BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 146—149 (1966)

Organic Syntheses by Means of Noble Metal Compounds. XV. The Carbonylation of 1, 5, 9-Cyclododecatriene Catalyzed by Palladium

By Jiro Tsuji and Tatsuo Nogi

Basic Research Laboratories, Toyo Rayon Company, Kamakura

(Received May 27, 1965)

The carbonylation of 1, 5, 9-cyclododecatriene has been carried out in ethanol in the presence of palladium chloride; mono- and diesters have thus been obtained without ring contraction. It has been observed, by means of a study of the NMR and infrared spectra, that the first attack of carbon monoxide occurred at the trans double bond, giving ethyl cyclododecadienecarboxylate. The second attack of carbon monoxide occurred randomly, giving an isomeric mixture of ethyl cyclododecenedicarboxylate. No triester was obtained even under prolonged carbonylation. The true catalyst has been found to be metallic palladium, and the presence of hydrogen chloride has been found to be essential for the catalysis. The oxidation of ethyl cyclododecadienecarboxylate, followed by esterification, has given ethyl succinate and 1, 3, 6-hexanetricarboxylate. This result indicates that the double bonds of ethyl cyclododecadienecarboxylate remain at the original positions.

We have reported that pallaium chloride or metallic palladium, in the presence of hydrogen chloride, is an active catalyst for the carbonylation of olefins in alcohol, thus forming carboxylic esters.[1] The reaction proceeds quite smoothly under rather mild conditions. The palladium-catalyzed carbonylation reaction was then extended to various allylic compounds[2] and conjugated dienes[3] to form β, γ-unsaturated esters. Furthermore, it was found that 1, 5-cyclooctadiene (1, 5-COD) can be carbonylated smoothly to form mono- or diester, depending on the reaction conditions.[4] The above-mentioned olefinic compounds are known to form π- or π-allylic complexes with palladium chloride,[5] and certainly their carbonylations proceed through the formation of these complexes.

Like 1, 5-COD, 1, 5, 9-cyclododecatriene (1, 5, 9-CDT) can be easily prepared from butadiene by the catalytic action of several transition metal complexes. However, unlike 1, 5-COD, which is known to form a stable palladium chloride complex, 1, 5, 9-CDT does not easily form a complex with palladium chloride. Only recently it was reported that a complex can be prepared after the prolonged contact of 1, 5, 9-CDT with palladium chloride-benzonitrile complex, but its structure is not yet known.[6] It seems likely that the three double bonds of 1, 5, 9-CDT are not orientated in a way suitable for forming a stable complex with palladium chloride. From these considerations, it seemed worthwhile investigating the carbonylation of 1, 5, 9-CDT by the catalytic action of palladium. The carbonylation of 1, 5, 9-CDT has been reported by Rull,[7] who obtained methyl cyclododecanecarboxylate by the catalytic action of cobalt carbonyl in methanol. In this case, two double bonds were hydrogenated. In addition, the carbonylation of 1, 5, 9-CDT by the catalytic action of Lewis acids to give carboxylic acids is known, but in this case ring contractions due to transannular reaction have occurred, giving a variety of carboxylic acids.[8a,b] In contrast, the carbonylation reaction reported in this paper gives mono- and dicarbonylation products without ring contraction or the reduction of the double bonds.

Experimental

The gas chromatographic analyses were carried out on a Thermol-3 column, 2 m. long, at 220°C. All the boiling points are uncorrected. The molecular weights were determined in benzene by the ebullioscopic method, using a Mechrolab vapor pressure osmometer. The NMR spectra were recorded on a high resolution spectrometer, model DP 60, and the peak positions are expressed in τ values. The infrared spectra were recorded on a Hitachi infrared spectrometer, model EPI-S2.

---

[1] J. Tsuji, M. Morikawa and J. Kiji, *Tetrahedron Letters*, **1963**, 1437.

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

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

[4] J. Tsuji, S. Hosaka, J. Kiji and T. Susuki, This Bulletin, **39**, 141 (1966).

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

[6] E. Kuljian and H. Frye, *Z. Naturforsch.*, **19b**, 651 (1964).

[7] T. Rull, *Bull. soc. chim. France*, **1964**, 2680.

[8] a) K. E. Moller, *Brennstoff Chemie*, **45**, 129 (1964); *Angew. Chem.*, **75**, 1122 (1963). b) M. Genas and T. Rull, *Bull. soc. chim. France*, **1962**, 1837.

Materials. — Commercially-available palladium chloride was used without further purification. *cis, trans, trans*-1, 5, 9-CDT was prepared in the Central Research Laboratories, Toyo Rayon Company, and distilled before use.

The Carbonylation of 1, 5, 9-CDT—The reaction conditions and the amounts of the reactants used are shown in Table I. A typical example of the carbonylation is as follows. One gram of palladium chloride, 20 ml. of ethanol containing a certain amount of hydrogen chloride, and 10 g. of 1, 5, 9-CDT were introduced into a glass vessel with a gas-inlet capillary. The vessel was then set in a stainless steel autoclave (made by Sakashita Seisakusho), and carbon monoxide was introduced (100 kg./cm^2). After the autoclave had been set in an electrical furnace preheated to 100°C, the furnace was shaken. After a certain period of time, the autoclave was quenched in a water bath. The catalyst was removed by filtration, and the solution was distilled. The 1, 5, 9-CDT recovered was collected at 90—95°C/8 mmHg. Ethyl cyclododecadiencarboxylate (140—145°C/5 mmHg) and ethyl cyclododecenedicarboxylate (165—175°C/4 mmHg) were easily separated by fractional distillation.

The presence of four olefinic protons was confirmed by a study of the NMR spectrum of ethyl cyclododecadienecarboxylate (Fig. 1). Also, the monoester was hydrogenated in ethanol in the presence of an Adams platinum catalyst, with the absorption of 2 mol. of hydrogen; it gave ethyl cyclododecanecarboxylate.

Found: C, 74.57; H, 11.60; mol. wt., 240. Calcd. for $C_{15}H_{28}O_2$: C, 74.95; H, 11.74%; mol. wt., 240.

The hydrolysis of ethyl cyclododecanecarboxylate was carried out by refluxing it in a 10% alcoholic potassium hydroxide solution for 5 hr. After the usual work-up, cyclododecanecarboxylic acid was recrystallized from hexane, m. p. 97—98°C (reported m. p. 99.5°C[7]).

Found: C, 73.45; H, 11.39%. Calcd. for $C_{13}H_{24}O_2$: C, 73.53; H, 11.39%.

An NMR spectrum of ethyl cyclododecenedicarboxylate showed the presence of 2 olefinic protons (Fig. 2), and the hydrogenation of the diester consumed 1 mol. of hydrogen. The hydrolysis of the hydrogenated diester with 10% ethanolic potassium hydroxide gave the corresponding solid acid, which did not show a sharp melting point, even after chromatographic purfication.

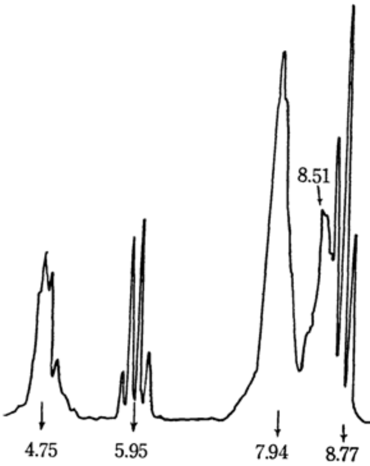


Fig. 1. NMR spectrum of ethyl cyclododecadienecarboxylate.

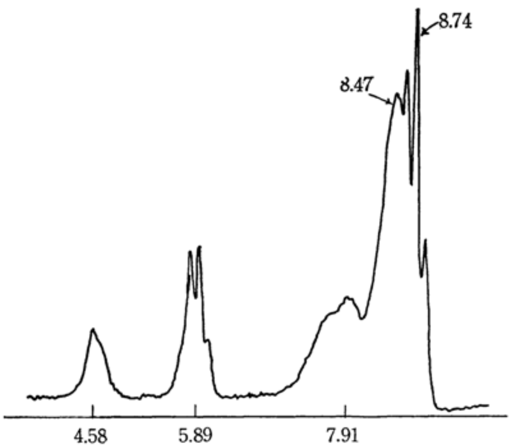


Fig. 2. NMR spectrum of ethyl cyclododecenedicarboxylate.

Found: C, 65.41; H, 9.41. Calcd. for $C_{14}H_{24}O_4$: C, 65.59; H, 9.44%.

The Carbonylation of Cyclododecene.—A mixture of 1 g. of palladium chloride, 20 ml. of ethanol containing hydrogen chloride (7.5%), and 6 g. of cyclododecene was placed in a glass vessel; the reaction was then carried out at 120°C for 20 hr. under a pressure of carbon monoxide (100 kg./cm^2). After the usual work-up, 8.0 g. (93%) of ethyl cyclododecanecarboxylate was obtained by distillation (148—150°C/10 mmHg). The ester was then hydrolyzed to crystalline cyclododecanecarboxylic acid.

The Oxidation of Ethyl Cyclododecadienecarboxylate.—The ester (10 g.) was mixed with 20 ml. of cyclohexane and 20 ml. of water in a 1-l. round-bottomed flask. To the mixture there was then vigorously stirred 250 ml. of a sodium permanganate solution (12.5%) over a 3-hr. period, with the occasional addition of small pieces of dry ice. The oxidation product was then esterified in a manner described before,[4] and distilled. A lower-boiling fraction was confirmed to be ethyl succinate by gas chromatography and infrared spectrum; then it was hydrolyzed to succinic acid, m. p. 186—188°C. A higher-boiling fraction (b. p. ca. 150°C/2 mmHg, mol. wt., 300; yield 4 g.) was identified by infrared and NMR spectra, with the ethyl 1, 3, 6-hexanetricarboxylate obtained from ethyl cyclooctenecarboxylate, and by converting it into ethyl 2-oxocyclopentanepropionate.

Results and Discussion

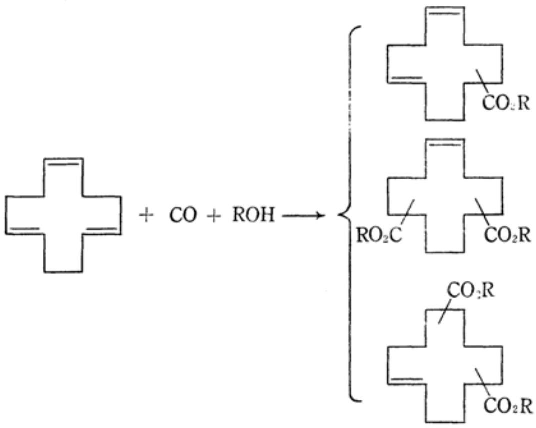
There are three isomers of 1, 5, 9-CDT, namely, cis-trans-trans, cis-cis-trans and trans-trans-trans. In this study, the most easily obtainable cis-trans-trans isomer was used. The carbonylation proceeded smoothly, and mono- and di-carbonylation were observed, giving ethyl cyclododecadienecarboxylate and ethyl cyclododecenedicarboxylate respectively. The presence of, respectively, two and one double bonds in these esters was confirmed clearly by the

TABLE I. CARBONYLATION OF 1,5,9-CDT[a]

Cat.[b]	HCl/EtOH[c] wt.%	Reaction Temp. °C	Reaction Time hr.	CO kg./cm²	Yield, %[d] monoester	Yield, % diester
$PdCl_2$	0	100	24	100	20	0
$PdCl_2$	7.5	100	1	100	54	37
$PdCl_2$	15	100	1	100	50	41
$PdCl_2$	15	30	15	100	0	0
$PdCl_2$	7.5	100	1/3	100	30	0
$PdCl_2$	7.5	100	1/2	100	64	3
$PdCl_2$	7.5	100	10	100	trace	85
$PdCl_2$	7.5	100	5	50	33	45
$PdCl_2$	7.5	100	1	150	60	25
Pd-C	0	100	24	100	0	0
Pd-C	7.5	100	1	100	50	30

a) Amount of 1,5,9-CDT 10 g.
b) Amount of $PdCl_2$ 1 g. Pd-C (10%) 3 g.
c) Volume of ethanol 20 ml.
d) Yield based on 1,5,9-CDT (10 g.).

NMR spectra (Fig. 1 and 2) and hydrogenation, showing that no ring contraction occurs during the carbonylation reaction.



When 1, 5-COD was carbonylated, it was rather easy to control the reaction so that mono- and diester were selectively obtained,[4] because the double bonds of 1, 5-COD behave as a bidentate ligand, forming a stable complex with palladium. Although the trans double bond was attacked first, as will be described later, there was not much difference in the reaction rate between mono- and dicarbonylation, as is shown in Table I, and it seemed likely that the double bonds of 1, 5, 9-CDT behaved almost independently. The only way to obtain the monoester as a main product was to stop the reaction after a comparatively short period. A longer reaction time gave rise to the diester exclusively. The reaction stopped at the dicarbonylation stage and the further carbonylation of the remaining double bond to form a saturated triester was almost impossible. It is supposed that the two ester groups of cyclododecenedicarboxylate inhibit the access of palladium to the remaining double bond, thus making the carbonylation almost impossible. On the other hand, cyclododecene, which has no such steric hindrance, was carbonylated easily to give ethyl cyclododecanecarboxylate.

It is known that there is considerable diffrence in reactivity between the cis and trans double bonds of *cis, trans, trans*-1, 5, 9-CDT.[9] In general, one of the trans double bonds is attacked first. In this carbonylation reaction, as was expected, it was found, by comparing the changes of intensities of the infrared bands at 968 cm⁻¹ (trans) and 707 cm⁻¹ (cis), that the first attack of carbon monoxide occurred at the trans double bond. As is shown in Figs. 3, 4 and 5, the intensity ratio of the cis and trans bonds of 1, 5, 9-CDT is about 1 : 2, while those of the monoester and diester are nearly equal. Therefore, it is apparent that the second attsck is not selective and that both the cis and trans double bonds are randomly attacked.

By mono- and dicarbonylation, considerable numbers of isomers can be formed on the basis

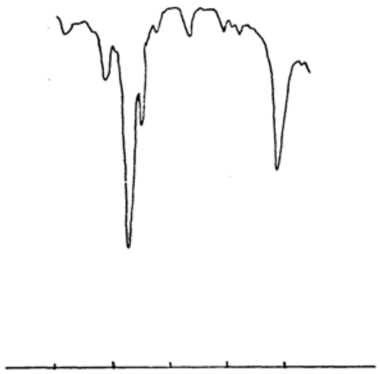


Fig. 3. Infrared spectrum of 1,5,9-cyclododecatriene (in CCl_4).

---

[9] M. Ohno and S. Torimitsu, *Tetrahedron Letters*, **1964**, 2259.

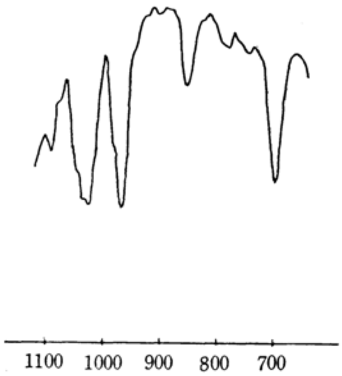


Fig. 4. Infrared spectrum of ethyl cyclododecadienecarboxylate (in CCl_4).

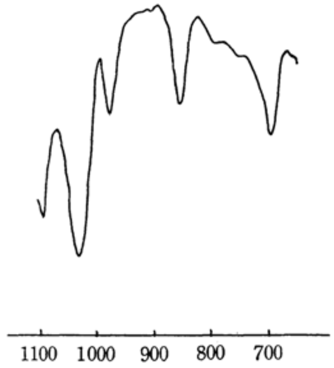
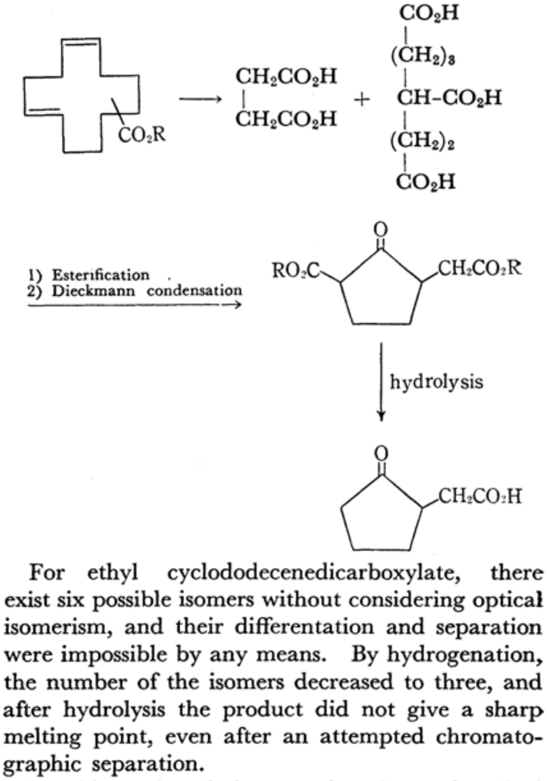


Fig. 5. Infrared spectrum of ethyl cyclododecenedicarboxylate (in CCl_4).

of the relative position of the carbethoxy groups. There are two possible sites of the carbethoxy group in ethyl cyclododecadienecarboxylate relative to the remaning cis and trans double bonds. Actually, two peaks were observed closely by gas chromatography, but it was impossible to separate them by any means. By hydrogenation, a single peak was observed; this was identified with the ethyl cyclododecanecarboxylate obtained by the carbonylation of cyclododecene catalyzed by palladium chloride. The hydrolysis of the hydrogenated ester gave cyclododecanecarboxylic acid as a crystal.

It is known that palladium chloride is an active catalyst for double bonds migration. For example, 1, 5-COD can be isomerized to 1, 3-COD by the action of palladium chloride.[10] In view of this the possibility of the double bond migration after the monocarbonylation was investigated by the oxidation of the monoester with sodium permanganate. When the oxidation product was esterified, the presence of ethyl succinate was detected by gas chromatography. The ester was isolated by distillation. Ethyl 1, 3, 6-hexanetricarboxylate was also isolated. This ester's identity with the ester isolated from the oxidation product of ethyl 4-cyclooctenecarboxylate was confirmed by means of a study of their infrared and NMR spectra. Furthermore, the structure of ethyl 1, 3, 6-hexanetricarboxylate was confirmed by its conversion into ethyl 2-oxocyclopentanepropionate, as has been described in the structural determination of ethyl 4-cyclooctenecarboxylate.[4] Thus, the oxidation studies have confirmed that the double bonds of ethyl cyclododecadienecarboxylate remain at the original positions, at least usually, even in the presence of palladium chloride.



For ethyl cyclododecenedicarboxylate, there exist six possible isomers without considering optical isomerism, and their differentation and separation were impossible by any means. By hydrogenation, the number of the isomers decreased to three, and after hydrolysis the product did not give a sharp melting point, even after an attempted chromatographic separation.

In this carbonylation, as has been described before,[4] metallic palladium and hydrogen chloride are essential for the catalysis. Palladium on carbon alone was inactive. The concentration of hydrogen chloride in the reaction medium has a marked influence on the reaction rate, as can be seen in Table I.

---

[10] Rhono-Poulene, French Pat. 1337889 (1963); *Chem. Abstr.*, **60**, 2802 (1964).