Synthesis, Properties, and Oxidizing Ability of 9,11-Dimethylbenzocyclohepta[6,7-b]pyrimido[5,4-d]furan-10(9H),12(11H)-dionylium Tetrafluoroborate

Shin-ichi Naya, Takeshi Tokunaka, and Makoto Nitta*

Department of Chemistry, School of Science and Engineering, Waseda University, Shinjuku-ku, Tokyo 169-8555, Japan

nitta@waseda.jp

Received September 1, 2003

Convenient preparation of novel 9,11-dimethylbenzocyclohepta[6,7-b]pyrimido[5,4-d]furan-10(9H),12(11H)-dionylium tetrafluoroborate **11·BF$_4$**⁻ consisted of a condensation reaction of benzo[d]tropone with dimethylbarbituric acid and following oxidative cyclization reaction by using DDQ-Sc(OTf)$_3$ or photoirradiation under aerobic conditions. Alternative synthesis of **11·BF$_4$**⁻ was also accomplished by a condensation reaction of 2-methoxybenzo[d]tropone with dimethylbarbituric acid and a subsequent cyclization reaction by using 42% aq HBF$_4$. The X-ray crystal analysis and MO calculation were carried out to clarify the structural characteristics. Properties of the cation **11** were studied by the pK_{R^+} value (4.7) and reduction potentials (−0.46 and −1.07 V vs Ag/AgNO$_3$) as well as the reaction with some nucleophiles. The oxidizing ability of **11·BF$_4$**⁻ toward alcohols in the autorecycling process was demonstrated as well.

Introduction

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. Combination of more than one π system can endow new properties to the original π system. Previously, we have studied the synthesis and structural and chemical properties of catacondensed aromatic π systems, azuleno[1,2-a]azulene derivatives,[1] and azuleno-annulated 1,6-methano[10]annulene derivatives.[2] We have now focused our attention on the cycloheptatrienylium (tropylium) ion **1** (Figure 1), which has fair thermodynamic stability (pK_{R^+} 3.9).[3] While the tropylium ion **1** is destabilized by benzo-annulation as demonstrated by the benzotropylium ion **2** (pK_{R^+} 1.6),[4] tropylium ions annulated with five-membered aromatic heterocycles, **3a**[5] and **3b**,[6] have been appreciably stabilized (**3a**, pK_{R^+} 6.7; **3b**, pK_{R^+} 6.0). We have recently reported the oxidative cyclization of heptafulvenes **4a,b**

FIGURE 1.

by using DDQ to afford tropylium ions annulated with furo[2,3-d]pyrimidine-1(2H),3(4H)-dione, **5a,b·BF$_4$**⁻.[7] In this context, the synthesis, properties, and reactivity of **6a−c·BF$_4$**⁻ [8b,c] and **7a,b**[9] were investigated as well. Furthermore, novel photoinduced autorecycling oxidizing reactions of **5a·BF$_4$**⁻ [8a] and **6a−c·BF$_4$**⁻ [8b,c] toward some

* Author to whom correspondence may be addressed. Telephone: +81-(0)3-5286-3236. Fax: +81-(0)3-3208-2735.

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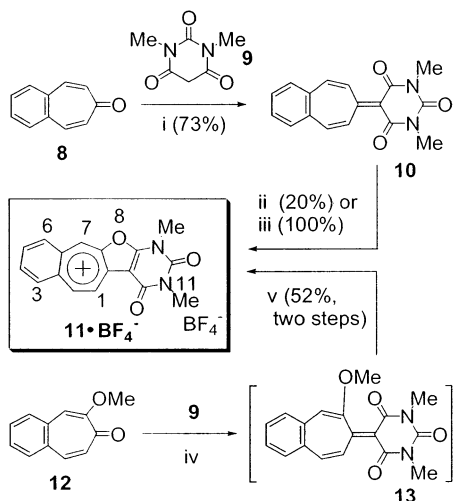
SCHEME 1[a]

[a] Reagents and conditions: (i) Ac$_2$O, reflux, 1 h; (ii) (a) DDQ, Sc(OTf)$_3$, xylene, reflux, 48 h, (b) 42% aq HBF$_4$, Ac$_2$O, 0 °C, 1 h; (iii) *hv*, aerobic, 42% aq HBF$_4$, CH$_3$CN–CH$_2$Cl$_2$, rt, 36 h; (iv) (EtCO)$_2$O, 135 °C, 1 h; (v) 42% aq HBF$_4$, (EtCO)$_2$O, 135 °C, 0.25 h.

alcohols to give the corresponding carbonyl compounds are studied. From this viewpoint, we studied 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 **11·BF$_4$**$^-$ (Scheme 1). The benzo-annulation onto **5a·BF$_4$**$^-$, giving **11·BF$_4$**$^-$, can endow regioselectivity toward nucleophiles and a change of the redox potentials. We report here the results in detail.

Results and Discussion

Synthesis. A condensation reaction of benzo[*d*]tropone (**8**)[10] with dimethylbarbituric acid (**9**) in Ac$_2$O under reflux afforded 3-[1′,3′-dimethyl-2′(1′*H*),4′(3′*H*),6′(5′*H*)-trioxopyrimidin-5′-ylidene]benzocycloheptatriene (**10**) as orange needles (Scheme 1). Compound **10** was fully characterized on the basis of the NMR, IR, UV–vis, mass spectral data, and elemental analysis. Unlike in the cases of **4a,b**, compound **10** did not cyclize with DDQ in xylene under reflux for 48 h and **10** was recovered quantitatively. Recently, Fukuzumi and co-workers have reported that Sc^{3+} catalyzes the electron-transfer reaction of DDQ,[11] and the method was applied to the synthesis of the porphyrin allays.[12] Thus, the reaction of **10** with DDQ and Sc(OTf)$_3$ in xylene under reflux for 48 h and subsequent treatment with 42% aq HBF$_4$ in Ac$_2$O at 0 °C afforded the desired compound **11·BF$_4$**$^-$ (Scheme 1). On the other hand, oxidative cyclization of **10** was also accomplished by photoirradiation (RPR-100, 350-nm lamps) under aerobic conditions in the presence of 42% aq HBF$_4$ to result in the formation of compound **11·BF$_4$**$^-$ in quantitative yield. Alternative synthetic procedure of **11·BF$_4$**$^-$ is also studied. A condensation reaction of **9** with 2-methoxybenzo[*d*]tropone **12**[13] in boiling Ac$_2$O followed

TABLE 1. λ_{max} and pK_{R^+} Values and Reduction Potentials[a] of Cations **11**[b] and Reference Compounds **1**, **2**, and **5a**

compd	λ_{max}	pK_{R^+}	reduction potential	
			$E1_{red}$	$E2_{red}$
11	441	4.7	−0.46	−1.07
1[d]	273	3.9	−0.51	
2[d]	426	1.6		
5a[c]	397	∼6.0	−0.58	

[a] V vs Ag/AgNO$_3$; cathodic peak potential. [b] Salt **11·BF$_4$**$^-$ was used for the measurement. [c] Reference 12. [d] Reference 15.

by treatment with 42% aq HBF$_4$ afforded **11·BF$_4$**$^-$, probably via the intermediate **13**.

Properties. Compound **11·BF$_4$**$^-$ was characterized on the basis of the NMR, IR, UV–vis, mass spectral data, and elemental and X-ray structure analyses. The mass spectrum of **11·BF$_4$**$^-$ ionized by FAB exhibited the correct M$^+$ − BF$_4$ ion peak, which is indicative of the cationic structure. The characteristic band for the anion BF$_4$$^-$ was observed at 1084 cm^{-1} in the IR spectrum of **11·BF$_4$**$^-$. The ORTEP drawing[14] clarified that compound **11·BF$_4$**$^-$ has a nearly planar structure. The bond length of O8–C8a is much shorter than that of O8–C7a, suggesting that the former bond has a larger bond order. MO calculation of **11** was carried out by the 6-31G* basis set of the MP2 levels,[15] and the bond length alternation obtained by the MO calculation for **11** is very similar to that obtained by X-ray analysis. Although the bond alternation is also observed for **5b·BF$_4$**$^-$ [7] and **6a–c·BF$_4$**$^-$,[8b,c] such tendency for **11·BF$_4$**$^-$ is apparently stronger than that for **5b·BF$_4$**$^-$.

In the UV–vis spectrum, the longest wavelength absorption maximum (λ_{max}) of **11** appears at a longer wavelength (441 nm) than that of **5a** (397 nm),[8a] while the difference in the wavelength ($\Delta\lambda$) between **11** and **5a** is smaller (44 nm) than the $\Delta\lambda$ between **1** and **2** (153 nm). Thus, the benzo-annulation onto **5a** seems to cause smaller perturbation than the benzo-annulation onto **1**.

The affinity of the carbocation toward hydroxide ions expressed by the pK_{R^+} value is the most common criterion of carbocation stability.[16] The pK_{R^+} value of cation **11** was determined spectrophotometrically in buffer solutions prepared in 50% aqueous CH$_3$CN and summarized in Table 1, along with those of reference compounds **1**,[3] **2**,[4] and **5a**.[8a] The pK_{R^+} value of **11** was determined to be 4.7, which is smaller by 1.3 pH units than that of **5a**, while

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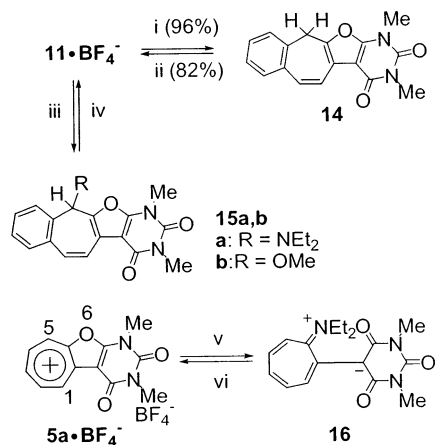(15) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.11; Gaussian, Inc.: Pittsburgh, PA, 1998.
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SCHEME 2[a]

[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) Et₂NH or MeOH, CH₃CN, rt, 0.5 h; (iv) 42% aq HBF₄, Ac₂O, 0 °C, 1 h; (v) Et₂NH, CH₃CN, rt; (vi) 42% aq HBF₄, Ac₂O, 0 °C, 1 h.

the pK_{R^+} value of **2** is smaller by 2.3 pH units than that of **1**. Accordingly, the benzo-annulation onto **5a** seems to cause smaller perturbation than the benzo-annulation onto **1**. These features are rationalized as follows: we have recently clarified that perturbations derived from benzo-annulation onto the cyclohepta[*a*]azulenylium ion were highly dependent on the annulating position.[17] While the benzo-annulation on the double bond having a smaller bond order of the cation significantly perturbs the original π-system and the benzene ring, the benzo-annulation on the double bond having a larger bond order causes smaller perturbation. Since the C3−C4 bond of **5a** has a larger bond order,[7] the benzo-annulation onto **5a** at this position would cause smaller perturbation than the benzo-annulation onto a fully delocalized **1**.

The reduction potential of **11** was determined by cyclic voltammetry (CV) in CH₃CN. Two reduction waves of **11** are irreversible under the conditions of the CV measurements; the peak potentials ($E1_{red}$ and $E2_{red}$) are summarized in Table 1, together with those of the reference compounds **1**[3] and **5a**.[8a] The irreversible nature is probably due to the formation of a tropyl radical and its dimerization. This reduction behavior seems to be a typical property of tropylium ions[18] and is similar to those of **5a**[8a] and **6a−c**.[8b,c] The $E1_{red}$ of **11** is more positive by 0.12 V than that of **5a**, and then, it is the most positive value among those of uracil-annulated heteroazulenes **5a,b·BF₄⁻** and **6a−c·BF₄⁻**.

Reactivity. To clarify the reactivity, the reactions of **11·BF₄⁻** with some nucleophiles were carried out. While the reaction of **5a·BF₄⁻** with NaBH₄ proceeded at the 1-, 3-, and 5-positions to afford a mixture of three regio-isomers,[8a] the reaction of **11·BF₄⁻** proceeded at only the 7-position to afford a single isomer **14** in good yield due to the benzo-annulation (Scheme 2). Compound **14** is oxidized by DDQ to regenerate **11·BF₄⁻** in good yield.

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TABLE 2. Autorecycling Oxidation of Some Alcohols by 11a·BF₄⁻ and 5a·BF₄⁻ under Photoirradiation[a]

entry	compd	alcohol	carbonyl compound[b]	yield[c]/%
1	**11a·BF₄⁻**	PhCH₂OH	PhCHO	5161
2	**11a·BF₄⁻**	PhCH(OH)Me	PhCOMe	4380
3	**5a·BF₄⁻**	PhCH₂OH	PhCHO	3175

[a] CH₃CN solution was irradiated by a 450-W high-pressure Hg lamp. [b] Isolated as 2,4-dinitrophenylhydrazone. [c] On the basis of **11·BF₄⁻**; the yield, called "blank", is subtracted from the yield of the carbonyl compound in the presence of **11·BF₄⁻**. [d] Reference 8a.

The reaction of **5a·BF₄⁻** with diethylamine afforded a **5a** adduct, which underwent a ring-opening reaction to give **16** (Scheme 2).[8a] In contrast, the reaction of **6a−c·BF₄⁻** with diethylamine afforded a 3-adduct and/or a mixture of a 3-adduct and a 5-adduct.[8b,c] Thus, a reaction of **11·BF₄⁻** with diethylamine in CD₃CN was carried out. The diethylamine addition of **11·BF₄⁻** occurred at only the 7-position to afford **15a** (Scheme 2), which is stable in CD₃CN for a few days in the presence of diethylamine in the dark; however, it decomposes during concentration in vacuo. Moreover, the reaction of **11·BF₄⁻** with MeOH in the presence of NaHCO₃ was also carried out to afford 7-adducts **15b**. Satisfactory ¹H and ¹³C NMR were obtained for **15a,b**; however, HRMS of **15a** gives only the (M − NEt₂)⁺ peak instead of the M⁺ peak. Thus, compound **11·BF₄⁻** is endowed by benzo-annulation to react with nucleophiles to exhibit complete regioselectivity. Upon treatment with 42% aq HBF₄ in Ac₂O, compounds **15a,b** regenerated **11·BF₄⁻** in good yields.

Autorecycling Oxidation. We have previously reported that compounds **5a·BF₄⁻** [8a] and **6a−c·BF₄⁻** [8b,c] undergo autorecycling oxidation toward some alcohols under photoirradiation (high-pressure Hg lamp). In this context and in a search for functions of **11·BF₄⁻**, we examined the oxidation of some alcohols by using **11·BF₄⁻**. We found that compound **11·BF₄⁻** has oxidizing ability toward benzyl alcohol and 1-phenylehtanol to give benzaldehyde and acetophenone, respectively, under aerobic and photoirradiation conditions. The results are summarized in Table 2, together with those of the reference compound **5a·BF₄⁻**.[8a] Direct irradiation of the alcohols in the absence of **11·BF₄⁻** (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 **11·BF₄⁻**. Carbonyl compounds are obtained in more than 100% yield (based on compound **11·BF₄⁻**) under photoirradiation, and thus, autorecycling oxidation clearly proceeds. Furthermore, the $E1_{red}$ of **11·BF₄⁻** is more positive than that of **5a·BF₄⁻** (Table 1), and oxidizing ability seems to be more efficient for **11·BF₄⁻** as compared with **5a·BF₄⁻** (Table 2). Attempted detection of the intermediate such as reduced compound **14** in the oxidation reaction was unsuccessful at the present stage. We propose that the present autorecycling oxidation proceeds via electron transfer from alcohol to the excited cation **11·BF₄⁻**;[8] however, further investigations are required to clarify the present autorecycling oxidation reaction.

Summary

A convenient preparation of novel 9,11-dimethylben-zocyclohepta[6,7-*b*]pyrimido[5,4-*d*]furan-10(9*H*),12(11*H*)-dionylium ion **11·BF₄⁻** was accomplished. The structural characteristics of **11·BF₄⁻** were studied by X-ray crystal analysis and MO calculation. The physical properties of **11·BF₄⁻** were clarified by measurement of the UV−vis spectrum, the pK_{R^+} value, and the reduction potential. The regioselectivity of the 7-position of **11·BF₄⁻** toward some nucleophiles was clarified. The photoinduced au-torecycling oxidation reaction of **11·BF₄⁻** toward some alcohols was carried out to afford the corresponding carbonyl compounds in more than 100% yield.

Experimental Section

General experimental conditions and spectroscopic instru-mentation used have been described previously.[8]

Preparation of 3-[1′,3′-Dimethyl-2′(1′*H*),4′(3′*H*),6′(5′*H*)-trioxapyrimidin-5′- ylidene]benzocycloheptatriene (10). A solution of benzo[*d*]tropone **8** (78 mg, 0.5 mmol) and 1,3-dimethylpyrimidine-2(1*H*),4(3*H*),6(5*H*)-trione **9** (156 mg, 1 mmol) in Ac₂O (2 mL) was heated under reflux for 1 h. To the mixture was added EtOH (50 mL), and the precipitates were collected by filtration to give **10** (104 mg, 73%).

Data for 10: orange needles; mp 243−244 °C (from CH₂-Cl₂/AcOEt); ¹H NMR (500 MHz, CDCl₃) δ 3.39 (6H, s, Me), 7.60 (2H, d, *J* = 12.5 Hz, H-1, 5), 7.62 (2H, dd, *J* = 7.6, 7.3, H-7, 8), 7.71 (2H, d, *J* = 7.6, H-6, 9), 8.76 (2H, d, *J* = 12.5 Hz, H-2, 4); ¹³C NMR (150.9 MHz, CDCl₃) δ 28.5, 107.2, 130.6, 131.9, 133.0, 138.0, 141.7, 151.2, 161.8, 163.2; IR (CHCl₃) ν 1653, 1272 cm⁻¹; MS (rel int.) *m/z* 294 (M⁺, 100%). Anal. Calcd for C₁₇H₁₄N₂O₃: C, 69.38; H, 4.79; N, 9.52. Found: C, 69.2; H, 4.8; N, 9.5.

Oxidative Cyclization of 10 with DDQ and Sc(OTf)₃. To a stirred solution of **10** (59 mg, 0.2 mmol) in xylene (10 mL) was added DDQ (150 mg, 0.66 mmol) and Sc(OTf)₃ (324 mg, 0.66 mmol), and the mixture was heated under reflux for 48 h until the reaction complete. The mixture was concentrated in vacuo, and to the resulting residue was added 4% aq NaOH. The mixture was extracted with CH₂Cl₂, and the extract was dried over Na₂SO₄ and concentrated in vacuo. The residue was dissolved in a mixture of acetic anhydride (2 mL) and 42% aq HBF₄ (0.4 mL) at 0 °C, and the mixture was stirred for 1 h. To the mixture was added Et₂O (20 mL), and the precipitates were collected by filtration to give **11·BF₄⁻** (15 mg, 20%).

Data for 11·BF₄⁻: orange plates; mp 293−295 °C dec (from CH₃CN); ¹H NMR (500 MHz, CD₃CN) δ 3.44 (3H, s, Me), 3.76 (3H, s, Me), 8.35−8.41 (2H, m, H-4,5), 8.62−8.64 (1H, m, H-3), 8.67−8.68 (1H, m, H-6), 9.03 (1H, d, *J* = 11.3 Hz, H-2), 9.13 (1H, d, *J* = 11.3 Hz, H-1), 9.51 (1H, s, H-7); ¹³C NMR (150.9 MHz, CD₃CN) δ 28.6, 31.2, 100.6, 126.0, 135.9, 136.1, 136.6, 137.2, 138.1, 138.9, 140.3, 149.8, 150.5, 153.2, 154.8, 157.0, 167.5; IR (CHCl₃) ν 1744, 1680, 1220, 1083 cm⁻¹; MS (FAB) *m/z* 293 (M⁺ − BF₄⁻). HRMS calcd for C₁₇H₁₃BF₄N₂O₃: 293.0927 (M − BF₄⁻). Found: 293.0923 (M⁺ − BF₄⁻). Anal. Calcd for C₁₇H₁₃BF₄N₂O₃: C, 53.72; H, 3.45; N, 7.37. Found: C, 53.7; H, 3.3; N, 7.2.

Oxidative Cyclization of 10 by Photoirradiation. A solution of **10** (29 mg, 0.1 mmol) and 42% aq HBF₄ (0.1 mL) in CH₃CN (10 mL) and CH₂Cl₂ (6 mL) in a Pyrex tube was irradiated by RPR-100, 350-nm lamps under aerobic conditions for 36 h until the reaction was complete. The mixture was concentrated in vacuo, the resulting residue was dissolved in a mixture of acetic anhydride (2 mL) and 42% aq HBF₄ (0.4 mL) at 0 °C, and the mixture was stirred for 1 h. To the mixture was added Et₂O (20 mL), and the precipitates were collected by filtration to give **11·BF₄⁻** (38 mg, 100%).

Preparation of 11·BF₄⁻ from 9 and 12. A solution of **9** (156 mg, 1.0 mmol) and 2-methoxybenzo[*d*]tropone (**12**) (93 mg, 0.5 mmol) in (EtCO)₂O (3 mL) was heated at 135 °C for 1 h.

To the mixture was added 42% aq HBF₄ (0.6 mL), and the mixture was heated at 135 °C for 0.25 h. To the mixture was added Et₂O (50 mL), and the precipitates were collected by filtration to give **11·BF₄⁻** (98 mg, 52%).

X-ray Structure Determination of 11·BF₄⁻: orange plate, C₁₇H₁₃BF₄N₂O₃, *M* = 380.10, triclinic, space group *P*1̄, *a* = 7.862(2) Å, *b* = 7.873(2) Å, *c* = 14.511(4) Å, α = 93.47(2)°, β = 97.190(1)°, γ = 114.54(1)°, *V* = 780.9(4) Å³, *Z* = 2, *D_c* = 1.616 g cm⁻³, crystal dimensions 1.00 × 1.00 × 0.20 mm. The data were measured on a radiation diffractometer with graphite monochromated Mo Kα radiation. A total of 7357 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,[14] with 257 variables and 2 395 observed reflections (*I* > 3.00σ(*I*)). The nonhydrogen atoms were refined anisotropically. The weighting scheme *w* = (3.0000σ_c²(F₀) + 0.0010F₀² + 0.5000)⁻¹ gave satisfactory agree-ment analysis. The final *R* and *Rw* values were 0.0510 and 0.0630. The maximum peak and minimum peak in the final difference map were 0.26 and −0.38 e⁻ Å³.

Determination of pK_{R^+} Value of 11·BF₄⁻. Buffer solu-tions 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 phtha-late (0.1M) and NaOH (0.1 M) (for pH 4.1−5.9), and KH₂PO₄ (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 3 mg of compound **11·BF₄⁻** in MeCN (20 mL), were diluted to 10 mL with the buffer solution (8 mL) and MeCN (1 mL). The UV−vis spectrum was recorded for each cation **11** in 20 different buffer solutions. Immediately after the spectrum was recorded, the pH of each solution was determined on a pH meter calibrated with standard buffers. The observed absorbance at the specific absorption wavelength (439 nm) of cation **11** was plotted against pH to give a classical titration curve, whose midpoint was taken as the pK_{R^+} value.

Cyclic Voltammetry of Cation 11. 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 cation **11** (0.5 mmol dm⁻³) and Bu₄NClO₄ (0.1 mol dm⁻³) to deaerate it. The measure-ments were made at a scan rate of 0.1 V s⁻¹. Immediately after the measurements, ferrocene (0.1 mmol) (*E*₁/₂ = +0.083) was added as the internal standard and the observed peak poten-tial was corrected with reference to this standard. The cation **11** exhibited two reduction waves, and they are summarized in Table 1.

Reaction of 11·BF₄⁻ with NaBH₄. A solution of **11·BF₄⁻** (380 mg, 1 mmol) and NaBH₄ (38 mg, 1 mmol) in CH₃CN (10 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 Na₂-SO₄ and concentrated in vacuo to give **14** (282 mg, 96%).

Data for 14: colorless powder; mp >300 °C dec (from CH₂-Cl₂); ¹H NMR (600 MHz, CDCl₃) δ 3.38 (3H, s, Me), 3.55 (3H, s, Me), 3.89 (2H, s, H-7), 7.05 (1H, d, *J* = 11.7 Hz, H-2), 7.07 (1H, d, *J* = 11.7 Hz, H-1), 7.22 (1H, d, *J* = 7.6 Hz, H-3), 7.28 (1H, d, *J* = 7.6 Hz, H-6), 7.35 (1H, dd, *J* = 7.6, 6.7 Hz, H-4), 7.36 (1H, dd, *J* = 7.6, 6.7 Hz, H-5); ¹³C NMR (150.9 MHz, CDCl₃) δ 28.2, 29.4, 33.2, 96.1, 115.4, 119.9, 126.7, 128.7, 129.4, 130.3, 132.3, 133.0, 135.8, 142.8, 150.6, 154.3, 158.5; IR (CHCl₃) ν 1707, 1668 cm⁻¹; MS (FAB) *m/z* 295 (M⁺ + H). HRMS calcd for C₁₇H₁₄N₂O₃: 295.1084 (M + H). Found: 295.1011 (M⁺ + H). Anal. Calcd for C₁₇H₁₄N₂O₃ + ¹/₅CH₂Cl₂: C, 66.36; H, 4.66; N, 9.00. Found: C, 66.7; H, 4.3; N, 8.9.

Oxidation of 14. To a stirred solution of **14** (0.5 mmol) in CH₂Cl₂ (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 CH₂Cl₂, the residue was dissolved in a mixture of acetic anhydride (5 mL) and 42% aq HBF₄ (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 **11·BF₄⁻** (156 mg, 82%).

¹H NMR Monitoring of Reaction of 11·BF₄⁻ with Diethylamine. To a solution of **11·BF₄⁻** (0.01 mmol) in CD₃-CN (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).

Data for 15a: ¹H NMR (600 MHz, CD₃CN) δ 0.83 (6H, t, J = 7.1 Hz, CH₃), 2.23 (2H, qd, J = 13.5, 7.1 Hz, CH₂), 2.27 (2H, qd, J = 13.5, 7.1 Hz, CH₂), 3.28 (3H, s, Me), 3.47 (3H, s, Me), 5.21 (1H, s, H-7) 7.05 (1H, d, J = 11.5 Hz, H-2), 7.08 (1H, d, J = 11.5 Hz, H-1), 7.38−7.51 (4H, m, H-3, 4, 5, 6); ¹³C NMR (150.9 MHz, CD₃CN) δ 11.8, 28.3, 29.9, 43.1, 64.2, 96.7, 118.0, 118.4, 128.2, 130.2, 132.6, 132.7, 133.1, 135.4, 136.4, 146.2, 156.2, 159.7 (one carbon overlapping); MS (FAB) m/z 293 (M⁺ − NEt₂). HRMS calcd for C₂₁H₂₃N₃O₃: 293.0927 (M⁺ − NEt₂). Found: 293.0919 (M⁺ − NEt₂).

¹H NMR Monitoring of Reaction of 11·BF₄⁻ with MeOH. To a solution of **11·BF₄⁻** (0.01 mmol) in CD₃CN (0.5 mL) in a NMR tube was added MeOH (one drop) and NaHCO₃ (14 mg). The NMR measurement was carried out immediately (after ca. 30 s).

Data for 15b: ¹H NMR (600 MHz, CD₃CN) δ 3.02 (3H, s, Me), 3.41 (3H, s, Me), 3.51 (3H, s, Me), 5.67 (1H, s, H-7), 7.18 (1H, d, J = 11.6 Hz, H-2), 7.21 (1H, d, J = 11.6 Hz, H-1), 7.50 (1H, dd, J = 7.6, 7.3 Hz, H-4), 7.54 (1H, dd, J = 7.6, 7.3 Hz, H-5), 7.59 (1H, d, J = 7.6 Hz, H-6), 7.61 (1H, d, J = 7.6 Hz, H-3); ¹³C NMR (150.9 MHz, CD₃CN) δ 28.5, 30.2, 50.7, 79.1, 96.8, 118.2, 119.3, 129.2, 130.4, 132.2, 133.2, 133.2, 134.1, 135.7, 145.8, 151.8, 156.8, 160.0; MS (FAB) m/z 325 (M⁺ + H). HRMS calcd for C₁₈H₁₆N₂O₄: 325.1189 (M⁺ + H). Found: 325.1169 (M⁺ + H).

Reaction of 15a,b with HBF₄. To a solution of **15a** or **15b** (0.05 mmol) in CH₃CN (20 mL) was added a mixture of acetic anhydride (5 mL) and 42% aq HBF₄ (1 mL) at 0 °C. The mixture was stirred for 1 h. To the mixture was added Et_2O (50 mL) and the precipitates were collected by filtration to give **11·BF₄⁻** (for **15a**, 86%; for **15b**, 82%).

General Procedure for Autorecycling Oxidation of Alcohols in the Presence of 11·BF₄⁻. A CH₃CN (16 mL) solution of compound **11·BF₄⁻** (0.005 mmol) and benzyl alcohol or 1-phenylethanol (2.5 mmol, 500 equiv) in a Pyrex tube was irradiated by 450-W high-pressure Hg lamp 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.

Supporting Information Available: ¹H and ¹³C NMR spectra of **10**, **11·BF₄⁻**, **14**, **15a**, and **15b**, HMQC and HMBC spectra of **10** and **11·BF₄⁻**, UV−vis spectra of **11** and reference compound **5a**, calculated data for **11·BF₄⁻**, and ORTEP drawing of **11·BF₄⁻** (PDF) and X-ray crystallographic data for **11** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

JO035274U