

α -Allylation of Carbonyl Compounds *via* Silyl Enol Ethers and Silyl Ketene Acetals using a Hypervalent Iodine Reagent†

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Oxidation of allyltrimethylsilane with iodosobenzene and trimethylsilyl trifluoromethanesulfonate followed by treatment with trimethylsilyl enol ethers of ketones or trimethylsilyl ketene acetals of esters/lactones provides a new method for the α -allylation of the corresponding carbonyl compounds.

There is considerable interest in the hypervalent iodine oxidation of a wide variety of organic compounds.¹ One important goal achieved using this approach is the formation of carbon–carbon bonds.² Oxidation of silyl enol ethers reported from our laboratory³ and other research groups^{4,5} has offered a useful way of accomplishing such a goal.

We have reported that oxidation of silyl enol ethers with iodosobenzene in the presence of boron trifluoride–diethyl ether produces symmetrical 1,4-diones [e.g. **4**, R = Ph in eqn. (1)].³ The method could not be used to synthesise unsymmetrical products. Zhdankin *et al.* modified this approach by generating *in situ* the hypervalent iodine intermediate, phenacyliodonium tetrafluoroborate (**2**, X = BF₄), to synthesise cross-coupled products.⁴ Only the α -(trimethylsilyloxy) styrene was employed as a substrate. As an effort to introduce a new method for carbon–carbon cross coupling, we now report the α -allylation of carbonyl compounds *via* silyl enol ethers and silyl ketene acetals.

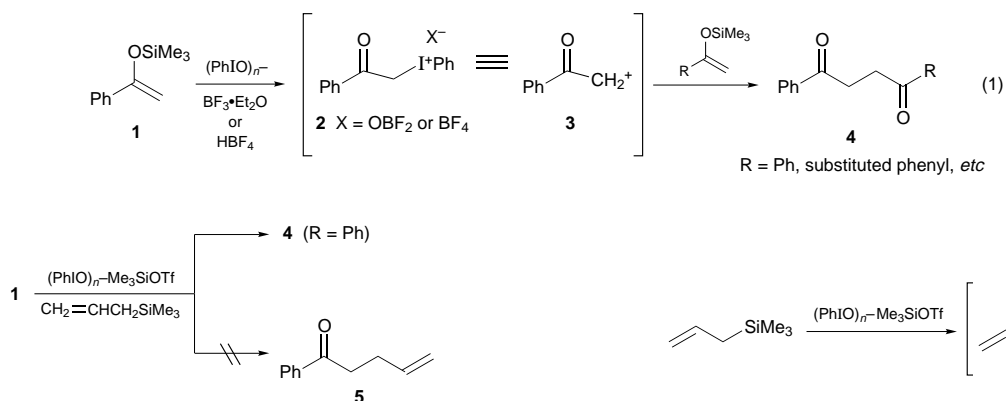
Based on previous results that the iodine(III) intermediate **2**, generated from the oxidation of a silyl enol ether, is equivalent to carbocation **3** and capable of forming a carbon–carbon bond with silyl enol ether itself or with external carbon nucleophiles thereby producing **4** [eqn. (1)], we first investigated the α -allylation by treating silyl enol ether **1** with iodosobenzene and trimethylsilyl trifluoromethanesulfonate followed by addition of allyltrimethylsilane. The reaction, however, gave the self coupling product butane-1,4-dione **4** (R = Ph) and the expected allylated ketone **5** was not obtained in any detectable amount (Scheme 1). Use of iodosobenzene and boron trifluoride–diethyl ether also gave **4**.

The above observations led us to change the strategy with the addition of allyltrimethylsilane followed by the addition of the trimethylsilyl enol ether. Thus, allyltrimethylsilane was added to a solution of (PhIO)_n-Me₃SiOTf in dichloromethane. The reaction was monitored by ¹H NMR and the formation of allyliodonium intermediate **6** was indicated by the observation of a downfield shift of the methylene protons from δ 1.8 to 5.0. Addition of silyl enol ether **1** afforded the α -allylated product **5**⁶ in 69% yield (Scheme 2). A similar approach was successfully used for the α -allylation of other silyl enol ethers (Table 1, entries 1–3). The method is regioselective as **8** gave only **9** in 76% yield (Table 1, entry 2). Furthermore, trimethylsilyl ketene acetals of esters and lactones can also be α -allylated using this approach (Table 1, entries 4–6).

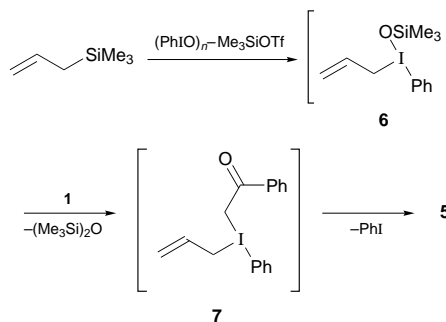
A plausible mechanism for this reaction involves the generation of the reactive I^{III} species PhI(OSiMe₃)OTf⁷ from the reaction of iodosobenzene and trimethylsilyl trifluoromethanesulfonate. Allyltrimethylsilane then forms the initial intermediate **6** which then reacts with the silyl enol ether (e.g. **1**) to give another intermediate **7**. Finally, ligand coupling and reductive elimination of iodobenzene gives the α -allylated product (Scheme 2).

Experimental

Typical Procedure.—To an ice cooled suspension of iodosobenzene (528 mg, 2.4 mmol) in dry dichloromethane (75 ml) under nitrogen was added trimethylsilyl trifluoromethanesulfonate (0.48 ml, 566 mg, 2.4 mmol). To the resulting yellow solution was added allyltrimethylsilane (0.38 ml, 274 mg, 2.4 mmol) which turned the solution colourless. The cooling bath was then removed and the



Scheme 1




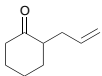

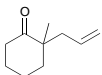
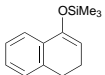
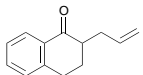

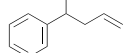

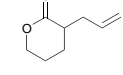

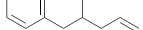
Scheme 2

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†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1997, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

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Table 1 α -Allylation of carbonyl compounds

Entry	Substrate	Product ^a	Yield (%)	(Lit.)
1			52	(8)
2			65	(9)
3			61	(8)
4			70	(10)
5			40	(11)
6			75	(12)

^aSpectral data (IR, ¹H NMR and MS) of all products were in agreement with those previously reported or required.

trimethylsilyl enol ether of acetophenone (**1**) (384 mg, 2.0 mmol) was added. After stirring overnight at room temperature, the reaction mixture, now violet, was washed with water (2 × 25 ml) and saturated aqueous sodium hydrogen carbonate (25 ml). Drying of the organic phase (MgSO₄) followed by removal of solvent *in vacuo* yielded the crude product as a slightly coloured liquid. Purification by flash chromatography on silica gel with ethyl acetate–hexane as eluent gave 208 mg (69%) of 1-phenylpent-4-en-1-one (**5**) as a colourless oil, IR (neat) ν/cm^{-1} 1660, 1705; δ_{H} (CDCl₃, 200 MHz) 2.5 (m, 2 H), 3.1 (t, 2 H), 5.1 (m, 2 H), 5.9 (m, 1 H), 7.5–8.0 (m, 5 H); δ_{C} (100 MHz) 28.1 (C3), 37.7 (C2), 115.3 (C5), 128, 128.5, 133 (aromatic), 136.9 (aromatic or C4), 137.3 (aromatic or C4), 199.43 (C1). Following the above procedure, other silyl enol ethers and

silyl ketene crystals were converted into the corresponding α -allyl-carbonyl compounds (Table 1).

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