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Preliminary communication

PALLADIUM-CATALYSED SYNTHESIS OF THE CINNAMIC METHYL ESTER FROM STYRENE, CARBON MONOXIDE AND METHANOL

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Summary

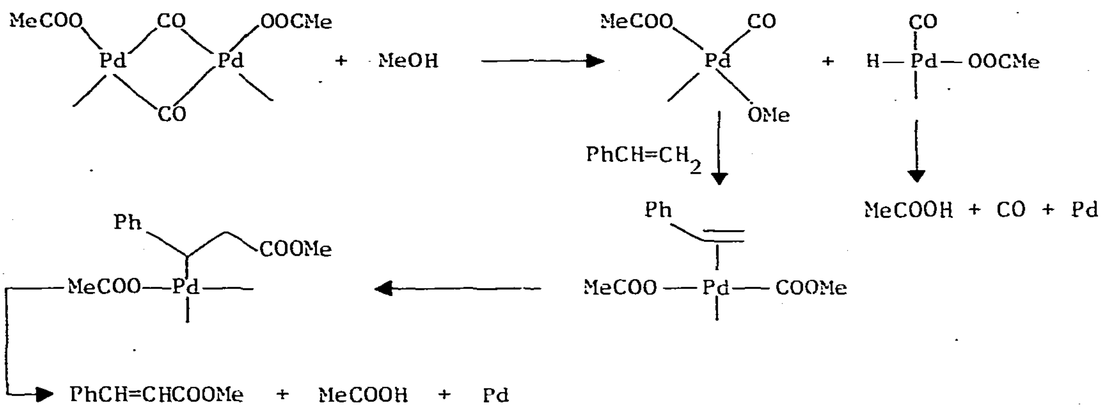
Methyl cinnamate, together with dimethyl phenylsuccinate, is obtained from carbomethoxylation of styrene catalysed by a palladium salt, coupled with a copper(II) reoxidizing system and an alkali metal salt, at room temperature and lower than atmospheric pressures of carbon monoxide.

Methyl cinnamate has previously been obtained from carbomethoxylation of styrene with palladium complexes only as by-product in less than stoichiometric amount [1,2], dimethyl phenylsuccinate being the preferred product. In spite of the availability of many palladium-based catalytic systems for carbomethoxylation [1—5] none of them gave satisfactory results for methyl cinnamate.

Recently Moiseev et al. reported a tetrameric palladium complex: $[Pd(CO)(OCOMe)]_4 \cdot 2MeCOOH$, which decomposed in methanol to give dimethyl carbonate [6]. We now have observed that when the same cluster is dissolved in styrene under a carbon monoxide atmosphere and methanol is added dropwise at 28°C, the main product is methyl cinnamate. We interpret this in terms of an attack of methanol at one of the two dimeric units composing Moiseev's cluster (non-reactive ligands are omitted) (Scheme 1).

Oxidative addition of an alcohol across a metal—metal bond has been recently described by Cotton [7]. An intermediate containing both carbomethoxy and acetato groups coordinated to palladium was trapped with triphenylphosphine [8]. After styrene insertion a proton is transferred to the acetato group and methyl cinnamate is formed.

In the attempt to convert this reaction into a catalytic process we added MeO—Cu—Cl as reoxidant and found that 4—5 mol of methyl cinnamate was formed before palladium black separated out. To utilize the palladium carbonyl system in methanolic solution we used palladium acetate (or palladium chloride



SCHEME 1

and sodium acetate) with a large excess of MeO—Cu—Cl, but this time the main product was dimethyl phenylsuccinate. When copper chloride/sodium acetate was used in methanol as a steady source of MeO—Cu—Cl, however, we observed an increase of the proportion of methyl cinnamate to ca. 50%. Further improvement was obtained by adding a salt such as magnesium chloride or lithium chloride, which prevented separation of palladium black, probably by stabilizing an anionic palladium species. At the same time the solubility of carbon monoxide is lowered by salting out; this favours hydrogen abstraction from the coordinated precursor of methyl cinnamate rather than the carbon monoxide addition which leads to dimethyl phenylsuccinate. When a carbon monoxide/nitrogen mixture, containing only 20% of carbon monoxide, was used, the selectivity in cinnamic ester approached 80% (methyl 3-methoxy-3-phenylpropionate, dimethyl phenylsuccinate and traces of other products were also formed). More than 100 molecules of methyl cinnamate could be formed per molecule of palladium complex [9] even though the reaction conditions were not optimized. The procedure was also applied to substituted styrenes to yield the corresponding cinnamates. If higher pressures of carbon monoxide are used, dimethyl phenylsuccinate can also be synthesized with a high turn over.

Experimental

Palladium chloride (0.1 g, 0.56 mmol), styrene (10.40 g, 100 mmol), anhydrous copper chloride (13.44 g, 100 mmol), sodium acetate (8.21 g, 100 mmol) and magnesium chloride (5 g, 52 mmol) were dissolved in methanol (100 ml) under nitrogen. A 20/80 mixture of CO and N_2 (0.6 l/h) was passed through at 28°C for 24 h. Saponification with sodium hydroxide solution and extraction with ether after acidification gave an acid portion (8 g) containing (GLC) cinnamic acid (6.05 g, 37.2 mmol), 3-methoxy-3-phenylpropionic acid (1.4 g, 7.23 mmol), and phenylsuccinic acid (0.54 g, 2.4 mmol). The neutral portion consisted of styrene, with traces of acetophenone and 1,1-dimethoxy-2-phenylethane. If new $CuCl_2$ (100 mmol), sodium acetate (100 mmol), and styrene (5 g, 48 mmol) were added to the reaction mixture after the first 24 h and reaction was allowed to proceed a further 24 h, the cinnamic acid obtained by saponification as above corresponded to 104 mol per mol of Pd complex.

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