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CARBONYLATION WITH ACETYLENE INSERTION FOLLOWING THE TRAPPING OF ACYL GROUPS ON COORDINATED KETONES OR ALDEHYDES

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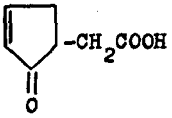
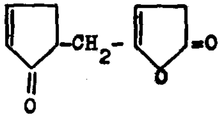
Recently we reported on the easy formation of the products


I

and


II

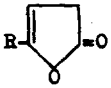
by reaction of allyl halides with acetylene and nickel carbonyl in ketonic solvents(1). An hexadienoyl-nickel carbonyl halide resulting from the linear addition of the allylic group, acetylene and carbon monoxide is likely to be the precursor of I and II.

In order to elucidate the nature of the effect exerted by the ketonic solvent we caused hexadienoyl chloride :

$$CH_2=CH-CH_2-CH=CH-CO-Cl$$

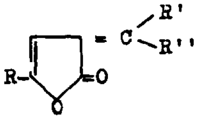
to react with acetylene and nickel carbonyl in acetone and obtained the products I and II in good yields. The same reaction gave a very low yield in tetrahydrofuran.

This result strongly suggests that the ketonic solvent exerts a stabilizing effect on the acyl group. Moreover we found that the carbonylation with insertion of acetylene becomes in ketonic solvents a general reaction for aliphatic, alicyclic and aromatic acid halides RCOX (X=Cl,Br,I). The products thus formed are β,γ-unsaturated γ-lactones:



III

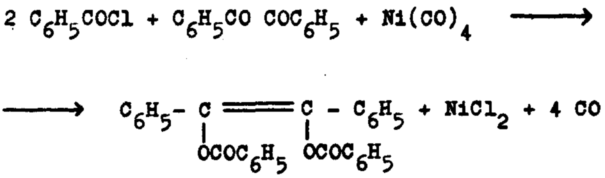
In the absence of water, products deriving from Reformatsky-type reactions between coordinated π-allyl-lactones and ketones R'COR'' are also formed :



IV

The way by which ketones stabilize the acyl group is likely to be a trapping of this latter on the oxygen atom of the coordinated ketones. In trying to prove this point we found a strong support in the reaction of benzoyl chloride with nickel carbonyl studied by Bauld (2).

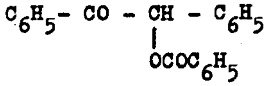
Benzyl, the coupling product of two benzoyl groups, captures two new benzoyl groups forming a dienol ester :



$$2\ C_6H_5COCl + C_6H_5CO\ COC_6H_5 + Ni(CO)_4 \longrightarrow$$

$$\longrightarrow C_6H_5-\underset{\displaystyle OCOC_6H_5}{\overset{}{C}}=\underset{\displaystyle OCOC_6H_5}{\overset{}{C}}-C_6H_5 + NiCl_2 + 4\ CO$$

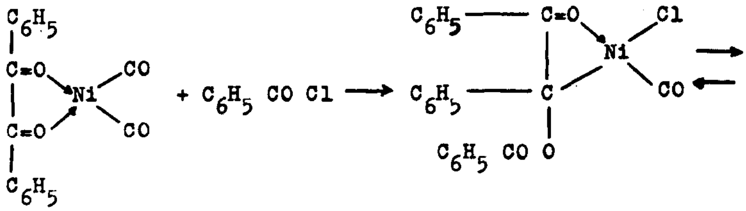
We carried out this reaction in moist acetone and found the benzoate of benzoin as the main product :

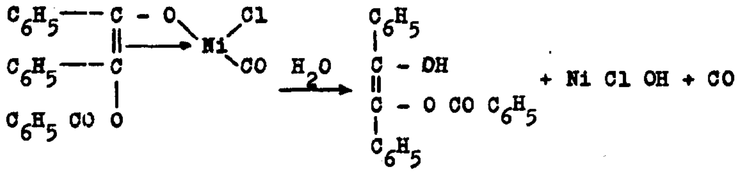


$$C_6H_5-CO-\underset{\displaystyle OCOC_6H_5}{CH}-C_6H_5$$

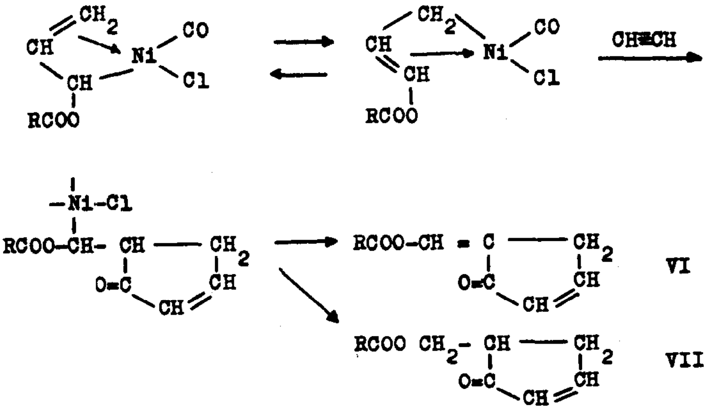
V

According to our previous observations (3) on the behaviour of the C-Ni bond, hydrogenation occours instead of carbonylation if an adjacent electron-attractor substituent such as -C=O is present. In a similar way the formation of V can be explained by a trapping reaction of the acyl group, forming a C-Ni bond adjacent to a C=O group, followed by the capture of a proton from water :

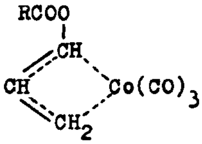




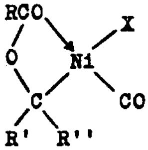
If this way of reasoning is correct a ketone with an adjacent double bond instead of the electron attracting group should give rise to an allylic system,which is reactive with acetylene and carbon monoxide. This assumption is proved to be true by reacting an acyl chloride, acrolein, acetylene and nickel carbonyl in an inert solvent : the products VI and VII are obtained, resulting from the linear addition of an acyl group, acrolein, acetylene and carbon monoxide, followed by cyclization and loss or capture of H (probably H^- and H^+ respectively) :



This scheme of reaction is supported by the recent isolation of cobalt complexes from the reaction of acyl cobalt carbonyls and unsaturated aldehydes (4) :



Based upon the experiments mentioned above we hold as likely that ketonic solvents R'COR'' act as scavengers of acyl groups RCO in complexes such as the following :



The acyl group should subsequentely react with acetylene. The above complex is analogous to those postulated in Friedel-Crafts reactions for explaining the loss of reactivity of the acyl group in the absence of a sufficient amount of $AlCl_3$ (5).
In this case the acyl group should be blocked by ketones as follows :

$$[RCO : OC\ R'\ R'']^{+}\ [AlCl_4]^{-}$$

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