

MIZOROKI-HECK TYPE REACTION THROUGH C-SI OR C-H BOND ACTIVATION

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Mizoroki-Heck (MH) reaction of silanols with olefins is a feasible method to synthesize substituted olefins by means of catalytic palladium(II) acetate. The hydroxy group of silanol is reported to play an important role in the reaction.

A series of reactions were carried out using silanols and silanediols and found that silanediols have comparable reactivity towards olefins bearing electron-withdrawing groups in the presence of stoichiometric amounts of palladium acetate. Catalytic reactions also took place although the reactions were less effective.

The reaction of *p*-methoxyphenyl(ethyl) silanediol with ethyl acrylate, butyl acrylate, N,N-dimethylacryl amide and N-*tert*-butylacrylamide gave the corresponding coupling products; ethyl (2*E*)-3-(*p*-methoxy-phenyl)propenoate, butyl (2*E*)-3-(*p*-methoxyphenyl)propenoate, N,N-dimethyl (2*E*)-3-(*p*-methoxyphenyl) propenamide and N-*tert*-butyl (2*E*)-3-(*p*-methoxyphenyl)propenamide, in 39%, 45%, 60% and 40% yields, respectively. The reactions were carried out with catalytic amounts of Pd(OAc)₂ in the presence of Cu(OAc)₂ and LiOAc in DMF at 100°C.

Carbon-carbon bond formation through catalytic activation of C-H bonds also has a considerable interest in the pharmaceutical industry. Differently substituted benzene derivatives were subjected to reaction with olefins in the presence the catalyst palladium (II) acetate, and successively achieved the corresponding products in good yields. Benzene derivatives having electron-donating groups gave higher yields when compared to those having electron-withdrawing groups.

Further, symmetrically substituted benzene derivatives such as, 1,4-dimethoxybenzene with ethyl acrylate, in the presence catalytic amount of Pd(OAc)₂ in DMF at 100°C, afforded ethyl (2*E*)-3-(2,5-dimethoxyphenyl)propenoate in 57% yield. Unsymmetrically substituted benzene derivatives such as anisole, 1,2-dimethoxybenzene and 1,3-dimethoxybenzene were subjected to the coupling reaction, under similar reaction conditions and obtained mixtures of regioisomers in 77%, 73% and 77%, respectively. The major regioisomers in each case was identified as ethyl (2*E*)-3-(4-methoxyphenyl) propenoate, ethyl (2*E*)-3-(2,3-dimethoxyphenyl)propenoate and ethyl (2*E*)-3-(2,4-dimethoxyphenyl)propenoate, respectively.