

STEREOSPECIFIC CHARACTER OF CYCLISING CARBONYLATION OF
ALLYL HALIDES

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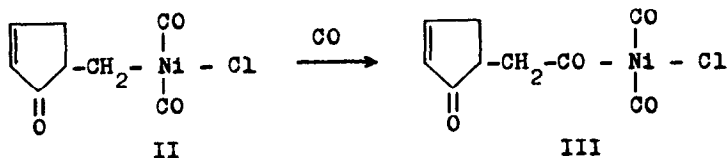
(Received 25 October 1966)

We recently reported (1) the reaction of acyl chlorides with nickel carbonyl and acetylene giving rise to products of the formula I :

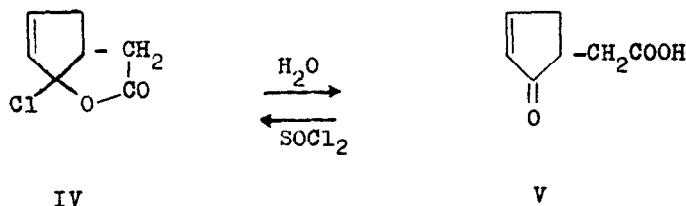


We wish now to describe the behaviour of cis and trans hexa-2,5-dienoyl chloride and of allyl chloride or bromide in this reaction.

cis-Hexadienoyl chloride reacts with nickel carbonyl in diethyl ether, benzene or heptane at room temperature by cyclising, probably to II and III (where other ligands may replace carbonylic groups) :

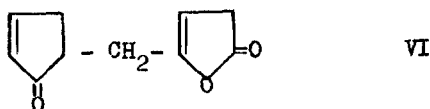


In the absence of acetylene the main product is 2-oxocyclopent-3-en-1-ylacetic acid V, which is present in the mixture as the chloride IV (isomeric form of the acyl chloride, preparable also from V and SOCl_2) :



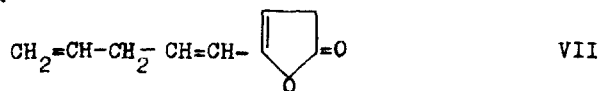
Minor amounts of phenol, phenyl hexa-2,5-dienoate, 3-oxocyclohex-4-ene-1-carboxylic acid and of nickel complexes are also found.

If acetylene is present the further course of the reaction strongly depends on the type of solvent employed. Ketones and in lower measure esters lead to the formation of VI :



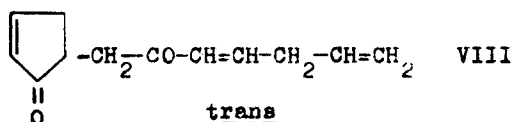
Under the same conditions employed for the cis isomer, trans-hexadienoyl chloride does not cyclise and reacts as a normal acyl chloride.

Thus in acetone in the presence of acetylene it gives mainly VII :

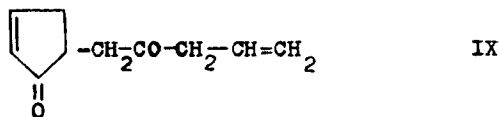


cis-Hexadienoyl halides are formed in diethyl ether (bromide more easily than chloride) directly from allyl halides, acetylene and nickel carbonyl (in the same way as hexadienoic acid and esters (2)), or from π -allylnickel halides, acetylene and carbon monoxide (3).

Only a little amount of hexadienoyl halide however is found as such. If water is present even in very low percentage, hexadienoic acid is formed. In the absence of water cyclisation occurs, possibly at the stage of hexadienoylnickel halide, with formation of IV and trans VIII as the main products (about 30% of IV and 20% of VIII from allyl bromide in diethyl ether at 30° with C₂H₂ and CO 1:1)



Several other by-products, among which the diketone IX, are contained in the reaction mixture in low amounts.



If moist acetone is employed the main product is VI (1, 4).

Beside ketones, other solvents, mainly esters display a moderate activity in promoting carbonylation with formation of VI.

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References

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- 3) R.F.Heck, J.Amer.Chem.Soc. 85, 2013 (1963)
- 4) L.Cassar and G.P.Chiusoli, Tetrahedron Letters n°37, 3295 (1965).