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Novel synthesis and properties of 7,9-dimethylcyclohepta[b]-pyrimido[5,4-*d*]furan-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 barbituric acid afforded novel 7,9-dimethylcyclohepta[b]pyrimido[5,4-*d*]-furan-8(7*H*),10(9*H*)-dionylium tetrafluoroborate (**9**·BF_4^-), which is the isoelectronic compound of the 5-ethyl-3-methyllumiflavinium ion. The stability of cation **9** is expressed by the pK_{R+} value, which was determined spectrophotometrically, as ca. 6.0. The electrochemical reduction of **9** exhibited low reduction potential at −0.58 (V vs $Ag/AgNO_3$), upon cyclic voltammetry (CV). In a search for the reactivity, reactions of **9**·BF_4^- with some nucleophiles, hydroxide, hydride, amines, thiols, and methanol, were carried out to exhibit that the introduction of nucleophiles is dependent on the nucleophile itself. The photo-induced oxidation reactions of some alcohols catalyzed by **9**·BF_4^- under aerobic conditions were carried out to give the corresponding carbonyl compounds in more than 100% yield [based on compound **9**·BF_4^-], suggesting the oxidizing function of **9**·BF_4^- toward alcohols in the autorecycling process. The UV–vis and fluorescence spectra of **9** were studied to suggest the electron transfer from alcohols to the excited **9**.

1. Introduction

The importance of fused uracils, which are common sources for the development of new potential therapeutic agents, is well known.[1,2] Among these, flavins are known to play an important role as cofactors in a wide variety of biological redox reactions. Dehydrogenation reactions represent a major family of processes mediated by the 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.[3] In this relation, 5-deazaflavins (**1a**) has been studied extensively in both enzymatic[4] and model systems[5,6] in the hope of providing 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, Fig. 1), in which the nitrogen atom of the 5-deazaflavin (**1a**) is replaced by an oxygen, has been synthesized and found to possess a strong function to oxidize alcohols to the corresponding carbonyl compounds.[7] 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**) and 9-methylcyclohepta[*b*]pyrimido[5,4-*d*]-furan-8,10(9*H*)-dione (**2b**), which are structural isomers of 5-deazaflavin (**1a**) and 5-deaza-10-oxaflavin (**1b**), and their function in oxidizing some alcohols to the corresponding carbonyl compounds.[8] In relation to the studies, we have investigated the synthesis and properties of heteroazulene-substituted methyl cations[9–12] and tropylium ions.[13] In 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. Moreover, the heteroazulenes are demonstrated to stabilize not only cations but also radical species. On the other hand, the photo-induced oxidizing reaction of amines by 3-methyllumiflavin (**3**) and its related 5-ethyl-3-methyllumiflavinium ion (**4**) has been investigated to clarify the mechanistic aspects.[14] In addition, photo-induced oxidizing reaction by using the acridinium ion have also been reported.[15–17] The oxidation of *p*-xylene to *p*-tolualdehyde was initiated by

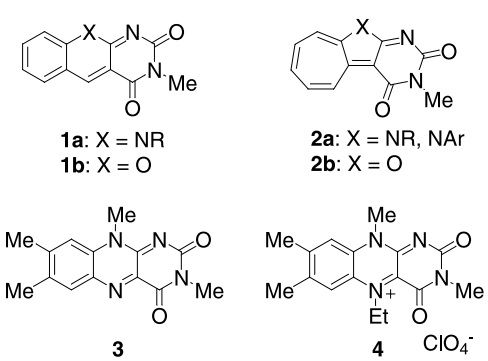

Figure 1.

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

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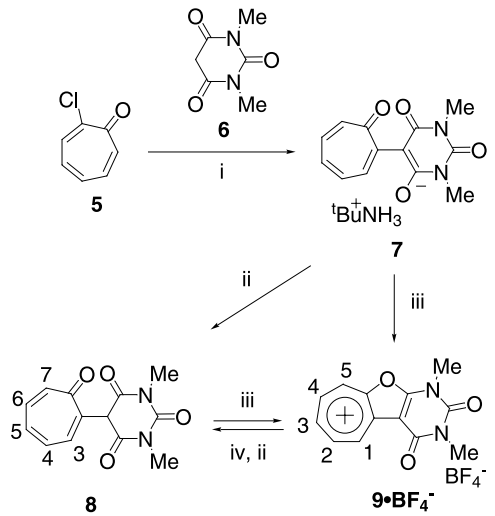


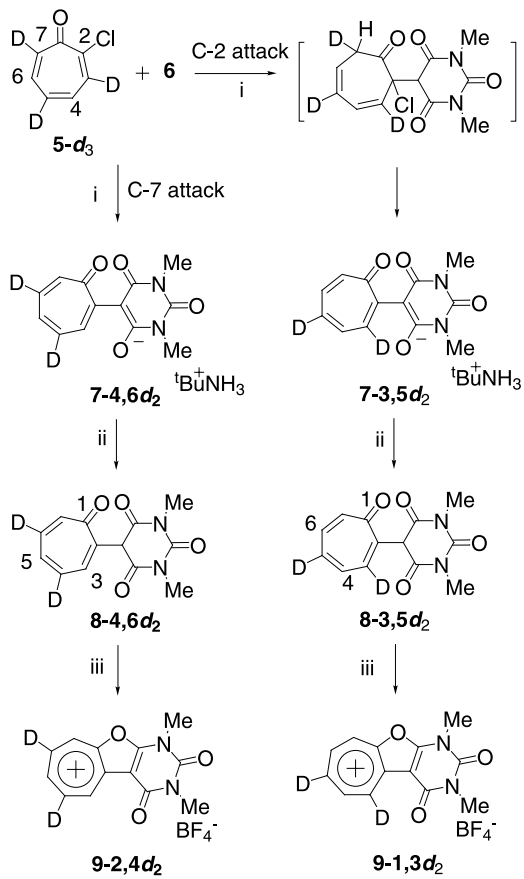
Scheme 1. *Reagents and conditions*: (i) Bu^tNH_2, CH_2Cl_2, rt, 24 h; (ii) 3% HCl; (iii) 42% aq. HBF_4, propanoic anhydride, 0°C, 1 h; (iv) aq. $NaHCO_3$, CH_3CN, rt, 6 h.

photo-induced electron transfer from *p*-xylene to the singlet excited state of the 10-methyl-5-phenylacridinium ion under photo-irradiation.[17] Thus, in search for the reactivity and oxidizing function of uracil-annulated heteroazulenes, we studied the synthesis and properties of novel 7,9-dimethylcyclohepta[*b*]pyrimido[5,4-*d*]furan-8(7*H*),10(9*H*)-dionylium tetrafluoroborate (**9**·BF_4^-). The photo-induced oxidizing reaction of **9**·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

Reactions of 2-chlorotropone (**5**) with dimethylbarbituric acid (**6**) was performed in CH_2Cl_2 in the presence of Bu^tNH_2 at rt for 24 h to give **7** as yellow solid, which is contaminated with Bu^tNH_3Cl (Scheme 1). The solid of **7** was dissolved in 3% HCl and extracted with CH_2Cl_2 to give **8** as colorless prisms in 94% yield. Compounds **7** and **8** were treated with aq. HBF_4 in Ac_2O at 0°C for 1 h to result in the formation of 7,9-dimethylcyclohepta[*b*]pyrimido[5,4-*d*]-furan-8(7*H*),10(9*H*)-dionylium tetrafluoroborate (**9**·BF_4^-) in 91 and 96% yields, respectively. Compound **9**·BF_4^- was easily hydrolyzed by aq $NaHCO_3$ to regenerate **8** in good yield. Nucleophilic substitution onto a tropone carrying a mobile substituent is known to take place at C-2 (usual substitution) or at C-7 (unusual substitution) to give 2-substituted tropones.[18] In order to confirm this point and the cyclization pathways to give **9**·BF_4^-, the reaction of 2-chloro-3,5,7-trideuteriotropone **5**-d_3 with **6** was studied (Scheme 2). Reaction of **5**-d_3 with **6** afforded a mixture of **7-4,6d$_2$** and **7-3,5d$_2$** in a ratio of 9:1, suggesting that the nucleophilic attack of **6** occurred at both C-7 and C-2 of the tropone nucleus in that ratio. Treatment of a mixture of **7-4,6d$_2$** and **7-3,5d$_2$** with 3% HCl afforded **8-4,6d$_2$** and **8-3,5d$_2$** in a ratio of 9:1. The mixture was treated with aq. HBF_4 in Ac_2O to afford a mixture of **9-2,4d$_2$**·BF_4^- and **9-1,3d$_2$**·BF_4^- in a similar ratio. The structures and the ratios



Scheme 2. *Reagents and conditions*: (i) Bu^tNH_2, CH_2Cl_2, rt, 24 h; (ii) 3% HCl; (iii) 42% aq. HBF_4, propionic anhydride, 0°C, 1 h.

of the deuterated compounds were based on the HRMS and assigned ^{1}H NMR spectra (Section 4). Thus, the cyclization reaction of **8** giving furan moiety is also confirmed to proceed via C-1 attack, but not C-3 attack, on the tropone nucleus (Scheme 2).

2.2. Properties

Compounds **7**, **8**, and **9**·BF_4^- were fully characterized on the basis of IR, UV–vis, mass spectral data as well as elemental analyses or X-ray structure analysis. In the ^{1}H NMR spectrum, protons of the seven-membered ring of **7** appeared as sharp signals in DMSO-d_6. On the contrary, these protons of **8** exhibited broad signals in DMSO-d_6, $CDCl_3$, and CD_3CN and an active methyne-proton (H-5 in the barbituric acid moiety) signal appeared at δ 4.16 in $CDCl_3$. In CD_3OD, these protons of **8** exhibited sharp signals and the active methyne-proton signal disappeared. The features show that compound **8** exists as the keto-form in DMSO-d_6, $CDCl_3$, and CD_3CN and as the enol-form in CD_3OD. In addition, broad signals of the seven-membered ring protons of **8** are probably due to the large steric hindrance between the carbonyl functions of barbituric acid and the troponyl moieties restricting free rotation in the NMR time scale. Moreover, the tautomeric change depending on the solvent was confirmed by ^{13}C NMR and UV–vis spectra. In a ^{13}C NMR spectrum of **8**, an active methyne-carbon signal appeared at δ 57.2 ($CDCl_3$), although this carbon signal appeared at δ 97.3 in CD_3OD. Other carbon signals exhibited slight change. The signal of the

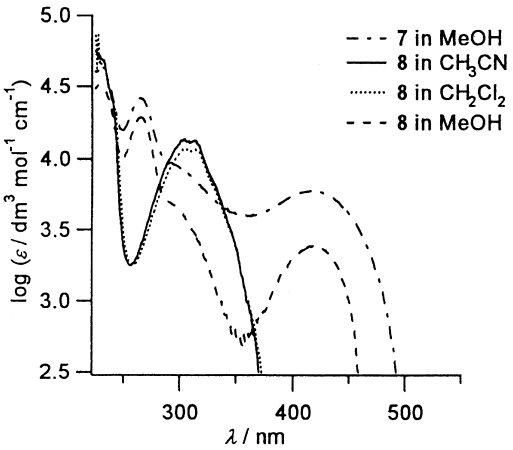


Figure 2. UV–vis spectra of **7** and **8**.

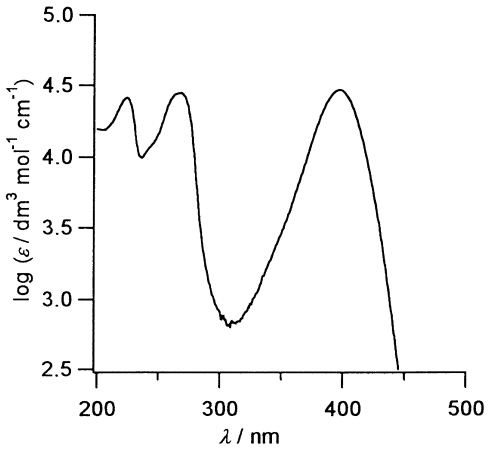


Figure 4. UV–vis spectrum of **9** in CH_3CN.

corresponding carbon of **7** appeared at δ 89.5 (DMSO-d_6), and thus, the structure of **8** in CD_3OD exists as the enol form. UV–vis spectra of **8** in CH_3CN and CH_2Cl_2 as well as **7** and **8** in MeOH are shown in Figure 2. The spectra of **8** in CH_3CN and CH_2Cl_2 are similar, while the spectrum of **8** in MeOH shows remarkable change. In contrast, the spectra of **7** and **8** in MeOH are similar, suggesting that **8** exists as the enol-form in MeOH. Although the single crystal of **9**·BF_4^- could not be obtained, the X-ray crystal analysis clarified the structural details of **8**, and the ORTEP drawing is shown in Figure 3. The troponyl moiety is nearly planar. The angles of C2–C8–C9, C2–C8–C10, and C9–C8–C10 are 111.8, 110.3, and 115.2°, respectively. These values show that the C8 atom exists in sp^3 hybridization. The dihedral angle of H–C8–C2–C1 is 179.2°, suggesting that the troponyl moiety and the barbituric acid moiety are nearly perpendicular to each other.

The characteristic band for the counter anion BF_4^- was observed at 1084 cm^{-1} in the IR spectrum of **9**·BF_4^-. The UV–vis spectrum of cation **9** in CH_3CN is shown in Figure 4. The longest wavelength of absorption maximum of **9** is 397 nm. These spectroscopic properties as well as the NMR spectral data are in good accordance with the structure of **9**·BF_4^-.

The affinity of carbocations toward the hydroxide ion, expressed by the pK_{R+} value, is the most common criterion of carbocation stability.[19] The pK_{R+} value of cation **9** was determined spectrophotometrically in buffer solutions prepared in 50% aqueous CH_3CN and summarized in Table 1, along with those of reference compounds **4**,[20] **10**,[21] and **11** (Fig. 5).[22] On treatment with aqueous $NaHCO_3$ solution, compound **9**·BF_4^- undergoes ring-opening reaction to give **8** (Scheme 1). Thus, the sharp titration curve for neutralization of cation **9** was not obtained, and the pK_{R+} value of **9** was estimated to be ca. 6.0. The pK_{R+} value of **9** is larger than that of **10**[21] (pK_{R+}, 3.9) and it is smaller by about 1.0 pH unit than those of the corresponding parent cation **11** (pK_{R+} 6.9).[22] In addition, the pK_{R+} value of **9** is larger than that of **4**.

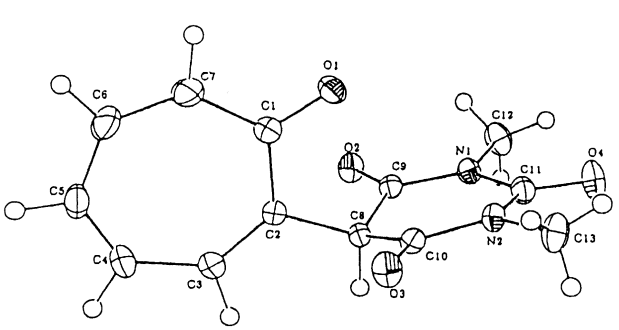


Figure 3. An ORTEP drawing of **8** with thermal ellipsoid plot (50% probability). Selective bond lengths (Å) and angles (°); O1–C1 1.244(2), C1–C2 1.466(2), C2–C3 1.357(2), C3–C4 1.424(3), C4–C5 1.345(3), C5–C6 1.418(3), C6–C7 1.352(3), C7–C1 1.445(2), C2–C8–C9 111.8(1), C2–C8–C10 110.3(1), C9–C8–C10 115.2(1).

The reduction potential of **9** was determined by cyclic voltammentry (CV) in CH_3CN. The reduction wave of **9** was irreversible under the conditions of the CV measurements; the peak potential is summarized in Table 1, together with those of the reference compound **2b** as well as **4**[14] and **10**.[21] The irreversible nature is probably due to the formation of tropyl radical and its dimerization. This

Table 1. pK_{R+} Values and reduction potentials (peak potential in *V* vs Ag/$AgNO_3$) of cations **9** (Reversible process is shown in parentheses. Salts **9**·BF_4^- were used for the measurement; the measurement was made at a scan rate of 0.1 V s^{-1}) and reference compounds **2b**, **4**, **10**, and **11**

Compd.	pK_{R+}	Reduction potential $E1_{red}$ (V)
9	ca. 6.0	−0.58
2b	–	−1.12[a]
4	4.15[b]	(+0.29)[c]
10[d]	3.9	−0.51
11[e]	6.9	–

[a] This work.
[b] Ref. 20.
[c] Ref. 14.
[d] Ref. 21.
[e] Ref. 22.

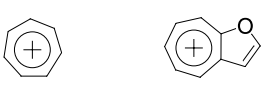


Figure 5.

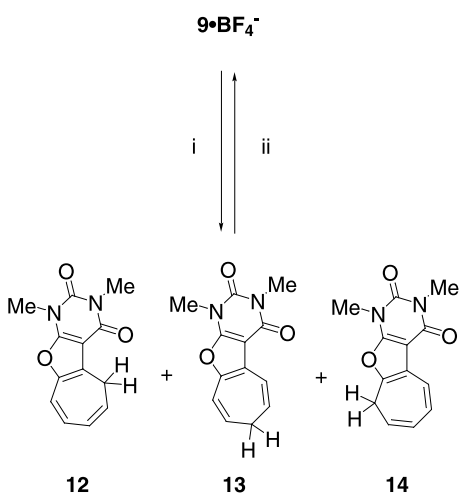
Table 2. Results for the addition reaction of cations **9**·BF_4^- with some nucleophiles

Entry	Nucleophile	Product (combined Yield)	Ratio of adduct				Regeneration of cation
			1-Adduct	3-Adduct	5-Adduct	5a-Adduct	**9**·BF_4^-/%
1	$NaBH_4$	**12**–**14** (97%)	**12** (29)	**13** (12)	**14** (59)		90
2	$BnNH_2$	**17** (95%)				**17** (100)	91
3	Et_2NH	**18** (100%)				**18** (100)	100
4	PhSH	**19**, **20** (60%)	**19** (58)	**20** (42)			99
5	BnSH	**21**–**23** (100%)	**21** (59)	**22** (32)	**23** (9)		60
6	MeOH	**24**–**26** (100%)	**24** (40)	**25** (47)		**26** (12)	95

Table 3. ^{1}H NMR spectral data (500 MHz) of addition products

Compd.		H-1	H-2	H-3	H-4	H-5	Remaining signals
12	δ_H	3.42	5.51	6.03	6.27	6.62	3.39 (Me), 3.54 (Me)
	J	6.2	10.5	6.3	11.4		
13	δ_H	7.00	5.44	2.50	5.39	6.63	3.42 (Me), 3.59 (Me)
	J	9.4	6.3	6.9	9.7		
14	δ_H	7.02	6.40	6.11	5.47	3.36	3.39 (Me), 3.53 (Me)
	J	11.2	6.3	10.4	6.2		
19	δ_H	5.60	5.80	6.05	5.83	6.28	3.37 (Me), 3.52 (Me), 7.11-7.29 (5H, m, Ph)
	J	7.8	11.2	7.3	11.7		
20	δ_H	6.96	5.71	4.52	5.65	6.67	3.39 (Me), 3.54 (Me), 7.11–7.29 (5H, m, Ph)
	J	10.2	7.8	8.5	10.5		
21	δ_H	5.36	5.73	6.12	6.18	6.58	3.39 (Me), 3.49 (Me), 3.78 (2H, s, CH_2), 7.11–7.32 (5H, m, Ph)
	J	8.0	11.0	7.2	11.4		
22	δ_H	7.12	5.58	3.89	5.47	6.62	3.41 (Me), 3.56 (Me), 3.67 (2H, s, CH_2), 7.11–7.32 (5H, m, Ph)
	J	10.8	7.4	7.6	10.5		
23	δ_H	7.00	6.31	6.21	5.76	4.95	3.39–3.78 (8H, s, CH_2, Me), 7.11–7.32 (5H, m, Ph)
	J	11.1	7.3	11.0	8.1		
24	δ_H	5.75	6.16	6.51	6.55	6.93	3.42 (Me), 3.60 (Me), 3.23 (3H, s, OMe)
	J	7.3	10.3	7.9	10.3		
25	δ_H	7.04	5.60	3.62	5.54	6.64	3.42 (Me), 3.60 (Me), 3.42 (3H, s, OMe)
	J	10.0	4.7	4.8	10.3		
26	δ_H	7.29	6.85	6.60	6.73	5.97	3.44 (Me_2), 3.14 (3H, s, OMe)
	J	7.3	11.2	7.6	10.8		

reduction behavior seems to be a typical property of tropylium ions.[23] Since the $E1_{red}$ of **9** is more positive by 0.54 V than that of **2b**, **9** is thus expected to have higher oxidation ability. In addition, the $E1_{red}$ of **9** is more negative by 0.87 V than that of **4**. This feature suggests that the oxidizing ability of **9** may be lower than that of **4**.



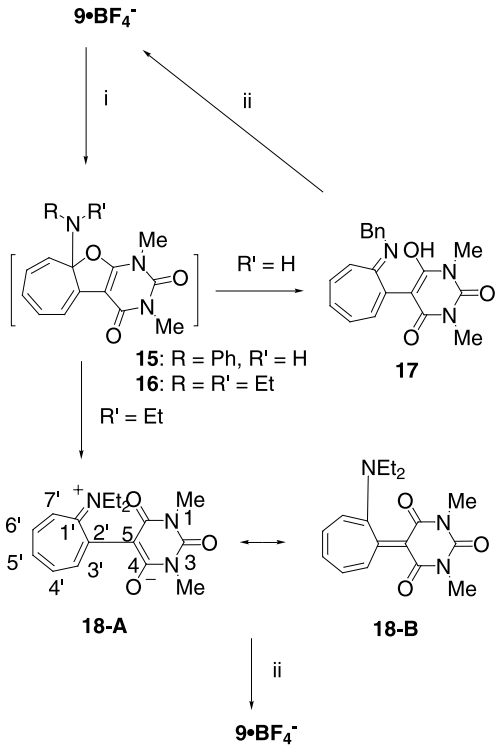
Scheme 3. *Reagents and conditions*: (i) $NaBH_4$, CH_3CN, rt, 1 h; (ii) (a) DDQ, CH_2Cl_2, rt, 1 h; (b) 42% aq. HBF4, Ac_2O, 0°C, 1 h.

2.3. Reactivity of 9·BF_4^-

The reactions of heteroazulenylium ion **9**·BF_4^- with some nucleophiles were carried out. The reaction site of the cation showed remarkable difference depending on the nucleophile. The results are summarized in Table 2. Since the products were unstable on SiO_2 and Al_2O_3, regio-isomers except **25** could not be separated. Thus, the structural assignments were based on the ^{1}H and ^{13}C NMR spectra and IR spectra as well as high-resolution mass spectra of the mixtures. The ^{1}H NMR spectra of the mixtures of each regio-isomer except the ring-opened products, **17** and **18**, could be assigned by using H–H COSY spectra, and they are summarized in Table 3.

Reduction of **9**·BF_4^- with $NaBH_4$ in CH_3CN afforded a mixture of three compounds **12**, **13**, and **14**, and the mixture was oxidized by DDQ to regenerate **9**·BF_4^- in good yield (Scheme 3, Table 2, entry 1).

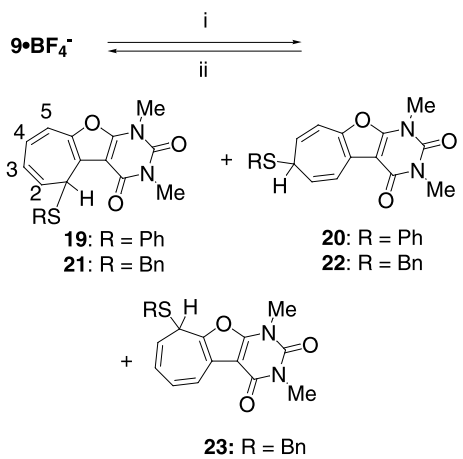
The reactions of **9**·BF_4^- with benzylamine and diethylamine afforded single products **17** and **18**, respectively, which derive from 5a-adducts **15** and **16**, respectively (Scheme 4, Table 2, entries 2 and 3). The physical data (Section 4) could rationalize their structures. The coupling constants of protons on the seven-membered ring of **18** are 8.4, 10.8, 7.1, and 11.6, respectively, suggesting the bond-length



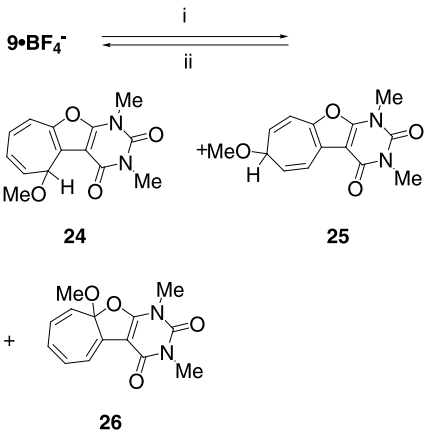
Scheme 4. *Reagents and conditions*: i (a), $BnNH_2$ or Et_2NH, CH_3CN, rt, 0.5 h; (b) 3% HCl; (ii) 42% HBF_4, Ac_2O.

alternation and important contribution of canonical structure **18-A** rather than **18-B**. The ^{13}C NMR spectral datum of **18** was fully assigned by using the H-C COSY spectra (HMQC and HMBC). Signals of C-5, C-4(6), and C-1′ appearing at δ_c 87.3, 162.1, and 174.4, respectively, are similar to those of **7** (C-5: 89.8; C-4(6): 160.8; C-1′: 188.2). Furthermore, two ethyl groups of **18** are not equivalent, and thus, **18** has a structure involving imminium and enol characters. Upon treatment with aq. HBF_4 in Ac_2O, compounds **17** and **18** regenerated **9**·BF_4^- in good yields.

The reactions of **9**·BF_4^- with benzenethiol and benzylmercaptane were carried out (Scheme 5, Table 2, entries 4 and 5). The addition reactions of **9** occurred at 1-, 3-, and 5-positions, and a mixture of two or three regio-isomers,



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



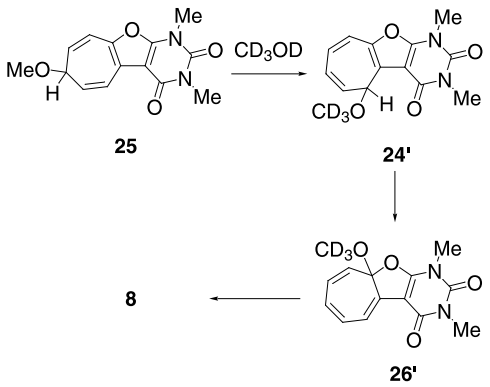
Scheme 6. *Reagents and conditions*: (i) MeOH, $NaHCO_3$, CH_3CN, rt; (ii) 42% HBF_4, Ac_2O.

19–**23** were obtained in good combined yields. The mixtures of addition products regenerated **9**·BF_4^- in good yields upon treatment with aq. HBF_4 in Ac_2O. The addition products were obtained preferentially in the order of 1>3>5-adducts. In compounds **19** and **21**, the coupling constants between H-1 and H-2 are large. Similarly, the coupling constant between H-4 and H-5 in compound **23** is large. Thus, these coupling constants suggest that the sulfide groups are located at the pseudo-axial position in the cycloheptatriene moiety.[24]

The reaction of **9**·BF_4^- with MeOH afforded a mixture of compound **24**, **25**, and **26** in a ratio of 40: 47: 12 as a reddish oil. As mentioned below, since these products rearrange each other, this ratio depends on the reaction time (Scheme 6, Table 2, entry 6). A mixture of compounds **24**, **25**, and **26** was characterized by the ^1H and ^{13}C NMR and IR spectra as well as high-resolution mass spectra. In the ^{13}C NMR of a mixture of compounds **24**–**26**, twelve signals of the sp^3-carbon were observed. Nine of these signals were assigned to three methyl groups of three addition products and the remaining three signals were assigned to the MeO-introduced carbons. Regarding the H–C COSY spectra (HMQC), one of these signals is not coupled with a proton, suggesting the introduction of the methoxy-group to the 5a-position in compound **26**. The ^1H NMR signals of the seven-membered ring support also this characterization. Only compound **25** was crystallized partially from CCl_4 solution of **24**–**26**, and, the analytical data of **25** is not satisfactory because of its instability under recrystallization, however, correct HRMS is obtained. Although **25** is inert in $CDCl_3$ and CD_3CN, isomerization reaction was observed by addition of a drop of CD_3OD. To verify this rearrangement, the reaction of **25** was monitored by NMR spectroscopy in CD_3OD (Scheme 7, Table 4). Compound **25** isomerized gradually to **24′** and **26′**, and hydrolysis of **26′** in the presence of stray H_2O gave **8**. In this reaction, the signal of δ 3.14, which is a methyl proton of MeOH in CD_3OD, was observed. Only compounds **24**–**26** undergo rearrangement, and compounds **17**–**23** do not undergo rearrangement in the presence of a nucleophile, respectively.

2.4. Autorecycling oxidation of alcohols by 9·BF_4^-

3-Methyllumiflavin (**3**) and cationic species **4** have been



Scheme 7.

Table 4. Time dependent rearrangement of **25**

Time (h)	Ratio			
	25	**24'**	**26'**	**8**
0	100	0	0	0
0.1	73	27	0	0
1	53	47	0	0
6	29	22	49	0
24	0	0	35	65
48	0	0	0	100

studied to oxidize some amines under photo-irradiation.[14] We have previously reported that compounds **2a**,**b** oxidize some alcohols to the corresponding carbonyl compounds.[8] In this context and in a search for functions of **9**·BF_4^-, we examined the oxidation of some alcohols by using **9**·BF_4^-. We have found that compound **9**·BF_4^- has remarkable oxidizing ability toward some alcohols, 1-phenylethanol, diphenylmethanol, and 9-fluorenol, to give acetophenone, benzophenone, and 9-fluorenone, respectively, under aerobic and photo-irradiation conditions. The results are summarized in Table 5. Although direct irradiation of the alcohols in the absence of **9**·BF_4^- gives the corresponding carbonyl compounds in a trace or modest amount, they are obtained in more than 100% yield [based on compound **9**·BF_4^-] under photo-irradiation in the presence of **9**·BF_4^-, and thus, autorecycling oxidation clearly proceeds (Table 5). Since decoloration of acidic aqueous $KMnO_4$ 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 and diphenylmethanol, photo-induced oxidation reactions afforded not only ketones but also ethers, which derive from the dehydration of alcohols, probably because of the generation of HBF_4 (Table 5). Moreover, time dependency of the photo-induced oxidation reaction of 1-phenylethanol was investigated in dilute CH_3CN solution, and the results are summarized in Table 6. As the time of photo-irradiation was prolonged, the yield of acetophenone was increased gradually. After 15 h irradiation, the highest yield of acetophenone is obtained, while after 40 h irradiation, the yield is decreased, suggesting plausible decomposition of the catalyst **9**·BF_4^-. Furthermore, **9**·BF_4^- oxidize methyl 1-phenylethyl ether, but the rate of oxidation seems to be slower than that of 1-phenylethanol (Table 6). Thus, the formation of ether caused by generation of HBF_4^- reduces the rate of alcohol oxidation. The ^1H NMR monitoring of the photo-oxidation reaction of 1-phenylethanol in the presence of **9**·BF_4^- was studied, and 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.

Table 6. Time dependency of autorecycling oxidation of 1-phenylethanol and methyl 1-phenylethyl ether in the presence of **9**·BF_4^- under photo-irradiation

Time (h)	Alchohol or ether	Yield[a] of acetophenone[b] (%)
5	PhCH(OH)Me	793
6	PhCH(OH)Me	873
10	PhCH(OH)Me	1433
15	PhCH(OH)Me	1960
40	PhCH(OH)Me	1173
15	PhCH(OMe)Me	780

Acetonitrile solution was irradiated by 450-W high-pressure Hg lamp.
[a] Based on **9**·BF_4^-; the yield, called the **9**·BF_4^- blank, is subtracted from the total yield of ketone in the presence of **9**·BF_4^-.
[b] Isolated as acetophenone 2,4-dinitrophenylhydrazone.

In a search for the mechanistic aspect of the present photo-induced oxidation reaction, the fluorescence spectral studies of **9**·BF_4^- were carried out. The fluorescence spectrum of **9** in CH_3CN under irradiation of the longest wavelength of the absorption maximum is shown in Figure 7. The wavelength of the fluorescence of **9** was 491 nm, and then, storks-shift was 94 nm. The quantum yield (Φ) of **9** was determined to be 0.087 by using quinine bisulfate as standard.[25] By addition of 1-phenylethanol to the solution of **9**, quenching of the fluorescence was observed, suggesting interaction of the singlet excited state of **9** with the alcohol (the fluorescence was quenched completely by gradual addition of 1-phenylehtanol). Moreover, 9-fluorenol was oxidized to give 9-fluorenone. This fact would suggest that

Table 5. Autorecycling oxidation of some alcohols by **9**·BF_4^- under photo-irradiation

Entry	Additive	Alcohol	Ketone	Yield[a] (%)	Yield[b] (%)	Ether	Yield[a] (%)
1	**9**·BF_4^-	PhCH(OH)Me	PhCOMe	4	200	$(PhMeCH)_2O$	30
2	None	PhCH(OH)Me	–	–	–	–	–
3	**9**·BF_4^-	Ph_2CHOH	Ph_2CO	8	356	$(Ph_2CH)_2O$	41
4	None	Ph_2CHOH	Ph_2CO	1	–	–	–
5	**9**·BF_4^-	9-Fluorenol	9-Fluorenone	12	311	–	–
6	None	9-Fluorenol	9-Fluorenone	6	–	–	–

Acetonitrile solution was irradiated by 450-W high-pressure Hg lamp.
[a] Based on alcohol used.
[b] Based on **9**·BF_4^-; the yield, called the **9**·BF_4^- blank, is subtracted from the total yield of ketone in the presence of **9**·BF_4^-.

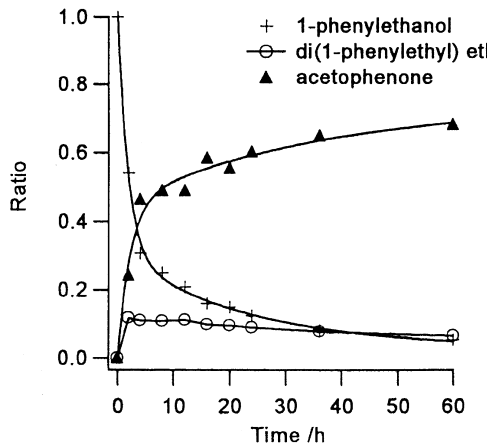


Figure 6. ^{1}H NMR monitoring of autorecycling oxidation of 1-phenylethanol by **9**·BF_4^-.

electron-transfer reaction from 9-fluorenol to the excited **9** 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 8. The electron-transfer from alcohol to the excited cation **9** generates a radical species **27** and **28**; the latter reacts with molecular oxygen to afford a carbonyl compound, hydroperoxyl radical, and proton. The radical species **27** would undergo radical coupling to give dimers **29** (Path A). This feature is suggested by the irreversible $E1_{red}$ of **9** (vide supra). Furthermore, transformation of bitropyl **30** into the corresponding tropylium ion **32** by photo-induced electron transfer (Scheme 8) has been reported.[26] Thus, the radical species **27** as well as its dimers **29** would be oxidized to regenerate cation **9** 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 **27** and **28**; the former compounds are oxidized under aerobic conditions to regenerate **9**. The reduced-products **12**, **13**, and **14**, prepared by $NaBH_4$ reduction (Table 2), are easily oxidized to give **9**·BF_4^- by 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

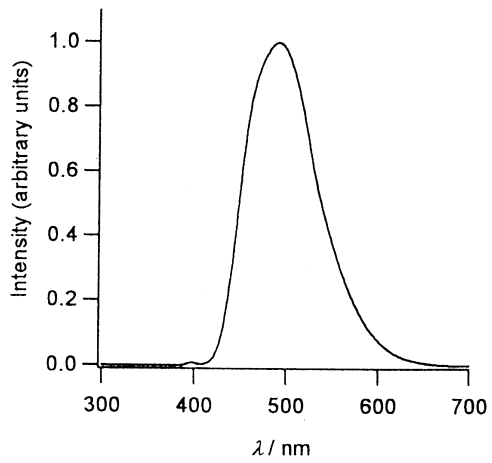
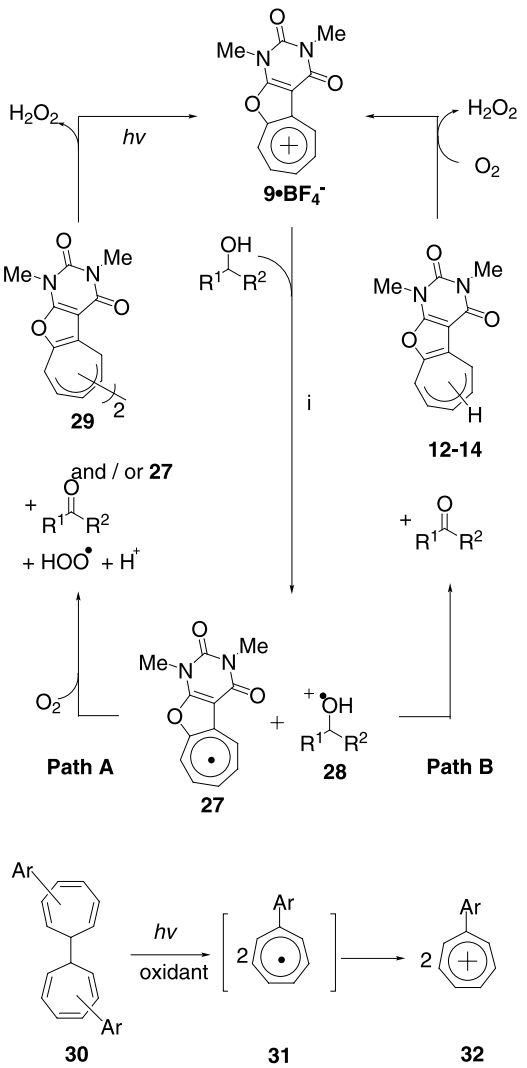


Figure 7. Fluorescence spectrum of **9** in CH_3CN.



Scheme 8. *Reagents and conditions*: (i) CH_3CN, rt, aerobic, *hν*.

compound **27** and its dimer or compounds **12**, **13**, and **14** was unsuccessful in the present photo-oxidation reaction. 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*]furan-8(7*H*),10(9*H*)-dionylium tetrafluoroborate (**9**·BF_4^-), which is isoelectronic system of 5-ethyl-3-methyllumiflavinium ion (**4**), was accomplished. The properties of **9**·BF_4^- were clarified by measurements of the pK_{R+} value, reduction potential, UV–vis spectrum, and fluorescence spectrum. Moreover, the reactions with some nucleophiles were carried out to clarify reactivities of **9**·BF_4^-. Photo-induced autorecycling oxidation reaction of **9**·BF_4^- toward some alcohols was carried out for the first time to afford the corresponding carbonyl compounds in autorecycling process. Thus, a preliminary mechanistic aspect of the autorecycling oxidation reaction is postulated. Further studies concerning synthesis, properties, and functions including mechanistic aspects of other uracil-annulated heteroazulenylium ions are under way.

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 a 450-W high-pressure Hg lamp Pyrex filter.

4.2. Preparation of 1,3-dimethyl-5-(1′-oxocyclohepta-trien-2′-yl)-pyrimidine-2(1*H*),4(3*H*),6(5*H*)-trione (8)

A solution of 2-chlorotropone (**5**) (1.41 g, 10 mmol), 1,3-dimethyl-2(1*H*),4(3*H*),6(5*H*)-pyrimidinetrione (**6**) (1.56 g, 10 mmol), and Bu^tNH_2 (1.83 g, 25 mmol) in CH_2Cl_2 (50 mL) was stirred at rt for 24 h. After evaporation of the CH_2Cl_2 and Bu^tNH_2, the residue was filtered and washed with Et_2O to give **7**, which is contaminated with Bu^tNH_3Cl. The 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 **8** (2.44 g, 94%).

4.2.1. *tert*-Butylammonium 1,3-dimethyl-2,6-dioxo-5-(1′-oxocycloheptatrien-2′-yl)-1,3*H*-pyrimidin-4-oxide (7). Yellow powder; ^{1}H NMR (500 MHz, DMSO-d_6) δ 1.24 (9H, s, Bu^t), 3.07 (6H, s, NMe), 6.60 (1H, d, *J*=12.0 Hz, H-7), 6.64 (1H, dd, *J*=11.6, 7.8 Hz, H-5), 6.86 (1H, dd, *J*=11.6, 9.2 Hz, H-4), 6.91 (1H, dd, *J*=12.0, 7.8 Hz, H-6), 7.56 (1H, d, *J*=9.2 Hz, H-3), 7.87 (3H, br s, NH_3); ^{13}C NMR (125.7 MHz) δ 26.9, 27.1, 51.0, 89.5, 128.2, 131.8, 132.5, 133.0, 135.3, 150.2, 152.6, 160.6, 188.4; IR (KBr) ν 3428, 1665, 1576 cm^{-1}; MS (FAB) *m*/*z* 261 (M^++H−Bu^tNH_2).

4.2.2. Compound 8. Colorless needles; mp 217–218°C (from AcOEt); ^{1}H NMR (500 MHz) δ 3.36 (6H, s, NMe), 4.16 (1H, s, CH), 7.08–7.14 (3H, m), 7.23–7.30 (1H, m), 7.48–7.52 (1H, m); ^{1}H NMR (400 MHz, DMSO-d_6) δ 3.17 (6H, s, NMe), 4.93 (1H, s, CH), 7.01 (1H, d, *J*=12.0 Hz), 7.25–7.34 (2H, m), 7.40–7.47 (1H, m), 7.72–7.78 (1H, m); ^{1}H NMR (400 MHz, CD_3CN) δ 3.23 (6H, s, NMe), 4.42 (1H, s, CH), 7.02 (1H, d, *J*=12.0 Hz), 7.15–7.25 (2H, m), 7.32–7.38 (1H, m), 7.58–7.64 (1H, m); ^{13}C NMR (125.7 MHz) δ 28.9, 57.2, 133.7, 135.4, 137.3, 140.2, 141.3, 148.7, 151.7, 166.4, 185.2; ^{13}C NMR (125.7 MHz, CD_3OD) δ 28.9, 97.3, 135.6, 137.1, 139.7, 141.5, 142.7, 150.2, 153.2, 168.7, 187.2; IR ($CHCl_3$) ν 1681 cm^{-1}; MS (FAB) *m*/*z* 261 (M^++H); Anal. calcd for $C_{13}H_{12}N_2O_4$: C, 60.00; H, 4.65; N, 10.76. Found: C, 59.8; H, 4.7; N, 10.9.

4.3. Preparation of a mixture of 8-4,6d_2 and 8-3,5d_2

A solution of **5**-d_3 (141 mg, 1 mmol), **6** (156 mg, 1 mmol), and Bu^tNH_2 (183 mg, 2.5 mmol) in CH_2Cl_2 (10 mL) was stirred at rt for 24 h. After evaporation of the CH_2Cl_2 and Bu^tNH_2, the residue was filtered and washed with Et_2O to give a mixture of **7-4,6d_2** and **7-3,5d_2**, which is contaminated with Bu^tNH_3Cl. The 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 a mixture of **8-4,6d_2** and **8-3,5d_2** (185 g, 71%).

4.3.1. A mixture of 7-4,6d_2 and 7-3,5d_2. HRMS calcd for $C_{13}H_9N_2O_4D_2$+$C_4H_{12}N$: 263.0985 (M+H−Bu^tNH_2). Found: 263.0968 (M^++H−Bu^tNH_2). **7-4,6d_2**. ^{1}H NMR (500 MHz, DMSO-d_6) δ 1.25 (9H, s, Bu^t), 3.07 (6H, s, NMe), 6.60 (1H, br s, H-7), 6.64 (1H, br s, H-5), 7.56 (1H, br s, H-3), 7.87 (3H, br s, NH_3). **7-3,5d_2**. ^{1}H NMR (500 MHz, DMSO-d_6) δ 1.25 (9H, s, Bu^t), 3.07 (6H, s, NMe), 6.60 (1H, br d, *J*=12.0 Hz, H-7), 6.86 (1H, br s, H-4), 6.91 (1H, br d, *J*=12.0 Hz, H-6), 7.87 (3H, br s, NH_3).

4.3.2. A mixture of 8-4,6d_2 and 8-3,5d_2. HRMS calcd for $C_{13}H_{10}N_2O_4D_2$: 263.1001 (M+H). Found: 263.1033 (M^++H). **8-4,6d_2**. ^{1}H NMR (500 MHz, CD_3OD) δ 3.30 (6H, s, NMe), 7.10 (1H, br s, H-7), 7.30 (1H, br s, H-5), 7.73 (1H, br s, H-3). **8-3,5d_2**. ^{1}H NMR (500 MHz, CD_3OD) δ 3.30 (6H, s, NMe), 7.10 (1H, br d, *J*=12.5 Hz, H-7), 7.30 (1H, br s, H-4), 7.45 (1H, br d, *J*=12.5 Hz, H-6).

4.4. Preparation of 7,9-dimethylcyclohepta[*b*]pyrimido-[5,4-*d*]furan-8(7*H*),10(9*H*)-dionylium tetrafluoroborate (9·BF_4^-) or a mixture of 9-4,6d_2·BF_4^- and 9-3,5d_2·BF_4^-

A solution of **8** (130 mg, 0.5 mmol) [or a mixture of **8-4,6d_2** and **8-3,5d_2** (185 mg, 0.7 mmol)] in propanoic anhydride (2.5 mL) and 42% aq. HBF_4 (0.5 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 **9**·BF_4^- (158 mg, 96%) [or a mixture of **9-2,4d_2**·BF_4^- and **9-1,3d_2**·BF_4^- (154 mg, 83%)].

4.4.1. Compound 9·BF_4^-. Yellow powder; mp 243–244°C (from CH_3CN–AcOEt, decomp.); ^{1}H NMR (500 MHz, CD_3CN) δ 3.43 (3H, s, Me), 3.73 (3H, s, Me), 8.73–8.76 (2H, m, H-3, 4), 8.82–8.86 (1H, m, H-2), 9.07–9.09 (1H, m, H-5), 9.53 (1H, d, *J*=10.1 Hz, H-1); ^{13}C NMR (125.7 MHz) δ 29.2, 31.6, 98.2, 135.3, 139.9, 144.8, 148.2, 148.7, 149.3, 150.6, 157.8, 163.1, 166.2; IR (KBr) ν 1722, 1683, 1657, 1084 cm^{-1}; MS (FAB) *m*/*z* 243 (M^+−BF_4); HRMS calcd for $C_{13}H_{11}BF_4N_2O_3$: 243.0770 (M−BF_4). Found: 243.0760 (M^+−BF_4). Anal. calcd for $C_{13}H_{11}BF_4N_2O_3$: C, 47.31; H, 3.36; N, 8.49. Found: C, 47.2 H, 3.2; N, 8.5.

4.4.2. A mixture of 9-2,4d_2·BF_4^- and 9-1,3d_2·BF_4^-. HRMS calcd for $C_{13}H_9BF_4N_2O_3D_2$: 245.0895 (M−BF_4). Found: 245.0930 (M^+−BF_4). **9-2,4d_2**·BF_4^-. ^{1}H NMR (500 MHz, CD_3CN) δ 3.43 (3H, s, Me), 3.73 (3H, s, Me), 8.74 (1H, br s, H-3), 9.08 (1H, br s, H-5), 9.53 (1H, br s, H-1). **9-1,3d_2**·BF_4^-. ^{1}H NMR (500 MHz, CD_3CN) δ 3.43 (3H, s, Me), 3.73 (3H, s, Me), 8.73 (1H, br d, *J*=9.5 Hz, H-4), 8.83 (1H, br s, H-2), 9.08 (1H, br d, *J*=9.5 Hz, H-5).

4.5. Direct preparation of 9·BF_4^- from 5 and 6

A solution of **7** (3.686 g, contaminated with Bu^tNH_3Cl), which was prepared by the reaction of **6** (1.56 g, 10 mmol), **5** (1.41 g, 10 mmol), and Bu^tNH_2 (1.83 g, 25 mmol), in

propanoic anhydride (50 mL) and 42% aq. HBF_4 (10 mL) was stirred at 0°C for 1 h. To the mixture was added Et_2O (300 mL) and the precipitates were collected by filtration to give **9**·BF_4^- (3.00 g, 91%).

4.6. Reaction of 9·BF_4^- with $NaHCO_3$

To a solution of **9**·BF_4^- (165 mg, 0.5 mmol) in CH_3CN (10 mL) was added saturated aqueous $NaHCO_3$ solution (1 mL), and the mixture was stirred at rt for 6 h. To the mixture was added 3% HCl, and the solution was extracted with CH_2Cl_2. The extract was dried over Na_2SO_4 and concentrated in vacuo to give **8** (130 mg, 100%).

4.7. Reaction of 9·BF_4^- with $NaBH_4$

A solution of **9**·BF_4^- (989 mg, 3.0 mmol) and $NaBH_4$ (114 mg, 3.0 mmol) in CH_3CN (50 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** (711 mg, 97%) (Table 2).

4.7.1. A mixture of 1,7-dihydro-7,9-dimethylcyclohepta-[*b*]pyrimido[5,4-*d*]furan-8(7*H*),10(9*H*)-dione (12), 3,7-dihydro-7,9-dimethylcyclohepta[*b*]pyrimido[5,4-*d*]furan-8(7*H*),10(9*H*)-dione (13), and 5,7-dihydro-7,9-dimethylcyclohepta[*b*]pyrimido[5,4-*d*]furan-8(7*H*),10(9*H*)-dione (14). Yellow powder; mp 85–86°C (from EtOH); ^{13}C NMR (150.9 MHz) δ 21.8, 26.8, 27.5, 28.1, 28.1, 28.2, 29.4, 29.4, 29.5, 96.0, 96.1, 115.1, 117.0, 117.9, 118.3, 118.6, 120.4, 120.8, 121.3, 122.3, 124.3, 127.2, 127.3, 128.4, 128.4, 140.1, 146.6, 149.5, 150.5, 150.6, 150.7, 154.4, 154.7, 156.4, 158.5, 158.5, 158.7 (two carbons overlapping); IR (KBr) ν 1707, 1666 cm^{-1}; MS (FAB) *m*/*z* 245 (M^++H); HRMS calcd for $C_{13}H_{12}N_2O_3$: 245.0927 (M+H). Found: 245.0907 (M^++H). Anal. calcd for $C_{13}H_{12}N_2O_3$: C, 63.93; H, 4.95; N, 11.47. Found: C, 63.4; H, 4.6; N, 11.4.

4.8. Oxidation of a mixture of 12–14

To a solution of a mixture of **12**–**14** (122 mg, 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 **9**·BF_4^- (149 mg, 90%).

4.9. Reaction of 9·BF_4^- with benzylamine and diethylamine

A solution of **9**·BF_4^- (165 mg, 0.5 mmol) and benzylamine (214 mg, 2.0 mmol) [or diethylamine (147 mg, 0.5 mmol)] in CH_3CN (10 mL) was stirred at rt for 0.5 h. After evaporation of the CH_2Cl_2 and excess amine, the residue was acidified with 3% HCl and extracted with CH_2Cl_2. The extract was dried over Na_2SO_4 and concentrated in vacuo to give **17** (166 mg, 95%) [or **18** (158 mg, 100%)] (Table 2).

4.9.1. 1,3-Dimethyl-4-hydroxy-5-(1′-benzyliminocyclo-heptatrien-2′-yl)pyrimidine-2(3*H*),6(1*H*)-dione (17). Red-dish needles; mp 198–199°C (from $CHCl_3$); ^1H NMR (500 MHz, DMSO-d_6) δ 3.23 (6H, s, Me), 4.76 (2H, s, $PhCH_2$), 7.31–7.61 (8H, m, Ph, H-5, 6, 7), 7.78 (1H, dd, *J*=10.2, 9.6 Hz, H-4), 8.21 (1H, d, *J*=9.6 Hz, H-3), 9.76 (1H, br s, OH); ^{13}C NMR (125.7 MHz, DMSO-d_6) δ 27.2, 47.1, 89.0, 123.6, 126.9, 127.4, 128.5, 134.0, 135.4, 138.0, 142.2, 143.6, 145.8, 152.5, 160.7, 166.0; IR (KBr) ν 3259, 1672, 1592 cm^{-1}; MS (FAB) *m*/*z* 350 (M^++H); Anal. calcd for $C_{20}H_{19}N_3O_3$: C, 68.75; H, 5.48; N, 12.03. Found: C, 68.4; H, 5.3; N, 11.9.

4.9.2. 5-(2′-Diethylaminocyclohepta-2′,4′,6′-trienylidene)-pyrimidine-2(1*H*),4(3*H*),6(5*H*)-trione (18). Orange pow-der; mp 167–168°C (from AcOEt); ^1H NMR (500 MHz) δ 1.05 (3H, t, *J*=7.3 Hz, CH_3), 1.36 (3H, t, *J*=7.3 Hz, CH_3), 3.34 (6H, s, NMe), 3.50 (2H, q, *J*=7.3 Hz, CH_2), 3.69 (2H, q, *J*=7.3 Hz, CH_2), 6.66 (1H, dd, *J*=10.8, 7.1 Hz, H-3), 6.79 (1H, d, *J*=11.6 Hz, H-5), 6.98 (1H, dd, *J*=11.6, 7.1 Hz, H-4), 7.07 (1H, dd, *J*=10.8, 8.4 Hz, H-2), 8.69 (1H, d, *J*=8.4 Hz, H-1); ^{13}C NMR (125.7 MHz) δ 11.3 (CH_3), 11.8 (CH_3), 27.7 (NCH_3), 44.2 (CH_2), 46.3 (CH_2), 87.3 (C-5), 113.0 (C-7′), 123.2 (C-3′), 124.5 (C-5′), 127.2 (C-2′), 129.8 (C-6′), 133.2 (C-4′), 152.7 (C-2), 162.1 (C-4, 6), 174.4 (C-1′); IR ($CHCl_3$) ν 1672, 1603, 1580, 1431 cm^{-1}; MS (FAB) *m*/*z* 316 (M^++H); HRMS calcd for $C_{17}H_{21}N_3O_3$: 316.1661 (M+H). Found: 316.1672 (M^++H). Anal. calcd for $C_{17}H_{21}N_3O_3$: C, 64.75; H, 6.71; N, 13.32. Found: C, 64.5; H, 6.7; N, 13.4.

4.10. Reaction of 9·BF_4^- with PhSH or BnSH

To a suspension of **9**·BF_4^- (66 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 BnSH (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. The residue was dissolved in CH_2Cl_2 and filtered to remove $NaBF_4$, and the filtrate was evaporated to give a mixture of **19** and **20** [or **21**–**23**] (Table 2).

4.10.1. A mixture of 1,7-dihydro-7,9-dimethyl-1-phenylthiocyclohepta[*b*]pyrimido[5,4-*d*]furan-8(7*H*),10(9*H*)-dione (19) and 3,7-dihydro-7,9-dimethyl-3-phenylthio-cyclohepta[*b*]pyrimido[5,4-*d*]furan-8(7*H*),10(9*H*)-dione (20). Yellow oil; ^{13}C NMR (150 MHz) δ 28.1, 28.2, 29.4, 29.5, 43.2, 46.5, 95.6, 117.1, 118.2, 118.6, 120.9, 121.5, 122.5, 122.7, 125.6, 125.7, 125.8, 127.2, 127.5, 128.3, 128.5, 128.7, 129.1, 129.2, 129.4, 130.7, 132.2, 133.0, 135.6, 147.2, 150.5, 155.9, 158.0, 158.3; IR ($CHCl_3$) ν 1709, 1276 cm^{-1}; HRMS calcd for $C_{19}H_{17}N_2O_3S$: 353.0960 (M+H). Found: 353.1005 (M^++H).

4.10.2. A mixture of 1-benzylthio-1,7-dihydro-7,9-dimethylcyclohepta[*b*]pyrimido[5,4-*d*]furan-8(7*H*),10(9*H*)-dione (21), 3-benzylthio-3,7-dihydro-7,9-dimethylcyclo-hepta[*b*]pyrimido[5,4-*d*]furan-8(7*H*),10(9*H*)-dione (22), and 5-benzylthio-5,7-dihydro-7,9-dimethylcyclohepta-[*b*]pyrimido[5,4-*d*]furan-8(7*H*),10(9*H*)-dione (23). Yellow oil. ^{13}C NMR (150 MHz) δ 28.1, 28.1, 28.2, 28.9, 29.3, 29.5, 34.4, 34.5, 34.9, 38.9, 41.6, 43.3, 53.5, 95.8, 96.0, 118.0, 118.1, 119.1, 120.6, 121.2, 121.3, 122.2, 122.6, 122.1, 122.8, 125.3, 125.9, 16.5, 126.7, 126.8, 127.0, 127.0, 128.0, 128.2, 128.4, 128.5, 128.6, 128.7, 128.8, 128.8,

128.9, 137.9, 138.1, 141.1, 146.5, 149.0, 150.4, 150.5, 154.7, 155.6, 158.2, 158.3 (two carbons overlapping); IR ($CHCl_3$) ν 1708, 1277 cm^{-1}; HRMS calcd for $C_{20}H_{19}N_2O_3S$: 367.1117 (M+H). Found: 367.1083 (M^++H).

4.11. Reaction of 9·BF_4^- with MeOH

To a suspension of **9**·BF_4^- (165 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 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 **24**–**26** (Table 2).

4.11.1. A mixture of 1,7-dihydro-7,9-dimethyl-1-methoxycyclohepta[*b*]pyrimido[5,4-*d*]furan-8(7*H*),10(9*H*)-dione (24), 3,7-dihydro-7,9-dimethyl-3-methoxycyclohepta[*b*]-pyrimido[5,4-*d*]furan-8(7*H*),10(9*H*)-dione (25), and 5a,7-dihydro-7,9-dimethyl-5a-methoxycyclohepta[*b*]pyrimido[5,4-*d*]furan-8(7*H*),10(9*H*)-dione (26). Reddish oil. ^{13}C NMR (150 MHz) δ 27.9, 28.2, 28.7, 29.0, 29.5, 29.6, 54.6, 55.2, 56.4, 67.3, 77.5, 89.4, 114.2, 115.0, 116.3, 117.6, 118.5, 122.7, 122.8, 122.9, 123.9, 125.2, 125.6, 125.8, 127.4, 128.8, 130.5, 133.7, 138.3, 139.8, 145.2, 148.4, 149.1, 150.5, 150.7, 153.0, 154.9, 156.0, 158.4, 158.4, 163.0, 164.6; IR ($CHCl_3$) ν 1710, 1668, 1265 cm^{-1}; HRMS calcd for $C_{14}H_{14}N_2O_4$: 275.1032 (M+H). Found: 275.1021 (M^++H).

4.11.2. Compound 25. Colorless powder; mp 151–154°C (from CCl_4, decomp.); ^{13}C NMR (100 MHz) δ 28.2, 29.5, 56.4, 77.5, 89.4, 114.2, 117.6, 122.7, 122.8, 123.9, 149.1, 150.5, 154.9, 158.4; IR ($CHCl_3$) ν 1710, 1668, 1265 cm^{-1}; MS (ret. int.) *m*/*z* 274 (M^+, 36), 259 (17), 243 (45), 186 (87), 58 (100%); HRMS calcd for $C_{14}H_{14}N_2O_4$: 275.1032 (M+H). Found: 275.1024 (M^++H). Anal. calcd for $C_{14}H_{14}N_2O_4$: C, 61.31; H, 5.14; N, 10.21. Found: C, 60.6; H, 4.3; N, 10.5.

4.12. Reaction of 17, 18, a mixture of 19 and 20, a mixture of 21–23, and a mixture of 24–26 with HBF_4

A solution of each of **17**, **18**, a mixture of **19** and **20**, a mixture of **21**–**23**, and a mixture of **24**–**26** (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 **9**·BF_4^-. The results are summarized in Table 3.

4.13. Determination of pK_{R+} value of 9·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 3 mg of cation **9**·BF_4^- in CH_3CN (20 mL), were diluted to 10 mL with the buffer solution (5 mL) and MeCN (4 mL). The UV–vis spectrum was recorded for cation **9a** 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 (394 nm) of cation was plotted against pH to give a classical titration curve, whose midpoint was taken as the pK_{R+} value (Table 1).

4.14. Cyclic voltammetry of cation 9·BF_4^-

The reduction potentials of **9**·BF_4^- were 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 an CH_3CN solution (4 mL) of cation **9**·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: the reduction potential was measured through independent scan (Table 1).

4.15. X-Ray structure determination of 8[†]

Colorless prisms, $C_{13}H_{12}N_2O_4$, M=260.25, monoclinic, space group $P2_1/c$, a=11.1404(7), b=7.6870(3), c=14.9663(7) Å, β=110.982(3)°, V=1196.7(1) $Å^3$, Z=4, Dc=1.444 g cm^{-3}, crystal dimensions 0.50×0.20×0.20 mm^3. Data were measured on a Rigaku RAXIS-RAPID radiation diffractomater with graphite monochromated Mo Kα radiation. A total 10,804 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,[27] with 185 variables and 2224 observed reflections [I>3.00σ(I)]. The non-hydrogen atoms were refined anisotropically. The weighting scheme $w=[\sigma_c^2(F_0)+0.0070F_0^2]^{-1}$ gave satisfactory agreement analysis. The final R and Rw values were 0.060 and 0.089. The maximum peak and minimum peak in the final difference map were 0.62 and −0.35 e^- $Å^{-3}$.

4.16. General procedure of autorecycling oxidation of some alcohols by 9·BF_4^-

An CH_3CN (1 mL) solution of compound **9**·BF_4^- (16.5 mg, 0.05 mmol) and an alcohol (2.5 mmol, 50 equiv.) in a Pyrex tube was irradiated by 450-W high-pressure Hg lamp under aerobic conditions for 40 h. The reaction mixture was concentrated in vacuo and separated by column chromatography on SiO_2. The results are summarized in Table 5.

4.17. Time dependency of autorecycling oxidation of 1-phenylethanol by 9·BF_4^-

A CH_3CN (16 mL) solution of compound **9**·BF_4^- (16.5 mg, 0.05 mmol) and 1-phenylethanol (305 mg, 2.5 mmol) in a Pyrex tube was irradiated by 450-W high-pressure Hg lamp under aerobic conditions for the periods indicated in

[†] CCDC reference number 194281.

Table 6. The reaction mixture was concentrated in vacuo and diluted with ether and filtered. The filtrate was treated with 2,4-dinitrophenylhydrazine in 6% HCl to give 2,4-dinitrophenylhydrazone. The results are summarized in Table 6.

4.18. ^{1}H NMR monitoring of autorecycling oxidation of 1-phenylethanol by 9·BF_4^-

A CD_3CN (0.5 mL) solution of compound **9**·BF_4^- (0.660 mg, 0.002 mmol) and 1-phenylehtanol (12.2 mg, 0.10 mmol) in NMR tube was irradiated by 450-W high-pressure Hg 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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