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Organic Syntheses by Means of Noble Metal Compounds. XLIX.[1] Oxidation of 3-Hexenedioate to 2,4-Hexadienedioate Catalyzed by Palladium Chloride and Copper(II) Chloride

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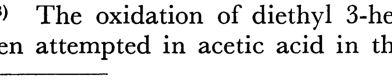
Divalent palladium is a unique oxidizing agent and it can abstract hydrogen from various organic compounds.[2] This is exemplified in the nucleophilic substitution of olefins and coupling of aromatic compounds in its presence. This led us to investigate the possibility of liquid phase oxidative dehydrogenation of carbonyl compounds to α,β-unsaturated compounds as shown below.



$$\underset{\underset{\mathrm{O}}{\|}}{-\mathrm{C}}-\mathrm{CH_2CH_2}- \longrightarrow \underset{\underset{\mathrm{O}}{\|}}{-\mathrm{C}}-\mathrm{CH{=}CH}-$$

An attempted oxidation of cyclohexanone with palladium chloride in acetic acid gave phenol, probably formed through cyclohexenone, but it was impossible to stop the reaction at the stage of cyclohexenone formation.[3] The oxidation of diethyl 3-hexenedioate (I) was then attempted in acetic acid in the presence of sodium acetate. As expected, the ester was dehydrogenated smoothly to give 2,4-hexadienedioate(II) (diethyl *trans,trans*-muconate) in 78% yield.

$$\underset{\mathrm{I}}{\mathrm{EtO_2C{-}CH_2CH{=}CHCH_2{-}CO_2Et}}$$

$$\longrightarrow \underset{\mathrm{II}}{\mathrm{EtO_2C{-}CH{=}CH{-}CH{=}CH{-}CO_2Et}}$$

As is often the case in the oxidation reaction with divalent palladium, addition of cupric chloride made the reaction catalytic with regard to palladium chloride.

The reaction can be explained in the following way. At first, the acidic α hydrogen of I is abstracted with the base to give anion, which attacks palladium chloride to form μ-dichlorobis(1-carbethoxy-3-carbethoxymethyl-π-allyl)dipalladium(III). The formation of π-allylic complexes from β,γ-unsaturated esters is a known reaction.[5] The acidic hydrogen α to the ester group in the complex III is then abstracted, followed by reductive elimination of palladium to give rise to II. Reoxidation of the reduced palladium with cupric

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[1] Part XLVIII. J. Tsuji, M. Hara, and Y. Mori,, *Tetrahedron*, **28**, 3721 (1972).

[2] J. Tsuji, *Accounts Chem. Res.*, **2**, 144 (1969).

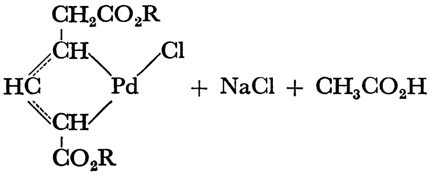
[3] Selective oxidation of cyclohexanone and other ketones to α,β-unsaturated ketones using bis(triphenylphosphine)dichloropalladium was recently reported.[4]

[4] R. J. Theissen, *J. Org. Chem.*, **36**, 752 (1971).

[5] J. Tsuji and S. Imamura, This Bulletin, **40**, 197 (1967).

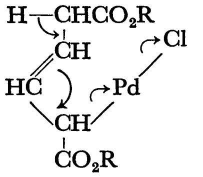
chloride makes the reaction a catalytic cycle with palladium. As an evidence of this mechanism, complex III was isolated when a part of the reaction mixture was taken out during the course of reaction.

$\mathrm{I} + PdCl_2 + CH_3CO_2Na \longrightarrow$



III

$\mathrm{III} + CH_3CO_2Na \longrightarrow$



$\longrightarrow \mathrm{II} + Pd + NaCl + CH_3CO_2H$

$Pd + 2CuCl_2 \longrightarrow PdCl_2 + 2CuCl$

The reaction is another example of the unique oxidation catalyzed by palladium chloride. It is feasible because of two properties of divalent palladium, π-allylic complex formation from β,γ-unsaturated esters and abstraction of active hydrogens.

Experimental

A mixture of palladium chloride (3.6 g, 0.02 mol), sodium acetate (6.0 g), ethyl 3-hexenedioate (8.0 g, 0.04 mol) in acetic acid (60 ml) was stirred at 70° for 50 min, during which period metallic palladium precipitated gradually. After filtration, the solution was diluted with water and extracted with ether. Distillation of the ethereal solution gave an oily mixture (7.0 g, 125—130°C/6 mm) which partly crystal lized on cooling. Filtration and recrystallization from *n*-hexane gave crystals (3.1 g, 78%) which proved to be diethyl *trans*, *trans*-muconate, and were identified by their IR and NMR spectra and mixed mp determination (60—61°C) with an authentic sample.

Catalytic process was carried out in the following way. Diethyl 3-hexenedioate (10 g) was heated with a mixture of palladium chloride (1.8 g), cupric chloride (13 g) and sodium acetate (6 g) in acetic acid (60 ml) at 80° for 7 hr stirring. After the usual work-up, an oily distillate was isolated (8.5 g, 110—120°C/6 mm). Gas chromatographic analysis showed that the distillate contained 6.4 g of ethyl muconate.