Chem. Pharm. Bull. 38(4) 1104—1106 (1990)

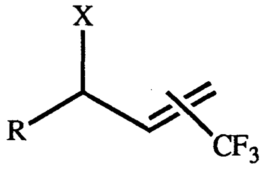
TRIFLUOROMETHYLATED ALLYLIC ANION AND RADICAL; GENERATION BY THE ELECTRONIC INVERSION OF Π-ALLYLIC PALLADIUM COMPLEX BY SAMARIUM DIIODIDE

Yuji HANZAWA, Seiji ISHIZAWA, Yoshiro KOBAYASHI, and Takeo TAGUCHI*
Tokyo College of Pharmacy, 1432-1 Horinouchi, Hachioji, Tokyo 192-03, Japan

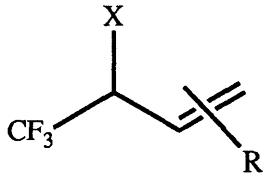
Trifluoromethylated π-allylic Pd-complex was treated with samarium diiodide to generate the trifluoromethylated allylic anion and radical species.

KEYWORDS π-allylic palladium-complex; samarium diiodide; trifluoromethyl group; electronic inversion

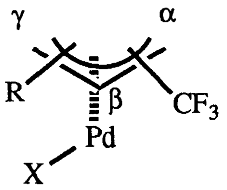
Recently we reported on the reaction of trifluoromethylated allylic alcohol derivatives (**1**, **2**) with a soft carbon nucleophile in the presence of palladium catalyst $[Pd(PPh_3)_4, Pd(DPPE)_2]$ and its application to the synthesis of trifluoromethylatyed pyrethroid.1) In this nucleophilic substitution reaction, the position of the trifluoromethyl group, the kind of ester group as a leaving group, and the ligand of palladium metal are crucial factors for the formation of the trifluoromethylated π-allylic complex (**3**).



1



2



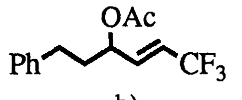
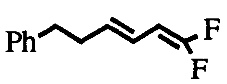
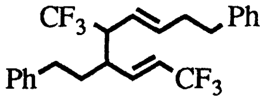
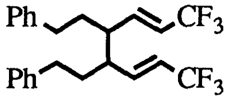
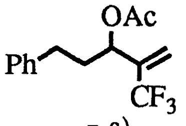
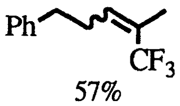
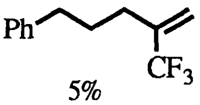
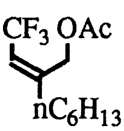
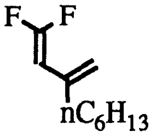
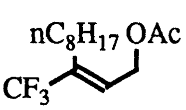
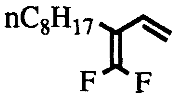
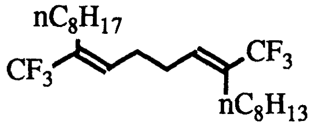
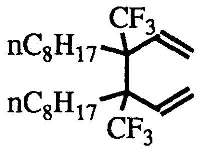
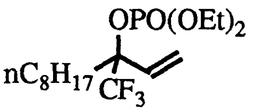
3

R=alkyl
X=OAc, OCOOEt, $OPO(OEt)_2$, OTs

On the other hand, trifluoromethylated allylic anions and/or the radicals are considered to be very important reactive species for the synthesis of highly functionalized fluorine-containing compounds in the fields of organic and medicinal chemistry.2) Here, we report the generation of the trifluoromethylated allylic anion and radical by the electronic inversion of the trifluoromethylated π-allylic palladium complex using samarium diiodide (SmI_2).3) The results, obtained by the reactions of trifluoromethylated π-allylic palladium complexes derived from alcohol derivatives (**4**-**8**) with SmI_2 (2 eq mol) in THF and isopopyl alcohol (1 eq mol),4) are shown in Table I. The compounds

(**4**, **6**, **7**, **8**), whose trifluoromethyl groups are located at either end (α or γ) of the π-allylic complex system (**3**), gave the difluorodiene compound as the major product along with the dimeric compound even in the presence of the alcohol.5) The compound (**5**) which has a trifluoromethyl group at the central carbon (β-position) of **3** yielded the reduced products as a mixture of regiochemical isomers without giving any of the fluorine-eliminated diene or the coupled dimer. We believe that difluorodienes are obtained through the formation of allylic anion species followed by the β-elimination of a fluoride ion6) and the dimers are derived from the coupling between the allylic radicals (Chart 1). The reduction in compound (**5**) is considered to be derived by the abstraction of hydrogen atom from alcohol by the anion or radical species in which the β-elimination of fluoride ion is impossible. When the reaction was attemoed in the absence of Pd(0) catalyst, no reaction took place. As an equivalent to the trifluoromethylated allylic anion, the reaction of compound (**5**) with 2-octanone in the presence of palladium catalysist and SmI_2 (2 eq) was examined to give a 4:3 diastereomeric mixture of the products in 76% yield (Chart 2). Although we have no plausible explanation for the different regioselectivity of **5** in reduction and carbonyl addition, it might be the result of the different reaction mechanism, that is the radical or anionic reaction.

Table I. Reaction of Allylic Estere (**4**-**8**) with $Pd(PPh_3)_4$ and SmI_2 a)

Starting material	Product (yield)		
 **4** b)	 42%	 22%	 7%
 **5** c)	 57%	 5%	
 **6** d)	 45%		
 **7** d)	 28%	 14%	 7%
 **8** d)	49%	22%	3%

a) Reaction was carried out by using $Pd(PPh_3)_4$ (0.05 eq.), iso-PrOH (1 eq) and SmI_2 (2 eq) in THF. b) Room temperature, 2 h. c) 50 °C, 20 h. d) Reflux, 2 h.

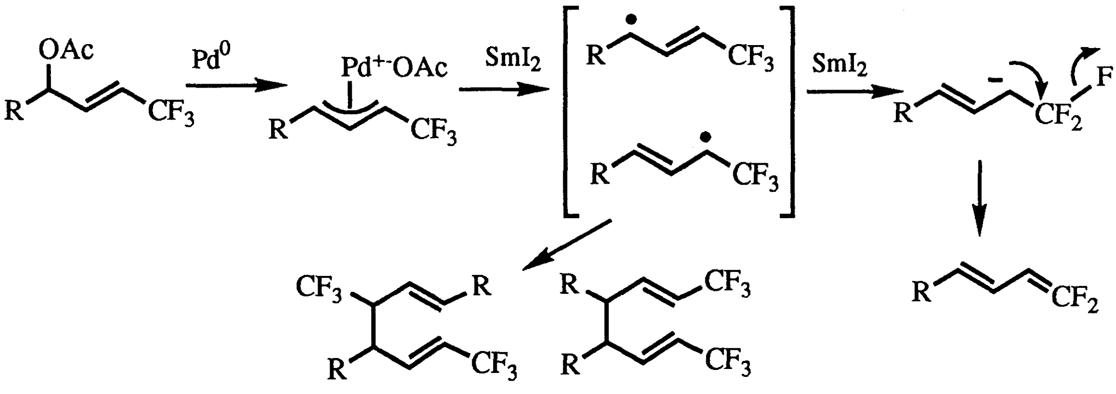


Chart 1

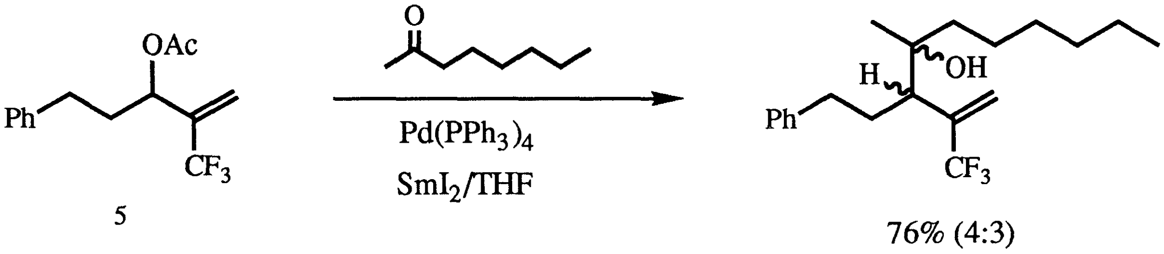


Chart 2

The easy availability of the trifluoromethylated allylic alcohol derivatives[7] and the clear reactivity with the carbonyl compound in compound (5)[8] have opened a new way to create the new fluorinated bioactive compounds.

REFERENCES AND NOTES

1) Y. Hanzawa, S. Ishizawa and Y. Kobayashi, Chem. Pharm. Bull., 36, 4209 (1988).
2) R. Filler and Y. Kobayashi, "Biomedicinal Aspects of Fluorine Chemistry," Kodansha, Tokyo (1982).
3) H. B. Kagan, J. L. Namy and P. Girard, Tetrahedron, 37, 175 (1981). About the inversion of the electronic reactivity of allylic alcohol derivatives with SmI_2; T. Tabuchi, J. Inanaga and M. Yamaguchi, Tetrahedron Lett., 27, 601, 195 (1986).
4) Source to trap the anion or radical species by hydrogen atom.
5) None of the reduced products were isolated from the reaction mixture. All of the isolated products were identified by ^{1}H- and ^{19}F-NMR, and mass spectra.
6) Although the carbon-fluorine bond is very strong, a double bond can be easily formed by the elimination of the fluoride through a β-elimination process. See Ref. 2.
7) See Ref. 1 and the references cited therein.
8) Reductive coupling of allylic acetate with carbonyl compound with Pd(0)–SmI_2 system; T. Tabuchi, J. Inanaga and M. Yamaguchi, Tetrahedron Lett., 27, 1195 (1986). The trifluoromethylated allylic anion, generated by the reaction of the trifluoromethylated allyltrimethylsilane with fluoride ion, has been reported to react with carbonyl compound. T. Yamazaki, K. Takita and N. Ishikawa, Nippon Kagaku Kaishi, 2131 (1985).

(Received November 30, 1989)