Boron Trifluoride Mediated Allylation of Aromatic α-Bromoketones by Allyltributyltin

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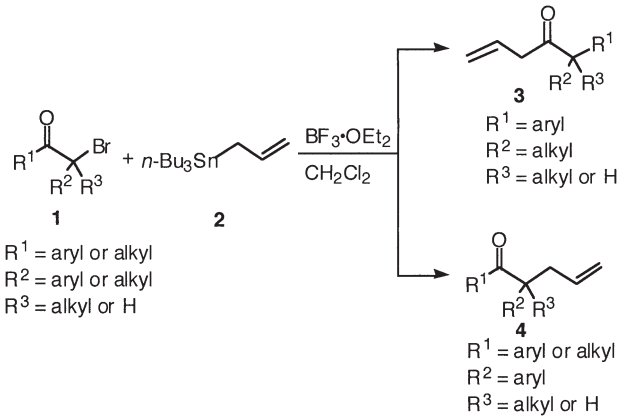
Replacement of bromine atom of aromatic α-brormoketones by allyltributyltin in the presence of BF_3 was described. The reaction proceeds with or without migration of the aryl group, depending on the structure of the α-bromoketone.

Allylation of carbonyl compounds by allyltributyltin is a very useful reaction in organic synthesis.[1,2] The functional groups, adjacent to the carbonyl group, often influence the reaction to cause somewhat complicated results. For example, α-haloketone gives epoxide by the reaction with allyltributyltin in the presence of Pd(0),[3] Pd(II),[4] and *n*-Bu_2SnCl_2-HMPT.[5] Simple replacement of halogen with allyl group occurs in the presence of radical initiator.[3] Aromatic α-haloketone gives allyl ketone or homoallyl alcohol by the reaction with allyltributyltin, in the presence of $SnCl_2$, and it proceeded with migration of the aryl group.[6] Formation of aldehydes in the presence of Pd(0) was also reported.[3] In this paper, we wish to report new type reactions between aromatic α-bromoketone and allyltributyltin.

When aromatic α-bromoketone (**1**) was treated with allyltributyltin (**2**) and $BF_3{\cdot}OEt_2$, two different types of reaction proceeded, depending on the structure of **1**. The reaction pathway is shown in Sheme 1. If R^1 was an aryl group and R^2 was not an aryl group, the reaction proceeded with migration of the aryl group to give allylketone (**3**). Although the reaction of tertiary bromoketone such as **1a** proceeded smoothly to give **3a**, that of secondary bromoketone such as **1d** proceeded slowly, and gave **3a** and considerable amount of unidentified products.[7]



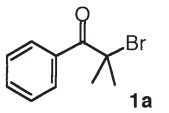
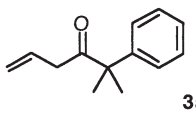
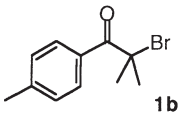
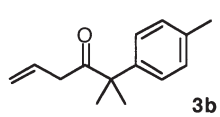
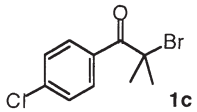
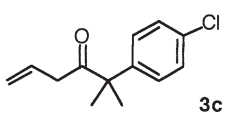
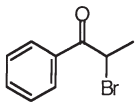
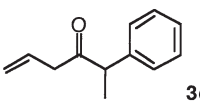
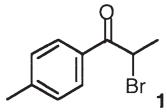
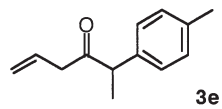
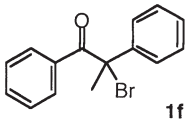
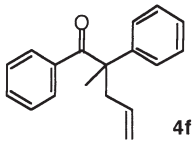
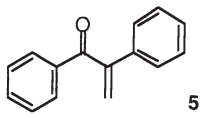
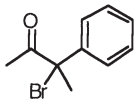
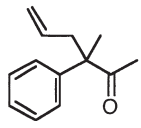
Scheme 1.

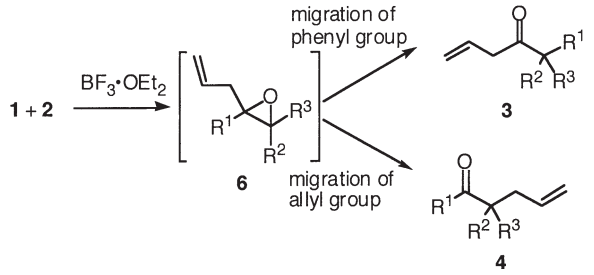
When R^2 was an aryl group, simple replacement of the bromine by allyl group occurred. Results are summarized in Table 1. When neither R^1 nor R^2 was aryl group the replacement of bromine did not occur. For example, 3-bromo-3-methyl-1-phenyl-2-butanone did not react under the similar conditions.

Allyl epoxides such as **6** in Scheme 2 seem to be a plausible intermediate in these reactions. When R^1 is aryl group, it migrates to the adjacent carbon during the course of the isomerization of epoxides to ketones. It means that an aryl group migrates more easily than an allyl group. When R^1 is an alkyl group, the allyl group migrates to give **4**; an allyl group migrates more easily than an alkyl group does.

However, these mechanisms cannot explain the allylation of **1f**. If the reaction proceeds by the mechanisms shown in Scheme 2, **1f** gives epoxide **6f**, and the following migration does not give

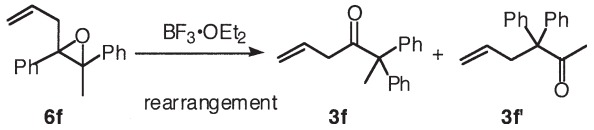
Table 1. Allylation of **1**

Bromoketone	Products	Yield/%
 **1a**	 **3a**	79
 **1b**	 **3b**	86
 **1c**	 **3c**	62
 **1d**	 **3d**	55
 **1e**	 **3e**	66
 **1f**	 **4f**	48
	 **5**	29
 **1g**	 **4g**	74

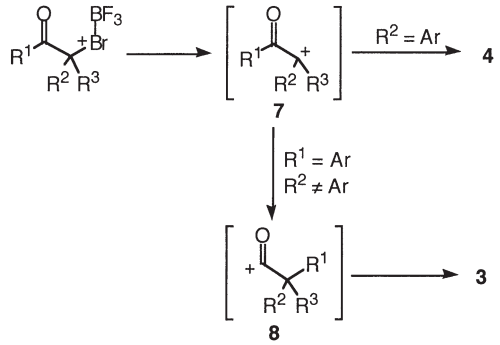


Scheme 2.

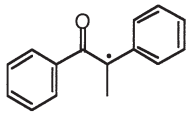
4f, but **3f** and **3f′** (Scheme 3),[8–11] and neither **3f** nor **3f′** was obtained by the allylation of **1f**. The consideration described above leads us to the different mechanisms. One plausible mechanism is as follows (Scheme 4). Initially, BF_3 mediates the formation of carbocation **7**. When R^1 is an aryl group and R^2 is not, the migration of the aryl group occurrs to give the acyl cation **8**. On the other hand, if R^2 is an aryl group, the positive charge of **7** is stabilized by the aryl group, and it is allylated by **2** without rearrangement of the intermediate. The formation of **5** as a byproduct of **3f** is explained as the product of an E1 type reaction of a carbocation like **7**. However, the reasons why **1g** did not give the corresponding alkene are under investigation.



Scheme 3.



Scheme 4.



9

Scheme 5.

Free radical such as **9** is another plausible intermediate in the case of **1f**. If BF_3 or tin can assist the generation of **9**, the subsequent radical substitution with allyltributyltin gives **4f**.

Typical procedure: The procedure of the allylation of **1a** is as follows. To a CH_2Cl_2 (5 ml) solution of **1a** (0.57 g, 2.51 mmol) and allyltributyltin (**2**) (0.99 g, 2.99 mmol), was added a CH_2Cl_2 (1 ml) solution of $BF_3{\cdot}OEt_2$ (0.71 g, 5.00 mmol) at 0 °C. After stirring at room temperature for 6 h, the solution was poured into water, and extracted with ether. The ether layer was washed with 10% aqueous solution of KF, and the solid of *n*-Bu_3SnF was removed. The solution was dried over $MgSO_4$. After removing the solvent under reduced pressure, the residue was purified by column chromatography on silica gel. The yield of **3a** was 79% (0.37 g, 1.97 mmol).

References and Notes

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7 Baba and co-workers have reported (Ref. 6) that α-haloketone **1d** reacted with allyltributyltin (**2**) in the presence of $BF_3{\cdot}OEt_2$ at 0 °C to give 2-bromo-3-phenyl-5-hexen-3-ol. Probably because we used 2-equivalent of $BF_3{\cdot}OEt_2$ at higher temperature, further reaction proceeded to give **3d**.
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