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Novel synthesis and properties of 7,9-dimethylcyclohepta[*b*]pyrimido[5,4-*d*]thiophen-8(7*H*),10(9*H*)-dionylium tetrafluoroborate: autorecycling oxidation of some alcohols under photo-irradiation

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Abstract—Three-step reactions starting from 2-chlorotropone with dimethylthiobarbituric acid afforded 7,9-dimethylcyclohepta[*b*]-pyrimido[5,4-*d*]thiophen-8(7*H*),10(9*H*)-dionylium tetrafluoroborate **5**·BF_4^-, which is the isoelectronic compound of the 5-ethyl-3-methyllumiflavinium ion. The X-ray crystal analysis and MO calculation were carried out to clarify the structural characteristics of **5**·BF_4^-. The stability of cation **5** is expressed by the pK_{R+} value, which was determined spectrophotometrically as 5.1. The electrochemical reduction of **5** exhibited low reduction potential at −0.53 (V vs $Ag/AgNO_3$), upon cyclic voltammetry (CV). In a search for the reactivity, reactions of **5**·BF_4^- with some nucleophiles, hydride, diethylamine, thiols, and methanol, were carried out, which revealed that the introduction of nucleophiles to give regio-isomers is dependent on the nucleophile. The photo-induced oxidation reactions of **5**·BF_4^- toward some alcohols under aerobic conditions were carried out to give the corresponding carbonyl compounds in more than 100% yield [based on compound **5**·BF_4^-], suggesting the oxidizing function of **5**·BF_4^- toward alcohols in the autorecycling process. The UV–vis and fluorescence spectra of **5** were studied to suggest the electron transfer from alcohols to the excited **5**.

1. Introduction

Flavins are known to play an important role as cofactors in a wide variety of biological redox reactions. Among these, dehydrogenation reactions represent a major family of processes mediated by a subclass of flavoenzymes known as oxidases. Included in this group are the oxidative transformations of alcohols to carbonyl compounds, of amines to imines, and of fatty acid esters to their α,β-unsaturated analogs.[1] In this context, 5-deazaflavins **1a** has been studied extensively in both enzymatic[2] and model systems[3,4] in the hope of gaining mechanistic insight into flavin-catalyzed reactions. In addition, 5-deaza-10-oxaflavin **1b** [2*H*-chromeno[2,3-*d*]pyrimidine-2,4(3*H*)-dione][5] and 5-deaza-10-thiaflavin **1c** [1-benzothiopyrano[2,3-*d*]pyrimidine-2,4(3*H*)-dione][6] (Fig. 1), in which the nitrogen atom of the 5-deazaflavin **1a** is replaced by an oxygen and a sulfur, respectively, have been synthesized and found to possess a function to oxidize alcohols to the corresponding carbonyl compounds. On the basis of the above observations, we have previously studied convenient preparations of 6,9-disubstituted cyclohepta[*b*]pyrimido[5,4-*d*]pyrole-8(6*H*),10(9*H*)-diones **2a**[7] and 9-methylcyclohepta[*b*]pyrimido[5,4-*d*]furan-8,10(9*H*)-dione **2b**,[8] which are structural isomers of 5-deazaflavin and 5-deaza-10-oxaflavin **1a**,**b**, respectively, and their function in oxidizing some alcohols to the corresponding carbonyl compounds. In relation to these studies, we have investigated the synthesis and properties of heteroazulene-substituted methyl cations[9–12] and tropylium ions.[13] Through the studies, the reduction potentials and pK_{R+} values of these cations were clarified to be strongly dependent on the heteroatoms in the heteroazulene moiety, which is demonstrated to stabilize not only

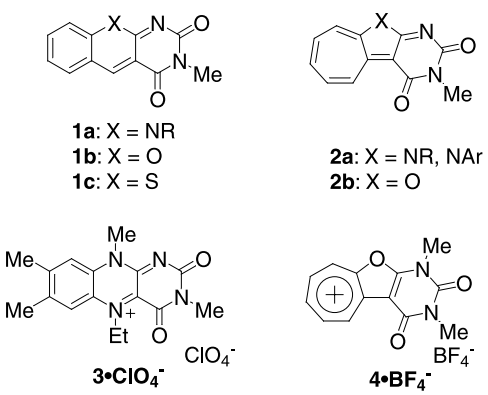

Figure. 1.

Keywords: 7, 9-dimethylcyclohepta[*b*]pyrimido[5,4-*d*]thiophen-8(7*H*),10(9*H*)-dionylium tetrafluoroborate; tropylium cation; oxidizing function; photo-reaction.

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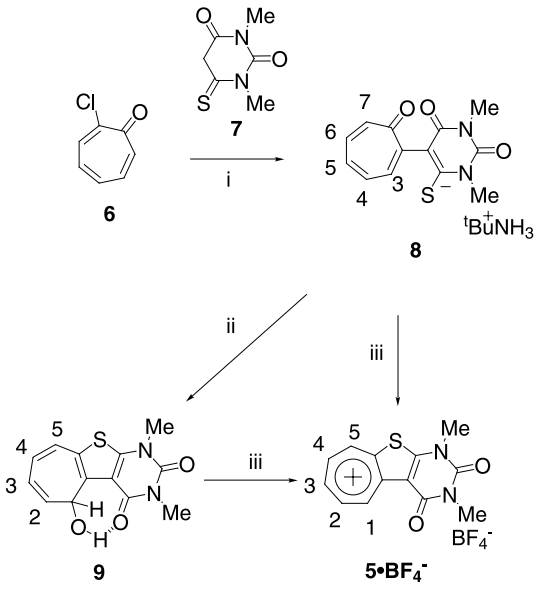
cations but also radical species. Since the photo-induced oxidizing reaction of amines by 3-methyllumiflavin and related 5-ethyl-3-methyllumiflavinium ion **3**,[14] and photo-induced oxidation reaction of *p*-xylene to *p*-tolualdehyde by using the acridinium ion have also been reported,[15–17] we have previously studied the synthesis and oxidizing function of 7,9-dimethylcyclohepta[*b*]pyrimido[5,4-*d*]furan-8(7*H*),10(9*H*)-dionylium tetrafluoroborate **4**·BF_4^-.[18] Thus, it would be expected that 7,9-dimethylcyclohepta[*b*]-pyrimido[5,4-*d*]thiophen-8(7*H*),10(9*H*)-dionylium tetra-fluoroborate **5**·BF_4^- has some chemical and functional analogies to compound **4**·BF_4^-, however, the synthesis of this ring system has not yet been accomplished. Thus, in a search for the reactivity and oxidizing function, we studied the synthesis and properties of novel 7,9-dimethylcyclo-hepta[*b*]pyrimido[5,4-*d*]thiophen-8(7*H*),10(9*H*)-dionylium tetrafluoroborate **5**·BF_4^- for the first time. The structural characterization of **5**·BF_4^- was also carried out by X-ray crystal analysis and MO calculation. The photo-induced autorecycling oxidiation reaction of **5**·BF_4^- toward some alcohols to give the corresponding carbonyl compounds was studied as well. We report herein the results in detail.

2. Results and discussion

2.1. Synthesis and properties

Reaction of 2-chlorotropone **6** with dimethylthiobarbituric acid **7** was performed in CH_2Cl_2 in the presence of Bu^tNH_2 at rt for 24 h to give **8** as a yellow solid, which is contaminated with Bu^tNH_3Cl (Scheme 1). Treatment of solid **8** with 3% HCl and subsequent extraction with CH_2Cl_2 resulted in the formation of cyclized compound **9** (31% yield based on **6**), which afforded 7,9-dimethylcyclo-hepta[*b*]pyrimido[5,4-*d*]thiophen-8(7*H*),10(9*H*)-dionylium tetrafluoroborate **5**·BF_4^- in 96% yield upon treatment with aq. HBF_4 in Ac_2O. Furthermore, reaction of **8** with aq. HBF_4 in Ac_2O gave directly salt **5**·BF_4^- in 50% yield based on **6**. Structures of compounds **8**, **9**, and **5**·BF_4^- are fully characterized on the basis of ^1H and ^{13}C NMR, IR, UV–vis, and mass spectral data as well as elemental analyses. The structural characterization of **5**·BF_4^- was also performed by the X-ray crystal analysis. In the ^1H NMR spectrum, protons of the seven-membered ring of **8** appeared as sharp signals in DMSO-d_6, suggesting the proposed structure. On the other hand, the structural feature of **9** is noteworthy and the signal of the hydroxy proton appears at δ_H 11.10 in the ^1H NMR spectrum. Moreover, the coupling constant between H-1 and H-2 is J 5.0, suggesting that the hydroxy group is located at the pseudo-equatorial position in the cycloheptatriene moiety,[19] and it forms an intramolecular hydrogen bond with the carbonyl-oxygen. The IR spectrum of compound **5**·BF_4^- exhibited no thiocarbonyl group. Although the chemical shift of thiocarbonyl-carbon appears at lower-field by ca. 20 ppm than that of the carbonyl-carbon,[20] the chemical shifts of carbonyl-carbons of **4**·BF_4^- exhibit δ_c 163.1 and δ_c 166.2[18] and those of **5**·BF_4^- exhibit δ_c 159.3 and δ_c 168.8. These values are similar to each other, and this feature suggests no thiocarbonyl group in **5**·BF_4^-. The characteristic band for the counter anion BF_4^- was observed at 1084 cm^{-1} in the IR spectrum of **5**·BF_4^-. The UV–vis spectrum of cation **5** in CH_3CN is shown in Figure 2; the longest wavelength of absorption maximum is 414 nm. These spectroscopic properties as well as the ^1H NMR spectra are in good accordance with the structure of **5**·BF_4^-. The X-ray crystal analysis revealed compound **5**·BF_4^- exhibits two structures in the solid state. These structures resemble each other. Two ORTEP drawings of the structures **I** and **II** are shown in Figure 3, where both have a nearly planar structure. The selected bond lengths of both **I** and **II** are summarized in Table 1. The bond lengths of C1–C2, C3–C4, and C5–C5a are shorter than those of C2–C3, C5a–C10b, and C10b–C1 in structure **I** and **II**, existing in bond-length alternation in the seven-membered ring, as shown in **5-A**,**5-B**, and **5-C** (Fig. 4). In addition, since the bond length of C5a–S6 was longer than that of S6–C6a, the contribution of **5-D** seems to be less important. MO calculation of **5** was carried out by the 6-31G* basis set of the MP2 levels[21] and the selected bond lengths are also



Scheme 1. *Reagents and conditions*: (i) Bu^tNH_2, CH_2Cl_2, rt, 24 h; (ii) 3% HCl; (iii) 42% aq. HBF_4, propanoic anhydride, 0°C, 1 h.

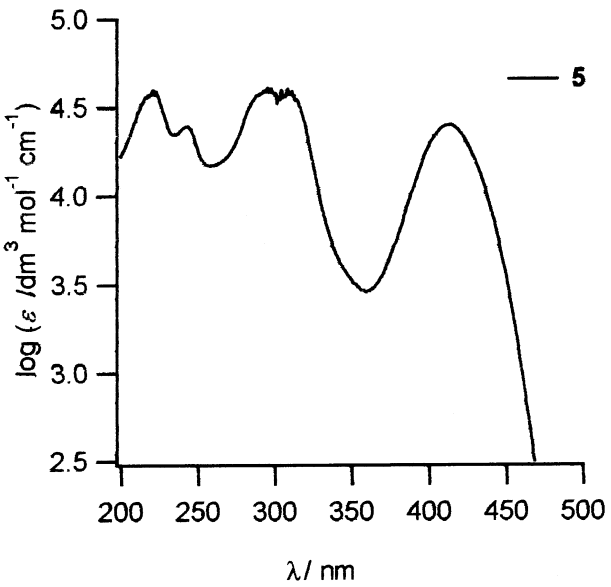


Figure 2. UV–vis spectrum of **5** in CH_3CN.

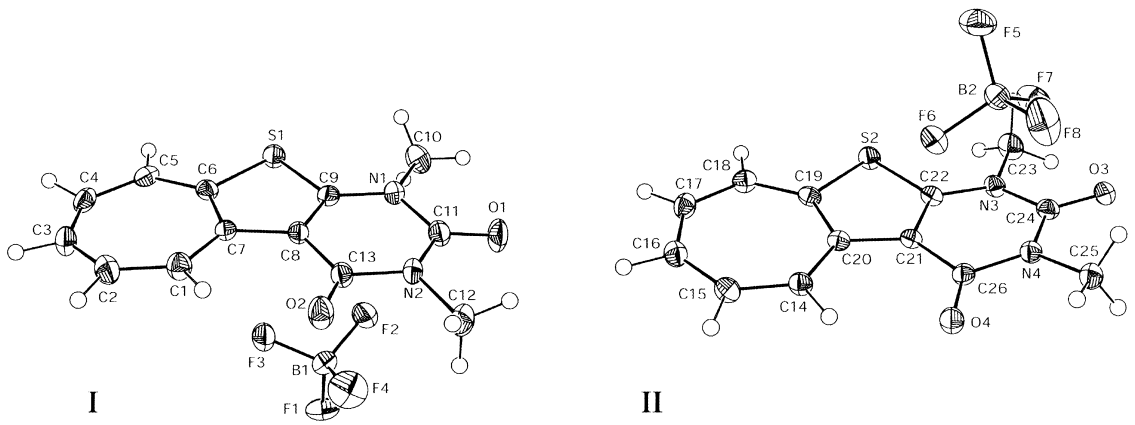


Figure 3. An ORTEP drawing of **5**·BF_4^- with thermal ellipsoid plot (50% probability).

Table 1. Bond lengths of **5**·BF_4^- obtained by X-ray structure analysis and MO calculation

Cation	Method	Bond length[a] (Å)											
		C1–C2	C2–C3	C3–C4	C4–C5	C5–C5a	C5a–C10b	C10b–C1	C5a–S6	S6–C6a	C6a–N7	C6a–C10a	C10a–C10b
5	X-Ray **I**	1.38	1.39	1.38	1.39	1.39	1.43	1.41	1.75	1.72	1.35	1.38	1.43
	X-Ray **II**	1.39	1.40	1.39	1.39	1.39	1.44	1.41	1.75	1.72	1.34	1.38	1.42
5	MP2/6-31G*	1.37	1.41	1.37	1.40	1.36	1.42	1.41	1.82	1.79	1.32	1.37	1.42

[a] The numbering is shown in Figure 4.

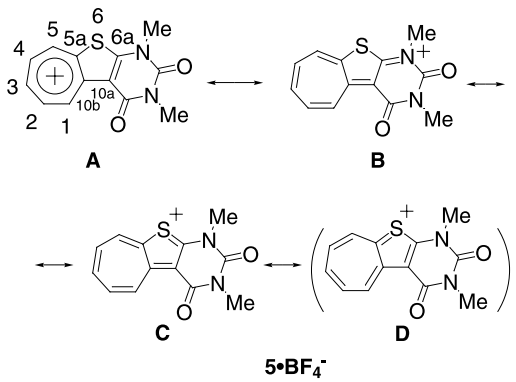


Figure 4.

Table 2. pK_{R+} Values and reduction potentials of cation **5** and reference compounds **2b**, **3**, **4**, **10**, and **11**

Compound	Reduction potentials (V)	
	pK_{R+}	$E1_{red}$
5	5.1	−0.53
2b	–	−1.12[a]
3	4.15[b]	(+0.29)[c]
4[d]	ca. 6.0	−0.58
10[e]	3.9	−0.51
11[f]	6.0	–

Peak potential in V vs. $Ag/AgNO_3$. Reversible process is shown in parentheses. Salts **5**·BF_4^- was used for the measurement; the measurement was made at a scan rate of 0.1 V s^{-1}.
[a] This work.
[b] Ref. 23.
[c] Ref. 14; reversible process.
[d] Ref. 18.
[e] Ref. 24.
[f] Ref. 25.

summarized in Table 1. The bond length alternation obtained by MO calculation for **5** is similar to that obtained by X-ray analysis.

The affinity of carbocations toward the hydroxide ion, expressed by the pK_{R+} value, is the most common criterion of carbocation stability.[22] The pK_{R+} value of cation **5** was determined spectrophotometrically as 5.1 in buffer solutions prepared in 50% aqueous CH_3CN and summarized in Table 2, along with those of reference cations **3**·ClO_4^-,[23] **4**BF_4^-,[18] and **10**,[24] and **11**[25] (Fig. 5). The pK_{R+} value of **5** is larger than that of **3** and tropylium ion **10**, and it is smaller by about 1.0 pH unit than those of **4** and **11**. The reduction potential of **5** was determined by cyclic voltammentry (CV) in CH_3CN. The reduction wave of cation **5** was irreversible under the conditions of the CV measurements; the peak potential is summarized in Table 2, together with those of the reference compounds **2b** and **3**[14] as well as **4**[18] and **10**.[24] The irreversible nature is probably due to the formation of a tropyl radical and its dimerization. This reduction behavior seems to be a typical property of tropylium ions.[26] Since the $E1_{red}$ of **5** is more positive by 0.59 and 0.05 V than that of **2b** and **4**, respectively, thus, **5** would be expected to have higher oxidizing ability than **2b** and **4**. In addition, the $E1_{red}$ of **5** is more negative by 0.82 V than that of **3**, suggesting that the oxidizing ability of **5** would be lower than that of **3**.

2.2. Reactivity of 5·BF_4^-

The reactions of **5**·BF_4^- with some nucleophiles were carried

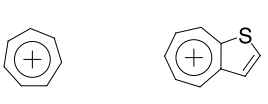


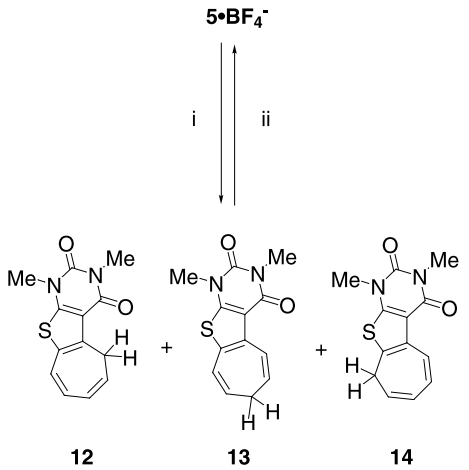
Figure 5.

Table 3. Results for the reaction of **5**·BF_4^- with some nucleophiles

Entry	Nucleophile	Product	Combined yield (%)	Ratio of adduct			Regeneration of cation **5**·BF_4^- (%)
				1-Adduct	3-Adduct	5-Adduct	
1	$NaBH_4$	**12**-**14**	98	**12** (27)	**13** (12)	**14** (61)	86
2	Et_2NH	**15**, **16**	100		**15** (81)	**16** (19)	90
3	PhSH	**17a**-**19a**	100	**17a** (47)	**18a** (41)	**19a** (12)	97
4	BnSH	**17b**-**19b**	100	**17b** (53)	**18b** (34)	**19b** (13)	81
5	MeOH	**20**-**22**	66	**20** (21)	**21** (58)	**22** (21)	93

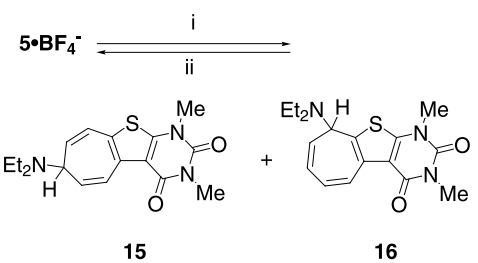
Table 4. ^1H NMR spectral data (500 MHz) of addition products **12**-**16**, **17a**-**19a**, **17b**-**19b**, and **20**-**22**

Compound		H-1	H-2	H-3	H-4	H-5	Remaining signals
12	δ_H	3.52	5.52–5.66	6.15	6.55	6.82	3.43 (Me), 3.53 (Me)
	J	6.6	9.9	5.7	11.0		
13	δ_H	7.37	5.52–5.66	2.45	5.52–5.66	6.60	3.44 (Me), 3.58 (Me)
	J	9.8	6.9	7.1	10.2		
14	δ_H	7.73	6.61	6.14	5.52–5.66	3.08	3.42 (Me), 3.53 (Me)
	J	11.6	5.7	9.7	6.6		
15	δ_H	7.32	5.65	2.74–2.84	5.73	6.55	3.44 (Me), 3.58 (Me) 1.07 (6H, t, *J*=7.1 Hz, CH_3), 2.74–2.84 (4H, m, CH_2)
	J	10.0	5.3	5.3	9.8		
16	δ_H	7.73	6.47	6.13	5.60	4.20	3.42 (Me), 3.55 (Me) 1.11 (6H, t, *J*=7.1 Hz, CH_3), 2.74–2.84 (4H, m, CH_2)
	J	11.6	6.1	10.6	4.7		
17a	δ_H	6.55	5.89	6.22	6.32	6.62	3.43 (Me), 3.50 (Me), 7.12–7.38 (5H, m, Ph)
	J	8.4	10.6	6.6	11.2		
18a	δ_H	7.54	5.79	4.15	5.69	6.58	3.44 (Me), 3.54 (Me), 7.12–7.38 (5H, m, Ph)
	J	10.3	7.1	7.2	10.1		
19a	δ_H	7.87	6.53	6.26	5.76	4.86	3.41 (Me), 3.54 (Me), 7.12–7.38 (5H, m, Ph)
	J	11.3	6.7	10.2	8.2		
17b	δ_H	6.22	5.83	6.19	6.43	6.72	3.40 (Me), 3.46 (Me), 3.60–3.78 (2H, s, CH_2) 7.06–7.31 (5H, m, Ph)
	J	8.6	10.5	6.6	11.4		
18b	δ_H	7.55	5.70	3.70	5.58	6.56	3.43 (Me), 3.54 (Me), 3.60–3.78 (2H, s, CH_2) 7.06–7.31 (5H, m, Ph)
	J	10.3	7.2	7.2	10.1		
19b	δ_H	7.87	6.55–6.59	6.18–6.23	5.62	4.36	3.41 (Me), 3.52 (Me), 3.60–3.78 (2H, s, CH_2) 7.12–7.38 (5H, m, Ph)
	J	11.6	6.4	10.1	7.7		
20	δ_H	6.39	6.18	6.56	6.65	6.99	3.42 (Me), 3.55 (Me), 3.14 (3H, s, OMe)
	J	7.6	10.5	6.8	11.2		
21	δ_H	7.36	5.73	3.58	5.65	6.56	3.44 (Me), 3.57 (Me), 3.42 (3H, s, OMe)
	J	10.2	4.7	4.6	10.1		
22	δ_H	7.90	6.66	6.28	5.74	4.58	3.45 (Me), 3.58 (Me), 3.58 (3H, s, OMe)
	J	11.6	6.2	10.5	5.3		

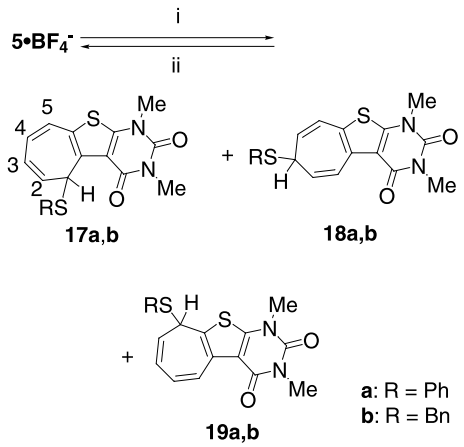


Scheme 2. *Reagents and conditions*: (i) $NaBH_4$, CH_3CN, rt, 1 h; (ii) (a) DDQ, CH_2Cl_2, rt, 1 h; (b) 42% aq. HBF_4, Ac_2O, 0°C, 1 h.

out. The reaction site of the cation showed remarkable difference depending on the nucleophile. The results are summarized in Table 3. Since the products were unstable on SiO_2 and Al_2O_3, regio-isomers could not be separated. Thus, the structural assignments were based on the ^1H and ^{13}C NMR spectra and IR spectra as well as high-resolution mass spectra of the mixtures. The ^1H NMR spectra of the

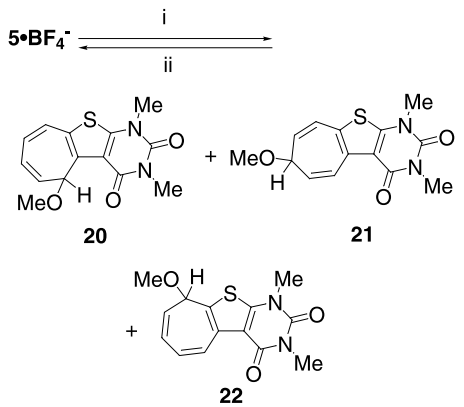


Scheme 3. *Reagents and conditions*: (i) Et_2NH, CH_3CN, rt, 0.5 h; (ii) 42% aq. HBF_4, Ac_2O.



Scheme 4. *Reagents and conditions*: (i) PhSH or BnSH, $NaHCO_3$, CH_3CN, rt; (ii) 42% aq. HBF_4, Ac_2O.

mixtures of each regio-isomer could be assigned by using H-H COSY spectra, and they are summarized in Table 4. Reduction of **5**·BF_4^- with $NaBH_4$ in CH_3CN afforded a mixture of three compounds **12**, **13**, and **14**, and the mixture is oxidized by DDQ to regenerate **5**·BF_4^- in good yield (Scheme 2, Table 3, entry 1). The diethylamine addition of **5**·BF_4^- occurred at 3- and 5-positions to afford a mixture of **15** and **16** in good yield (Scheme 3, Table 3, entry 2). Upon treatment with aq. HBF_4 in Ac_2O, a mixture of **15** and **16** regenerated **5**·BF_4^- in good yield. The reactions of **5**·BF_4^- with benzenethiol and benzylmercaptane were carried out (Scheme 4, Table 3, entries 3 and 4). The addition reactions of **5** occurred at 1, 3, and 5-positions, and two mixtures of three regio-isomers **17a**-**19a** and **17b**-**19b** were obtained in good combined yields, respectively, and the mixtures of addition products regenerated **5**·BF_4^-, respectively, in good yields upon treatment with aq. HBF_4 in Ac_2O. The addition products were obtained preferentially in the order 1->3->5-adducts. In compounds **17a**,**b**, the coupling constants between H-1 and H-2 are large. In compounds **19a**,**b**, the coupling constants between H-5 and H-4 are large, similarly. Thus, these coupling constants suggest that the sulfide groups are located at the pseudo-axial position in the cycloheptatriene moiety (vide supra).[19] Similarly, the reaction of **5** with MeOH afforded a mixture of compounds **20**–**22** in a ratio of 21:58:21 as a pale yellow powder (Scheme 5, Table 3, entry 5). Furthermore, upon treatment with aq. HBF_4 in Ac_2O, a mixture of compounds **20**–**22**



Scheme 5. *Reagents and conditions*: (i) MeOH, $NaHCO_3$, CH_3CN, rt; (ii) 42% aq. HBF_4, Ac_2O.

Table 5. Autorecycling oxidation of some alcohols by **5**·BF_4^- and **4**·BF_4^- under photo-irradiation

Entry	Additive	Alcohol	Carbonyl compounds	Yield[a] (%)
1	**5**·BF_4^-	PhCH(OH)Me	PhCOMe[b]	1627
2	**5**·BF_4^-	Cyclohexanol	Cyclohexanone[b]	2652
3	**5**·BF_4^-	9-Fluorenol	9-Fluorenone	2167
4	**4**·BF_4^-	PhCH(OH)Me	PhCOMe[b]	1860
5	**4**·BF_4^-	Cyclohexanol	Cyclohexanone[b]	3405
6	**4**·BF_4^-	9-Fluorenol	9-Fluorenone	2467

Acetonitrile solution was irradiated by RPR-100 350 nm lamp.
[a] Isolated as 2,4-dinitrophenylhydrazone.
[b] Based on **5**·BF_4^- or **4**·BF_4^-; the yield, called **5**·BF_4^- and **4**·BF_4^- blank, is subtracted from the total yield of ketone in the presence of **5**·BF_4^- or **4**·BF_4^-.

regenerated **5**·BF_4^- in good yield. Thus, the introduction of nucleophiles to give regio-isomers is dependent on the nucleophile.

2.3. Autorecycling oxidation of alcohols

3-Methyllumiflavin and cationic species **3** have been studied to oxidize some amines under photo-irradiation.[14] We have previously reported that compound **4**·BF_4^- undergoes autorecycling oxidation toward some alcohols under photo-irradiation (high pressure Hg lamp). In this context and in a search for functions of **5**·BF_4^-, we examined the oxidation of some alcohols by using **5**·BF_4^-. We have found that compound **5**·BF_4^- has remarkable oxidizing ability toward some alcohols, 1-phenylethanol, cyclohexanol, and 9-fluorenol to give acetophenone, cyclohexanone, and 9-fluorenone, respectively, under aerobic and photo-irradiation conditions (350 nm lamp). The results are summarized in Table 5 (entries 1–3). Oxidizing reaction of the alcohols by using **4**·BF_4^- under similar conditions was also carried out to give similar results to those of **5**·BF_4^- (Table 5, entries 4–6). Although direct irradiation of the alcohols in the absence of **5**·BF_4^- gives the corresponding carbonyl compounds in small amount, they are obtained in more than 100% yield [based on compound **5**·BF_4^- or **4**·BF_4^-] under photo-irradiation in the presence of **4**·BF_4^- and

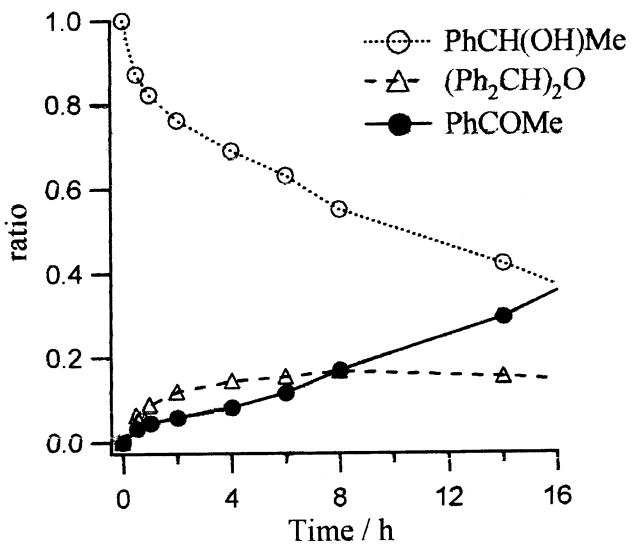


Figure 6. ^1H NMR monitoring of autorecycling oxidation of 1-phenylethanol by **5**·BF_4^-.

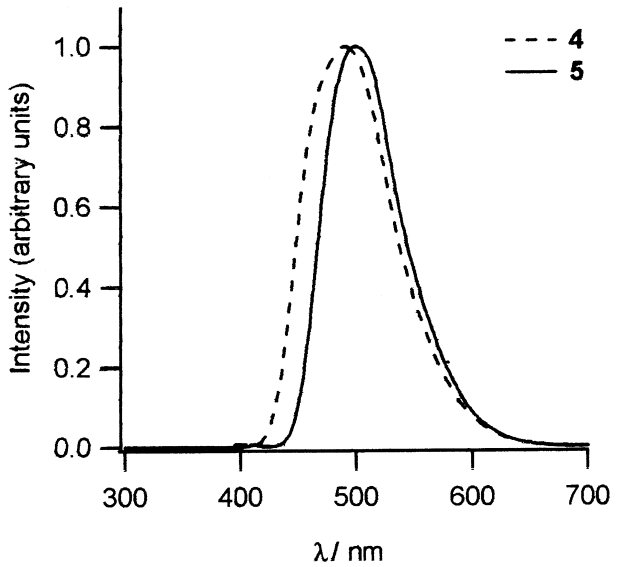
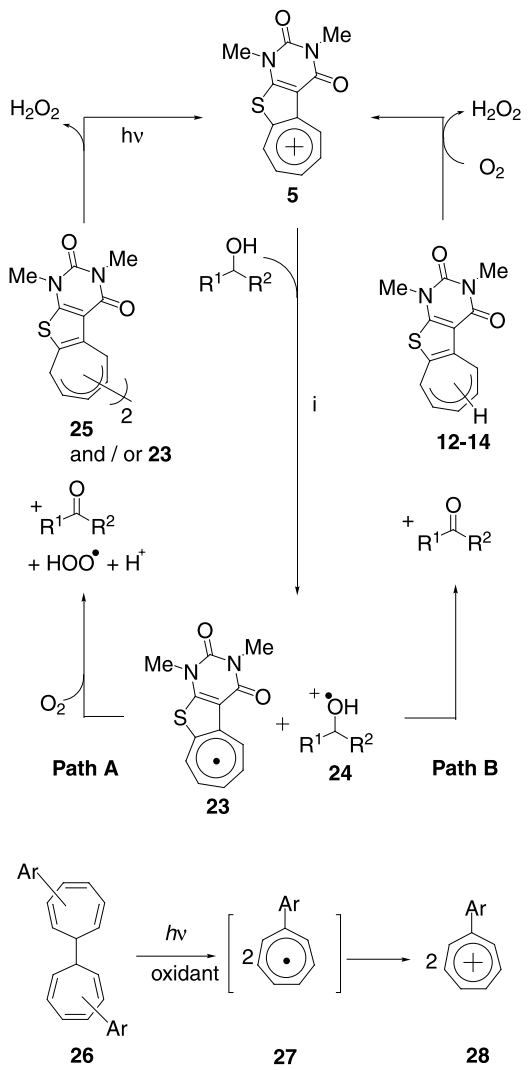


Figure 7. Fluorescence spectra of **4** and **5** in CH_3CN.

5·BF_4^-, and thus, autorecycling oxidation clearly proceeds. Since decoloration of acidic aqueous $KMnO_4$ solution was observed by addition of photo-irradiated solution, the generation of H_2O_2 during the photo-induced oxidation was thus suggested. In the case of 1-phenyethanol, photo-induced oxidation reactions afforded not only acetophenone but also di(1-phenylethyl) ether, which derives from the dehydration of 1-phenyethanol, probably because of the generation of HBF_4. We have reported that **4**·BF_4^- oxidized di(1-phenylethyl) ether, but the rate of oxidation was slower than that of 1-phenylethanol.[18] Thus, the formation of ether catalyzed by HBF_4 reduces the rate of alcohol oxidation. In order to clarify the time dependency of autorecycling oxidation, the ^1H NMR monitoring of the photo-oxidation reaction of 1-phenylethanol in the presence of **5**·BF_4^- was studied. The ratios of alcohol, ketone, and ether were plotted against the reaction time (Fig. 6). As the ratio of alcohol decreases simply, the ratio of ketone increases. In contrast, the ratio of ether is nearly constant.

In a search for the mechanistic aspect of the present photo-induced oxidation reaction, the fluorescence spectrum of **5**·BF_4^- was investigated. The fluorescence spectrum of **5**·BF_4^- in CH_3CN under irradiation of the longest wavelength of the absorption maximum is shown in Figure 7, together with that of **4**·BF_4^-.[18] The wavelengths of the fluorescence of **4** and **5** are 491 and 500 nm, and then, storks-shifts were 94 and 86 nm, respectively. The quantum yield (Φ) for **5** was determined to be 0.054, which is similar to that (0.087) for **4**,[18] by using quinine bisulfate as standard.[27] By gradual addition of 1-phenylethanol to the solution of **5**, quenching of the fluorescence was observed, suggesting interaction of the singlet excited state of **5** with the alcohol as in the case of **4**.[18] Moreover, 9-fluorenol was oxidized to give fluorenone. This fact would suggest that electron-transfer reaction from 9-fluorenol to the exited **5** seems to be favorable rather than direct hydride-transfer reaction, which would generate an antiaromatic fluorenyl cation. Thus, the postulated mechanistic pathways for the present photo-induced oxidation of alcohols are depicted in Scheme 6. The electron-transfer from alcohol to the excited



Scheme 6. *Reagents and conditions*: (i) CH_3CN, rt, aerobic, hv.

cation **5** generates a radical species **23** and **24**; the latter reacts with molecular oxygen to afford a carbonyl compound, hydroperoxyl radical, and proton. The radical species **23** would undergo radical coupling to give dimers **25** (Path A). This feature is suggested by the irreversible $E1_{red}$ of **5** (vide supra). Furthermore, transformation of bitropyl **26** into the corresponding tropylium ion **28** by photo-induced electron transfer (Scheme 6) has been reported.[28] Thus, the radical species **23** as well as its dimers **25** would be oxidized to regenerate cation **5** under photo-irradiation and aerobic conditions. On the other hand, there is an alternative mechanistic pathway (Pathway B), in which compounds **12**–**14** in addition to the carbonyl compound are generated from **23** and **24**; the former compounds are oxidized under aerobic conditions to regenerate **5**. The reduced-products **12**, **13**, and **14**, synthesized by reduction of **5**·BF_4^- with $NaBH_4$, are easily oxidized to give **5**·BF_4^- under aerobic and photo-irradiation conditions in the presence of $NaBF_4$. Thus, autorecycling oxidation would also be possible in this Path B. However, attempted detection of compound **23** and its dimer **25** or compounds **12**, **13**, and **14** was unsuccessful at the present stage. Thus, further investigations are required to clarify the mechanistic aspect of the reaction.

3. Conclusion

Convenient synthesis of novel 7,9-dimethylcyclohepta[*b*]-pyrimido[5,4-*d*]thiophen-8(7*H*),10(9*H*)-dionylium tetrafluoroborate **5**·BF_4^-, which is a sulfur analogue of **4**·BF_4^- and isoelectronic with **1a**,**b** and **2a**,**b** as well as **3**·ClO_4^- and **4**·BF_4^-, was accomplished. The structural characterization of **5**·BF_4^- was performed by the X-ray crystal analysis and MO calculation. The properties of **5**·BF_4^- were clarified by measurement of the pK_{R+} value, reduction potential, UV–vis spectrum, and fluorescence spectrum. Moreover, reactions with some nucleophiles were carried out to clarify reactivities of **5**·BF_4^-. Photo-induced autorecycling oxidation reaction of **5**·BF_4^- toward some alcohols was carried out to afford the corresponding carbonyl compounds in yields more than 100%. Mechanistic aspect of the autorecycling oxidation is postulated as well.

4. Experimental

4.1. General

IR spectra were recorded on a HORIBA FT-710 spectrometer. Mass spectra and high-resolution mass spectra were run on JMS-AUTOMASS 150 and JMS-SX102A spectrometers. Unless otherwise specified, ^{1}H NMR spectra and ^{13}C NMR spectra were recorded on JNM-AL 400, JNM-lambda 500, and AVANCE 600 spectrometers using $CDCl_3$ as the solvent, and the chemical shifts are given relative to internal $SiMe_4$ standard: *J*-values are given in Hz. Mps were recorded on a Yamato MP-21 apparatus and were uncorrected. Photo-irradiation was carried out by using RPR-100 apparatus fitted with 350 nm lamps through a Pyrex filter. The desired dimethylthiobarbituric acid (**7**)[29] was prepared by the methods described in the literature.

4.2. Preparation of 7,9-dimethyl-1,7-dihydro-1-hydroxycyclohepta[*b*]pyrimido[5,4-*d*]thiophene-8(7*H*),10(9*H*)-dione (9)

A solution of **6** (1.69 g, 12 mmol), **7** (2.09 g, 12 mmol), and Bu^tNH_2 (2.19 g, 30 mmol) in CH_2Cl_2 (50 mL) was stirred at rt for 24 h. After evaporation of the CH_2Cl_2 and Bu^tN H_2, the precipitates were collected by filtration and washed with Et_2O to give **8**, which was contaminated with Bu^tNH_3Cl. The resulting crystals were dissolved in 3% HCl and extracted with CH_2Cl_2. The extract was dried over Na_2SO_4 and concentrated in vacuo to give **9** (3.77 mmol, 31%).

4.2.1. *tert*-Butylammonium 1,3-dimethyl-2,6-dioxo-5-(1′-oxocycloheptatrien-2′-yl)-1,3*H*-pyrimidin-4-oxide (8). Orange powder; ^{1}H NMR (500 MHz, DMSO-d_6) δ 1.26 (9H, s, Bu^t), 3.09 (3H, s, Me), 3.56 (3H, s, Me), 6.76 (1H, d, *J*=12.0 Hz, H-7), 6.83 (1H, dd, *J*=11.0, 7.8 Hz, H-5), 6.92 (1H, dd, *J*=11.0, 8.8 Hz, H-4), 7.02 (1H, dd, *J*=12.0, 7.8 Hz, H-6), 7.16 (1H, d, *J*=8.8 Hz, H-3), 7.87 (3H, br s, NH_3); ^{13}C NMR (127.5 MHz) δ 27.0, 27.2, 33.6, 51.0, 109.6, 131.2, 133.7, 133.8, 138.0, 139.9, 152.2, 153.2, 158.1, 173.3, 186.3; IR (KBr) ν 3420, 1705, 1649, 1584 cm^{-1}; MS (FAB) *m*/*z* 277 (M^++H−Bu^tNH_2).

4.2.2. Compound 9. Yellow prisms; mp 139–140°C (from AcOEt); ^{1}H NMR (500 MHz) δ 3.37 (3H, s, Me), 3.50 (3H, s, Me), 4.30 (1H, dd, *J*=5.0, 1.6 Hz, H-1), 5.66 (1H, dd, *J*=9.6, 5.0 Hz, H-2), 5.98 (1H, ddd, *J*=9.6, 5.4, 1.6 Hz, H-3), 6.39 (1H, dd, *J*=11.8, 5.4 Hz, H-4), 6.67 (1H, d, *J*=11.8 Hz, H-5), 11.10 (1H, s, OH); ^{13}C NMR (127.5 MHz) δ 28.9 (Me), 35.1 (Me), 49.1 (C-1), 106.4, 110.1, 122.8 (C-2), 124.1 (C-3), 129.1 (C-4), 130.6 (C-5), 146.4, 150.2, 160.1, 161.0; IR ($CHCl_3$) ν 3385, 1700, 1627, 1606 cm^{-1}; MS (rel. int.) *m*/*z* 276 (M^+, 28.5), 89 (100%). Anal. calcd for $C_{13}H_{12}N_2O_3S$: C, 56.51; H, 4.38; N, 10.14. Found: C, 56.2; H, 4.3; N, 10.1.

4.3. Preparation of 7,9-dimethylcyclohepta[*b*]pyrimido-[5,4-*d*]thiophene-8(7*H*),10(9*H*)-dionylium tetrafluoroborate (5·BF_4^-)

To a stirred solution of **9** (55.2 mg, 0.2 mmol) in propanoic anhydride (2 mL) was added 42% aq. HBF_4 (0.4 mL) dropwise, and the mixture was stirred at 0°C for 1 h. To the mixture was added Et_2O (50 mL) and the precipitates were collected by filtration to give **5**·BF_4^- (66 mg, 96%).

4.3.1. Compound 5·BF_4^-. Dark green powder; mp 201–202°C (from CH_3CN–AcOEt, decomp.); ^{1}H NMR (500 MHz, CD_3CN) δ 3.46 (3H, s, Me), 3.76 (3H, s, Me), 8.59–8.65 (1H, m), 8.79–8.85 (2H, m), 9.43 (1H, d, *J*=9.8 Hz, H-1), 10.34–10.40 (1H, m); ^{13}C NMR (150.9 MHz, CD_3CN) δ 29.2, 37.1, 111.8, 142.2, 143.9, 146.7, 147.8, 150.4, 150.9, 155.9, 156.5, 159.3, 168.8; IR (KBr) ν 1718, 1660, 1084 cm^{-1}; MS (FAB) *m*/*z* 259 (M^+-BF_4). HRMS calcd for $C_{13}H_{11}BF_4N_2O_2S$: 259.0541 ($M-BF_4$). Found: 259.0551 (M^+-BF_4). Anal calcd for $C_{13}H_{11}N_2O_2SBF_4$: C, 45.11; H, 3.20; N, 8.09. Found: C, 44.85; H, 2.96; N, 7.90.

4.4. Direct preparation of 5·BF_4^- from 6 and 7

A solution of **8** (1.837 g, contaminated with Bu^tNH_3Cl), which was prepared by the reaction of **6** (1.69 g, 12 mmol), **7** (2.09 g, 12 mmol), and Bu^tNH_2 (2.19 g, 30 mmol), in propanoic anhydride (20 mL) and 42% aq. HBF_4 (4 mL) was stirred at 0°C for 1 h. To the mixture was added Et_2O (100 mL) and the precipitates were collected by filtration to give **5**·BF_4^- (863 mg, 50%).

4.5. Reaction of 5·BF_4^- with $NaBH_4$

A solution of **5**·BF_4^- (173 mg, 0.5 mmol) and $NaBH_4$ (19 mg, 0.5 mmol) in CH_3CN (10 mL) was stirred at rt for 1 h. To the mixture was added saturated aqueous NH_4Cl solution, and the mixture was extracted with CH_2Cl_2. The extract was dried over Na_2SO_4 and concentrated in vacuo to give a mixture of **12**–**14** (127 mg, 98%) (Table 3, entry 1).

4.5.1. A mixture of 1,7-dihydro-7,9-dimethylcyclohepta-[*b*]pyrimido[5,4-*d*]thiophene-8(7*H*),10(9*H*)-dione (12), 3,7-dihydro-7,9-dimethylcyclohepta[*b*]pyrimido[5,4-*d*]thiophene-8(7*H*),10(9*H*)-dione (13), and 5,7-dihydro-7,9-dimethylcyclohepta[*b*]pyrimido[5,4-*d*]thiophene-8(7*H*),10(9*H*)-dione (14). Pale yellow powder; mp 135–136°C (from EtOH); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ_c 25.9, 27.0, 27.1, 28.1, 28.2, 28.3, 34.3, 34.4, 34.6, 111.8, 111.9, 112.6, 121.4, 121.5, 121.6, 122.5, 122.7, 123.1,

124.0, 124.4, 126.9, 127.0, 127.1, 128.0, 129.5, 129.7, 130.9, 131.3, 133.1, 136.5, 150.7, 150.9, 151.0, 152.6, 155.1, 158.8, 158.9, 159.1 (one carbon overlapping); IR (KBr) ν 1701, 1653 cm^{-1}; MS (FAB) *m/z* 261 (M^++H). HRMS calcd for $C_{13}H_{12}N_2O_2S$: 261.0698 (M^++H). Found: 261.0686 (M^++H). Anal calcd for $C_{13}H_{12}N_2O_2S$: C, 59.98; H, 4.65; N, 10.76. Found: C, 59.3; H, 4.3; N, 10.3.

4.6. Oxidation of a mixture of 12–14

To a stirred solution of a mixture of **12**–**14** (0.5 mmol) in CH_2Cl_2 (5 mL) was added DDQ (176 mg, 0.75 mmol), and the mixture was stirred at rt for 1 h. After evaporation of the CH_2Cl_2, the residue was dissolved in a mixture of acetic anhydride (5 mL) and 42% HBF_4 (1 mL) at 0°C, and the mixture was stirred for another 1 h. To the mixture was added Et_2O (50 mL) and the precipitates were collected by filtration to give **5**·BF_4^- (151 mg, 87%).

4.7. Reaction of 5·BF_4^- with diethylamine

A solution of **5**·BF_4^- (86 mg, 0.25 mmol) and $HNEt_2$ (73 mg, 1.0 mmol) in CH_3CN (5 mL) was stirred at rt for 0.5 h. After evaporation of the CH_2Cl_2 and excess NEt_2, the residue was dissolved in CH_2Cl_2 and filtered. The resulting filtrate was evaporated to give a mixture of **15** and **16** (83 mg, 100%) (Table 3, entry 2).

4.7.1. A mixture of 3-diethylamino-7,9-dimethyl-3,7-dihydrocyclohepta[*b*]pyrimido[5,4-*d*]thiophene-8(7*H*),10(9*H*)-dione (15), and 7-diethylamino-7,9-dimethyl-5,7-dihydrocyclohepta[*b*]pyrimido[5,4-*d*]thiophene-8(7*H*),10(9*H*)-dione (16). Pale yellow powder; mp 145–146°C (from CH_2Cl_2); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 12.6, 13.1, 28.1, 28.2, 34.1, 34.6, 43.8, 44.6, 44.8, 58.7, 60.5, 112.1, 112.3, 117.9, 121.2, 123.4, 125.7, 126.2, 126.5, 128.3, 130.4, 130.7, 132.3, 136.7, 150.9, 151.0, 152.3, 152.8, 158.8, 159.2; IR ($CHCl_3$) ν 1700, 1653 cm^{-1}; MS (FAB) *m/z* 331 (M^+). HRMS calcd for $C_{17}H_{21}N_3O_2S$: 331.1354 (M). Found: 331.1371 (M^+).

4.8. Reaction of 5·BF_4^- with PhSH or $PhCH_2SH$

To a suspension of **5**·BF_4^- (69 mg, 0.2 mmol) and $NaHCO_3$ (168 mg, 2.0 mmol) in CH_3CN (2 mL) was added PhSH (22 mg, 0.2 mmol) [or $PhCH_2SH$ (25 mg, 0.2 mmol)], and the mixture was stirred at rt for 1 h. The mixture was filtered and the filtrate was concentrated in vacuo. After the residue was dissolved in CH_2Cl_2 and filtered to remove $NaBF_4$, the filtrate was evaporated to give a mixture of **17a**-**19a** [or a mixture of **17b**-**19b**] (Table 3, entries 3 and 4).

4.8.1. A mixture of 1,7-dihydro-7,9-dimethyl-1-phenylthiocyclohepta[*b*]pyrimido[5,4-*d*]thiophene-8(7*H*),10(9*H*)-dione (17a), 3,7-dihydro-7,9-dimethyl-3-phenylthio cyclohepta[*b*]pyrimido[5,4-*d*]thiophene-8(7*H*),10(9*H*)-dione (18a), and 5,7-dihydro-7,9-dimethyl-5-phenylthiocyclohepta[*b*]pyrimido[5,4-*d*]thiophene-8(7*H*),10(9*H*)-dione (19a). Yellow oil; ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 28.1, 28.2, 34.3, 34.4, 34.6, 44.4, 45.7, 47.6, 53.4, 111.6, 112.4, 121.7, 123.7, 123.9, 124.7, 124.8, 124.9, 125.6, 126.5, 127.1, 127.3, 127.4, 127.5, 127.8, 128.1, 128.4, 128.6, 128.7, 128.9, 129.0, 129.1, 129.2, 129.3, 129.4, 130.7, 131.0, 132.0, 132.2, 132.3, 132.8, 133.2, 133.5, 134.4, 134.6, 136.5, 150.4, 150.7, 152.9, 154.6, 158.5, 158.6; IR ($CHCl_3$) ν 1708 cm^{-1}; MS (FAB) *m/z* 369 (M^++H). HRMS calcd for $C_{19}H_{17}N_2O_2S_2$: 369.0731 (M+H). Found: 369.0725 (M^++H).

4.8.2. A mixture of 1-benzylthio-1,7-dihydro-7,9-dimethylcyclohepta[*b*]pyrimido[5,4-*d*]thiophene-8(7*H*),10(9*H*)-dione (17b), 3-benzylthio-3,7-dihydro-7,9-dimethylcyclohepta[*b*]pyrimido[5,4-*d*]thiophene-8(7*H*),10(9*H*)-dione (18b), and 5-benzylthio-5,7-dihydro-7,9-dimethylcyclohepta[*b*]pyrimido[5,4-*d*]thiophene-8(7*H*),10(9*H*)-dione (19b). Yellow oil; ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 28.0, 28.1, 28.2, 28.9, 29.3, 29.5, 34.4, 34.5, 34.9, 38.9, 41.6, 111.7, 112.4, 121.8, 123.8, 124.2, 124.5, 124.7, 124.9, 125.8, 126.2, 127.0, 127.1, 127.2, 127.3, 127.4, 127.9, 128.1, 128.2, 128.3, 128.4, 128.5, 128.6, 128.7, 128.8, 128.9, 129.1, 129.4, 130.8, 133.3, 133.5, 136.3, 138.0, 138.4, 141.1, 150.3, 150.7, 152.9, 154.6, 158.7, 158.9 (three carbons overlapping); IR ($CHCl_3$) ν 1699 cm^{-1}; MS (FAB) *m/z*383 (M^++H). HRMS calcd for $C_{20}H_{19}N_2O_2S_2$: 383.0887 (M+H). Found: 383.0912 (M^++H).

4.9. Reaction of 5·BF_4^- with MeOH

To a suspension of **5**·BF_4^- (172 mg, 0.5 mmol) and $NaHCO_3$ (420 mg, 5.0 mmol) in CH_3CN (5 mL) was added MeOH (5 mL) and the mixture was stirred at rt for 2 h. The mixture was filtered and the filtrate was concentrated in vacuo. The residue was dissolved in CH_2Cl_2 and filtered to remove $NaBF_4$. The resulting filtrate was evaporated to give a mixture of **20**–**22** (Table 3, entry 5).

4.9.1. A mixture of 1,7-dihydro-7,9-dimethyl-1-mehtoxycyclohepta[*b*]pyrimido[5,4-*d*]thiophene-8(7*H*),10(9*H*)-dione (20), 3,7-dihydro-7,9-dimethyl-3-methoxy cyclohepta[*b*]pyrimido[5,4-*d*]thiophene-8(7*H*),10(9*H*)-dione (21), and 5,7-dihydro-7,9-dimethyl-5-methoxycyclohepta[*b*]pyrimido[5,4-*d*]thiophene-8(7*H*),10(9*H*)-dione (22). Pale yellow powder; mp 129–130°C (from CH_2Cl_2); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 28.1, 28.2, 28.3, 34.2, 34.5, 34.6, 53.5, 54.8, 56.7, 56.9, 69.0, 74.8, 77.5, 111.8, 112.2, 112.4, 117.6, 120.8, 123.3, 125.4, 125.7, 126.2, 126.5, 126.7, 127.7, 128.7, 128.8, 130.5, 130.6, 130.8, 132.4, 135.8, 136.5, 150.5, 150.7, 150.8, 152.1, 152.9, 154.8, 158.7, 158.9, 159.0; IR ($CHCl_3$) ν 1700, 1652 cm^{-1}; MS (FAB) *m/z* 291 (M^++H). HRMS calcd for $C_{14}H_{14}N_2O_3S$: 291.0803 (M+H). Found: 291.0804 (M^++H).

4.10. Reactions of mixtures of 12–14, 15 and 16, 17a–19a, 17b–19b, and 20–22 with aq. HBF_4

A solution of each mixture (0.5 mmol) in acetic anhydride (10 mL) and 42% aq. HBF_4 (2 mL) was stirred at 0°C for 1 h. To the mixture was added Et_2O (50 mL) and the precipitates were collected by filtration to give **5**·BF_4^- (Table 3, entries 1–5).

4.11. Determination of pK_{R+} value of 5·BF_4^-

Buffer solutions of slightly different acidities were prepared by mixing aqueous solutions of potassium hydrogen phthalate (0.1 M) and HCl (0.1 M) (for pH 2.2–4.0),

potassium hydrogen phthalate (0.1 M) and NaOH (0.1 M) (for pH 4.1–5.9), and KH_2PO_4 (0.1 M) and NaOH (0.1 M) (for pH 6.0–8.0) in various portions. For the preparation of sample solutions, 1 mL portions of the stock solution, prepared by dissolving 4 mg of cation **5**·BF_4^- in MeCN (20 mL), were diluted to 10 mL with the buffer solution (5 mL) and MeCN (4 mL). The UV–vis spectrum was recorded for each cation **5** in 30 different buffer solutions. Immediately after recording the spectrum, the pH of each solution was determined on a pH meter calibrated with standard buffers. The observed absorbance at the specific absorption wavelengths (410 nm) of each cation was plotted against pH to give a classical titration curve, whose midpoint was taken as the pK_{R+} value. The results are summarized in Table 2.

4.12. Cyclic voltammetry of cation 5·BF_4^-

The reduction potential of **5**·BF_4^- was determined by means of CV-27 voltammetry controller (BAS Co). A three-electrode cell was used, consisting of Pt working and counter electrodes and a reference $Ag/AgNO_3$ electrode. Nitrogen was bubbled through a CH_3CN solution (4 mL) of **5**·BF_4^- (0.5 mmol dm^{-3}) and Bu_4NClO_4 (0.1 mol dm^{-3}) to deaerate it. The measurements were made at a scan rate of 0.1 V s^{-1} and the voltammograms were recorded on a WX-1000-UM-019 (Graphtec Co) X–Y recorder. Immediately after the measurements, ferrocene (0.1 mmol) ($E_{1/2}$=+0.083) was added as the internal standard, and the observed peak potentials were corrected with reference to this standard. The compounds exhibited no reversible reduction wave: each of the reduction potentials was measured through independent scan, and they are summarized in Table 2.

4.13. X-Ray structure determination of 5·BF_4^-[†]

Orange prisms, $C_{13}H_{11}BF_4N_2O_2S$, M=346.11, monoclinic, space group $P2_1/c$, a=13.744(7) Å, b=14.771(8) Å, c=14.181(6) Å, β=104.25(4)°, V=2790.4(2) $Å^3$, Z=8, D_c=1.648 g cm^{-3}, crystal dimensions 0.80×0.50×0.30 mm^3. Data were measured on a Rigaku RAXIS-RAPID radiation diffractomater with graphite monochromated Mo Kα radiation. A total 25835 reflections were collected, using the ω–2θ scan technique to a maximum 2θ value of 55.0°. The structure was solved by direct methods and refined by a full-matrix least-squares method using SIR92 structure analysis software,[30] with 437 variables and 3408 observed reflections [I>3.00$\sigma(I)$]. The non-hydrogen atoms were refined anisotropically. The weighting scheme $w=[0.2000\times\sigma_c^2(F_0)+0.0005\times F_0^2+0.1000]^{-1}/(4\times F_0^2)$ gave satisfactory agreement analysis. The final R and Rw values were 0.0290 and 0.0750. The maximum peak and minimum peak in the final difference map were 0.36 and −0.24 $e^-/Å^3$.

4.14. General procedure for autorecycling oxidation of 1-phenylethanol and cyclohexanol catalyzed by 4·BF_4^- and 5·BF_4^-

An CH_3CN (16 mL) solution of compound **4**·BF_4^- or **5**·BF_4^- (0.005 mmol) and 1-phenylethanol or cyclohexanol (2.5 mmol, 500 equiv.) in a Pyrex tube was irradiated by 350 nm lamp under aerobic conditions for 16 h. The reaction mixture was concentrated in vacuo and diluted with ether and filtered. The filtrate was treated with 2,4-dinitrophenylhydrazine in 2N-HCl to give 2,4-dinitrophenylhydrazone. The results are summarized in Table 5.

4.15. Autorecycling oxidation of 9-fluorenol catalyzed by 4·BF_4^- and 5·BF_4^-

An CH_3CN (16 mL) solution of compound **4**·BF_4^- or **5**·BF_4^- (0.005 mmol) and 9-fluorenol (2.5 mmol, 500 equiv.) in a Pyrex tube was irradiated by 350 nm lamp under aerobic conditions for 16 h. The reaction mixture was concentrated in vacuo and separated by column chromatography on SiO_2. The results are summarized in Table 5.

4.16. ^{1}H NMR monitoring of autorecycling oxidation of 1-phenylehtanol catalyzed by 5·BF_4^-

An CD_3CN (0.5 mL) solution of compound **5**·BF_4^- (1.73 mg, 0.005 mmol) and 1-phenylehtanol (30.5 mg, 0.25 mmol) in NMR tube was irradiated by 350 nm lamp under aerobic conditions. The NMR measurement was carried out at intervals, and the ratios of 1-phenylethanol, acetophenone, and di(1-phenylethyl) ether were plotted against them (Fig. 6).

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