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Photoinduced Allylation of Aromatic Carbonyl Compounds by Allylic Stannanes

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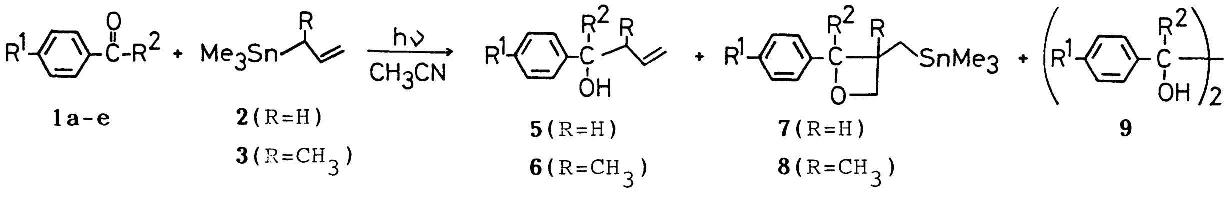
Irradiation of aromatic carbonyl compounds and allyl-, 2-methyl-2-propenyl-, or 3-methyl-2-butenyltrimethylstannanes in acetonitrile afforded δ,γ-unsaturated alcohols as major product. A photoinduced electron transfer mechanism is proposed for the allylations.

The development of versatile methods for forming carbon-carbon bonds is a central objective of synthetic organic chemistry. It has been elucidated that an allylstannane is a useful reagent for the thermal allylation of quinones[1-2] or simple carbonyl compounds[3] in the presence of Lewis acid. Recently, the photochemical carbon-carbon bond forming reactions via photoinduced electron transfer from allylic stannanes to iminium salts,[4] dicyanoethylenes,[5] and quinones[6] have been reported independently by Mariano, Mizuno, and our group. In this paper we describe a new method for the preparation of δ,γ-unsaturated alcohols by photoinduced allylation of aromatic carbonyl compounds by allylic stannanes. This is the first example of the allylation of simple carbonyl compounds by photochemical processes using allylic stannanes. The present photoallylation occurs under neutral conditions, in contrast to the thermal allylation by allylic stannanes that proceeds in the presence of Lewis acid.[1-2]



Scheme 1.

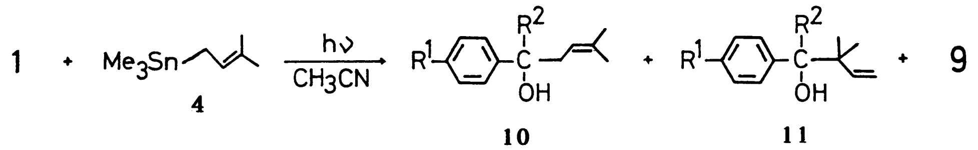
Irradiation of an acetonitrile solution containing benzophenone(**1a**, 0.5 mmol) and allyltrimethylstannane(**2**, 1.0 mmol) with a high pressure mercury lamp through a Pyrex filter for 5 h under nitrogen atmosphere afforded homoallyl alcohol(**5a**, 64%), oxetane(**7a**, 18%), and 1,1,2,2-tetraphenylethane-1,2-diol(**9a**, 10%). These products were isolated by preparative thin layer chromatography. The structures of the products were assigned from spectral properties.[7] Similar irradiations of other aromatic carbonyl compounds(**1b-e**) with allyl-(**2**) and 2-methyl-2-propenyltrimethylstannane (**3**) also afforded the corresponding homoallyl alcohols, oxetanes, and 1,2-diols (Scheme 1). The results are summarized in Table 1. No photoinduced reaction of benzophenone with **2** proceeded in the presence of naphthalene. The addition reactions did not occur in the dark, and benzophenone did not react with **2** even in the presence of BF_3OEt_2.

Table 1. Photochemical Reaction of Aromatic Carbonyl Compounds with Allylic Stannanes in Acetonitrile

Carbonyl compd	Allylic stannane	Product yields/%			Regioisomer ratio(**10**/**11**)[b]
		Alcohol	Oxetane	Pinacol	
1a(R^1=H, R^2=C_6H_5)	**2**	**5a**(64)	**7a**(18)	**9a**(10)	
	3	**6a**(50)	**8a**(23)	**9a**(5)	
	4	**10a**+**11a**(62)	-	**9a**(13)	63/37
1b(R^1=Cl, R^2=C_6H_5)	**2**	**5b**(68)	**7b**(11)	**9b**(10)	
	3	**6b**(53)	**8b**(22)	**9b**(17)	
	4	**10b**+**11b**(62)	-	**9b**(22)	66/34
1c(R^1=Me, R^2=C_6H_4-Me-p)	**2**	**5c**(63)	**7c**(10)	**9c**(10)	
	4	**10c**+**11c**(74)	-	**9c**(20)	67/33
1d(R^1=CN, R^2=Me)	**2**	**5d**(61)	-	**9d**(14)	
	4	**10d**+**11d**(52)	-	**9d**(16)	54/46
1e(R^1=CN, R^2=H)	**4**	**10e**+**11e**(40)	-	**9e**(33)	30/70

*a)*Isolated yields based on the ketone used. *b)*Determined by ^{1}H NMR integration.

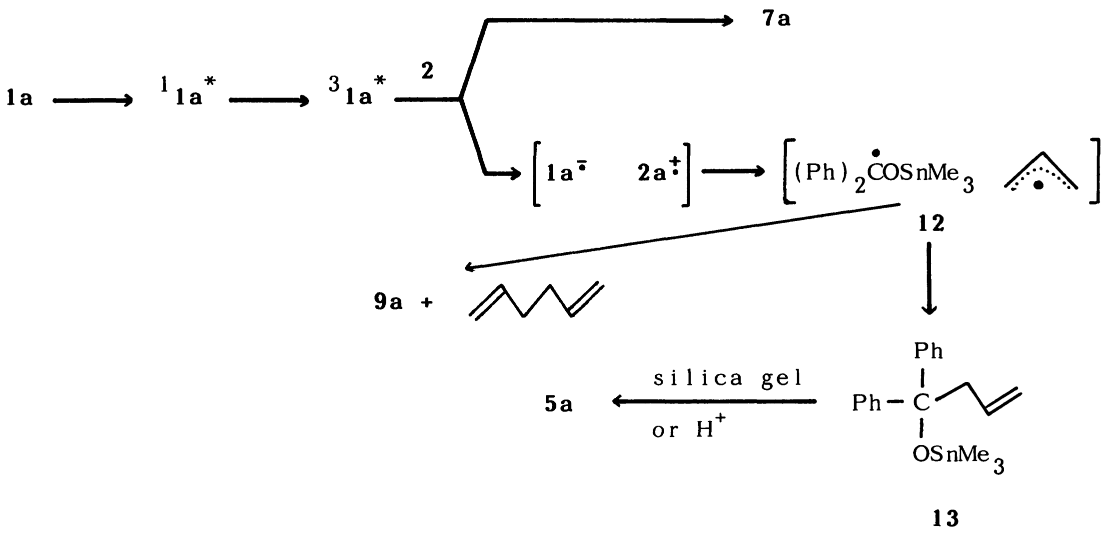
In order to clarify the regiochemistry of introduced allylic moiety, we examined the reaction with 3-methyl-2-butenyltrimethylstannane(**4**). Contrary to the thermal reactions in the presence of Lewis acid,[8] the photoallylation with **4** gave regioisomeric adducts (**10** and **11**) as shown in Scheme 2 and Table 1. The



Scheme 2.

regioisomeric ratio(α vs.γ) was controlled by the steric interaction between R^2 on **1** and allylic moiety. Thus the regioselectivities were low in the photoallylation compared to those in thermal reaction.8) No formation of oxetane in the photoallylation with **4** is probably owing to the lower oxidation potential of **4** as compared to **2**.

From these results, we tentatively propose electron transfer mechanism as shown in Scheme 3 for the photoallylation of benzophenone(**1a**) with allyltrimethylstannane(**2**). The initial step is one-electron transfer from **2** to the excited triplet benzophenone to produce the radical ion pair (**1a**$^{\cdot-}$ **2**$^{\cdot+}$). The nucleophilic attack of the ketyl radical toward **2**$^{\cdot+}$ gives radical pair(**12**) which recombines to give **13**.9) During chromatographic separation, **13** would be hydrolyzed to afford the adduct(**5a**). The radicals escaped from the cage would give rise to 1,1,2,2-tetraphenylethane-1,2-diol(**9a**) and 1,5-hexadiene.10) Oxetane(**7a**) is probably produced via Paterno-Büchi reaction. The details of the reaction mechanism are under investigation.



Scheme 3.

Thus the allylation of benzophenones, acetophenones, and benzaldehydes was achieved by the photochemical reaction with allylic stannanes. No photoinduced electron transfer reaction occurred for benzophenone when allyltrimethylsilane was used instead of allyltrimethylstannane.11)

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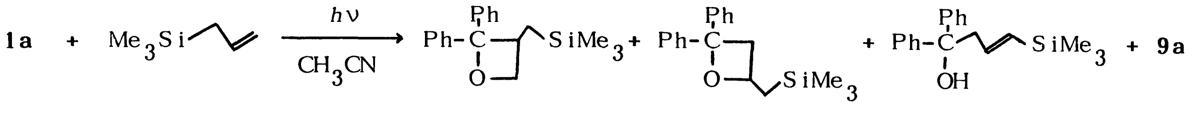
7)Compound **5a**: IR($CHCl_3$) 3550 cm^{-1}(OH); ^1H NMR(CCl_4) δ=2.50(s, 1H), 3.05(d, 2H, J=8 Hz), 5.12(m, 2H), 5.75(m, 1H), and 7.13-7.70(m, 10H). Compound **7a**: IR($CHCl_3$); 3000, 2950, 2870, 1490, 1450, and 970 cm^{-1}; ^1H NMR(270 MHz,$CDCl_3$) δ=0.06(9H, $J_{Sn^{117}-H}$=51 and $J_{Sn^{119}-H}$=53 Hz), 0.79(1H, t, J=13 Hz), 1.03(1H, dd, J=4 and 13 Hz), 3.94(1H, m), 4.31(1H, dd, J=5 and 7 Hz), 4.85(1H, dd, J=5 and 8 Hz), and 7.34-7.54(m, 10H). The orientation of **7a** was confirmed by comparison with that of oxetanes obtained from the photocycloaddition of benzophenone with allyltrimethylsilane(see Ref. 11).

8)The 3-methyl-2-butenyl group in **4** is exclusively introduced at γ-allyl terminus into benzaldehyde in the thermal reaction with **4** in the presence of BF_3OEt_2 (see Ref.3).

9)Unfortunately, in spite of several efforts isolation of **13** was unsuccessful. However, presence of **13** could be estimated by ^1H NMR spectrum of the irradiating mixture of **1a** and **2** in acetonitrile. After removal of the solvent in vacuo, two kinds of methyl protons (δ=0.06 and 0.39) were observed. The signal at δ=0.06 is due to the methyl protons of oxetane **7a**. The signal at δ=0.39 could be assignable to methyl protons of **13** on the basis of their chemical shift, integration, and also of disappearance of the signal after hydrolysis of the irradiating mixture with dilute hydrochloric acid.

10)1,5-Hexadiene could be detected by GLC analysis.

11)Irradiation of benzophenone and allyltrimethylsilane in acetonitrile solution for 16 h afforded isomeric oxetanes(41%; **14**:**15**=95:5), hydrogen abstraction product(**16**; 26%), and 1,1,2,2-tetraphenylethane-1,2-diol(**9a**, 5%).



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