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DICHLOROBIS(ORGANONITRILE)PALLADIUM(II) CATALYSIS OF CIS- TO TRANS- ISOMERIZATION OF ETHYLCHRYSANTHEMATE AND CHRYSANTHEMIC ACID

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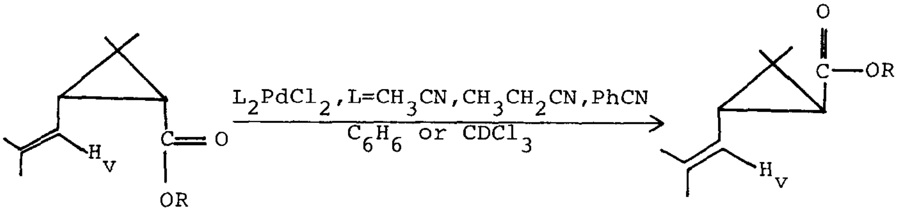
Summary: Complexes of the type L_2PdCl_2 (L = CH_3CN, CH_3CH_2CN, PhCN) in benzene or chloroform act as homogeneous catalysts in the room temperature cis to trans isomerization of ethylchrysanthemate and chrysanthemic acid.

The trans-isomer of chrysanthemic acid (**2b**) is an important structural unit in the pyrethrin insecticides. The pyrethrins are a class of natural (and synthetic) insecticides,[1,2] many of which are esters of cis and trans chrysanthemic acids. These insecticides are noted for their rapid action and low toxicity to mammals. Although the trans arrangement of the vinyl and ester groups (e.g. **2**) is observed in the natural pyrethrins, both synthetic cis and trans pyrethrin analogues have also been found to have insecticidal activity.[3] In general the synthetic materials are cis/trans mixtures.[4] If one of the mixed isomers is more active than the other, it would be desirable to have at hand efficient interconversion methodology. Base catalyzed,[5] thermal,[6] and light[7] promoted interconversions of chrysanthemic acid esters have been reported. We now report isomerizations homogeneously catalyzed by complexes of palladium(II) (eq. 1).

Esters **1a** and **2a** were separated by gas chromatography (QF 1, 30% on Chromosorb P, 10'x3/8", column temperature 120-150° C) or by high pressure liquid chromatography (silica column, hexane eluent). The **1a** → **2a** conversion was observed with commercial **1a**/**2a** mixture and with pure **1a** separated as above. The reaction was monitored by observation of the disappearance of the ^1H nmr



(1)

1

a) R=CH_3CH_2

b) R=H

2

a) R=$CH_3CH_2^-$

b) R=H

resonance of H_v in **1a** (5.4δ in $CDCl_3$) and the appearance of the H_v resonance of **2a** (4.9δ in $CDCl_3$).[4d] At low concentrations of $(PhCN)_2PdCl_2$, only partial **1a** → **2a** isomerization is observed over a period of several hours. Thus, the reaction in $CDCl_3$ of **1a** (0.077 M) with $(PhCN)_2PdCl_2$ (0.01 M) essentially stopped after 15.5 h, at which time 87% of **1a** was converted to **2a** (in this experiment, there was 35% conversion within the first five minutes, and the final turnover number was 6.7). Experiments with lower concentrations of L_2PdCl_2 catalysts resulted in correspondingly lower turnovers. Addition of more L_2PdCl_2 to the stopped reactions resulted in additional **1a** → **2a** conversion. The use of equimolar concentrations of $(PhCN)_2PdCl_2$ and **1a** (0.077 M) resulted in complete conversion to **2a** within 25 minutes. Ester **2a** does not appear to complex Pd(II) in this system, as there is no change in the vinyl proton resonance in the ^1H nmr (by comparison with **2a** in the absence of $(PhCN)_2PdCl_2$) and, in addition, $(PhCN)_2PdCl_2$ precipitates on treatment of the solution with hexane at a -30°C. After 24 h the solution which was originally 0.077 M in both $(PhCN)_2PdCl_2$ and **1a** is partially converted to new and yet uncharacterized products (presumably from reaction of **2a** formed from **1a** with Pd(II) species).

The cis → trans isomerization is not limited to ethyl chrysanthemate. We have also observed analogous isomerization with chrysanthemic acid, **1b**. The acid reaction was monitored by observation of the disappearance of the ^1H nmr resonance of H_v in **1b** (5.4δ in $CDCl_3$) and the appearance of the H_v resonance of **2b** (4.9δ in $CDCl_3$).[10] The reaction of **1b** (0.060 M) with $(PhCN)_2PdCl_2$ (0.0091 M) in $CDCl_3$ resulted in complete conversion of **1b** → **2b** in 5.5 h. The turnover number was 6.8. At lower concentrations of $(PhCN)_2PdCl_2$, only partial **1b** → **2b** isomerization is observed over a period of several hours. Addition of more L_2PdCl_2 to the stopped reactions results in additional **1b** → **2b** conversion. The use of equimolar concentrations of $(PhCN)_2PdCl_2$ (.35 M) and **1b** (.35 M) results in complete conversion to **2b** within 25 minutes. Unlike the ester reaction, the product **2b** is partially further converted to new and yet uncharacterized products. Between 0° and 11°C however, the **1b** → **2b** conversion is clean and stops at **2b**.

We are now studying the disadvantageous "stopping" of the reactions after only a few turnovers when either **1a** or **1b** is in excess. We believe that precipitation of $PdCl_2$ during the reaction may be the cause of loss of activity In separate experiments we find that solid $PdCl_2$ has no effect on solutions of **1a**.

The mild conditions employed in the palladium catalyzed isomerizations contrast with the high temperature base catalysis approach (190°C),[5] with the acid chloride[11] thermolysis (150°C), and with the thermal[6] reactions at 240-260°C. The novelty of the rearrangements reported here is highlighted by earlier studies of vinylcyclopropanes and their reactions with chloropalladium complexes. The earlier workers[12,13] reported chloropalladation of various vinylcyclopropanes, with cyclopropane ring opening and formation of π-allylic palladium complexes.

We shall defer comment on the mechanism of these interesting reactions until our stereochemical studies with optically active materials are completed.[14]

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