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Regioreversed Allylation in Lewis Acid-mediated and Photochemical Addition Reactions of Unsymmetric α-Diketones with Allylic Stannanes

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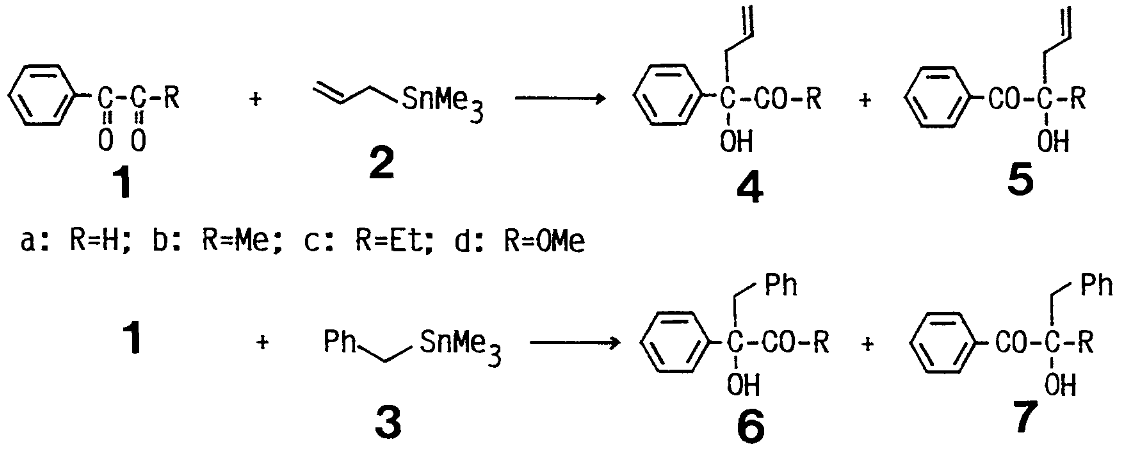
In the photochemical reaction of allyl- and benzyltrimethylstannanes with unsymmetric α-diketones (PhCOCOR), the allylic group was introduced to the benzoyl carbon in high or excellent selectivity, whereas the acyl carbon was allylated either exclusively or predominantly under BF_3-mediated reaction.

The Lewis acid-catalyzed addition of allylic stannanes to aldehydes,1) ketones,2) and other functions3) is powerful carbon-carbon bond-forming reaction. However, the applicable substrates are limited to unhindered compounds.1) Recently, we revealed that the hindered carbonyl compounds such as benzophenone could be successfully allylated under photochemical conditions via single electron-transfer mechanism.4) More recently studies in our laboratories have elucidated that diphenylethanediones (benzils) afforded α-allylbenzoins in high yields under photochemical conditions.5) Thus the photochemical addition of allylic stannanes to carbonyl compounds will also open a carbon-carbon bond-forming reaction. We report here opposite regioselectivities of allylating position of unsymmetric α-diketones under photochemical and Lewis acid-mediated reactions with allylic stannanes.

Reaction of α-diketones (**1**, 0.5 mmol) with allyltrimethylstannane (**2**, 1.0-2.0 mmol) in the presence of BF_3OEt_2 (0.5-1.5 mmol) was performed in dichloromethane at -78 or -5 °C under nitrogen in the dark,6) followed by chromatographic purification (TLC on silica gel) to give a mixture of homoallylic alcohols, **4** and **5**, in high or excellent yields. The products could be easily separated into each isomer through a Lobar column (Merck; LiChroprep Si 60).7) The results are summarized in Table 1. The product ratios were invariant at reaction temperature and equivalent of Lewis acid, but the yield of the products was improved at -5 °C and with excess (2-3 equiv.) of Lewis acid.



The product ratios of **4a**/**5a** and **4b**/**5b** were 0/100 and 23/77, respectively. Thus, the allyl group was introduced exclusively or predominantly into the acyl carbon in the reaction of phenylglyoxal (**1a**) and 1-phenyl-1,2-propanedione (**1b**) with **2** (Runs 1 and 3). This selectivity is interpreted by both steric and electronic effects. It is well known that less hindered carbonyl group is generally allylated in the addition reaction of allylic stannanes with carbonyl compounds under Lewis acid conditions.[8)] This was supported by the fact that the regioselectivity

Table 1. Lewis Acid-mediated and Photochemical Reactions of α-Diketones with Allylic Stannanes

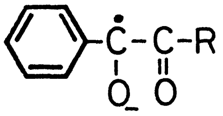
Run	Diketone	Stannane	Condition[a)]	Product ratio[b)] 4(6) / 5(7)	Total yield[c)] %
1	**1a**	**2**	L	0 / 100	90
2			P	90 / 10	25
3	**1b**	**2**	L	23 / 77	79
4			P	76 / 24	89
5	**1b**	**3**	L	-[d)]	-[d)]
6			P	74 / 26	79
7	**1c**	**2**	L	40 / 60	88
8			P	74 / 26	60
9	**1c**	**3**	P	78 / 22	65
10	**1d**	**2**	L	100 / 0	89
11			P	100 / 0	71

a) L: BF_3-mediated reaction at -5 °C in the presence of 2 or 3 equiv. of Lewis acid (see Text); P: Photochemical reaction (see Text).
b) Determined by ^1H NMR. c) Isolated yield. d) No reaction.

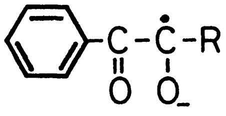
decreased in the order of **1a** (R=H), **1b** (R=Me), and 1-phenyl-1,2-butanedione (**1c**; R=Et) (Runs 1, 3, and 7). Examination of ^{13}C NMR of **1b** at -50 °C in $CDCl_3$ clearly showed that the acetyl carbon (δ 201.11) was stronger electrophile than benzoyl carbon (δ 191.43).[9] Furthermore, the benzoyl carbonyl group was more weakly complexed with BF_3OEt_2 than the acetyl carbonyl from the inspection of ^{13}C NMR of **1b** in the presence of 1 equivalent of BF_3OEt_2 at -50 °C.[10]

Irradiation (λ>400 nm) of α-diketones (**1**, 0.5 mmol) in the presence of **2** (1 mmol) in acetonitrile (10 ml) at ambient temperature afforded again a mixture of homoallylic alcohols, **4** and **5**. The results are summarized in Table 1. In the addition reaction of **1a**, **1b**, and **1c** with **2**, the product ratios (**4**/**5**) were 90/10,[11] 76/24, and 74/26, respectively (Runs 2, 4, and 8). Contrary to Lewis acid conditions (Run 5), benzylation of **1b** by benzyltrimethylstannane (**3**) smoothly proceeded under photochemical conditions to give **6b** and **7b** in a ratio of 74:26 (Run 6). Similar ratio was observed in the reaction with **1c** (Run 9). Thus, the allylic group was selectively introduced to the benzoyl carbon. It is interesting that the opposite regioselectivity to that of Lewis acid-mediated reaction can be achieved under photochemical conditions.

This regioreversed selectivity can be rationalized by the stability of the semidione radical produced from single electron-transfer from **2** to photo-excited **1**.[4,5] Since the semidione radical **A** is more stable than **B**, the allylic radical derived from destannylation from $\mathbf{2}^{\ddagger}$ or $\mathbf{3}^{\ddagger}$ couples predominantly with benzoyl carbon to give **4** or **6** as a major product. As the semidione radical **Ba** (R=H) is less stable than **Bb** (R=Me) or **Bc** (R=Et), higher selectivity was observed in **1a** than **1b** or **1c** (Runs 2, 4, and 8).



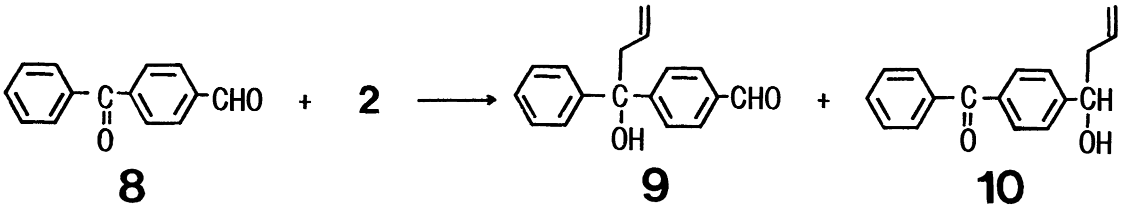
A



B

a: R=H
b: R=Me
c: R=Et

In contrast, methyl benzoylformate (**1d**) afforded exclusively methyl 2-hydroxy-2-phenyl-4-pentenoate (**4d**) under both photochemical and Lewis acid conditions (Runs 10 and 11). This is rationalized that ester-carbonyl group could not be enough activated by BF_3 toward nucleophilic attack by the allylic stannanes.



When 4-benzoylbenzaldehyde (**8**) was treated with **2** at -78 °C using 2 equivalent of BF_3OEt_2, the aldehyde group was exclusively allylated in 90% yield. On the other hand, benzophenone-carbonyl group was also allylated under photochemical conditions (**9**/**10** = 30/70; 65% yield). It is noteworthy that the photochemical procedure can also introduce allyl group into the hindered carbonyl group.

In conclusion, the present photoinduced allylation of unsymmetric diketones using allylic stannanes showed exactly regioreversed selectivity to Lewis acid-mediated one. Therefore, photoallylation will be a new methodology for carbon-carbon bond-forming reaction of hindered carbonyl compounds in the reaction with allylic stannanes.

References

1) For recent reviews, see: Y. Yamamoto, Acc. Chem. Res., 20, 243 (1987); Y. Yamamoto, Aldrichem. Acta, 20, 45 (1987).

2) Y. Yamamoto, T. Komatsu, and K. Maruyama, J. Chem. Soc., Chem. Commun., 1983, 191.

3) A. Hosomi, H. Iguchi, M. Endo, and H. Sakurai, Chem. Lett., 1979, 977; A. Takuwa, Y. Naruta, O. Soga, and K. Maruyama, J. Org. Chem., 49, 1857 (1984); G. E. Keck and E. J. Enholm, ibid., 50, 146 (1985); Y. Naruta, Y. Nishigaichi, and K. Maruyama, Chem. Lett., 1986, 1703.

4) A. Takuwa, H. Tagawa, H. Iwamoto, O. Soga, and K. Maruyama, Chem. Lett., 1987, 1091.

5) A. Takuwa, Y. Nishigaichi, K. Yamashita, and H. Iwamoto, Chem. Lett., 1990, 639.

6) This experiment was performed using normal-addition, i.e., addition of allylic stannane to a CH_2Cl_2 solution of containing Lewis acid and α-diketone.

7) The each isomer exhibited satisfactory spectroscopic data.

8) Y. Yamamoto, N. Maeda, and K. Maruyama, J. Chem. Soc., Chem. Commun., 1983, 742.

9) Assignment of acetyl carbon was established by proton non-decoupling technique.

10) The benzoyl carbon was weakly complexed as noted by downfield shift of the carbonyl signal from 191.43 (control) to 191.68 ppm, while the acetyl signal downfield shifted from 201.11 (control) to 202.70 ppm. Two groups recently have shown spectroscopically the role of Lewis acids in the reaction between allyltins and aldehydes. S. E. Denmark, T. Wilson, and T. M. Willson, J. Am. Chem. Soc., 110, 984 (1988); G. E. Keck, M. B. Andrus, and S. Castellio, ibid., 111, 8136 (1989).

11) Irradiation of **1a** with **2** was carried out at -40 °C, because **1a** partially reacted with **2** at room temperature even in the dark.

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