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Novel Synthesis and Oxidizing Ability of Tropylium Ions Annulated with Two 2,4-Dimethylfuro[2,3-*d*]pyrimidine-1(2*H*),3(4*H*)-diones

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Convenient preparation of novel tropylium ions annulated with two 2,4-dimethylfuro[2,3-*d*]-pyrimidine-1(2*H*),3(4*H*)-diones, **12a**$^+$·BF_4^- and **12b**$^+$·BF_4^-, consists of a reaction of 2-methoxytropone with dimethylbarbituric acid to give 7,9-dimethyl-3-[1′,3′-dimethyl-2′(1′*H*),4′(3′*H*),6′(5′*H*)-trioxopyrimidin-5′-ylidene]cyclohepta[*b*]pyrimido[5,4-*d*]furan-8(7*H*),10(9*H*)-dione **8** and the following oxidative cyclization by using DDQ or photoirradiation under aerobic conditions. On the basis of the MO calculations, the selectivity of two types of oxidative cyclization reactions of **8** was rationalized. X-ray crystal analyses and MO calculations were carried out to clarify the structural characteristics of **12a**$^+$·BF_4^- and **12b**$^+$·BF_4^-. The stability of cations **12a**$^+$ and **12b**$^+$ is expressed by the pK_{R^+} values which were determined spectrophotometrically as 8.8 and 8.6. The electrochemical reduction of **12a**$^+$ and **12b**$^+$ exhibited reduction potential at −0.63 and −0.62 (V vs Ag/$AgNO_3$), respectively. Reactions of **12a**$^+$·BF_4^- and **12b**$^+$·BF_4^- with some nucleophiles, hydride and diethylamine, were carried out to clarify that the reactivity of **12a**$^+$·BF_4^- and **12b**$^+$·BF_4^- was substantially dependent on the annulating position. The oxidizing ability of **12a**$^+$·BF_4^- and **12b**$^+$·BF_4^- toward alcohols and amines in the autorecycling process was demonstrated as well.

Introduction

Flavins are known to play an important role as cofactors in a wide variety of biological redox reactions.[1] Dehydrogenation reactions represent a major category 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 analogues.[2] The flavin-redox systems have been investigated extensively through synthetic model systems and theoretical calculations.[3] Among these compounds, 5-deazaflavins **1a** (Figure 1) have been studied extensively in both enzymatic[4] and model systems,[5] in the hope of providing mechanistic insight into flavin-catalyzed reactions. In this relation, 5-deaza-10-oxaflavin **1b** (2*H*-chromeno[2,3-*d*]pyrimidine-2,4(3*H*)-dione), in which the nitrogen atom is replaced by an oxygen, has been synthesized and found to possess a strong ability to oxidize alcohols to the corresponding carbonyl compounds.[6] On the basis of the above observations, the synthesis and properties of polycyclic flavin derivative **2a**[7] and its analogue **2b**[8] (double 5-deazaflavin) have been reported. The double 5-deazaflavins **2a** and **2b** have an extended conjugation and a more positive reduction potential as compared with **1a**. Thus, **2a** and **2b** are more effective than **1a** for oxidation of alcohols.

On the other hand, we have previously studied convenient preparations of 6-substituted 9-methylcyclohepta[*b*]pyrimido[5,4-*d*]pyrrole-8(6*H*),10(9*H*)-diones[9] and 9-methylcyclohepta[*b*]pyrimido[5,4-*d*]furan-8,10(9*H*)-dione,[10] which are structural isomers of **1a** and **1b**, respectively, and their reactions in oxidizing some alco-

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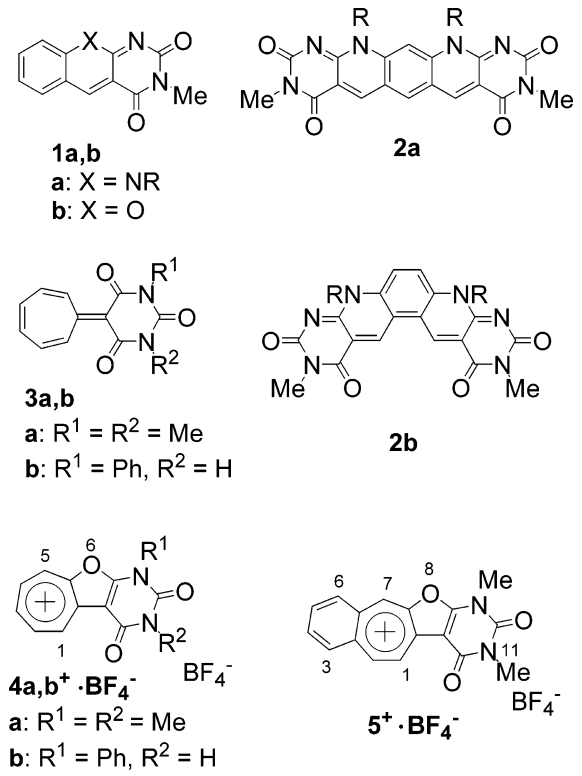
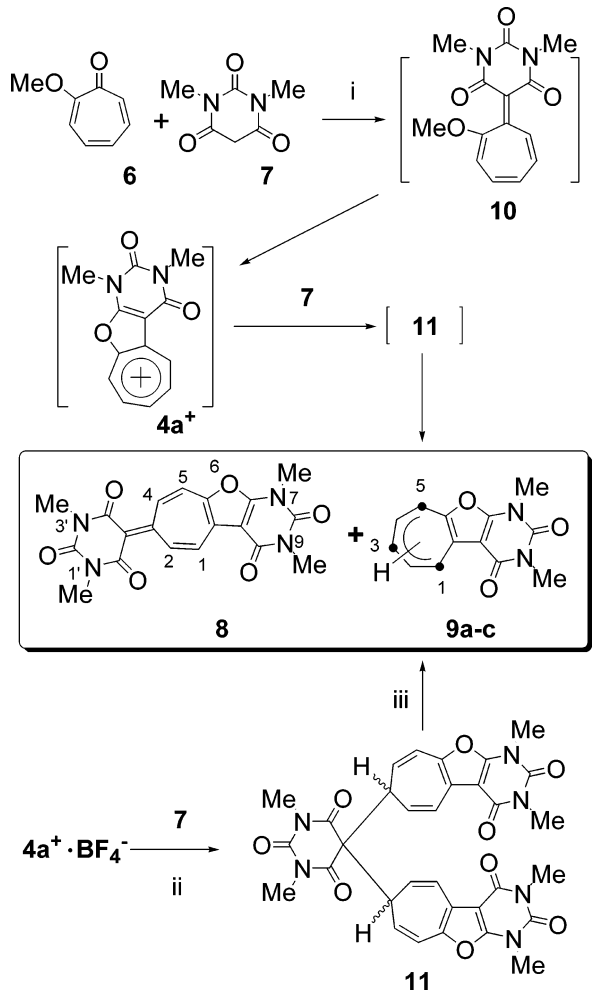


FIGURE 1.

hols to the corresponding carbonyl compounds. In this relation, we have reported the oxidative cyclization of heptafulvenes **3a** and **3b** by using DDQ to afford cyclohepta[*b*]pyrimido[5,4-*d*]furan-8(7*H*),10(9*H*)-dionylium tetrafluoroborates **4a**$^{+}$·BF_4^- and **4b**$^{+}$·BF_4^-, respectively.[11] Novel photoinduced autorecycling oxidizing reactions of **4a**$^{+}$·BF_4^- toward some alcohols were studied as well.[12] On the other hand, the π-conjugation mode in polycyclic conjugated π-systems containing more than one $(4n+2)$ conjugation loop is an important subject from both theoretical and experimental viewpoints. A combination of more than one π-system can endow the original π-system with new properties. From this viewpoint, we have recently reported the synthesis, properties, and oxidizing ability of 9,11-dimethylbenzocyclohepta[6,7-*b*]pyrimido-[5,4-*d*]furan-10(9*H*),12(11*H*)-dionylium ion **5**$^{+}$·BF_4^-.[13] The properties and reactivity of compound **5**$^{+}$·BF_4^- were much perturbed by the benzo-annulation on **4a**$^{+}$·BF_4^-. Thus, the aromatic ring-annulation onto **3a** and **4a**$^{+}$·BF_4^- is a very interesting project from the viewpoint of exploration of novel functions. In this study, we report the synthesis and properties of a novel type of heptafulvene **8** (Scheme 1), which is converted to novel tropylium ions annulated with two 2,4-dimethylfuro[2,3-*d*]pyrimidine-1(2*H*),3(4*H*)-diones, **12a**$^{+}$·BF_4^- and **12b**$^{+}$·BF_4^- (Scheme 2). Compounds **12a**$^{+}$·BF_4^- and **12b**$^{+}$·BF_4^- are expected to be a double uracil-annulated heteroazulene having an extended conjugation. The structural details and chemical

SCHEME 1[a]



[a] Reagents and conditions: (i) Ac_2O, reflux, 0.5 h; (ii) Et_3N, CH_3CN, rt, 2 h; (iii) xylene, 90 °C, 3 h.

properties as well as the photoinduced oxidizing reaction of **12a**$^{+}$·BF_4^- and **12b**$^{+}$·BF_4^- toward some alcohols and amines are investigated as well.

Results and Discussion

Synthesis. Preparation of 1,3,8,10-tetramethyldipyrimido[6,5-*b*:6′,5′-*b*′]cyclohepta[1,2-*d*:5,4-*d*′]difuran-2(1*H*),4(3*H*),7(8*H*),9(10*H*)-tetraonylium tetrafluoroborate **12a**$^{+}$·BF_4^- and its isomer **12b**$^{+}$·BF_4^- was easily accomplished by the reaction of 2-methoxytropone **6** with dimethylbarbituric acid **7** and subsequent oxidative cyclization. The reaction of 2-methoxytropone **6** with 2 molar equiv of dimethylbarbituric acid **7** in Ac_2O under reflux for 0.5 h afforded a novel heptafulvene, 7,9-dimethyl-3-[1′,3′-dimethyl-2′(1′*H*),4′(3′*H*),6′(5′*H*)-trioxopyrimidin-5′-ylidene]cyclohepta[*b*]pyrimido[5,4-*d*]furan-8(7*H*),10(9*H*)-dione **8** (38% based on **6** used) and a mixture of 1,7-, 3,7-, and 5,7-dihydro-7,9-dimethylcyclohepta-[*b*]pyrimido[5,4-*d*]furan-8(7*H*),10(9*H*)-diones **9a**−**c**[12] (50% based on **6** used) (Scheme 1). The reaction of **6** with even 1 molar equiv of **7** did not afford **4a**$^{+}$ but afforded **8** and **9a**−**c** in lower yields and compound **6** was not recovered in the reaction. Thus, compound **11** is postulated as the intermediate for the formation of **8** and **9a**−**c**. The

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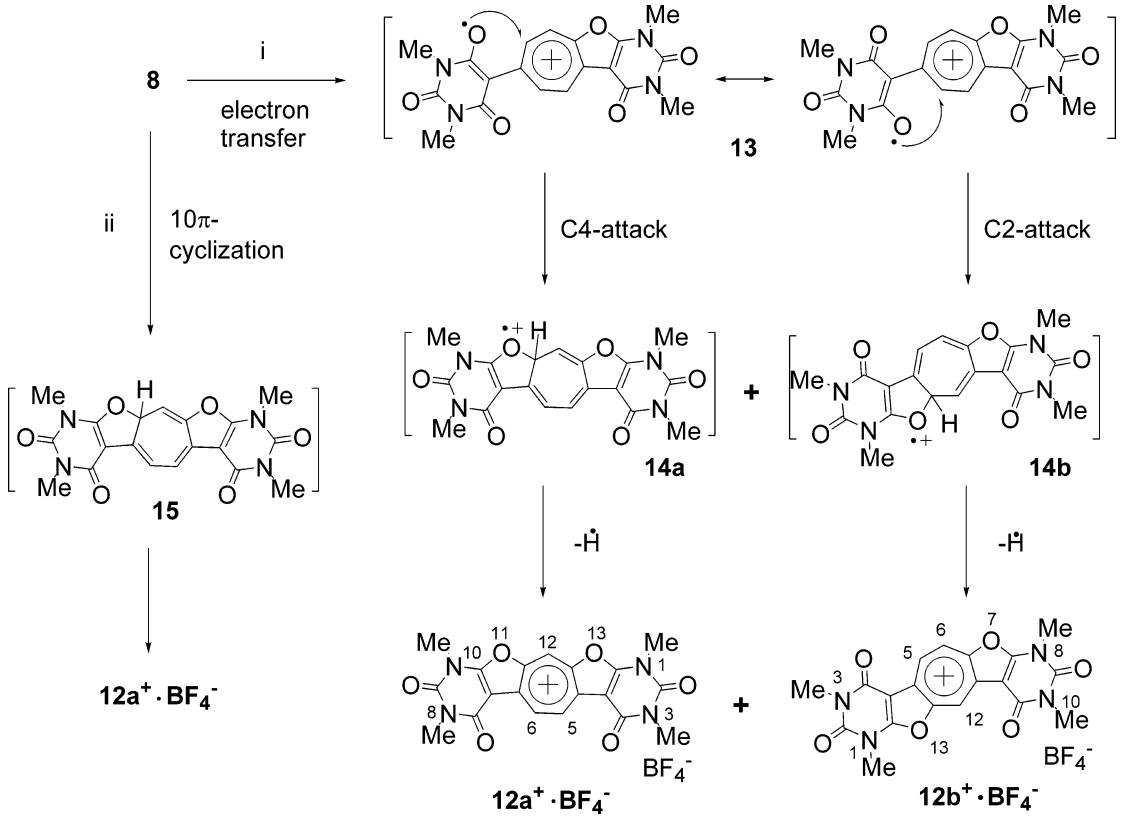
SCHEME 2 [a]



[a] Reagents and conditions: (i) (a) DDQ, $CHCl_3$, reflux, 1 h; (b) 42% aq HBF_4, Ac_2O, 0 °C, 1 h; (ii) (a) *hν*, aerobic, 42% aq HBF_4, $CH_3CN-(CH_2Cl)_2$, rt, 48 h; (b) 42% aq HBF_4, Ac_2O, 0 °C, 1 h;

reaction of **4a**$^+$·BF_4^- with **7** in the presence of Et_3N afforded compound **11** quantitatively. The structure of **11** was determined on the basis of the ^1H and ^{13}C NMR and IR spectral data, as well as elemental analysis. A careful study of the NMR signals of **11** led us to conclude it is a 3:2 chromatographically inseparable mixture of meso and racemic forms. However, FABMS of **11** gives only the $(M + H)^+$ peak of **8** instead of the $(M + H)^+$ peak of **11** probably due to easy elimination of **9a**−**c**. A solution of **11** in xylene was heated at 90 °C for 3 h to afford **8** (83%) and a mixture of **9a**−**c** (33%). Thus, the reaction of **6** with **7** giving **8** and **9a**−**c** would proceed as follows: the condensation of 2-methoxytropone **6** with dimethylbarbituric acid **7** gives intermediate **10**, which undergoes demethoxylating cyclization to give cation **4a**$^+$. The addition reaction of **4a**$^+$ with another dimethylbarbituric acid **7** occurs quickly to give the intermediate **11**, which undergoes an elimination reaction to give **8** and **9a**−**c**.

The reaction of **8** with DDQ in $CHCl_3$ under reflux for 1 h and subsequent anion exchange reaction by using aq HBF_4 in Ac_2O afforded a mixture of **12a**$^+$·BF_4^- and **12b**$^+$·BF_4^- in a good combined yield (90%, Scheme 2).[11] The ratio of **12a**$^+$·BF_4^- and **12b**$^+$·BF_4^- is determined to be 1:4 from the ^1H NMR spectrum of the mixture. The mixture of **12a**$^+$·BF_4^- and **12b**$^+$·BF_4^- was separated by fractional recrystallization from CH_3CN/AcOEt to give pure samples of **12a**$^+$·BF_4^- and **12b**$^+$·BF_4^-. According to the redox properties of **8** under CV measurement (vide infra), the DDQ-prompted oxidative cyclization of **8** would proceed via a similar pathway to that of compounds **3a**,**b**[11] as outlined in Scheme 2. The radical cation **13**, which is generated by one-electron oxidation of **8**, undergoes a cyclization reaction to give intermediates **14a** and **14b**, the hydrogen abstraction of which gives cations **12a**$^+$ and **12b**$^+$, respectively. Subsequent anion exchange reaction with aq HBF_4 solution results in the formation of **12a**$^+$·BF_4^- and **12b**$^+$·BF_4^-. On the other hand, oxidative cyclization of **8** was also accomplished by photoirradiation (RPR-100, 350-nm lamps) under aerobic conditions in the presence of 42% aq HBF_4. The reaction proceeded selectively to give **12a**$^+$·BF_4^- as a single product in quantitative yield. The photoinduced oxidative cyclization of **8** would proceed as shown also in Scheme 2. The photoinduced 10*π*-cyclization of **8** gives intermediate **15**, which would undergo 1,7-hydrogen shift and oxidation under photoirradiation and aerobic conditions in the presence of 42% aq HBF_4 leading to **12a**$^+$·BF_4^-.

To clarify the selectivity of the two cyclizations, MO calculations of **8** and **13** were carried out with use of the AM1 method (MOPAC97).[14] At C2 and C4, the charge density of **8** and **13** as well as the coefficients of LUMOs of **8** and **13** are depicted in Figure 2. Regarding the charge density and the coefficients of the LUMO for radical cation **13**, both values are larger for C2 than those for C4, suggesting that intramolecular radical addition of the former position occurs preferentially to that of the latter position, irrespective of whether addition occurs charge controlled or frontier orbital controlled. On the contrary, the photoinduced 10*π*-cyclization of **8** would

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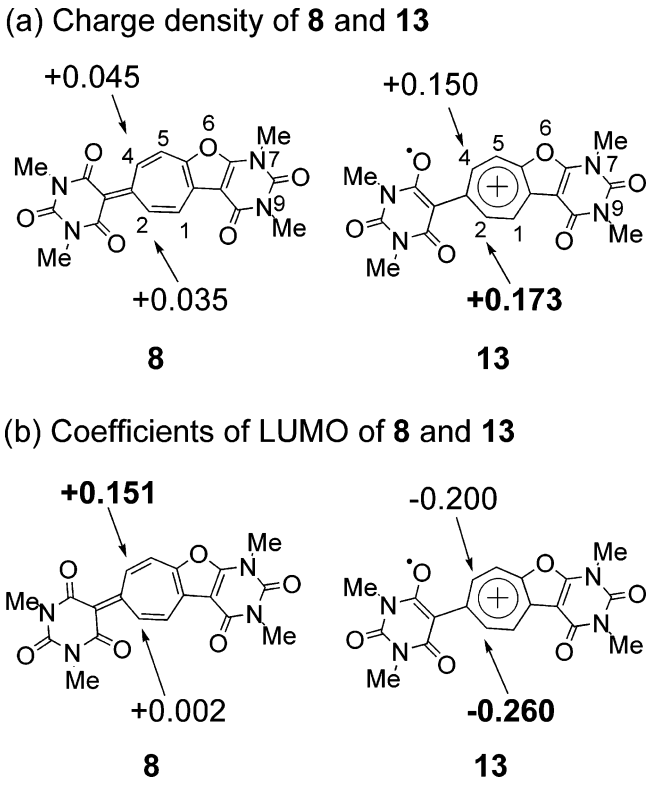

FIGURE 2.

occur frontier orbital controlled. Regarding the coefficients of the LUMO for **8**, the value is much larger for C4 than for C2, suggesting that the 10π-cyclization of the former position occurs preferentially to that of the latter position. Consequently, **15** would be generated selectively to result in the formation of only **12a**$^+$·BF_4^-. Thus, the selectivity of the two cyclizations of **8** seems to be rationalized.

Properties. The structure of **8** was determined on the basis of the ^{1}H and ^{13}C NMR, IR, and mass spectral data, as well as elemental analysis. Two methyl groups on the N1′ and N3′ of the pyrimidine moiety appear equivalent. This is probably due to the free rotation around the exocyclic double bond of the fulvene system on the NMR time scale. In the ^{13}C NMR spectrum, a signal of the C5′ of the barbituric acid moiety in **8** appears at similar field (δ_C 103.7) to those of **3a**,**b** (**3a**, δ_C 102.7; **3b**, δ_C 101.2),[11] suggesting a similar electron density. Thus, a polarization of the exocyclic double bond of the fulvene system of **8** seems to be similar to that of **3a**,**b**. In the UV−vis spectrum, the longest wavelength absorption maximum (λ_{max}) of **8** appears at a longer wavelength (487 nm) than that of **3a**[11] (431 nm), and thus the difference in the wavelength ($\Delta\lambda$) between **8** and **3a** is 56 nm. Although 42% aq HBF_4 was added to the solution, the visible region of the spectrum of **8** was not changed. By addition of TFA to the CH_3CN solution of **8**, new absorption appeared at 420 nm, which probably corresponds to the absorption of the 7,9-dimethyl-3-[1′,3′-dimethyl-2′(1′*H*),4′(3′*H*)-dioxo-6′-hydroxypyrimidin-5′-yl]cyclohepta[*b*]pyrimido[5,4-*d*]furan-8(7*H*),10(9*H*)-dionylium ion **16**$^+$ (Figure 3) generated by protonation on the baribituric acid moiety in **8**. In contrast, addition of TFA to the CH_3CN solution of **3a** causes no change in the UV−vis spectrum, suggesting

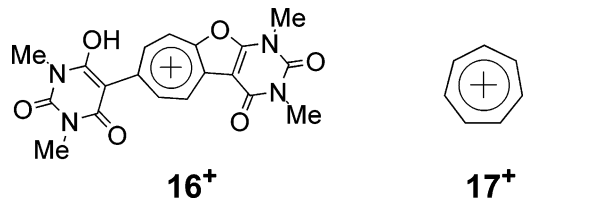

FIGURE 3.

that protonation of **3a** would not occur. The feature is rationalized by the difference in thermodynamic stability between **4a**$^+$ (pK_{R^+}, ca. 6.0) and simple tropylium ion **17**$^+$ (pK_{R^+}, 3.9).[18] However, the absorption of **8** did not disappear completely by addition of a larger amount of TFA, suggesting that the basicity of **8** is not so high, and thus, the complete protonation of **8** does not occur. The mixture regenerated **8** quantitatively upon the addition of Et_3N, and thus, the protonation−deprotonation cycle is completely reversible.

The redox property of **8** was determined by cyclic voltammetry (CV) in acetonitrile. The reduction and oxidation waves of **8** were irreversible under the conditions of CV measurements, and the peak potentials are −1.16 ($E1_{red}$) and +0.87 V ($E1_{ox}$). At the first reduction potential ($E1_{red}$) of **8**, a radical anion would be generated. The value ($E1_{red}$) of **8** is similar to those of **3a**,**b** (**3a**, −1.15 V; **3b**, −1.13 V).[11] On the other hand, radical cation **13** (Scheme 2) seems to be generated at the first oxidation potential ($E1_{ox}$). The value ($E1_{ox}$) of **8** is more negative than those of **3a**,**b** (**3a**, +1.08 V; **3b**, +1.11 V)[11] due to the larger stability of **4a**$^+$ as compared with tropylium ion **17**$^+$. After the first cycle of CV measurement of **8**, another reduction wave was recorded at −0.62 V. This wave is suggested to be the reduction waves of **12a**$^+$ and **12b**$^+$, which are generated by oxidative cyclization reactions of **8** under CV measurement. This feature is similar to the behavior of compounds **3a**,**b**.[11] Thus, DDQ-prompted oxidative cyclization of **8** affording cations **12a**$^+$ and **12b**$^+$ would proceed via a similar pathway to that of compounds **3a**,**b** (vide supra).

In a similar fashion, compounds **12a**$^+$·BF_4^- and **12b**$^+$·BF_4^- were fully characterized on the basis of the ^{1}H and ^{13}C NMR, IR, UV−vis, and mass spectral data, as well as the elemental analyses. In the UV−vis spectra, the longest wavelength absorption maxima (λ_{max}) of **12a**$^+$ and **12b**$^+$ appear at longer wavelength (**12a**$^+$, 460 nm;

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TABLE 1. λ_{max} and pK_{R^+} Values and Reduction Potentials[a] of Cations 12a$^+$ [b] and 12b$^+$ [b] and Reference Cations 4a$^+$, 5$^+$, and 17$^+$

			reduction potential/V	
compd	λ_{max}	pK_{R^+}	$E1_{red}$	$E2_{red}$
12a$^+$	460	8.8	−0.63	
12b$^+$	456	8.6	−0.62	
4a$^+$ [c]	397	ca. 6.0	−0.58	
5$^+$ [d]	441	4.7	−0.46	−1.07
17$^+$ [e]	273	3.9	−0.51	

[a] *V* vs Ag/AgNO$_3$; cathodic peak potential. [b] Salt **12a**$^+$·BF$_4^-$ and **12b**$^+$·BF$_4^-$ were used for the measurement. [c] Reference 12. [d] Reference 13. [e] Reference 18.

12b$^+$, 456 nm) than those of **4a**$^+$ [12] and **5**$^+$ [13] (**4a**$^+$, 397 nm; **5**$^+$, 441 nm), suggesting that cations **12a**$^+$ and **12b**$^+$ have a more extended conjugation as compared with those of **4a**$^+$ and **5**$^+$ (Table 1). X-ray crystal analyses of **12a**$^+$·BF$_4^-$ and **12b**$^+$·BF$_4^-$ were performed, and the ORTEP drawings are shown in Figure 4.[15] Compounds **12a**$^+$·BF$_4^-$ and **12b**$^+$·BF$_4^-$ have a nearly planar structure. On both compounds **12a**$^+$·BF$_4^-$ and **12b**$^+$·BF$_4^-$, the bond lengths of O1−C15 and O2−C9 are shorter than those of O1−C2 and O2−C6, suggesting that the former bonds have a larger bond order. Furthermore, on compound **12a**$^+$·BF$_4^-$, the bond length of C4−C5 is shorter than those of C3−C4 and C5−C7. On compound **12b**$^+$·BF$_4^-$, the bond length of C1−C2 is shorter than that of C1−C7. These facts suggest the existence of bond alternation as shown in the canonical structures of **12a,b**$^+$**-B** and **12a,b**$^+$**-C** (Figure 5). The feature shows also that cations **12a**$^+$ and **12b**$^+$ have a more extended conjugation as compared with **4a**$^+$ and **5**$^+$.[12,13] MO calculations of **12a**$^+$ and **12b**$^+$ were carried out by the 6-31G* basis set of the MP2 level,[16] and it was found that the bond length alternations obtained by the MO calculations are very similar to those obtained by the X-ray analyses.

The affinity of the carbocation toward hydroxide ions expressed by the pK_{R^+} value is the most common criterion of carbocation stability.[17] The pK_{R^+} values of cations **12a**$^+$ and **12b**$^+$ were determined spectrophotometrically in buffer solutions prepared in 50% aqueous CH$_3$CN and are summarized in Table 1, along with those of reference cations **4a**$^+$,[12] **5**$^+$,[13] and tropylium ion **17**$^+$.[18] The pK_{R^+} values of **12a**$^+$ and **12b**$^+$ (**12a**$^+$, pK_{R^+}, 8.8; **12b**$^+$, pK_{R^+}, 8.6) are larger than those of **4a**$^+$ (pK_{R^+}, ca. 6.0), **5**$^+$ (pK_{R^+}, 4.7), and **17**$^+$ (pK_{R^+}, 3.9), suggesting that the two 2,4-dimethylfuro[2,3-*d*]pyrimidine-1(2*H*),3(4*H*)-dione moieties stabilize the tropylium ion quite effectively. While the benzo-annulation onto **4a**$^+$ has a destabilization effect on the cation **5**$^+$, one more annulation of the furopyrimidine-ring onto **4a**$^+$ has a stabilizing effect on the cations **12a**$^+$ and **12b**$^+$. Although the pK_{R^+} value of **12a**$^+$ is larger than that of **12b**$^+$, the difference is small, suggesting that the difference in perturbations due to the position of annulation by the furopyrimidine-ring is small.

The reduction potentials of **12a**$^+$ and **12b**$^+$ were determined by cyclic voltammentry (CV) in CH$_3$CN. The reduction waves of **12a**$^+$ and **12b**$^+$ were irreversible under the conditions of the CV measurements; the peak potential is also summarized in Table 1, together with those of the reference cations **4a**$^+$,[12] **5**$^+$,[13] and tropylium ion **17**$^+$.[18] The irreversible nature is probably due to the formation of the tropyl radical and its dimerization, which seems to be a typical property of tropylium ions.[19] The $E1_{red}$ values of dodecyl derivatives of **2a**,**b** (**2a**, −0.84 V; **2b**, −0.99 V) have been reported to be less negative than that of a dodecyl derivative of **1a** (−1.44 V).[7,8] On the contrary, the $E1_{red}$ of **12a**$^+$ and **12b**$^+$ are slightly more negative by 0.04 and 0.05 V than that of **4a**$^+$, but the values are less negative than those of **1a**, **2a**, and **2b**.

Reactivity. While the reaction of **4a**$^+$·BF$_4^-$ with NaBH$_4$ proceeded at the 1-, 3-, and 5-positions to afford a mixture of three regioisomers **9a**−**c**,[12] the reduction of **12a**$^+$·BF$_4^-$ and **12b**$^+$·BF$_4^-$ occurs on the C12 to afford **18a** and **18b**, respectively, in good yields due to two closed furopyrimidine-rings (Scheme 3). The reaction is similar to that of **5**$^+$·BF$_4^-$.[13] Upon hydride abstraction with DDQ and subsequent anion exchange reaction, compounds **18a** and **18b** regenerated **12a**$^+$·BF$_4^-$ and **12b**$^+$·BF$_4^-$, respectively, in quantitative yields. On the other hand, the reaction of **4a**$^+$·BF$_4^-$ with diethylamine afforded a C5a-adduct, which underwent a ring-opening reaction to give **22** (Scheme 4).[12] In contrast, the diethylamine addition of **5**$^+$·BF$_4^-$ occurred at only C7 to give **23**, which is stable and does not undergo a further isomerization reaction.[13] Thus, the reactivity of **12a**$^+$·BF$_4^-$ and **12b**$^+$·BF$_4^-$ with diethylamine is very interesting, and the reaction of **12a**$^+$·BF$_4^-$ with diethylamine was monitored by ^{1}H NMR spectroscopy in CD$_3$CN. Initially, diethylamine addition to **12a**$^+$·BF$_4^-$ occurred at C12 to afford **19a** (Scheme 4). Although compound **19a** is stable in dilute solution, it decomposes during concentration in vacuo. Satisfactory ^{1}H and ^{13}C NMR spectra were obtained for **19a**. While the C12-adduct **19a** is stable under ^{1}H NMR measurement (1 h), a slow isomerization reaction seemed to occur (48 h) to give **20a**, which underwent ring-opening reaction to afford **21a** (Scheme 4). On the other hand, a reaction of **12b**$^+$·BF$_4^-$ with diethylamine gives only C6a-adduct **20b**, which undergoes ring-opening reaction to give **21b**. Compound **21b** was stable and no isomerization reaction was observed. On the basis of the study of ^{1}H and ^{13}C NMR, we have reported that compound **22** has a larger contribution of the canonical structure **22-B**.[12] On the contrary, considering the large coupling constant (10.4 Hz) between the H1 and H2, as well as the high-field chemical shift of C4 (δ_C 125.0 ppm), compound **21a** has a larger contribution of the canonical structure **21a-A**, probably due to the stability of the closed furan ring. The large coupling constant (11.4 Hz) between the H1 and the H2 and the low-field chemical shift of C4 (δ_C 175.4 ppm) suggest that compound **21b** has a larger contribution of the canonical structure **21b-B**, probably due to the stability of the closed furan ring. Upon treatment with aq HBF$_4$ in Ac$_2$O, compounds **19a**, **21a**, and **21b** regenerated **12a**$^+$·BF$_4^-$ and **12b**$^+$·BF$_4^-$ in good yield.

Autorecycling Oxidation. The double 5-deazaflavins **2a** and **2b** have been studied as photocatalysts for cyclohexanol under photoirradiation.[7,8] Moreover, we have previously reported that compound **4a**$^+$·BF$_4^-$ acts as a photocatalyst for some alcohols under photoirradiation.[12] In this context and in a search for functions of

(19) (a) Doering, W. von E.; Knox, L. H. *J. Am. Chem. Soc.* **1954**, *76*, 3203−3206. (b) Doering, W. von E.; Knox, L. H. *J. Am. Chem. Soc.* **1957**, *79*, 352−356. (c) Okamoto, K.; Komatsu, K.; Kinoshita, T.; Shingu, H. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 1901−1902.

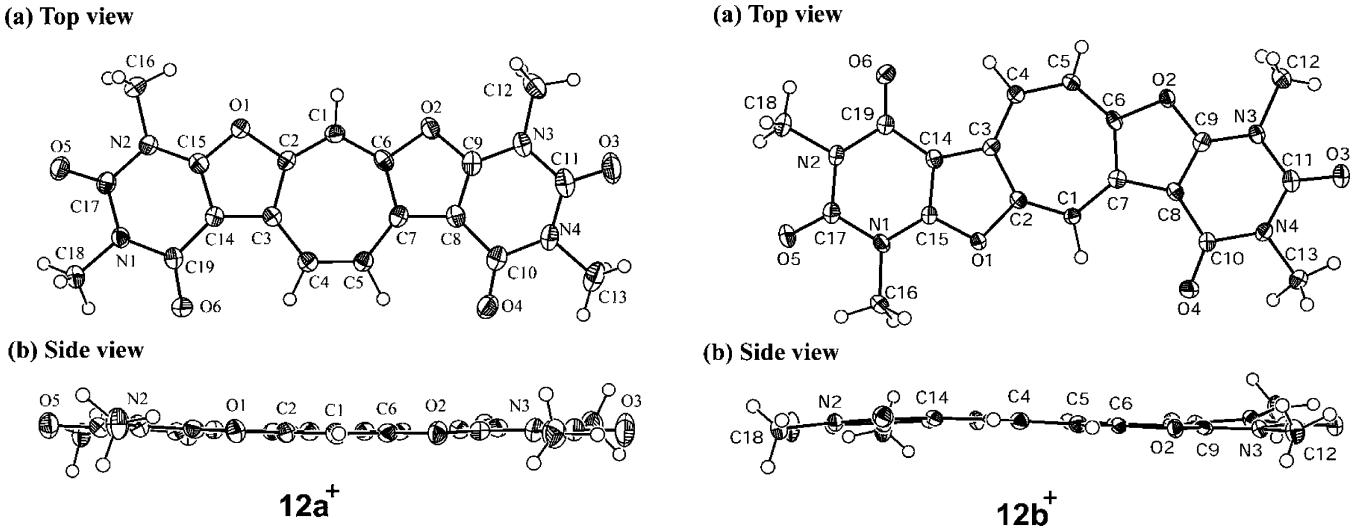


FIGURE 4. ORTEP drawings of **12a**$^+$·BF_4^- and **12b**$^+$·BF_4^- with thermal ellipsoid plot (50% probability). Selected bond lengths (Å) of **12a**$^+$·BF_4^-: O1−C2 1.392(4), O1−C15 1.341(4), O2−C6 1.390(4), O2−C9 1.348(5), C1−C2 1.361(5), C2−C3 1.423(5), C3−C4 1.421(5), C4−C5 1.373(5), C5−C7 1.413(5), C6−C7 1.424(5), C1−C6 1.374(5), C3−C14 1.426(5), C7−C8 1.416(5), C8−C9 1.364(5), C14−C15 1.371(5). Selected bond lengths (Å) of **12b**$^+$·BF_4^-: O1−C2 1.394(3), O1−C15 1.345(3), O2−C6 1.384(3), O2−C9 1.347(3), C1−C2 1.366(3), C2−C3 1.436(3), C3−C4 1.401(3), C4−C5 1.376(3), C5−C6 1.383(3), C6−C7 1.420(3), C1−C7 1.409(3), C3−C14 1.417(3), C7−C8 1.428(3), C8−C9 1.358(3), C14−C15 1.369(3).

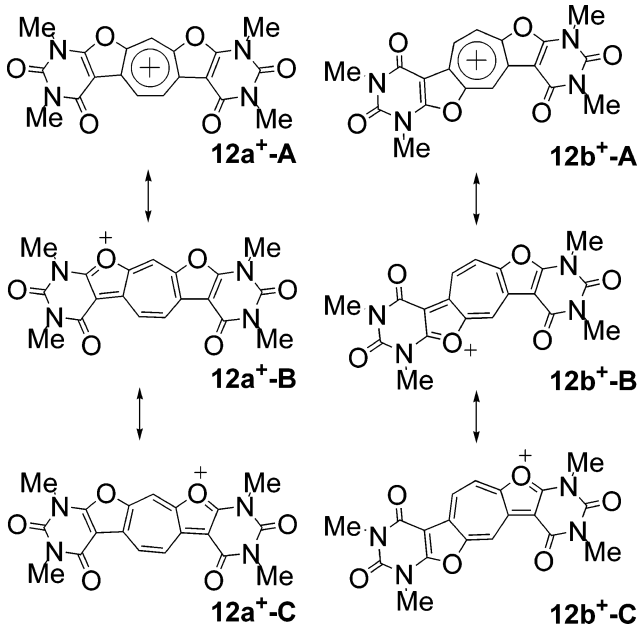
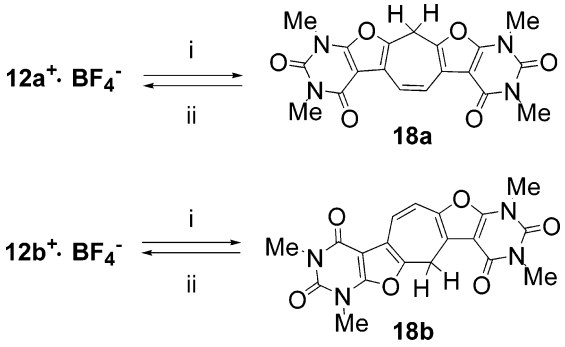


FIGURE 5.

SCHEME 3[a]



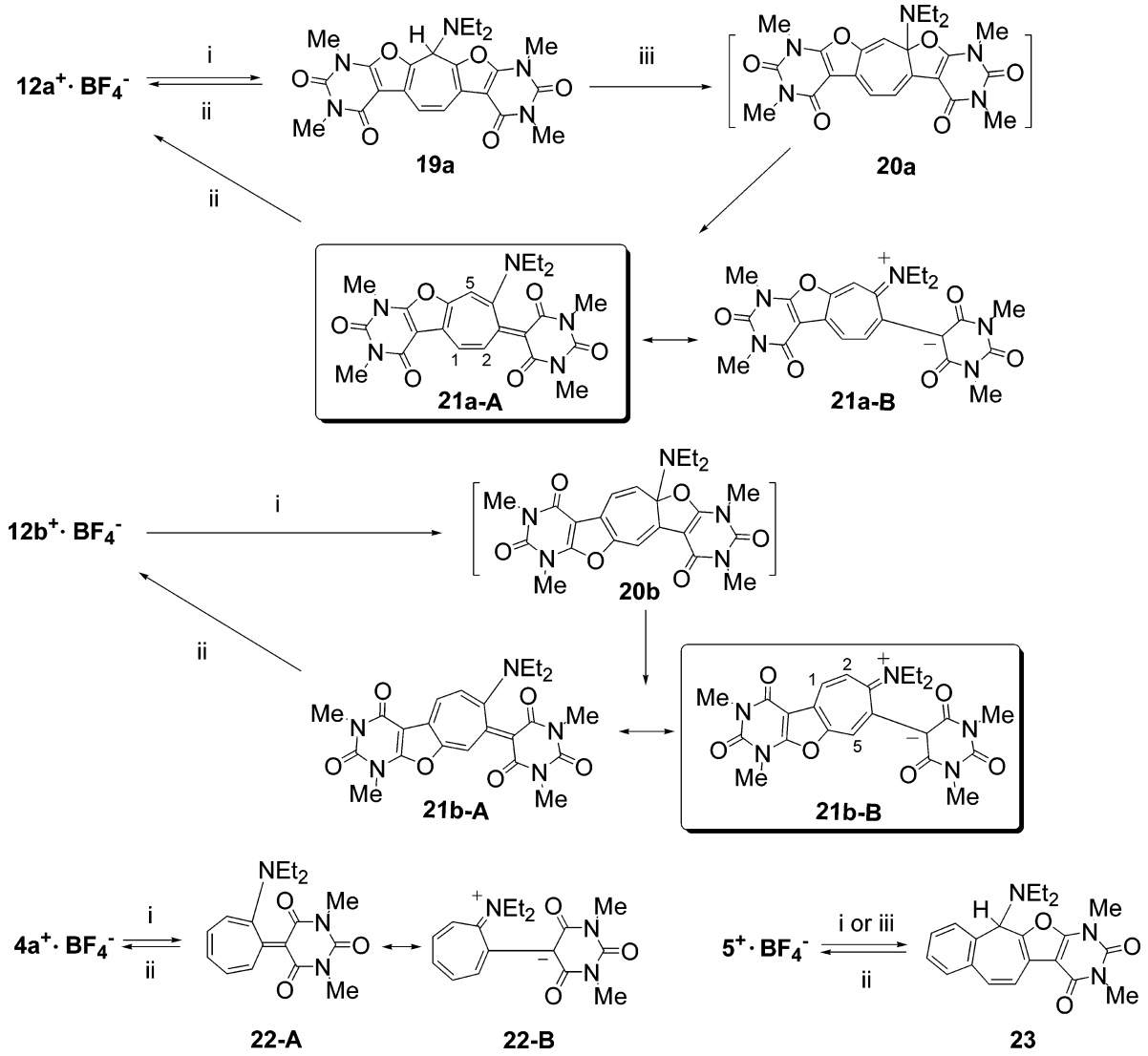
[a] Reagents and conditions: (i) $NaBH_4$, CH_3CN, rt, 1 h; (ii) (a) DDQ, CH_2Cl_2, rt, 1 h; (b) 42% aq HBF_4, Ac_2O, 0 °C, 1 h

12a$^+$·BF_4^- and **12b**$^+$·BF_4^-, we examined the oxidation of some alcohols and amines by using **12a**$^+$·BF_4^- and **12b**$^+$·BF_4^-. We found that salts **12a**$^+$·BF_4^- and **12b**$^+$·BF_4^- can oxidize benzyl alcohol and cyclohexanol to give benzaldehyde and cyclohexanone, respectively, under aerobic and photoirradiation conditions. Furthermore, we found that salts **12a**$^+$·BF_4^- and **12b**$^+$·BF_4^- can oxidize benzylamine and 1-phenylethylamine to give the corresponding imines. The photooxidation results are summarized in Table 2. Oxidation of benzyl alcohol and benzylamine with reference salt **4a**$^+$·BF_4^- under similar conditions was also carried out (Table 2, entries 9 and 10). Those reactions gave better yields as compared with those of **12a**$^+$·BF_4^- and **12b**$^+$·BF_4^-. Direct irradiation of the alcohols and amines in the absence of **12a**$^+$·BF_4^- or **12b**$^+$·BF_4^- (named "blank") gives the corresponding carbonyl compounds in small amounts. Thus, the yield in Table 2 is calculated by subtraction of the "blank" yield from the yield of the carbonyl compound in the presence of **12a**$^+$·BF_4^- or **12b**$^+$·BF_4^-. Carbonyl compounds are obtained in more than 100% yield [based on salts **12a**$^+$·BF_4^- or **12b**$^+$·BF_4^-] under photoirradiation, and thus the autorecycling oxidation clearly proceeds. Attempted detection of the intermediate such as reduced compounds **18a** and **18b** in the oxidation reaction of alcohols and amines was unsuccessful at the present stage. We propose that the present autorecycling oxidation proceeds via electron transfer from alcohol or amine to the excited cation **12a**$^+$·BF_4^- or **12b**$^+$·BF_4^-;[12,20] however, further investigations are required to clarify details of the present autorecycling oxidation reaction.

In summary, a convenient synthesis of novel tropylium ions annulated with two 2,4-dimethylfuro[2,3-*d*]pyrimidine-1(2*H*),3(4*H*)-diones **12a**$^+$·BF_4^- and **12b**$^+$·BF_4^- was accomplished. On the basis of MO calculations of a novel

(20) Naya, S.; Iida, Y.; Nitta, M. *Tetrahedron* **2004**, *60*, 459−467.

SCHEME 4 [a]



[a] Reagents and conditions: (i) Et_2NH, CD_3CN, rt, 30 s; (ii) 42% aq HBF_4, Ac_2O, 0 °C, 1 h; (iii) Et_2NH, CH_3CN, rt, 48 h;

TABLE 2. Autorecycling Oxidation of Some Alcohols and Amines by $12a^+ \cdot BF_4^-$, $12b^+ \cdot BF_4^-$, and Reference Salt $4a^+ \cdot BF_4^-$ under Photoirradiation[a]

entry	salt	alcohol or amine	carbonyl compd[b]	yield[c]/%
1	**12a**$^+ \cdot BF_4^-$	$PhCH_2OH$	PhCHO	2224
2	**12b**$^+ \cdot BF_4^-$	$PhCH_2OH$	PhCHO	1429
3	**12a**$^+ \cdot BF_4^-$	cyclohexanol	cyclohexanone	669
4	**12b**$^+ \cdot BF_4^-$	cyclohexanol	cyclohexanone	432
5	**12a**$^+ \cdot BF_4^-$	$PhCH_2NH_2$	$PhCH{=}NCH_2Ph$	7699
6	**12b**$^+ \cdot BF_4^-$	$PhCH_2NH_2$	$PhCH{=}NCH_2Ph$	6601
7	**12a**$^+ \cdot BF_4^-$	$PhCH(Me)NH_2$	$PhMeC{=}NCHMePh$	5213
8	**12b**$^+ \cdot BF_4^-$	$PhCH(Me)NH_2$	$PhMeC{=}NCHMePh$	3600
9	**4a**$^+ \cdot BF_4^-$ [d]	$PhCH_2OH$	PhCHO	4468
10	**4a**$^+ \cdot BF_4^-$ [e]	$PhCH_2NH_2$	$PhCH{=}NCH_2Ph$	8161

[a] CH_3CN solution was irradiated by RPR-100, 350-nm lamps under aerobic conditions. [b] Isolated by conversion to 2,4-dinitrophenylhydrazone. [c] Based on **12a**$^+ \cdot BF_4^-$ or **12b**$^+ \cdot BF_4^-$ used; the yield is calculated by subtraction of the "blank" yield from the total yield of carbonyl compound in the presence of **12a**$^+ \cdot BF_4^-$ or **12b**$^+ \cdot BF_4^-$. [d] Reference 12. [e] This work.

heptafulvene **8**, the selectivity of two types of oxidative cyclization was clarified. The structural characteristics of **12a**$^+ \cdot BF_4^-$ and **12b**$^+ \cdot BF_4^-$ were studied by X-ray crystal analyses and MO calculations. The physical properties of **12a**$^+ \cdot BF_4^-$ and **12b**$^+ \cdot BF_4^-$ were investigated by measurement of the UV−vis spectra, the pK_{R^+} values, and the reduction potentials. Reactivity of **12a**$^+ \cdot BF_4^-$ and **12b**$^+ \cdot BF_4^-$ with diethylamine was substantially dependent on the annulating position. The photoinduced autorecycling oxidation reaction of **12a**$^+ \cdot BF_4^-$ and **12b**$^+ \cdot BF_4^-$ toward some alcohols and amines was carried out to afford the corresponding carbonyl compounds in yields of more than 100%.

Experimental Section

General experimental conditions and spectroscopic instrumentation used have been previously described.[11]

Preparation of 7,9-Dimethyl-3-[1′,3′-dimethyl-2′(1′*H*),4′-(3′*H*),6′(5′*H*)-trioxopyrimidin-5′-ylidene]cyclohepta[*b*]pyrimido[5,4-*d*]furan-8(7*H*),10(9*H*)-dione (8). A solution of 2-methoxytropone **6** (136 mg, 1 mmol) and dimethylbarbituric acid **7** (313 mg, 2 mmol) in Ac_2O (2 mL) was heated under reflux for 0.5 h. After the reaction was completed, the mixture was concentrated in vacuo. The resulting residue was chro-

matographed on SiO_2 with AcOEt as the eluent to give **8** (150 mg, 38%) and a mixture of **9a**−**c** (122 mg, 50%). The mixture of compounds **9a**−**c** was identified on the basis of the comparison of the physical data with those reported in the literature.[12]

Independent Preparation of Compounds 11. A solution of **4a**$^+$·BF_4^- [11] (132 mg, 0.4 mmol) and **7** (31 mg, 0.2 mmol) in CH_3CN (5 mL) in the presence of Et_3N (50 mg, 0.5 mmol) was stirred at room temperature for 2 h. To the mixture was added H_2O, and the mixture was extracted with CH_2Cl_2. The extract was dried over Na_2SO_4 and concentrated in vacuo to give compound **11** (128 mg, 100%).

Thermal Elimination Reaction of 11. A solution of **11** (192 mg, 0.3 mmol) in xylene (5 mL) was heated at 90 °C under N_2 for 3 h. After evaporation of the solvent, the residue was separated by column chromatography on SiO_2 (hexane−AcOEt, 1:1) to give **8** (99 mg, 83%) and **9a**−**c** (24 mg, 33%).

Oxidative Cyclization of 8 with DDQ. To a stirred solution of **8** (396 mg, 1 mmol) in $CHCl_3$ (20 mL) was added DDQ (467 mg, 2 mmol) and the mixture was heated under reflux for 1 h until the reaction was complete. After evaporation of the $CHCl_3$, the residue was dissolved in a mixture of Ac_2O (10 mL) and 42% aq HBF_4 (2 mL) at 0 °C and the mixture was stirred for 1 h. To the mixture was added Et_2O (200 mL) and the precipitate was collected by filtration and washed with Et_2O to give a mixture of **12a**$^+$·BF_4^- and **12b**$^+$·BF_4^- (431 mg, 90%) in the ratio of 4:1.

Oxidative Cyclization of 8 by Photoirradiation. A solution of **8** (198 mg, 0.5 mmol) and 42% aq HBF_4 (2 mL) in CH_3CN (180 mL) and $(CH_2Cl)_2$ (20 mL) in a Pyrex tube was irradiated by RPR-100, 350-nm lamps under aerobic conditions for 48 h until the reaction was complete. The mixture was concentrated in vacuo, and the resulting residue was dissolved in a mixture of Ac_2O (10 mL) and 42% aq HBF_4 (2 mL) at 0 °C. The mixture was stirred for 1 h. To the mixture was added Et_2O (100 mL) and the precipitate was collected by filtration to give **12a**$^+$·BF_4^- (238 mg, 99%).

Determination of pK_{R+} Values of 12a$^+$·BF_4^- and 12b$^+$·BF_4^-. Buffer solutions of slightly different acidities were prepared by mixing aqueous (H_2O−CH_3CN 5:4) solutions of potassium hydrogen phthalate (0.1 M) and NaOH (0.1 M) (for pH 4.1−5.9), KH_2PO_4 (0.1 M) and NaOH (0.1 M) (for pH 6.0−8.0), KH_2PO_4 (0.1 M) and NaOH (0.1 M) (for pH 6.0−8.0), $Na_2B_4O_7$ (0.025 M) and HCl (0.1 M) (for pH 8.2−9.0), and $Na_2B_4O_7$ (0.025 M) and NaOH (0.1 M) (for 9.2−10.8) in various portions. For the preparation of sample solutions, 1-mL portions of the stock solution, prepared by dissolving 3 mg of compounds **12a**$^+$·BF_4^- and **12b**$^+$·BF_4^- in CH_3CN (20 mL), were diluted to 10 mL with the buffer solution (9 mL). The UV−vis spectrum was recorded for each cation **12a**$^+$ and **12b**$^+$ in 20 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 wavelength (**12a**$^+$, 458 nm; **12b**$^+$, 453 nm) of cations **12a**$^+$ and **12b**$^+$ was plotted against pH to give a classical titration curve, whose midpoint was taken as the pK_{R^+} value.

Cyclic Voltammetry of Cations 12a$^+$ and 12b$^+$. The reduction potential of **12a**$^+$ and **12b**$^+$ was determined by using a 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 cations **12a**$^+$ and **12b**$^+$ (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 potential was corrected with reference to this standard. The cations **12a**$^+$ and **12b**$^+$ exhibited a reduction wave, and they are summarized in Table 1.

Reaction of 12a$^+$·BF_4^- or 12b$^+$·BF_4^- with $NaBH_4$. A solution of **12a**$^+$·BF_4^- or **12b**$^+$·BF_4^- (482 mg, 1 mmol) and $NaBH_4$ (38 mg, 1 mmol) in CH_3CN (10 mL) was stirred at room temperature 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 compound **18a** (396 mg, 100%) or **18b** (396 mg, 100%), respectively.

Oxidation of 18a and 18b. To a stirred solution of **18a** or **18b** (198 mg, 0.5 mmol) in CH_2Cl_2 (5 mL) was added DDQ (176 mg, 0.75 mmol), and the mixture was stirred at room temperature for 1 h. After evaporation of the CH_2Cl_2, the residue was dissolved in a mixture of Ac_2O (5 mL) and 42% aq 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 precipitate was collected by filtration to give **12a**$^+$·BF_4^- (241 mg, 100%) or **12b**$^+$·BF_4^- (241 mg, 100%), respectively.

^{1}H NMR Monitoring of the Reaction of 12a$^+$·BF_4^- and 12b$^+$·BF_4^- with Diethylamine. To a solution of **12a**$^+$·BF_4^- or **12b**$^+$·BF_4^- (0.01 mmol) in CD_3CN (0.5 mL) in a NMR tube was added diethylamine (7.3 mg, 0.1 mmol). The NMR measurement was carried out immediately (after ca. 30 s).

Reaction of 12a$^+$·BF_4^- and 12b$^+$·BF_4^- with Diethylamine. A solution of **12a**$^+$·BF_4^- (241 mg, 0.5 mmol) and diethylamine (147 mg, 2 mmol) in CH_3CN (10 mL) was stirred at room temperature for 48 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 **21a** (234 mg, 100%).

Reaction of 12b$^+$·BF_4^- with Diethylamine. A solution of **12b**$^+$·BF_4^- (241 mg, 0.5 mmol) and diethylamine (147 mg, 2 mmol) in CH_3CN (10 mL) was stirred at room temperature for 1 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 **21b** (224 mg, 97%).

Reaction of 19a with HBF_4. To a solution of **19a** (0.05 mmol) and diethylamine in CH_3CN, prepared by the reaction of **12a**$^+$·BF_4^- (0.05 mmol) with diethylamine (7.3 mg, 0.1 mmol) in CH_3CN (20 mL), was added a mixture of Ac_2O (5 mL) and 42% aq HBF_4 (1 mL) at 0 °C. The mixture was stirred for 1 h. To the mixture was added Et_2O (50 mL) and the precipitate was collected by filtration to give **12a**$^+$·BF_4^- (24 mg, 100%).

Reaction of 21a and 21b with HBF_4. A solution of **21a** or **21b** (234 mg, 0.5 mmol) in Ac_2O (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 precipitate was collected by filtration to give **12a**$^+$·BF_4^- or **12b**$^+$·BF_4^-, respectively (**12a**$^+$·BF_4^-, 217 mg, 90%; **12b**$^+$·BF_4^-, 234 mg, 97%).

General Procedure for the Oxidation of Alcohols in the Presence of 12a$^+$·BF_4^- and 12b$^+$·BF_4^-. A CH_3CN (16 mL) solution of salt **12a**$^+$·BF_4^- or **12b**$^+$·BF_4^- (0.005 mmol), an alcohol (2.5 mmol, 500 equiv), and K_2CO_3 (138 mg, 1 mmol) in a Pyrex tube was irradiated by RPR-100, 350-nm lamps under aerobic conditions for 16 h. The reaction mixture was concentrated in vacuo and diluted with Et_2O and filtered. The filtrate was treated with a saturated solution of 2,4-dinitrophenylhydrazine in 6% HCl to give 2,4-dinitrophenylhydrazone. The results are summarized in Table 2.

General Procedure for the Oxidation of Amines in the Presence 12a$^+$·BF_4^- and 12b$^+$·BF_4^-. A CH_3CN (16 mL) solution of salt **12a**$^+$·BF_4^- and **12b**$^+$·BF_4^- (0.005 mmol) and amines (2.5 mmol, 500 equiv) in a Pyrex tube was irradiated by RPR-100, 350-nm lamps under aerobic conditions for 16 h. The reaction mixture was concentrated in vacuo and diluted with Et_2O and filtered. The filtrate was treated with a saturated solution of 2,4-dinitrophenylhydrazine in 6% HCl to give 2,4-dinitrophenylhydrazone. The results are summarized in Table 2.

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Supporting Information Available: Detailed descriptions of the X-ray crystal analyses and calculated data for **12a**$^+$·BF_4^- and **12b**$^+$·BF_4^- as well as determination of pK_{R^+} values and cyclic voltammetry of **12a**$^+$·BF_4^- and **12b**$^+$·BF_4^-; UV−vis spectra of **12a**$^+$·BF_4^- and **12b**$^+$·BF_4^- and reference compound **4a**$^+$·BF_4^-. Analytical and spectroscopic data of **8**, **11**, **12a**$^+$·BF_4^-, **12b**$^+$·BF_4^-, **18a**,**b**, **19a**, and **21a**,**b**; and NMR data of **8**, **11**, **12a**$^+$·BF_4^-, **12b**$^+$·BF_4^-, **18a**,**b**, **19a**, and **21a**,**b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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