

Preliminary communication

SYNTHESIS OF ARYL ESTERS FROM OLEFINS AND PHENOLS VIA PALLADIUM CARBONYL CHLORIDE

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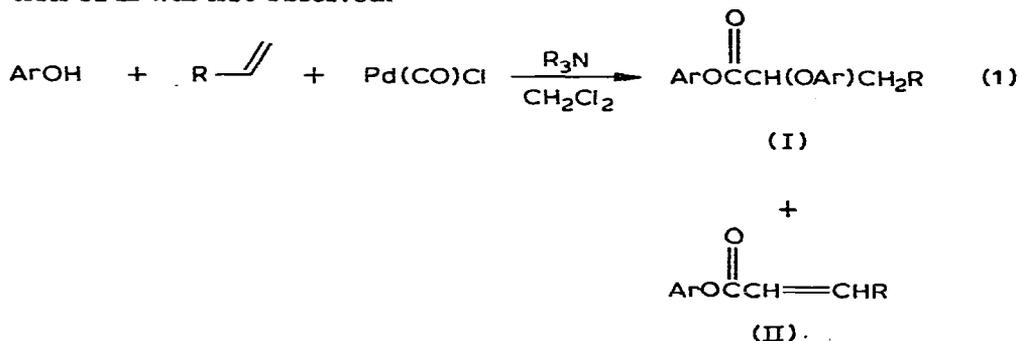
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Summary

The carboarylation of monosubstituted 1-olefins with 2,6-dichlorophenol, carbon monoxide, and palladium carbonyl chloride in the presence of a tertiary amine is described. In most cases, high yields of the unsaturated aryl esters were obtained.

Recently, the synthesis of methyl cinnamate from carbon monoxide, methanol, and styrene in the presence of a palladium(I) compound was reported by Cometti and Chiusoli [1]. Only small amounts of dimethyl phenylsuccinate were obtained in sharp contrast to previous efforts which resulted in phenylsuccinates as the major products [2, 3]. Similarly, we have observed that treatment of substituted 1-alkenes with palladium carbonyl chloride and 2,6-dichlorophenol* in the presence of a tertiary amine resulted in the formation of the esters I and II in high yield (Equation 1). Further reaction of II was not observed.

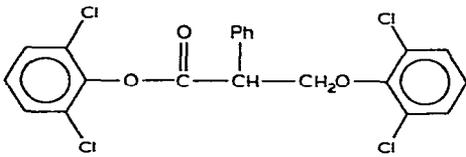
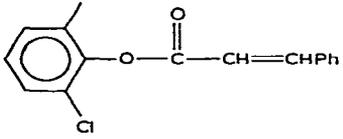
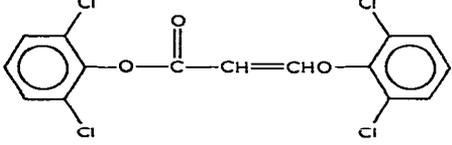
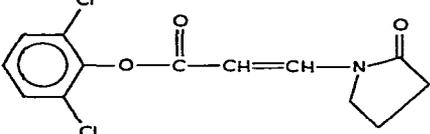
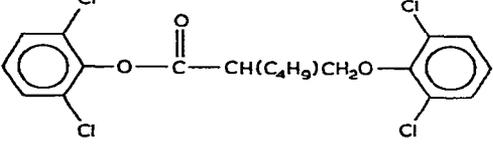


*Although other phenols could be employed, replacement of 2,6-dichlorophenol by phenol resulted in a mixture of products; both the expected olefin carbonylation and diphenyl carbonate were observed, for example, *N*-vinylpyrrolidone acrylate (V, R = pyrrolidone, 76%), diphenyl carbonate (7%). Carbonates derived from 2,6-dichlorophenol were not observed (see also ref. 4).

Reactions were generally performed employing 1.0 equiv of freshly prepared palladium carbonyl chloride, 5.0 equiv of olefin, and 4.0 equiv of 1,2,2,6,6-pentamethylpiperidine in methylene chloride or benzene solution. The reactions were allowed to proceed at room temperature under a carbon monoxide atmosphere for two hours, filtered, then the products were isolated by column chromatography (silica gel : hexane/CH₂Cl₂ eluent) and characterized by IR, NMR, mass spectrometry and combustion analysis.*

A variety of functional olefins were found to undergo reaction under these conditions (Table 1). Products derived from carbonylation at both the terminal carbon and the internal carbon were observed. In the absence of a strongly electron donating substituent, carbonylation occurred preferentially at the substituted carbon. This regioselectivity has been noted previously [5]. When strongly electron donating substituents were present, carbonylation occurred at the terminal carbon, followed by elimination of dichlorophenol to form the un-

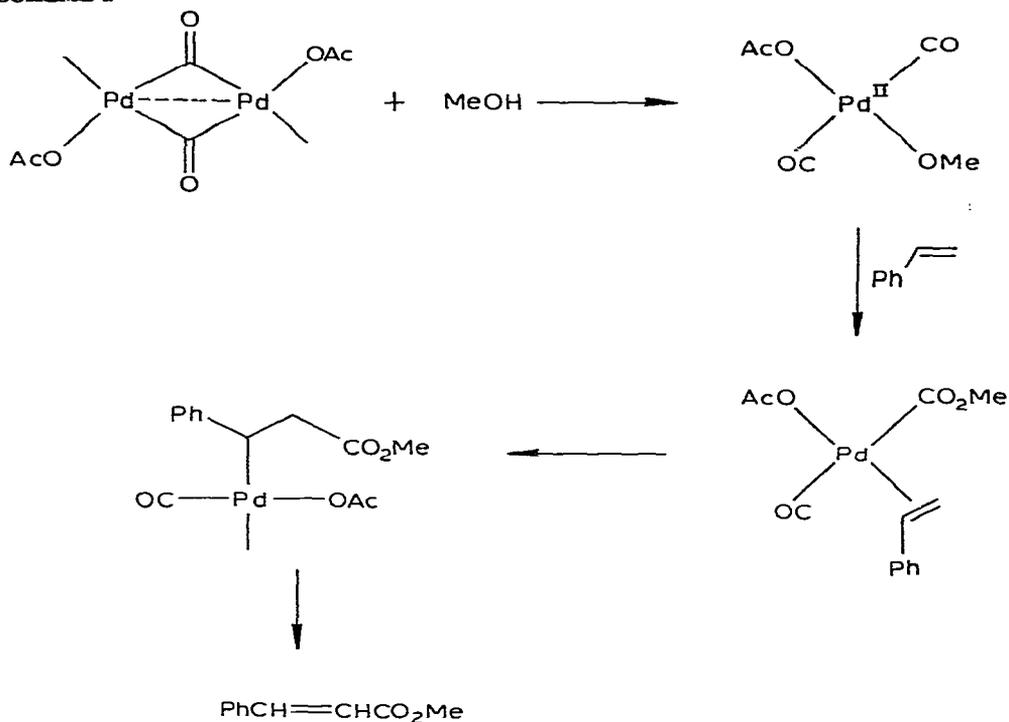
TABLE 1
PREPARATION OF ARYL ESTERS

Olefin	Ester	% Yield ^a
styrene		18
		69
vinyl acetate		65
N-vinylpyrrolidone		85
1-hexene		90

^aYield based on Pd(CO)Cl.

*Satisfactory combustion analyses (C, H \pm 0.4% and N, Cl where applicable) were obtained for all products.

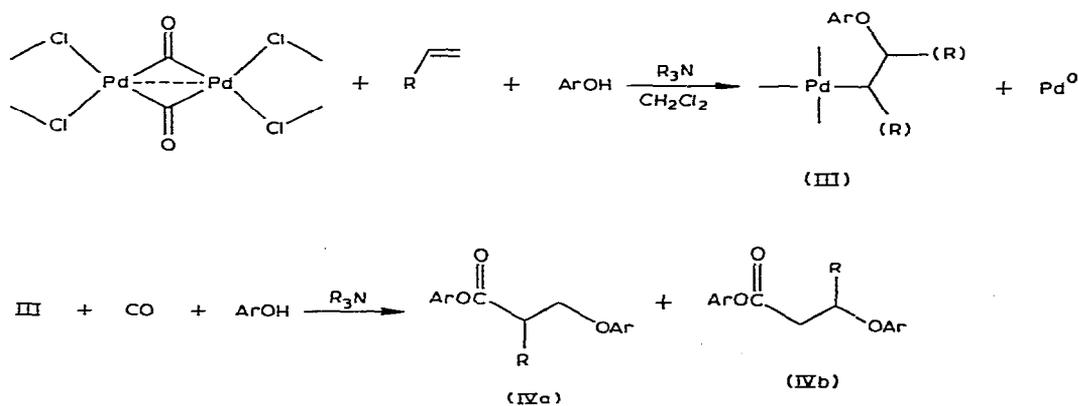
SCHEME 1

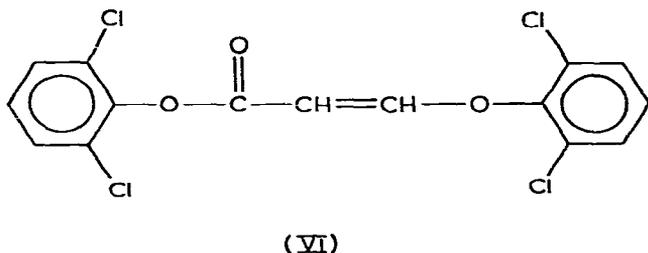
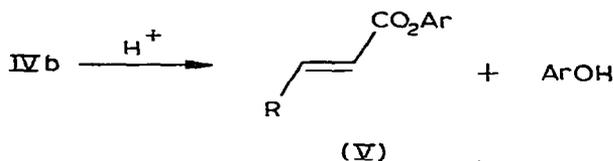


saturated ester. Electron deficient olefins failed to react under these conditions, explaining, in part, the absence of phenyl succinate esters in the preparation of the aryl cinnamate.

Extension of the above procedure to internal olefins or geminal disubstituted olefins was unsuccessful. Cyclohexene, 3-hexene, α -methylstyrene, and even methyl acrylate failed to react and the olefin could be recovered unchanged.

The reaction scheme for the carboarylation of olefins with palladium carbonyl chloride is not known. For the carbomethoxylation of styrene Cometti and Chiusoli favor an attack of methanol on palladium carbonyl acetate to form a palladium(II) methoxide and palladium metal followed by carbonyl insertion, then the addition of styrene (Scheme 1).





Although a similar scheme may be operative in our case also (phenol in place of methanol), we favor a disproportionation of the palladium(I) species followed by an oxypalladium reaction to form a β -phenoxy-alkylpalladium intermediate, III, followed by a sequence similar to that proposed by Tsuji [6] to form the substituted esters, IV.

Elimination of the phenol from IVb catalyzed by the amine hydrochloride generated during the course of the reaction would result in the formation of the observed *Z*-isomer, V. In the case where R = AcO, elimination of acetic acid occurred resulting in the formation of the β -phenoxyacrylate, VI.

Experimental

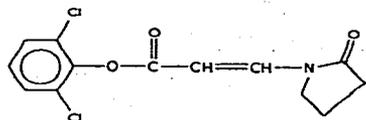
Reactions were run under an atmosphere of either nitrogen or carbon monoxide. Diisopropylethylamine (Aldrich), 2,6-dichlorophenol (Aldrich), styrene (Aldrich), *N*-vinylpyrrolidone (Aldrich), vinyl acetate (Eastman), 1-hexene (Phillips), 3-hexene (Phillips), α -methylstyrene (Aldrich), cyclohexene (Eastman), and methyl acrylate (Rohm and Haas) were distilled prior to use. Palladium carbonyl chloride [7] and 1,2,2,6,6-pentamethylpiperidine [8] were prepared by literature procedures.

All compounds gave satisfactory combustion analyses ($\pm 0.4\%$ for C, H, N) and were identified by IR, NMR, and mass spectrometry data and by hydrolysis and comparison of the free acids with authentic samples.

General procedure for carbonylation

A 25 ml three-neck flask equipped with a spin bar, a subsurface carbon monoxide inlet and an exit tube was charged with 0.34 g (2.0 mmol) of palladium carbonyl chloride, 0.33 g (2.0 mmol) of 2,6-dichlorophenol, 1.1 g (10.0 mmol) of *N*-vinylpyrrolidone and 10 ml of methylene chloride. Carbon monoxide was bubbled through the stirred mixture and 0.52 g (4.0 mmol) of diisopropylethyl amine added. After four hours, the mixture was analyzed by

HPLC to indicate the presence of 0.25 g (85%) of



isolated by column chromatography and characterized by IR, NMR, and mass spectrometry.

Acknowledgments

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