

SYNTHESIS OF ORGANIC COMPOUNDS BY DIRECT CARBOXYLATION REACTIONS USING METAL CARBONYLS

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I. INTRODUCTION

Although the Fischer-Tropsch process (181) for the conversion of water gas into hydrocarbons has been known since 1925, its dependence on the *in situ* formation of metal carbonyls was not recognized immediately and most of the pioneering work in the application of metal carbonyls to organic synthesis was carried out by W. Reppe and his co-workers at I. G. Farben during the Second World War (30, 142). One of the main results of this work was the "Oxo" process for the conversion of olefins into the homologous aldehydes or alcohols by reaction with synthesis gas and a cobalt catalyst (58, 122, 168, 190).

It is in fact only over the last few years that the synthetic applications of metal carbonyls have attracted the attention of academic rather than industrial chemists. Much of this awakening interest seems to stem from the revival of interest in organo-metallic compounds engendered by new concepts of bonding as typified by ferrocene (42, 203).

The object of this review is to summarize our present knowledge as regards the application of transition metal carbonyls in the synthesis of organic compounds in which one or more carbon monoxide units have become incorporated. In order to avoid overlap with other reviews, discussion of such related topics as the chemistry of metal carbonyls, their organo-metallic derivatives, and their use in polymerization reactions has not been included except where germane to the present topic. Various modes of classification of the reactions herein reviewed are feasible, but none is pre-eminent as many reactions can be accomplished by the use of more than one metal carbonyl and, not infrequently, a reaction may give rise to a multitude of products.

For the purposes of this review a classification in terms of type of product has been selected. Since much uncertainty still surrounds the precise mode of formation of most of the observed products it seems desirable to defer a discussion of the mechanism of these reactions to the end of the review.

The literature has been surveyed through *Chemical Abstracts* to the end of 1960, but many additional papers have been included.

II. α,β -UNSATURATED CARBOXYLIC ACIDS

The fundamental reaction is typified by the exothermic conversion of acetylene to acrylic acid when reacting with nickel carbonyl under aqueous acidic conditions, at about 40°. The reaction may be carried out with either the stoichiometric quantity of nickel carbonyl or catalytically by formation of nickel carbonyl *in situ* from carbon monoxide and a nickel salt. Typical reaction conditions for the latter are 150° and 30 atmospheres.

Iron pentacarbonyl also has been employed (143) but the yields obtained, about 28%, are much lower than with nickel carbonyl, usually over 50%.

A wide variety of solvent systems has been employed successfully (78) including primary, secondary, and tertiary alcohols, acetone, methyl ethyl ketone, dioxane, tetrahydrofuran, ethyl acetate, pyridine, and anisole. However, water must be present and in anhydrous alcoholic solvents only much reduced yields of acids are obtained. Most of the carboxylation reactions reported in the literature have been carried out in aqueous ethanol and the product is the ethyl ester, formed by subsequent esterification of the acid. This may be minimized by buffering the reaction medium.

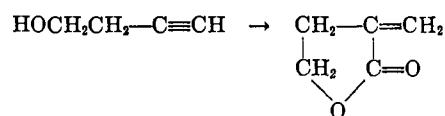
Side-reactions are favored by non-hydroxylic solvents such as dioxane (16, 98). A wide range of esters may be obtained by conducting the reaction in the presence of the appropriate alcohol or thiol, and amides in the presence of amines (143).

The prime purpose of the acid does not seem to be the production of a hydrogen ion concentration since both hydrochloric and acetic acids function equally effectively although trichloroacetic acid, of intermediate dissociation constant, was unsatisfactory (78). The over-all stoichiometry of the carboxylation reaction has been shown (78) to be (acetylene): (nickel carbonyl): (α -methylene acid) in the ratio 10:2:5 in the presence of adequate amounts of water and acid.

The reaction is characterized by an induction period the length of which depends on the individual acetylene and the reaction temperature. Thus it is one minute for acetylene at 40° and for diphenylacetylene at 75°. A transient deep brown coloration is also frequently observed during the reaction. The efficiency of, and the precise conditions for, the carboxylation reaction depend on the individual acetylene and it has been possible to divide substituents into two classes: (A) those which facilitate carboxylation: alkyl; aryl; $-\text{CH}_2\text{OH}$; $-\text{CH}_2\text{OAc}$; $-\text{CHROAc}$; $-\text{CH}_2\text{CH}_2\text{OH}$; $-\text{CH}_2\text{CH}(\text{CH}_3)\text{OH}$, $-\text{CH}_2\text{CH}_2\text{OAc}$, $-\text{CH}_2\text{CH}_2\text{OCHO}(\text{CH}_2)_4$

$\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$; and (B) those which hinder carboxylation: H, $-\text{CHROH}$; $-\text{CR}_2\text{OH}$; $-\text{CR}_2\text{OAc}$; $\text{CH}_2\text{C}(\text{CH}_3)_2\text{OH}$; $-\text{Ac}$; $-\text{CO}_2\text{H}$; $-\text{CO}_2\text{C}_2\text{H}_5$. Thus in an acetylene $\text{XC}\equiv\text{CY}$ if both X and Y belong to class A the reaction is smooth. Similarly, if X comes from A and Y from B the reaction proceeds smoothly also with the formation of $\text{YCH}=\text{CXCO}_2\text{H}$, but if both X and Y come from group B the reaction is not exothermic and gives only a low yield of unsaturated acid after prolonged heating. Of course, acetylene where $\text{X} = \text{Y} = \text{H}$ reacts smoothly.

In general the addition of the elements of formic acid ($\text{H}-\text{CO}_2\text{H}$) is always *cis* and obeys the Markownikoff rule (76) (see Table 1). In only three cases, namely, phenylacetylene, phenylprop-1-yne and non-2-yne, have products resulting from anti-Markownikoff addition been reported (143), where they only appear to have been present in minor amounts. This carboxylation reaction particularly lends itself to the synthesis of α -methylene acids as illustrated by the synthesis of the antibiotic α -methylenebutyrolactone (75).

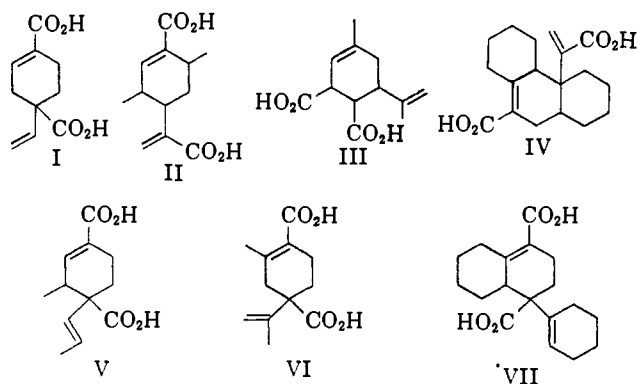


Vinylacetylenes are not very readily carboxylated

TABLE 1
CARBOXYLATION OF ACETYLENES

Acetylene	Products	Yield, %	References
Acetylene	Acrylic acid	95	38, 143, 204
But-1-yne	But-1-ene-2-carboxylic acid	45	204
Propyne	α -Methacrylic acid	50	204
Hex-1-yne	Hex-1-ene-2-carboxylic acid	35	75, 204
Oct-1-yne	Oct-1-ene-2-carboxylic acid	20	143
Non-2-yne	α -Hexyl- β -methylacrylic and α -methyl- β -hexylacrylic acid	32.5	143
Dec-5-yne	Dec-5-ene-5-carboxylic acid	52	76
Phenylacetylene	Atropic acid and traces cinnamic acid	48	75, 143
1-Phenylprop-1-yne	α -Methylcinnamic and α -phenylcrotonic acid	54	143
Diphenylacetylene	α -Phenyl- <i>trans</i> -cinnamic acid	48	76, 98, 143
Prop-2-yn-1-ol acetate	3-Acetoxyprop-1-ene-2-carboxylic acid	40	75
But-1-yn-3-ol	2-Hydroxybut-3-ene-carboxylic acid	...	143
But-3-yn-1-ol	4-Hydroxybut-1-ene-2-carboxylic acid lactone	23	75
But-3-yn-1-ol acetate	4-Acetoxybut-1-ene-2-carboxylic acid	47	75
But-3-yn-1-ol tetrahydropyranyl ether	4-Hydroxybut-1-ene-2-carboxylic acid tetrahydropyranyl ether	20	75
But-2-yn-1, 4-diol diacetate	1,4-Diacetoxybut-2-ene-2-carboxylic acid	58	76
Pent-1-yn-5-ol <i>p</i> -toluenesulfonate	5-Hydroxypent-1-ene-2-carboxylic acid <i>p</i> -toluenesulfonate	1.5	77
Pent-4-yn-2-ol	4-Hydroxypent-1-ene-2-carboxylic acid lactone	30	75
Pent-3-yn-2-ol	4-Hydroxypent-2-ene-2-carboxylic acid	60	76
Hex-1-yn-3-ol acetate	3-Acetoxyhex-1-ene-2-carboxylic acid	48	75
2-Methylpent-4-yn-2-ol	4-Hydroxy-4-methylpent-1-ene-2-carboxylic acid lactone	7.4	75
1-Ethynylcyclohexyl acetate	α -(1-Acetoxy-cyclohexyl)-acrylic acid	3.5	75
1-Phenylprop-2-yn-1-ol acetate	3-Acetoxy-3-phenylprop-1-ene-2-carboxylic acid	50	75
1-Phenylprop-2-yn-1-ol	3-Hydroxy-3-phenylprop-1-ene-2-carboxylic acid	10	75
5-Bromopent-1-yne	5-Bromopent-1-ene-2-carboxylic acid	40	77
Pent-3-yn-2-one	<i>cis</i> and <i>trans</i> 4-Ketopent-2-ene-2-carboxylic acid	30	76
Oct-3-yn-2-one	2-Keto-oct-3-ene-4-carboxylic acid	40	76
Pent-4-yn-1-ol	5-Hydroxypent-1-ene-2-carboxylic acid lactone	21	75
Ethyl propiolate	No reaction	...	80
Sodium propiolate	<i>trans-trans</i> -Muconic acid	1	80
Ethyl but-3-ynoate	Ethyl 3-carboxybut-3-enoate	28	80
Ethyl pent-4-ynoate	Ethyl 4-carboxypent-4-enoate	46	80
Ethyl hex-5-ynoate	Ethyl 5-carboxyhex-5-enoate	40	80
Ethyl hept-6-ynoate	α - <i>n</i> -Butyl- β -carbethoxyacrylic acid	37	76, 80
Hept-6-ynoic acid	<i>n</i> -Butylfumaric acid	28	76
Hex-5-ynonitrile	1-Cyanopent-4-ene-4-carboxylic acid	39	80
Diethyl acetylenedicarboxylate	Ethyl mellitate	18	76

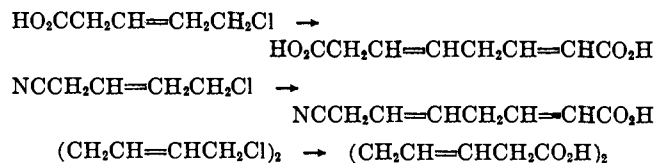
but the reaction appears to be catalyzed by pyridine (77). The initially formed diene acids rapidly dimerize to products which are formulated as I from vinylacetylene (143, 204) after some controversy, II from pent-3-en-1-yne (77), III from 3-methylbut-3-en-1-yne (14), and IV from cyclohex-1-enylacetylene (77). Compound I is known as mikanecic acid (36) and has been isolated from the alkaline hydrolysis of the alkaloid sarracine. It seems to the reviewer that compounds II, III, and IV might be better formulated as V, VI, and VII, respectively.



Attempts to carboxylate diacetylenes were unsuccessful (76).

Application of this reaction to halogenoacetylenes has been investigated (77). In compounds where the halogen is remote from the acetylene grouping the reaction takes place in the normal way. Where the halogen is directly attached to the acetylenic group as in iodobut-1-yne the product is the dehalogenated acetylene, namely, but-1-yne. The position with regard to α -halogenoacetylenes is more complex, the products are allenic and maleic acids, and will be considered in the following section.

If the carboxylation of acetylene is carried out in the presence of an allyl chloride instead of acid the product is a 2,5-dienoic acid. The following examples have been reported (28)

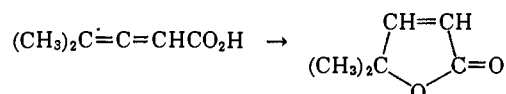


Carboxylation of diphenylacetylene also has been achieved under alkaline conditions (176), although in lower yields, with nickel carbonyl in methanolic sodium hydroxide solution at room temperature. A 30% yield of *trans*- α -phenylcinnamic acid and 58% of 1,2,3,4-tetraphenylbuta-1,3-diene were obtained.

Methyl methacrylate is obtained by the carbonylation of allene using iron or ruthenium carbonyl in methanol at temperatures in the range of 130–225° and carbon monoxide pressures from 300 to 1000 atmospheres. Other products are methyl 2-methylene-3,3-dimethylglutarate, and methyl 3-methylene-1-methylcyclobutane-carboxylate (13).

III. ALLENIC ACIDS

The formation of allenic acids by the reaction of α -halogenoacetylenes with nickel carbonyl under aqueous conditions was mentioned in the preceding section. Other products including substituted maleic anhydrides and ketones also are formed (6). The formation of these latter products is minimized by the use of α -chloroacetylenes and published examples are recorded in Table 2. The presence of acid is not essential for this reaction and the stoichiometric ratio (nickel carbonyl):-(α -chloroacetylene):(chloride ion):(allenic acid) is roughly 2:2:2:1 (81). In the presence of mineral acids, such as hydrochloric, the allenic acids lactonize, *e.g.*



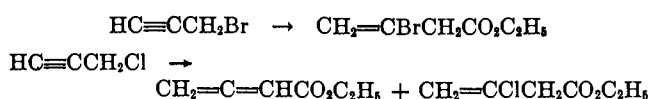
The precise orientation of the product seems to depend on both electronic and steric factors. Initial rearrangement of the α -chloroacetylene to the chloroallene has been precluded by comparing the behavior of $(\text{CH}_3)_2\text{CClC}\equiv\text{CH}$ and $(\text{CH}_3)_2\text{C}=\text{C}=\text{CHCl}$ under the

TABLE 2
PREPARATION OF ALLENIC ACIDS

Acetylene	Allene acid ^a	Yield, ^b %	References
3-Chloroprop-1-yne	Buta-2,3-dienoic acid	6	81, 169
3-Chlorobut-1-yne	Penta-2,3-dienoic acid	10	81
1-Chlorobut-2-yne	2-Methylbuta-2,3-dienoic acid	15	6
3-Chloro-3-methylbut-1-yne	4-Methylpenta-2,3-dienoic acid	45	81
3-Chlorohex-1-yne	Hepta-2,3-dienoic acid	12.5	81
1-Chlorohept-2-yne	2-Butylbuta-2,3-dienoic acid	51	6, 81
1-Bromohept-2-yne	2-Butylbuta-2,3-dienoic acid	11.5	6
1-Iodohept-2-yne	2-Butylbuta-2,3-dienoic acid	22	6
Hept-2-yn-1-ol <i>p</i> -toluenesulfonate	2-Butylbuta-2,3-dienoic acid	31	6
2-Chloro-2-methyloct-3-yne	2-Butyl-4-methylpenta-2,3-dienoic acid	13	81
3-Chloro-3-phenylprop-1-yne	4-Phenylbuta-2,3-dienoic acid	12	81

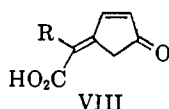
^a In some cases the acid was obtained partly as the ethyl ester. ^b This is the combined yield of acid and ester.

same reaction conditions (81). The chloroallene did not react. Further interesting observations have been made on the reaction of propargyl bromide and chloride with nickel carbonyl in ethanol at 70° (169).



No allenecarboxylic ester could be isolated from the reaction with propargyl bromide, but it was the sole product from the reaction with propargyl chloride at room temperature.

If other α -halogeno or *p*-toluenesulfonyloxyacetylenes are used, much lower yields of allenic acids are obtained and two new types of product are observed. These are substituted maleic anhydrides and ketoacids of structure VIII.



The relative amounts depend on the halogen. Thus carboxylation of 1-substituted hept-2-yne gave the following products (6).

1-Substituent	Allene acid, %	VIII (R = <i>n</i> -butyl), %
Cl	40	None
<i>p</i> -CH ₃ C ₆ H ₄ SO ₃	31	2
Br	11.5	10
I	20	14

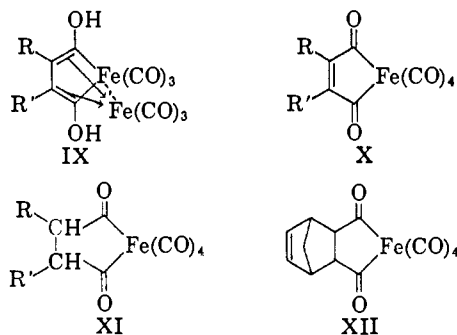
It is thought that small amounts of methylbutylmaleic anhydride may have been missed. All three products were observed in the carboxylation of 1-halogenobut-2-yne (6).

α -Substituent	Allenic acid, %	VIII (R = methyl), %	Dimethylmaleic anhydride, %
Cl	15	2	..
Br	..	5	3
I	..	1	14

IV. MALEIC ACIDS

In addition to the formation of maleic anhydrides as described in the preceding section, they also can be obtained *via* the reaction of an acetylene and an iron carbonyl in aqueous alkali. The initial product is a complex of structure (IX) (65), together with, in the case of acetylene, some ethylene and hydrogen (172). Oxidation of the complex (IX, R = R' = CH₃) with potassium ferricyanide (29) or nitric acid (26) gives the maleic anhydride. Complex (IX) can be converted to complex (X) by oxidation with ferric chloride. This has been done (26) for R = H; R' = H, CH₃, C₂H₅, *n*-C₄H₉, C₆H₅ and for R = R' = H, CH₃, C₂H₅, C₆H₅. Complex (X, R = R' = H) may be reduced with zinc and acetic acid to a dihydro-complex (XI) which may then be oxidized to succinic acid (26). Alternatively

complex (X, R = R' = H) will undergo a Diels-Alder reaction with cyclopentadiene to give complex (XII),



probably also convertible to the corresponding diacid. Complex X (R = R' = Ph) is also obtained from the reaction of diphenylcyclopropenone with iron enneacarbonyl (17).

V. SATURATED CARBOXYLIC ACIDS

Acids of this type are formed by the reaction of olefins with nickel carbonyl under aqueous acidic conditions, in general more stringent than for acetylenes. Thus, for the stoichiometric method, temperatures around 160° at pressures of about 50 atmospheres of carbon monoxide are normally employed, while catalytically temperatures in the region of 250° and carbon monoxide pressures around 200 atmospheres are used. However, highly reactive olefins such as bicyclo[2.2.1]-heptenes react under "acetylene" conditions (16). Cobalt and iron carbonyls also have been employed but the latter particularly appears to be less effective. There are also indications that cobalt tends to cause more side-reactions, for example in the carboxylation of ethylene appreciable amounts of diethyl ketone are formed (46).

The kinetics of carboxylation of cyclohexene using dicobalt octacarbonyl have been investigated (40). The rate was found to be proportional to the concentration of water and the half power of the olefin concentration. The maximum rate at 156° was attained at carbon monoxide pressures between 165 and 210 atmospheres. At lower pressures the rate was directly proportional to the carbon monoxide pressure and at higher pressures decreased proportionately becoming inversely proportional above 340 atmospheres. The rate also depended on the cobalt concentration but to a less than proportional extent.

The direction of addition of the elements of formic acid to olefins does not appear to be as selective as with acetylenes, Table 3, although once more, relatively few quantitative estimates are available.

Alcohols may be used in place of olefins but a higher temperature and the addition of a nickel halide are necessary, Table 4. Secondary and tertiary alcohols react at 275° and primary at 300° (3). The reaction

TABLE 3
CARBOXYLATION OF OLEFINS

Olefin	Product	Yield, %	References
Ethylene	Propionic acid	90	46, 48, 54, 86, 146, 147
Propylene	Butyric and isobutyric acids (1:1)	60	46, 54, 147
But-1-ene	<i>n</i> - and iso-valeric acids	..	147
Isobutene	Isovaleric acid and trimethylacetic acid (6:1)	..	46, 147
Hex-1-ene	2-Methylhexanoic and heptanoic acids	70	38
Oct-1-ene	2-Methyloctanoic and nonanoic acids	84	147, 157
2-Ethylhex-1-ene	2-Ethylheptanoic acid	60	147
Dodec-1-ene	2-Methyldodecanoic and tridecanoic acids	28	147
Octadec-1-ene	2-Methyloctadecanoic acid	67	147
Cyclohexene	Cyclohexanecarboxylic acid	78	38, 40, 146, 147
Cyclooctene	Cyclooctanecarboxylic acid	31	150
Cyclooctatetraene	Cyclooctanecarboxylic acid	51	150
Bicyclo[2.2.1]heptene	Bicyclo[2.2.1]heptane-2-carboxylic acid	80	16
Bicyclo[2.2.1]heptadiene	Bicyclo[2.2.1]hept-5-ene-2-carboxylic acid	80	16
Carvomenthene	Little reaction	..	38
Pinene	Little reaction	..	38
Hexa-1,5-diene	2-Methylhex-5-enoic acid	20	146, 147
Buta-1,3-diene	2-(Carboxycyclohexyl)-propionic acid	..	146
Undecylenic acid	Dodecane-1,12-carboxylic acid	44	38, 147
But-3-en-2-one	Levulinic and 2-methylacetoacetic acid	..	147
Dihydrofuran	Tetrahydrofuran carboxylic acid	..	147

TABLE 4
CARBOXYLATION OF ALCOHOLS

Alcohol	Products	Yield, %	References
Methanol	Acetic acid	87	23, 54, 148
Ethanol	Propionic acid	69	148
Propanol	<i>n</i> -Butyric and isobutyric acids (4:1)	70	148
2-Propanol	Isobutyric acid	..	54
Butanol	α -Methylbutyric acid	47	3, 56
Butan-2-ol	α -Methylbutyric acid	30	3
<i>tert</i> -Butyl alcohol	Isovaleric and trimethylacetic acids (9:1)	57	148
Pentanol	α -Methylvaleric acid	16	3
Neopentanol	C ₄ Acids	21	3
2-Methylbutan-2-ol	Dimethylthylacetic acid	35	3
Hexanol	2-Methylhexanoic acid	55	3
2-Ethylbutan-1-ol	Diethylmethylacetic acid	40	3
Heptanol	2-Methylheptanoic acid	33	3
Heptan-2-ol	2-Methylheptanoic acid	70	3
Octanol	2-Methyloctanoic acid	30	3
Octan-2-ol	2-Methyloctanoic acid	76	3
3-Cyclohexylpropanol	3-Cyclohexyl-2-methylpropionic acid	36	3
Cyclopentanol	Cyclopentanecarboxylic acid	84	3
4-Methylcyclohexanol	4-Methylcyclohexanecarboxylic acid	53	3
Decal-2-ol	Decahydro-1 and 2-naphthoic acids	77	3
2-Phenylethanol	Ethylbenzene	12	3
3-Phenylpropanol	<i>n</i> -Propylbenzene	40	3
4-Phenylbutanol	<i>n</i> -Butylbenzene	40	3
Ethane-1,2-diol	Succinic acid	..	148
Butane-1,3-diol	Adipic and α -methylglutaric acids (2:3)	12.5	148
Butane-1,4-diol	Adipic acid	70	30, 148
Pentane-1,5-diol	Pimelic acid	..	148
	α -Methylvaleric acid	10	3
Hexane-1,6-diol	Suberic acid	..	148
	2-Methylhexanoic acid	30	3
Decane-1,10-diol	Decane-1,10-dicarboxylic acid	54	148
Dodecane-1,12-diol	Dodecane-1,12-dicarboxylic acid	57	148
Tetradecane-1,14-diol	Tetradecane-1,14-dicarboxylic acid	62	148

generally appears to proceed *via* formation of the olefin. Phenyl substituted alcohols appear to undergo preferential hydrogenolysis to the parent hydrocarbon; for example 4-phenylbutanol gives phenylbutane. Carboxylic acid derivatives such as esters (117, 145, 147), thioesters (145, 147), amides (35, 117, 145, 147), or anhydrides (48, 54, 147) are obtained by conducting the reaction in the presence of the appropriate alcohol, thiol, amine, or carboxylic acid.

It is interesting that diols appear to give mainly straight chain acids. A similar observation applies to the carboxylation of cyclic ethers under the same conditions as for alcohols (Table 5).

Esters of carboxylic acids are sometimes encountered among the products of the hydroformylation reaction (Section VII). The reaction of allylic halides with nickel carbonyl at ambient temperatures is reported (28) to give allylcarboxylic acids. Thus allyl chloride is

TABLE 5
 CARBOXYLATION OF CYCLIC ETHERS AND LACTONES

Starting compound	Catalyst	Products	Reference
Tetrahydrofuran	Ni	46% Adipic acid, 37% valeric acid, and valerolactone, α -methylglutaric acid, α -ethylsuccinic acid, α - and γ -methylbutyrolactones	149
	Co	Valerolactone, C ₄ and C ₅ diols, 2-hydroxymethyl-tetrahydropyran	149
Valerolactone	Ni, Pt	46% α -methylbutyric and 3% adipic acids	45
α -Methylbutyrolactone	Ni	Adipic and valeric acids	149
Butyrolactone	Ni	α -Methylglutaric acid	149
2-Methyltetrahydrofuran	Ni	Glutaric acid	149
2,5-Dimethyltetrahydrofuran	Ni	2-Methyladipic acid	149
Tetrahydropyran	Ni	2,5-Dimethyladipic acid	149
Dioxane	Ni	Pimelic acid	149
Thiophane	Ni, Pt	Succinic acid	149
		Adipic acid	64a

converted to but-3-enoic acid, crotyl chloride to pent-4-enoic acid and 1-chloro-4-cyanobut-2-ene to 7-cyanohepta-2,5-dienoic acid.

Acetylene can be carboxylated with dicobalt octacarbonyl in methanol at 95° and a carbon monoxide pressure of 250 atmospheres to give as a major product dimethyl succinate (127), or in the presence of aniline the dianilide (131). Other products in decreasing amounts are methyl acrylate, dimethyl fumarate, dimethyl α -carbomethoxysuccinate, cyclopent-2-enone, dimethyl γ -oxopimelate, methyl γ -oxohexanoate, *trans-trans*-dimethyl muconate, dimethyl hex-3-enedioate, and cyclopentanone (130, 133). Dimethyl succinate apparently is not formed *via* methyl acrylate as the reaction is too slow (177). In the presence of hydrogen the products, when carried out in ethanol, are ethyl propionate, propionaldehyde and its ethyl acetal together with traces of ethyl acrylate, diethyl succinate, and ethyl γ,γ -diethoxybutyrate (33, 34).

VI. ARYL CARBOXYLIC ACIDS

The conversion of aryl halides into aryl carboxylic acids using metal carbonyls has attracted attention as a route to the industrially important terephthalic acid. Treatment of an aryl halide with nickel carbonyl, aqueous acid, and carbon monoxide at temperatures around 300° and carbon monoxide pressures of about 600 atmospheres gives the corresponding benzoic acid, Table 6, in around 30% yield. Apart from nickel carbonyl the use of iron (18) and cobalt carbonyls (18, 205) also has been reported. The carboxylation of aryl halides using a copper-zinc catalyst has been patented (88) but whether this involves a metal carbonyl intermediate is uncertain.

A number of modifications to the general procedure have been employed. Thus, the corresponding esters are obtained if an anhydrous alcohol (87, 138) or lower ester (87, 183), such as methyl formate is used as reaction medium. Amides or nitriles are the products in the presence of formamide, urea, or oxamide (184). The aryl fluoride is formed by the use of sodium fluo-

ride under anhydrous conditions (135). The same product is also obtained by treating the aryl diazonium fluoroborate with nickel carbonyl in an anhydrous alcohol as solvent saturated with hydrogen chloride (90). This reaction proceeds at ambient temperature and pressure, but if carbon monoxide is used in place of nickel carbonyl, pressures up to 1000 atmospheres are required.

Another reaction which may be mentioned conveniently at this stage is the disproportionation of benzoic anhydrides to phthalic anhydrides and benzene, when heated with nickel carbonyl at 325°, and a carbon monoxide pressure of 100 atmospheres (Table 6). Yields of 6 to 70% are claimed (139, 140). Similarly *N,N*-dibenzoylaniline disproportionates into *N*-phenylphthalimide and benzene (139). It is possible to carry out both the carboxylation and disproportionation concurrently if an alkali metal carbonate is present

 TABLE 6
 PREPARATION OF ARYL ACIDS AND DERIVATIVES

Starting material	Product	Reference
Chlorobenzene	Methyl benzoate	138
Iodobenzene	Benzoic acid	205
<i>p</i> -Chlorotoluene	<i>p</i> -Toluic acid	18
<i>p</i> -Chlorotoluene	40% Toluonitrile and 40% <i>p</i> -toluamide	184
<i>p</i> -Dichlorobenzene	<i>p</i> -Chlorobenzoic and terephthalic acids	205
<i>p</i> -Dichlorobenzene	Above as methyl esters	138
<i>p</i> -Dibromobenzene	<i>p</i> -Bromobenzoic and terephthalic acids	182
<i>o</i> -Dichlorobenzene	<i>o</i> -Chlorobenzoic and phthalic acids	205
1-Chloronaphthalene	1-Naphthoic acid	205
Benzenediazonium fluoroborate	Benzoyl fluoride	90
Chlorobenzene	Benzoyl fluoride	135
Bromobenzene	Benzoyl fluoride	135
<i>o</i> -Dichlorobenzene	<i>o</i> -Chlorobenzoyl fluoride	135
<i>p</i> -Dichlorobenzene	<i>p</i> -Chlorobenzoyl fluoride	135
Benzoic anhydride	Phthalic anhydride and benzene	139
<i>o</i> -Toluic anhydride	3-Methylphthalic anhydride	139
<i>p</i> -Methoxybenzoic anhydride	4-Methoxyphthalic anhydride	139
1-Naphthoic anhydride	1,8-Naphthoic anhydride	139
<i>N,N</i> -Dibenzoylaniline	<i>N</i> -Phenylphthalimide	139
Bromobenzene	Phthalic anhydride	140
<i>o</i> -Bromotoluene	3-Methylphthalic anhydride	140
4-Bromobiphenyl	4-Phenylphthalic anhydride	140
1-Chloronaphthalene	1,8-Naphthoic anhydride	140

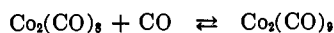
(140). The carbonyl groups in phthalic anhydride will exchange with ^{14}CO in the presence of dicobalt octacarbonyl (194) or nickel carbonyl (178, p. 37). When treated with hydrogen and dicobalt octacarbonyl phthalic anhydride is quantitatively converted to benzoic acid (194).

VII. ALDEHYDES AND ALCOHOLS

The reaction of an olefin with synthesis gas, a mixture of carbon monoxide and hydrogen, to form an aldehyde is frequently referred to as the "Oxo" synthesis. Since the reaction may be visualized as entailing the addition of the elements of formaldehyde ($\text{H}-\text{CHO}$) across the double bond it is also referred to as the "hydroformylation" reaction. Insofar as the products of such reactions are primarily aldehydes the term hydroformylation is preferable.

As customarily performed a cobalt catalyst is employed and is added either as preformed dicobalt octacarbonyl, a cobalt salt, or as the reduced metal. Iron and nickel catalysts also have been indicated for the hydroformylation reaction in the patent literature (47, 56) but both in fact appear to be inactive under the usual conditions. The use of rhodium or iridium catalysts also has been advocated (164) as allowing the reaction to be carried out at lower temperatures than with cobalt. This seems perfectly feasible since both are known to form carbonyl hydrides analogous to cobalt hydrocarbonyl, which is now recognized to be the true intermediate in the hydroformylation reaction (83). The temperatures normally employed are in the region $100\text{--}120^\circ$, as at higher temperatures, $150\text{--}180^\circ$, subsequent reduction of the aldehyde to a primary alcohol occurs. Carbon monoxide-hydrogen pressures of 200–300 atmospheres are typical.

The optimum conditions can be deduced from the extensive kinetic studies that have been made of the hydroformylation reaction (71, 93, 110, 112, 113, 115, 116, 129). The first stage is the formation of cobalt hydrocarbonyl. Although conversion of dicobalt octacarbonyl is rapid, that of other cobalt catalysts is slower and then the reaction rate increases as the reaction proceeds. The cobalt hydrocarbonyl then reacts with the olefin forming the aldehyde and dicobalt octacarbonyl. At constant catalyst concentration over the pressure range 120–380 atmospheres the reaction is first order with respect to olefin concentration and independent of pressure. At pressures below 100 atmospheres the reaction is first order with respect to hydrogen. At constant hydrogen pressure the reaction rate is a maximum for partial carbon monoxide pressures of 8 to 12 atmospheres. At higher carbon monoxide pressures the rate is lower. This probably is the result of a competing reaction of carbon monoxide with dicobalt octacarbonyl (95), thus



decreasing the concentration of cobalt hydrocarbonyl. As it has been shown (22, 71, 83, 121, 202) that olefins will react with cobalt hydrocarbonyl at room temperature and atmospheric pressure and further that the hydrocarbonyl can be formed from the octacarbonyl at room temperature, it seems possible that the conditions customarily employed are excessive.

The reaction rate is reported (73) to be increased by the presence of small amounts of certain organic bases and decreased by large amounts. Pyridine and its homologs, with the exception of 2,6-lutidine, are particularly effective (74), whereas primary and secondary amines are much less efficient and tertiary amines almost inhibit the reaction. Variations in solvent medium have little effect on the reaction rate (199). Thus the reaction proceeds at essentially the same rate in paraffin hydrocarbons, aromatic hydrocarbons, ethers, ketones, or alcohols.

The rate of hydroformylation of an olefin decreases with increasing alkyl substitution so that straight chain terminal olefins > straight chain internal olefins > branched chain olefins (199). The effect is larger the closer the branching is to the double bond. In cyclic olefins the reaction rate is at a minimum in cyclohexene so that the order of reactivity is cyclopentene > cyclohexene < cycloheptene > cyclooctene. Double bond isomerization which is known to be catalyzed by dicobalt octacarbonyl (7) occurs infrequently and then only at temperatures above 150° . However, if Fischer-Tropsch catalysts, usually cobalt oxide and thoria, are employed as in the earlier investigations (82, 152) double-bond isomerization is extensive.

The direction of addition seems to be governed largely by steric effects, the aldehyde group being attached preferentially to the less hindered end of the double bond. Additionally the proportion of branched chain aldehyde appears to increase at higher reaction temperatures (71). These generalizations are best illustrated by a perusal of Table 7. Unfortunately some workers appear to have failed to recognize that their products are a mixture of isomers and in other cases, where relative amounts of isomers isolated are recorded, it seems likely that these were not the original proportions and that one of the isomers may have been removed as a result of a side reaction. One such reaction is the aldol condensation and another a Tischenko type oxidation-reduction between two molecules of aldehyde giving rise to an ester. The former reaction in particular probably is responsible for the very low proportion of straight chain aldehyde observed. Thus the reported increase in the ratio of *n*- to iso-products by the addition of water to the reaction mixture (57) probably is due to partial inhibition of aldol condensation. Often in order to minimize side-reactions either alcohols or orthoformic esters are added and the aldehydes converted as formed into acetals. Alternatively by conducting the

TABLE 7
 HYDROFORMYLATION OF OLEFINS

Olefin	Products	Yield, %	References
Ethylene	Propionaldehyde	72	2, 9, 10, 15, 37, 47, 49, 57, 115, 118, 129, 131, 134, 152, 171
Propylene	Butyraldehyde and isobutyraldehyde	80	37, 44, 47, 49, 56, 57, 111, 118, 129, 131, 144, 152, 164, 171
But-1-ene	1- and 2-Butanol	..	40, 82, 167
But-2-ene	Pentan-1-ol and 2-methylbutanol	..	82
Isobutene	Pentan-1-ol and 2-methylbutanol	..	37, 82
	3-Methylbutan-1-ol (47%) and neopentyl alcohol (1%)	48	10, 82, 192
	Isovaleraldehyde	90	8, 59, 60, 129, 131
Pent-1-ene	Hexanol, 2-methylpentanol, 2-ethylbutanol (5:4:1)	..	82
Pent-2-ene	C ₅ aldehydes	75	1, 2
2-Methylbut-1-ene	β -Methylvaleraldehyde	53	2
	4-Methylpentanol, 3-methylpentanol, 2,3-dimethylbutanol (11:9:1)	..	82
3-Methylbut-1-ene	As above	..	82
2-Methylbut-2-ene	4-Methylpentanol, 3-methylpentanol, 2,3-dimethylbutanol (11:9:1)	..	82
Hex-1-ene	Heptylaldehyde and 2-methylhexylaldehyde (1:1)	64	2, 129, 198
	2-Methylhexanol (17%) and heptan-1-ol (29%)	46	82, 198
2-Methylpent-3-ene	5-Methylhexanol, 3-methylhexanol, 2,4-dimethylpentanol (4:3:3)	..	82
2-Ethylbut-1-ene	β -Ethylvaleraldehyde	55	2
2,3-Dimethylbut-1-ene	3,4-Dimethylpentanal	45	4
	3,4-Dimethylpentanol	..	82
2,3-Dimethylbut-2-ene	3,4-Dimethylpentanol	..	82
3,3-Dimethylbut-1-ene	4,4-Dimethylpentanol	..	82
Heptenes	Heptylaldehyde	66	50, 185
Oct-1-ene	C ₇ aldehydes	13	198
	C ₇ alcohols	61	198
Di-isobutylene	3,5,5-Trimethylhexanol	60	53, 82, 186
"Di- <i>n</i> -butene"	3-Ethylheptanol	..	185
2-Ethylhex-1-ene	C ₇ aldehydes	23	111
Octadec-1-ene	C ₁₇ aldehydes	54	2, 109
Cyclopentene	Cyclopentanealdehyde	65	2
	Cyclopentylcarbinol	..	82
Cyclohexene	Cyclohexanealdehyde	80	37, 49, 111, 127, 131
	Cyclohexylcarbinol	..	82
Cyclooctene	Cyclooctylcarbinol	..	150
Octalins	C ₁₁ aldehydes	32	2
Δ^8 -Octalin	No reaction	..	2
Limonene	β -(4-Methylcyclohex-2-en-1-yl)-butyraldehyde and small amounts of β -(4-methylcyclohexyl)-butyraldehyde	33	21
Camphene	Homoisocamphenylaldehyde	68	91
α -Pinene	2 or 3-formyl-2,6,6-trimethylbicyclo[3,1,1]heptane	..	114, 127
Dihydrodicyclopentadiene	Tricyclo[5,2,1,0 ^{2,4}]decane-4-methylol	90	159
Dicyclopentadiene	C ₁₁ aldehyde and C ₁₂ dialdehyde	..	158
	C ₁₁ alcohol and C ₁₂ diol	..	41
3 β ,20 β -Dihydroxypregn-5-ene	6 α -Hydroxymethylallopregnane-3 β ,20 β -diol	58	119
3 β -Acetoxypregn-5-en-20-one	3 β -Acetoxy-6 α -hydroxymethyl-5 α -pregnan-20-one	50	12
Styrene	Methylphenylacetaldehyde	30	1, 2, 127, 131
1-Vinylnaphthalene	Methyl-(1-naphthyl)-acetaldehyde	29	2
2-Vinylfuran	Aldehydes formed, but not isolated	..	2
3-Vinylcyclohexene	C ₇ unsaturated aldehyde	..	37, 180
	C ₁₀ glycols and 3- and 4-ethylcyclohexylcarbinols	..	41
Vinyl acetate	α -Acetoxypropionaldehyde (30%) and β -acetoxypropionaldehyde (22%)	52	2, 47
Methyl vinyl ether	β -Methoxypropionaldehyde	..	47
Butyl vinyl ether	α -Butoxypropionaldehyde	31	2
Vinyltrimethylsilane	α - and β -trimethylsilylpropionaldehydes (1:1)	16	24
Allyl alcohol	γ -Hydroxybutyraldehyde	30	1, 2, 122, 127
Allyl acetate	γ -Acetoxybutyraldehyde	75	1, 2
Allyl ethyl ether	β -Ethoxyisobutyraldehyde (30%), methylacrolein (6%), γ -ethoxybutyraldehyde (4%)	..	2
Allyl phenyl ether	C ₁₀ aldehydes	50	2
Crotyl alcohol	3-Formylbutanol	..	127
Methylallyl acetate	γ -Acetoxy- β -methylbutyraldehyde	64	123
Allyltrimethylsilane	Trimethylsilylbutyraldehyde	6	24
Acraldehyde	Propionaldehyde	..	2
Acraldehyde diethyl acetal	Aldehydes formed but not isolated	..	2
4-Methyl-2-vinyl- <i>m</i> -dioxane	2-(2-Formylethyl)-4-methyl- <i>m</i> -dioxane	28	51
1,1-Diacetoxyprop-1-ene	Succindialdehyde-1,1-diacetate	75	2
Crotonaldehyde	Butyraldehyde	..	2
Crotonaldehyde diethyl acetal	Methylsuccindialdehyde mono diethyl acetal	50	127
Cyclohex-1-en-3-ylaldehyde	Cyclohexanedialdehyde	24	52
Cyclohex-1-en-3-ylaldehyde diethyl acetal	Cyclohexanedialdehyde mono diethyl acetal	..	52
Methyl vinyl ketone	Methyl ethyl ketone	..	2
Mesityl oxide	Methyl isobutyl ketone	..	2
Methyl acrylate	Methyl γ -oxobutyrate	54	37, 47, 49, 189
Ethyl acrylate	Ethyl γ -oxobutyrate	74	2, 55, 74, 120

TABLE 7 (Concluded)

Olefin	Products	Yield, %	References
Acrylonitrile	Aldehyde formed but not isolated	..	2
Ethyl crotonate	Ethyl β -formylbutyrate and ethyl 5-oxopentanoate	71	1, 2, 55, 57, 127, 132
Butyl crotonate	Butyl 5-oxopentanoate	37	55
Methyl undecylenate	C ₁₁ aldehydes	71	1, 2
Methyl oleate	Mixed aldehyde esters	..	37, 109
Methyl cyclohex-3-enyl carboxylate	Methyl formylcyclohexylcarboxylate	..	37
Ethyl cinnamate	Ethyl β -phenylpropionate	..	2
Ethyl β -(2-furan)-acrylate	Ethyl β -(2-furan)-propionate	..	2
Ethyl sorbate	Ethyl diformylacproates	49	55
Diethyl maleate	Diethyl α -formylsuccinate	62	55
Diethyl fumarate	Diethyl α -formylsuccinate	48	1
Diethyl itaconate	Diethyl α -(formylmethyl)-succinate	56	55
Buta-1,3-diene	<i>n</i> -Valeraldehyde and α -methylbutyraldehyde (1:1)	24	4
Isoprene	Isomeric C ₅ aldehydes	16	4
1,2-Dimethylbuta-1,3-diene	C ₇ aldehydes	22	4
2,3-Dimethylbuta-1,3-diene	3,4-Dimethylpentanal	45	4
Cyclopentadiene	Cyclopentanealdehyde	37	4
Alloöcimene	4,8-Dimethylnonanal	70	20
Myrcene	4,8-Dimethylnonanal	..	20
1-Phenylbuta-1,3-diene	Trace of <i>n</i> -butylbenzene and polymer	..	2, 4
Phenanthrene	No reaction	..	2
Furan	2-Tetrahydrofurfuryl alcohol	35	37, 198
2,5-Dimethylfuran	2,5-Dimethyl-3-tetrahydrofurfuryl alcohol	23	198
Pyridine	N-Formylpiperidine and N-methylpiperidine	..	128
Indole	44% of indole recovered	..	170
N-Methylindole	No apparent reaction	..	170
N-Phenylindole	No apparent reaction	..	170
N-Acetylindole	No apparent reaction	..	170
2-Methylindole	2,3-Dihydro-2-methylindole	26	170
2-Phenylindole	2,3-Dihydro-2-phenylindole	9	170
2-Allylindole	Reaction apparently occurred but no product isolatable	..	170

reaction at a higher temperature the aldehyde is immediately reduced to the corresponding alcohol.

Conjugated dienes are converted to the saturated aldehyde (4). This may proceed *via* the unsaturated aldehyde which is known to be reduced under hydroformylation conditions (2, 198). Unsaturated acids and esters, however, are generally hydroformylated at the β -carbon atom. Ethyl cinnamate is an exception in giving ethyl dihydrocinnamate. This difficulty with α,β -unsaturated aldehydes may be circumvented by first converting them to the acetals (51, 52, 127). Furan is converted under hydroformylation conditions

to tetrahydrofurfuryl alcohol and 2,5-dimethylfuran to 2,5-dimethyl-3-tetrahydrofurfuryl alcohol (198). Attempts to hydroformylate indoles led only to low yields of dihydroindoles (170) and from pyridine a mixture of N-methyl- and N-formylpiperidine was obtained (128).

Alcohols may be used in place of olefins, Table 8. Where feasible the reaction appears to proceed *via* olefin formation. Thus ¹⁴CH₃OH gives ethanol and acetic acid with all the carbon-14 at C.2 and propionaldehyde with the carbon-14 equally distributed between C.2 and C.3 (25). In the case of pinacol the reaction pro-

TABLE 8
HYDROFORMYLATION OF ALCOHOLS

Alcohol	Products	References
Methanol	Acetaldehyde, propionaldehyde, methyl acetate 39% Ethanol, 5% propanol, 1% butanol, 9% methyl acetate, 6.3% ethyl acetate, 8.5% methane	23 144, 193, 206
Ethanol	<i>n</i> - and isobutyl alcohol, <i>n</i> - and isoamyl alcohol	197, 206
1-Propanol	11% <i>n</i> - and isobutyl alcohols	197
<i>tert</i> -Butyl alcohol	55% isovaleraldehyde, 10.5% pivalaldehyde 60% isoamyl alcohol, 4% neopentyl alcohol, 3% isobutane, 3% isobutene	84, 97 192, 197, 206
Cyclohexanol	Cyclohexylcarbinol	206
Pinacol	26% 3,4-dimethylpentanol, 17% pinacolone, 4% pinacolyl alcohol	200
Benzyl alcohol	31% 2-phenylethanol, 63% toluene	195
<i>p</i> -Methylbenzyl alcohol	24% 2-(<i>p</i> -methylphenyl)-ethanol, 58% <i>p</i> -xylene	195
<i>m</i> -Methylbenzyl alcohol	36% 2-(<i>m</i> -methylphenyl)-ethanol, 52% <i>m</i> -xylene	195
<i>p-tert</i> -Butylbenzyl alcohol	28% 2-(<i>p-tert</i> -butylphenyl)-ethanol, 54% <i>p-tert</i> -butyltoluene	195
2,4,6-Trimethylbenzyl alcohol	18% 2-(2,4,6-trimethylphenyl)-ethanol, 58% 1,2,3,5-tetramethylbenzene	195
<i>p</i> -Hydroxymethylbenzyl alcohol	39% 2-(<i>p</i> -methylphenyl)-ethanol, 12% <i>p</i> -phenylene- β,β' -diethanol, 27% <i>p</i> -xylene	195
<i>p</i> -Methoxybenzyl alcohol	44% 2-(<i>p</i> -methoxyphenyl)-ethanol, 16% <i>p</i> -methoxytoluene	195
<i>m</i> -Methoxybenzyl alcohol	2% 2-(<i>m</i> -methoxyphenyl)-ethanol, 23% <i>m</i> -methoxytoluene	195
<i>p</i> -Chlorobenzyl alcohol	16% 2-(<i>p</i> -chlorophenyl)-ethanol, 41% <i>p</i> -chlorotoluene	195
<i>m</i> -Trifluoromethylbenzyl alcohol	5% <i>m</i> -methylbenzotrifluoride	195
<i>p</i> -Carbomethoxybenzyl alcohol	27% ethyl (<i>p</i> -methyl)-benzoate	195
<i>p</i> -Nitrobenzyl alcohol	Polymer of <i>p</i> -aminobenzyl alcohol	195

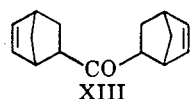
ceeds in part *via* rearrangement to pinacolone and subsequent reduction to pinacolyl alcohol (200). Other products frequently encountered are formate esters and hydrocarbons; for example, methyl alcohol apart from the previously mentioned products gives methyl formate and methane (193). Such hydrogenolyses occur particularly frequently with benzyl alcohols (195, 197, 206), and in some cases may be the predominant reaction. It has been shown (195) that both the rate of reaction and extent of hydrogenolysis are increased by the introduction of nuclear *para* or *meta* electron releasing substituents. Nitro groups are reduced to amino groups under these conditions (195).

Acetylenes react very sluggishly under hydroformylation conditions (43). Pent-1-yne gave only small amounts of 1-hexanol and 2-methylpentanol; diphenylacetylene gave stilbene.

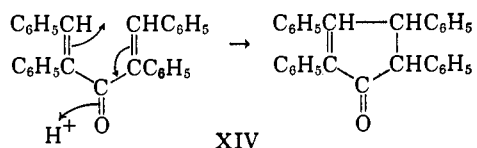
Alcohols are also formed by the reaction of olefins with iron pentacarbonyl under aqueous alkaline conditions (151, 173). At temperatures in the region of 100–150° and pressures of 160–180 atmospheres ethylene is converted to propanol and propionic acid (151), propylene to butanol (141), but-1-ene to *n*-amyl alcohol and 2-methylbutanol (151) and cyclopentene to cyclopentylcarbinol (174). Under less strongly alkaline conditions the products are mainly the corresponding aldehydes (173, 174). The reactive species in the reaction seems to be $H_2Fe_2(CO)_8$ as its salt (27). The reaction medium is a very powerful reducing agent capable of reducing benzaldehyde to benzyl alcohol (173, 174), acetone to 2-propanol (174), allyl alcohol to propanol (151), methyl acrylate to methyl propionate (189), methyl vinyl ether to ethanol and methanol, and but-2-en-1,4-diol or dihydrofuran to butan-1,4-diol (151). Terminal olefins are isomerized by these solutions, hex-1-ene giving a mixture of hex-2-ene and hex-3-ene.

VIII. KETONES, TROPONES, AND QUINONES

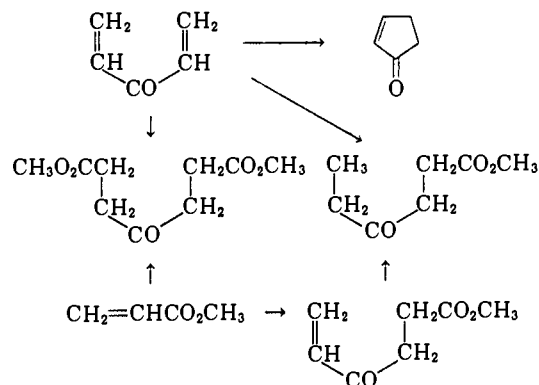
Ketones are not infrequently formed as by-products in carboxylation and hydroformylation reactions and may become major products under some conditions. Thus carboxylation of ethylene gives diethyl ketone in 15% yield together with propionic acid, using a cobalt catalyst (46). Similarly under hydroformylation conditions ethylene gives appreciable amounts of diethyl ketone (152) and propylene gives some dipropyl ketone (171). In the carboxylation of bicyclo[2.2.1]heptadiene and bicyclo[2.2.1]heptene in acidic aqueous ethanol-dioxane mixtures with nickel carbonyl the amount of the ketone XIII or its tetrahydro derivative increases with the proportion of dioxane (16).



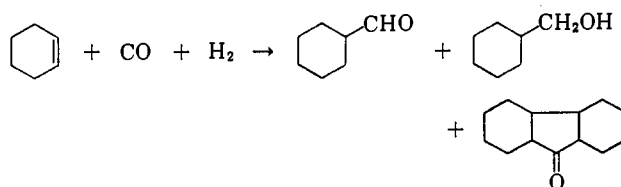
Analogous observations have been made with acetylenes. When diphenylacetylene is carboxylated with nickel carbonyl in dioxane containing a little acidic aqueous ethanol, the main product is 1,2,3,4-tetraphenylcyclopent-2-en-1-one and only a small amount of ethyl *trans*- α -phenylcinnamate is formed (98). It was suggested originally that this product arose from reduction of tetraphenylcyclopentadienone but a more likely mode of formation is the Nazarov type cyclization of the intermediary divinyl ketone XIV.



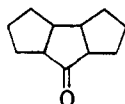
Similar reactions would account for some of the products obtained from the reaction of acetylene with dicobalt octacarbonyl in methanol at 95° and a carbon monoxide pressure of 250 atmospheres. Apart from methyl acrylate and dimethyl succinate which are the major products (130), there have also been isolated (133) cyclopent-2-en-1-one, dimethyl γ -ketopimelate, and methyl γ -ketoheptanoate. These compounds may all be considered as being formed from divinyl ketone. Alternatively dimethyl γ -ketopimelate could be formed from two molecules of methyl acrylate, and methyl γ -ketoheptanoate *via* formation of methyl 3-ketohept-4-enoate and a subsequent reduction for which there are analogies (*cf.* Section VII).



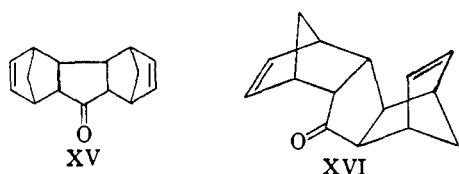
In non-aqueous systems the products are cyclopentanones or cyclopentadienones, from olefins or acetylenes, respectively. Cyclohexene reacts with carbon monoxide and hydrogen in a stainless steel autoclave at 300° and 800 atmospheres pressure forming cyclohexylaldehyde, cyclohexylcarbinol, and perhydrofluorenone (85).



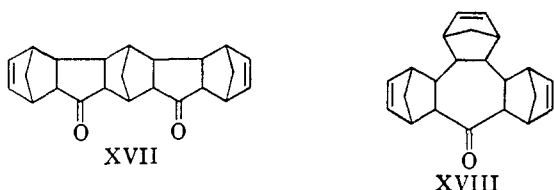
Perhydrofluorenone also was formed when a platinum lined autoclave was employed at 350° and it was claimed that this obviated a metal carbonyl intermediate. However, it is known from recent work that definite carbonyl complexes are formed on platinum surfaces (39). Cyclopentene reacted under similar conditions to give a compound which, presumably (85), is



The reaction of bicyclo[2.2.1]heptadiene with iron carbonyls has been examined in some detail (16, 125). The reaction with iron pentacarbonyl takes place at 80° and appears to be an autocatalytic. Apart from several hydrocarbons and a bicycloheptadiene-iron tricarbonyl complex three ketones have been isolated. The major ketone compound has structure XV and stereochemistry XVI (16).



The other two ketones have structures XVII and XVIII (16) with probably the same endo fusion of the new rings to the bicycloheptane nucleus.



Bicyclo[2.2.1]heptene does not react with iron pentacarbonyl under comparable conditions, but with iron enneacarbonyl at room temperature it gives reasonable yields of tetrahydro XV. Bicyclo[2.2.1]heptadiene under the latter conditions gives mostly hydrocarbon dimers and small amounts of XV together with lesser amounts of other ketones. Benzobicyclo[2.2.1]heptadienes react more sluggishly with iron pentacarbonyl forming ketones of structure XIX having the same stereochemistry as XVI (16).

Closely analogous reactions have been observed between metal carbonyls and acetylenes. Diphenylacetylene reacts with nickel carbonyl in benzene at 80° forming tetraphenylcyclopentadienone together with hexaphenylbenzene (17). The reaction is inhibited by carbon monoxide pressures. Under similar conditions acetylene is converted to indan-1-one XX presumably *via* formation of the cyclopentadienone dimer XXI (151).



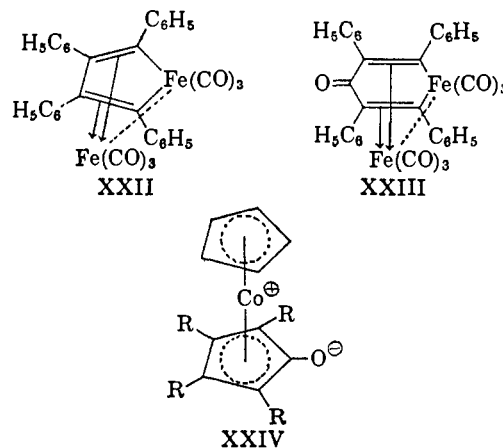
The most extensively investigated reaction of this type is that of iron carbonyls with diphenylacetylene under non-aqueous conditions (69, 165, 191). The reaction is carried out in benzene either by irradiating the refluxing solution and iron pentacarbonyl, heating with iron dodecacarbonyl, or stirring with iron enneacarbonyl at room temperature. Some tetraphenylcyclopentadienone is formed directly and isolated as its iron tricarbonyl complex. Other complexes also are formed, including XXII and XXIII which are readily converted to tetraphenylcyclopentadienone or its iron tricarbonyl complex by irradiation, heating with carbon monoxide, reaction with bromine in acetic acid, or reduction with lithium aluminum hydride. Essentially the same products are obtained from diphenylcyclopropenone and iron enneacarbonyl (17). A number of other cyclopentadienones have been prepared by similar methods, Table 9. Acetylene (70) and probably also

TABLE 9
FORMATION OF CYCLOPENTADIENONES

Acetylene	Cyclopentadienone	References
Phenylacetylene	2,5-Diphenylcyclopentadienone ^a	69, 79, 89, 166, 191
Phenylprop-1-yne	2,5-Diphenyl-3,4-dimethylcyclopentadienone ^a	191
<i>p</i> -Bromophenylacetylene	Di- <i>p</i> -bromophenylcyclopentadienone ^a	191
Trimethylsilylacetylene	Bis-(trimethylsilyl)-cyclopentadienone ^a	191
Phenyltrimethylsilylacetylene	Diphenylbis-(trimethylsilyl)-cyclopentadienone ^a	191
Diphenylacetylene	Tetraphenylcyclopentadienone	17, 69, 165

^a Isolated as iron tricarbonyl complexes.

phenylacetylene (69) form tropone iron tricarbonyl complexes. The cyclopentadienone ring also is formed when diphenyl- or dimethylacetylene is irradiated with π -cyclopentadienylcobalt dicarbonyl, the product being the complex XXIV (R = CH₃ or C₆H₅) (92).



Under appropriate conditions the reaction of acetylenes with metal carbonyls may lead to the formation of quinones. Irradiation of iron pentacarbonyl in dimethylacetylene gives a duroquinone iron tricarbonyl complex and similar products are obtained with pent-1-yne and hex-1-yne (175). These complexes are decomposed by air to the quinone and by dilute acid to the hydroquinone. Similarly irradiation of dimethylacetylene in a solution containing the manganese pentacarbonyl anion and then acidification gave some durohydroquinone (92). Tetraphenylquinone or the hydroquinone has been obtained from complex XXIII either by reduction with lithium aluminum hydride, sodium in liquid ammonia or stannous chloride (69), or by oxidation with nitric acid (165).

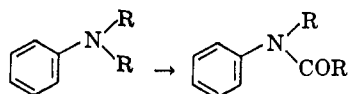
A relatively extensive collection of hydroquinones has been prepared by the reaction of acetylenes with iron pentacarbonyl in aqueous alkali together with small amounts of acrylic acids (151). Mono-substituted acetylenes give the 2,5-disubstituted hydroquinones, Table 10. Probably the initial product is the quinone, which is known to be reduced under these conditions.

TABLE 10
FORMATION OF HYDROQUINONES (151)

Acetylene	Hydroquinone	Yield, %
Propyne	2,5-Dimethylhydroquinone	30
But-2-yne	2,3,5,6-Tetramethylhydroquinone	15
Phenylacetylene	2,5-Diphenylhydroquinone	22
Prop-1-yn-3-ol	2,5-Di-(hydroxymethyl)-hydroquinone	..
But-2-yn-1,4-diol-dimethyl ether	2,3,5,6-Tetra-(methoxymethyl)-hydroquinone	27.5
Hex-3-yn-2,5-diol-dimethyl ether	2,3,5,6-Tetra- α -(α -methoxyethyl)-hydroquinone	2
3-Dimethylaminoprop-1-yne	2,5-Di-(dimethylaminomethyl)-hydroquinone	4
3-Diethylaminoprop-1-yne	2,5-Di-(diethylaminomethyl)-hydroquinone	2
Bis-1,4-dimethylamino-but-2-yne	2,3,5,6-Tetra-(dimethylaminomethyl)-hydroquinone	22

IX. FORMAMIDES AND UREAS

Primary and secondary amines react with a wide variety of metal carbonyls forming the N-formyl derivatives and ureas, Table 11. Many of these reactions take place at room temperature and pressure. The behavior of tertiary amines on carbonylation is very interesting. Aliphatic tertiary amines are reported (143, 147) to give N,N-dialkylformamides; the fate of the alkyl group is not reported. Aryl tertiary amines on the other hand are reported to react as shown where R is an alkyl group.



The only two examples quoted are N,N-diethylaniline and N,N-dimethyl- β -naphthylamine.

TABLE 11
PREPARATION OF FORMAMIDES AND UREAS

Amine	Metal carbonyl	Product	References
Ammonia	Re(CO) ₄ Cl	Formamide	64
Ammonia	Ru(CO) ₅ I ₂	Formamide	62
Methylamine	HgCo(CO) ₄ ^a	N-Methylformamide	64
Butylamine	Ni(CO) ₄ ^a	N-Butylformamide and N,N'-dibutylurea	143, 147
Ethylenediamine	HgCo(CO) ₄ ^a	N,N'-Diformylethylenediamine	64
Aniline	Ni(CO) ₄ ^a	Formanilide and N,N'-diphenylurea	143
	Co ^a	N,N'-Diphenylurea	147
Dimethylamine	Co ₂ (CO) ₈	Dimethylformamide and tetramethylurea	179
Dibutylamine	Ni(CO) ₄ ^a	Dibutylformamide	143, 147
Diisobutylamine	Ni(CO) ₄ ^a	Diisobutylformamide	147
Pyrrolidine	Ni(CO) ₄ ^a	N-Formylpyrrolidine	143, 147
Piperidine	Fe(CO) ₅	N-Formylpiperidine	63
Piperidine	Co ₂ (CO) ₈ ^a	N-Formylpiperidine	179
Piperidine	Ni(CO) ₄ ^a	N-Formylpiperidine	63, 143, 147
Morpholine	Fe(CO) ₅	N-Formylmorpholine	63
Morpholine	Ni(CO) ₄ ^a	N-Formylmorpholine	63, 143, 147
Perhydrocarbazole	Ni(CO) ₄ ^a	N-Formylperhydrocarbazole	143, 147
Hexamethyleneimine	Co ^a	N-Formylhexamethyleneimine	147
Trimethylamine	Co ^a	Dimethylformamide	147
Tributylamine	Co ^a	Dibutylformamide	147
Tributylamine	Ni(CO) ₄ ^a	Dibutylformamide	143

^a Catalytic reactions.

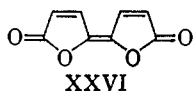
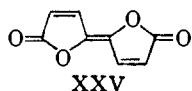
The conversion of urea to hydrazine may be achieved, using iron, cobalt, nickel, molybdenum, or tungsten metal at temperatures from 40 to 150° depending on the metal (124). When iron is used semicarbazide is formed as a major by-product. Conversely hydrazine hydrate reacts with iron pentacarbonyl at 45° under a carbon monoxide pressure of 900 atmospheres to give semicarbazide, while at 100° and 500 atmospheres both urea and semicarbazide are formed (160). Totally different products are obtained from hydrazine hydrate and carbon monoxide in the absence of a catalyst (161). The reversible nature of this reaction is further demonstrated by the exchange of ¹⁴CO with N,N'-diphenylurea at 230° in the presence of dicobalt octacarbonyl (194).

Azobenzenes are converted, in part, to N,N'-diarylureas when reacting with dicobalt octacarbonyl and carbon monoxide and hydrogen (67, 68, 103, 104). Under the same conditions both nitrobenzene and hydrazobenzene also were converted to N,N'-diphenylurea. In the case of unsymmetrically substituted azobenzenes all three possible N,N'-diarylureas are formed although the one containing two different aryl nuclei predominates (103, 104). Ureas also have been obtained from oximes under similar conditions. Thus, benzaldoxime gave N,N'-dibenzylurea (35%) and N-benzylurea (10%) (154) and analogous products were obtained from the oxime of 2-acetylnaphthalene (151), together with heterocyclic compounds (see the following section).

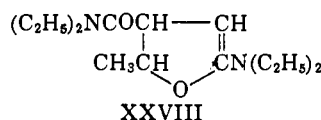
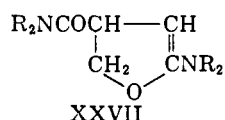
X. HETEROCYCLIC COMPOUNDS

A variety of heterocyclic compounds have been pre-

pared by reactions with metal carbonyls. A curious type of compound is formed by the reaction of acetylene with dicobalt octacarbonyl and 100–1000 atmospheres of carbon monoxide at 90–120°. The product is mainly the *trans* bifurandione XXV together with smaller amounts of the *cis* compound XXVI (5, 66, 162).

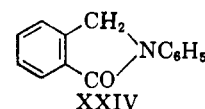


The *cis* form XXVI apparently is more stable than the *trans* XXV from which it is formed rapidly by acid or base treatment. Substituted acetylenes such as hex-3-yne, propyne, hex-1-yne, as well as phenyl-, 2-naphthyl-, *p*-chlorophenyl-, and *o*-methoxyphenyl-acetylene give analogous compounds (162). Unsymmetrically substituted acetylenes appear to give mixtures of positional isomers. Under the same conditions 3-dialkylamino-prop-1-yne give products formulated as XXVII (R = CH₃, C₂H₅); 3-methyl-3-diethylaminoprop-1-yne gave XXVIII (163).



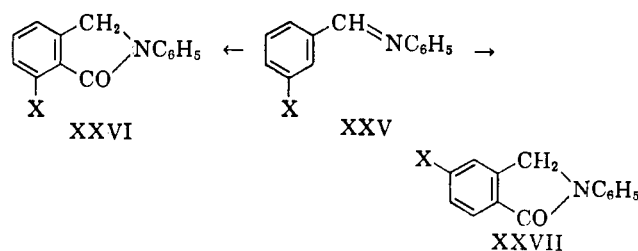
Other routes to heterocyclic compounds have started with compounds containing carbon–nitrogen double bonds as in Schiff bases or oximes and nitrogen–nitrogen double bonds as in azobenzenes. Anils, such as benzalaniline, are converted by reaction with dicobalt octacarbonyl in benzene at 200–230° and carbon

monoxide pressures in the range 100 to 200 atmospheres into 2-phenylphthalimidines XXIV (99, 103, 107, 108, 137).



A wide variety of Schiff bases have been employed in this reaction, Table 12. Iron pentacarbonyl also catalyzes the reaction, but less effectively. No reaction occurred with nickel carbonyl (103, 105), although its use is claimed in a patent (137). The reaction is inhibited by polar solvents such as ethanol, tetrahydrofuran, and water (103, 105). In the presence of hydrogen the anils are reduced to the corresponding amines (103, 104).

The factors controlling the direction of cyclization are not obvious; only a few *m*-substituted benzaldehyde anils XXV have been employed.

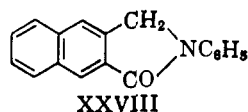


When X was dimethylamino or hydroxyl, phthalimidine XXVI was obtained in good yield, but when X was methoxyl the product was XXVII in very low yield. It is noteworthy that 2-naphthaldehyde anil gave XXVIII in high yield.

TABLE 12
CONVERSION OF SCHIFF BASES TO PHTHALIMIDINES

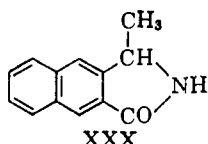
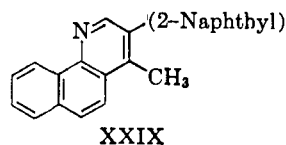
R—CR ² =N—R ¹	Phthalimidine	Yield, %	References		
R	R ¹	R ²			
C ₆ H ₅	C ₆ H ₅	H	2-C ₆ H ₅ —	72	99, 103, 105, 107, 137
C ₆ H ₅	<i>p</i> -CH ₃ OC ₆ H ₄	H	2- <i>p</i> -CH ₃ OC ₆ H ₄	86	103, 106, 107
C ₆ H ₅	<i>p</i> -HOC ₆ H ₄	H	2- <i>p</i> -HOC ₆ H ₄	65	103, 106, 107
C ₆ H ₅	<i>p</i> -ClC ₆ H ₄	H	2- <i>p</i> -ClC ₆ H ₄	75	103, 106, 107
C ₆ H ₅	<i>p</i> -NO ₂ C ₆ H ₄	H	103, 106, 107
C ₆ H ₅	C ₆ H ₅ CH ₂	H	2-C ₆ H ₅ CH ₂	82	103, 106, 107
C ₆ H ₅	CH ₃	H	2-CH ₃	49	103, 106, 107, 137
C ₆ H ₅	(CH ₂) ₂ ^a	H	2-(—CH ₂) ₂	..	137
C ₆ H ₅	<i>p</i> -(C ₂ H ₅) ₂ NC ₆ H ₄	H	2- <i>p</i> -(C ₂ H ₅) ₂ NC ₆ H ₄	..	137
C ₆ H ₅	1-naphthyl	H	2-(1-naphthyl)	..	137
<i>p</i> -(CH ₃) ₂ NC ₆ H ₄	C ₆ H ₅	H	2-C ₆ H ₅	82	106, 107, 137
<i>p</i> -HOC ₆ H ₄	C ₆ H ₅	H	2-C ₆ H ₅	77	99, 106, 107
<i>p</i> -CH ₃ OC ₆ H ₄	C ₆ H ₅	H	2-C ₆ H ₅	..	137
<i>p</i> -ClC ₆ H ₄	C ₆ H ₅	H	2-C ₆ H ₅	..	137
<i>o</i> -NO ₂ C ₆ H ₄	C ₆ H ₅	H	103, 106, 107
<i>o</i> -HOC ₆ H ₄	C ₆ H ₅	H	103, 106
<i>o</i> -CH ₃ OC ₆ H ₄	C ₆ H ₅	H	2-C ₆ H ₅	18	103, 106, 107
<i>m</i> -CH ₃ OC ₆ H ₄	C ₆ H ₅	H	2-C ₆ H ₅	5	103, 106, 107
<i>m</i> -HOC ₆ H ₄	C ₆ H ₅	H	2-C ₆ H ₅	77	103
<i>m</i> -(CH ₃) ₂ NC ₆ H ₄	C ₆ H ₅	H	2-C ₆ H ₅	82	103
1-Naphthyl	C ₆ H ₅	H	2-C ₆ H ₅	96	99, 103, 106, 107
2-Naphthyl	C ₆ H ₅	H	2-C ₆ H ₅	80	99, 103, 106, 107
C ₆ H ₅	C ₆ H ₅	CH ₃	2-C ₆ H ₅	61	103, 106, 107, 108, 137
C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	2-C ₆ H ₅	97	103, 106, 107, 108, 137

^a Anil from ethylenediamine.



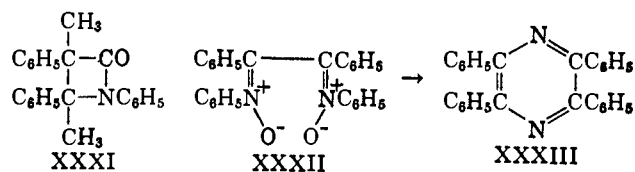
The effect of substituents on the rates of reaction of a series of anils $RN=CR^1, R^2$ have been observed (103). When $R = R^1 = C_6H_5$, the nature of $R^2 = H, CH_3$ or C_6H_5 had no appreciable effect on the rate. Ortho substituents on $R = C_6H_5$ such as 2-methyl, 2,6-dimethyl and 2,6-diethyl lowered the rate, although a *p*-methyl group enhanced it. No steric effect from the *ortho* substituents was observed for reduction of the anils. In the cases where $R = p$ -nitrophenyl, $R^1 = H$, $R^2 = C_6H_5$ and $R = C_6H_5$, $R^1 = H$, $R^2 = o$ -nitrophenyl no reactions occurred.

Attempts to prepare 2-hydroxyphthalimidines from aldoximes or ketoximes have been unsuccessful. Benzaldoxime is variously reported as giving *N,N'*-dibenzylurea and *N*-benzylurea (155) or benzamide (103, 107). 2-Acetylnaphthalene oxime gave analogous ureas together with a large amount of XXIX and a small amount of XXX, probably as a result of hydrogenolysis of the 2-hydroxyphthalimidine (156).



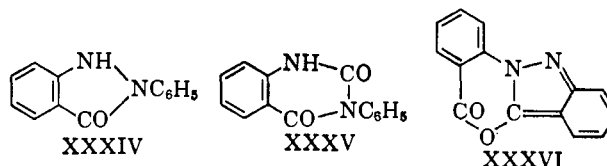
Benzophenone oxime (154) and its *O*-methyl ether (153) gave 3-phenylphthalimidine. Acetophenone oxime was converted to 3-methylphthalimidine and a compound tentatively formulated as XXXI, and phenyl benzyl ketoxime produced 3-benzylphthalimidine and small amounts of 3,4-dihydro-3-phenylisocarbostyryl (154). However, the prize transformation must be that of XXXII to XXXIII (153)!

Reaction of compounds containing a vinylogous carbon-nitrogen double bond such as 2-(2'-phenylvinyl)-



pyridine and 2-(2'-phenylvinyl)-quinoline gave violet-red unstable solids (68, 103, 106),

Azobenzene reacts with dicobalt octacarbonyl at 170–190° under a carbon monoxide pressure of 150 atmospheres forming 2-phenylindazolone XXXIV and small amounts of 3-phenyl-2,4-dioxo-1,2,3,4-tetrahydroquinazoline XXXV and diphenylurea (67, 68, 100, 103). At 220–230° the major product was XXXV with small amounts of diphenylurea and XXXVI (68, 100, 102, 103). Under the same conditions XXXIV is converted to XXXV (68, 100, 101, 103).



Identical observations have been made as regards catalysts and solvents as for conversion of anils to phthalimidines (68, 103). Reaction of azobenzene with nickel carbonyl in cyclohexane at 250° is claimed to give primarily XXXVI together with aniline, diphenylurea, and XXXV (136).

In all the cases reported, Table 13, cyclization always occurs on to the substituted ring. Attempts to carry out similar carbonyl insertions in indazole, indazolone, 2-phenylbenzoxazole and 2-phenylbenzimidazole were unsuccessful (68).

XI. THE MECHANISM OF CARBONYL INSERTION REACTIONS*

A variety of mechanisms have been proposed from

* For a stimulating account of some aspects of this topic see Reference 178.

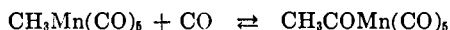
TABLE 13
CARBONYLATION OF AZOBENZENES $R-N=N-R^1$

R	R ¹	Product	Yield, %	References
C ₆ H ₅	C ₆ H ₅	2-Phenylindazolone	49	6, 7, 68, 100, 103
<i>p</i> -CH ₃ C ₆ H ₄	C ₆ H ₅	5-Methyl-2-phenylindazolone	35	68, 103
<i>p</i> -ClC ₆ H ₄	C ₆ H ₅	5-Chloro-2-phenylindazolone	24	68, 100, 103
<i>p</i> -(CH ₃) ₂ NC ₆ H ₄	C ₆ H ₅	5-Dimethylamino-2-phenylindazolone	80	68, 100, 103
C ₆ H ₅	C ₆ H ₅	3-Phenyl-2,4-dioxo-1,2,3,4-tetrahydroquinazoline	65	67, 68, 100, 102, 103, 136
<i>p</i> -CH ₃ C ₆ H ₄	C ₆ H ₅	6-Methyl-3-phenyl-2,4-dioxo-1,2,3,4-tetrahydroquinazoline	36	68, 103
<i>m</i> -CH ₃ C ₆ H ₄	C ₆ H ₅	7-Methyl-3-phenyl-2,4-dioxo-1,2,3,4-tetrahydroquinazoline	26	68, 103
<i>p</i> -ClC ₆ H ₄	C ₆ H ₅	6-Chloro-3-phenyl-2,4-dioxo-1,2,3,4-tetrahydroquinazoline	43	68, 100, 103
<i>p</i> -(CH ₃) ₂ NC ₆ H ₄	C ₆ H ₅	6-Dimethylamino-3-phenyl-2,4-dioxo-1,2,3,4-tetrahydroquinazoline	18	68, 100, 103
<i>p</i> -CH ₃ C ₆ H ₄	<i>p</i> -CH ₃ C ₆ H ₄	6-Methyl-3-(<i>p</i> -tolyl)-2,4-dioxo-1,2,3,4-tetrahydroquinazoline	40	68, 103
<i>p</i> -ClC ₆ H ₄	<i>p</i> -ClC ₆ H ₄	6-Chloro-3-(<i>p</i> -chlorophenyl)-2,4-dioxo-1,2,3,4-tetrahydroquinazoline	17	68, 103
<i>p</i> -CH ₃ OC ₆ H ₄	<i>p</i> -CH ₃ OC ₆ H ₄	6-Methoxy-3-(<i>p</i> -methoxyphenyl)-2,4-dioxo-1,2,3,4-tetrahydroquinazoline	28	68, 103
<i>p</i> -NCC ₆ H ₄	C ₆ H ₅	No appreciable reaction	..	68, 103
α -Naphthyl	α -Naphthyl	No appreciable reaction	..	68, 103
β -Naphthyl	β -Naphthyl	No appreciable reaction	..	68, 103

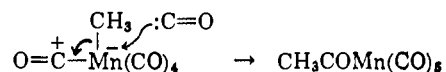
time to time for the carbonylation reactions discussed in this review. Originally (143, 147), it was pointed out that many of the observed results could be accounted for if an intermediate cyclopropanone or cyclopropenone were formed. This idea is still inherent even in some recent publications although it has become increasingly obvious that such an explanation was untenable. The final disproof was provided by a study of the reactions of the recently prepared diphenylcyclopropenone under carboxylation conditions (17). In the absence of nickel carbonyl it was found to be perfectly stable under the usual acidic conditions used for carboxylating diphenylacetylene, even when nickel chloride was present. In the presence of nickel carbonyl conversion to *trans* α -phenylcinnamic acid occurred. That this took place *via* diphenylacetylene was demonstrated by the ready decarbonylation of diphenylcyclopropenone with nickel carbonyl in benzene.

The reactions are currently envisioned as proceeding *via* three distinct stages. Initial reaction of the substrate with the metal carbonyl leads to the eventual formation of a carbon-metal σ -bond. A carbonyl insertion between the carbon and metal atoms then occurs and this is followed by cleavage of the acyl-metal bond.

The process of carbonyl insertion is now fairly well understood, largely as a result of the study of alkyl and acyl manganese pentacarbonyls (31). Acetyl, phenylacetyl, and benzoyl manganese pentacarbonyls are decarbonylated rapidly on heating to methyl, benzyl, and phenyl manganese pentacarbonyls, respectively. That this process was reversible was demonstrated by reconversion of methyl manganese pentacarbonyl to acetyl manganese pentacarbonyl by treatment with carbon monoxide at 35 atmospheres and room temperature.



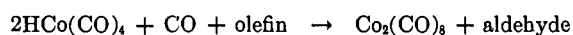
This reversible carbonylation occurred with all the groups investigated with the exception of trifluoromethyl. Trifluoroacetyl manganese pentacarbonyl was converted to the trifluoromethyl compound on heating but the reverse process could not be achieved. Further interesting information came from the carbonylation of methyl manganese pentacarbonyl with ^{14}C when the carbonyl group inserted was found not to contain any carbon-14. Additionally $\text{CH}_3^{14}\text{COMn}(\text{CO})_5$ gave after decarbonylation methyl manganese pentacarbonyl still retaining all of the original carbon-14. These observations indicate a mechanism in which the carbon monoxide residue inserted is one originally bonded to manganese and the over-all reaction may be envisioned as occurring *via* a metal to carbon migration of the methyl group. Whether or not the insertion of the carbonyl group and the coordination of another carbon monoxide molecule to the manganese atom are concerted processes is uncertain.



That this carbonyl insertion reaction was not only specific for carbon-manganese bonds was demonstrated (31) by the conversion of π -cyclopentadienylmethyl-dicarbonyliron to the corresponding acetyl compound by treatment with carbon monoxide at 140 atmospheres and 125°. π -Cyclopentadienylmethyltricarboxymolybdenum appeared to undergo a similar carbonylation. Subsequently it has been shown that methyl, ethyl, benzyl (22), and allyl (61) tetracarbonyl cobalt compounds also undergo reversible carbonylation to the corresponding acyltetracarbonylcobalt compounds. It is also claimed (22) that the alkyltetracarbonylcobalt compounds are in equilibrium with the acyltricarboxylcobalt derivatives, but the evidence so far presented is not convincing. Recently the reversible carbonylation of alkyl and aryl platinum, palladium, and nickel and cobalt tertiary phosphine complexes of general formula $[\text{MRX}(\text{PET}_3)_2]$ has been reported (19). The dialkyl and diaryl complexes $[\text{MR}_2(\text{PET}_3)_2]$ are also carbonylated and in the case of *trans*- $[\text{PtMe}_2(\text{PET}_3)_2]$ gave in addition diacetyl. It is suggested that these reactions occur through five or six coordinated intermediates. This is supported by the observed readier carbonylation of the palladium compounds as palladium expands its coordination shell more readily than platinum.

The reaction which has received the most thorough mechanistic investigation is the hydroformylation reaction. The main features of the kinetics of the reaction have been summarized already in Section VII. A variety of reaction sequences have been proposed by individual investigators to account for the observed interdependencies of the reactants; most however ignore the now proven intermediacy of cobalt hydrocarbonyl in the reaction.

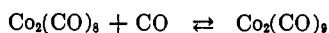
The main evidence for this conclusion may be summarized. Under normal hydroformylation conditions dicobalt octacarbonyl is converted rapidly to cobalt hydrocarbonyl (121). However, in the presence of an olefin, no free cobalt hydrocarbonyl is detectable until hydroformylation is complete. Furthermore it is found (83) that cobalt hydrocarbonyl reacts rapidly with olefins at room temperature and pressure absorbing carbon monoxide and giving as products an aldehyde and dicobalt octacarbonyl in accordance with the equation



Additional circumstantial evidence is supplied by the observation that the rate of this reaction with various olefins (83) parallels the relative rates at which the same olefins undergo hydroformylation (199). On the basis of these observations the sequence of equations (a) \rightarrow (d) fairly accurately summarizes the pathway of hydroformylation

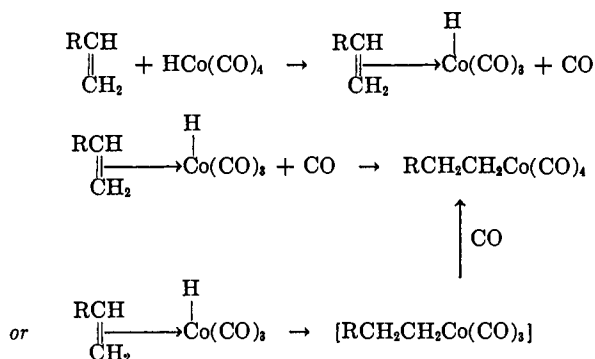
- (a) $\text{Co}_2(\text{CO})_8 + \text{H}_2 \rightarrow 2\text{HCo}(\text{CO})_4$
 (b) $\text{HCo}(\text{CO})_4 + \text{RCH}=\text{CH}_2 \rightarrow \text{RCH}_2\text{CH}_2\text{Co}(\text{CO})_4$
 (c) $\text{RCH}_2\text{CH}_2\text{Co}(\text{CO})_4 + \text{CO} \rightarrow \text{RCH}_2\text{CH}_2\text{COC}(\text{CO})_4$
 (d) $\text{RCH}_2\text{CH}_2\text{COC}(\text{CO})_4 + \text{HCo}(\text{CO})_4 \rightarrow$
 $\text{RCH}_2\text{CH}_2\text{CHO} + \text{Co}_2(\text{CO})_8$

In addition the equation

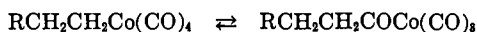


should be added (95).

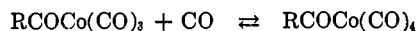
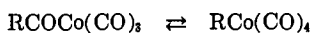
Whether step (b) is a single step as depicted is unknown; it seems likely, however, that it is in fact a multi-step process, *e.g.*,



The carbonyl insertion reaction also has been formulated (22) as proceeding

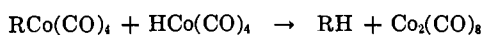


the latter acyltricarbonylcobalt complex being reduced by hydrogen. The evidence for such a route is not convincing, being based essentially on the successful reduction of an acyltetracarbonyl-cobalt compound by hydrogen at 25°, which process was completely inhibited by a high pressure of carbon monoxide. It is suggested that the entity actually reduced is the acyltricarbonylcobalt complex and the reported observations are explained on the basis of the equilibria



Objection was taken to step (d) in the original scheme as it was thought that the concentration of cobalt hydrocarbonyl would be too low; however, it depends entirely on the relative rates of the individual steps which are presently unavailable. In the absence of experimental detail it is as yet impossible to assess fairly the merits of the latter hydroformylation scheme.

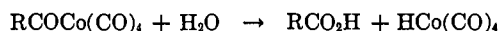
The formation of hydrocarbons in the hydroformylation reaction is readily envisioned in terms of the reaction



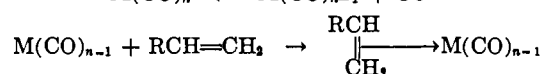
competing with prior carbonyl insertion. This is very well illustrated by the hydroformylation of nuclear substituted benzyl alcohols, where electron-withdrawing substituents favored hydrocarbon formation (195). In this connection the reluctance of trifluoromethyl-

pentacarbonylmanganese to undergo carbonyl insertion may be recalled (31).

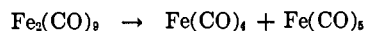
Knowledge regarding the mechanism of the other reactions considered in this review is much more fragmentary. The carboxylation of olefins using dicobalt octacarbonyl exhibits kinetics which, as might be expected, seem to roughly parallel those of the hydroformylation reaction (40). It is tempting to think in terms of hydrolysis of an acyltetracarbonylcobalt complex, *e.g.*



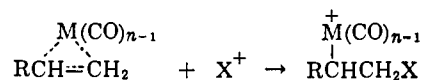
The primary step in the reactions with iron or nickel carbonyls seems to occur *via* an initial dissociation of the metal carbonyl to a coordinatively unsaturated species which then coordinates with the substrate. Some re-



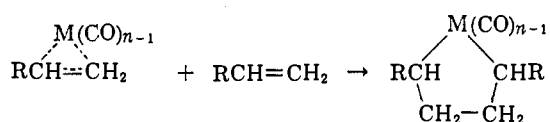
actions, as already noted, exhibit marked temperature dependence or are aided by irradiation with ultraviolet light. Dissociation of metal carbonyls is known to occur under such conditions. The reaction of nickel carbonyl with diphenylacetylene is inhibited by high carbon monoxide pressures (17), probably through inhibition of initial dissociation of the nickel carbonyl. It has been demonstrated that nickel carbonyl exchanges with carbon monoxide (11) and that nickel dicarbonyldiphosphines exchange with phosphines (94), through formation of a tricoordinated nickel intermediate. A similar intermediate is involved in the thermal and photochemical decompositions of nickel carbonyl (187). The position with regard to iron pentacarbonyl is much less certain; in some cases at least reactions appear to be autocatalytic and are also aided by irradiation with ultraviolet light. The latter suggests either the intermediacy of an iron tetracarbonyl species or the initial formation of di-iron enneacarbonyl which frequently gives the same reactions as iron pentacarbonyl and tri-iron dodecacarbonyl but at much lower temperatures. This then could dissociate into $\text{Fe}(\text{CO})_4$ and iron pentacarbonyl.



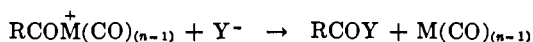
The subsequent reaction of the substrate metal carbonyl complex then may be



where X may be a proton or an incipient allylcarbenium ion as in a modification of the carboxylation of acetylenes. This satisfactorily accounts for the observed over-all *cis*-addition of formic acid in the carboxylation of acetylenes (76). Alternatively the complex may react in an analogous way with another olefin or acetylene molecule, *e.g.*

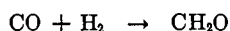


Such a scheme entailing essentially carbanionic addition would account for the apparent absence of skeletal rearrangements in the carbonylation reactions of bicyclo[2.2.1]heptadiene (16). Carbonyl insertion then can be envisioned as occurring in the normal way. The cleavage of the acyl metal carbonyl complexes has not been investigated experimentally. However, consideration of the products obtained suggests a generalized reaction scheme of the type



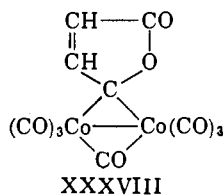
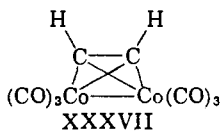
where Y^- , for example, may be a hydride ion as in hydroformylation, hydroxide ion in carboxylation, or fluoride anion as in formation of acyl fluorides. The metal subcarbonyl thus produced is then available for further reaction with another molecule of substrate, thus providing a chain reaction, or combination with a carbon monoxide molecule.

Reactions entailing the incorporation of the elements of formaldehyde such as hydroformylation and formation of divinyl or dialkyl ketones entail an over-all reduction, in the purely stoichiometric sense



In hydroformylation this is achieved by direct supply of hydrogen, while in the reactions with iron carbonyls in alkaline solution the over-all reduction entailed in the reaction is at the expense of oxidation of carbon monoxide. In other reactions such as the formation of open chain ketones along with carboxylation the source of "hydrogen" is presumably oxidation of zero-valent metal to the corresponding cation.

Thus far reactions in which only one carbon monoxide unit has been introduced have been considered. Recently some light has been thrown on the way in which more than one carbon monoxide unit may be introduced. It has been found that when the acetylenedicobalt hexacarbonyl complex XXXVII (177) reacts with carbon monoxide at 200 atmospheres and 70° three moles of carbon monoxide are taken up and the complex XXXVIII (96) is formed.



The conversion of this complex to succinic acid is readily conceivable as is also its conversion to bifurandione (XXV). It is probably no coincidence that reactions leading to di-carbonyl compounds only appear

to occur under conditions where polynuclear metal carbonyls may be present, as in the formation of duroquinone from but-2-yne and iron pentacarbonyl in sunlight (175). Iron pentacarbonyl is converted to di-iron enneacarbonyl under such conditions. Evidence recently has been produced that formation of complexes of type (IX) from acetylenes and iron carbonyls in alkaline solution occurs most readily in the presence of salts of $\text{H}_2\text{Fe}_2(\text{CO})_8$ (27).

In conclusion, it is obvious that much remains to be investigated in this field, especially with regard to the mechanism of these reactions, which present many unique features combining aspects of carbonium ion, carbanion, and free radical processes. Recent press reports of the discovery of organic compounds in meteorites (which are normally composed of iron and nickel with lesser amounts of other transition metals) spotlights the possibility that the initial formation of organic compounds on Earth may have entailed reactions akin to those discussed in this review.

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