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ORGANIC SYNTHESES BY MEANS OF NOBLE METAL COMPOUNDS.

II. SYNTHESES OF SATURATED CARBOXYLIC ESTERS FROM OLEFINS[1]

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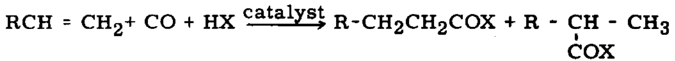
Direct carbonylation of olefins to form saturated acid derivatives, as shown by the following scheme, can be carried out mainly in two ways :[2] namely 1) through the formation of carbonium ion by the action of Lewis acids, such as $AlCl_3$, BF_3, H_2SO_4 etc., on olefins, followed by carbonylation with carbon monoxide, and 2) by the catalytic action of nickel compounds.



$$RCH = CH_2 + CO + HX \xrightarrow{\text{catalyst}} R\text{-}CH_2CH_2COX + R - \underset{\displaystyle COX}{CH} - CH_3$$

X = Cl, OR, OH.

In the course of our studies on the reaction of carbon monoxide with olefins in the presence of noble metal compounds, we have found that some noble metals and their salts have catalytic action on the carbonylation of olefins with carbon monoxide in an alcoholic solution of hydrogen chloride under mild conditions. This method is essentially different from the two

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[1] A previous communication by J. Tsuji, M. Morikawa and J. Kiji, Tetrahedron Letters, No. 16, 1061 (1963) is regarded as Part I.

[2] M. Orchin and J. Wender, Catalysis, Vol. 5, p. 1, Reinhold Pub. Corp., New York (1957).

known methods mentioned above.

Recently the use of noble metal halide as a catalyst for the carbonylation reaction was reported in the patent assigned to du Pont.[3] The patent deals with the synthesis of acyl halide by the reaction of olefin with carbon monoxide and hydrogen chloride in an inert solvent at an elevated temperature and high pressure in the presence of a catalytic amount of halide, carbonyl or chelate of a group VIII noble metal. This report prompted us to reveal the result of our investigation.

Our method is explained by an example of ethylene in the following. 1 g. of palladium chloride and 30 ml. of alcoholic solution of hydrogen chloride (15 %) were added in a glass vessel equipped with a gas inlet capillary. The glass vessel was placed in a 300 ml. pressure reactor. Then carbon monoxide : ethylene mixture (1 : 1) was introduced in an amount sufficient to provide a pressure of 100 atm. The reaction was carried out at 80° with shaking for several hours until no more pressure drop was observed. After usual work-up, the products were separated by distillation, and 22 g. of ethyl propionate was obtained as a main product. In addition, 0.3 g. of ethyl β-ethoxypropionate and 0.8 g. of a higher boiling ester (b.p. 100-110°/20 mm.) were obtained. The structure of the latter ester was determined in the following way. Its infrared absorption bands at 1710 and 1730 cm^{-1} indicate that the ester is a saturated keto ester. Reduction of the keto ester with sodium borohydride gave γ-lactone (I.R. 1780 cm^{-1}, b.p. 140°/70 mm.) showing that the original keto ester

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[3] T. Alderson and V. A. Engelhardt, U. S. Pat. 3,065,242 (1962) ; C. A. 58, 8912 (1963).

was γ-keto ester. Hydrolysis of the ester afforded a crystalline keto acid (m.p. 35-36°, b.p. 140°/10 mm.). The keto acid was reduced by the Wolf-Kishner method to give an oily acid, which was identified with caproic acid. Ethyl γ-ketocaproate was synthesized by the known two methods[4] for the identification. The identity of the authentic sample with the carbonylation product was confirmed by N. M. R. and I. R. spectra and retention time of gas chromatograph. The formation of ethyl γ-ketocaproate from two moles of ethylene and carbon monoxide is understandable. The formation of this compound was not reported in the du Pont's patent. Under the similar reaction conditions, propylene gave ethyl iso-butyrate and ethyl n-butyrate in a ratio of 2 to 1.

An inevitable side reaction of this carbonylation reaction is the addition of hydrogen chloride to olefins. With higher olefins and higher concentration of hydrogen chloride, the ratio of the hydrogen chloride addition to the carbonylation increases. Thus, in addition to ethyl-cyclohexanecarboxylate, chlorocyclohexane was obtained as a byproduct from cyclohexene. Styrene formed ethyl α- and β-phenylpropionate in a ratio of 2 to 1. In addition, α-chloroethylbenzene and ethylbenzene were detected in the reaction mixture.

With halogenated olefins, reductive dehalogenation occurred concurrently with the carbonylation. For example, vinyl chloride yielded ethyl propionate as a main product and ethyl α-chloropropionate as a minor product. In the same way, allyl chloride gave ethyl n- and iso-butyrate

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[4] M. T. Taylor, <u>J. Chem. Soc</u>. 1958, 3822 ; M. C. Klotzel, <u>J. Am. Chem. Soc</u>. **70**, 3571 (1948).

and ethyl β-chloro-iso-butyrate.

In this novel carbonylation reaction, the presence of both palladium chloride and hydrogen chloride is essential. It is known that palladium salt is easily reduced to palladium metal with carbon monoxide in an aqueous or alcoholic solution. Actually after the reaction, black reduced palladium powder was recovered. Interestingly enough, it was found that palladium metal such as palladium on carbon or palladium powder obtained by prior reduction of palladium chloride with carbon monoxide is equally effective catalyst. In conformity with our observation, the catalytic activity of palladium metal on the carbonylation reaction of acetylene has recently been reported.[5] In addition to palladium, metallic rhenium and rhodium as well as their salts are effective.

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[5] G. Jacobsen and H. Spathe, Ger. Pat. 1, 138, 760, 1962 ; C. A. **58** 6699 (1963).