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# Palladium-catalyzed Reaction of Phenyl Fluoroalkanesulfonates with Alkynes and Alkenes

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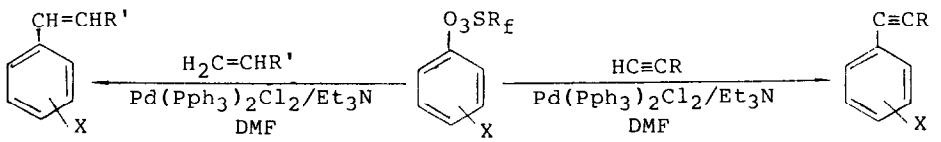
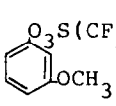
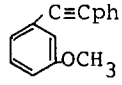
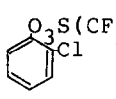
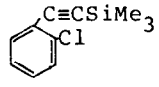
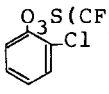
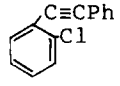
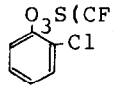
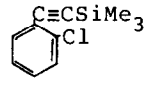
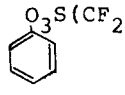
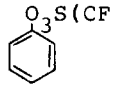
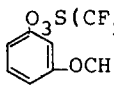
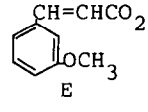
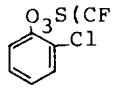
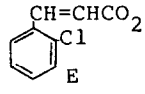
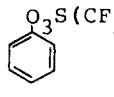
Abstract: Palladium-catalyzed reaction of phenyl fluoroalkanesulfonates with alkynes and alkens under mild conditions givesthe corresponding alkynyl and alkenyl substituted benzenes in good yields.

The palladium catalyzed reactions of alkynes and alkenes with organic halides have been extensively studied to provide a good approach to form caron-carbon bond. However, this type of substitution at $sp^2$ carbon is limited to aryl halides and alkenyl halides[1,2]. Recently, Cacchi[3] and Scott[4] extended the palladium catalyzed olefination to vinyl triflates, i.e. vinyl halide could be replaced by vinyl triflate in the Heck reaction. To our knowledge,no example on palladium catalyzed alkynation and olefination of phenyl fluoroalkanesulfonates has been described. Herein, we wish to report that phenyl fluoroalkanesulfonates, similar to halobenzene, can be used as substrates for the palladium catalyzed carbon-carbon bond formation.




The representative results are listed in the Table. Phenyl fluoroalkane-

Table Palladium-catalyzed reaction of phenyl fluoroalkanesulfonate with alkynes and alkenes

| fluoroalkanesulfonate | alkyne | time(h) | product | isolated yield % |
|---|---|---|---|---|
| $phOSO_2CF_3$ | HC≡CPh | 3 | PhC≡CPh | 91 |
| $phOSO_2CF_3$ | $HC≡CSiMe_3$ | 7 | $PhC≡CSiMe_3$ | 87 |
| $phO_3S(CF_2)_2O(CF_2)_2H$ | HC≡CPh | 7 | PhC≡CPh | 84 |
| $phO_3S(CF_2)_2O(CF_2)_2H$ | $HC≡CSiMe_3$ | 7 | $PhC≡CSiMe_3$ | 92 |
|  | HC≡CPh | 12 |  | 87 |
|  | $HC≡CSiMe_3$ | 14 |  | 73 |
|  | HC≡CPh | 7 |  | 89 |
|  | $HC≡CSiMe_3$ | 8 |  | 94 |
|  | HC≡CPh | 12 | PhC≡CPh | 77 |
|  | $H_2C=CHCO_2Et$ | 14 | $PhCH=CHCO_2Et$ E | 83 |
|  | $H_2C=CHCO_2Et$ | 18 |  E | 87 |
|  | $H_2C=CHCO_2Et$ | 13 |  E | 83 |
|  | $H_2C=CHCN$ | 14 | PhCH=CHCN E:Z=71:29 | 75 |

a. Reaction conditions: 5mmol of phenyl fluoroalkanesulfonate, 2-3mmol% $PdCl_2(PPh_3)_2$ 7.5mmol of alkyne or alkene and 3ml $Et_3N$ in 15ml DMF at 90°C for 3-17h under nitrogen.

b. All Compounds have been fully characterized spectrally (IR,'H NMR and MS).

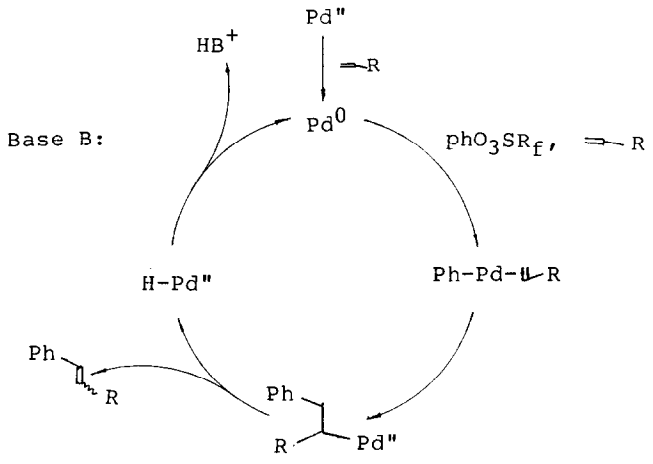
c. When phenyl fluoroalkanesulfonates reacted with alkynes, the conversion was 100%. Reaction with alkenes the converison was 80-90%.

d. Ratio of E and Z isomers was determined by NMR.

sulfonates with either electron withdrawing or electron donating substituents on the benzene ring reacted with alkynes and alkenes to give the corresponding products in good yields. Owing to the accessibility of a wide variety of such esters the new method provides an effective means for the specific transformation of phenols into alkynyl and alkenyl substituted benzenes, thus broadening existing methodologies in the area commonly referred to as phenylic substitution.

A typical procedure is as follows: A mixture of phenyl triflate, 1.1g (5mmol), phenylacetylene, 0.7g (7mmol), triethylamine, 3ml, and dichlorobis (triphenylphosphine)palladium,100mg(0.143mmol) in 15ml DMF was stirred at 90°C for 4h under nitrogen. The reaction mixture was then diluted with water, extracted with 1:1 petroleum ether/ether,washed with water until neutral,dried ($Na_2SO_4$),and evaporated. Chromatography of the residue on silica gel(petroleum ether/ethyl acetate=100:2 as eluate)provided pure diphenylacetylene 0.81g(91%).

This reaction may proceed through the reduction of the Pd(II) catalyst to Pd(O) species, presumably by the olefin. The resulting Pd(O) species is then capable of entering the catalytic cycle by oxidative addition of phenyl fluoroalkanesulfonate and coordination with the olefin to form a Pd(II) species as shown in Scheme.




Previously we have reported exclusive sulfur-oxygen bond cleavage in the reaction of phenyl fluoroalkanesulfonates with nucleophiles[5]. The present method shows that the palladium catalyzed alkynation and olefination of phenyl fluoroalkanesulfonates apparently provides the exclusive carbon-oxygen bond fragmentation.

Employment of phenyl tosylate instead of phenyl fluoroalkanesulfonate under the same conditions in these reactions met only with failure.

**ACKNOWLEDGMENT**

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References and notes:

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