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Palladium(0)-catalyzed addition of $CFBr_3$ to olefins: synthesis of 1,1,3-tribromo-1-fluoroalkanes and 1,2-difluoroalkenes

B. Rama Raju, E. K. Pramod Kumar and Anil K. Saikia*

Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati 781 039, India

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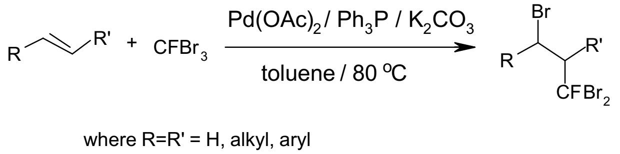
Abstract—It has been observed that Pd(0) can be used as a catalyst for the addition of $CFBr_3$ to olefins to give 1,1,3-tribromo-1-fluoroalkanes with good yields. Both terminal and internal olefins react under these conditions. Treatment of the addition product with zinc and methanol gave 1,2-fluoroalkenes.

The introduction of fluorine(s) into organic materials is prevalent in fields such as pharmacology or functionalized materials because of the unique biological and physical properties of the resulting compounds.[1] Several β-fluorophenethylamines,[2] 3-fluoroalkylamines,[3] and vinyl fluorides,[1c,4] have been shown to be irreversible inhibitors of certain enzymes. 1,2-Difluoroethylenes are especially interesting intermediates in organic chemistry due to their use in fluorinated analogues of natural products,[5] polymers[6] and liquid crystals.[7] In particular, reactions using fluoroorganometallic reagents derived from fluorohalohydrocarbons are versatile for constructing fluorinated target molecules.[8] There are a few methods reported for the addition of perfluoroalkyl monobromides to olefins catalyzed by radical initiators.[9] However, reports on the metal catalyzed addition of fluorohaloalkanes to olefins are few.[10] In this letter we report the palladium(0)-catalyzed addition of $CFBr_3$ to various olefins and subsequent reduction of the addition products with Zn and methanol to give 1,2-difluoroolefins.

In continuation of our interest in Freon,[11] we required a method for the addition of $CFBr_3$ to olefins. Following a literature procedure for the addition of perfluoroalkyl monobromide under free radical conditions,[9] where $CFBr_3$ was treated with olefin in the presence of sodium dithionite, the reaction resulted in a complex mixture. A variety of addition reactions of organic halides to alkenes catalyzed by palladium(0) have been reported.[12] Klabunde and Low have studied the stabilities and properties of some oxidative addition products of palladium and perfluoroalkyl halides.[13] They studied various fluorohaloalkanes, however, there was no mention of $CFBr_3$. Taking cues from this and in continuation of our own work on palladium-catalyzed reactions,[14] it was envisaged that palladium(0) might be a suitable reagent for the addition reaction of $CFBr_3$ to olefins. Thus, when $CFBr_3$ was treated with olefins in the presence of a catalytic amount of palladium(II) acetate, triphenylphosphine and anhydrous potassium carbonate in toluene at 80 °C, the corresponding addition products were obtained in good yields.[15] The reaction is represented in Scheme 1.

To generalize the reaction, various olefins were reacted with $CFBr_3$ as shown in Table 1. It was observed that both terminal and internal olefins could be converted to the corresponding fluorobrominated alkanes. In both cases, no Heck products (olefins) were isolated. Terminal olefins gave only one product whereas cyclic olefins



Scheme 1.

Keywords: Tribromofluoromethane; Palladium; Catalyst; Addition; Olefins; Reduction; Zinc–methanol.

* Corresponding author. Tel.: +91 361 2582316; fax: +91 361 2690762; e-mail: asaikia@iitg.ernet.in

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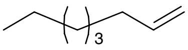
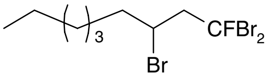
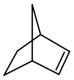
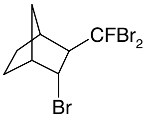
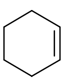
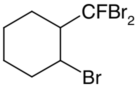
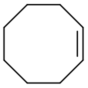
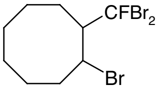
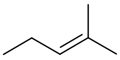
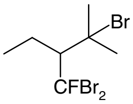
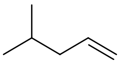
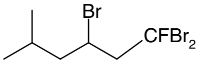
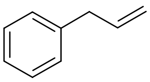
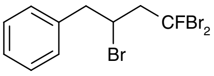
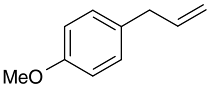
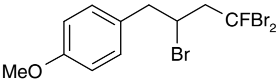
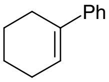
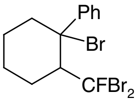
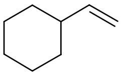
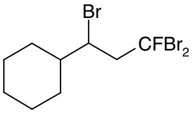
Table 1. Palladium catalyzed addition of $CFBr_3$ to olefins

Entry	Substrate (**a**)	Time (h)	Product (**b**)	Yield[a] (%)
1		30		79
2		16		79
3		31		78
4		49		96
5		27		63[b]
6		21		79
7		15		81
8		17		75
9		71		33
10		18		85

[a] Isolated yields. Compounds were characterized by IR, ^1H, ^{13}C and ^{19}F NMR.

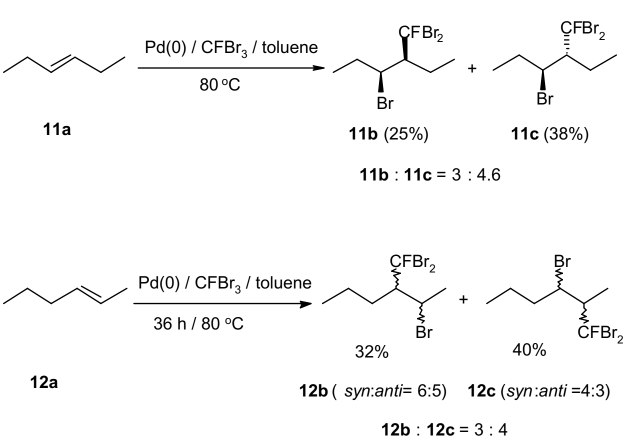
[b] Determined by ^1H NMR.

gave *cis* and *trans* products. Internal olefins gave a mixture of diastereomers.

trans-3-Hexene **11a** gave diastereomers[16] **11b** and **11c** in a ratio of 3:4.6.[17] The unsymmetrical olefin **12a** gave a mixture of four isomers[16] (Scheme 2). It was observed that CF_2Br_2 did not react with olefins under these reaction conditions due to the instability of the $CFBr_2PdBr$ species.[13]

The mechanism of the reaction may be as follows (Scheme 3). The first step is the oxidative addition of palladium(0) to $CFBr_3$ followed by olefin insertion. Reductive elimination of palladium(II) to palladium(0) with addition of bromine gives the product. With unfunctionalized olefins, the insertion occurs placing the $CFBr_2$ group at the less-substituted position of the olefin. Thus, the regioselectivity of the insertion is controlled by steric, not electronic factors with these substrates. β-Hydrogen elimination as occurs in the Heck reaction does not take place.

The reduction of 1,1,3-tribromo-1-fluoroalkanes with Zn and methanol gave *cis*- and *trans*-1,2-difluoroolefins (Scheme 4).[18]



Scheme 2.