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NEW TYPES OF CARBONYLATION WITH INSERTION OF ACETYLENE

L.Cassar and G.P.Chiusoli

Donegani Research Institute, Montecatini Co.

Novara, Italy

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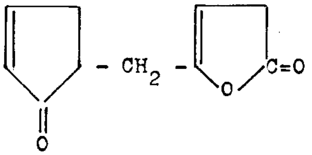
We recently reported (1) on the reactions of substituted acetylenes with allylic halides and nickel carbonyl in acetone-water at room temperature and atmospheric pressure. Unsaturated ketones and lactones derived from cyclopentenones and cyclohexenones were obtained.

Under the same conditions acetylene gives rise to hexadienoic acids, as shown in our previous papers(2).

We wish now to report on a dramatic change in the type of product formed from allyl chloride, acetylene and nickel carbonyl, caused by the solvent employed.

This reaction was carried out at 20°C in several solvents whose water content did not exceed 0,5%. After distillation of the solvent and addition of water to the mixture, the product was extracted with ether and chromatographed on silica.

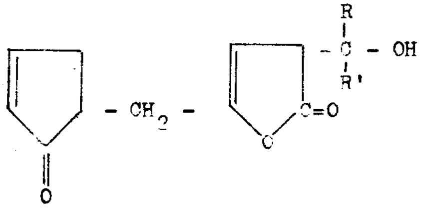
Whereas 2,5-hexadienoic acid (or its functional derivatives) constitutes the main product obtained from reactions in most solvents, compound I forms predominantly in ketonic solvents such as acetone, cyclopentanone, acetophenone etc., containing small amounts of water (0,1-0,4%) :



I

It results from one molecule of allyl chloride, two of acetylene and three of carbon monoxide, through an intermediate nickel complex which is splitted by water.

If the amount of water is further reduced, a new reaction takes place between the lactonic ring (probably coordinated with the nickel ion as a π -allylic complex (3)) and the ketone employed RCOR' with formation of products of the type II and III :



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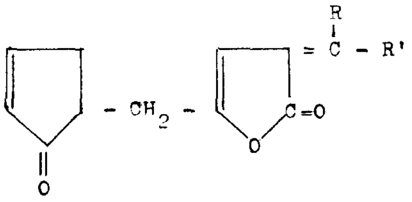
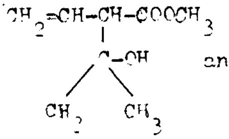


III

Other allylic halides bearing electron-attracting substituents on the double bond react in a similar way. Thus methyl bromocrotonate $BrCH_2\ CH=CH\ COOCH_3$ reacts with nickel carbonyl in acetone giving rise in part to the products of an allylic rearrangement in the ratio IV : V = 88 : 12:



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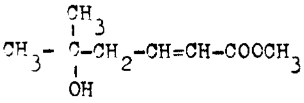


$CH_3-C(CH_3)(OH)-CH_2-CH=CH-COOCH_3$

IV

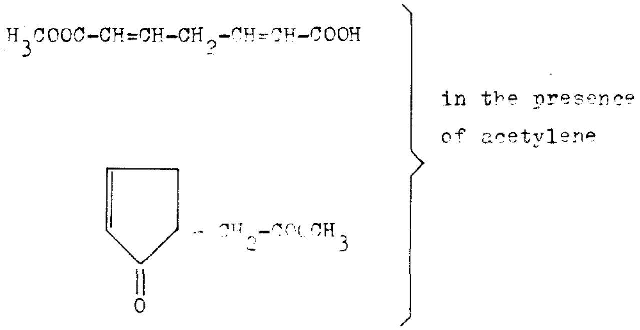
V

These facts strongly suggests that a Reformatsky-type reaction has occurred(1).

The influence of ketones is not confined to the reaction leading to product I. It appears that ketones generally promote the carbonylation of otherwise unreactive materials.

Thus allylic halides with electron-attracting substituents such as methyl bromocrotonate, which upon treatment with nickel carbonyl in hydroxylic solvents give rise to substitutive hydrogenation of the halogenated carbon(5) and mainly to coupling reactions in inert solvents(6), form in ketonic solvents the products which might be expected from the carbonylation of normal allylic halides :

$H_3COOC\text{-}CH{=}CH\text{-}CH_2\text{-}COOH$ in the absence of acetylene



$H_3COOC\text{-}CH{=}CH\text{-}CH_2\text{-}CH{=}CH\text{-}COOH$

in the presence of acetylene

The mechanism by which ketones promote the carbonylation will be further studied.Work in progress suggests that coordinated acyl groups are stabilised by ketones.

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