

ORGANIC AND BIOLOGICAL CHEMISTRY

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Organic Syntheses by Means of Noble Metal Compounds. VII.¹ Reactions of Olefin-Palladium Chloride Complexes with Carbon Monoxide

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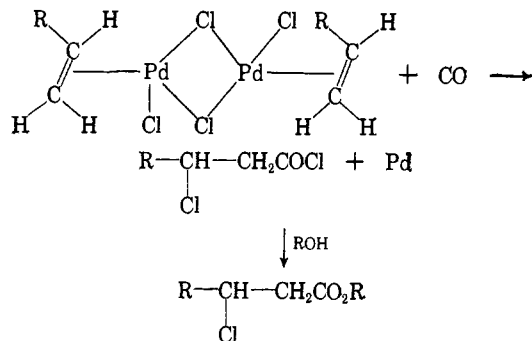
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Olefin-palladium chloride complexes and carbon monoxide react to form β -chloroacyl chlorides. The mechanism of this reaction is discussed.

Introduction

Olefin-palladium chloride complexes can be prepared easily² by the method of Kharasch, *et al.* Recently, the industrial production of acetaldehyde from ethylene by catalytic action of palladium chloride was established. In this reaction, the formation of an ethylene-palladium chloride complex as an intermediate was assumed.³ Since then, the reactivity of olefin-palladium chloride complexes has attracted attention from the viewpoint of synthetic organic chemistry. The formation of vinyl acetate by the reaction of ethylene and sodium acetate in the presence of palladium chloride is understandable as a nucleophilic attack of acetate anion on the complex.⁴ As another example, reaction of amines with the complex was studied.⁵

We have confirmed the formation of β -chloroacyl chlorides by the reaction of olefin-palladium chloride complexes with carbon monoxide. The reaction can be expressed in the general scheme



A preliminary account of this work has been given.⁶

Results and Discussion

Reactions of the various complexes were carried out in a stainless steel autoclave under 40 to 100 kg./cm.² pressure of carbon monoxide; a rapid pressure drop was observed at room temperature. The formation of acyl chlorides was confirmed by infrared absorption spectra of crude products. The products were converted to the corresponding esters which were isolated by distillation. The reaction products and their yields are shown in Table I. The yields are generally

(1) Part VI: J. Tsuji, M. Morikawa, and N. Iwamoto, *J. Am. Chem. Soc.*, **86**, 2095 (1964).

(2) M. S. Kharasch, R. C. Seyler, and F. R. Mayo, *ibid.*, **60**, 882 (1938).

(3) J. Smidt, W. Hafner, R. Jira, R. Sieber, J. Sedlmeier, and A. Sabel, *Angew. Chem.*, **74**, 93 (1962); *Chem. Ber.*, **95**, 102 (1962).

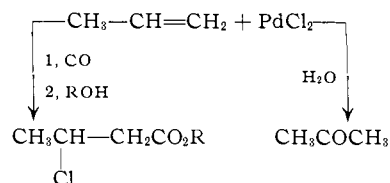
(4) (a) I. I. Moiseev, M. N. Vargaftik and Ya. K. Syrkin, *Dokl. Akad. Nauk, SSSR.*, **133**, 377 (1960); (b) E. W. Stern, *Proc. Chem. Soc.*, 111 (1963).

(5) E. W. Stern and M. L. Spector, *ibid.*, 370 (1961).

(6) J. Tsuji, M. Morikawa, and J. Kiji, *Tetrahedron Letters*, No. 16, 1061 (1963).

not high and it seems likely that a considerable part of the olefin complex is decomposed by the action of carbon monoxide to form the original olefin or a chlorinated hydrocarbon.

One of the characteristic features of this reaction is the formation of a straight chain β -chloroester from α -olefins, lower than 1-hexene. Attack of carbon monoxide on a terminal olefin always occurs at a terminal carbon atom. For example, only methyl β -chloro-*n*-butyrate was obtained from propylene. On the other hand, on hydrolysis of the propylene-palladium chloride complex, hydroxide ion attack is observed predominantly at the central carbon atom to give acetone.



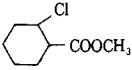
It is apparent that the carbonylation reaction of the olefin-palladium chloride complex does not proceed through a simple nucleophilic attack of carbon monoxide.

In the case of cyclohexene, the formation of two products was shown by gas chromatography. These *cis*- and *trans*-methyl 2-chlorocyclohexanecarboxylates were separated by preparative gas chromatography. In the *trans* isomer, the Cl and COOR groups are expected to assume a more stable equatorial-equatorial conformation. As expected for an axial hydrogen attached to the carbomethoxy-bearing carbon, H₁ showed a sextet centered at 7.5 τ , and H₂, attached to the chlorine-bearing carbon, a sextet at 5.9 τ .⁷ On the other hand, the Cl and COOR groups in the *cis* isomer have an equatorial-axial conformation and their interconversion is expected to be rather easy. As a result, the signal attributed to H₁ was observed at 7.4 τ and that of H₂ at 5.3 τ . Complete analyses of the n.m.r. spectra of the *cis*- and *trans*-chloroesters and related compounds will be given in a separate paper. The relative amounts of the *cis* and *trans* isomers vary with reaction conditions, but usually the more stable *trans* isomer was predominant.

The presence of chlorocyclohexane in the reaction mixture was confirmed. The amount of chlorocyclohexane relative to the chloroester varied with reaction conditions, especially with the pressure of carbon

(7) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, 1959, p. 387.

TABLE I
CONDITIONS, PRODUCTS, AND YIELDS OF THE CARBONYLATION AND SUBSEQUENT ESTERIFICATION REACTION

Olefin	PdCl ₂ , g.	CO pressure, kg./cm. ²	Products	B.p., °C. (mm.)	Yields, based on PdCl ₂ used, %
Ethylene	5	55	CH ₃ (Cl)CH ₂ COOC ₂ H ₅	65-70 (27)	41
Propylene	3	100	CH ₃ CH(Cl)CH ₂ COOCH ₃	159 (760)	27
1-Butene	10	60	CH ₃ CH ₂ CH(Cl)CH ₂ COOCH ₃	61-66 (22)	11
1-Pentene	10	60	CH ₃ CH ₂ CH ₂ CH(Cl)CH ₂ COOCH ₃	84-94 (30)	10
1-Hexene	10	50	CH ₃ CH ₂ CH ₂ CH ₂ CH(Cl)CH ₂ COOCH ₃ (minor part) and other chloroesters	81-93 (15-17)	Total 1.6 g.
2-Butene (<i>cis</i>)	10	50	CH ₃ CH(Cl)CH(CH ₃)COOCH ₃	81-85 (65)	13
2-Butene (<i>trans</i>)	10	50			6
Isobutene	10	60	CH ₃ C(CH ₃)(Cl)CH ₂ COOCH ₃	Unconfirmed	12
Vinyl chloride	10	50	Cl ₂ CHCH ₂ COOCH ₃	77-81 (23)	5
Allyl chloride	12	40	ClCH ₂ CH(Cl)CH ₂ COOCH ₃	95-100 (30)	5
Cyclohexene	Complex 5.2	50	 (<i>cis, trans</i>)	110 (10) ^b	36 ^a

^a Based on cyclohexenepalladium chloride complex prepared by the Kharasch method. ^b Bath temperature.

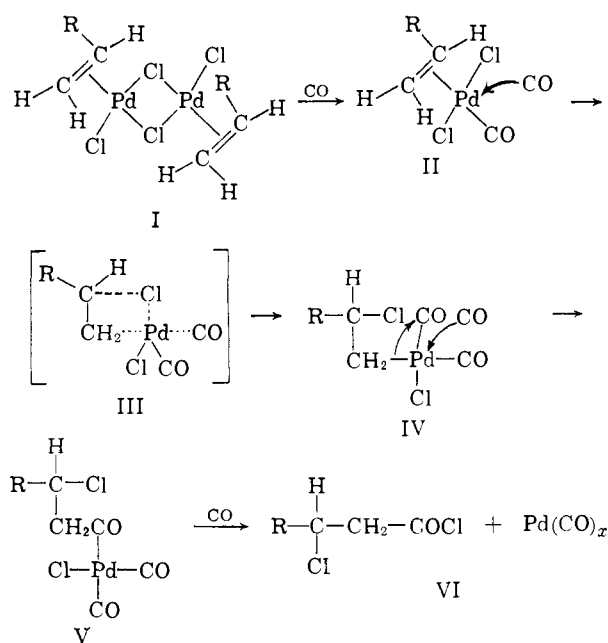
monoxide. The reaction at high carbon monoxide pressure (100 kg./cm.²) gave chiefly chlorocyclohexane. The optimum pressure to obtain the chloroester seems to be about 50 kg./cm.².

The reactivities of *cis* and *trans* olefins were compared by carrying out the carbonylation of *cis*- and *trans*-2-butene under the same reaction conditions. The products obtained from the *cis* and *trans* isomers were the same according to the infrared and n.m.r. spectra; the only difference observed was in yields.

Carbonylation of 1-pentene followed by esterification of the product gave the expected 3-chlorohexanoate. However, a complicated mixture of chloroesters was obtained by carbonylation of 1-hexene. The normal product, 3-chloroheptanoate, was formed but it was not the major product. Other products were found from n.m.r. spectra to be isomeric chloroesters formed after migration of the terminal double bond. 1-Heptene behaved similarly giving a mixture of isomeric chloroesters.

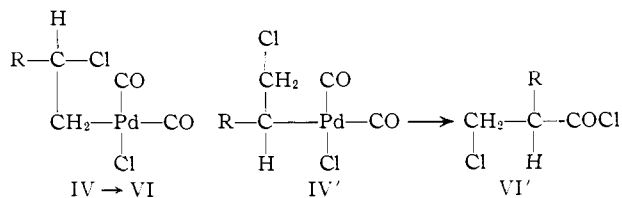
In addition to simple olefins, the reaction of some chlorinated olefins was studied. Allyl chloride gave β,γ -dichlorobutyrate. It is of interest that allyl chloride forms a π -allylpalladium chloride complex which reacts with carbon monoxide to give 3-butenoyl chloride at a somewhat higher temperature.⁸ It is apparent that the complexes formed from allyl chloride at room temperature and higher temperature are different, and hence the products of the carbonylation reaction are also different.

Reaction Mechanism.—Possibly the first step of the reaction is the coordination of one or two moles of carbon monoxide to palladium to form the complex II. The chlorine atom is transferred from palladium to the coordinated olefinic carbon atom with a concerted transformation from the π -complex II to the σ -complex IV. Carbon monoxide is then inserted between palladium and the methylene group to give the β -chloroacylpalladium complex V which then collapses to form β -chloroacyl chloride. Carbonylation of the palladium-*t*-phosphine complex with carbon monoxide to form an acyl complex was reported by Chatt, *et al.*,⁹ and the same type of carbonylation to



form an acyl complex might be responsible for the present reaction. A similar mechanism has been proposed for the related nickel carbonyl-catalyzed carboxylation reaction.¹⁰

According to this mechanism, the formation of the straight chain acyl chloride is understandable, since the first attack on the coordinated olefin is by chlorine, not by carbon monoxide. The main factor in the formation of the straight chain acyl chloride VI seems to be steric. The σ -complex IV may be one of two possibilities, IV or IV'. The less-crowded IV may be



favored over IV'. This may explain the exclusive attack of carbon monoxide at the less hindered terminal carbon atom to form VI, not VI'.

(8) J. Tsuji, J. Kiji, and M. Morikawa, *Tetrahedron Letters*, No. 26, 1811 (1963).

(9) G. Booth and J. Chatt, *Proc. Chem. Soc.*, 67 (1961).

(10) R. Heck, *J. Am. Chem. Soc.*, 85, 2013 (1963). For general reference, see C. W. Bird, *Chem. Rev.*, 62, 283 (1962).

Experimental

The n.m.r. spectra were determined by the Varian high-resolution spectrometer Model DP 60 and HR 100 using tetramethylsilane as an internal standard. Gas chromatographic analyses were carried out on the column, silicon DC 550 on Celite, 2 m. length, at 100 or 180°. All boiling points are uncorrected.

Materials.—Commercially available anhydrous palladium chloride was used without further purification. Carbon monoxide (99.5% pure) was purchased from the Matheson Co.

Identification of all the β -chloroester was done by comparing the retention time on the gas chromatograph, and the infrared and n.m.r. spectra with those of authentic samples. Unless specified, the authentic samples were prepared by the addition of hydrogen chloride to the corresponding α,β -unsaturated acids in ether and subsequent esterification with diazomethane.

Reaction of Ethylene.—Five grams of palladium chloride was suspended in 50 ml. of dry benzene in a 100-ml. stainless steel autoclave. Ethylene was introduced (55 kg./cm.²) and the mixture was stirred magnetically for 5 hr. at room temperature. The excess ethylene was replaced with carbon monoxide and the mixture was stirred at room temperature for several hours. The benzene solution was separated by centrifugation from precipitated palladium, and the palladium was washed with dry benzene. The infrared spectrum of the crude benzene solution showed a band at 1800 cm.⁻¹ attributed to an acyl chloride. Ethanol (2 ml.) was added to the combined benzene solution and the solution was refluxed for 1 hr. The solution was washed with dilute sodium carbonate solution, then with water, and dried. By distillation, a total of 1.6 g. of ethyl β -chloropropionate, b.p. 65–70° (27 mm.), was obtained. The n.m.r. spectrum showed three triplets, centered at 8.75 (methyl protons in ethoxy group), 7.31 (C- α , two protons), 6.33 (C- β , two protons), and a quartet, centered at 5.97 τ (methylene protons in ethoxy group). The chloroester was identified with commercially available ethyl β -chloropropionate by infrared and n.m.r. spectra and by gas chromatography.

Reaction of the Other Olefins.—The reaction conditions of the other olefins are given in Table I. All reactions were carried out at room temperature in the 100-ml. stainless steel autoclave, and 50 ml. of dry benzene was used as solvent. Large excess of olefins (about 10 ml. of liquid or liquefied olefins) was used in all cases. Carbonylation was carried out in the presence of excess olefins except in the cases of ethylene and propylene. The confirmation of the products is described in the following.

Methyl β -Chloro-*n*-butyrate.—An authentic sample was prepared from crotonic acid. The n.m.r. spectrum of the product showed two doublets at 8.44 (methyl protons) and 7.28 (methylene protons), a singlet at 6.35 (methyl protons in methoxy group), and a multiplet centered at 5.52 τ (C- β proton).

Methyl β -Chloro-*n*-valerate.—An authentic sample was prepared from 2-pentenoic acid.¹¹ The n.m.r. spectrum gave a triplet at 9.00 (methyl protons), a doublet at 7.27 (C- α two protons), a singlet at 6.39 (methyl protons in methoxy group), and two multiplets centered at 8.27 (C- γ two protons) and at 5.80 τ (C- β proton).

Methyl β -Chloro- α -methylbutyrate.—The ester obtained from *cis*- and *trans*-2-butene showed the same n.m.r. spectrum: two doublets at 8.79 (methyl protons) and at 8.50 (C- γ three protons),

(11) J. R. Johnson, "Organic Reactions," Vol. 1, R. Adams, Ed., John Wiley and Sons, Inc., New York, N. Y., 1957, p. 240.

two quintets centered at 7.33 (C- α proton) and at 5.62 (C- β proton), and a singlet at 6.39 τ (methyl protons in methoxy group).

Methyl β -Chloroisovalerate.—An authentic sample was prepared by the method of Smith and Spillane.¹² The n.m.r. spectrum showed three singlets at 8.30 (six protons in methyl groups), 7.19 (methylene protons), and 6.34 τ (methyl protons in methoxy group).

Methyl 3-Chlorohexanoate.—The n.m.r. spectrum showed a triplet at 9.07 (methyl protons), an unresolved multiplet (four protons in methylene groups), a doublet at 7.27 (C- α two protons), a singlet at 6.34 (methyl protons in methoxy group), and a multiplet at 5.68 τ (C- β proton). The authentic sample was prepared from 2-hexenoic acid.¹¹

Methyl *cis*-2-Chlorocyclohexanecarboxylate.—1-Cyclohexanecarboxylic acid was synthesized by the method of Joly and Warnant¹³ from 1-bromocyclohexanecarboxylic acid. By the procedure given by Vaughan, *et al.*,¹⁴ the acid was treated with hydrogen chloride in acetic acid at 100° for 15 hr. The chloroacid was methylated with diazomethane. The methyl ester was purified by preparative gas chromatography.

Methyl *trans*-2-Chlorocyclohexanecarboxylate.—The procedure given by Vaughan, *et al.*, was somewhat modified. *trans*- β -Chloroacrylic acid (m.p. 84°) was synthesized by the addition of propiolic acid to a hot solution of 33% hydrochloric acid. Reaction of butadiene and *trans*- β -chloroacrylic acid in benzene was carried out in an autoclave for 30 hr. at 150°. The acidic fraction was separated from the reaction mixture with sodium carbonate solution. The solution was acidified with hydrochloric acid and extracted with ether. When the solvent was removed, the residue solidified to give *trans*-2-chloro-4-cyclohexanecarboxylic acid (m.p. 109°). The hydrogenation of the acid was carried out in ethyl acetate to afford *trans*-2-chlorocyclohexanecarboxylic acid (m.p. 84°). The chloro acid was methylated with diazomethane and purified by distillation; b.p. 100° (bath temperature, 10 mm.).

Methyl β,β -Dichloropropionate.—An authentic sample was prepared in the following way. β -Chloroacrylic acid, used in the synthesis of the 2-chlorocyclohexanecarboxylate, was dissolved in acetic acid saturated with hydrogen chloride and the solution was kept at 100° for 1 day. Most of the acetic acid was removed under reduced pressure and the residue was dissolved in ether. The ethereal solution was washed with water and then treated with diazomethane. Crude product was isolated by distillation, b.p. 77–81° (23 mm.), and then purified by preparative gas chromatography. The n.m.r. spectrum showed a doublet at 6.77 (C- α two protons), a singlet at 6.29 (methyl protons in methoxy group), and a triplet at 3.87 τ (C- β proton).

Methyl β,γ -Dichloro-*n*-butyrate.—Chlorine gas was passed into 70 ml. of an ethereal solution of vinylacetic acid¹⁵ (7 g.) for 15 min. The resulting ethereal solution was washed with water and methylated with diazomethane. The product was distilled with considerable decomposition to give 2.5 g. of methyl β,γ -dichloro-*n*-butyrate, b.p. 95–100° (30 mm.). The n.m.r. spectrum of this product is somewhat complicated.

(12) L. I. Smith and L. J. Spillane, *J. Am. Chem. Soc.*, **65**, 288 (1943).

(13) R. Joly and J. Warnant, *Bull. soc. chim. France*, 367 (1958).

(14) W. R. Vaughan, R. L. Craven, R. Q. Little, and A. C. Schoenthaler, *J. Am. Chem. Soc.*, **77**, 1594 (1955).

(15) E. C. Horning, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1960, p. 851.