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Pages 2875 to 2879 were originally printed in the wrong sequence in issue 33 of the 1965 volume. They are now printed in the correct sequence at the front of this issue.

DIRECTION OF ADDITION AND EFFECT OF SUBSTITUENTS IN THE REACTIONS OF ALLYLIC HALIDES WITH ALKYNES AND NICKEL CARBONYL

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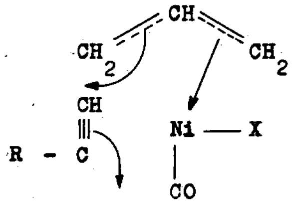
Our previous work on carboxylation of allylic halides with insertion of alkynes (1) led us to the isolation of acids, ketones and lactones derived from cyclopentenones and cyclohexenones(1, IX).

We regarded the course of the reaction as a series of stepwise additions probably initiated by a concerted addition of the coordinated allylic group to the alkyne and of this latter to the carbonyl group :



Further steps involve closure of the cyclopentenone or cyclohexenone rings, insertion of carbon monoxide and splitting to cyclopentenonic or cyclohexenonic acids. Alternatively, a new addition to the alkyne and a new insertion of carbon monoxide may occur with formation of ketones and lactones.

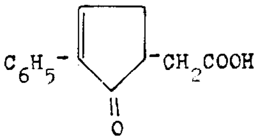
We thus observed a step by step growing up of a complex molecule on a transition metal, this process being interrupted at different stages by the uptake of a proton or of an hydroxide ion.

In order to get more information on the type of addition we examined the orientation in the reaction of allyl chloride with phenylacetylene and nickel carbonyl and the effect of replacing the hydrogen atoms of the allylic double bond by methyl groups.

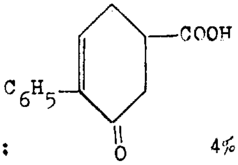
The reaction was carried out in acetone-water at 20°C.

Weight percentages of the main constituents of the products obtained from phenylacetylene, allyl chlorides and nickel carbonyl (estimated by quantitative thin layer chromatography) are given below. Melting points of the compounds isolated as such (all white solids) are also given.

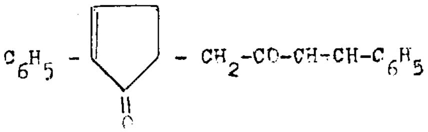
1) From allyl chloride :



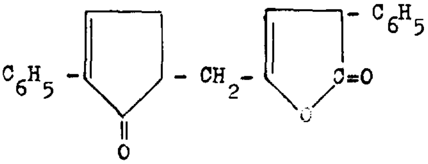
m.p. 110-111°, 21% ;



4% ;

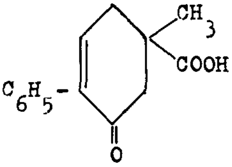


m.p. 104-105°. 64% :

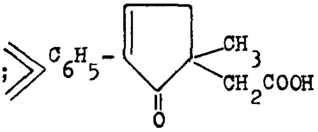


4% .

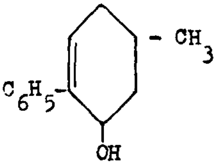
2) From methallyl chloride :



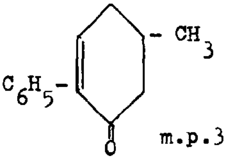
m.p.180-181°;



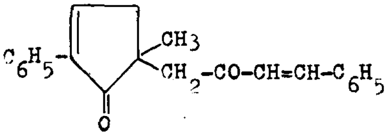
13%



34% ;

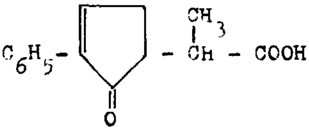


m.p.38-40°, 6% ;

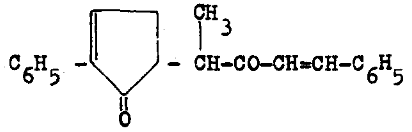


m.p. 127-128°, 37% .

3) From crotyl chloride :



m.p. 130-131°, 20%



m.p. 95-96°C, 71%

From these and previous results we draw the following conclusions :

1) Allylic groups add to the unsubstituted acetylenic carbon atom to a large extent (at least 93% for allyl chloride, the remaining 7% corresponding to unidentified products).

2) Cyclopentenonic or cyclohexenonic rings always form, the former generally more easily than the second.

3) Cyclopentenonic or cyclohexenonic groups add to carbon monoxide with formation of acyl-nickel carbonyls.

4) Alternatively, the cyclohexenonic group may loose or acquire hydrogen with formation of phenols or cyclohexenones.

5) Acyl-carbonyls may split to acids under the action of water.

6) Cyclopentenonic acyl-carbonyls may add further to a molecule of alkyne. At this stage, splitting to unsaturated diketones may be caused by proton addition.

7) Alternatively, a new molecule of carbon monoxide may be taken up, followed by lactonisation and proton addition with formation of unsaturated keto-lactones. This reaction was observed mainly for alkyl-acetylenes.

8) A methyl group on the carbon atom 2 of the allylic group favours the six carbons cycle formation.

9) The 3-methyl substituted allylic group reacts at the unsubstituted side.

Authors thank prof. A.Quilico for helpful discussions.

References

1) I, II, III, IV, G.P.Chiusoli, Chimica e Industria(Milan), 41, 503, 506, 512, 762 (1959); V, G.P.Chiusoli and S.Merzoni, id. 43, 259 (1961); VI, G.P.Chiusoli, G. Bottaccio and A.Cameroni, id. 44, 131(1962); VII, G.P. Chiusoli and S.Merzoni, id 45, 6(1963); VIII, G.P.Chiusoli, S.Merzoni and G.Mondelli, id 46, 743 (1964); IX, G.P.Chiusoli and G.Bottaccio, id 47, 165(1965); M.Dubini, G.P.Chiusoli and F. Montino, Tetrahedron Letters n°24, 1591 (1963); G.P.Chiusoli, S.Merzoni and G.Mondelli, Tetrahedron Letters n°38, 2777(1964).