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varied from crotyltrifluoroborate to allyltrifluoroborate.

A new organic transformation by introducing crotyl/allyltrifluoroborates in cross-coupling reaction with aroyl chlorides

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ABSTRACT

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The major development and extensively used methods in organic synthesis for carbon-carbon bond formation reactions are palladium-catalyzed allylation reactions.¹ Our interest is to introduce crotyl- and allyltrifluoroborates in a new organic transformation. Compared to highly reactive, less stable allylboronic acid and allylboronic ester, potassium allyltrifluoroborate is an air- and water-stable unique solid compound. Its use in organic transformations is increasing dramatically.² Recently, potassium allyltrifluoroborate is successfully applied in Michael type reaction.³ In addition to this, cross-coupling reaction of potassium allyltrifluoroborate and aryl halides is developed very recently.⁴ The oxidative addition of aroyl chloride to a palladium (0) complex vielding ArCO-Pd-Cl is a new entity for cross-coupling chemistry. Very few reports demonstrated the direct cross-coupling reaction of aryl metals with aroyl chloride in the presence of a palladiumcatalyst.⁵ But, palladium catalyzed cross-coupling reaction of allyl metals with aroyl halides is yet to be known. In this communication, we demonstrate the palladium-catalyzed microwave irradiated cross-coupling reaction of potassium crotyltrifluoroborate with aroyl chlorides and potassium allyltrifluoroborate with aroyl chlorides as well (Scheme 1). The results of this new cross-coupling process, which facilitates smooth organic transformation, are presented in Tables 2 and 3.

In earlier works of palladium-catalyzed cross-coupling reaction of potassium allyltrifluoroborate with aryl halides reported by Yamamoto group^{4b} and Al-Masum group^{4a}, 2.5 equiv of potassium allyltrifluoroborate gave best results. In the initial experiments, we

* Corresponding author. *E-mail address:* malmasum@tnstate.edu (M. Al-Masum). applied the same palladium-catalyst system that we had previously found effective for trans- β -methyl styrene synthesis^{4a} and no promising transformation was observed. Changing the molar ratio and solvent system with the same palladium complex merited the successful cross-coupling of potassium allyltrifluoroborate and aroyl chlorides (Table 1). Both microwave and conventional heating systems are almost equally effective and we explore the transformation under microwave heating for minute reaction.

Microwave irradiated PdCl₂(d^tbpf) catalyzed direct cross-coupling reaction of aroyl chlorides with potas-

sium crotyl/allyltrifluoroborates has been developed. Regioselectivity of the cross-coupling product is

When aroyl chloride treated with crotyltrifluoroborate 1a in the presence of palladium-catalyst, major cross-coupling products obtained in α -selectivity (Table 2, entries 1–4). In the case of 4chloro-aroyl chloride, potassium crotyltrifluoroborate gave a mixture of α -adduct and γ -adduct (Table 2, entry 5). The reaction success of crotyltrifluoroborate with aroyl chloride is mixed. Yields are moderate and aroyl group coupling at the α -position of the allyl moiety is interesting which we thought could proceed with γ selectivity (Table 2, entry 5). Probably, the electron donating methyl group enhances α -selectivity. In the case of potassium allyltrifluoroborate, a more selective transformation was observed. The best successful conditions leading to the formation of crotonophenone 5a from the cross-coupling of potassium allyltrifluoroborate **1b** and aroyl chloride **2a** is shown as a representative procedure. A dry microwave pyrex tube was purged with argon. Potassium allyltrifluoroborate, 73.0 mg (0.5 mmol), anhydrous potassium carbonate, 414 mg (3.0 mmol), PdCl₂(d^tbpf) catalyst, 9.9 mg (0.015 mmol), benzoyl chloride, $114 \,\mu L$ (1.0 mmol), and a magnetic bar were packed in a microwave tube. The reactants were then flushed with argon for 1-2 min to prevent the presence of air from causing the decomposition of the Pd catalyst followed by the addition of 2.0 mL of dry 1,4-dioxane from a sure-seal bottle. The





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Scheme 1.

Table 1Microwave versus thermal heating

Method	Molar ratio of 1b:2	Heating	Product	Yields (%)
1	2.5:1	MW, 20 min	Mixed regioisomers	65
2	1:2	MW, 20 min	5 (selective)	95
3	1:2	140 °C, 12 h thermal	5 (selective)	90
4	1:1	MW, 20 min	Mixed regioisomers	<50

Table 2

Palladium-catalyzed cross-coupling reaction of crotyltrifluoroborate $\mathbf{1a}$ and aroyl chlorides $\mathbf{2}^a$



^a Yields are isolated pure products by column chromatography.

^b Major product was **6** (γ -selectivity).

resulting mixture in the microwave tube was subsequently inserted into the microwave (CEM, Discover microwave 300 W

Table 3 Palladium-catalyzed cross-coupling reaction of allyltrifluoroborate 1b and aroyl chlorides 2^a



^a Yields are isolated pure products by column chromatography.

^b 4,4'-Dibromobenzil (**7**) was the major product.

power) and heated at 140 °C for 20 min. After removal from the microwave, the product mixture was extracted with diethyl ether and separated from the inorganic byproducts through filtration. The crude product was subjected to silica gel chromatography or preparative thin layer chromatography with hexane/ethyl acetate (50:1, 25:1, 10:1) as eluents and the pure product was isolated, dried, and characterized by GC/MS (Saturn 2200 Benchtop GC/MS) and NMR (Varian 300 MHz).



Scheme 2. Probable mechanism.

By adding potassium allyltrifluoroborate, the scope of this new transformation was established with a variety of different aroyl chlorides. On changing the electron-rich or electron-deficient groups in the phenyl ring of the aroyl chlorides, the reaction proceeded essentially in the same rate affording the corresponding aryl propenyl ketones (crotonophenones) in good to high yields (Table 3, entries 1–6, 9 and 10). In the case of para-bromo-aroyl chloride and allyltrifluoroborate, the cross-coupling product 5g was formed as a minor product (Table 3, entry 7) and homocoupling product 4,4'-dibromobenzil (7) was the major one. Probably, possible palladium insertion to bromide inhibits the transmetallation process and led to the homo-coupling product. Interestingly, when 4-nitro-aroyl chloride reacted with potassium allyltrifluoroborate under the same reaction conditions, a 50:50 mixture of β -adduct and γ -adduct was obtained (Table 3, entry 8) in good yields. Compared to other bases, potassium carbonate was the most effective for this transformation. This new cross-coupling reaction requires an excess amount of potassium carbonate. Control experiments without potassium carbonate did not give any product. Also, adding a stoichiometric amount of potassium carbonate had very little effect on the formation of the desired product. The palladium inserted aroyl chloride, ArCO-Pd-Cl displays excellent chemoselectivity in cross-coupling reaction when treated with potassium allyltrifluoroborate. Initially, we speculated that central carbon selectivity appears to be accomplished through palladacycle. But the mixture of products observed in

the case of 4-nitro-aroyl chloride and allyltrifluoroborate (Table 3, entry 8) convinces us to propose that the nucleophile may attack the terminal carbon of the π -allyl intermediate and subsequently isomerizes to the more stable α , β -unsaturated ketone (Scheme 2).

The application of potassium crotyltrifluoroborate cross-coupled with aroyl chlorides and potassium allyltrifluoroborate crosscoupled with aroyl chlorides has been successfully established. Further synthetic and mechanistic studies of these new processes will be explored in due course.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2011.07.107.

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