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In situ generated tris(*p*-bromophenyl)amine radical cation promoted electron transfer reaction of cyclopropyl silyl ethers

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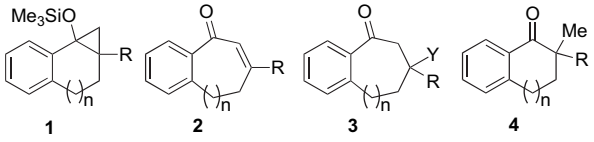
ABSTRACT

Tris(*p*-bromophenyl)aminium hexachloroantimonate and perchlorate were utilized to promote the oxidative ring-opening reaction of cyclopropyl silyl ethers giving ring-expanded ketones. Exploration of salt quantity effect on the reaction allowed us to hypothesize that amine radical cation is regenerated through the oxidation of neutral amine by hexachloroantimonate anion. Based on this hypothesis, amine radical cation was initially generated by the treatment of parent amine with either antimony pentachloride or the mixture of silver perchlorate and molecular iodine, and subsequently reacted with same substrates. The in situ generated amine radical cation was found to promote the reaction, and the expected products were obtained in better yields than via use of the corresponding salt reagents.

1. Introduction

Radical ions that are generated by single electron transfer (SET) processes of neutral organic molecules possess various chemical reactivities.[1,2] For example, radical cations undergo fragmentation, radical addition, dimerization, disproportionation, and reaction with nucleophiles. In addition to these chemical reactions, radical cations can abstract an electron from other molecules to return to their neutral forms, and therefore they are expected to act as SET oxidants. Among radical cations to behave in this manner are triarylamine radical cations, and they in fact promote various oxidative transformations of organic compounds.[3] In many cases, the appropriate amine radical cation salts are generally prepared before conducting reactions, and tris(*p*-bromophenyl)aminium hexachloroantimonate, $(p\text{-}BrC_6H_4)_3NSbCl_6$, has been most frequently used for this purpose. Recently, we also used this radical cation salt to promote oxidative ring-opening reaction of cyclopropyl silyl ethers to give ring-expanded ketones.[4] In addition, in situ generated radical cations are often used to promote SET reactions of other molecules under the electrochemical[1f,5] as well as photochemical conditions.[1b,c,g,4a] We became interested in determining whether the amine radical cation, $(p\text{-}BrC_6H_4)_3N^{\bullet+}$, could be generated in situ by certain chemical oxidants and subsequently used to promote the transformation of cyclopropyl silyl ethers.[6]

In this paper, we first describe the reactions of cyclopropyl silyl ethers with $(p\text{-}BrC_6H_4)_3NSbCl_6$ and tris(*p*-bromophenyl)aminium perchlorate, $(p\text{-}BrC_6H_4)_3NClO_4$, and hypothesize a reaction mechanism involving regeneration of $(p\text{-}BrC_6H_4)_3N^{\bullet+}$ promoted by $SbCl_6$ anion. Then, we report the results of the experiments in which $(p\text{-}BrC_6H_4)_3N^{\bullet+}$ is initially generated by the treatment of $(p\text{-}BrC_6H_4)_3N$ with $SbCl_5$ or the mixture of $AgClO_4$ and I_2, and subsequently used for the reaction with same substrates. Compounds investigated are shown in Chart 1.



1 2 3 4

a (n = 1, R = Me) , **b** (n = 1, R = $(CH_2)_2CH{=}CH_2$),
c (n = 1, R = $(CH_2)_3CH{=}CH_2$), **d** (n = 2, R = Me), Y = Cl, OH

Chart 1.

2. Results and discussion

2.1. Reactions with aminium salt reagents, $(p\text{-}BrC_6H_4)_3NX$

Our preliminary investigation revealed that $(p\text{-}BrC_6H_4)_3NSbCl_6$ promoted the regioselective ring-opening of cyclopropyl silyl ethers **1** to give ring-expanded chloro adducts **3**-Cl, that were finally converted to the ring-expanded enones **2** by treatment with NaOAc.[4] In the reaction with the corresponding ClO_4 salt, **2** is directly produced from **1** without base treatment because of weak nucleophilicity of ClO_4 anion. The results of these salts promoted reactions of **1** performed in CH_2Cl_2, MeCN and benzotrifluoride (BTF) are summarized in Table 1.

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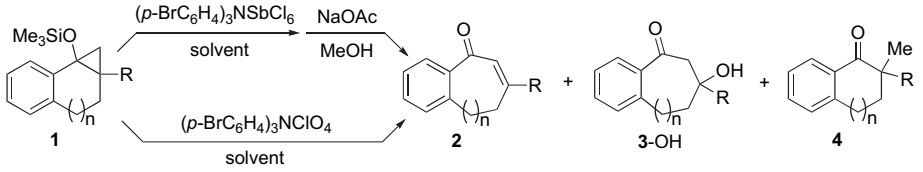
Table 1
$(p\text{-}BrC_6H_4)_3NX$ promoted ring-opening reaction of **1**[a] and subsequent treatment with NaOAc[b]



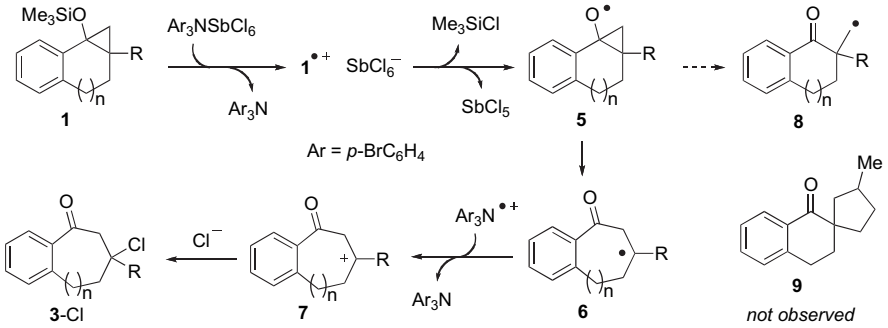
Entry	1	X	Solvent	Salt (equiv vs **1**)	Yields (%)		
					2	**3**-OH[c]	**4**
1[d]	**1a**	$SbCl_6$	CH_2Cl_2	2.0	79	0	Trace
2	**1a**	$SbCl_6$	CH_2Cl_2	1.0	74	0	8
3	**1a**	$SbCl_6$	CH_2Cl_2	0.5	66	2	8
4[d]	**1a**	$SbCl_6$	MeCN	2.0	43	0	Trace
5	**1a**	$SbCl_6$	MeCN	0.5	63	5	4
6[d]	**1a**	$SbCl_6$	BTF	2.0	67	0	Trace
7[d]	**1a**	$SbCl_6$	BTF	1.0	89	0	Trace
8	**1a**	$SbCl_6$	BTF	0.5	67	Trace	2
9	**1a**	$SbCl_6$	BTF	0.1	24	19	2
10	**1b**	$SbCl_6$	CH_2Cl_2	2.0	78	0	4
11	**1b**	$SbCl_6$	CH_2Cl_2	1.0	66	0	10
12	**1b**	$SbCl_6$	CH_2Cl_2	0.7	75	0	6
13	**1b**	$SbCl_6$	CH_2Cl_2	0.5	61	0	10
14[d]	**1b**	$SbCl_6$	BTF	1.0	74	0	1
15	**1b**	$SbCl_6$	BTF	0.5	63	0	4
16	**1b**	ClO_4	CH_2Cl_2	2.0	18	0	0
17	**1b**	ClO_4	CH_2Cl_2	1.0	48	0	26
18	**1b**	ClO_4	CH_2Cl_2	0.5	24[e]	0	36[e]

[a] **1** (0.40 mmol), solvent (8 mL), N_2, room temperature, 30 min.
[b] NaOAc (5.1–6.0 equiv vs **1**), MeOH (8.0 mL), 85 °C, 2–3 h.
[c] Isolated before base treatment.
[d] Reported in Ref. 4b.
[e] Average of two experiments.

In Table 1, we see that **2** was a major product and its yield varied depending on the conditions employed in the reactions with $SbCl_6$ salt (entries 1–15). Hydroxy adduct **3**-OH as well as external bond cleavage product **4** were also obtained although the yields are relatively low. Notably, as the quantity of $SbCl_6$ salt decreased, the formation of **4** became sizeable. Decreasing the salt quantity to 0.1 equiv vs **1a** led to the formation of a small amount of deprotected cyclopropanol (8%), not shown in entry 9. We were rather surprised to find that the yields of **2** did not significantly drop even when 0.5 equiv of the salt was used because the transformation of **1** to **3** in principle requires two electron transfers from **1** (entries 3, 5, 8, 13, 15).[4a,b,7] While the effect of solvent polarity on the reaction is not obvious, it should be noted that BTF could be an alternative solvent for CH_2Cl_2 in these reactions because BTF was proposed as an environmentally benign solvent and potential substitute to CH_2Cl_2 as well as benzene.[4b,8–10] In comparison, use of the ClO_4 salt was somewhat complicated; the yield of **2b** was quite low using 2.0 equiv of the salt (entry 16).[11] Decreasing the quantity of the salt to 1.0 equiv (entry 17) and 0.5 equiv (entry 18) increased the formation of **2b** to a different extent. It is difficult to rationalize the unpredictable yields of **2b**. While the formation of **4b** was negligible in the reactions with 2.0 equiv of the salt (entry 16), it became significant using less than 2.0 equiv of the salt (entries 17 and 18).

On the basis of these results, the following working hypotheses can be made. First, $SbCl_5$ originated from $SbCl_6$ anion oxidizes $(p\text{-}BrC_6H_4)_3N$ to regenerate its radical cation, which is consistent with the fact that $SbCl_5$ can accept two electrons to become $SbCl_3$.[1i,12] If so, $(p\text{-}BrC_6H_4)_3NSbCl_6$ should act as three electron transfer reagent. Thus, about 0.7 equiv of this salt could be a stoichiometric amount to convert **1** to **3**-Cl (see entry 12 in Table 1). Second, **4** is not produced from SET reaction of **1** with the salt reagents. In other words, the precursor of **4** would not be the corresponding primary alkyl radical (will be discussed below).[13]

A plausible reaction mechanism for **1** and $(p\text{-}BrC_6H_4)_3NSbCl_6$ is proposed in Scheme 1. SET between **1** and the aminium salt gives the ion pair of the radical cation of **1** ($\mathbf{1}^{\bullet+}$) and $SbCl_6$ anion ($SbCl_6^-$).[14,15] Subsequently, desilylation of $\mathbf{1}^{\bullet+}$ is assisted by Cl^-, that is, derived from $SbCl_6^-$, to produce cyclopropoxy radical **5** and $SbCl_5$. Regioselective internal-bond cleavage of cyclopropane ring of **5** occurs to produce tertiary alkyl radical **6**. Efficient SET between **6** and



Scheme 1.

(p-$BrC_6H_4)_3N^{\bullet+}$, which comes form either starting $SbCl_6$ salt or in situ generated one by $SbCl_5$ is expected to give stable tertiary carbocation **7**. Nucleophilic capture of **7** by Cl^- gives the adduct **3**-Cl, while hydroxy adduct **3**-OH is formed by the reaction between **6** and H_2O, most probably moisture, under the low concentration of Cl^-.[16] Because of the possibility of external bond cleavage of **5** to give primary alkyl radical **8**,[4,7] we initially expected the formation of diagnostic spirocyclization product **9**, which is formed through a fast 5-*exo* radical cyclization of **8b**, in the reaction of **1b**. However, **9** has been never observed, and therefore we concluded that sequential processes from **5** to **7** via **6** could take place faster than the process from **5** to **8**.

2.2. Reaction with in situ generated amine radical cation, (p-$BrC_6H_4)_3N^{\bullet+}$

Our results and the preceding discussion prompted us to investigate whether methods based on the salt preparations could also generate (p-$BrC_6H_4)_3N^{\bullet+}$ in situ (respective method A and method B in Scheme 2),[17] and the resulting radical cation could promote the transformation of **1**–**2**.

(method A)

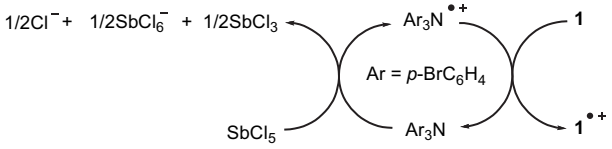
$$2(p\text{-}BrC_6H_4)_3N + 3SbCl_5 \longrightarrow 2(p\text{-}BrC_6H_4)_3NSbCl_6 + SbCl_3$$

(method B)

$$2(p\text{-}BrC_6H_4)_3N + 2AgClO_4 + I_2 \longrightarrow 2(p\text{-}BrC_6H_4)_3NClO_4 + 2AgI$$

Scheme 2.

We first needed to learn how $SbCl_5$ and $AgClO_4/I_2$ interacted with **1** in the absence of (p-$BrC_6H_4)_3N$. When **1b** was treated with $SbCl_5$ (1.1 equiv) in CH_2Cl_2, the reaction became complicated, and **3b**-Cl could not be obtained.[18] In the presence of (p-$BrC_6H_4)_3N$, the expected reaction pathways are shown in Scheme 3.[19] Then, we performed the reaction in which catalytic quantity of (p-$BrC_6H_4)_3N$ (0.1 equiv) was used, and found that the reaction was also complicated, which is probably due to the presence of an excess of $SbCl_5$ (see above). Therefore, we decided to use enough (p-$BrC_6H_4)_3N$ to fully consume $SbCl_5$. Under these conditions, the generation of (p-$BrC_6H_4)_3N^{\bullet+}$ was confirmed by the evolution of characteristic deep blue color (method A).[17]



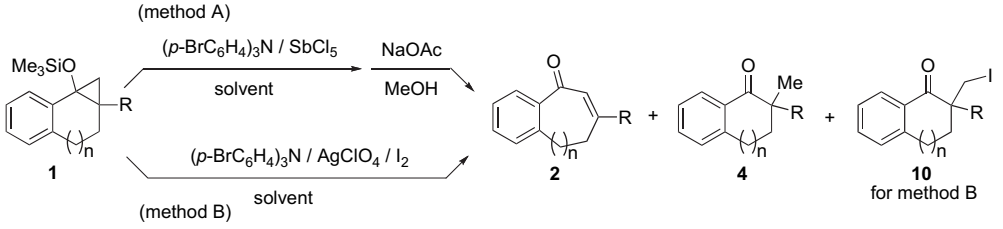
Scheme 3.

We also examined the reaction of **1b** with $AgClO_4$ and I_2 (method B) in CH_2Cl_2 and found the formation of iodo adduct **10b** (24%) and small amount of **2b** (4%).[20]

As described above, neither $SbCl_5$ nor the mixed reagent system of $AgClO_4$ and I_2 promoted the desired regioselective ring-opening reaction of **1**. Therefore, we applied both methods A and B to promote this transformation and the results are summarized in Table 2.

Depending upon the conditions under which $SbCl_6$ salt reagent is prepared (Scheme 2),[1i,17] 1.5 equiv of (p-$BrC_6H_4)_3N$ is enough to

Table 2
In situ generated (p-$BrC_6H_4)_3N^{\bullet+}$ promoted ring-opening reaction of **1**[a] and subsequent treatment with NaOAc[b]



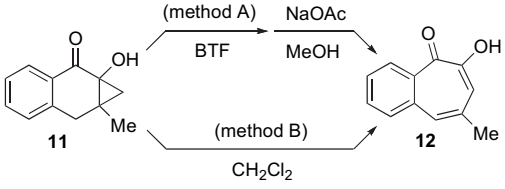
Entry	1	Method	Solvent	Yields (%)			
				2	4	10	2 for salt[c]
1	**1a**	A	CH_2Cl_2	80	0	—	66–79
2[d]	**1b**	A	CH_2Cl_2	58	0	—	61–78
3	**1b**	A	CH_2Cl_2	77	0	—	
4	**1b**	A	MeCN	57	0	—	52[g]
5	**1b**	A	BTF	78	0	—	63–74
6	**1c**	A	BTF	65	0	—	47[h]
7	**1d**	A	BTF	72	0	—	68[h]
8	**1a**	B	CH_2Cl_2	76	0	10	—
9	**1b**	B	CH_2Cl_2	74[f]	0[f]	Trace[f]	18–48
10	**1b**	B	MeCN	35	5[g]	5	—
11[e]	**1b**	B	BTF	56	3[g]	4	—
12[e]	**1b**	B	BTF	74	5[g]	4	—
13[e]	**1b**	B	BTF	45	4[g]	1	—
14	**1c**	B	CH_2Cl_2	47	0	17	—
15	**1d**	B	CH_2Cl_2	47	0	0	—

[a] **1** (0.40 mmol), solvent (8 mL), N_2, room temperature, 30 min; method A: (p-$BrC_6H_4)_3N$ (2.5 equiv), $SbCl_5$ (1.1 equiv); method B: (p-$BrC_6H_4)_3N$ (2.5 equiv), $AgClO_4$ (2.2 equiv), I_2 (1.1 equiv); Before addition of **1**, reagent mixture is stirred for 15–20 min (see Experimental).
[b] NaOAc (5.1–6.0 equiv vs **1**), MeOH (8.0 mL), 85 °C, 2–3 h.
[c] Yields of **2** for salt reagent promoted reactions.
[d] (p-$BrC_6H_4)_3N$ (1.5 equiv).
[e] Stirring of reagent mixture: 1 h, 2 h, 15 h for entries 11–13, respectively.
[f] Average of three experiments (see Experimental).
[g] Reported in Ref. 4a.
[h] Reported in Ref. 4b.

react with 1.1 equiv of $SbCl_5$, and a modest yield of **2b** was obtained in CH_2Cl_2 (entry 2). However, it is not sufficient to consume $SbCl_5$ generated in situ from $SbCl_6^-$ (Scheme 1), and therefore we decided to use 2.5 equiv of $(p\text{-}BrC_6H_4)_3N$, which significantly increased the yield of **2b** (entry 3) and similarly produced **2a** (entry 1). Method A was also applied to other substrates **1c** and **1d** (entries 6 and 7). Generally, the yields of **2** using method A are better than those obtained in $SbCl_6$ salt promoted reactions. Method B in CH_2Cl_2 was also effective affording **2a** in 76% yield (entry 8), and the yield of **2b** was improved compared to that for ClO_4 salt promoted reaction (entry 9). This method was also applied to **1c** and **1d** to give **2c** and **2d** in modest yields (entries 14 and 15). Both methods proved effective in MeCN and BTF (entries 4–7 for method A, entries 10–13 for method B). In the case of method B, because of the lower solubility of the reagents in BTF, the mixture was necessarily stirred for longer times before addition of **1b** (entries 11–13).

Comparison of the two methods reveals that method A provides more consistent results than method B on the basis of the yield of **2** although some results of latter method is compatible with those of former. Also, it should be noted that small though not insignificant amounts of byproducts such as **4** and **10** were obtained occasionally using method B. In principle, the nature of the counter anion should influences the stability of a radical cation in its salt form. In fact, it is known that $SbCl_6^-$ stabilizes the counter radical cations more significantly than other anions, with the latter anions triarylamine radical cations readily react with water.[1i] Thus, avoiding contamination by water is more strictly required when using method B, and this situation should be also considered in salt reagent promoted reactions (see Table 1).

Also, we applied these methods to the oxidative ring-opening reaction of bicyclic keto cyclopropanol **11**, and the expected benzotropolone **12** was obtained although not optimized (Scheme 4).[21] When **11** was subjected to method A using BTF as the solvent, incomplete reaction occurred giving a low yield of **12** (29% based on 53% conversion of **11**) after treatment with NaOAc. On the other hand, method B in CH_2Cl_2 completely consumed **11** and produced **12** in moderate yield (37%).



Scheme 4.

3. Conclusion

As demonstrated above, we have developed a new means of accessing the well-known tris(*p*-bromophenyl)amine radical cation catalyst. Compared to the ordinary salt reagent based method, both methods A and B are practical and effective and even more convenient because isolation of the radical cation salts is not required. This would be advantageous particularly when counter anions that do not stabilize the radical cations are associated, unlike $SbCl_6^-$. Also notably, although not quantitative, we found that most of the amine could be recovered and reused (see Experimental). We are investigating further applications of method A and B to other SET reactions. In principle, these in situ generation methods should be applicable to other oxidizable compounds, and therefore it must promises to be particularly interesting to examine compounds whose radical cations could not be easily isolated but behave as SET oxidants. Investigation related to this issue is also in progress in our group.

4. Experimental section[22]

4.1. Reaction with $(p\text{-}BrC_6H_4)_3NX$

Both $(p\text{-}BrC_6H_4)_3NSbCl_6$ and $(p\text{-}BrC_6H_4)_3NClO_4$ were prepared from $(p\text{-}BrC_6H_4)_3N$, that was obtained by bromination of Ph_3N with Br_2, according to the literature procedures.[17] $(p\text{-}BrC_6H_4)_3NSbCl_6$, 90% yield: mp 141.2–141.8 °C (decomp.) (lit.[17] 141–142 °C, decomp.). $(p\text{-}BrC_6H_4)_3NClO_4$, 55% yield: mp 119.4 °C (decomp.) (lit.[17] 129 °C).

The procedure for $(p\text{-}BrC_6H_4)_3NSbCl_6$ promoted reactions in BTF was previously reported.[4b] Reactions of **1** with $SbCl_6$ salt under various conditions described in this paper were similarly performed. Procedure of the reaction with $(p\text{-}BrC_6H_4)_3NClO_4$ was essentially same as that with $SbCl_6$ salt except for not performing base treatment of the crude reaction products. Details follow.

4.2. Reaction with in situ generated $(p\text{-}BrC_6H_4)_3N^{\bullet+}$

*4.2.1. Reaction of **1b** with $(p\text{-}BrC_6H_4)_3N^{\bullet+}$ generated by $SbCl_5$, represented by entry 3 in Table 2.* To $(p\text{-}BrC_6H_4)_3N$ (482.1 mg, 1.00 mmol) and $SbCl_5$ (0.056 mL, 0.44 mmol) in CH_2Cl_2 (7 mL) was added **1b** (114.7 mg, 0.40 mmol) in CH_2Cl_2 (1 mL) under N_2. The resulting mixture was stirred for 30 min and followed by addition of satd aqueous $NaHCO_3$. Then, filtration was performed, and the filtrate was extracted with Et_2O. The extract was treated with water, satd aqueous $NaHCO_3$, satd aqueous NaCl, and dried over anhydrous $MgSO_4$. The residue obtained after concentration was subjected to column chromatography (CH_2Cl_2/*n*-C_6H_{14}=1/1) to give the mixture of **2a** and **3a**-Cl together with tris(*p*-bromophenyl)amine. Subsequently, the product mixture was refluxed with NaOAc (2.40 mmol) for 3 h in MeOH (8 mL). Then, extraction with Et_2O was performed, and the extract was treated with water, satd aqueous $NaHCO_3$, satd aqueous NaCl, and dried over anhydrous $MgSO_4$. The residue obtained after concentration was subjected to preparative TLC (CH_2Cl_2/*n*-C_6H_{14}=1/1) giving **2b** (65.7 mg, 0.31 mmol, 77%).

Reactions of **1b** under other conditions and reactions of other **1** and **12** were similarly performed. The average recovery of $(p\text{-}BrC_6H_4)_3N$ was 80%.

*4.2.2. Reaction of **1b** with $(p\text{-}BrC_6H_4)_3N^{\bullet+}$ generated by $AgClO_4$ and I_2, represented by entry 9 in Table 2.* To a mixture of $(p\text{-}BrC_6H_4)_3N$ (482.6 mg, 1.00 mmol), $AgClO_4$ (182.4 mg, 0.88 mmol) and I_2 (111.7 mg, 0.44 mmol) cooled at −30 °C was added CH_2Cl_2 (7 mL) under N_2. Then, it was warmed to room temperature and followed by addition of **1b** (114.7 mg, 0.40 mmol) in CH_2Cl_2 (1 mL). The resulting mixture was stirred for 30 min and followed by addition of water. Then, extraction with Et_2O was performed. The extract was treated with water, satd aqueous $Na_2S_2O_3$, satd aqueous $NaHCO_3$, satd aqueous NaCl, and dried over anhydrous $MgSO_4$. The residue obtained after concentration was subjected to column chromatography (CH_2Cl_2/*n*-C_6H_{14}=1/1) to remove tris(*p*-bromophenyl)amine from crude **2b**. Subsequently, crude **2b** was purified by preparative TLC using same solvent system to give **2b** (70.5 mg, 0.33 mmol, 83%). Other two trials of same experiment gave **2b** in 84% and 55% yields.

Reactions of **1b** under other conditions and reactions of other **1** and **12** were similarly performed. The average recovery of $(p\text{-}BrC_6H_4)_3N$ was 97%.

Substrates (**1a**,[4a] **1b**,[4a] **1c**,[4a] **1d**,[4a] **11**[21]) and products (**2a**,[4a] **2b**,[4a] **2c**,[4b] **2d**,[4a] **3a**-Cl,[4a] **3a**-OH,[7b] **4a**,[4a] **10a**,[7b] **12**[21]) are known compounds. Spectral data of **4b**, **10b**, **10c** are presented below. Deprotected alcohols of **1a** and **1b** obtained in the reactions were identified by direct comparison of their ^1H NMR charts to those of the precursor alcohols of **1a** and **1b**. The spectral data of deprotected alcohols of **1a** and **1b** are also reported.

4.2.2.1. ***4b***. Pale yellow oil; IR (Neat) 2924, 1678, 1220 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.20 (s, 3H), 1.56–1.82 (m, 2H), 1.89–2.14 (m, 4H), 2.91–3.06 (m, 2H), 4.90–5.04 (m, 2H), 5.72–5.87 (m, 1H), 7.20–7.32 (m, 2H), 7.42–7.48 (m, 1H), 8.02–8.06 (m, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 22.2, 25.4, 28.4, 33.7, 35.6, 44.5, 114.4, 126.5, 127.9, 128.5, 131.5, 132.8, 138.5, 143.0, 202.0; LRMS (EI) *m/z* (relative intensity) 214 (M^+, 5), 160 (100); HRMS (EI) calcd for $C_{15}H_{18}O$ 214.1358, found 214.1362.

4.2.2.2. ***10b***. Pale yellow oil; IR (Neat) 2904, 1658, 1594, 1214 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.71–2.22 (m, 6H), 2.92–3.05 (m, 2H), 3.44 (d, *J*=10.3 Hz, 1H), 3.59 (d, *J*=10.3 Hz, 1H), 4.91–5.04 (m, 2H), 5.68–5.80 (m, 1H), 7.20–7.34 (m, 2H), 7.45–7.51 (m, 1H), 8.02–8.05 (m, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.8, 25.0, 27.9, 33.0, 33.8, 47.5, 115.0, 126.8, 128.0, 128.7, 131.1, 133.5, 137.5, 142.8, 197.3; LRMS (EI) *m/z* (relative intensity) 340 (M^+, 3), 213 (100); HRMS (EI) calcd for $C_{15}H_{17}IO$ 340.0324, found 340.0321.

4.2.2.3. ***10c***. Brown oil; IR (Neat) 2900, 1636, 1594, 1212 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.23–1.78 (m, 4H), 1.98–2.06 (m, 2H), 2.12–2.22 (m, 2H), 2.91–3.04 (m, 2H), 3.44 (d, *J*=10.0 Hz, 1H), 3.59 (d, *J*=10.3 Hz, 1H), 4.91–5.01 (m, 2H), 5.67–5.80 (m, 1H), 7.22–7.34 (m, 2H), 7.45–7.51 (m, 1H), 8.02–8.05 (m, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 15.2, 22.9, 25.1, 33.0, 34.0, 34.1, 47.7, 114.9, 126.8, 128.0, 128.7, 131.2, 133.5, 138.0, 142.9, 197.6; LRMS (EI) *m/z* (relative intensity) 354 (M^+, 1), 141 (100); HRMS (EI) calcd for $C_{16}H_{19}IO$ 354.0481, found 354.0481.

4.2.2.4. Deprotected alcohol of ***1a***. White solid; mp 82–85 °C, IR (KBr) 3212, 2916, 1448 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.87 (d, *J*=5.7 Hz, 1H), 1.26 (d, *J*=5.7 Hz, 1H), 1.41 (s, 3H), 1.53–1.65 (m, 1H), 1.92–2.01 (m, 1H), 2.18 (br s, 1H), 2.43 (td, *J*=6.4, 14.8 Hz, 1H), 2.59–2.67 (m, 1H), 7.03–7.15 (m, 2H), 7.22–7.28 (m, 1H), 7.70–7.73 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 19.0, 22.0, 26.4, 26.6, 27.0, 58.4, 123.9, 125.3, 126.2, 128.0, 133.1, 140.7; LRMS (EI) *m/z* (relative intensity) 174 (M^+, 48), 118 (100); HRMS (EI) calcd for $C_{12}H_{14}O$ 174.1043, found 174.1045.

4.2.2.5. Deprotected alcohol of ***1b***. White solid; mp 91–93 °C; IR (KBr) 3236, 2912, 1436 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.88 (d, *J*=5.9 Hz, 1H), 1.27 (d, *J*=5.9 Hz, 1H), 1.56–1.79 (m, 2H), 1.92–2.03 (m, 2H), 2.20–2.44 (m, 3H), 2.47–2.71 (m, 1H), 4.95–5.10 (m, 2H), 5.81–5.96 (m, 1H), 7.03–7.15 (m, 2H), 7.22–7.28 (m, 1H), 7.69–7.72 (m, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 21.8, 23.4, 27.0, 30.4, 31.2, 32.4, 58.7, 114.8, 123.8, 125.3, 126.2, 127.9, 132.9, 138.9, 140.8; LRMS (EI) *m/z* (relative intensity) 214 (M^+, 10), 159 (100); HRMS (EI) calcd for $C_{15}H_{18}O$ 214.1358, found 214.1354.

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14. Oxidation potentials ($E^{ox}_{1/2}$ V vs. SCE) of **1** were reported to be +1.53, +1.36, +1.36, and +1.80 for **1a**, **1b**, **1c**, and **1d**, respectively.[4a] Therefore, SET from **1** to $(p\text{-BrC}_6\text{H}_4)_3\text{N}^{\bullet+}$ is estimated to be endergonic on the basis of the oxidation potential of the amine (+1.05 V vs. SCE).[15] This thermodynamic disadvantage would be overcome by the irreversible post-SET process, such as nucleophile assisted desilylation of $\mathbf{1}^{\bullet+}$.[4a,b,7]
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19. Although one may consider the competitive SET of **1** and $(p\text{-BrC}_6\text{H}_4)_3\text{N}$ to $SbCl_5$, SET with $(p\text{-BrC}_6\text{H}_4)_3\text{N}$ should be more efficient than that with **1** based on their oxidation potentials.[14]
20. When **1b** was reacted with $AgClO_4$ in CH_2Cl_2, deprotection took place quantitatively to give the alcohol. Reaction of **1b** with I_2 gave **10b** (25%). Reaction of **1a** with I_2 in THF giving **10a** (91%) was also reported in our previous paper.[7b] Relatively low yield of **10b** might be due to the possibility of reaction of I_2 with olefin moiety of **1b**.
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