

A Convenient Method for the Synthesis of α -Imidostyrenes from Styrenes and Imides via Diphenylstyrylsulfonium Salts

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Styrenes having a hydrogen atom at the α -position reacted with diphenyl(trifluoromethanesulfonyloxy)sulfonium triflate (**1**) to form diphenylstyrylsulfonium triflates **2** that were in turn converted into the corresponding α -imidostyrenes on treatment with sodium or potassium salts of cyclic imides.

Substituted vinylsulfonium salts are frequently used as useful synthetic intermediates that react with various nucleophiles. Formation of cyclopropanes by the reaction of dimethylvinylsulfonium salts with enolates¹ or anionic species of active methylene compounds² is among the best known examples. Recently, convenient methods for the syntheses of 2-arylaziridines³ and allylamines⁴ via diphenylvinylsulfonium salts were reported from our laboratory.

In this communication, we would like to describe a new method for the synthesis of α -imidostyrenes, useful precursors of vinylamines, by introducing an imido group to the α -position of styrenes via diphenylstyrylsulfonium salts.

In the first place, a reaction of isolated [(*E*)-2-(4-chlorophenyl)ethenyl]diphenylsulfonium triflate (**2a**)^{3,5} with several cyclic imide compounds was tried (Table 1, Entries 1–4). Several α -imidostyrenes were synthesized smoothly in DMSO⁶ at room temperature although the reaction with sodium 1,8-naphthalimide proceeded much more slowly than the cases with the other imides, which was presumably due to its steric effect (Entry 1). Moreover, isatin, a cyclic amide, gave the similar product in moderate yield (Entry 5). 4-Chloro- α -phthalimidostyrene was obtained in 90% yield by using potassium phthalimide (Entry 4); however, when [(*E*)-2-(4-chlorophenyl)ethenyl]dimethylsulfonium triflate was used instead of **2a**, 4-chloro- α -phthalimidostyrene was not detected and *N*-methylphthalimide (58%) was obtained along with (*E*)-4-chlorostyryl methyl sulfide (88%).

Next, α -phthalimidation of several styrenes in one vessel according to the present method was examined (Table 2, Entries 1–4). Styrene and 4-chlorostyrene were converted into the corresponding α -phthalimidostyrene in high yields without isolating the intermediate sulfonium salts **2** (Entries 1 and 2). Electron-donating groups in a benzene ring lowered the yield and allowed several unknown by-products to be obtained (Entries 3 and 4). Furthermore, *N*-vinylphthalimide gave the desired 1,1-diphthalimidoethylene in moderate yield (Entry 5). In the above reactions, 1 equiv. of potassium phthalimide was used for neutralizing 1 equiv. of triflic acid generated during the preparation of the sulfonium salt; therefore, when 1 equiv. of potassium phthalimide was used, the reaction did not proceed at all.

The overall synthetic route with a proposed reaction mechanism is shown in Scheme 1. Initially, diphenyl(trifluoromethanesulfonyloxy)sulfonium triflate (**1**), prepared from diphenyl

Table 1. Reactions of **2a** with metal salts of cyclic imide or amide compounds

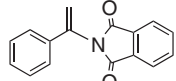
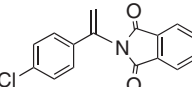
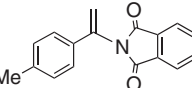
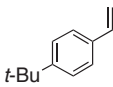
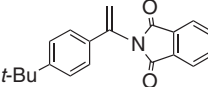
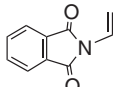
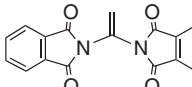
Entry	R ¹ R ² NM	Method ^b	Conditions	Yield /% ^c
1		A	rt, 40 h	36
2		A	rt, 3 h	69
3		A	rt, 12 h	84
4		B	rt, 12 h	90
5		A	rt, 1 h	62

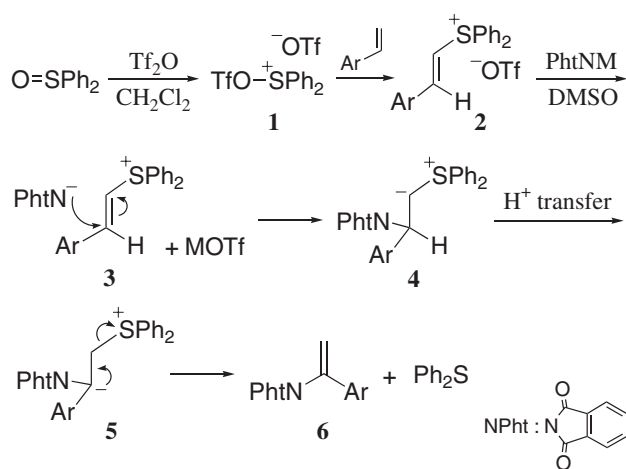
^aSingle isomer with *E*-configuration. ^bMethod A: Imide or amide (1.1 equiv.) was added to a stirred suspension of sodium hydride (1.1 equiv.) in DMSO at rt. After 0.5 h, **2a** was added. Method B: A mixture of **2a** and potassium phthalimide (1.1 equiv.) in DMSO was stirred. ^cIsolated yield.

sulfoxide and triflic anhydride (Tf₂O), reacted with styrenes to form the corresponding diphenylstyrylsulfonium triflate **2**. Then, nucleophilic addition of phthalimide anion, for example, to the α -position of **2** gave **4** in which 1,2-prototropic shift took place to form **5**. Subsequent regeneration of a double bond by eliminating diphenyl sulfide produced the α -phthalimidostyrenes **6**. The behavior of diphenylvinylsulfonium salts shown in the steps **4** to **6** is a unique one and is quite different from that of similar intermediates, vinylphosphonium salts that undergo the so-called Schweizer reaction.⁷

Thus, an effective and convenient method for the synthesis of α -imidostyrenes from styrene derivatives and cyclic imides was established.

Table 2. Reactions of olefins with potassium phthalimide via diphenylvinylsulfonium salts

$ \begin{array}{c} \text{R}-\text{CH}=\text{CH}_2 \xrightarrow[\text{-78}^{\circ}\text{C}]{\text{CH}_2\text{Cl}_2} \xrightarrow[\text{Temp., Time}]{\text{DMSO}} \text{R}-\text{CH}=\text{CH}-\text{N} \begin{array}{c} \text{O} \\ \diagup \diagdown \\ \text{C}_6\text{H}_4 \\ \diagdown \diagup \\ \text{O} \end{array} \\ \text{Ph}_2\text{SO (1.0 equiv.)} \quad \text{KPhthal (3.0 equiv.)} \\ \text{Tf}_2\text{O (1.0 equiv.)} \end{array} $				
Entry	Substrate	Conditions ^a	Product	Yield /% ^b
1		rt, 16 h		87
2		rt, 3 h		86
3		rt, 24 h		50
4		rt, 15 h		51
5		60 °C, 1 h		48

^aFor the second step. ^bIsolated yield.**Scheme 1.**

Further studies for the scope and limitation of the present reaction are now in progress.

A typical experimental procedure for the synthesis of α -imido-styrenes is as follows (Table 2, Entry 1): To a stirred solution of diphenyl sulfoxide (30.3 mg, 0.15 mmol) in dichloromethane (0.3 mL) was added triflic anhydride (0.025 mL, 0.15 mmol) under an argon atmosphere at -78°C , followed by dropwise addition of styrene (15.6 mg, 0.15 mmol) in dichloromethane (0.3 mL) at the same temperature. After 10 min, the reaction mixture was warmed up to 0°C , and the solvent was removed in vacuo. To the residue were added DMSO (0.3 mL) and potassium phthalimide (83.3 mg, 0.45 mmol), and the mixture was stirred at room temperature for 16 h. The reaction mixture was quenched with cold water (10 mL), and the organic material was extracted with ether (10 mL $\times$ 2). The combined organic layers were dried over anhydrous sodium sulfate, filtrated, and evaporated. After crude precipitates formed by addition of a small amount of chloroform were removed by filtration, the filtrate was evaporated. The resulting crude products were purified by preparative TLC to give α -phthalimidostyrene (32.5 mg, 87%).

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References and Notes

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