Pergamon

Tetrahedron Letters, Vol. 37, No. 21, pp. 3721-3722, 1996

0040-4039/96 $15.00 + 0.00

PII: S0040-4039(96)00668-5

An Efficient Ligand Exchange Reaction of β-(Trifyloxy)vinyliodonium Triflates with Aryllithium Reagents Leading to Diaryliodonium Triflates

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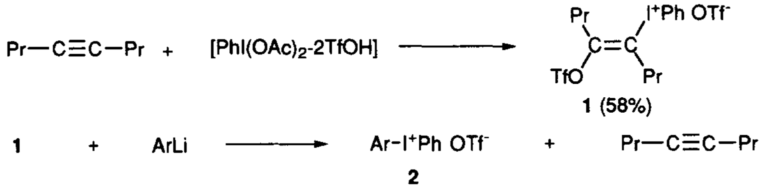
Abstract: Reaction of β-[[(trifluoromethylsulfonyl)oxy]vinyl](phenyl)-iodonium triflates with aryllithiums gave (aryl)(phenyl)iodonium triflates selectively. This reaction indicates that ligand exchange reaction takes place efficiently at iodine atom and provides another approach to unsymmetrical diaryliodonium salts. Copyright © 1996 Elsevier Science Ltd

Recently much attention has been paid to hypervalent iodine compounds in organic synthesis.[1] Diaryliodonium salts are useful for arylation reactions, photopolymerization, and chemical amplification in imaging process.[1] Heterocyclic aryliodonium salts are shown to possess a biological activity.[1] Previously we have reported reactive hypervalent iodine reagents prepared from trifluoromethanesulfonic acid (TfOH) and iodosylbenzene (PhIO) or iodobenzene diacetate [PhI(OAc)$_2$].[2] These reagents exhibit a high electrophilicity to react with alkynes to yield (E)-β-(trifyloxy)vinyliodonium triflates stereoselectively.[3]

On the other hand, ligand exchange reactions are well-known reactions of hypervalent species.[4] However, ligand exchange reactions using vinyliodonium salts are little attractive for synthetic applications for lack of the utility and the selectivity and there are only few successful examples applied to synthesis of symmetrical heterocyclic iodonium salts.[5]

The β-(trifyloxy)vinyliodonium triflates[3] have a good leaving group, OTf, with the geometry *trans* to phenyliodonio group. The high nucleofugacity of OTf is very suitable to cause elimination at the stage of ligand exchange. Thus we considered that β-(trifyloxy)vinyliodonium triflates undergo ligand exchange effectively. In this paper we want to report an efficient ligand exchange reaction of β-(trifyloxy)vinyliodonium triflates giving unsymmetrical diaryliodonium triflates

The iodine reagent [PhI(OAc)$_2$-2TfOH][6] could be used for the preparation of β-(trifyloxy)vinyliodonium triflates. Addition of 4-octyne to a stirred solution of PhI(OAc)$_2$ and TfOH in CH$_2$Cl$_2$ gave phenyl[5-(trifyloxy)-4-octen-4-yl]iodonium triflate (1) in 58% yield.

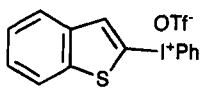


General procedure of the ligand exchange reaction is as follows. An aryllithium (2 mmol) solution in ether or THF was added to a stirred solution of β-(trifyloxy)vinyliodonium triflate 1 (1 mmol) in CH$_2$Cl$_2$ at -75

°C and the mixture was stirred at that temperature for 2 h. Then, the reaction mixture was treated with TfOH (1 mmol) and concentrated under reduced pressure. Trituration of the residue with ether gave crystals of diaryliodonium triflate (**2**) which were further purified by reversed phase liquid chromatography and fully characterized by spectral means and combustion analyses. GC analysis of the mother liquor indicated that 4-octyne was formed in almost equal yield with diaryliodonium triflate **2**. The results are given in Table 1.

Table 1. Ligand exchange reactions of vinyliodonium triflates **1** with aryllithium reagents.

aryllithium reagent	reaction temp. (°C)	aryliodonium salt **2**	isolated yield (%)
PhLi	-75	$Ph_2I^+OTf^-$(**2a**)	76
2-lithiobenzothiophene	-75	**2b**	78
2-lithiothiophene	-75	**2c**	71
2-lithiotoluene	-75	**2d**	90
2-lithioanisole	-35	**2e**	93
3-lithioanisole	-75	**2f**	67



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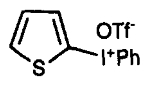

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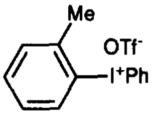

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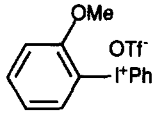

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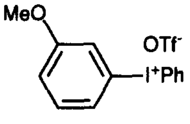

2f

Table 1 shows that the reaction of **1** with aryllithium reagents affords unsymmetrical diaryliodonium salts **2**, which include synthetically difficult *ortho* and *meta*-substituted aryliodonium salts. The presence of high nucleofugal OTf group at the vinyl ligand brings about effective elimination of the vinyl group accompanying decomposition to 4-octyne and triflate ion since the reaction of β-(chlorovinyl)(phenyl)iodonium chloride with lithiothiophene results in a low yield of phenyl(thienyl)iodonium chloride.[5a]

In summary, we have found an efficient ligand exchange reaction of vinyliodonium salts bearing a high nucleofugal triflate group at the β position. Most of the preparations of diaryliodonium salts have been so far conducted by electrophilic aromatic substitution of hypervalent iodine reagents which yields *para*-substituted aryliodonium salts.[1] The present ligand exchange reaction gives unsymmetrical diaryliodonium salts in good yields even in the *ortho* and *meta*-substituted cases and provides another route to synthesis of diaryliodonium salts.

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(*Received in Japan* 20 *February* 1996; *accepted* 8 *April* 1996)