% of the stoichiometric quantity of nickel carbonyl is used, $\alpha\beta:\delta\epsilon$-dienoic acids and their esters are obtained:

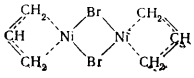
$$RCH{=}CHCH_2X + CO + R^1OH + CH{\equiv}CH \rightarrow RCH{=}CHCH_2CH{=}CHCOOR^1 + HX$$

(X = Hal). The reaction goes best at room temperature and atmospheric pressure, with yields up to 80%.[116,129,130] Allyl chloride is converted into hexa-2,5-dienoic acid and its methyl, ethyl, and other esters, which possess a pleasant odour and are stable compounds. Hepta-2,5-dienoic and 5-methylhexa-2,5-dienoic acids are obtained from but-2-enyl and methylallyl chlorides respectively. Secondary react more slowly than primary chloro-derivatives to form the same unbranched dienoic acids. Carbonylation is slowed down or completely inhibited by an electronegative substituent at the double bond. The reactions are favoured by an allyl and also by a phenyl group conjugated with the double bond[131-136]. The following mechanism has been suggested for the reaction involving tetracarbonylnickel[123]:

$$RR^1C{=}CR^2CHR^3Cl + Ni(CO)_4 \rightarrow [(CO)_3NiCHR^3CR^2{=}CRR^1]^+Cl^- \xrightarrow{C_2H_2} \rightarrow \text{cis-}[(CO)_3NiClCOCH{=}CHCHR^3CR^2{=}CRR^1 \xrightarrow{CO} \rightarrow \text{cis-}[(CO)_3NiCOCH{=}CHCHR^3CR^2{=}CRR^1]^+Cl^- \xrightarrow{CO+R^4OH} \rightarrow \text{cis-}\ RR^1C{=}CR^2CHR^3CH{=}CHCOOR^4 + Ni(CO)_4 + HCl\ .$$

The *cis*-configuration of the alkenoyl complex, which favours cyclisation, is confirmed also by the formation of up to 97% yields of acetic esters of phenols when the resulting dienoic acids are treated with acetic anhydride in the presence of zinc, aluminium, or tin(IV) chloride or sulphuric acid as catalyst[123,137].

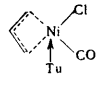
A mixture of carbon monoxide and acetylene reacts with the dimer of π-allylnickel bromide (XLVII) in ether at 0°C to form a dienoyl bromide[124]:



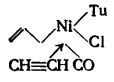
(XLVII)

$$+ 10\,CO + 2\,C_2H_2 \rightarrow 2\,CH_2{=}CHCH_2CH{=}CHCOBr + 2\,Ni(CO)_4\ .$$

The carbonylation of allyl compounds by carbon monoxide in the presence of acetylene can be accomplished in three ways—by the use of nickel carbonyl previously prepared at 20°C and atmospheric pressure, by generating an intermediate compound as catalyst *in situ* at the same temperature and pressure, and finally by using nickel compounds at 150–200°C and pressures of carbon monoxide and acetylene of 30–100 atm—the latter two of which did not require use of the extremely toxic tetracarbonylnickel. For example, a mixture of Raney nickel with thiourea or a mixture of nickel dichloride, thiourea, and iron powder is employed, when the nickel chloride is reduced by the iron powder[117,131,138]. The catalyst may be the five-coordinated nickel complex formed by reducing nickel dichloride hexahydrate with an iron alloy containing 80% of manganese and with thiourea as ligand[139]. The structure of the complex was based on data on five-coordinated halogeno(carbonyl)triphenylphosphine-π-allylnickel[140] and halogeno(thiourea)-π-allylnickel[141] complexes. In the presence of carbon monoxide and acetylene at room temperature and atmospheric pressure the complex catalyst converts methanolic allyl chloride into methyl hexa-2,5-dienoate in ~75% yield. The chief side-products are hexa-1,5-diene, methyl but-3-enoate, 2-oxocyclopent-3-enylacetate, and γ-oxo-δ-2-oxocyclopent-3-enylvalerate, phenyl hexa-2,5-dienoate, and *S*-allylisothiourethane chloride. The five-coordinated nickel complex

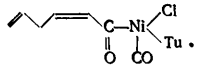


(Tu = thiourea) gives hexa-1,5-diene with allyl chloride, methyl but-3-enoate with carbon monoxide, and *S*-allylisothiourethane chloride with urea[139]. These molecules easily displace acetylene from the complex



(XLVIII)

before reaction with the allyl group. In the presence of carbon monoxide this reaction yields



(XLIX)

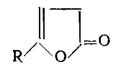
This is followed either by cyclisation to a cyclopentene ring and then the formation of methyl 2-oxocyclopent-3-enyl acetate on the absorption of carbon monoxide, or by cyclisation to phenol and its reaction with carbon monoxide to form phenyl hexa-2,5-dienoate. Further reactions of the 2-oxocyclopent-3-enylacetic ester followed by hydrogenation of the double bond lead to formation of the γ-oxo-δ-2-oxocyclopent-3-enylvaleric ester[142,143].

The course of the reaction is affected by the nature of the solvent. When allyl halides react with carbon monoxide and acetylene in the presence of tetracarbonylnickel in ethereal or ketonic solution, the main products are not unsaturated acids and their esters, as is observed in aqueous or alcoholic medium, but cyclopentenonic acids or lactones. In a ketone solution allyl halides with electron-accepting substituents give satisfactory yields of the corresponding dienoic acids[144]. Acetone, ethyl acetate, dioxan, and oxolan are used as solvents. Methylallyl chloride yields derivatives of cyclohexane and bicyclo-[3,1,0]hexane; but allyl bromide yields hexa-2,5-dienoic and 2-oxocyclopent-3-enylacetic acids, and also lactones of 4-hydroxy-2-isopropylidene-5-(2-oxocyclopent-3-enyl)-pent-3-enoic and 4-hydroxy-5-(2-oxocyclopent-3-enyl)-pent-3-enoic acids. The reaction of allyl chloride with propyne in the presence of tetracarbonylnickel in aqueous acetone leads to the formation of 4-methyl-5-oxocyclohex-3-enecarboxylic acid[145].

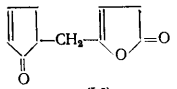
The reactions of allyl halides in ketone solutions are accompanied by the intermediate formation of carbonylhexadienoylnickel chloride[146]. The effect of the solvent on the reaction is due to stabilisation of the acyl group resulting from donor–acceptor interaction with the carbonyl group of the solvent, perhaps in a complex of the type

$$[R^1R^2C\dot{O}{-}CRO{-}\dot{N}i(X)CO].$$

Allyl chloride, carbon monoxide, and substituted acetylenes in the presence of tetracarbonylnickel yield ketone and lactone derivatives containing oxocyclopentenylacetic and oxocyclohexenecarboxylic acids. An intermediate complex of the acetylenic compound with the carbonyl reacts with allyl chloride to close the cyclopentene or cyclohexene ring with the addition of carbon monoxide. After this the ring opens to form the acid or, with further addition of carbon monoxide and acetylene, also ketones and lactones[147]. In ketone solutions allyl halides, acetylene, and carbon monoxide in the presence of tetracarbonylnickel form $\beta\gamma$-unsaturated γ-lactones of the types[146,148,149]

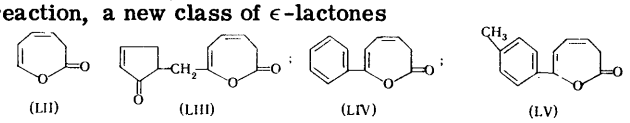


(L)



(LI)

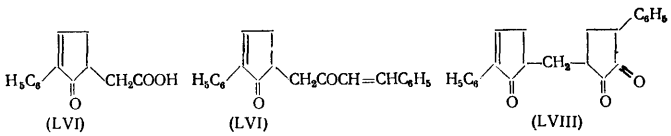
The reaction takes place with the stoichiometric quantity of the carbonyl at 40–50°C. If the concentration of carbon monoxide is low, and water is added at the end of the reaction, a new class of ϵ-lactones



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

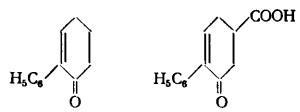
is obtained having two double bonds in the ring. They are formed by the addition of two molecules of acetylene and one molecule of carbon monoxide to an acyl group followed by lactonisation [150].

In the reaction of allyl halides with phenylacetylene and tetracarbonylnickel the allyl group usually adds by means of its primary carbon atom to the unsubstituted carbon in the acetylene, whereas the carbonyl group attacks the hydrocarbon on the opposite side, to form the compound $CH_2:CHCH_2CH:C(C_6H_5)CONiX$. Ring closure results in the formation of cyclopentenone derivatives



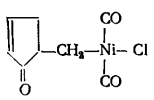
(LVI) (LVI) (LVIII)

or cyclohexenone derivatives

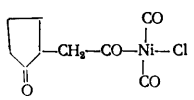


(LIX) (LX)

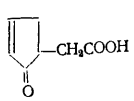
together with γ-lactones similar to the above [151]. The carbonylation of allyl halides with cyclisation is stereospecific. *cis*-Hexa-2,5-dienyl chloride reacts with tetracarbonylnickel in diethyl ether, benzene, or heptane forming



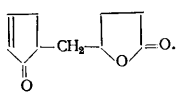
or



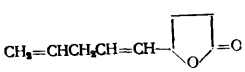
in both of which the carbonyl group can be replaced by other ligands, but in the absence of acetylene



is formed. In the presence of acetylene the course of the reaction is strongly dependent on the solvent; in a ketone medium a γ-lactone



is formed. *trans*-Hexa-2,5-dienyl chloride is not cyclised under the same conditions, but reacts similarly to an acid chloride. In acetone it is mainly converted into a γ-lactone [152].



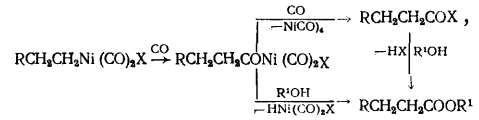
4. Saturated Halogeno-derivatives

(*a*) Catalysts based on Group VIII metals

The preparation of carboxylic acids from alkyl halides, carbon monoxide, and water is accomplished in the presence of tetracarbonylnickel at 350–450°C and 100 atm.[153,154] The alkyl halide may react directly with the carbonyl [124]:

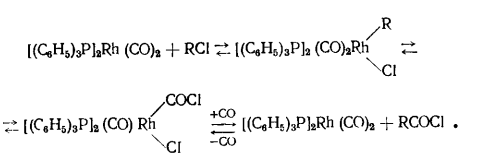
$$Ni(CO)_4 + RCH_2CH_2Cl \rightarrow RCH_2CH_2Ni(CO)_3X,$$

Reaction then takes place with carbon monoxide and an alcohol:



Cobalt carbonyls also catalyse this reaction. In the presence of sodium tetracarbonylcobaltate in alcoholic solution at atmospheric pressure carboxylic esters are obtained in yields up to 80% from alkyl halides. Methyl iodide gives an acetic ester, pentyl iodide forms a hexanoic ester, and 1-chloro- and 2-iodo-octanes give a nonanoic ester. Other catalysts are pent-4-enoyltricarbonylacrylonitrilecobalt, tricarbonyl-π-allylcobalt, acetyltricarbonyltriphenylphosphinecobalt, and sodium tetracarbonylferrate [155]. Ethyl butyrate and isobutyrate are obtained from butyl iodide and carbon monoxide in the presence of potassium tetracarbonylcobaltate in an alcoholic medium. Isomeric compounds are formed by the isomerisation of alkyl- and acyl-cobalt tricarbonyls [156]. In the presence of bistetracarbonylcobalt aldehydes are obtained from alkyl halides and mixtures of carbon monoxide and hydrogen in the proportions 1:4–4:1 at 130–140 atm and 160°C: e.g. octyl bromide yields nonanal (90%). [157] Fluoroalkenes form a complex with bistetracarbonylcobalt at 100°C: tetrafluoroethylene yields μ-tetrafluoroethylene-bistetracarbonylcobalt $(CO)_4Co.CF_2:CF_2.Co(CO)_4$. [158]

Rhodium(II) complexes are also effective catalysts for the carbonylation of alkyl halides to form halides of carboxylic acids [159]. The reaction with chloro-carbonyl-bistriphenylphosphinerhodium(II) can be written [160]



(*b*) Acid catalysts

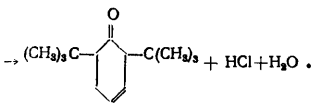
High yields of acid chlorides are obtained by the reaction of alkyl chlorides with carbon monoxide (at 120 atm) in the presence of aluminium trichloride at 50°C. Polyhalogenated alkanes react at 200°C and 900 atm. Carbon tetrachloride gives a 37% yield of trichloroacetyl chloride, chloroform 21% of dichloroacetyl chloride, and dichloromethane 2% of chloroacetyl chloride. Compounds $C_6H_{6-n}Cl_{n-1}COCl$ and $C_2H_{6-n}Cl_n$ are formed in low yields. [161] In the presence of iron trichloride the reaction takes place under milder conditions (150°C and 50 atm), but with still smaller yields [162]. The following

series of reactions is assumed between t-butyl chloride and carbon monoxide (150 atm) in the presence of aluminium or iron(III) chloride at 5°C:[163]

$$(CH_3)_2C{=}CH_2 + HCl \rightleftarrows (CH_3)_3CCl \overset{+CO}{\underset{-CO}{\rightleftarrows}}$$

$$\rightleftarrows \underset{6-12\%}{(CH_3)_3CCOCl} \overset{+CH_2=C(CH_3)_2}{\rightleftharpoons} \underset{12-21\%}{(CH_3)_3CCOCH{=}C(CH_3)_2} + HCl;$$

$$(CH_3)_2C{=}CH_2 + 2\,(CH_3)_3CCOCl \xrightarrow[-AlCl_4^- \text{ or } FeCl_4^-]{AlCl_3 \text{ or } FeCl_3} \rightarrow$$



$$\rightarrow (CH_3)_3C\text{–}C_6H_4\text{–}C(CH_3)_3 + HCl + H_2O\,.$$

Carboxylic acids are prepared from alkyl halides, carbon monoxide, and water in the presence of hydrogen fluoride at 150°C and 45 atm [164]. With carbon monoxide and hydrogen fluoride in the presence of boron trifluoride secondary alkyl chlorides and bromides give high yields of the fluorides of carboxylic acids [165]. t-Pentyl chloride reacts with carbon monoxide and water at high pressures of the former in the presence of silver perchlorate or fluoroborate in nitrobenzene solution to form $\alpha\alpha$-dimethylbutyric acid in quantitative yield [166]. Alkyl halides are converted into carboxylic acid by using, instead of carbon monoxide, formic acid with a large excess of concentrated sulphuric acid at atmospheric pressure and 20–40°C. This method has been employed to obtain α-methylbutyric acid (30%) from s-butyl chloride, and $\alpha\alpha$-dimethylpropionic acid (76%) from t-butyl chloride [167,168]. In the presence of boron trifluoride dihydrate at 25°C and 150 atm methylallyl chloride yields chloro-$\alpha\alpha$-dimethylpropionic acid, and in the presence of a mixture of orthophosphoric acid and boron trifluoride at 70°C and 50 atm carbon monoxide pressure 8-bromo-octene gives a mixture of two isomeric acids—7-bromo-2,2-dimethylheptanoic and 6-bromo-2-ethyl-2-methylhexanoic [169].

Ethyl fluoride in anhydrous hydrogen fluoride under carbon monoxide pressures of 40–400 atm at 120–180°C is converted into a high yield of propionic acid, the reaction being catalysed by the hydrogen fluoride [170]:

$$C_2H_5F \rightarrow C_2H_5^+ + F^-;\ C_2H_5^+ + CO \rightarrow C_2H_5CO^+ \xrightarrow{F^-} C_2H_5COF\,.$$

5. Aromatic Halogeno-derivatives

Aromatic acyl fluorides can be prepared from aryl halides in the presence of tetracarbonylnickel and sodium fluoride at 380°C and 600 atm of carbon monoxide [171]. The same compounds are formed when arenediazonium fluoroborates are heated with carbon monoxide in absolute alcohol saturated with hydrogen chloride in the presence of tetracarbonylnickel [172]. Aryl iodides and acetylene in the presence of this carbonyl at 120–140°C and 30 atm give high yields of γ-keto-acids [173]:

$$C_6H_5I + C_2H_2 + Ni(CO)_4 + ROH + HX \rightarrow C_6H_5COCH_2CH_2COOR + NiIX + 2CO$$
(X=OH, OR, Cl, Br, I; R=Alk.)

Chloro- and iodo-benzenes in the presence of nickel and its di-iodide (1 : 3) under 240–320 atm of carbon monoxide at 250–300°C give 95–100% yields of benzoic acid. This method is used to prepare terephthalic (~ 30%), *o*-toluic (60%), 2-naphthoic (52%) acids [174]. An unusual reaction takes place with aryl halides at 250 to 375°C and 300–600 atm of carbon monoxide in toluene or cyclohexane solution in the presence of tetracarbonylnickel and an alkali-metal carbonate or phosphate: bromobenzene gives a mixture of phthalic anhydride (up to 75%) and benzoic anhydride (intermediate product) with benzene, *p*-chlorotoluene forms 4-methylphthalic anhydride (20%), *o*-bromotoluene produces 3-methylphthalic anhydride (45%), *p*-bromobiphenyl yields phenylphthalic anhydride (35%), and 1-chloronaphthalene gives naphthoic anhydride (4%). [175,176] In the presence of alloy catalysts formed by nickel with copper and chromium singly and together methyl terephthalate is obtained in 55–80% yield from *p*-dichlorobenzene, carbon monoxide, and methanol at 250–450°C and 200–1500 atm. Under similar conditions trichlorobenzene is converted into a mixture of benzene-mono-, -di-, and -tri-carboxylic esters [177]. Raney nickel catalyses the formation of carboxylic acids from aryl halides and carbon monoxide at 210–320°C and 100 atm [178]. Nickel formate and dichloride are less active in this reaction.

In the presence of small quantities of tetracarbonylnickel and water at 190–260°C and 200 atm aryl bromides are converted into the corresponding carboxylic acids. Additions of potassium acetate and sodium benzoate increase the yield of acids to 90% and above by keeping down the concentration of the strongly inhibiting hydrogen bromide formed in the reaction. The rate of the reaction is directly proportional to the concentrations of bromobenzene, tetracarbonylnickel, and water and inversely proportional to the pressure of carbon monoxide. When the composition of the reaction mixture is close to stoichiometric, the yield of aromatic carboxylic acids in the presence of nickel diacetate tetrahydrate at 250–260°C increases sharply [179].

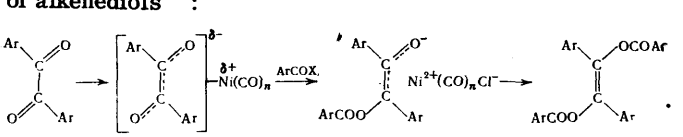
Methyl *p*-chlorobenzoate and dimethyl terephthalate are obtained in 30% and 10% yield respectively from *p*-dichlorobenzene in the presence of dicarbonylbistriphenylphosphinenickel in methyl acetate under 350 atm of carbon monoxide at 345–360°C. [180] In benzene solution under 250–350 atm of carbon monoxide at 200–300°C, with the complex $((C_6H_5)_3P)_2NiBr_2.C_4H_9Br$ or a mixture of nickel and iodine as catalyst, a mixture of terephthalic (17–25%) and *p*-chlorobenzoic (75–83%) acids is obtained [181]. The carbonyls of nickel [182–184], cobalt [185,186], and iron [185] are also used in this reaction. *p*-Chlorobenzoic acid, which is an intermediate in the synthesis of terephthalic acid, may be formed either from the acid chloride obtained from carbon monoxide and dichlorobenzene [181] or via a complex of the catalyst with dichlorobenzene [182]. However, the true reaction mechanism has not been finally elucidated.

Tetracarbonylnickel is able to undergo different stoichiometric reactions with aryl halides depending on the solvent employed. Boiling an aryl iodide with the carbonyl and a solvent is assumed to produce an intermediate complex (LXI), which in alcoholic solution then gives esters in quantitative yield, but in an aprotic solvent, e.g. oxolan or n-hexane, is converted into a diketone:

$$ArI + Ni(CO)_4 \rightarrow \underset{(LXI)}{ArCONi(CO)_nI} \rightarrow \begin{cases} \xrightarrow{ROH} ArCOOR + HI + Ni(CO)_n \\ \xrightarrow{oxolan} ArCOCOAr + NiX_2 + CO \end{cases}$$

$$\rightarrow ArC{=}CAr \quad (ArCOO,\ OOCAr)$$

Aryl chlorides, aryl bromides, and alkyl halides do not react with the carbonyl under these conditions [187–190]. Sterically hindered aryl iodides, such as *o*-tolyl and 1-naphthyl iodides, form not only diketones but also esters of alkenediols [188]:



Esters are obtained by the reaction of aryl halides with carbon monoxide and alcohols under high pressures at 350–400°C in the presence of nickel, cobalt, and strontium salts, especially the chlorides, nitrates, naphthenates, and oleates [191].

The reaction of benzyl chloride with potassium tetracarbonylcobaltate has led to the isolation not only of phenylacetyltricarbonylcobalt but also of *o*-toluoyltricarbonylcobalt, an isomerisation product whose formation is strongly promoted by adding hydrogen tetracarbonylcobaltate and also by conducting the reaction in an atmosphere of nitrogen. This isomerisation, which is not observed at 0°C, already occurs at 30–50°C. [192]

Aryl and cycloalkyl halides undergo carbonylation in the presence of palladium, its salts, and its complexes [127,128,193]. This involves the intermediate formation of a complex similar to that obtained in the decarbonylation of acid halides to aryl halides at 35–60°C. [194] The carbonylation of aryl halides takes place also in the presence of alkali metals at 300–380°C and 5–500 atm of carbon monoxide to form high yields of carboxylic acids. Excess of water stops the reaction. Intermediate formation of an alkali-metal formate is assumed [195–197].

Esters are obtained in up to 95% yield from aryl halides and certain alkyl halides in methanolic or butanolic medium in the presence of tetracarbonylnickel and potassium or sodium methoxide or butoxide. The relative proportions of halide, carbonyl, and alkoxide are 1:6:1–3. The reactivity of the halides increases in the sequence RCl < RBr < RI. The system containing the t-butoxide is considerably more active than that containing the methoxide [198].

Among non-aromatic cyclic halogeno-derivatives that undergo carbonylation are also those of adamantane. 1-Bromoadamantane and carbon monoxide in the presence of an acid catalyst yield adamantanecarboxylic acid [199].

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The results cited in this Review show that catalysts based on nickel, cobalt, and rhodium carbonyls are the most active in the carbonylation of the compounds under consideration [200]. Catalysts based on platinum and palladium chlorides are also extremely active in the carbonylation of halogeno-derivatives. Carbonylation of almost all the compounds takes place also in the presence of acid catalysts such as sulphuric, orthophosphoric, and hydrofluoric acids, boron trifluoride, etc. Special interest attaches to the possibility of effecting the reaction in the presence of these catalysts at atmospheric pressure, with the use of formic acid as carbonylating agent. Carbonylation catalysts based on Group VIII metals, especially with the addition of phosphines, arsines, and amines, are usually more selective than acid catalysts.

So called "stoichiometric" methods, in which tetracarbonylnickel is most often the source of the carbonyl group, can be used as well as catalytic methods.

The conditions of carbonylation and the nature of catalysts and solvents have a marked effect on the course of the reactions. Thus unsaturated monocarboxylic and saturated dicarboxylic acids and their esters, lactones, and chlorides can be obtained from di- and poly-unsaturated hydrocarbons. Saturated and unsaturated acids, their esters, and lactones have been obtained from alcohols. Halogeno-derivatives yield saturated and unsaturated acids, their esters, $\alpha\beta:\gamma\epsilon$-dienoic acids and esters, the difficultly accessible $\beta\gamma$-unsaturated γ-lactones, chloroalkanoic and chloroalkenoic esters, and acid chlorides and fluorides of carboxylic acids.

The production of acetic acid from methanol and the carbonylation of cyclododeca-1,5,9-triene in order to obtain 13-tridecalactam have been accomplished on an industrial scale.

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