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CARBOXYLATION OF ORGANIC HALIDES WITH INSERTION OF ACETYLENE: NEW SYNTHESES OF γ-KETOACIDS AND ESTERS

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In the attempt of extending to other compounds the carboxylation reactions of allylic derivatives described in our preceding papers (1-5), for example:

$$CH_2{=}CHCH_2X + CH{\equiv}CH + CO + ROH \xrightarrow{Ni\ cat.} CH_2{=}CHCH_2CH{=}CHCOOR + HX$$

(where X=Cl,Br,I,OR,OCOR and R=H or Alkyl), we examined several aliphatic and aromatic halides as well as new catalysts; we thus observed a behaviour which largely differs from that of the allylic compounds.

It is known that aromatic halides are carboxylated by nickel carbonyl (6-8). Aryl iodides have been shown to give esters in unusually mild conditions (7). We found however that acetylene, even under pressure, does not react in alcoholic medium at temperatures between 0° and 60°C, in spite of what is commonly observed in the carboxylation of allylic compounds. At temperatures of 120-140°C and pressures of about 30 atm of acetylene and carbon monoxide, iodobenzene gave benzoylpropionates in high yield. The overall reaction may be expressed as follows:

$$C_6H_5I + CH{\equiv}CH + Ni(CO)_4 + ROH + HX \longrightarrow C_6H_5COCH_2CH_2COOR + NiIX + 2CO$$

(where R= alkyl, X= OH,OR,Cl,Br,I)

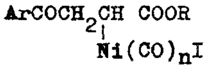
The insertion of acetylene in low yield was also observed at temperatures between 40 and 60°C, starting up the carboxylation of acetylene with hydrochloric acid and nickel carbonyl, according to Reppe (8,9).

Under the conditions experienced the benzoylnickel carbonyl iodide, which is likely to be the intermediate, appears to be stable and does not liberate carbon monoxide. Under the same conditions the analogous vinylacetyl derivative formed from an allylic halide is not stable and the allylic group joins directly to acetylene. Accordingly, an experiment performed by refluxing vinylacetyl chloride and nickel carbonyl in tetrahydrofuran gave prevailingly 1,5-hexadiene:

$$2CH_2{=}CHCH_2COCl + Ni(CO)_4 \longrightarrow CH_2{=}CHCH_2CH_2CH{=}CH_2 + NiCl_2 + 6\ CO$$

The aroyl group reacting with acetylene and carbon monoxide might be expected to give rise to the unsaturated compound: $C_6H_5COCH{=}CHCOOR$. However, the corresponding saturated compound was found instead.

Experiments on benzoylacrylates show that the double bond is hydrogenated under reaction conditions. This is likely to occur through intermediates containing a nickel-carbon bond such as:



$$ArCOCH_2\underset{\displaystyle Ni(CO)_nI}{\underset{|}{CH}}COOR$$

which are splitted by the hydroxylic solvent in $RCOCH_2CH_2COOR$ and NiIX.

This behaviour was observed by us in the synthesis of β-allylpropionic compounds from allylic halides and activated olefins (10):

$$RCH{=}CHCH_2X + CH_2{=}CHY + H_2O + Ni \longrightarrow RCH{=}CHCH_2CH_2CH_2Y + NiX^+ + OH^-$$

(X=Cl,Br,I; Y=CN,COOR,CHO etc) and in the substitutive hydrogenation of allylic halides (3):

$$XCH_2CH{=}CHY + Ni + H_2O \longrightarrow CH_2{=}CHCH_2Y + NiX^+ + OH^-$$

It is not likely, however, that free benzoylacrylates are involved in the synthesis of benzoylpropionates. As shown by the experiments at the lower temperatures, the synthesis seems to occur only if the carboxylation of acetylene to acrylic and unsaturated dicarboxylic esters according to Reppe is first started. This leads to the suggestion that the benzoyl group reacts with a complex containing the precursors of these acids, and the hydrogenating splitting may then occur in the complex thus formed.

A similar reaction with aliphatic halides, was observed by reacting salts of cobalt hydrocarbonyl with acetylene and carbon monoxide in aqueous media under mild pressures. The reaction with carbon monoxide alone was studied by Heck and Breslow (11) who obtained the direct substitutive carboxylation. Working in the absence of bases under low partial pressures of acetylene and at temperatures between 60 and 120°C (depending on the reactivity of the halide),compounds of the formula $RCOCH_2CH_2COOH$ (R=Alkyl) are obtained (12) along with the acids formed in the direct carboxylation.

The reaction was found to occur through cobalt complexes which are splitted by acids.

It is to be noted that Natta and Pino(13)isolated some γ-ketonic acids as by-products of the synthesis of succinic acid from acetylene and carbon monoxide.

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