

Microwave-assisted Palladium Catalyzed Cross-coupling Reaction of Sodium Tetraphenylborate with Carboxylic Anhydrides

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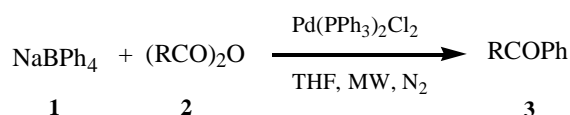
Abstract: A rapid and efficient method for synthesis of unsymmetrical ketones under microwave irradiation is reported.

Keywords: Cross-coupling, microwave irradiation, ketones, palladium catalyst.

The palladium-catalyzed cross-coupling reaction of organoboron compounds with organic electrophiles is very attractive in organic synthesis¹. Further these coupling reactions have been used successfully for the synthesis of natural products pharmaceutical, intermediates and combinational libraries of organic compounds². Recently Ryuki Kakino³ reported that Pd(PPh₃)₄ catalyzed reaction of carboxylic anhydrides with arylboronic acid under neutral conditions has a wide scope in application to synthesis of various ketones. However the reaction time is long (5-24 h) and the reaction of sodium tetraphenylborate with carboxylic anhydrides is not reported.

In recent years microwave irradiation of organic reactions has gained in popularity⁴. We have also reported the palladium and cobalt-catalyzed reactions⁵. Herein we report a very simple, fast, economic and general method for the Pd(PPh₃)₂Cl₂ catalyzed cross-coupling reaction of sodium tetraphenylborate with carboxylic anhydrides under microwave irradiation (**Scheme 1**) and the corresponding results are shown in **Table 1**.

Scheme 1



To determine the optimum condition of this reaction, we investigated the effects of

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various solvents, the power and time of microwave irradiation. It was found that the highest yield of compound **3** was obtained at 525 W for 12 min in THF.

Table 1 Synthesis of ketones^a

3	R	Product ^b	M.P(Lit)/	Yield (%) ^c
a	Ph	PhCOPh	47-48/47	92
b	4-BrPh	4-BrPhCOPh	79-80	90
c	4-NO ₂ Ph	4-NO ₂ PhCOPh	134-135	91
d	4-ClPh	4-ClPhCOPh	75-76	84
e	4-CH ₃ Ph	4-CH ₃ PhCOPh	56-57	90
f	4-CH ₃ OPh	4-CH ₃ OPhCOPh	58-59	91
g	3-NO ₂ Ph	2-NO ₂ PhCOPh	96-97	88
h	2-ClPh	2-Cl PhCOPh	43-44	82
i	PhCH=CH	PhCH=CHCOPh	52-53/53-54	84
j	CH ₃	PhCOCH ₃	17-19	90

^aMicrowave irradiation is carried out with an improved reflux Ganlanz WP750B commercial microwave oven at 2450MHz; ^bAll products gave satisfactory ¹HNMR and IR; ^cYield of isolated product.

General procedure: Mixture of sodium tetraphenylborate (1.1 mmol) with carboxylic anhydrides (1.0 mmol), [PdCl₂(PPh₃)₂] (0.05 mmol) and THF (12 mL) was irradiated at 525W for 12 min by microwaves under a nitrogen atmosphere. After the reaction mixture was cooled, the solvent was removed and diethyl ether (10 mL) and H₂O (20 mL) was added and the aqueous layer was extracted with diethyl ether (3×20 mL), the organic phase was dried (MgSO₄) and the solvent was evaporated in *vacuo*. The crude product was purified by recrystallized from ethanol and column chromatography on silica gel (200-300 mesh) using petroleum/ethyl acetate (v/v =15:1) as eluent.

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