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Organic Syntheses by Means of Noble Metal Compounds. XIV. The Carbonylation of Cyclooctadienes

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The 1, 5-cyclooctadiene - palladium chloride complex and carbon monoxide react in ethanol to form ethyl 4-cyclooctenecarboxylate. The carbonylation of 1, 5-cyclooctadiene catalyzed by palladium chloride has given ethyl 4-cyclooctenecarboxylate and cyclooctanedicarboxylate. It has been found that the monoester can be obtained selectively under certain conditions; the further carbonylation of the monoester gives the diester. Under the same reaction conditions, 1, 3-cyclooctadiene gives ethyl 2-cyclooctenecarboxylate in a low yield. Metallic palladium has been found to be the true catalyst and the presence of hydrogen chloride has been found to be essential for the catalysis. It has also been found that the 1, 5-cyclooctadiene - palladium chloride complex can be formed from 1, 5-cyclooctadiene, metallic palladium and hydrogen chloride by heating them in an autoclave under nitrogen. It seems likely that the catalytic carbonylation of 1,5-cyclooctadiene proceeds through the formation of the 1,5-cyclooctadiene - palladium chloride complex.

Previous work in this series has shown that palladium chloride complexes of simple olefins,[1] allylic compounds,[2,3] and conjugated dienes[4] can be carbonylated easily to form saturated or unsaturated esters in an alcoholic solution, and acid chlorides in a benzene solution. In the present paper, we wish to report the carbonylation of the 1, 5-cyclooctadiene (1, 5-COD) - palladium chloride complex (I). It was of special interest to study the carbonylation of 1, 5-COD complex in view of the fact that the complex is unusually stable and has a monomeric structure which is different from halogen-bridged olefinic and π-allylic complexes of palladium chloride.[5] In addition, the direct carbonylation of 1, 5-COD to form a mono- or a di-ester in the presence of a catalytic amount of palladium chloride seemed to be worthy of study.

Experimental

The NMR spectra were determined with high-resolution spectrometer, models DP 60 and HR 100, using tetramethylsilane as an internal standard; the peak positions are expressed in terms of τ values. Gas chromatographic analyses were carried out on a Thermol-3 column, 2 m. long, at 220°C for higher-boiling products, or on a Silicone DC 550 columm, 2 m. long, at 180°C for lower-boiling products. All boiling points are uncorrected. The molecular weights were determined in benzene using a Mechrolab vapor-pressure osmometer, or by mass spectroscopy.

Materials. — Commercially available anhydrous palladium chloride was used without further purification. Carbon monoxide (99.5% pure) was purchased from the Matheson Co., U.S.A. 1, 5-COD was also a commercial product (99% pure). 1, 3-COD was prepared from 1, 5-COD by Devaprabhakara's method.[6]

3-Bromocyclooctene was prepared by refluxing a mixture of cyclooctene (80 g.), N-bromosuccinimide (110 g.), benzoyl peroxide (0.2 g.), and carbon tetrachloride (400 ml.) for 1 hr. The product (b. p. 73—75°C/ 7mmHg) was obtained in a 69% (96 g.) yield.

The Carbonylation of 1, 5-COD in Ethanol.— The reaction conditions are given in Table I. The general procedure is as follows. To avoid the effect of the metal surface of a stainless steel autoclave, the reaction was carried out in a glass vessel with a gas-inlet capillary. In the glass vessel, a mixture of ethanol (or an ethanolic solution of hydrogen chloride), 1, 5-COD, and palladium chloride (or metallic palladium, or palladium acetylacetonate) was placed; the vessel was then set in the autoclave. Then carbon monoxide was introduced (100 kg./cm^2), and the mixture was shaken at 100°C for a certain period of time. After the reaction, the reaction mixture was poured into five times its volume of water, and the solution was extracted several times with ether. The ethereal solution was dried over anhydrous magnesium sulfate. Distillation under reduced pressure gave COD (40°C/14 mmHg), the monoester (102°C/15 mmHg), and the diesters (143°C/4 mmHg). The recovered COD consisted of 1, 5- and 1, 3-isomers. Their relative amounts varied

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[1] J. Tsuji, M. Morikawa and J. Kiji, *Tetrahedron Letters*, **1963**, 1061; *J. Am. Chem. Soc.*, **86**, 4851 (1964).

[2] J. Tsuji, J. Kiji, S. Imamura and M. Morikawa, *Tetrahedron Letters*, **1963**, 1811; *J. Am. Chem. Soc.*, **86**, 4350 (1964).

[3] R. Long and G. H. Whitfield, *J. Chem. Soc.*, **1964**, 1852.

[4] J. Tsuji, J. Kiji and S. Hosaka, *Tetrahedron Letters*, **1964**, 605.

[5] For general reference, see E. O. Fischer and H. Werner, "Metall π-Komplexe mit di- und oligoolefinischen Liganden," Verlag Chemie, Weinheim (1963).

[6] D. Devaprabhakara, C. G. Cardenas and P. D. Gardner, *J. Am. Chem. Soc.*, **85**, 1553 (1963).

with the reaction conditions. Ethyl 4-cyclooctenecarboxylate was converted into crystalline amide by heating it with excess concentrated ammonia in a sealed tube at 100° for 10 hr; m. p. 203°C[7] (from ethanol). When the ester was hydrogenated in ethanol in the presence of palladium on carbon, ethyl cyclooctanecarboxylate was obtained (b. p. 120°C/20 mmHg.). On hydrolysis with 15% alcoholic potassium hydroxide, cyclooctane-carboxylic acid was obtained (b. p. 110—120°C/1 mmHg). The acid was converted into acid chloride by treatment with oxalyl chloride in benzene. The crude acid chloride was converted into amide by treatment with ammonia; m. p. 194—196°C (from ethanol) reported m. p. 195.8°C),[8] hydrazide, m. p, 67—68°C.

The Carbonylation of Cyclooctene.—To a mixtrue of 30 ml. of ethanol, 3g. of palladium chloride, and 17 g. of cyclooctene in a glass vessel set in the autoclave, carbon monoxide was introduced (97 kg./cm^2); this mixture was then shaken at 100°C for 25 hr, After the usual work-up, 8.4 g. of cyclooctanecarboxylate was collected by distillation (108—115°C/14 mmHg). The ester was converted into crystalline amide in the manner described above.

The Carbonylation of 1, 3-COD.—A mixture of 1, 3-COD (16 g.), ethanol (30 ml.), and palladium chloride (5 g.) was allowed to react under 155 kg./cm^2 of carbon monoxide at 100°C for 23 hr. After the usual work-up, distillation gave 1, 3-COD (4.3 g., 50—75°C/46 mmHg) and crude ester (5.0 g., 75—145°C/46 mmHg). The purification of the crude ester by preparative gas chromatography gave ethyl 2-cyclooctenecarboxylate and a small amount of 3-ethoxycyclooctene. Analytical results of the monoester;

Found: C, 72.21; H, 9.89; mol. wt., 184. Calcd. for $C_{11}H_{18}O_2$; C, 72.49; H, 9.96%; mol. wt., 182.

NMR spectrum: 8.77 (triplet, 3 methyl protons), 8.44 (multiplet, ring methylenes), 7.92 (multiplet, 2 allylic protons), 6.70 (multiplet, 1 proton at the carbethoxy-bearing carbon), 5.95 (diffuse quartet, 2 protons $-O-CH_2-$), and 4.34 (multiplet, 2 vinyl protons). Ethyl 2-cyclooctenecarboxylate was converted into amide by treating it with ammonia in a sealed tube at 100°C for 10 hr; m. p. 185—186°C (from ethanol).

Found: C, 70.50; H, 9.87; N, 9.11. Calcd. for $C_9H_{15}O_1N$; C, 70.55; H, 9.87; N, 9.14%.

3-Ethoxycyclooctene was identified, by means of its NMR and infrared spectra, with an authentic sample prepared by refluxing 3-bromocyclooctene with sodium ethoxide in ethanol. Mol. wt., Found: 154 (mass spectroscopy). Calcd. for $C_{10}H_{18}O_1$: 154.

The ether had the following NMR peaks; 8.87 (triplet, 3 methyl protons), 8.51 (diffuse multiplet, ring methylenes), 7.87 (multiplet, 2 allylic protons), 6.65 (multiplet, 2 protons $-O-CH_2-$), 5.91 (multiplet, 1 proton $-CH-O-$), and 4.52 (multiplet, 2 vinyl protons). Two protons of the ethoxy (5.91) and carbethoxr groups (5.95) do not show a clear quartet, because of the effect of the neighboring asymmetric carbon (the carbethoxy- or ethoxy-bearing carbon). A similar observation has been reported with cortisone acetate.[9]

In addition, 1.5 g. of unidentified diester (mol. wt., 240) was obtained.

The Carbonylation of 3-Bromocyclooctene.—A mixture of 3-bromocyclooctene (8 g.) and palladium chloride (1.8 g.) in ethanol (60 ml.) was allowed to react under 92 kg./cm^2 of carbon monoxide at 100°C for 14 hr. The crude product then obtained by distillation (62—94°C/5 mmHg) was purified by preparative gas chromatography; 3-ethoxycyclooctene (yield based on 3-bromocyclooctene 16.9%) and ethyl 2-cyclooctenecarboxylate (yield 36.4%) were thus obtained.

The Carbonylation of the 1, 5-COD Complex.—The complex (15 g.) was suspended in 30 ml. of ethanol in a glass vessel. Carbon monoxide was then introduced (100 kg./cm^2), and the mixture was shaken for 24 hr. at 110°C. After the usual work-up, 2.4 g. of crude monoester (100—120°C/21 mmHg), together with a small amount of 1, 5-COD, was obtained. Further distillation gave 0.3 g. of the diesters (140°C/5 mmHg).

The Formation of the 1, 5-COD Complex from Metallic Palladium.—In a glass vessel, 20 ml. of a 15% alcoholic solution of hydrogen chloride, 0.2 g. of palladium black, and 8 ml. of 1, 5-COD were mixed. The mixture was then shaken in the autoclave at 110°C under a nitrogen atmosphere (40 kg./cm^2). After 18 hr., a yellow precipitate contaminated with palladium black was collected by filtration and recrystallized from acetic acid to give 0.12 g. of the 1, 5-COD palladium chloride complex. The complex was identified by a comparison of its infrared spectrum with that of an authentic sample.

Found: C, 33.76; H, 4.28; Cl, 24.62. Calcd. for $C_8H_{12}Pd_1Cl_2$: C, 33.62; H, 4.23; Cl, 24.80%.

The recovered COD consisted of a 1 : 2.3 muxture of 1, 5- and 1, 3-isomers.

The Carbonylation of Di-μ-chloro-bis(8-methoxycyclooct-4-enyl)-dipalladium.—This complex was prepared by the treatment of the 1, 5-COD complex with sodium carbonate in methanol following the method of Chatt et al.[10] To a suspension in the autoclave of the complex (5.5 g.) in 50 ml. of benzene, carbon monoxide was introduced (50 kg./cm^2). The mixture was then stirred at 60°C for 20 hr. After the reaction, the palladium which had precipitated was removed. An infrared spectrum of the crude solution showed an absorption band at 1735 cm^{-1} due to an ester. No absorption at 1800 cm^{-1} due to an acid chloride was observed. To ensure the conversion of an acid chloride, if present, into an ester, the solution was then refluxed with 10 ml. of methanol for 30 min. When the solvent was removed, 1.2 g. of an oily residue was obtained. Gas chromatographic analysis showed the presence of two main products, which were separated by preparative gas chromatography. The first fraction was identified as 1, 5-COD. The second fraction was determined to be methyl 8-methoxy-4-cyclooctenecarboxylate.

Found: C, 66.39; H, 9.03 mol. wt. 198. Calcd. for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15%; mol. wt. 198.3.

The NMR spectrum had the following peaks; 4.43τ (multiplet, 2 vinyl protons), 6.43τ (singlet, methyl protons of the ester,), 6.79τ (singlet methoxy protons),

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[7] G. Stork and H. K. Landesman, *J. Am. Chem. Soc.*, **78**, 5129 (1956).

[8] A. C. Cope, M. Grug and S. W. Fenton, ibid., **74**, 174 (1952); E. Muller and H. Hubner, *Chem. Ber.*, **96**, 670 (1963).

[9] J. N. Shoolery and M. T. Rogers, *J. Am. Chem. Soc.*, **80**, 5121 (1958).

[10] J. Chatt, L. M. Vallarino and L. M. Venanzi, *J. Chem. Soc.*, **1957**, 3413.

7.28τ (multiplet, proton at the carbomethoxy-bearing carbon), 6.5τ (multiplet, 1 proton at the methoxy-bearing carbon), broad multiplets centered at 7.8 (4 allylic protons), and 8.24 (4 ring methylene protons). Furthermore, a small amount of methyl 4-cyclooctenecarboxylate was detected.

The Conversion of Ethyl 4-Cyclooctenecarboxylate (II) into Ethyl 3-Carbethoxyl-2-oxocyclopentanepropionate.—Fourteen grams of II were oxidized by the drop-by-drop addition of 220 ml. of a sodium permanganate solution (12%) for 3 hr., with the occasional addition of small pieces of dry ice. After the oxidation, sulfur dioxide gas was passed through until the solution became clear. Then the product was extracted with ether. The ether was then evaporated, and the residue was esterified in a mixture of benzene and ethanol by the azeotropic method. The benzene and ethanol were then evaportaed; the distillation of the residue gave 9 g. of ethyl 1, 3, 6-hexanetricarboxylate (b. p. 145—152°C/2 mmHg. Found: mol. wt., 293, Calcd. for $C_{15}H_{26}O_6$: 302).

The triester (5 g.) in 50 ml. of benzene was refluxed overnight with 1.2 g. of sodium hydride. The reaction mixture was washed with aqueous acetic acid and then with water. Distillation gave 2.1 g. of ethyl 3-carbethoxy-2-oxocyclopentanepropionate (b. p. 130—140°C (bath temp.)/ 1 mmHg). The ester gave a positive test with ferric chloride.

The ester (2 g.) was dissolved in a mixture of concentrated hydrocholric acid (8 ml.) and acetic acid (8 ml.); the mixture was then refluxed for 5 hr. The reaction mixture was concentrated under reduced pressure, and the residue was treated with 2, 4-dinitrophenylhydrazine to give the hydrazone of 2-oxocyclopentanepropionic acid; m. p. 171—172°C (reported m. p. 170°C[11]).

Found: C, 49.57; H, 4.69; N, 16.60. Calcd. for $C_{14}H_{16}O_6N_8$: C, 50.00: H, 4.76; N, 16.66%. Furthermore, the residue was esterified in a mixture of benzene and ethanol by the azeotropic method. After the solvents had been evaporated, the residue was treated with 2, 4-dinitrophenylhydrazine. The hydrazone of ethyl 2-oxocyclopentanepropionate thus obtained was recrystallized from ethanol; m. p. 87.5—88.5°C.

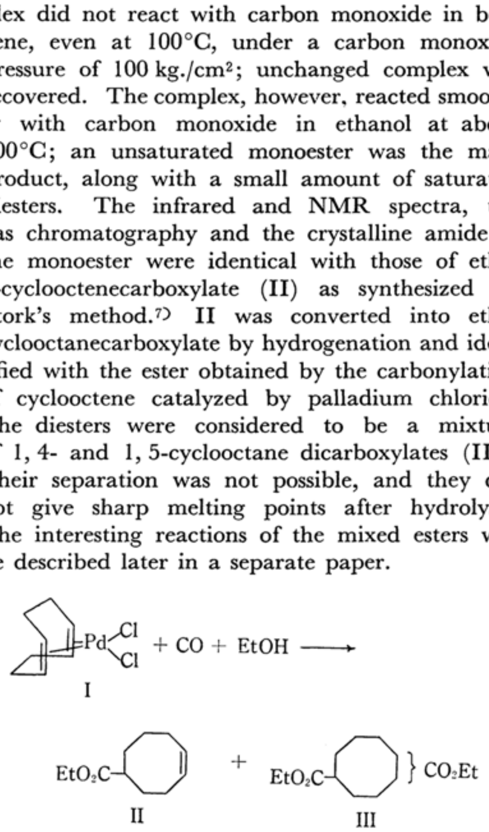
Found: C, 52.61; H, 5.56; N, 15.08. Calcd. for $C_{16}H_{20}O_6N_4$: C, 52.74; H, 5.53; N, 15.38%.

The Synthesis of Ethyl 2-Oxocyclopentanepropionate.—An enamine (30 g.) was prepared from cyclopentanone (21 g.) and pyrrolidine (30 g.) by the usual azeotropic method.[12]

The enamine (7 g.) was dissolved in 30 ml. of ethanol. To the solution 7 g. of ethyl 3-bromopropionate was added; then the mixture was refluxed for 5 hr. The enamine was hydrolyzed by warming it with excess dilute hydrochloric acid. After most of the ethanol had been evaporated, the residue was dissolved in ether. The ethereal solution was washed successively with a sodium bicarbonate solution and with water. The distillation of the solution gave 2 g. of ethyl 2-oxocyclopentanepropionate (b. p. 114—115°C/5 mmHg). 2, 4-Dinitrophenylhydrazone was prepared; its melting point was undepressed on admixture with the 2, 4-dinitrophenylhydrazone obtained above. (Found: C, 52.87; H, 5.61; N, 15.50%).

Results and Discussion

The Carbonylation of the 1, 5-COD Complex.—It was found that, unlike the other olefinic complexes previously studied,[1,2] the 1, 5-COD complex did not react with carbon monoxide in benzene, even at 100°C, under a carbon monoxide pressure of 100 kg./cm^2; unchanged complex was recovered. The complex, however, reacted smoothly with carbon monoxide in ethanol at about 100°C; an unsaturated monoester was the main product, along with a small amount of saturated diesters. The infrared and NMR spectra, the gas chromatography and the crystalline amide of the monoester were identical with those of ethyl 4-cyclooctenecarboxylate (II) as synthesized by Stork's method.[7] II was converted into ethyl cyclooctanecarboxylate by hydrogenation and identified with the ester obtained by the carbonylation of cyclooctene catalyzed by palladium chloride. The diesters were considered to be a mixture of 1, 4- and 1, 5-cyclooctane dicarboxylates (III). Their separation was not possible, and they did not give sharp melting points after hydrolysis. The interesting reactions of the mixed esters will be described later in a separate paper.



I

II

III

The Carbonylation of 1, 5-COD.—Considering that the complex can easily be formed from palladium chloride and 1, 5-COD, we attempted the direct carbonylation of 1, 5-COD without the prior formation of the complex. When 1, 5-COD in ethanol was smoothly carbonylated in the presence of palladium chloride, the monoester (II), accompanied by the mixed diesters (III), was obtained. As is shown in Table I, it was confirmed that only a catalytic amount of palladium chloride is necessary. Interestingly, it was found that a metallic palladium such as palladium on carbon or palladium black can be used as an active catalyst when the reaction is carried out in ethanol containing hydrogen chloride. Palladium acetylacetonate was found effective only when hydrogen chloride was added to the reaction medium. The concentration of hydrogen chloride has a marked effect on the reaction products. When the concentration was high, the yield of the diesters increased. When palladium iodide, instead of chloride, was used,

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[11] M. Lamant and M. Delepine, *Compt. rend.*, **242**, 380 (1956).

[12] G. Stork, A. Brizzolara, H. Landesman and J. Szmuszkovics, *J. Am. Chem. Soc.*, **84**, 1755 (1962).

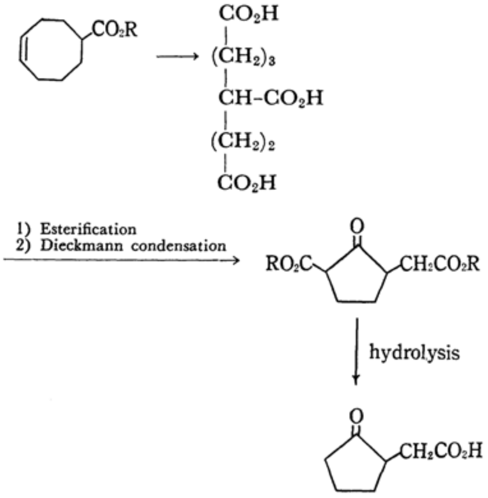
TABLE I. REACTION OF 1, 5-COD WITH CARBON MONOXIDE[d]

Expt.	1, 5-COD ml.	Solvent	Catalyst, g.	Reaction		Yield, %[a]	
				Temp. °C	Time hr.	Monoester	Diester
1	20	EtOH 30	$PdCl_2$ 3	100	3	58.4	19.8
2	20	EtOH 30	$PdCl_2$ 0.5	100	24	16.8	trace
3	20	EtOH 30	$PdCl_2$ 3	200—250	4	58.0	0.8
4	8	EtOH 12	$PdBr_2$ 1.2	100	1.5	52.2	45.5
5	8	EtOH 12	PdI_2 1.2	100	3.5	5.0	95.0
6	20	10% HCl[c]/EtOH 30	$Pd(acac)_2$[b] 1	100	2	75.0	3.8
7	20	30% HCl/EtOH 30	$Pd(acac)_2$[b] 1	100	1	37.5	59.0
8	20	10% HCl/EtOH 30	Pd-black 0.5	100	24	18.6	trace
9	20	10% HCl/EtOH 30	10% Pd on charcoal 5	100	24	31.0	31.0

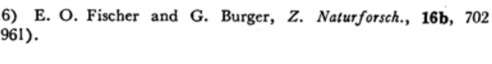
a) Yield based on 1,5-COD
b) Palladium acetylacetonate
c) 10% hydrogen chloride in absolute ethanol
d) Carbon monoxide pressure was 100 kg./cm^2 in all cases.

an almost exclusive formation of the diesters was observed. The catalytic action of the hydrogen chloride-palladium system in the carbonylation of olefins,[13] allylic compounds[2] and acetylene[14] has already been reported.

It is known that 1, 5-COD can be easily isomerized to 1, 3-COD by the catalytic action of palladium chloride.[15] Therefore, we should consider the possibility of the double bond migration during the carbonylation reaction to give isomers of ethyl cyclooctenecarboxylate. The position of the double bond in the monoester II was determined in the following way. The oxidation of II with sodium permanganate gave 1, 3, 6-hexanetricarboxylic acid, which was then esterified. The Dieckmann condensation of the ester gave ethyl 3-carbethoxy-2-oxocyclopentanepropionate, which in turn gave a low melting 2, 4-dinitrophenylhydrazone. The ketoester was converted into 2-oxocyclopentanepropionic acid and then to ethyl 2-oxocyclopentanepropionate, both of which gave 2, 4-dinitrophenylhydrazones as crystalline substances with sharp melting points. An authentic sample of ethyl 2-oxocyclopentanepropionate was synthesized by the reaction of cyclopentanone with ethyl 3-bromopropionate by the enamine method. Its identity was confirmed by a mixed melting point determination. Thus, the reaction sequences described above give convincing evidence for the structure of ethyl 4-cyclooctenecarboxylate. It can be concluded that the double bond of the monocarbonylation product remained at the original position, at least in the major portion, though not necessarily all, even in the presence of palladium; this suggests that the rate of carbonylation is larger than that of the double bond migration.



The first step in the carbonylation reaction of 1, 5-COD catalyzed by palladium-hydrogen chloride is evidently the formation of the 1, 5-COD complex. The complex is known to be formed by the direct contact of 1, 5-COD with palladium chloride or its complex.[10] Interestingly, we have confirmed that the complex can be prepared by the reaction of metallic palladium, not palladium chloride, with 1, 5-COD in ethanol containing hydrogen chloride (15%) at 100°C.



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In connection with our observation, it should be mentioned that π-allylpalladium bromide can be prepared from metallic palladium and allyl bromide.[16]

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[13] J. Tsuji, M. Morikawa and J. Kiji, *Tetrahedron Letters*, **1964**, 1437.

[14] G. Jacobsen and H. Spathe, German Pat. 1138760 (1962); *Chem. Abstr.*, **58**, 6699 (1963).

[15] S. A. Rhone-Poulenc, French. Pat. 1337889 (1963); *Chem. Abstr.*, **60**, 2802 (1964).

[16] E. O. Fischer and G. Burger, *Z. Naturforsch.*, **16b**, 702 (1961).

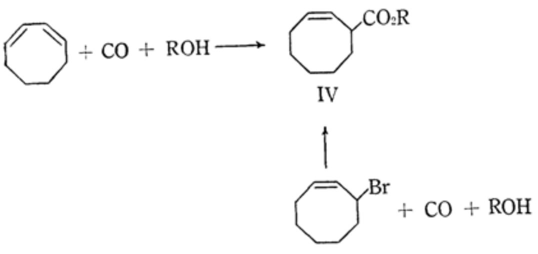
Table II. Comparative studies of carbonylation of dienes

CO pressure: 100 kg./cm^2; reaction temp.: 100°C

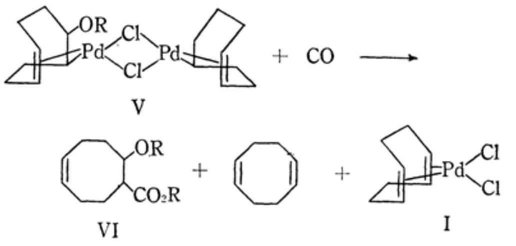
Diene ml.	EtOH ml.	PdCl$_2$ g.	Time hr.	Yield of monoester %	By-product %
1,3-COD 20	30	3	23	2-Cyclooctene-carboxylate (IV) 9.5	3-Ethoxycyclooctene 1.3
1,5-COD 20	30	3	3	4-Cyclooctene-carboxylate (II) 58.4	1,4- and 1,5-Cyclo-octanedicarboxylate 19.8
1,3-Cyclohexa-diene 5	12	1.2	24	2-Cyclohexene-carboxylate 79.8	

The second step in the carbonylation is the coordination of carbon monoxide on the palladium of the complex. When the 1, 5-COD complex in ethanol was shaken under 100 kg./cm^2 of carbon monoxide at room temperature, the complex changed into another yellow complex, while absorbing carbon monoxide. The new complex was quite unstable and decomposed when exposed to the air. Although no further elucidation of the new complex has been undertaken because of its instability, it is reasonable to expect that the complex is an intermediate in the carbonylation.

The Carbonylation of 1, 3-COD.—As has been mentioned, the COD recovered from the carbonylation was a mixture of 1, 5- and 1, 3-isomers. Therefore, the carbonylation of pure 1, 3-COD was studied. Ethyl 2-cyclooctenecarboxylate (IV) was obtained in a low yield. As is shown in Table II, the carbonylation of 1, 3-COD is much slower than that of 1, 5-COD. Under comparable conditions, 1, 3-cyclohexadiene gave 2-cyclohexenecarboxylate in a higher yield. In general, conjugated dienes such as butadiene can be carbonylated easily to form β, γ-unsaturated esters,[4] the steric factors of 1, 3-COD seem to be responsible for this difference in reactivity. The same ester was obtained by the carbonylation of 3-bromocyclooctene. The formation of the β, γ-unsaturated ester by a carbonylation of the allylic halogen catalyzed by palladium is a general reaction.[2]



The Carbonylation of Di-μ-chloro-bis (8-methoxycyclooct-4-enyl)-dipalladium. — The 1, 5-COD complex can be converted into a halogen-bridged alkoxy-substituted complex (V) by means of the action of sodium carbonate on the complex in alcohol.[10] The complex involves σ-bonds, which may be expected to be carbonylated more easily than the original 1, 5-COD complex. Actually the complex was carbonylated in benzene at 60°C to form an alkoxycyclooctenecarboxylate. Although no identification with an authentic sample has been made, it is highly probable that the product is methyl 8-methoxy-4-cyclooctenecarboxylate (IV); this suggestion is based on its NMR spectrum. In addition, 1, 5-COD and its palladium chloride complex were detected in the reaction mixture.



Although the reaction was carried out in a benzene solution, a methyl ester was obtained, instead of the expected acid chloride.[1] Undoubtedly the methoxy group is supplied by the decomposition of the methoxysubstituted complex.

Summary

1, 5-Cyclooctadiene - palladium chloride complex and carbon monoxide react in ethanol to form ethyl 4-cyclooctenecarboxylate. The carbonylation of the 1, 5-cyclooctadiene catalyzed by palladium chloride has given 4-cyclooctenecarboxylate and cyclooctanedicarboxylate. Under the same conditions, 1, 3-cyclooctadiene has given 2-cyclooctenecarboxylate in a low yield.