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REACTION OF OLEFIN-PALLADIUM CHLORIDE COMPLEX WITH CARBON MONOXIDE.

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Reaction of olefin-palladium chloride complex with water to form a carbonyl compound is well known and acetaldehyde is produced industrially from ethylene by the catalytic action of palladium chloride. By the elaborate work of Smidt on the mechanism of this reaction,[1] it was firmly established that the first step of the reaction is a nucleophilic attack of hydroxide ion to the olefin-palladium chloride complex. Consideration of this reaction mechanism leads us to the expectation that other nucleophilic reagents can also attack the olefin-palladium chloride complex. Until present, however, few studies have been carried out from this point of view. For example, nucleophilic attacks of amines[2] and acetate anion[3] have been reported.

We have carried out the reaction of carbon monoxide with various olefin-palladium chloride complexes, since nucleophilic nature of carbon

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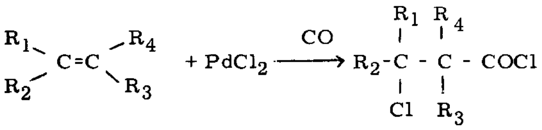
[1] J. Smidt, Angew. Chem. **74**, 93 (1962), Chem. Ind. 54 (1962).

[2] E. W. Stern and M. L. Spector, Proc. Chem. Soc. 370 (1961).

[3] I. I. Moiseev, M. N. Vargaftik and Ya. K. Syrkin, Daklady Akad. Nauk S.S.S.R. **133**, 377 (1960).

monoxide is well known. The complexes reacted smoothly with carbon monoxide in aprotic solvents to form β-chloroacyl chloride. The reaction can be shown by the following general scheme ;



$$\begin{matrix} R_1 & & R_4 \\ & C{=}C & \\ R_2 & & R_3 \end{matrix} + PdCl_2 \xrightarrow{CO} R_2\text{-}\underset{Cl}{\overset{R_1}{C}}\text{-}\underset{R_3}{\overset{R_4}{C}}\text{-}COCl$$

R=H, alkyl, halogen.

In this reaction, the prior isolation of olefin-palladium chloride complex is not always necessary. The complex was formed simply by mixing olefin and powdered palladium chloride in benzene and stirring for 5 hours in an autoclave. Then carbon monoxide was added up to the pressure of 50 kg/cm^2. A rapid absorption of carbon monoxide was observed during the first one hour. Stirring was continued for additional 5 hours. Formation of the acyl chloride was confirmed by observing an infrared absorption band of the crude product at 1800 cm^{-1}. Thus ethylene-palladium chloride complex was allowed to react with carbon monoxide at a room temperature under the pressure of about 50 kg/cm^2 in benzene, yielding β-chloropropionyl chloride. After separating palladium by filtration or centrifugation, β-chloropropionyl chloride was converted into ethyl β-chloropropionate by the treatment with ethanol, and the ester was isolated by distillation.* The yield of ethyl β-chloropropionate was 40 % based on the complex.

Propylene gave ethyl β-chloro-n-butyrate in 30% yield. For asym-

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* Identification of all the β-chlor esters formed by the reaction was done by comparing the retention time of gas chromatogram, I. R. spectra and N. M. R. spectra of the products with those of the authentic samples.

metric olefins, there are two possible sites of raction and in general nucleophilic attack occurs at a more substituted carbon. It is known that the attack of hydroxide ion to the propylene-palladium chloride complex occurs at the center carbon of propylene to form acetone.[1] Interestingly enough, the attack of carbon monoxide occurred at the terminal carbon of propylene to form exclusively ethyl β-chloro-n-butyrate and not ethyl β-chloro-iso-butyrate, indicating that the attacks of hydroxide ion and carbon monoxide are somewhat different, although both the reagents are of nucleophilic nature. In the same way, with 1-butene and 1-pentene, the carbonylation was found to occur at the terminal carbon and thus ethyl β-chloro-n-valerate and β-chloro-n-caproate were formed respectively, both of them are straight chain chloroesters.

α-Olefins, higher than 1-pentene, reacted in a different way ; for example, the formation of ethyl 3-chloro-n-heptylate was only 9% of the reaction product of 1-hexene and the main product was a lower boiling ester. 1-Heptene behaved in the same manner. The structural studies on the main products from 1-hexene and 1-heptene are now in progress. In connection with the different modes of the reaction between the palladium chloride complexes of higher and lower olefins, it is interesting to notice that propylene is oxidized by palladium chloride to isopropenyl acetate in anhydrous acetic acid containing sodium acetate.[4] On the other hand, 1-hexene yields acetate of 2-hexen-1-ol. Isobutylene was also attacked at the terminal carbon and converted into ethyl β-chloro-iso-valerate.

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[4] I. I. Moiseev, M. N. Vargaftik and Ya. K. Syrkin, Izvest. Akad. Nauk Otd. Khim. Nauk 930 (1962).

It is known that a common nucleophilic reagent attacks isobutylene at the tertiary carbonium ion intermediate which is more stable than the terminal primary carbonium ion. From these results, it seems likely that the carbonylation reaction of olefin-palladium chloride complex does not proceed through a simple carbonium ion intermediate.

Chlorinated olefins also reacted. Vinyl chloride gave ethyl β, β-dichloropropionate in a low yield.

Thus, by this reaction, β-chloroacyl chlorides can be synthesized easily from olefins having one less carbon. The mechanistic and stereochemical aspects of this unique reaction will be discussed in detail in a forthcoming paper.