# Organic Syntheses by Means of Noble Metal Compounds. XXV. Palladium-Catalyzed Carbonylation of Ethyl Acetylenemono- and -dicarboxylates[1]

Jiro Tsuji and Tatsuo Nogi

*The Basic Research Laboratories, Toyo Rayon Company, Limited, Kamakura, Japan*

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Carbonylation of ethyl acetylenemonocarboxylate was carried out smoothly at room temperature by the catalytic action of palladium in ethanol; ethyl fumarate, ethyl ethenetricarboxylate, ethyl 1,1,2-ethanetricarboxylate, and ethyl 1,3-butadiene-1,1,4,4-tetracarboxylate were obtained. Under the same reaction conditions, ethyl acetylenedicarboxylate gave rise to ethyl ethenetricarboxylate, ethyl 1,1,2-ethanetricarboxylate, and ethyl 1,1,2,2-ethanetetracarboxylate. The concentration of hydrogen chloride in the reaction medium had a profound effect on the yields of these products.

The nickel, cobalt, and iron carbonyl catalyzed carbonylation of acetylene and its alkyl derivatives to form acids or esters has been studied extensively. However, only one report has been given, by Jones, *et al.*,[2] on the carbonylation of an acetylenic bond activated by a carbonyl group. They studied the carbonylation of 2-heptynoic acid catalyzed by nickel carbonyl and obtained butyl fumarate in 30% yield as the sole product of monocarbonylation. It was also reported that an attempted carbonylation of ethyl acetylenedicarboxylate was unsuccessful and ethyl mellitate was obtained by trimerization instead. It was thus concluded that an alkoxycarbonyl group hinders the carbonylation of a triple bond. No other report on the successful carbonylation of acetylenic esters has appeared.

We have reported that metallic palladium, combined with hydrogen chloride, is an active catalyst for the carbonylation of various olefinic compounds.[3] In addition, acetylenic compounds can also be carbonylated giving products different from those obtained with metal carbonyls. For example, the palladium-catalyzed carbonylation of diphenylacetylene gave rise to α,β-diphenyl-γ-crotono lactone in high yield as the main product.[4] The main characteristic of catalysis by palladium is extensive dicarbonylation rather than monocarbonylation. Concerning the interaction of palladium with acetylenic esters, it was reported by Bryce-Smith[5] that dimethyl acetylenedicarboxylate trimerized easily to give hexamethyl mellitate in 93% yield when refluxed in benzene with a catalytic amount of palladium on carbon, and methyl acetylenemonocarboxylate reacted vigorously with a palladium catalyst to give a yellow polymeric product, showing that metallic palladium and acetylenic esters react easily to form complexes as oligomerization intermediates. In view of the fact that acetylenecarboxylates interact with palladium, the carbonylation of ethyl acetylenemono- and dicarboxylates was undertaken and it was found that mono- and dicarbonylation are possible depending on the reaction conditions. An alkoxycarbonyl group actually facilitates the carbonylation of triple bonds and the reaction proceeds smoothly even at room temperature. The results of this new carbonylation reaction are described in this paper.

## Results and Discussion

We have reported that the carbonylation of olefinic and acetylenic compounds is catalyzed by palladium chloride or metallic palladium in the presence of hydrogen chloride in ethanol. Therefore, the carbonylation of ethyl acetylenemonocarboxylate was attempted in ethanol containing various concentrations of hydrogen chloride. The acetylenic bond is remarkably reactive and the reaction proceeds smoothly at room temperature, to give the products shown in Scheme I.



Scheme I
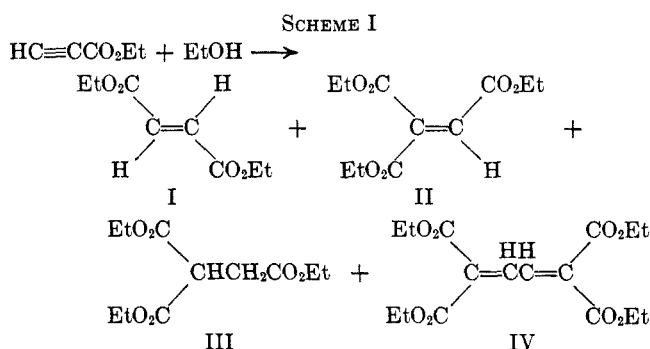
Ethyl fumarate is the product of a simple monocarbonylation reaction. The main reaction seems to be dicarbonylation; ethyl ethenetricarboxylate (II) and 1,1,2-ethanetricarboxylate (III) were obtained as predominant products. In addition, ethyl 1,3-butadiene-1,1,4,4-tetracarboxylate (IV) was obtained as a minor product. The ratio of these products and conversion were affected by the concentration of hydrogen chloride in the reaction medium as shown in Table I. When the conversion was low, a considerable amount of the starting material was recovered.

TABLE I

| Catalyst, g | HC≡CCO₂Et, g | Solvent, ml | I, g (%)[a] | II + III, g (%), ratio | IV, g (%) |
|---|---|---|---|---|---|
| PdCl₂, 1 | 10 | EtOH, 50 | 2.5 (14.3) | 1.5 (6.0), 5:1 | 1.2 (3.4) |
| 10% Pd/C, 2 | 10 | 10% HCl EtOH, 50 | 2.5 (14.3) | 3.0 (12.0), 1:1 | 1.0 (2.8) |
| PdCl₂, 2 | 5 | 10% HCl EtOH, 50 | 1.7 (19.4) | 5.0 (40), 1:4 | 1.7 (9.7) |

[a] The yield was based on ethyl acetylenemonocarboxylate.

A higher concentration of hydrogen chloride tended to give rise to dicarbonylation products, especially III. The same tendency was observed in the carbonylation

(1) Part XXIV: J. Tsuji and T. Nogi, *Tetrahedron Letters*, 1801 (1966).
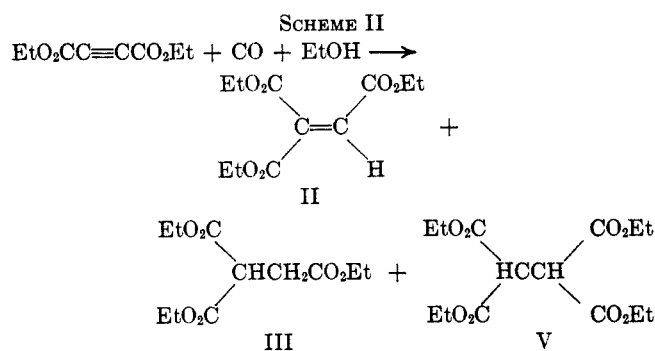(2) E. R. H. Jones, T. Y. Shen, and M. C. Whiting, *J. Chem. Soc.*, **48** (1951).
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of diphenylacetylene. Ethyl 1,3-butadiene-1,1,4,4-tetracarboxylate is a product of dimerization and dicarbonylation and is related to muconic acid. We have reported that muconyl chloride was formed by the carbonylation of acetylene in benzene in the presence of palladium chloride.[6] Thus, it can be said that the concerted reactions of dimerization and dicarbonylation are on a common reaction pathway of carbonylation of acetylenic compounds catalyzed by palladium. Of course, this route competes with the direct carbonylation of acetylene. It seems likely that the dicarbonylation products II and III are obtained by the concerted *cis* attack of carbon monoxide at the triple bond. The possibility that the further carbonylation of monocarbonylated product gives dicarbonylated products is unlikely, because the attempted carbonylation of ethyl fumarate under the same reaction conditions did not proceed and the starting material was recovered. Thus the carbonylation of ethyl acetylenemonocarboxylate consists of three competing reactions: namely, (1) monocarbonylation, (2) dicarbonylation by the concerted *cis* addition of carbon monoxide, and (3) the dimerization of the starting acetylenic ester followed by dicarbonylation.

The carbonylation of ethyl acetylenedicarboxylate was carried out in the presence of palladium catalyst and hydrogen chloride; the reactions in Scheme II were observed. Again, mono- and dicarbonylation products were obtained at room temperature. In this reaction too, the concentration of hydrogen chloride had a profound effect on the reaction; a higher concentration gave rise to higher yields of dicarbonylation products as shown in Table II.

SCHEME II



TABLE II

| Catalyst, g | $EtO_2CC{\equiv}CCO_2Et$, g (recovery, g) | Solvent, ml | II + III, g (%),[a] ratio | V, g (%) |
|---|---|---|---|---|
| PdCl₂, 1 | 5 (0.9) | EtOH, 50 | 2.5 (42.5), 1:2 | 0.5 (6.5) |
| PdCl₂, 2 | 5 (0.7) | 10% HCl, EtOH, 50 | 1.5 (III) (24.3) | 4.1 (51) |

[a] The yield was based on ethyl acetylenedicarboxylate consumed.

In these carbonylation reactions, both saturated and unsaturated esters were obtained. We have observed that palladium-catalyzed carbonylation of acetylene in ethanol gave rise to ethyl fumarate and ethyl maleate,

and no succinate was obtained.[7] In the present case, both saturated and unsaturated esters were obtained. It is apparent from the tables that a higher concentration of hydrogen chloride tends to increase the ratio of the saturated esters. However, no reasonable explanation can be given for the effect of the concentration of hydrogen chloride on the courses of the reaction to give the saturated and unsaturated esters and mono- and dicarbonylation products without evidence.

In this carbonylation reaction, no trimerization of acetylenic bonds to form a benzene derivative was observed. This is rather surprising in view of the fact that the trimerization of acetylenic esters goes easily in the presence of palladium catalysts.[5] The presence of carbon monoxide in the reaction medium strongly inhibits the coordination of the triple bond necessary for the trimerization. This suggests that a palladium–carbonyl complex which is active for carbonylation and dimerization, but not active enough for trimerization and oligomerization, is formed. Although true catalytic species in the reaction medium is not known, this is another example of the strong and efficient catalytic action of the palladium–hydrogen chloride system. The simple reaction procedure enhances the synthetic utility for the preparation of polycarboxylates.

## Experimental Section

The nmr spectra were determined on Varian high resolution spectrometer Models DP-60 and HR-100 using tetramethylsilane as an internal standard. The molecular weights were determined in benzene using a Mechrolab vapor pressure osmometer.

**Carbonylation of Ethyl Acetylenemonocarboxylate.**—The amount of materials used and the yields of the products are shown in the tables. Monoester (10 g) and palladium chloride (1 g) were mixed in 50 ml of ethanol and the mixture was placed in a glass vessel equipped with a gas-inlet capillary. The glass vessel was placed in a 300-ml autoclave. The reaction was carried out at room temperature for 18 hr under carbon monoxide pressure (100 kg/cm²) with constant shaking. After reaction, the mixture was diluted with a large amount of water and the solution was extracted with ether. After the usual work-up, the reaction product was subjected to distillation, giving the following products: the starting material, ethyl fumarate, 100–110° (30 mm), and a mixture of ethyl ethenetricarboxylate and ethanetricarboxylate which was separated by preparative gas chromatography, 90–105° (2 mm), and ethyl 1,3-butadiene-1,1,4,4-tetracarboxylate, 150–170° (2 mm). The structures of these products were determined in the following way.

Ethyl 1,1,2-ethanetricarboxylate was identified by infrared and nmr spectra ($\tau$ 5.78, 5.82, and 8.72 due to ethyl protons, 6.69 triplet due to CH, and 7.18 doublet due to CH₂) and compared with an authentic sample prepared by a known method.[8] The correct analysis and molecular weight were obtained.

For ethyl ethenetricarboxylate, a reasonable nmr spectrum was observed which showed two peaks at $\tau$ 8.86 and 5.69 due to ethyl protons and a singlet a 3.26 due to CH. Hydrogenation in the presence of palladium on carbon in ethanol produced ethyl ethanetricarboxylate.

Ethyl 1,3-butadiene-1,1,4,4-tetracarboxylate had mp 54° (lit.[9] mp 56°); infrared spectrum, 1725 and 1600 cm⁻¹; nmr spectrum, $\tau$ 8.64 and 5.69 due to ethyl protons, 2.53 singlet due to two diene protons; ultraviolet spectrum, $\lambda_{max}^{MeOH}$ 275 m$\mu$ ($\epsilon$ 50,400).

*Anal.* Calcd for $C_{16}H_{22}O_8$: C, 56.13; H, 6.48; mol wt, 342. Found: C, 56.12; H, 12; 6.44; mol wt, 335.

**Carbonylation of Ethyl Acetylenedicarboxylate.**—The diester (5 g), ethanol (50 ml), and palladium chloride (1 g) were allowed to react in the same way as shown above. After the usual

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work-up, the ether was evaporated. The residue on standing, at room temperature for 2 days, crystallized as ethyl ethanetetracarboxylate and was collected by filtration. Recrystallization was from hexane. The filtrate was subjected to distillation and separated into the following fractions; starting material and a mixture of ethene- and ethanetricarboxylates. Ethyl ethanetetracarboxylate was identified with an authentic sample by infrared and nmr spectra; the sample was prepared by the condensation of 2 moles of ethyl malonate. The identity was confirmed by a mixture melting point determination (75°).

# The Pyrolysis of Unsolvated Alkyllithium Compounds

WILLIAM H. GLAZE, JACOB LIN, AND E. G. FELTON[1]

*Department of Chemistry, North Texas State University, Denton, Texas 76203*

The rates of thermal decomposition of unsolvated ethyl-, n-butyl-, isopropyl-, and sec-butyllithium have been investigated at several temperatures in the range 82–130°. The rate constants for olefin product formation, obtained manometrically, indicate the following order of stability: ethyl ∼ n-butyl > isopropyl > sec-butyl. Activation parameters in each case are ca. 25 kcal ($\Delta H^*$) and $-10$ to $-16$ cal deg$^{-1}$ ($\Delta S^*$). The factors which distinguish the system from the decomposition in hydrocarbon solution are discussed.

Finnegan and Kutta[2] have reported recently on the thermal decomposition of n-butyllithium in decane solution in the temperature range 130–150°. The reaction is catalyzed by lithium n-butoxide and exhibits a hydrogen isotope effect consistent with the postulated cis-elimination mechanism. In this paper we would like to report the results of a similar study of the thermal decomposition of some alkyllithium compounds in the pure, liquid state. An unusual feature of the reaction under such conditions, reported earlier,[3] is the rather high percentage of cis-2-butene obtained from the pyrolysis of pure sec-butyllithium. This and other aspects of the pyrolysis in the undiluted state will be discussed in the following sections.

## Experimental Section

**Reagents.**—Alkyl halides were used as purchased or after distillation. In any case they were shown to be >99% pure by vapor–liquid partition chromatography. Lithium metal was enriched with 1% sodium (Lithium Corporation of America).

**Preparation, Purification, and Pyrolysis of Alkyllithiums.**—The same procedure was used as reported previously.[3] Alkyl chlorides were used for the preparations except for ethyl bromide. In most cases the alkyllithium solutions were filtered in the drybox and concentrated to thick syrupy liquids by removal of the pentane solvent. Ethyllithium was extracted from the reaction mixture with benzene and recrystallized by partial removal of the solvent in the drybox. The material was purified by distillation into U-tubes at ca. 90° and 50 μ as were each of the other alkyllithiums prior to decomposition.[3] The oil bath used for heating the pyrolysis tubes was regulated to ±0.05°. Decomposition rates were followed by observing the increase in vacuum-line pressure with a cathetometer to ±0.05 mm. Products were analyzed by vapor–liquid partition chromatography as before,[3] except for the pyrolysis products of ethyllithium, for which a silica gel column at 165° was employed. Infrared spectra confirmed the gas analyses.

The relative percentages of butene isomers from the decomposition of sec-butyllithium (neat) were invariant during a single run. This was established by sampling and analyzing the product gases in one run at several times after initiation of the decomposition.

## Results and Discussion

**Products.**—The pyrolytic elimination of lithium hydride from alkyllithium compounds such as n-butyl-, ethyl-, and isopropyllithium is apparently a nonfree-radical process[2,4] in which the olefinic product is contaminated only if the reaction is carried out under conditions in which the partial pressure of olefin is large. In that case, metallation of the olefin may occur followed by other complicating reactions resulting in a variety of products.[4a] Under the conditions employed, we find that the gaseous product consists of no less than 98% of the olefin to be expected from simple β elimination of lithium hydride. In the case of sec-butyllithium, the three expected olefins are found, and the distributions are shown in Table I. Until recently,

TABLE I

PRODUCT DISTRIBUTIONS FROM THE PYROLYSIS OF sec-BUTYLLITHIUM (NEAT)[a]

| Temp, °C | Distribution, % | | |
| --- | --- | --- | --- |
| | 1-Butene | cis-2-Butene | trans-2-Butene |
| 78.4 | 34 | 51 | 15 |
| 87.0 | 32 | 53 | 15 |
| 104.0 | 29 | 54 | 17 |

[a] <1% n-butane was observed in each case.

these data represented the only example of an elimination reaction in which the thermodynamically less favored cis-2-butene predominates. More recently, Brown and Klimisch[5] have reported that the E2 elimination of alkyl tosylates in t-butyl alcohol may yield predominately cis-2 olefin if the attacking base is sufficiently bulky, e.g., potassium t-butoxide.

The unusually high yield of cis-2-butene from the pyrolysis of sec-butyllithium may also be explained by a consideration of the steric factors associated with alkyllithium compounds. It is now well known that these species are found only in aggregates, usually tetramers or hexamers. The structures of ethyllithium[6] and methyllithium[7] have recently been determined by X-ray diffraction, and both consist of tetramers. Other workers have shown that t-butyllithium is tetrameric,[8] while ethyllithium[9] and n-butyllithium[10]

(1) National Science Foundation Research Participant, 1963–1964.

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