

New Synthesis, Properties, and Oxidizing Ability of 1,3-Dimethyl-5,10-methanocycloundeca[4,5]furo[2,3-d]pyrimidin-2,4(1,3H)-dionylium Tetrafluoroborate

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A novel synthesis of 1,3-dimethyl-5,10-methanocycloundeca[4,5]furo[2,3-d]pyrimidin-2,4(1,3H)dionylium tetrafluoroborate $(10^+ \cdot BF_4^-)$ was accomplished by the reaction of 3,8-methano[11]annulenone with dimethylbarbituric acid and following acidic cyclization, albeit in low yield. Remarkable structural characteristics were suggested on inspection of the spectral data and MO calculation, and it was clarified that the positive charge is largely localized at the C11. The pK_{R+} value of cation 10^+ was determined spectrophotometrically to be 4.6, which is much smaller by 4.1 pH unit than that of 1,3-dimethyl-7,12-methanocycloundeca[4,5]furo[2,3-d]pyrimidin-2,4(1,3H)dionylium tetrafluoroborate ($pK_{R+} = 8.7$). This value is also smaller by 1.6 pH unit than that of the parent 1,6-methano[11] annulenylium ion ($pK_{R+} = 6.2$). The feature is rationalized on the basis of the perturbation derived from the bond fixation of the parent cation. The electrochemical reduction of 10^+ exhibited less negative reduction potential at -0.39 (V vs Ag/AgNO₃) upon cyclic voltammetry (CV). In a search for reactivity, reactions of 10^+ with some nucleophiles, hydride and diethylamine, were carried out to give mixtures of C11- and C13-adducts. In both reactions, the methano-bridge controls the nucleophilic attacks to the C13 to favor exo selectivity. The photoinduced autorecycling oxidation reactions of 10^{+} BF₄⁻ toward some amines under aerobic conditions were carried out to give the corresponding imines (isolated by converting to the corresponding 2.4-dinitrophenylhydrazones) in 719–3286% yield (recycling number of $10^+ \cdot BF_4^-$: 7.2–32.9).

Introduction

Flavins are known to play an important role as cofactors in a wide variety of biological redox reactions.^{1,2} 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 enzymatic⁴ and model systems,⁵ in the hope of providing mechanistic insight into flavin-catalyzed reactions. In

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FIGURE 1.

this context, 5-deaza-10-oxaflavin **1b** (2*H*-chromeno[2,3-d]pyrimidin-2,4(3*H*)-dione), in which the nitrogen atom is replaced by an oxygen, has also 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, we have previously studied

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SCHEME 1^a



^a Reagents and conditions: (i) base, DMF, rt, 5 min; (ii) 35 °C, 48 or 72 h; (iii) 42% aq HBF₄, Ac₂O, 0 °C, 1 h.

convenient preparations of 10-substituted 3-methylcvclohepta[4,5]pvrro[2,3-d]pvrimidin-2,4(3H)-diones⁷ 2a and 3-methylcyclohepta[4,5]furo[2,3-d]pyrimidin-2,4(3H)dione 2b,⁸ which are the structural isomers of 1a and 1b, respectively, and their oxidation reactions toward some alcohols to the corresponding carbonyl compounds. In this relation, the synthesis, properties, and reactivity of $3a^+ \cdot BF_4^{-,9,10}$ and its sulfur and nitrogen analogues $3b - d^+ \cdot BF_4^{-11,12}$ as well as their novel photoinduced autorecycling oxidation reactions toward some alcohols also have been studied. Thus, structural modifications of the uracil-annulated heteroazulenes such as $3a-d^+\cdot BF_4^-$ are an interesting project from the viewpoint of exploration of novel functions. Much of the motivation for studying the properties of organic molecules stems from manipulation of the primary chemical structure. One strategy for raising or lowering the HOMO and LUMO levels includes conjugation length control. On the basis of this concept, we have recently reported the synthesis of 1,3-dimethyl-7,12-methanocycloundeca[4,5]furo[2,3-d]pyrimidin-2,4-(1,3H)-dionylium tetrafluoroborate $(4^+ \cdot BF_4^-, Scheme 1)$,¹³ which is a vinylogous compound of 3a, to involve 1,6methano[11]annulenylium ion 6⁺ instead of tropylium ion **5**⁺. The cation **6**⁺, which is an aromatic 10π -electron analogue of 5^+ , has higher thermodynamic stability (p $K_{\rm R+}$

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TABLE 1. Results for the Reactions of 12 with 13

run	base	time/h	yield/%	ratio of $10^+/4^+$
1	${ m Et_3N}$	48	6	83:17
2	(TMS) ₂ NH	48	trace	90:10
3	(TMS) ₂ NK	72	trace	90:10
4	NaH	48	8	100:0

 $= 6.2^{14}$ as compared with 5⁺ (p $K_{R+} = 3.9$).¹⁵ Due to this property, cation $4^+ \cdot BF_4^-$ exhibited higher thermodynamic stability (p $K_{R+} = 8.7$). Furthermore, the reactions of $4^+ \cdot BF_4^-$ with NaBD₄ and diethylamine exhibit that the methano-bridge controls the nucleophilic attacks to occur with endo selectivity. Thus, study of the methano-bridged compounds is an interesting project from the viewpoint of exploration of novel chiral auxiliaries.

Furthermore, 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. We have recently reported that perturbations derived from benzoannulation onto the cyclohepta[a]azulenylium ion are highly dependent on the annulating positions.¹⁶ From this viewpoint, the 1,6-methano[11]annulenylium ion annulated with the furopyrimidine on a different position from that of $4^+ \cdot BF_4^-$ seemed to be interesting. Thus, we have investigated the synthesis, properties, and reactivity of 1,3-dimethyl-5,10-methanocycloundeca[4,5]furo[2,3-d]pyrimidin-2,4(1,3H)-dionylium tetrafluoroborate ($10^+ \cdot BF_4^-$, Scheme 1) for the first time. Its structural characteristics are deduced based on the spectral data, pK_{R+} , redox potentials, and MO calculation. The photoinduced autorecycling oxidation of amines to give the corresponding imines is studied as well. We report here the results in detail.

Results and Discussion

Synthesis. A strategy for the preparation of 1,3dimethyl-5,10-methanocycloundeca[4,5]furo[2,3-d]pyrimidin-2,4(1,3*H*)-dionylium tetrafluoroborate $(10^+ \cdot BF_4^-)$ consisted of the reaction of 3,8-methano[11]annulenone $(12)^{17}$ with dimethylbarbituric acid (13) and following acidic cyclization. The reaction of 12 with 14, which is generated by the reaction of 13 with Et_3N , proceeded at the C2 and C11 to give a mixture of 15 and 16, as in the synthetic reaction of 17 and 18 (Figure 3).18 Compounds 15 and 16 are unstable on TLC (SiO₂ and Al_2O_3), and thus, without further isolation and purification, cyclization was carried out by using 42% aq HBF₄ to give $10^+ \cdot BF_4^-$ and 4⁺•BF₄⁻, respectively (Scheme 1, Table 1 run 1). Under similar conditions, (TMS)₂NH- and (TMS)₂NK-induced reactions of 12 and 13 afforded trace amounts of mixtures of $10^+ \cdot BF_4^-$ and $4^+ \cdot BF_4^-$ (Table 1, runs 2 and 3). In contrast, the NaH-induced reaction of 12 with 13 afforded

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FIGURE 2. UV-vis spectra of 10⁺ and reference compounds $3a^+$ and 4^+ in CH₃CN.



FIGURE 3. Coupling constants (*J*, in Hz) of $10^+ \cdot BF_4^-$, **4**⁺•BF₄⁻, **17**, and **18**.

a single product **15**, which is converted to $10^+ \cdot BF_4^-$ upon treatment with 42% aq HBF₄ in Ac₂O (Table 1, run 4). Unfortunately, the yields are poor, and thus, details of these reactions cannot be discussed at this stage.

Properties. Compound $4^+ \cdot BF_4^-$ is known¹³ and compound $10^+ \cdot BF_4^-$ was fully characterized on the basis of the ¹H NMR, ¹³C NMR, IR, UV-vis, and mass spectral data, as well as elemental analysis. The mass spectrum of $10^+ \cdot BF_4^-$ exhibited the correct $M^+ - BF_4^-$ ion peak, which is indicative of the cationic structure of the compound. The characteristic absorption band for the counterion of BF_4^- was observed at 1084 cm⁻¹ in the IR spectrum. The UV-vis spectrum of 10^+ ·BF₄⁻ in CH₃CN is shown in Figure 2, together with those of $3a^+ BF_4^$ and $4^+ \cdot BF_4^-$. The longest wavelength absorption maximum (λ_{max}) of $10^+ \cdot BF_4^-$ shows a red-shift by 110 nm as compared with that of $3a^+ \cdot BF_4^-$, suggesting the elongated π -conjugation. In addition, a red-shift (14 nm) of λ_{max} of $10^+ \cdot BF_4^-$ from that of $4^+ \cdot BF_4^-$ shows a larger perturbation due to the annulating position of the furopyrimidine ring. The¹H NMR spectrum of $10^+ \cdot BF_4^-$ is noteworthy, since the chemical shifts of bridged-annulene systems are quite useful in determining such structural properties as diatropicity and bond alternation. Unambiguous proton assignment was made by analyzing ¹H NMR, H-H COSY, and NOE spectra and selected coupling constants of the peripheral protons of $10^+ \cdot BF_4^-$ are shown in Figure 3 together with those of the reference compounds $4^+ \cdot BF_4^-$, 17,¹⁸ and 18.¹⁸ The large geminal coupling constant of

TABLE 2. ¹³C NMR Data and Calculated Charge Density of 10⁺

position	$\delta_{ m c}$	charge	position	$\delta_{ m c}$	charge
C2	150.6	1.106	C10	140.0	0.049
C4	164.9	0.944	C11	157.2	0.121
C4a	101.1	-0.275	C12	130.7	0.058
C4b	151.7	0.061	C13	129.3	0.052
C5	129.4	0.027	C13a	153.7	0.343
C6	139.0	0.157	C14a	158.4	0.895
C7	141.7	0.070	N1Me	31.4	0.392
C8	139.6	0.061	N3Me	29.6	0.379
C9	141.3	0.100	CH_2	31.3	0.044

the methylene protons ($J_{E,Z} = 12.4$ Hz) supports the absence of a norcaradiene structure for $10^+ \cdot BF_4^-$. The bridge protons of $10^+ \cdot BF_4^-$ appear at very high field (δ -0.53 and -1.33), and the peripheral protons appear in the aromatic region (δ 8.43 to 10.11), suggesting a large diatropic ring current.¹⁹ The vicinal coupling constants of protons of the aromatic perimeter of $10^+ \cdot BF_4^-$ suggest that the C6-C7-C8-C9 moiety exhibits small bond alternation $[J_{6,7} (8.6 \text{ Hz}), J_{7,8} (10.0 \text{ Hz}), J_{8,9} (8.6 \text{ Hz})]$. This feature is similarly observed for compound $4^+ \cdot BF_4^-$. In contrast, it is noteworthy that the C11-C12-C13 moiety of $10^+ \cdot BF_4^-$ exhibits large bond alternation [$J_{11,12}$ (9.7 Hz) $< J_{12,13}$ (12.5 Hz)]. While the vicinal coupling constants in the cycloheptatriene moiety of $4^+ \cdot BF_4^-$ and 18 are similar, a large difference in the vicinal coupling constants in 10^+ ·BF₄⁻ and 17 was observed. The ¹³C NMR spectral data for $10^+ \cdot BF_4^-$ were fully assigned by using the H-C Cosy spectra (HMQC and HMBC) as summarized in Table 2. Concerning the 11-membered ring, the chemical shift of the C13 carbon appeared at much higher field (δ_c 129.3) as compared with those of other carbons. In addition, the C11 carbon appeared at much lower field (δ_c 157.2) as compared with those of other carbons of the 11-membered ring, suggesting that the positive charge is localized largely at the C11-position. Unfortunately, a single crystal of $10^+ \cdot BF_4^-$ was not obtained by recrystallization from various solvents; however, we have reported that the structural details of 3b- \mathbf{d}^+ and $\mathbf{4}^+$ obtained by MO calculation show good agreement with those obtained by X-ray crystal analyses.^{9,11-13} Thus, MO calculation of 10^+ was carried out by the $6-31G^*$ basis set of the MP2 levels,²⁰ and the results are also summarized in Table 2. The calculated charge density of the C11 (+0.121) is relatively large, which accords with the feature of the ¹³C NMR spectrum. Thus, the canonical structures 10^+ -B and 10^+ -C would be important for 10^+ (Figure 4). Furthermore, the calculated bond length of C14a–O14 (1.349 Å) is shorter than that of C13a-O14 (1.395 Å), suggesting that a contribution of 10^+ -D is less important.

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FIGURE 4.

TABLE 3. pK_{R+} Values and Reduction Potentials of Cations 10^+ and Reference Compounds $3a^+$, 4^+ , 5^+ , and 6^+

compd	$pK_{ m R+}$	$(E1_{ m red})^b$
10 ^{+ a}	4.6	-0.39
$\mathbf{3a}^{+\ c}$	ca. 6.0	-0.58
$4^{+ d}$	8.7	-0.43
$5^{+ e}$	3.9	-0.51
6 ⁺ ^f	6.2	-0.42^{g}

^{*a*} Salts $10^+ \cdot BF_4^-$ are used for the measurement. ^{*b*} V vs Ag/AgNO₃; cathodic peak potential. ^{*c*} Reference 10. ^{*d*} Reference 13. ^{*e*} Reference 15. ^{*f*} Reference 14. ^{*g*} This work.

The affinity of the carbocation toward hydroxide ions expressed by the pK_{R+} value is the most common criterion of carbocation stability.²¹ The pK_{R+} values of cation 10^+ were determined spectrophotometrically in buffer solutions prepared in 50% aqueous CH₃CN and are summarized in Table 3, along with those of the reference compounds $3a^{+,9} 4^{+,13} 5^{+,15}$ and $6^{+,14}$ The p K_{R^+} value of 10^+ was determined to be 4.6, which is smaller by 4.1 pH unit than that of 4^+ (p $K_{R+} = 8.7$). In the reference compounds $3a^+$ and 4^+ , the annulation of the electrondonating furopyrimidine ring stabilizes the parent cations 5^+ and 6^+ , respectively. In contrast, the pK_{R+} value of 10⁺ is smaller by 1.6 pH unit than that of 6^+ (p K_{R^+} = 6.2), and thus, on the cation 10^+ , the annulation of the furopyrimidine ring destabilizes the parent cation 6^+ . The fact is quite different from those of $3a^+$ and 4^+ . The feature is rationalized on the basis of the perturbation derived from the bond fixation of the parent cation 6^+ . We have recently clarified that perturbations derived from benzo-annulation onto the cyclohepta[a]azulenylium ion are highly dependent on the annulating positions.¹⁶ While the benzo-annulation on the double bond having a large bond order of the parent cation causes smaller perturbation, the benzo-annulation on the double bond having a small bond order significantly perturbs both the original π -system and the annulating benzene ring. Regarding cation 6^+ , the X-ray crystal analysis has revealed that the bond length of C7-C8 (1.416 Å) is longer than that of C8-C9 (1.375 Å).²² Thus, the annulation of the furopyrimidine ring onto 6^+ at C7–C8 giving **10**⁺ would cause a larger perturbation than the annulation of the furopyrimidine ring onto 6^+ at C8–C9 giving





^{*a*} Reagents and conditions: (i) NaBH₄, CH₃CN, rt, 1 h; (ii) (a) DDQ, CH₂Cl₂, rt, 1 h, (b) 42% aq HBF₄, Ac₂O, 0 °C, 1 h; (iii) hv, aerobic, 42% aq HBF₄, CH₃CN-CH₂Cl₂, rt, 24 h.

4⁺. Due to this larger perturbation, the λ_{\max} of **10**⁺ would show a red-shift from that of **4**⁺ (vide supra). In the cation **10**⁺, this destabilizing effect is larger than the stabilizing effect derived from the electron-donating ability of furopyrimidine, and thus the cation **10**⁺ would exhibit a smaller pK_{R+} value as compared with that of **6**⁺.

The reduction potential of 10^+ was determined by cyclic voltammentry (CV) in CH₃CN. The reduction wave was irreversible under the conditions of the CV measurements; the peak potential is summarized in Table 3, together with those of the reference compounds 3a, 94^+ , 13 5^+ , 15 and 6^+ . 14 The $E1_{red}$ of 10^+ is less negative by 0.19 V than that of $3a^+$, suggesting the elongated π -conjugation of $10^+ \cdot BF_4^-$. Furthermore, the less negative $E1_{red}$ of 10^+ by 0.04 V as compared with that of 4^+ would be comparable to the lower pK_{R^+} value of 10^+ . 12,23 The irreversible nature is probably due to the formation of a radical species and its dimerization, as reported to be a typical property of uracil-annulated heteroazulenylium ions $3a-d^{+10-12}$ and 4^+ . 13

Reactivity. The reactions of $10^+ \cdot BF_4^-$ with some nucleophiles were investigated. While the reaction of $3a^+ \cdot BF_4^-$ with NaBH₄ proceeded at C5, C7, and C9 to give a mixture of three regioisomers 19–21 (19:20:21 29: 12:59),¹⁰ the reaction of $4^+ \cdot BF_4^-$ proceeded at the C13 to afford a single product 22.13 On the other hand, the reaction of $10^+ \cdot BF_4^-$ with NaBH₄ proceeded at C11 and C13 to give a mixture of 23 and 24 (in a ratio of 11:89) in quantitative yield (Scheme 2). There is a well-known tendency for double bond fixation in the methano[11]annulene system to favor a cycloheptatriene moiety predominantly over a 1,6-dimethylenecyclohepta-2,4diene moiety.²⁴ Thus, the formation of 23 and 24 would be ascribed to the stability of both the cycloheptatriene moiety and the closed furan ring. The formation of the C13-adduct predominates over the C11-adduct, although the positive charge is localized at C11 mainly (vide supra). The feature is similar to the reaction of $3a^+ \cdot BF_4^$ with NaBH₄, in which the ratio of C9-adduct 21 was

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TABLE 4. Autorecycling Oxidation of Some Amines by $10^+ \cdot BF_4^-$ under Photoirradiation^{*a*}

entry	compd	amine	imine	yield ^{b,c} /%	recycling no. d
1	$10^+ \cdot \mathrm{BF_4}^-$	$PhCH_2NH_2$	PhCH=NCH ₂ Ph	2238	22.4
2	$10^+ \cdot \mathrm{BF}_4^-$	PhCH(Me)NH ₂	PhMeC=NCHMePh	1733	17.3
3	$10^+ \cdot \mathrm{BF}_4^-$	hexylamine	N-hexylhexanal imine	3286	32.9
4	$10^+ \cdot BF_4^-$	cyclohexylamine	N-cyclohexylcyclohexanone imine	719	7.2
5	$3a^+ \cdot BF_4^-$	$PhCH_2NH_2$	PhCH=NCH ₂ Ph	8161	81.6
6	$4^+ \cdot BF_4^-$	$PhCH_2NH_2$	$PhCH=NCH_2Ph$	3007	30.1
7	$3a^+ \cdot BF_4^-$	PhCH(Me)NH ₂	PhMeC=NCHMePh	3947	39.5
8	$4^+ \cdot BF_4^-$	PhCH(Me)NH ₂	PhMeC=NCHMePh	2267	22.7

^{*a*} CH₃CN solution was irradiated by RPR-100, 350-nm lamps under aerobic conditions. ^{*b*} Isolated by converting to the corresponding carbonyl compounds and then to 2,4-dinitrophenylhydrazones. ^{*c*} Based on $10^+ \cdot BF_4^-$, $3a^+ \cdot BF_4^-$, and $4^+ \cdot BF_4^-$ used; the yield is calculated by subtraction of the "blank" yield from the total yield of imine in the presence of $10^+ \cdot BF_4^-$, $3a^+ \cdot BF_4^-$, and $4^+ \cdot BF_4^-$. ^{*d*} Recycling number of $10^+ \cdot BF_4^-$, $3a^+ \cdot BF_4^-$, and $4^+ \cdot BF_4^-$.

larger than those of C5- and C7-adducts, **19** and **20**.¹⁰ Recrystallization of a mixture of 23 and 24 from CH₃CN gave a pure sample of major product 24. To clarify the endo-exo selectivity, a reaction of $10^+ \cdot BF_4^-$ with NaBD₄ was carried out in an NMR tube to give a mixture of C11adduct 23-d and C13-adduct 24-d and 24. Since NaBD₄ used for the reaction is of 96% deuterium content, the reaction of $10^+ \cdot BF_4^-$ with the remaining hydride would give also compound 24. The ratio of 23-d, 24-d, and 24 was determined to be 16:76:10 by the ¹H NMR spectrum of the mixture. The structural assignment of 23, 24, 23d, and **24**-d was based on the NMR, IR, and mass spectral data. Furthermore, compounds 23-d and 24-d were determined to be the exo adduct by the H-H COSY and NOE spectra. Upon hydride abstraction with DDQ and subsequent anion exchange reaction, a mixture of compounds 23 and 24 regenerated $10^+ \cdot BF_4^-$ in quantitative yield. Furthermore, photoirradiation of a mixture of compounds 23 and 24 in CH₃CN and (CH₂Cl)₂ solution containing 42% aquaous HBF₄ under aerobic conditions for 24 h afforded 10⁺·BF₄⁻ mainly in addition to unidentified materials.

The reaction of $\mathbf{3a}^+ \cdot \mathbf{BF}_4^-$ with diethylamine has been shown to give a C9a-adduct, which underwent ringopening reaction to give 25 (Scheme 3).¹⁰ In contrast, the diethylamine addition of 4⁺·BF₄⁻ occurred at low temperature (-65 °C) to give C13-adduct **26**, which isomerized to 27 (Scheme 3) at higher temperature (>-35 °C).¹³ In the reaction of $10^+ \cdot BF_4^-$ with diethylamine, a mixture of **28a**, **b** and **29** was obtained in quantitative yield. Since the products were unstable on SiO_2 and Al_2O_3 , isomers 28a,b and 29 could not be separated. Thus, the structural assignment of **28a**,**b** and **29** was based on the ¹H NMR, IR, and HRMS spectra. The ¹H NMR spectra of **28a**,**b** and 29 are unequivocally assigned by using the H-H COSY and NOE spectra, and the ratio of 28a,b and 29 was determined to be 22:14:64 by the ¹H NMR spectrum of the mixture; exo adduct 28a predominates slightly. On the other hand, the addition reaction at the C13 proceeded selectively to give only exo adduct 29. This exo selectivity is similar to the reaction of $10^+ \cdot BF_4^-$ with $NaBD_4$ (vide supra). The results show the feasibility of the methano[11]annulene system for the exploration of a novel chiral auxiliary. Unlike in the case of 26,13 heating of 28a,b and 29 in CH₃CN did not undergo any isomerization, such as a reaction giving 30. Upon treatment with aq HBF_4 in Ac_2O , a mixture of compounds **28a,b** and **29** regenerated $10^+ \cdot BF_4^-$ in good yield.

Autorecycling Oxidation. Compounds $3a-d^+ \cdot BF_4^-$ act as a catalyst for oxidation of some alcohols under

SCHEME 3^a



 a Reagents and conditions: (i) Et_2NH, CH_3CN, rt, 1 h; (ii) 42% aq HBF4, Ac_2O, 0 °C, 1 h; (iii) CH_3CN, reflux, 24 h.

photoirradiation.¹⁰⁻¹² Moreover, compounds 2a and $\mathbf{\hat{4}^{+}}\cdot\mathrm{BF_{4}^{-}}$ have also been reported to undergo autorecycling oxidation toward some amines under photoirradiation.^{13,25} In this context, we examined the oxidation of some amines by using $10^+ \cdot BF_4^-$. We found that compounds $10^+ \cdot BF_4^-$ have an oxidizing ability toward benzylamine, 1-phenylethylamine, hexylamine, and cyclohexylamine to give the corresponding imines under aerobic and photoirradiation conditions. The results are summarized in Table 4, together with the results obtained by using reference compounds $3a^+ BF_4^-$ and $4^+ \cdot BF_4^-$. The reactions with $10^+ \cdot BF_4^-$ gave lower yields as compared with those of $3a^+ \cdot BF_4^-$ and $4^+ \cdot BF_4^-$. Direct irradiation of the amines in the absence of $10^+ \cdot BF_4^-$ (named "blank") gives the corresponding imines in small amounts. Thus, the yield in Table 4 is calculated by subtraction of the "blank" yield from the yield of the imine in the presence of $10^+ \cdot BF_4^-$. Imines are obtained in more

⁽²⁵⁾ Naya, S.; Iida, Y.; Nitta, M. Tetrahedron 2004, 60, 459-467.



FIGURE 5. Time dependency of autorecycling oxidation of benzylamine by using $10^+ \cdot BF_4^-$.

than 100% yield [based on compound $10^+ \cdot BF_4^-$] under photoirradiation, and thus, autorecycling oxidation clearly proceeds. To clarify the time dependency of the oxidizing reaction, ¹H NMR monitoring of the photooxidation reaction of $10^+ \cdot BF_4^-$ toward benzylamine was carried out. By using mesitylene as an internal standard, the yield of imine is recorded by using the ¹H NMR spectra at selected intervals. The results are summarized in Figure 5. The yield of benzaldimine was increased linearly as the irradiation time was prolonged to 48 h, suggesting that $10^+ \cdot BF_4^-$ would be stable under these conditions. Attempted detection of the intermediate such as reduced compounds 23 and 24 in the oxidation reaction of amines is unsuccessful at this stage. We propose that the present autorecycling oxidation proceeds via electron transfer from amines to the excited cation $10^{+} \cdot BF_{4}^{-}$;^{10,25} however, further studies will be required to clarify the detailed mechanistic aspect.

Summary

Novel synthesis of 1,3-dimethyl-5,10-methanocycloundeca[4,5]furo[2,3-d]pyrimidin-2,4(1,3H)-dionylium tetrafluoroborate $(10^+ \cdot BF_4^-)$ was accomplished albeit in low yield. The structural characteristics were clarified by the inspection of the spectral data and the MO calculation. The physical properties of $10^+ \cdot BF_4^-$ were studied by measurement of the UV-vis spectra, the pK_{R+} values, and the reduction potentials. Reactions of $10^+ \cdot BF_4^-$ with hydride and diethylamine afforded mixures of C11- and C13-adducts. In both reactions, the methano-bridge controls the nucleophilic attacks to the C13 to prefer exo selectivity. The results show that the methano[11]annulene system shows promise for the novel chiral auxiliary. The photoinduced oxidation reactions of $10^+ \cdot BF_4^-$ toward some amines under aerobic conditions were carried out to give the corresponding imines in 719-3286% yields (7.2-32.9 cycles).

Experimental Section

Preparation of 1,3-Dimethyl-5,10-methanocycloundeca-[4,5]furo[2,3-d]pyrimidin- 2,4(1,3H)-dionylium Tetrafluoroborate (10^+ ·BF₄⁻). A solution of dimethylbarbituric acid 13 (780 mg, 5 mmol) and base (4 mmol) in DMF (2 mL) was stirred at room temperature for 5 min. To the solution was added 12 (204 mg, 1 mmol) and the mixture was stirred at 35 °C for the period indicated in Table 1. To the mixture was added saturated 3% HCl, and the mixture was extracted with AcOEt. The extract was dried over Na₂SO₄ and concentrated in vacuo. The residue was dissolved in a mixture of Ac₂O (10 mL) and 42% HBF₄ (2 mL) at 0 °C, and the mixture was stirred for another 1 h. To the mixture was added Et₂O (50 mL) and the precipitates were collected by filtration to give $4^{+}\cdot BF_{4}^{-}$ and/ or $10^{+}\cdot BF_{4}^{-}$. The results are summarized in Table 1 (run 1, 23.6 mg, 6%; run 4, 31.5 mg, 8%).

Determination of pK_{R^+} Value of Cation 10⁺. Buffer solutions of slightly different acidities were prepared by mixing aqueous solutions of potassium hydrogen phthalate (0.1M) and HCl (0.1 M) (for pH 2.2-4.0), potassium hydrogen phthalate (0.1M) and NaOH $(0.1\ M)$ (for pH 4.1–5.9), and $KH_2PO_4\,(0.1M)$ 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 compound 10⁺·BF₄⁻ in CH₃CN (20 mL), were diluted to 10 mL with the buffer solution (8 mL) and CH_3CN (1 mL). The UV–vis spectrum was recorded for cation 10^+ 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 (500 nm) of cation 10^+ was plotted against pH to give a classical titration curve, whose midpoint was taken as the pK_{R+} value.

Cyclic Voltammetry of 10⁺. The reduction potential of **10**⁺·BF₄⁻ 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/AgNO₃ electrode. Nitrogen was bubbled through an acetonitrile solution (4 mL) of **10**⁺·BF₄⁻ (0.5 mmol dm⁻³) and Bu₄NClO₄ (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. Compound **10**⁺·BF₄⁻ exhibited an irreversible reduction wave, which is summarized in Table 3.

Reaction of 10^+ \cdot BF_4^- with NaBH₄. A solution of $10^+ \cdot BF_4^-$ (19.7 mg, 0.05 mmol) and NaBH₄ (8 mg, 0.20 mmol) in CH₃-CN (3 mL) was stirred at room temperature for 1 h. To the mixture was added saturated aqueous NH₄Cl solution, and the mixture was extracted with CH₂Cl₂. The extract was dried over Na₂SO₄ and concentrated in vacuo to give a mixture of **23** and **24** (15.5 mg, 100%).

¹H NMR Monitoring of the Reaction of $10^+ \cdot BF_4^-$ with NaBD₄. To a solution of compound $10^+ \cdot BF_4^-$ (3.9 mg, 0.01 mmol) in CD₃CN (0.5 mL) was added NaBD₄ (2.1 mg, 0.05 mmol) at room temperature in an NMR tube. After 1 h, the NMR measurement was carried out.

Oxidation of a Mixture of 23 and 24. To a stirred solution of **23** and **24** (15.4 mg, 0.05 mmol) in CH₂Cl₂ (2 mL) was added DDQ (17.6 mg, 0.075 mmol), and the mixture was stirred at room temperature for 1 h. After evaporation of the CH₂Cl₂, the residue was dissolved in a mixture of Ac₂O (2 mL) and 42% HBF₄ (0.4 mL) at 0 °C, and the mixture was stirred for another 1 h. To the mixture was added Et₂O (10 mL) and the precipitates were collected by filtration to give $10^+ \cdot BF_4^-$ (20 mg, 100%).

Oxidation of a Mixture of 23 and 24 by Photoirradiation. A solution of a mixture of 23 and 24 (16.7 mg, 0.054 mmol) and 42% aq HBF₄ (0.1 mL) in CH₃CN (1 mL) and CH₂-Cl₂ (2 mL) in a Pyrex tube was irradiated by RPR-100, 350-nm lamps under aerobic conditions for 24 h until the reaction was complete. The mixture was concentrated in vacuo, and the resulting residue was dissolved in a mixture of acetic anhydride (2 mL) and 42% aq HBF₄ (0.4 mL) at 0 °C. The mixture was stirred for 1 h. To the mixture was added Et₂O (20 mL) and the precipitate was collected by filtration to give 10⁺·BF₄⁻ mainly in addition to unidentified materials (13.5 mg).

Reaction of 10^+ \cdot BF_4^- with Diethylamine. To a solution of $10^+ \cdot BF_4^-$ (19.7 mg, 0.05 mmol) in CH₃CN (2 mL) was added diethylamine (11 mg, 0.15 mmol), and the mixture was stirred at room temperature for 1 h. To the mixture was added saturated aqueous NH₄Cl solution, and the mixture was extracted with CH₂Cl₂. The extract was dried over Na₂SO₄ and concentrated in vacuo to give a mixture of **28a,b** and **29** (19.0 mg, 100%).

Reaction of a Mixture of 28a,b and 29 with HBF₄. To a solution of a mixture of **28a,b** and **29** (19.0 mg, 0.05 mmol) in Ac₂O (2 mL) was added 42% aq HBF₄ (0.4 mL) at 0 °C. The mixture was stirred for 1 h. To the mixture was added Et₂O (10 mL) and the precipitate was collected by filtration to give 10^{+} ·BF₄⁻⁻ (20 mg, 100%).

General Procedure for Autorecycling Oxidation of Amines in the Presence of $10^+ \cdot BF_4^-$. A CH₃CN (16 mL) solution of compound $10^+ \cdot BF_4^-$ (1.97 mg, 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 Et₂O 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 4.

¹H NMR Monitoring of the Photooxidation of Benzylamine by Using 10^+ ·BF₄⁻. A CD₃CN (0.5 mL) solution of compound 10^{+} ·BF₄⁻ (0.197 mg, 0.0005 mmol), benzylamine (18.73 mg, 0.175 mmol), and mesitylene (internal standard; 3.6 mg, 0.03 mmol) in an NMR tube was irradiated by RPR-100, 350-nm lamps under aerobic conditions. The NMR measurement was carried out at intervals, and the yield of benzaldimine calculated by the ratio of the ¹H signal of benzaldimine and mesitylene was plotted against them (Figure 5).

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Supporting Information Available: Physical, analytical, and spectroscopic data for $10^+ \cdot BF_4^-$, 23, 24, 23-*d*, 24-*d*, 28a,b, and 29 and ¹H and ¹³C NMR spectra of $10^+ \cdot BF_4^-$, 23, 24, 23-*d*, 24-*d*, 28a,b, and 29. This material is available free of charge via the Internet at http://pubs.acs.org.

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