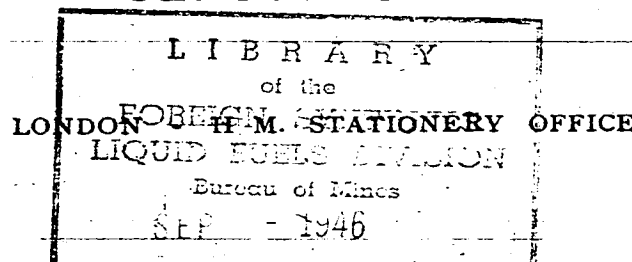FINAL REPORT No. 355.
ITEM No. 22.

RECENT ADVANCES IN THE CHEMISTRY OF CARBON MONOXIDE.

Rose, J. D.

" This report is issued with the warning that, if the subject matter should be protected by British Patents or Patent applications, this publication cannot be held to give any protection against action for infringement."

BRITISH INTELLIGENCE OBJECTIVES SUB-COMMITTEE

RECENT ADVANCES IN THE CHEMISTRY
OF
CARBON MONOXIDE

Translation of lecture by

Dr.W. Reppe, Ludwigshafen

Reported by

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RECENT ADVANCES IN THE CHEMISTRY OF CARBON MONOXIDE

Lecture by Dr. W. Reppe, Ludwigshafen, 26.4.45.

INTRODUCTION

Carbon monoxide has for many years been a substance of extraordinary interest to chemical industry. As examples of its large scale utilisation may be cited the synthesis of methanol from CO and hydrogen, of formic acid, of acetic acid from methanol and CO, the Fischer-Tropsch synthesis and the Mond nickel process. More recently American patent literature has shown an increasing interest in the addition of CO and water to olefines, and of CO to alcohols and ethers; these syntheses, however, are normally carried out at extremely high pressures and temperatures.

The great reactivity of carbon monoxide can be attributed to the free valencies (two lone electron pairs) and it was considered that CO should be capable of participating in many more reactions than had hitherto been reported. For example, reaction with acetylene could be expected, and this, if successful, would be doubly interesting as carbon monoxide and acetylene are formed in equimolecular proportions in the formation and utilisation of carbide, as shown in the following equation.

$$CaO + 3C \longrightarrow CaC_2 + CO$$
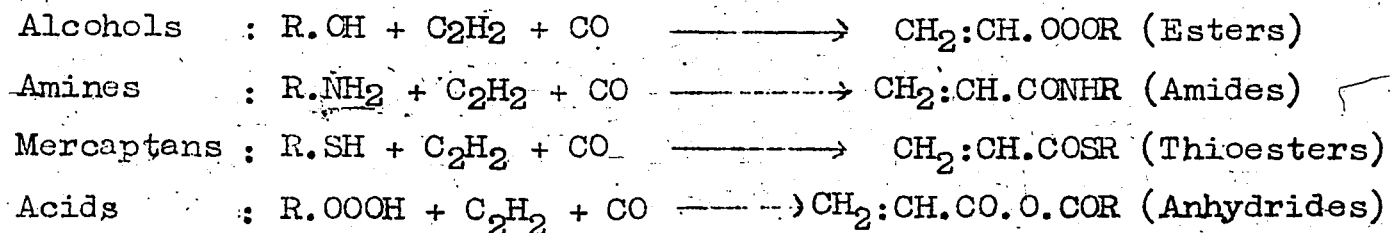$$\downarrow 2H_2O$$
$$C_2H_2$$
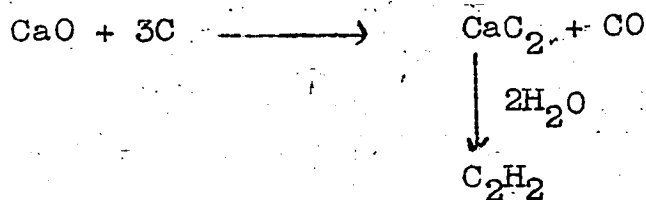
Normally, the carbon monoxide from a carbide oven is burnt, and its only value is that of a fuel.
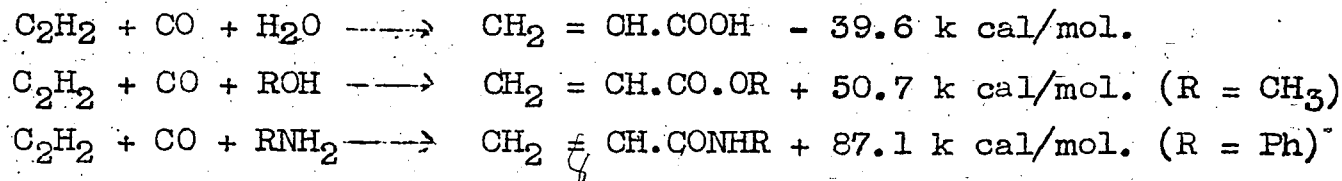
It was thought that CO and acetylene should give a mono- or di-aldehyde, and in the preliminary experiments in which nickel was used as catalyst, it became clear that the reaction which occurred was between acetylene and nickel carbonyl, and that the products of the reaction were not aldehydes but derivatives of acrylic esters.

# 1. SYNTHESIS OF ACRYLIC ACID AND ITS DERIVATIVES

The first experiments carried out used mixtures of acetylene and carbon monoxide with either nickel or nickel carbonyl as catalysts. When water was present, acrylic acid was formed and it was rapidly found that other substances containing active hydrogen atoms could be used in place of water with formation of corresponding derivatives of acrylic acid, thus:

Alcohols $\quad$: $R.OH + C_2H_2 + CO \longrightarrow CH_2:CH.OOOR$ (Esters)

Amines $\quad$: $R.NH_2 + C_2H_2 + CO \longrightarrow CH_2:CH.CONHR$ (Amides)

Mercaptans : $R.SH + C_2H_2 + CO \longrightarrow CH_2:CH.COSR$ (Thioesters)

Acids $\quad$: $R.OOOH + C_2H_2 + CO \longrightarrow CH_2:CH.CO.O.COR$ (Anhydrides)

The formation of acids, esters and amides from water, alcohols and amines, respectively, shows the following thermodynamics

$C_2H_2 + CO + H_2O \longrightarrow CH_2 = OH.COOH - 39.6$ k cal/mol.

$C_2H_2 + CO + ROH \longrightarrow CH_2 = CH.CO.OR + 50.7$ k cal/mol. (R = CH_3)

$C_2H_2 + CO + RNH_2 \longrightarrow CH_2 \neq CH.CONHR + 87.1$ k cal/mol. (R = Ph)

A tentative hypothesis put forward during the earlier work to account for the above reactions postulated the combination of acetylene and carbon monoxide with the formation of methylene ketene as an unstable intermediate product. The reactivity of ketene is well known, and it was thought that the fission of methylene ketene by water or alcohols would satisfactorily account for the formation of acrylic acid and esters.

$$CH \equiv CH + CO \longrightarrow [\; CH_2 = C = C = O\;]$$

$$H_2O \qquad\qquad R.OH$$
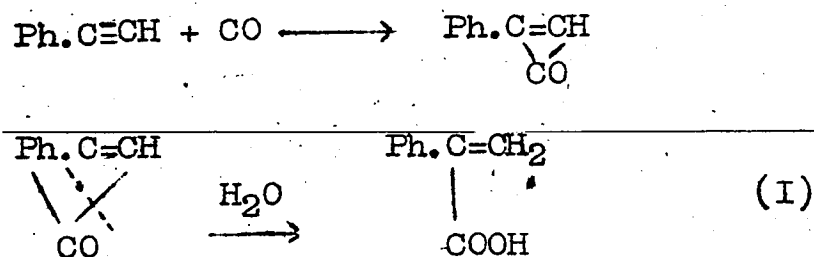
$$CH_2 = CH.COOH \qquad\qquad CH_2 = CH.COOR$$
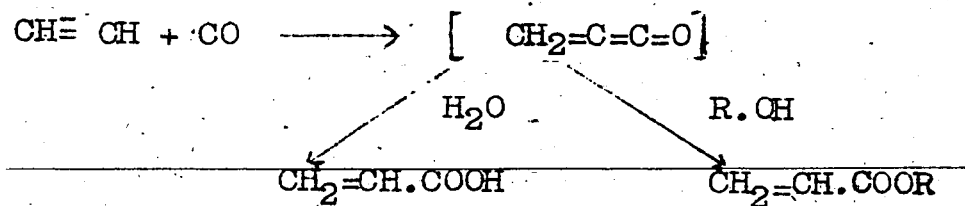
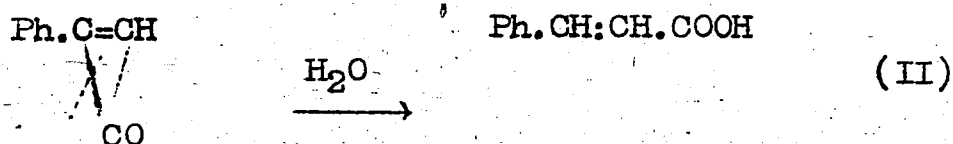This explanation is entirely unsatisfactory; it will not account for the activity of mono- and di-substituted acetylenes. Thus

phenylacetylene with CO gives a-phenylacrylic acid, $CH_2:CPh.COOH$, and not cinnamic acid, whilst on the above hypothesis disubstituted acetylenes should be incapable of reaction.

It is therefore postulated that the intermediate product in this type of reaction is <u>cyclopropenone</u> and that acrylic acid derivatives are formed by fission of this unstable ring system, as follows:
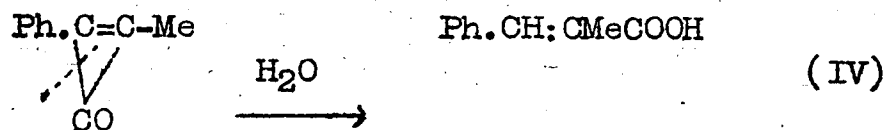
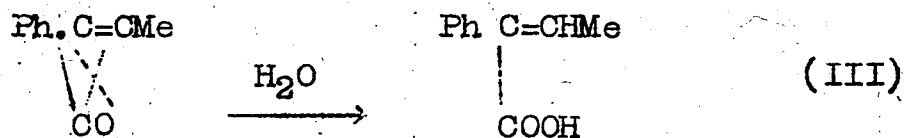$$CH{=}CH + CO \longrightarrow \underset{CO}{CH{=}CH}$$
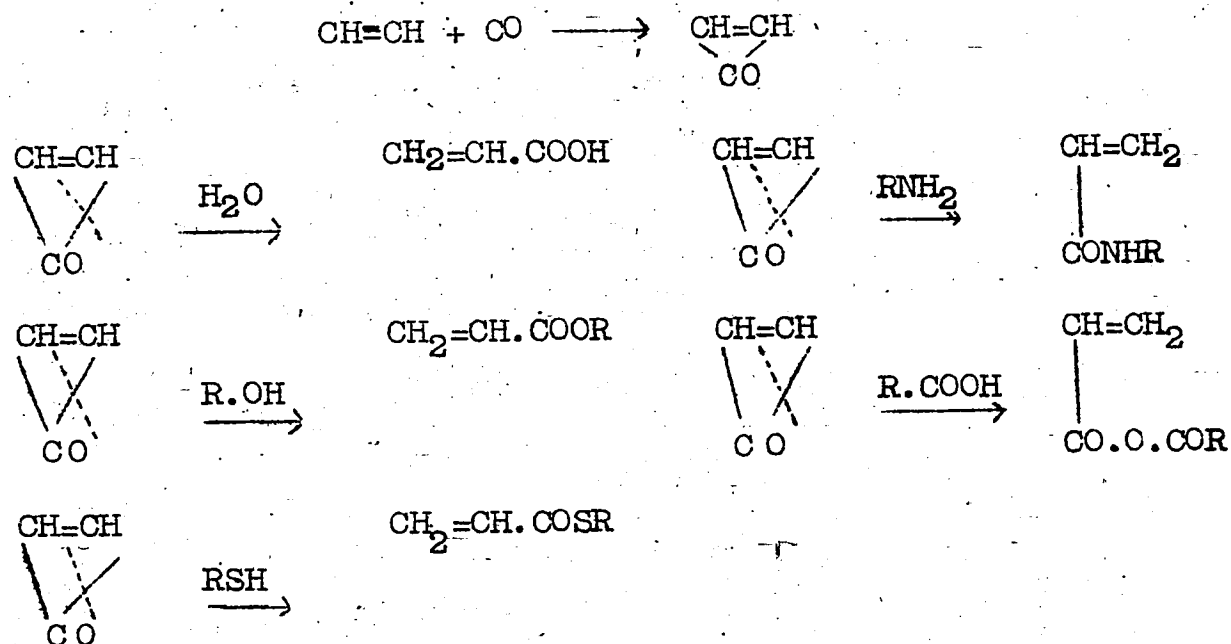
Similarly, using phenylacetylene, phenyl<u>cyclopropenone</u> is postulated as an intermediate and this might be expected to open in two ways giving a-phenylacrylic acid (I) and cinnamic acid (II).

$$Ph.C{\equiv}CH + CO \longrightarrow \underset{CO}{Ph.C{=}CH}$$

(I)

$$\underset{\underset{\text{CO}}{\diagup\!\!\diagdown}}{\text{Ph.C=CH}} \qquad \xrightarrow{\text{H}_2\text{O}} \qquad \text{Ph.CH:CH.COOH} \qquad\qquad (\text{II})$$
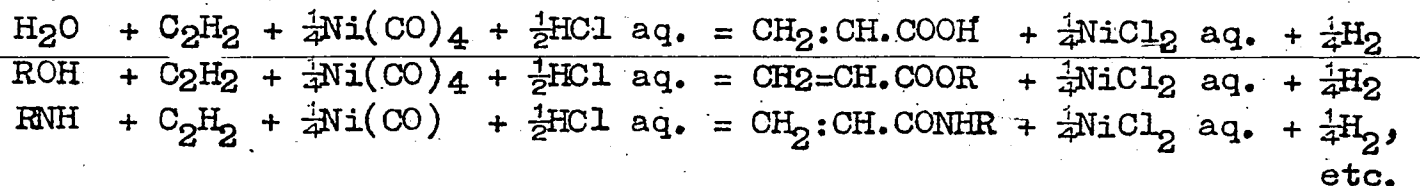
In fact only a-phenylacrylic acid is formed; with phenylmethylacetylene, fission of the hypothetical phenylmethylcyclopropenone can occur in both directions and both a-phenylcrotonic acid (III) and amethylcinnamic acid (IV) are obtained.

$$\text{Ph.C}\!\equiv\!\text{C-Me} + \text{CO} \xrightarrow{\hspace{2cm}} \underset{\underset{\text{CO}}{\diagdown\!\!\diagup}}{\text{Ph-C=C-Me}}$$

$$\underset{\underset{\text{CO}}{\diagdown\!\!\diagup}}{\text{Ph.C=CMe}} \qquad \xrightarrow{\text{H}_2\text{O}} \qquad \underset{\text{COOH}}{\overset{\text{Ph C=CHMe}}{\mid}} \qquad\qquad (\text{III})$$

$$\underset{\underset{\text{CO}}{\diagup\!\!\diagdown}}{\text{Ph.C=C-Me}} \qquad \xrightarrow{\text{H}_2\text{O}} \qquad \text{Ph.CH:CMeCOOH} \qquad\qquad (\text{IV})$$

The reactions of acetylene and carbon monoxide with compounds containing active hydrogen atoms are applicable to all acetylenic compounds, and can be carried out using Ni(CO)$_4$ in stoichiometric quantities, or catalytically using carbon monoxide and metals capable of forming carbonyls, or derivatives of such metals.

Stoichiometric method

Using metal carbonyls, it is necessary to use an acid to remove the metal, and the equation of the reaction is as follows:-

$$\text{H}_2\text{O} + \text{C}_2\text{H}_2 + \tfrac{1}{4}\text{Ni(CO)}_4 + \tfrac{1}{2}\text{HCl aq.} = \text{CH}_2\text{:CH.COOH} + \tfrac{1}{4}\text{NiCl}_2 \text{ aq.} + \tfrac{1}{4}\text{H}_2$$

$$\text{ROH} + \text{C}_2\text{H}_2 + \tfrac{1}{4}\text{Ni(CO)}_4 + \tfrac{1}{2}\text{HCl aq.} = \text{CH2=CH.COOR} + \tfrac{1}{4}\text{NiCl}_2 \text{ aq.} + \tfrac{1}{4}\text{H}_2$$

$$\text{RNH} + \text{C}_2\text{H}_2 + \tfrac{1}{4}\text{Ni(CO)} + \tfrac{1}{2}\text{HCl aq.} = \text{CH}_2\text{:CH.CONHR} + \tfrac{1}{4}\text{NiCl}_2 \text{ aq.} + \tfrac{1}{4}\text{H}_2,$$

etc.

Nickel carbonyl is the most generally useful carbonyl compound; similar results can be obtained from cobalt carbonyl but this is less accessible; the reaction does not work with iron carbonyl, and mixtures of nickel and iron carbonyls give only poor yields. The usual acids are hydrochloric, hydrobromic, phosphoric or acetic acids, and these are best used in aqueous solution. If the acid (e.g. acetic) is used in the anhydrous condition, then the hydrogen liberated (see above equation) adds to the double bond of the acrylic acid and a 25% yield of propionic acid is obtained. In the presence of water the hydrogen reduces part of the carbon monoxide liberated from the nickel carbonyl. Using technical 36% hydrochloric acid, a vigorous reaction occurs at temperatures as low as 40°C., and quantitative yields of acrylic acid derivatives are obtained.
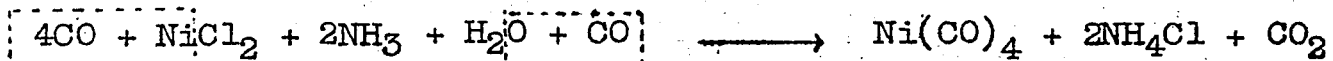
The formation of ethyl acrylate serves as an illustration of this reaction.

A three-necked flask contains ethanol and hydrochloric acid (36%) in the quantities calculated from the equation given. The contents are stirred vigorously and the air removed by an acetylene stream whilst the flask is warmed to 40-42°C. Nickel carbonyl (calculated amount) is added from a burette while the acetylene stream is passed in, and it should be noted that if the acetylene stream is not sufficiently vigorous, the flask can collapse due to the rapid absorption creating a vacuum. After absorption is complete, the ester-alcohol mixture is distilled from the aqueous nickel chloride and purified in the usual way.
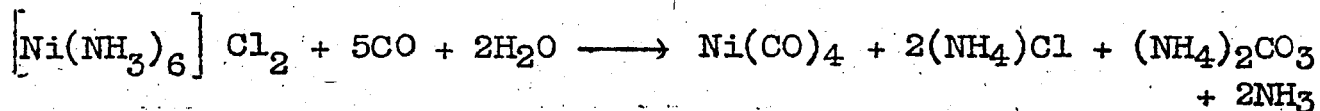
The regeneration of nickel carbonyl from nickel chloride is a relatively simple process. The nickel chloride solution is treated with rather more ammonia than is necessary for the formation of hexammino nickel chloride and then with carbon monoxide at 80°C. and 50-100 atmospheres pressure. The solution now contains nickel carbonyl, excess ammonia, ammonium chloride and ammonium carbonate. After removal of the nickel carbonyl the ammonia can be recovered by liming the aqueous phase.

The regeneration of nickel carbonyl can be done continuously in a specially designed tower, and is completely novel. It is considered to be a great advance over normal metallurgical practice, in which an

aqueous nickel solution is precipitated with sodium carbonate, the nickel carbonate filtered, dried, ignited and the dry oxide treated batchwise with carbon monoxide. The equation of the regeneration from aqueous solutions is as follows:
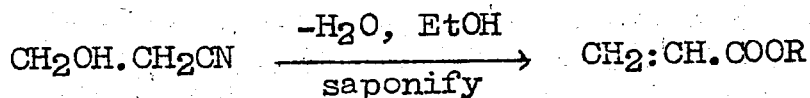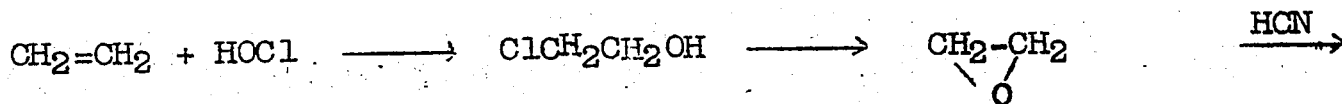
$$4CO + NiCl_2 + 2NH_3 + H_2O + CO \longrightarrow Ni(CO)_4 + 2NH_4Cl + CO_2$$

or, overall

$$[Ni(NH_3)_6]Cl_2 + 5CO + 2H_2O \longrightarrow Ni(CO)_4 + 2(NH_4)Cl + (NH_4)_2CO_3 + 2NH_3$$

The synthesis of acrylic esters from nickel carbonyl, hydrochloric acid, alcohol and water can be carried out continuously and at atmospheric pressure. The facility of the reaction combined with the ease of regenerating nickel carbonyl makes this a cheaper and technically, more attractive process than the normal one. The synthesis is also applicable to substituted acetylenes - methy-, ethyl-, phenyl-, vinyl- or divinyl-acetylene, to diacetylene, to alkinols and alkindiols their ethers and esters, and to acetylenes, carrying amine or mercaptan groups.

Catalytic process

Following the success of the "stoichiometric process" it was a natural consequence that a continuous catalytic process should be sought. This has been successful. Nickel is the most favourable metal catalyst and is best used as a halide. The reaction has to be carried out under pressure as it is under these conditions only that nickel carbonyl is formed from nickel salts. In the case of ethyl acrylate the alcohol is passed at 120-180° over catalysts contained in a pressure tower, and a counter stream of acetylene and carbon monoxide is circulated. A crude liquor containing a high percentage of ethyl acrylate is continuously removed from the foot of the tower.
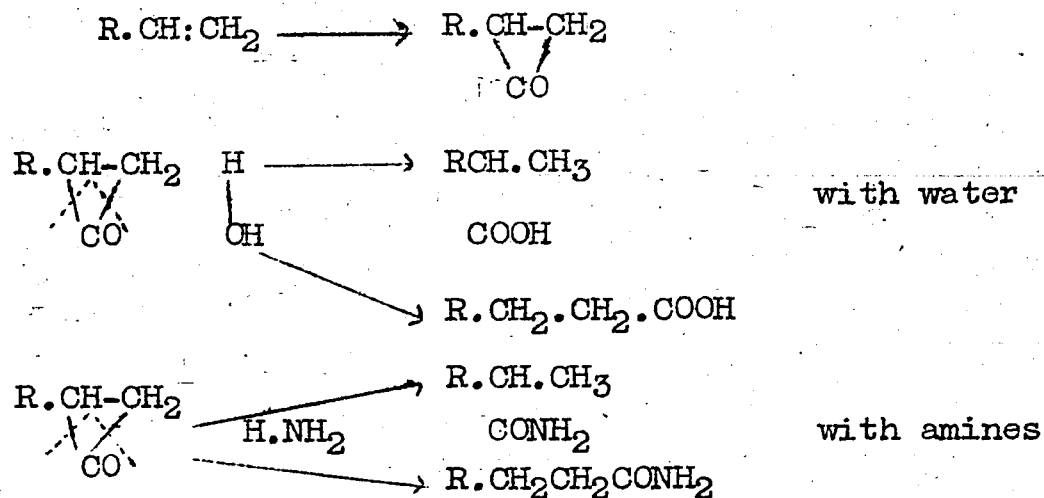
This contrasts with the normal commercial process for ethyl acrylate which is as follows:-

$$CH_2=CH_2 + HOCl \longrightarrow ClCH_2CH_2OH \longrightarrow \underset{O}{CH_2-CH_2} \qquad \overset{HCN}{\longrightarrow}$$

$$CH_2OH.CH_2CN \xrightarrow[\text{saponify}]{-H_2O, \ EtOH} CH_2:CH.COOR$$

II. SYNTHESIS OF CARBOXYLIC ACIDS AND DERIVATIVES

(a) From olefines and olefinic compounds

It was thought that if the process described in Section I using acetylene could be applied to olefines, the cyclopropanone ring would be formed as an intermediate product which should undergo hydrolytic fission with compounds containing active hydrogen atoms, thus:-

$$R.CH:CH_2 \longrightarrow \underset{CO}{R.CH-CH_2}$$

$$\underset{CO}{R.CH-CH_2} \quad H \longrightarrow \underset{COOH}{RCH.CH_3} \qquad \text{with water}$$
$$\qquad \qquad \overset{|}{OH}$$

$$\longrightarrow R.CH_2.CH_2.COOH$$

$$\underset{CO}{R.CH-CH_2} \longrightarrow \underset{CONH_2}{R.CH.CH_3} \qquad \text{with amines}$$
$$\qquad \qquad H.NH_2$$
$$\longrightarrow R.CH_2CH_2CONH_2$$

These expectations were realised, and it was in fact found that by interaction of olefines and carbon monoxide, both straight chain and a-methylated carboxylic acids were formed.

During the early part of this work information on the work of Ruhrchemie A-G (so called "Oxo process") became available. This firm following up observations made on the Fischer-Tropsch process, showed that carbon monoxide and hydrogen added to olefines to give aldehydes which could subsequently be reduced to alcohols. Work in the I.G.

demonstrated that nickel carbonyl was an intermediate product in this process.

The interaction of olefines with carbon monoxide proceeds easily at 200-300° and 150-300 atmospheres, and works equally well for the higher and the lower olefines, e.g., ethylene, propylene, butylene and C_5-C_{25} olefines. The C_{12}-C_{18} olefines prepared by cracking or by Fizcher-Tropsch synthesis are suitable starting materials. The acids formed can be hydrogenated to alcohols for use as detergents. An interesting application of the synthesis is the use of the acid originally formed as the agent for the fission of the cyclopropanone ring, giving anhydrides. Thus from ethylene, propionic anhydride, important for the manufacture of cellulose propionate, can be prepared.

$$CH_2=CH_2 + CO + H_2O \longrightarrow CH_3.CH_2.COOH$$

$$CH_2=CH_2 + CO \longrightarrow \left[\begin{array}{c} CH_2-CH_2 \\ \diagdown \diagup \\ CO \end{array} \right] \xrightarrow{CH_3CH_2COOH} \left[CH_3CH_2.CO \right]_2 O$$
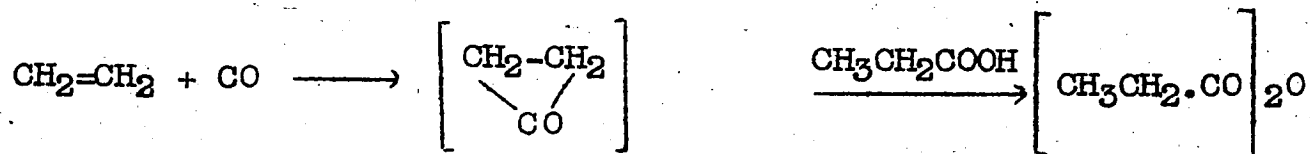
In this connection, it is interesting to note that Mailhe (Bull.Soc.Chim.,(4),5,1909,815-819) showed that anhydrides could be split over a nickel catalyst into olefines, carbon monoxide and carboxylic acids.

The mixed straight chain and a-methylated acids formed from the higher olefines have advantages over those obtained from natural fats inasmuch as they have higher solubility and dispersing power for lime soaps, and the same holds for the sulphates of the alcohols formed by catalytic reduction of the acids. Since higher olefines are cheap only as low percentage mixtures with paraffins, the above synthesis of acids from carbon monoxide and water is especially favourable since the separation of unreacted paraffin from the soaps of the acids formed is simple, and the regenerated fatty acids can easily be separated into fractions either as such, or after reduction to the corresponding alcohols.

It is clear from patent literature that American workers are

interested in this synthesis but the conditions they use (high pressures) are on the borderline of technical possibility. It is not known how far American work has gone, but our experience is that yields are almost quantitative.
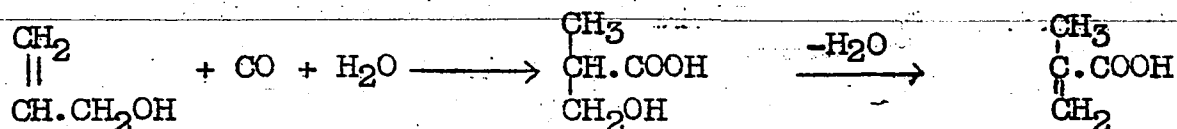
Cyclic olefines with carbon monoxide and water behave in the normal manner, thus cyclooctene gives cyclooctane carboxylic acid and cyclohexene gives cyclohexane carboxylic acid.
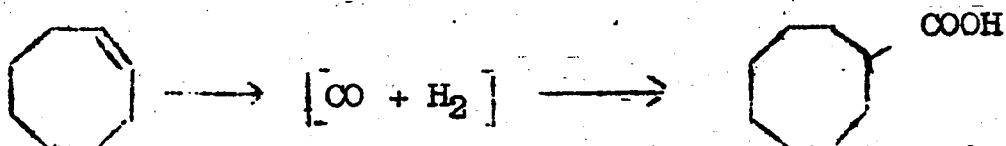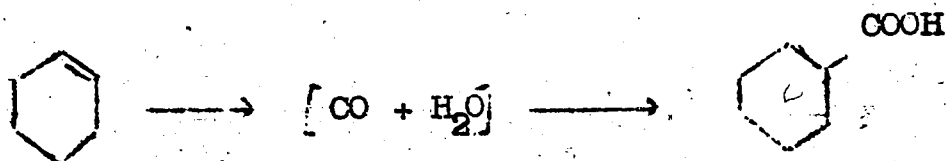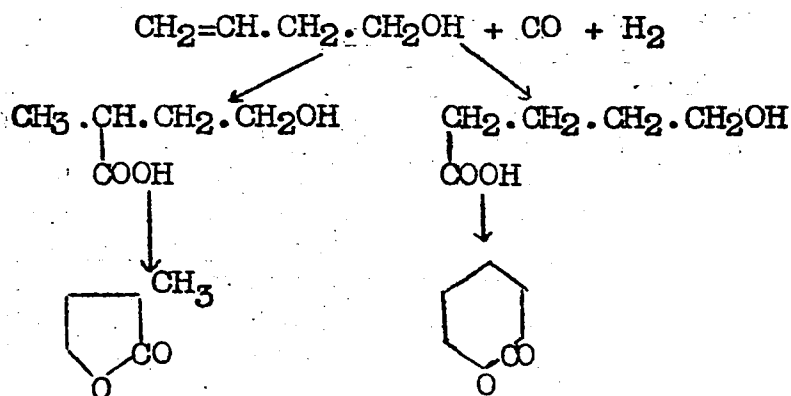

Butadiene, submitted to this reaction, first dimerises to vinyl cyclohexene, and from this a mixture of the following mono- and di-carboxylic acids are formed:

$$CH_2=CH.CH=CH_2$$
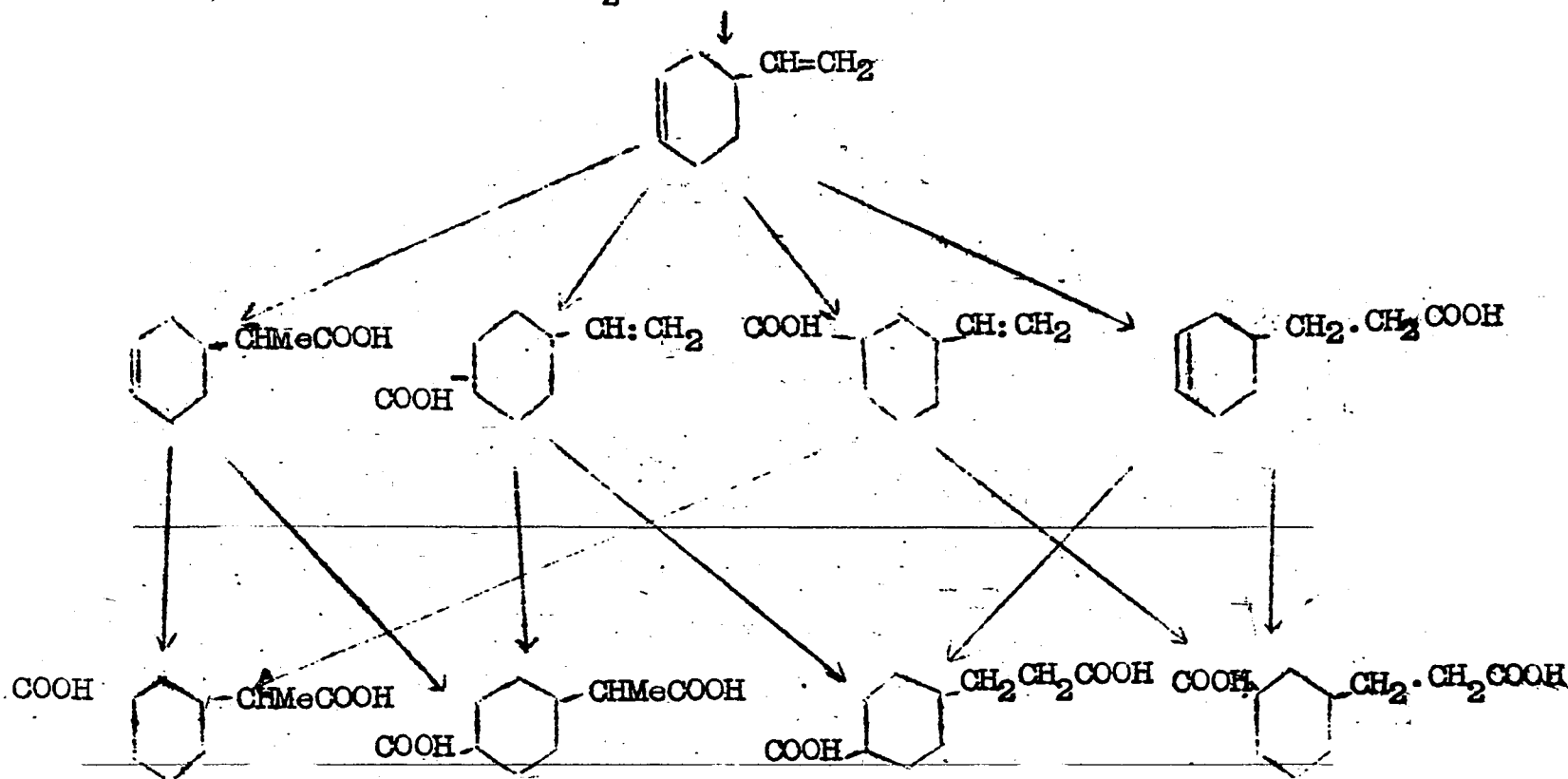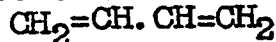
Similar reactions are shown by derivatives of olefines. Thus, allyl alcohol gives β-hydroxy isobutyric acid which on dehydration affords methacrylic acid.
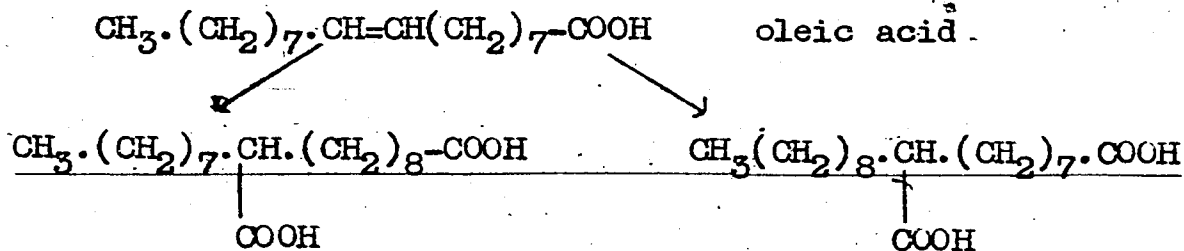
$$
\begin{array}{c}
CH_2 \\
\parallel \\
CH.CH_2OH
\end{array}
+ CO + H_2O \longrightarrow
\begin{array}{c}
CH_3 \\
CH.COOH \\
CH_2OH
\end{array}
\xrightarrow{-H_2O}
\begin{array}{c}
CH_3 \\
C.COOH \\
CH_2
\end{array}
$$

Buten-1-ol-4 yields, via the unstable hydroxy acids, a mixture of δ-valerolactone and methylbutyrolactone.

$$CH_2=CH.CH_2.CH_2OH + CO + H_2$$

$$
\begin{array}{c}
CH_3.CH.CH_2.CH_2OH \\
\downarrow \\
COOH
\end{array}
\qquad
\begin{array}{c}
CH_2.CH_2.CH_2.CH_2OH \\
\downarrow \\
COOH
\end{array}
$$

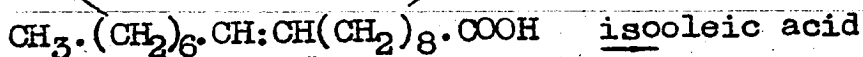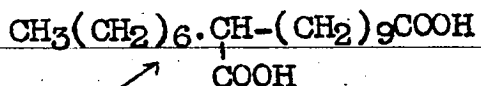methylbutyrolactone δ-valerolactone

Olefinic carboxylic acids

Oleic and undecylenic acids react with water and carbon monoxide yielding dicarboxylic acids suitable for use as intermediates for polyamides, alkyd resins, plasticisers, etc.
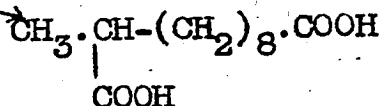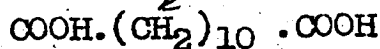
$$CH_3.(CH_2)_7.CH=CH(CH_2)_7-COOH \qquad \text{oleic acid}$$

$$
\begin{array}{c}
CH_3.(CH_2)_7.CH.(CH_2)_8-COOH \\
\downarrow \\
COOH
\end{array}
\qquad
\begin{array}{c}
CH_3(CH_2)_8.CH.(CH_2)_7.COOH \\
\uparrow \\
COOH
\end{array}
$$

a-octyl nonane dicarboxylic acid ⭢　　　　　　　　a-nonyl sebacic acid

$$CH_3(CH_2)_6.CH-(CH_2)_9COOH$$
$$| \\ COOH$$

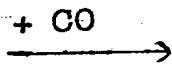$$CH_3.(CH_2)_6.CH:CH(CH_2)_8.COOH \quad \underline{isooleic \ acid}$$
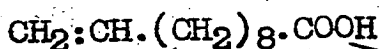
$$CH_2:CH.(CH_2)_8.COOH \quad\quad (undecylenic \ acid \ ex \ castor \ oil)$$

$$COOH.(CH_2)_{10}.COOH \quad\quad CH_3.CH-(CH_2)_8.COOH$$
$$| \\ COOH$$

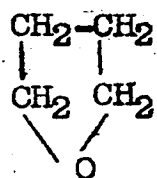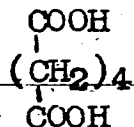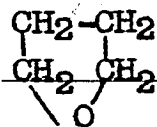## Ethers and alcohols

Aliphatic and cyclic ethers react with metal carbonyls giving
carboxylic acids, but, in contrast to the reaction with olefines in
which nickel carbonyl acts alone as catalyst; with ethers the simul-
taneous addition of a halogen is necessary. By this method tetra-
hydrofuran gives adipic acid, and this is visualised as the cheapest
and simplest route to adipic acid. Normally small quantities of
valeric acid are formed as a by-product, and by the use of special
conditions, the addition can be restricted to equimols of tetra-
hydrofuran and carbon monoxide, the product being δ-valerolactone
(which can be converted into caprolactam).

$$CH_2-CH_2$$
$$| \quad | \quad + CO \ \longrightarrow$$
$$CH_2 \ CH_2$$
$$\diagdown \diagup$$
$$O$$

δ-valerolactone

$$CH_2-CH_2$$
$$| \quad | \quad \longrightarrow$$
$$CH_2 \ CH_2$$
$$\diagdown O \diagup$$

$$COOH$$
$$|$$
$$(CH_2)_4 \quad\quad \underline{adipic \ acid}$$
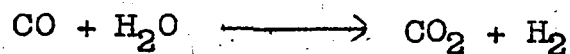$$|$$
$$COOH$$
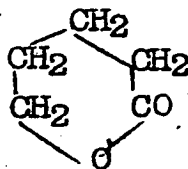
Tetrahydropyran, similarly treated, yields pimelic acid. The diols corresponding to these cyclic ethers can be used with equal efficiency; 1:4-butanediol gives adipic acid, 1:5-pentanediol pimelic acid, and 1:6-hexanediol suberic acid.

III. REACTIONS WITH HYDROCARBONYLS

The hydrocarbonyls were prepared according to Hieber's method by the action of solutions of alkalies or alkaline earths on metal carbonyls, especially iron pentacarbonyl. Later, experiments were conducted using sodium phosphate, sodium silicate, zinc aluminate and chromium aluminate. It was found that iron hydrocarbonyl, $Fe(CO)_4H_2$, in alkaline solution reacts quantitatively with carbon monoxide giving iron pentacarbonyl and hydrogen. The pentacarbonyl then reacts further with alkali, giving the hydrocarbonyl and CO_2, thus setting up a continuous reaction which ceases only when all the alkali present is converted into carbonate.

$$Fe(CO)_5 + H_2O \longrightarrow Fe(CO)_4H_2 + CO_2$$

$$Fe(CO)_4H_2 + CO \longrightarrow Fe(CO)_5 + H_2$$
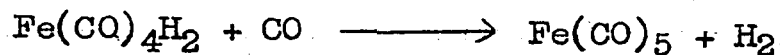
i.e., the overall reaction is:-

$$CO + H_2O \longrightarrow CO_2 + H_2$$

To convert the process from a discontinuous to a truly continuous one it was necessary to find some base which would fill the role played by caustic alkali in the discontinuous process. Such a base must have the following properties:-
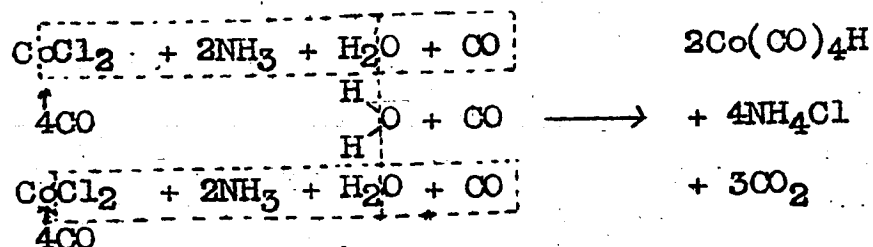
(1) Sufficiently basic to catalyse the reaction
$Fe(CO)_5 + H_2O \longrightarrow Fe(CO)_4H_2 + CO_2$, and to combine with the CO_2.

(2) The carbonate so formed should be thermally unstable and evolve CO_2 at higher temperatures.

(3) It should be water-soluble and non-volatile.

(4) It should be inert to the reactants (caustic soda forms formates with carbon monoxide).

Another method of preparation of hydrocarbonyls consists of an application of the process which has already been mentioned for the regeneration of nickel carbonyl from nickel salts. If this process is applied to ferrous or cobalt salts (e.g. ammoniacal Mohr salt), iron hydrocarbonyl, $Fe(CO_4)H_2$, can be prepared by regulating the rate of CO addition and stopping the addition at the right point. Using ammoniacal cobalt chloride the reaction stops automatically with the formation of $Co(CO)_4H$ which, in contrast to the iron compound, is stable to carbon monoxide. Pure cobalt hydrocarbonyl can be formed from such a solution by treatment with phosphoric acid.

The reaction can be represented as follows:

$$CoCl_2 + 2NH_3 + H_2O + CO \qquad 2Co(CO)_4H$$
$$4CO \qquad\qquad H\quad O + CO \longrightarrow + 4NH_4Cl$$
$$\qquad\qquad\qquad H$$
$$CoCl_2 + 2NH_3 + H_2O + CO \qquad + 3CO_2$$
$$4CO$$

or, including excess ammonia to interact with the CO_2,

$$2\left[Co(NH_3)_6\right]Cl_2 + 11CO + 6 H_2O \longrightarrow 2Co(CO)_4H + 4NH_4Cl + 3(NH_4)_2CO_3 + 2NH_3$$

Cobalt hydrocarbonyl $\left[Co(CO)_4H\right]$ is a stable compound. Its alkaline solution can be heated to 200° for long periods without decomposition. Iron hydrocarbonyl on the other hand can be obtained pure only with difficulty and is decomposed rapidly by alkali at 100°. Cobalt hydrocarbonyl is a strong inorganic acid; it can be titrated with caustic soda using methyl orange indicator, and the end-point can be approached from either the acid or the alkaline side. It can be titrated with methylene blue in acetic acid solution, giving a reduction value corresponding to the content determined alkimetrically. iron hydrocarbonyl, however, can be titrated with methylene blue only on the alkaline side. Iron hydrocarbonyl is a much weaker acid than
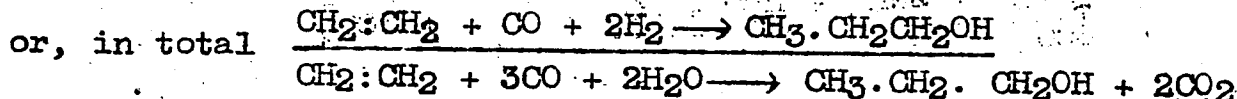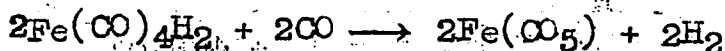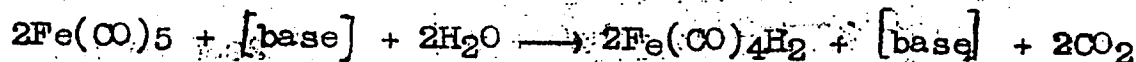
cobalt hydrocarbonyl.

Reaction of hydrocarbonyl with olefines

Interaction of alkaline iron hydrocarbonyl, $Fe(CO)_4H_2$, with ethylene gave, as main product, n-propanol; higher alcohols and organic acids (formic, propionic, etc.) were also formed. The same results were obtained if iron carbonyl, $Fe(CO)_5$, and ethylene were used in alkaline solution.

$$Fe(CO)_4H_2 + 2CH_2:CH_2 + 4H_2O \longrightarrow 2CH_3CH_2CH_2OH + Fe(HCO_3)_2$$
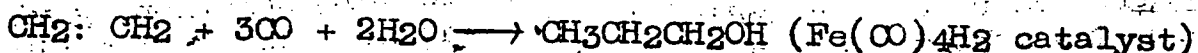
$$(or\ FeCO_3 + H_2O + CO_2)$$
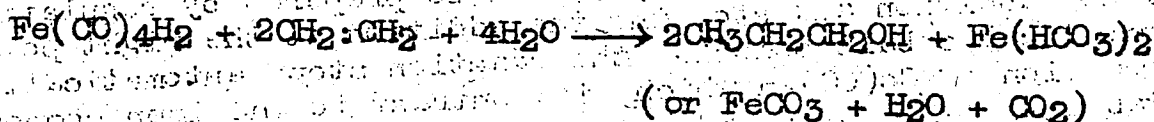
It was hoped to carry out the reaction using iron carbonyl itself as catalyst, with continuous addition of CO; the expected sequence of reactions was as follows:

$$2Fe(CO)_5 + [base] + 2H_2O \longrightarrow 2Fe(CO)_4H_2 + [base] + 2CO_2$$

$$2Fe(CO)_4H_2 + 2CO \longrightarrow 2Fe(CO_5) + 2H_2$$

or, in total

$$CH_2:CH_2 + CO + 2H_2 \longrightarrow CH_3.CH_2CH_2OH$$

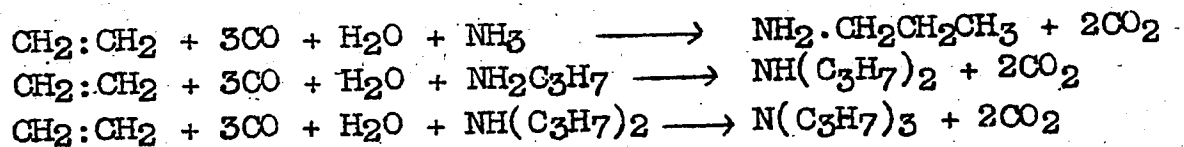$$CH_2:CH_2 + 3CO + 2H_2O \longrightarrow CH_3.CH_2.CH_2OH + 2CO_2$$

The actual reaction scheme, however, is much more complicated than the above, and has not been fully elucidated.

From what has been said, it is clear that the nature of the products to be obtained from identical reactants is entirely dependent on the nature of the catalyst used. Thus, ethylene, CO and water give propionic acid in presence of nickel carbonyl, and n-propanol in presence of iron hydrocarbonyl.

$$CH_2=CH_2 + CO + H_2O \longrightarrow CH_3CH_2COOH \quad (Ni(CO)_4 \quad catalyst)$$

$$CH_2:CH_2 + 3CO + 2H_2O \longrightarrow CH_3CH_2CH_2OH \quad (Fe(CO)_4H_2 \ catalyst)$$
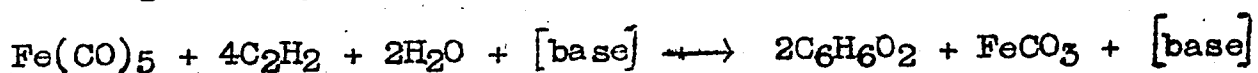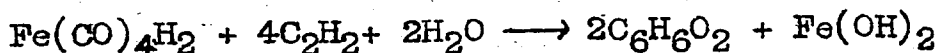
Further work showed that the formation of alcohols from olefines could be effectively accomplished only if the base were properly chosen, and that only tertiary bases would fulfil the necessary conditions of water solubility, non-volatility, and non-participation in side-reactions. Ammonia, primary and secondary amines, in these ethylene reactions are ineffective until they have been completely alkylated, thus:

$$CH_2:CH_2 + 3CO + H_2O + NH_3 \longrightarrow NH_2 \cdot CH_2CH_2CH_3 + 2CO_2$$

$$CH_2:CH_2 + 3CO + H_2O + NH_2C_3H_7 \longrightarrow NH(C_3H_7)_2 + 2CO_2$$

$$CH_2:CH_2 + 3CO + H_2O + NH(C_3H_7)_2 \longrightarrow N(C_3H_7)_3 + 2CO_2$$

The most effective bases are those containing a tertiary amino group, and a COOH or SO$_3$H group. The selected base was sodium dimethylamino acetate, $(CH_3)_2N \cdot CH_2 \cdot COONa$.

IV. SYNTHESIS OF HYDROQUINONE FROM ACETYLENE, CARBON MONOXIDE AND WATER

An attempt was made to synthesise unsaturated alcohols by submitting acetylene to the carbon monoxide-water reaction in presence of hydrocarbonyls. Surprisingly hydroquinone was formed, the conditions of the reaction being the same as those used for olefines, but at a rather lower temperature. A base (monoethanolamine) may be used, but is not essential; hydroxylic compounds (water or alcohol) must be present. The reaction is formulated as follows:

$$Fe(CO)_4H_2 + 4C_2H_2 + 2H_2O \longrightarrow 2C_6H_6O_2 + Fe(OH)_2$$

$$Fe(CO)_5 + 4C_2H_2 + 2H_2O + [base] \longrightarrow 2C_6H_6O_2 + FeCO_3 + [base]$$
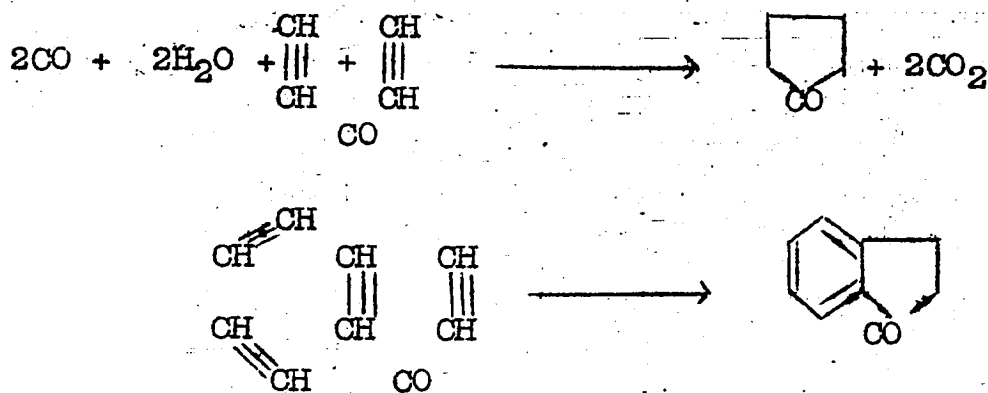
The yield at the moment is 20-30% of hydroquinone based on the hydrocarbonyl used.
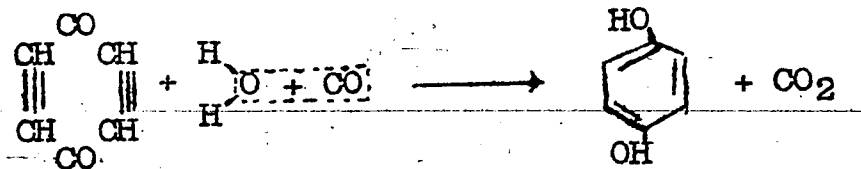
This reaction is also applicable to methyl, phenyl and dimethylacetylenes, to ethers of propargyl alcohol, butinol, butindiol, hexindiol and dimethylamino derivatives of acetylene, e.g. $Me_2N.CH_2.C{\equiv}CH$ and $Me_2N.CH_2.C{\equiv}C.CH_2.NMe_2$.

There is some preliminary evidence that the possibilities of acetylene in this connection are by no means exhausted. For example, the formation of <u>cyclopentanone</u> and hydrindone have been observed in certain cases, although these reactions have not yet been investigated further.

$$2CO \;+\; 2H_2O \;+\; \underset{CH}{\overset{CH}{|||}} \;+\; \underset{CH}{\overset{CH}{|||}} \longrightarrow \text{(cyclopentanone)} \;+\; 2CO_2$$

(CO below second acetylene)

$$\longrightarrow \text{(hydrindone)}$$

Aldehydes and ketones also react with acetylene in the presence of nickel carbonyl, but the course of the reaction is, at the moment unknown.