

ORGANIC SYNTHESIS BY MEANS OF NOBLE METAL COMPOUND
XXIV. PALLADIUM-CATALYZED CARBONYLATION OF PROPARGYL ALCOHOLS
AND PROPARGYL CHLORIDE¹

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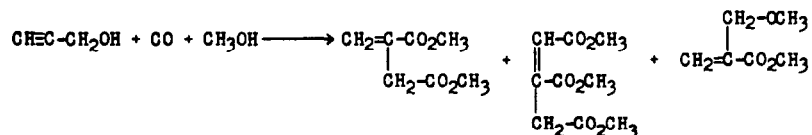
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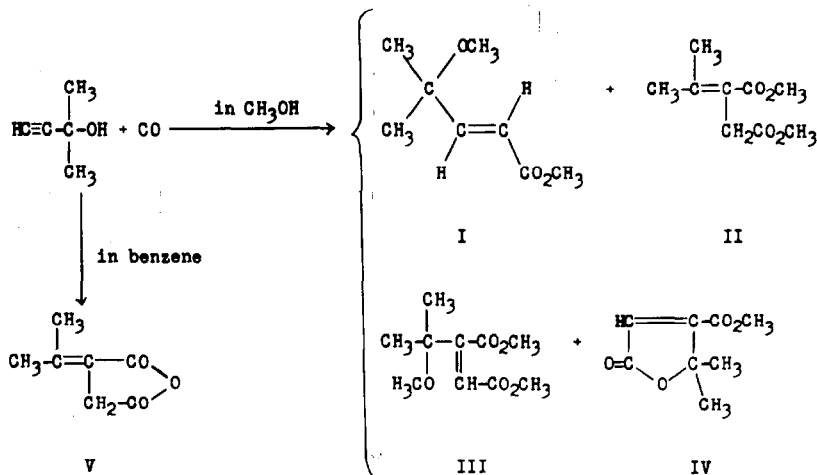
We have reported that palladium is a versatile catalyst for the carbonylation of various acetylenic compounds, e.g., acetylene to form muconyl chloride,² diphenylacetylene to form α,β -diphenyl- γ -crotonolactone,³ and acetylenic mono- and diesters to form several polycarboxylates.⁴ The characteristic of these palladium-catalyzed carbonylations is an extensive dicarbonylation, rather than monocarbonylation. These results are quite different from the reactions catalyzed by iron, nickel and cobalt carbonyls. We now studied the carbonylation of propargyl alcohols and chloride, and again reactions specific to palladium catalysis were observed; the results are presented in this communication.

The carbonylation of propargyl alcohol was carried out in methanol containing hydrogen chloride in the presence of a catalytic amount of palladium on carbon at 100° under a pressure of carbon monoxide (100 kg/cm²). The main product was methyl itaconate (yield 63%, one experiment), accompanied by methyl aconitate (yield 10%) and methyl 2-(methoxymethyl)acrylate (in a small amount). The ratio among these products is quite variable depending on the reaction conditions.



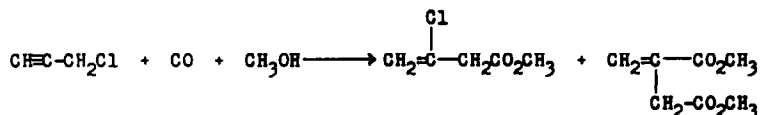
To our knowledge, this is the first example of formation of itaconate from propargyl alcohol. The addition of 3 moles of carbon monoxide to form acconitate is a new reaction. When the reaction was carried out in benzene, only resinous material was formed.

Substituted propargyl alcohols reacted similarly. Thus the carbonylation of 2-methyl-3-butyn-2-ol in methanol containing hydrogen chloride gave methyl 4-methoxy-4-methyl-2-pentenoate(I, trans form), methyl teraconate(II), methyl (1-methoxy-1-methylethyl)maleate(III) and methyl terebate(IV). When a concentration of hydrogen chloride in the medium was low, I was the main product; at a higher concentration, II and IV were obtained selectively.



When the reaction was carried out in benzene in the presence of palladium chloride, teraconic anhydride(V) was obtained selectively in 42% yield.

Propargyl chloride was carbonylated in methanol in the presence of a catalytic amount of palladium chloride under a pressure of carbon monoxide (100 kg/cm²). The reaction proceeded at room temperature and the products were methyl 3-chloro-3-butenate (in a small amount) and methyl itaconate (yield 66%, one experiment). Again the yields of these products were quite variable depending on the reaction conditions and always a considerable amount of resinous material was formed.



The formation of itaconic acid and 2,3-butadienic acid by nickel carbonyl-catalyzed carbonylation of propargyl chloride has been reported by Chiusoli et al.⁵ Rosenthal et al. reported that propargyl chloride reacts with nickel carbonyl to form ethyl 2,3-butadienoate and ethyl 3-chloro-3-butenate.⁶ The same authors obtained ethyl 2-(hydroxymethyl)acrylate and 4-hydroxycrotonate from the nickel carbonyl-catalyzed carbonylation of substituted propargyl alcohol.⁷ In addition, the nickel carbonyl-catalyzed carbonylation of substituted propargyl alcohols was studied by Jones et al.⁸; allenic esters were obtained by monocarbonylation.

Since the above-mentioned carbonylation can be carried out under rather mild conditions by a simple procedure, and the catalyst is easy to handle, it can be said that this method is quite useful for the syntheses of alkylidene-succinates.

References

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