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A REGIOSPECIFIC BENZOYLATION OF ALKYL VINYL ETHERS CATALYSED BY PALLADIUM

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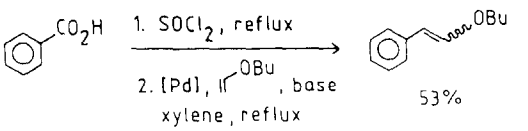
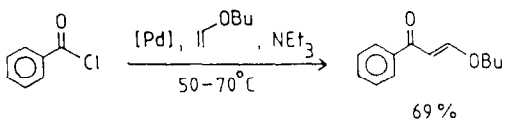
Abstract: A series of (E)-3-alkoxy-1-arylpropene-1-ones has been prepared by a regiospecific palladium-catalysed aroylation of alkylvinyl ethers.

The regiochemical outcome of the palladium-catalysed arylation of alkyl vinyl ethers is largely determined by electronic factors.[1] The halide, which acts as a ligand to palladium in the reaction, is one important factor, and arylation in the β-position increased in the order I Br Cl.[2] Chlorobenzenes are generally unreactive in Heck reactions,[3] but aroylchlorides provide access to intermediate arylpalladium chlorides.[4] This approach was successfully used in a regioselective synthesis of (E,Z)-2-butoxyethenylbenzenes, as exemplified in equation 1.[5]



eq. 1

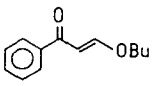
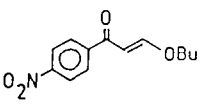
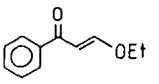
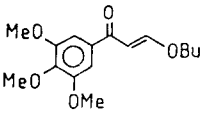
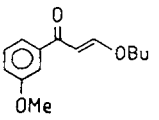
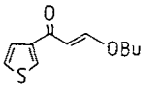
While the palladium-catalysed arylation of olefins has been extensively studied and is an important transformation in synthesis,[6] very few examples of palladium-catalysed aroylations of olefins have been reported.[7] We wish to report that nucleophilic olefins such as simple alkyl vinyl ethers serve as good substrates in the latter type of reaction. The aroylation takes place exclusively at the β-carbon atom, affording useful 1-aryl-1,3-dicarbonyl equivalents (eq. 2).



eq. 2

No reaction occurs in the absence of palladium catalyst. A detailed study of the scope and limitations of the synthesis is in progress. At this stage it should be noted that the reaction is simple to run (see below), and seems to be rather generally applicable.

Table: Products after palladium-catalysed benzoylation of alkyl vinyl ethers with various aroylchlorides[a].

Product	Yield (%)[b]	Product	Yield (%)[b]
	69		12
	54		57
	62		66

(a) Spectral and microanalytical data were in agreement with the proposed structures
(b) Isolated yield after chromatography

Typical procedure: palladium acetate (0.1 mmol) was charged together with the alkyl vinyl ether (5-10 mL) and triethyl amine (12 mmol) in a 50 mL thick-walled tube fitted with a teflon-lined screw cap. The mixture was stirred until a clear orange solution was obtained (10 min), whereupon the acid chloride (10 mmol) was added and the tube closed. Heating without stirring at 60-70 ^{o}C for 24 hours yielded a black slurry, which was diluted with ether (100 mL) and filtered to remove the triethyl amine hydrochloride. The resulting ethereal solution was concentrated at aspirator pressure and subjected to flash chromatography on silica,[8] using an ether/pentane mixture as eluent.

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References and notes:

1) See for example: a) Lee, T. D. and Daves Jr., G. D., J. Org. Chem. 48 399 (1983); b) Hallberg, A., Westfelt, L. and Holm, B., J. Org. Chem. 46, 5414 (1981); c) Hallberg, A., Westfelt, L. and Andersson, C.-M., Synth. Commun. 15, 1131 (1985).
2) Andersson, C.-M., Hallberg, A. and Daves Jr., G. D., to be published.
3) Exceptions have appeared; see: a) Davison, J. B., Simon, N. M. and Sojka, S. A., J. Mol. Catal. 22, 349 (1984); b) Julia, M. and Duteil, M., Bull. Soc. Chim. Fr. 2590 (1973).
4) Blaser, H.-U. and Spencer, A., J. Organomet. Chem. 233 (1982).
5) Andersson, C.-M. and Hallberg, A., to be published.
6) For reviews, see: a) Heck, R. F., Org. React. 27, 345 (1982); b) Heck, R. F., Palladium Reagents in Organic Syntheses (1985), Academic Press (London).
7) It has been reported that tetrakis(triphenylphosphine)palladium produces a ca. 7.5:1 mixture of methyl benzoylacrylate and methyl cinnamate from benzoyl chloride and methyl acrylate under conditions similar to those reported here. Biavati, A., Chiusoli, G. P., Costa, M. and Terenghi, G., Transition Met. Chem. 4, 398 (1979).
8) In the crude material, 10-15% of arylated vinyl ether was present.

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