Communication

Photo-allylation and photo-benzylation of carbonyl compounds using organotrifluoroborate reagents

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ARTICLE INFO

ABSTRACT

Allyl- and benzyl-trifluoroborates can be applied to the photoreaction of carbonyl compounds to afford the corresponding alcoholic adducts in acceptable yields via a photo-induced single electron transfer pathway. The results were confirmed from the reaction selectivity and the negative free energy change for the electron transfer process.

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1. Introduction

Organotrifluoroborates are known as air- and water-stable reagents and thus can be stored and handled easily [1]. In addition, some of them are either commercially available or can be readily prepared. They are currently used in a wide variety of applications in synthetic chemistry, transition metal catalyzed coupling reactions [2] (e.g., Suzuki–Miyaura coupling [3]), Lewis acid promoted allylation and other C–C bond formation reactions [1].

The stability of the organotrifluoroborates is due to the tetra-coordination of the boron atom, which is coordinatively saturated, and thus they possess an electron-rich character. Therefore, we anticipated its effectiveness as an electron-donating reagent in reactions via a photoinduced electron transfer (PET) process [4]. Previously, we reported photochemical allylation of carbonyl compounds via PET from allyltin reagents [5]. More recently, we used it in a similar photoreaction with silicon-based reagents [6] wherein extra coordination to the silicon atom (penta- or hexa-coordination) was the key to the effective PET. Here, we report that the photo-induced allylation and benzylation of carbonyl compounds can be further applied successfully to organotrifluoroborates [7].

2. Results and discussion

Because 1,2-dicarbonyl compounds are good substrates for a photoreaction via the PET mechanism with tin and silicon reagents

[5,6], we employed these substrates for a photoreaction with potassium allyl- and benzyl-trifluoroborate **1** and **2** (Scheme 1). Table 1 summarizes the results.

In all reactions conducted here, more than 80% of the substrates were consumed and the corresponding allyl- and benzyl-adducts were obtained in various yields. Methyl benzoylformate **3a** afforded the corresponding adducts in low yields (Entries 1 and 6). We did not obtain any products derived from the ester moiety. Aromatic diketones **3b** and **3c** afforded the corresponding adducts in good yields. Interestingly, phenylpropanedione **3b**, a non-symmetrical diketone, preferentially reacted with the aromatic ketone moiety (Entries 2 and 7), which is less reactive in the thermal reaction [5c]. Quinones **3d** (acenaphthenequinone) and **3e** (9,10-phenanthrenequinone) afforded higher yields of the corresponding adducts (Entries 4, 5, 9 and 10). These reactions proceeded photochemically, confirmed by the fact that no reaction occurred without photoirradiation at room temperature. Considering the reduction potentials of the carbonyl compounds (Table 2) [8,9], the more strongly electron-accepting substrate afforded higher yield of the product. Therefore, the PET mechanism is the most probable.

As stated in our previous reports, that γ-substituted allylic reagents preferentially afforded the α-adduct, which was derived from the reaction at the less crowded terminal of the allylic radical intermediate, is a characteristic feature of the photo-allylation [5a,10]. If the thermal allylation proceeded, the γ-adduct would be preferentially obtained as in the allylborane chemistry [11]. To confirm the mechanism and to expand the scope, the photoreaction of γ-substituted allyltrifluoroborates were attempted.

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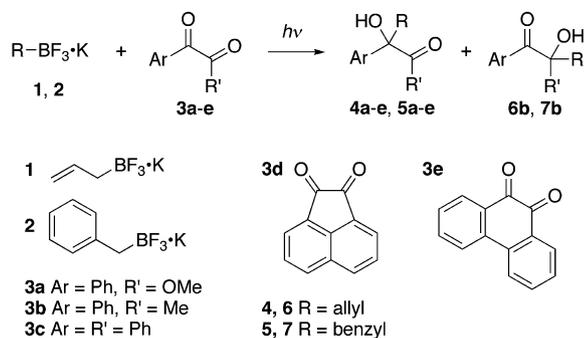
Scheme 1. Photo-induced allylation and benzylation of 1,2-dicarbonyl compounds.

Table 1
Photo-induced allylation and benzylation of 1,2-dicarbonyl compounds.[a]

Entry	Borate	Carbonyl comp.	Yield of **4**, **5** (**6**, **7**)/%
1	**1**	**3a**	21
2		**3b**	49 (19)
3		**3c**	58
4		**3d**	78
5		**3e**	91
6	**2**	**3a**	34
7		**3b**	62 (21)
8		**3c**	74
9		**3d**	90
10		**3e**	90

[a] Reaction conditions: $h\nu$ ($\lambda > 400$ nm), CH_3CN, N_2, 5 h.

Table 2
Reduction potentials, excitation energies, and free energy changes for the PET.[a]

Carbonyl comp.	E^{red}/V[b]	ΔE_T/kcal mol^{-1}	ΔG/kcal mol^{-1}
3a	−1.23	66 [9a]	−13.5
3b	−1.24	54.4 [9b]	−1.7
3c	−1.13	54.2 [9c]	−4.0
3d	−0.91	51.8 [9d]	−6.8
3e	−0.65	51.3 [9d]	−12.1
10	−1.59	68.6 [9c]	−7.7

[a] For PET with **1** (E^{ox} = +1.10 V).
[b] vs. SCE.

Mono-substituted cinnamylborate **8** and di-substituted prenyl borate **9** were employed as shown in Table 3.

Evidently, α-adducts were preferentially obtained as expected in good yields. The present α/γ ratios were similar to those observed in the reactions with tin and silicon reagents. Interestingly, in the case of the substrate **3e**, only α-adducts were obtained in both cinnamyl and prenyl additions (Entries 3 and 6).

The photo-allylation and photo-benzylation was also applied to an aromatic mono-ketone, however the efficiency appreciably decreased. As shown in Scheme 2, photoirradiation ($\lambda > 330$ nm) of benzophenone **10** with **1** in CH_3CN afforded 21% of the corresponding allyl adduct. Photo-benzylation with **2**, in turn, gave 25% of the benzyl-adduct. In both reactions, considerable amount of pinacol was also obtained as a by-product.

Scheme 3 depicts the plausible reaction pathway. As mentioned above, the PET process should be crucial. A photo-excited carbonyl compound is more reducible from its excitation energy than its ground state. Then a PET toward it from an organotrifluoroborate can occur exothermally because the free energy change ΔG for the PET was estimated to be negative by the Rehm–Weller equation [12] given the oxidation potentials of the borates [13]. Table 2 also summarizes the calculated values of ΔG for the reactions of borate **1**, which had less electron-donating potential than **2**. A

Table 3
Regioselectivity in photo-allylation with γ-substituted allyl-trifluoroborates[a]
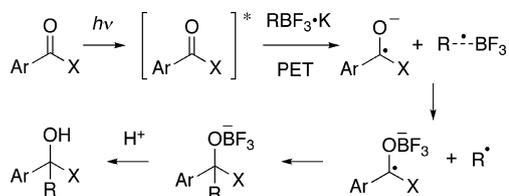

Entry	Borate	Carbonyl comp.	Yields of adducts (α/γ)/%
1	**8**	**3c**	44/9
2		**3d**	47/17
3		**3e**	85/tr
4	**9**	**3c**	65/17
5		**3d**	55/33
6		**3e**	67/tr

[a] Reaction conditions: $h\nu$ ($\lambda > 400$ nm), CH_3CN, N_2, 5 h.
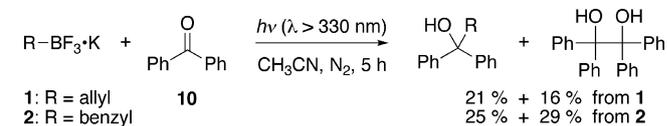
Scheme 2. Reaction of benzophenone.

Scheme 3. Proposed reaction path.

nucleophile such as the substrate and/or the solvent most likely cleaved the radical species of the borate reagent, and the resulting organo-radical coupled with the ketyl radical to give the adduct. The results shown in Table 1 (Entries 2 and 7) and Table 3 are very consistent with this reaction path. The higher reactivity of the benzoyl moiety indicates that the preferred resonance stabilization of the intermediate via the PET path determined the major product, and the a-selectivity of the allyl moiety implies the prior C–B bond cleavage to the C–C bond formation. The fact that a small amount of bibenzyl was observed in the reactions of **2** further supported the radicallic path. Rather low yields of the adduct for the reactions of **3a** and **10** could be attributed to their high triplet energies (Table 2) [9]; these substrates might also have undergone other photoreactions such as hydrogen abstraction [14].

3. Conclusion

Allyl- and benzyl-trifluoroborate reagents are found to be applied successfully to the photo-induced allylation and benzylation reactions of aromatic carbonyl compounds. We are currently working to extend the scope of this photoreaction to other substrates and to apply natural product synthesis, taking advantage of their ionic characters.

4. Experimental

A mixture of a carbonyl compound (**3**, 0.2 mmol) and allyl- and benzyl-trifluoroborate (**1** and **2**, 0.3 mmol) in dry acetonitrile

(10 mL) was degassed by bubbling nitrogen in a Pyrex test tube, which was irradiated for 5 h with a high pressure mercury lamp (300 W) through an appropriate filter solution under a nitrogen atmosphere at room temperature. After concentrating the reaction mixture under reduced pressure, the residue was chromatographed on a silica gel TLC plate to isolate the corresponding products.

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