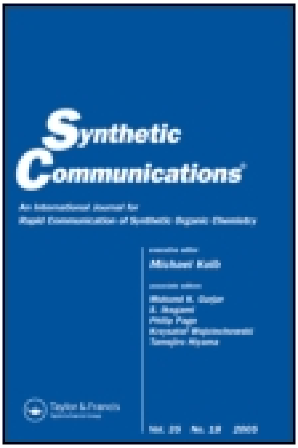

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The Reaction of [N-(p-Toluenesulfonyl)Imino]-Phenyliodinane with Enol Silanes

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THE REACTION OF [*N*-(*P*-TOLUENESULFONYL)IMINO]-PHENYLIODINANE WITH ENOL SILANES

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ABSTRACT: [*N*-(*p*-Toluenesulfonyl)imino]phenyliodinane reacts with enol silanes to provide α-tosylamino carbonyl compounds.

The amination of carbonyl compound is an important reaction because of its potential as a synthetic method for heterocyclic compounds and unnatural amino acids.[1] Several aminating methods including a direct amination of enol silane have been reported.[2] The amination of enol silane was achieved by either thermolysis or photolysis of ethylazidoformate, however, gave α-amino carbonyl compound in relatively low yield.[3]

High valent iodine compounds such as $PhIO/BF_3$ and PhI(OH)(OTs) have proven to be useful reagents in organic synthesis.[4] Enol silane reacts with the compounds to give synthetically useful α-substituted carbonyl compounds.[5] [*N*-(*p*-Toluenesulfonyl)imino]phenyliodinane (PhI=NTs), a nitrogen analog of PhIO, is relatively a new iodine(III) compound and has not been well studied until recently.[6] During our study of the application of the PhI=NTs to organic reaction, we have found the PhI=NTs also reacts with enol silanes to provide α-tosylamino carbonyl

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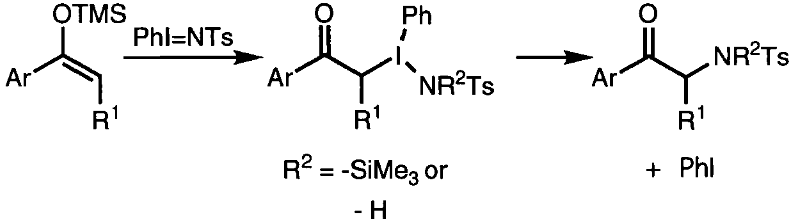
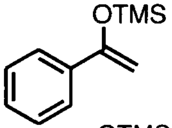
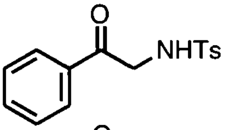
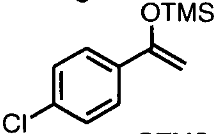
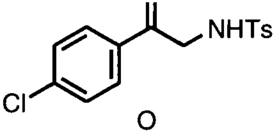
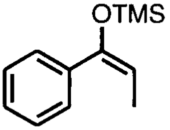
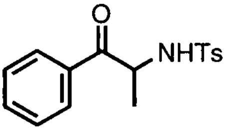
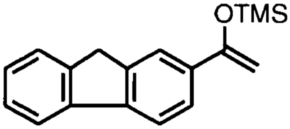
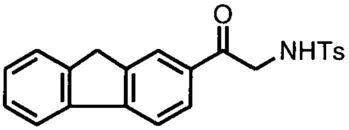
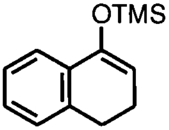
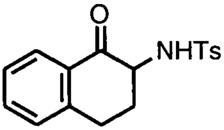
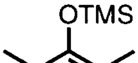
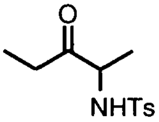
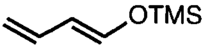
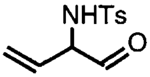
compounds. The PhI=NTs was found to be a good aminating reagent and readily reacts with enol silanes at warm temperature to provide α–tosylamino ketone and aldehyde in good yield. The aziridination of enol silanes reported by Evans' group[7] could afford the α-tosylamino ketone in the presence of copper catalyst, which was, however, found to be unnecessary in our reaction. Thus, we report here a facile synthetic method of α-tosylamino carbonyl compounds via the reaction between enol trimethylsilanes with *N*-tosyliminophenyliodinane.



1-(Trimethylsilyloxy)styrene readily reacts with the PhI=NTs in acetonitrile to give α-tosylaminoacetophenone in high yield (95%). When heated, the reaction was completed before the temperature of the reaction mixture reached to boiling point of acetonitrile. In contrast to the high efficiency of the reaction at warm temperature, a much longer reaction time was required at room temperature. The reaction was also performed in methylene chloride as a solvent but afforded the product in low yield (50%). Consequently, we carried out the rest of amination reactions in acetonitrile. Various aromatic enol silanes showed similar reactivities toward the PhI=NTs, as shown in Table 1, to provide α-tosylamino ketones in good yields.[8] The PhI=NTs also reacts with aliphatic enol silane such as 3-(trimethylsilyloxy)-2-pentene and 1-(trimethylsilyloxy)-1,3-butadiene, however, gave products in relatively low yields. Interestingly, 1-(trimethylsilyloxy)cyclohexene and 1-phenoxy-1-(trimethylsilyloxy)ethene did not react with PhI=NTs. The unreacted PhI=NTs was decomposed into iodobenzene and *p*-toluenesulfonamide.

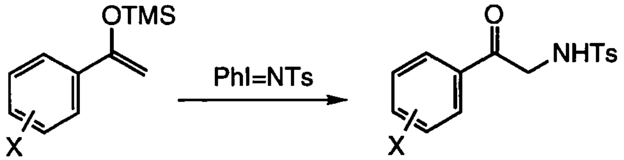
The electronic effect of the amination reaction was studied by reacting the PhI=NTs with 1-(trimethylsilyloxy)styrene derivatives containing substituent on the phenyl ring at room temperature. Since the PhI=NTs is not soluble in acetonitrile

Table 1. Reaction of Enol Silanes with PhI=NTs

Entry	Enol Silanes	Product	Yield[a]
1			95
2			95
3			94
4			70
5			67
6			53
7			52

[a]Isolated yield

Table 2. Reaction of Substituted Aromatic Enol Silanes with PhI=NTs at 25°C[a]



Entry	Enol Silanes	Yield	Reaction Time
1	o-Methyl-	51	18
2	m-Methyl-	96	11
3	p-Methyl-	97	1
4	p-Methoxy-	97	3.5
5	H-	95	4.5
6	p-Nitro-	85	6
7	p-Chloro-	99	>24

[a] All reactions were performed in dry acetonitrile (4 mL) with enol silane (0.3 mmol) and PhI=NTs (0.25 mmol).

because of its polymeric solid state structure,[9] the extent of the reaction may be followed by observing the dissolution of this reagent. As shown in Table 2 (entry 3-7), the reaction time necessary to complete the reaction depends upon the substituent on enol silanes. A long reaction time was required in the reaction with electron withdrawing substituent, indicating the electrophilic nature of the PhI=NTs. The position of substituent (entry 1-3) also influenced the yield and reaction time of the reaction, showing the steric effect of ortho substituent. In contrast to the large electronic effect of substituted enol silanes, a F_5PhI=NTs did not show any effect on the reaction. The reactivity of the F_5PhI=NTs was almost identical to the PhI=NTs.

In conclusion, we have shown a convenient synthetic method of α-tosylamino carbonyl compounds, being applicable to the synthesis of natural product such as Cathinone.[10] We are currently investigating the further details of the reaction.

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8. A typical experimental procedure is as follows. The PhI=NTs (0.6 mmol) was added to the solution of 1-(trimethylsilyloxy)styrene (0.5 mmol) in dry acetonitrile (7 mL) under nitrogen atmosphere. When the mixture was slightly heated, the solid PhI=NTs was immediately disappeared. After evaporation of the solvent, the residue was chromatographed with silica gel. Recrystallization with ethyl ether gave a pure 2-[*N*-(*p*-toluenesulfonyl)amino]acetophenone (0.48 mmol).[7]

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