

**Bis(pyridine)-Based Bromonium Ions. Molecular Structures of Bis(2,4,6-collidine)bromonium Perchlorate and Bis(pyridine)bromonium Triflate and the Mechanism of the Reactions of 1,2-Bis(2'-pyridylethynyl)benzenebromonium Triflate and Bis(pyridine)bromonium Triflate with Acceptor Olefins**

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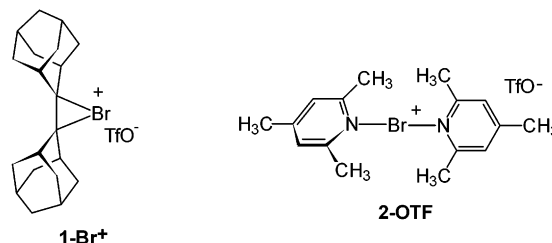
Received December 19, 2002

1,2-Bis(2'-pyridylethynyl)benzenebromonium triflate (**4**) and bis(pyridine)bromonium triflate (**5**) have been prepared and the mechanism of their reaction with various acceptors including eight alkenes of various structure, collidine, and Br<sup>-</sup> are reported. The reaction of **4** with neutral acceptors is second-order overall and involves a preequilibrium dissociation of the bidentate-bound Br<sup>+</sup> to form an unstable monodentate open form (**4-op**), which reacts with all neutral acceptors at or near the diffusion limit. Br<sup>-</sup> reacts with **4** by a different mechanism involving a direct nucleophilic attack on the Br<sup>+</sup>. The reaction of **5** with acceptors proceeds by a dissociative mechanism to reversibly form an unstable intermediate (pyr-Br<sup>+</sup>), which reacts with 4-penten-1-ol, 4-pentenoic acid adamantylideneadamantane and cyclohexene with nearly the same selectivity. The crystal and molecular structures of bis(2,4,6-collidine)bromonium perchlorate (**2-ClO<sub>4</sub>**) and **5** were determined by X-ray crystallography.

**Introduction**

In previous reports we have described mechanistic details of Br<sup>+</sup> transfer from the bromonium triflate of adamantylideneadamantane (Ad=Ad-Br<sup>+</sup>, **1-Br<sup>+</sup>**),<sup>1</sup> bis-(2,4,6-collidine)bromonium triflate (**2-OTf**)<sup>2</sup> and other bromonium ions based on ortho-substituted pyridines<sup>3</sup> to acceptor alkenes. Bis(collidine)halonium species have been used synthetically as sources of electrophilic halogen to promote halocyclization reactions of 1,*ω*-alkenoic acids and amides<sup>4</sup> and various alkenols and alkenoic acids.<sup>5</sup>

The mechanism for Br<sup>+</sup> transfer from **2-OTf** to 4-penten-1-ol proceeds through a complex sequence of events involving initial dissociation of one collidine from **2** to yield a reversibly formed coll-Br<sup>+</sup> ion, which is subsequently captured by the alkene leading to cyclized



products.<sup>2</sup> The stepwise process suggested to us several points of intervention in which structural changes on the Br<sup>+</sup>-pyridine complex might modify the reaction mechanism in interesting ways and furthermore might allow suitably decorated Pyr-Br<sup>+</sup> ions to transfer Br<sup>+</sup> to alkenes in a stereospecific way.<sup>3</sup>

In this study we consider reaction of various olefinic acceptors as well as 2,4,6-collidine with the bromonium triflate of 1,2-bis(2'-pyridylethynyl)benzene (**4**), which we have synthesized from its free ligand (**3**)<sup>6</sup> as in eq 1. The structures of the Ag<sup>+</sup> and PdCl<sub>2</sub> complexes of **3** indicate the ligand is essentially flat with the two nitrogens being ideally positioned to chelate the metal ions (N-Ag and N-Pd bond lengths being 2.15 and 2.01 Å),<sup>7</sup> suggesting that it should be able to bind Br<sup>+</sup> (N-Br bond length ca. 2.13–2.14 Å).<sup>8,9</sup> The chelating structure of this material should also retard dissociation of one of the Pyr-Br<sup>+</sup>–

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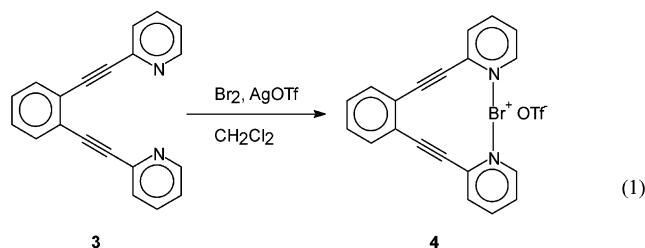
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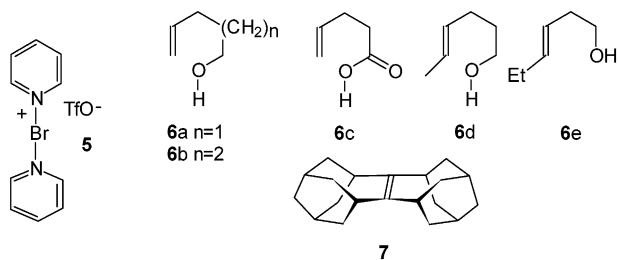
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Pyr bonds to give a reactive Pyr-Br<sup>+</sup> form and might thus modify the kinetics for Br<sup>+</sup> transfer in an interesting way. Although we have been unable to obtain a crystal of **4**



suitable for X-ray diffraction, we have obtained the structures of bis(2,4,6-collidine)bromonium perchlorate (**2-C1O<sub>4</sub>**) and bis(pyridine)bromonium triflate (**5**), which we present and compare here with the structure of two previously reported N-Br<sup>+</sup>-N species.<sup>8,9</sup> In addition we have studied the kinetics of Br<sup>+</sup> transfer from **5** to some olefinic acceptors, **6a–e**, cyclohexene (**6f**), Ad=Ad (**1**), and homoadamantane (**7**).



## Experimental Section

**(1) Materials and Methods.** Dichloromethane (Fisher) was treated with a small amount of bromine to remove reactive impurities, and then distilled from P<sub>2</sub>O<sub>5</sub> under Ar. Hexane (Fisher) was distilled from sodium under Ar. 1,2-Dichloroethane (Aldrich HPLC grade) was used as supplied. The olefinic acceptors (**6a–f**) were purchased from Aldrich and used as supplied as was 2,4,6-collidine and tetrabutylammonium bromide. Adamantylideneadamantane (Ad=Ad, **1**) was a gift from Dr. H. Šlebocka-Tilk, prepared as previously described,<sup>10</sup> and homoadamantane (**7**) was generously provided by Prof. Andrew Bennet, Simon Fraser University, Burnaby, British Columbia.

<sup>1</sup>H NMR spectra were obtained with Bruker Avance 300 and Avance 400 instruments. Mass spectra were obtained with a VG Quattro mass spectrometer. IR spectra were obtained with a Bomem Mb-120 FT-IR spectrophotometer, using KBr pressed disks. The X-ray diffraction structures were obtained with a Bruker P4 diffractometer by Dr. Yousheng Zhang and Dr. Ruiyao Wang of this department. UV-vis spectra and slower kinetic data were obtained with an OLIS modified Cary 17 UV-vis spectrophotometer. Faster reaction rates were monitored by using an Applied Photophysics SX-17MV stopped-flow reaction analyzer.

**(2) Synthesis. (a) Bis(pyridine)bromonium Triflate (**5**).** **5** was prepared according to a general procedure for the preparation of bis(collidine)bromonium triflate.<sup>2</sup> Silver triflate (1.41 g, 5.48 mmol) was suspended along with 1.0 mL of pyridine (0.982 g, 12.4 mmol) in 20 mL of dry dichloromethane (DCM) and the mixture was stirred until homogeneous. To the resulting colorless solution was added dropwise (with stirring)

a solution of 0.911 g of bromine (5.70 mmol) in 11 mL of dry DCM under Ar. The resulting mixture was filtered through Celite to remove AgBr and most of the solvent was subsequently removed with an Ar stream. The resulting crystals were purified by recrystallization from a DCM/hexane system and dried under vacuum to yield 1.59 g of a white crystalline product (75%), mp 87–89 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.83 (d, 4H, *J* = 5 Hz), 8.37 (t, 2H, *J* = 8 Hz), 7.89 (t, 4H, *J* = 7 Hz).

Crystals suitable for X-ray diffraction were grown by diffusing vapors of hexane into a solution of **5** in dichloroethane at 4 °C over a period of 10 days.

**(b) 1,2-Bis(2'-pyridylethynyl)benzene (**3**).** A modified procedure of the one reported by Thummel et al.<sup>6</sup> was followed. To a dried round-bottom flask was added 1,2-diiodobenzene (236 mg, 0.72 mmol), 2-ethynyl pyridine (222 mg, 2.16 mmol), Pd<sub>2</sub>(dibenzylideneacetone)<sub>3</sub> (56 mg, 0.06 mmol), PPh<sub>3</sub> (74 mg, 0.282 mmol), CuI (12 mg, 0.063 mmol), and dried Et<sub>3</sub>N (8 mL). The mixture was stirred under Ar at 45 °C for 8 h. After evaporation of the solvent, the oily residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (30 mL) and washed twice with water. The organic layer was dried with MgSO<sub>4</sub> and filtered, and the solvent was evaporated. The residue was first purified by chromatography on silica gel eluting with CH<sub>2</sub>Cl<sub>2</sub> and then CH<sub>2</sub>Cl<sub>2</sub>-MeOH (33/1); TLC *R<sub>f</sub>* 0.3 (CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 33/1). The crude product was purified further by a second chromatography on silica gel eluting with EtOAc/hexane (1/1); TLC *R<sub>f</sub>* 0.4 (EtOAc/hexane, 1/1). The product was obtained as a yellow solid (168 mg, 85%); Mp 113 °C (lit.<sup>6</sup> mp 113–115 °C). <sup>1</sup>H NMR (CD<sub>3</sub>CN, 400 MHz): δ 8.64 (d, *J* = 4.8 Hz, 2H), 7.78 (m, 4H), 7.69 (m, 2H), 7.48 (m, 2H), 7.36 (m, 2H). <sup>13</sup>C NMR (CD<sub>3</sub>CN, 100 MHz): δ 150.6, 143.1, 136.9, 132.6, 129.6, 128.0, 125.2, 123.8, 93.4, 87.0. MS (EI) *m/z* (rel intensity): 281 (5), 280 (M<sup>+</sup>, 29), 279 (18), 78 (50), 51 (100).

**(c) 1,2-Bis(2'-pyridylethynyl)benzene Bromonium Triflate (**4**).** The general procedure reported by Brown and Neverov<sup>2</sup> was followed to make compound **4** in 65% yield: Mp 145 °C, discolored at 129 °C. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 MHz): δ 8.89 (dq, *J* = 0.8, 5.7 Hz, 2H), 8.18 (td, *J* = 1.5, 7.8 Hz, 2H), 7.92 (d, *J* = 7.9 Hz, 2H), 7.78 (m, 2H), 7.64 (m, 2H), 7.60 (m, 2H). <sup>19</sup>F NMR (CD<sub>2</sub>Cl<sub>2</sub>, 376 MHz, CFCl<sub>3</sub> as reference): δ -79.4. <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 75 MHz): δ 148.6, 142.6, 134.3, 131.6, 131.4, 126.9. IR (KBr): 3070, 3026, 2223, 1587, 1496, 1156, 1029, 761, 636, 517, 440 cm<sup>-1</sup>. MS (ES<sup>+</sup>) *m/z* (rel intensity): 362 (22), 361 (M<sup>+</sup> - OTf, 100), 360 (22), 359 (M<sup>+</sup> - OTf, 99), 281 (6).

**(d) Bis(2,4,6-collidine)bromonium Perchlorate (**2-C1O<sub>4</sub>**).** **2-C1O<sub>4</sub>** was prepared in an analogous procedure to that reported by Brown and Neverov,<sup>2</sup> using AgClO<sub>4</sub> instead of AgOTf. The crude product was recrystallized with CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O. Yield 69%. Mp 247 °C. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 MHz): δ 7.22 (s, 4H), 2.80 (s, 12H), 2.46 (s, 6H). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 75 MHz): δ 155.8, 154.4, 126.1, 25.37, 21.15. MS (ES<sup>+</sup>) *m/z* (rel intensity): 324.2 (18), 323.2 (M, 98), 322.2 (18), 321.2 (M, 100), 243.2 (27), 122.0 (10). A crystal suitable for X-ray diffraction was grown by slow diffusion of diethyl ether into a concentrated CH<sub>2</sub>Cl<sub>2</sub> solution of **2-C1O<sub>4</sub>**.

**(3) Kinetics.** The kinetics of the reactions of bis(pyridine)-bromonium triflate **5** with cyclohexene, 4-penten-1-ol, and 4-pentenoic acid were monitored by observing the rate of disappearance of the bromonium ion at 232 nm (the wavelength of maximum change) in 1,2-dichloroethane (DCE) at 25 °C in the presence of excess olefin ((4.75–95.0) × 10<sup>-4</sup> M) and of added pyridine ((4.75–33.2) × 10<sup>-4</sup> M). The kinetics of the reaction of **5** with Ad=Ad were followed by monitoring the rate of appearance of product at 276 nm, the wavelength of maximum change for this reaction. In the former three cases, the rate constants were evaluated by NLLSQ fitting of the absorbance vs time traces for the disappearance of py<sub>2</sub>-Br<sup>+</sup>/OTf<sup>-</sup> to a standard exponential model (*A<sub>t</sub>* = *A<sub>∞</sub>* + (*A<sub>0</sub>* - *A<sub>∞</sub>*) exp(-*k<sub>obs</sub>t*)), while for Ad=Ad, they were evaluated by analogous fittings for the appearance of products. The UV spectrum of **5**

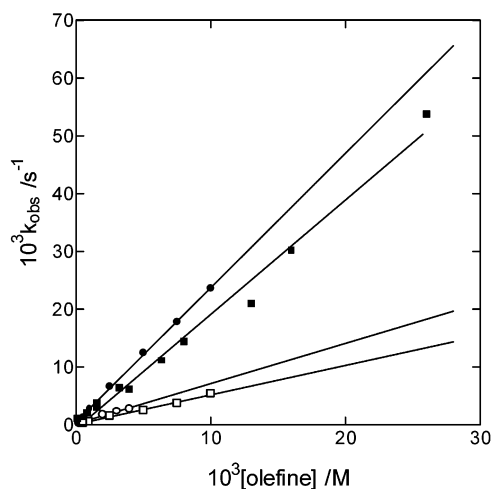
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**TABLE 1.** Second-Order Rate Constants Calculated for the Reactions of **4** with Various Acceptors in Dichloroethane at 25 °C

| acceptor                                       | $k_2$ ( $M^{-1} s^{-1}$ ) <sup>a</sup> |
|--|--|
| 4-penten-1-ol ( <b>6a</b> )                    | $2.0 \pm 0.1$                          |
| 4-pentenoic acid ( <b>6c</b> )                 | $0.5 \pm 0.1$                          |
| 5-hexen-1-ol ( <b>6b</b> )                     | $1.2 \pm 0.1$                          |
| <i>trans</i> -3-hexen-1-ol ( <b>6e</b> )       | $2.2 \pm 0.1$                          |
| 4-hexen-1-ol ( <b>6d</b> )                     | $1.9 \pm 0.1$                          |
| cyclohexene ( <b>6f</b> )                      | $2.3 \pm 0.1$                          |
| 2,4,6-collidine                                | $11.0 \pm 0.1$                         |
| Ad=Ad ( <b>1</b> )                             | $0.7 \pm 0.1$                          |
| homoadamantane ( <b>7</b> )                    | $1.2 \pm 0.2$                          |
| Bu <sub>4</sub> N <sup>+</sup> Br <sup>-</sup> | $>4.3 \times 10^4$                     |

<sup>a</sup> Quoted uncertainty in  $k_2$  is the standard error taken from linear regression of the plots of  $k_{obs}$  vs [acceptor].

**FIGURE 1.** Plot of  $k_{obs}$  vs [acceptor] for reaction of **4** with 4-penten-1-ol (■), 4-pentenoic acid (□), cyclohexene (●), and Ad=Ad (○),  $T = 25$  °C, in dichloroethane.

has a  $\lambda_{max}$  of 258 nm, with additional major absorbance bands at 252 and 265 nm. The  $\epsilon_{258}$  for the bromonium salt was calculated (according to Beer's law) to be  $9140 \pm 100 M^{-1} cm^{-1}$ . The wavelength of maximum change for the reaction of **5** with Ad=Ad was determined to be 276 nm. Comparison of the spectra for a  $9.5 \times 10^{-5} M$  solution of **5** in the presence and absence of  $4.7 \times 10^{-4} M$  Ad=Ad indicated that the products of the reaction had a significant absorbance at 260 nm with an  $\epsilon_{260}$  of  $\sim 9200 M^{-1} cm^{-1}$ .

The kinetics of the reaction of 1,2-bis(2'-pyridylethynyl)-benzene bromonium triflate **4** ( $1.0 \times 10^{-5} M$ ) with various alkenes were undertaken analogously in DCE at 25 °C under pseudo-first-order conditions of excess olefin. In DCE **4** has a maximum absorbance at 308 nm with an extinction coefficient ( $\epsilon$ ) of  $5.7 \times 10^4 M^{-1} cm^{-1}$ , which is also the wavelength of maximum change during the reaction. Each reaction was followed for at least 3 half-lives. The pseudo-first-order rate constants ( $k_{obs}$ ) were evaluated by NLLSQ fitting of the absorbance vs time traces for the disappearance of compound **4** to the standard exponential model. The pseudo-first-order kinetic constants ( $k_{obs}$ ) are given in Tables 1S to 10S in the Supporting Information. The second-order rate constants ( $k_2$ ) shown in Table 1 were determined from the slope of the plots of  $k_{obs}$  vs at least six [acceptor] varying between  $1.6 \times 10^{-4}$  and  $2.6 \times 10^{-2} M$ , see Figure 1 for examples, with 4-penten-1-ol, Ad=Ad, 4-pentenoic acid, and cyclohexene.

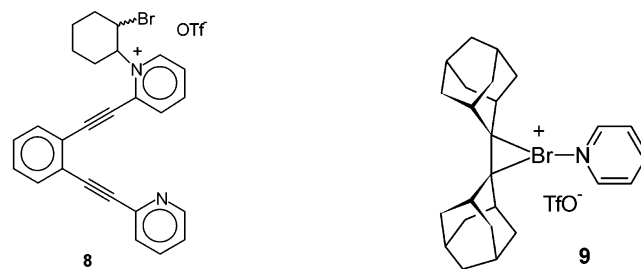
**(4) Equilibrium Constants for Reaction of 4 with A=Ad and 2,4,6-Collidine.** <sup>1</sup>H NMR spectroscopy was used for determination of the equilibrium constant for the reaction of **4** with Ad=Ad and with 2,4,6-collidine.

A CD<sub>2</sub>Cl<sub>2</sub> solution containing  $7.7 \times 10^{-3} M$  **4** and  $8.9 \times 10^{-3} M$  Ad=Ad was prepared in an NMR tube and the <sup>1</sup>H NMR spectrum determined after 15 min. The position of the equilibrium between **4** and 2,4,6-collidine was determined by <sup>1</sup>H NMR in two solvents, CD<sub>2</sub>Cl<sub>2</sub> (containing  $4.9 \times 10^{-3} M$  **4** and  $10.6 \times 10^{-3} M$  collidine) and CD<sub>3</sub>CN ( $4.6 \times 10^{-3} M$  collidine and  $7.0 \times 10^{-3} M$  **4**).

**(5) Reaction Products.** The identity of the products of reaction of each bromonium ion with the various acceptors was determined by <sup>1</sup>H NMR and mass spectrometry. The spectral parameters of all of the brominated products were compared with those of authentic material or with the corresponding data we obtained previously in the study of the same acceptors with bis(collidine)bromonium triflate<sup>2</sup> or in appropriate cases with Ad=Ad bromonium triflate.<sup>1c</sup> The product of reaction with homoadamantane (**7**) was not determined, but assumed to be either the bromonium ion (by analogy to Ad=Ad) or a cis addition product of Br and OTf since the molecular structure cannot allow a trans addition.

## Results

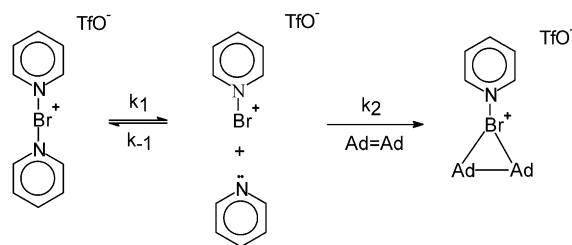
**(i) Reaction of Bromonium Ion 4 and 5 with Various Acceptors.** The reaction of **4** and **5** with the various acceptor alkenes produces substantially the same products of cyclization and addition as were observed previously when the Br<sup>+</sup> source was **2**.<sup>2</sup> From the reaction of **4** with cyclohexene two products were observed, *trans*-2-bromocyclohexane-1-trifluoromethanesulfonate and **8**, where both the Br<sup>+</sup> and pyridine ligand add to the double bond (stereochemistry not determined but presumed to be *trans*). In the case of the reaction of **5** with Ad=Ad, although we have not explicitly determined the product of the reaction, by analogy with the reaction of **2** with Ad=Ad, the product is assumed to be **9**.



The kinetics of the reaction of **4** with various alkenes (**1**, **6a–f**, **7**) were conducted under pseudo-first-order conditions of excess olefin. The original data for  $k_{obs}$ , the pseudo-first-order rate constant for reaction, are given in Tables S1–S10, Supporting Information. In the case of the reactions with **4**, the slopes of the plots of  $k_{obs}$  vs [alkene] generate the second-order rate constants given in Table 1. Also given in that table are the second-order rate constants for the reaction of **4** with 2,4,6-collidine and tetrabutylammonium bromide. The feature of note is the relative insensitivity of the  $k_2$  rate constants to the nature of the acceptor, except for Br<sup>-</sup>, which reacts with **4** at least 1000-fold faster than do neutral acceptors such as collidine and alkenes.

**(ii) Reaction of Bis(pyridine)bromonium Triflate (5) with Alkene Acceptors.** The kinetics for reaction of **5** with the olefin acceptors Ad=Ad, cyclohexene, 4-penten-1-ol, and 4-pentenoic acid were run under pseudo-first-order conditions of excess olefin in the presence of added pyridine. Given in Tables S11–S14 Sup-

## SCHEME 1



porting Information, are the original  $k_{\text{obs}}$  values as a function of varying [alkene] and [pyridine]. Typical examples of these data are shown graphically in Figure 2, showing a saturation behavior at increasing [Ad=Ad] suggestive of a two-step process involving a reversibly formed intermediate. The overall behavior is reminiscent of that exhibited by **2** (bis(2,4,6-collidine)bromonium triflate) in its reactions with Ad=Ad and other alkenes<sup>2</sup> for which the simplified process given in Scheme 1 is presented and analyzed in terms of the rate expression given in eq 2. In the case of Ad=Ad the product of the

$$k_{\text{obs}} = \frac{k_1 k_2 [\text{alkene}]}{k_{-1} [\text{py}] + k_2 [\text{alkene}]} = \frac{k_1 [\text{alkene}]}{\frac{k_{-1}}{k_2} [\text{py}] + [\text{alkene}]} = \frac{\frac{k_1 k_2}{k_{-1}} [\text{alkene}]}{[\text{py}] + \frac{k_2}{k_{-1}} [\text{alkene}]} \quad (2)$$

reaction is complex **9**, which cannot undergo subsequent reactions due to steric encumbrance, but in the case of other alkenes such as **6a–f**, the analogous  $\text{O}:\text{Br}^+:\text{pyr}$  complexes undergo subsequent fast reaction to form either cyclized or addition products.

Of the several ways to analyze the  $k_{\text{obs}}$  vs [alkene] and [pyridine] data the most satisfactory has the form  $k_{\text{obs}} = A/(B + [\text{py}])$ , where  $A = \{(k_1 k_2)/k_{-1}\}[\text{alkene}]$  and  $B = [\text{alkene}]/(k_{-1}/k_2)$ . Parameters  $A$  and  $B$  were determined by NLLSQ fits of the  $k_{\text{obs}}$  vs [py] data for each alkene concentration (see Supporting Information, Tables S11–S14) and subsequently plotted against [alkene] to give the values of  $k_1$ , the rate constant for dissociation of the bis(pyridine)bromonium complex, and the  $k_{-1}/k_2$  ratio. In the case of 4-pentenoic acid, which does not exhibit a saturation profile at the concentrations employed, a slightly different fitting procedure was employed. The value of  $k_1$ , which must be the same for all alkene acceptors, was taken as a constant defined as an average of the data for the first three alkenes in Table 2 after which the  $k_{-1}/k_2$  ratio was computed.

(iii) **<sup>1</sup>H NMR Determination of the Equilibrium Constants for the Reactions of **4** + Ad=Ad and **4** + Collidine.** When **4** was treated with Ad=Ad in  $\text{CD}_2\text{Cl}_2$  as described in the Experimental Section, the <sup>1</sup>H NMR spectrum showed three well-defined sets of peaks. Two sets appeared in the aromatic area and had the same chemical shifts as those of **4** and authentic ligand **3**. The third set of peaks was located in the aliphatic area with chemical shifts between those of free Ad=Ad and those

of the Ad=Ad bromonium ion.<sup>11</sup> The <sup>1</sup>H NMR data are consistent with the equilibrium process shown in Scheme 2, which is slow on the NMR time scale.

$K_{\text{eq}}$  in Scheme 2 was calculated from eq 3 by determining the amounts of the various species from the integrated <sup>1</sup>H NMR intensities of characteristic peaks of **3**, **4**, and Ad=Ad, under the assumption that for each molecule of **3** that is formed by  $\text{Br}^+$ -transfer from **4**, one Ad=Ad bromonium ion (**1-Br<sup>+</sup>**) will be generated. The so-determined value for  $K_{\text{eq}}$  is 7.1.

$$K_{\text{eq}} = [\mathbf{3}][\mathbf{1-Br}^+]/[\mathbf{4}][\mathbf{1}] \quad (3)$$

In the case of 2,4,6-collidine two separate <sup>1</sup>H NMR experiments were performed in  $\text{CD}_2\text{Cl}_2$  and in  $\text{CD}_3\text{CN}$ . Both <sup>1</sup>H NMR spectra showed three sets of peaks attributable to compounds **4**, **3**, and collidine (in a rapid equilibrium comprising free and  $\text{Br}^+$  complexed forms), corresponding to the process shown in Scheme 3. From the integrated intensities of the various peaks inserted into eq 4,  $K'_{\text{eq}}$  was computed to be 56 and 620  $\text{M}^{-1}$  in the two solvents.

$$K'_{\text{eq}} = [\mathbf{3}][\mathbf{2}]/[\mathbf{4}][\text{coll}]^2 \quad (4)$$

(iv) **Molecular Structures of Bis(pyridine)bromonium Triflate and Bis(2,4,6-collidine)bromonium Perchlorate.** Crystals of **5** and 2- $\text{ClO}_4$  suitable for X-ray diffraction were obtained by slow diffusion of hexane or ether, respectively, into a solution of the bromonium ion in dichloroethane or dichloromethane. Shown in Figures S1 and S3 are the ORTEP pictures for 2- $\text{ClO}_4$  and **5**, while in Figures S2 and S4 are the corresponding cell-packing diagrams. Selected bond lengths and angles are given in Table 3, along with those for two comparison materials, bis(quinoline)bromonium perchlorate (**10**)<sup>8</sup> and bis(quinuclidine)bromonium ion tetrafluoroborate (**11**).<sup>9</sup> Detailed structural information such as tables of bond lengths and angles, anisotropic displacement parameters, and atomic coordinates are given as Tables S15–S25 in the Supporting Information.

## Discussion

(i) **<sup>1</sup>H NMR Determination of the Equilibrium Constants for Reaction of **4** with Ad=Ad and Collidine.** The <sup>1</sup>H NMR spectrum of a  $\text{CD}_2\text{Cl}_2$  solution containing **4** and Ad=Ad was shown to contain a mixture of three components, residual **4**, its free ligand **3**, and the Ad=Ad-bromonium ion (**1-Br<sup>+</sup>**). From the sharpness of the peaks corresponding to **4** and **3**, establishment of the overall equilibrium suggested in Scheme 2 at ambient temperature is slow on the NMR time scale although the Ad=Ad-bromonium ion does undergo the well-known<sup>12</sup> rapid exchange with free Ad=Ad. By fitting the integrated intensities of characteristic peaks from each species to eq 3, an equilibrium constant of  $K_{\text{eq}} = 7.1$  is obtained suggesting the Ad=Ad bromonium ion is more stable than **4**.

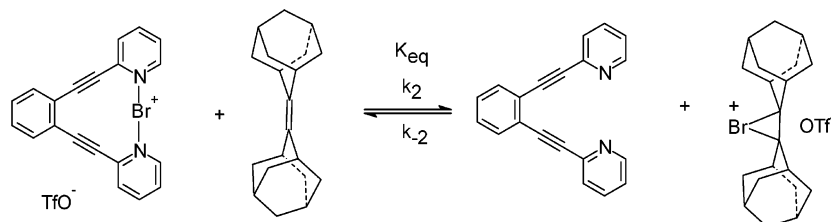
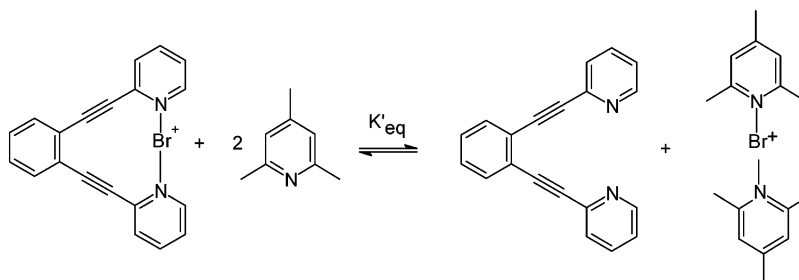
Similar experiments were conducted with  $\text{CD}_2\text{Cl}_2$  or  $\text{CD}_3\text{CN}$  containing **4** and 2,4,6-collidine, and the inte-

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**TABLE 2.**  $k_1$  and Partitioning Coefficient Values for the Reaction of Three Alkenes with Bis(pyridine)bromonium OTf<sup>-</sup> at 25 °C, As Obtained from Eq 2

| acceptor olefin                | $k_1 k_2 / k_{-1} / \text{s}^{-1}$ | $k_2 / k_{-1}$    | $k_{-1} / k_2$  | $k_1 / \text{s}^{-1}$ |
|--------------------------------|------------------------------------|-------------------|-----------------|-----------------------|
| Ad=Ad ( <b>1</b> )             | $1.20 \pm 0.01$                    | $0.105 \pm 0.003$ | $9.7 \pm 0.24$  | $11.50 \pm 0.31$      |
| cyclohexene ( <b>6f</b> )      | $3.10 \pm 0.16$                    | $0.21 \pm 0.02$   | $4.75 \pm 0.45$ | $14.8 \pm 1.6$        |
| 4-penten-1-ol ( <b>6a</b> )    | $2.57 \pm 0.08$                    | $0.17 \pm 0.05$   | $5.8 \pm 1.7$   | $14.9 \pm 4.4$        |
| 4-pentenoic acid ( <b>6c</b> ) |                                    |                   | $18.6 \pm 0.6$  | $12.8^a$              |

<sup>a</sup> Value taken as the average of those determined for the first three alkenes.

**SCHEME 2****SCHEME 3****TABLE 3.** Some Structural Parameters of Compounds with Linear N–Br<sup>+</sup>–N' Bonding

| compd                                    | N–Br–N'<br>(deg) | N–Br<br>(Å) | Br–N'<br>(Å)           | dihedral angle <sup>f</sup><br>(deg) |
|--|------------------|-------------|------------------------|--------------------------------------|
| <b>2</b> -ClO <sub>4</sub> <sup>-a</sup> | 176.31 (18)      | 2.086 (5)   | 2.143 (5) <sup>b</sup> | 33.2                                 |
|  | 180.0 (2)        | 2.115 (4)   | 2.115 (4) <sup>c</sup> | 0.0                                  |
| <b>5</b>                                 | 178.43(15)       | 2.075(4)    | 2.107(4)               | 10.34 <sup>g</sup>                   |
| <b>10</b> <sup>d</sup>                   | 176.6 (4)        | 2.100 (6)   | 2.185 (7)              | 13.02                                |
|  | 177.5 (3)        | 2.099 (7)   | 2.145 (7)              | 11.4                                 |
| <b>11</b>                                | 180 <sup>e</sup> | 2.120 (2)   | 2.156 (2)              | 4.2                                  |

<sup>a</sup> 1.5 independent molecules in the unit cell. <sup>b</sup> N' is related to N by a 2-fold axis. <sup>c</sup> N' is related to N by a mirror plane. <sup>d</sup> Two independent molecules in a unit cell.<sup>8</sup> <sup>e</sup> No error reported.<sup>9</sup> <sup>f</sup> Dihedral angle of the ligand-containing planes within the molecule. <sup>g</sup> Two dihedral angles calculated since the aromatic rings are not completely flat.

grated intensities for the various species fit to eq 4 to yield  $K'_{\text{eq}}$  values of 56 and 620 M<sup>-1</sup>, respectively. The 10-fold increase in the  $K'_{\text{eq}}$  value in CH<sub>3</sub>CN relative to CH<sub>2</sub>-Cl<sub>2</sub> may be related to the increased dielectric constant of the former (38.8<sup>13</sup>) relative to that of CH<sub>2</sub>Cl<sub>2</sub> (9.08).<sup>14</sup> Knowledge of the  $K'_{\text{eq}}$  value in CH<sub>2</sub>Cl<sub>2</sub> will prove valuable in determining the rate and equilibrium constants for the rather complex transfer of Br<sup>+</sup> from **4** to collidine and Ad=Ad discussed later (vide infra).

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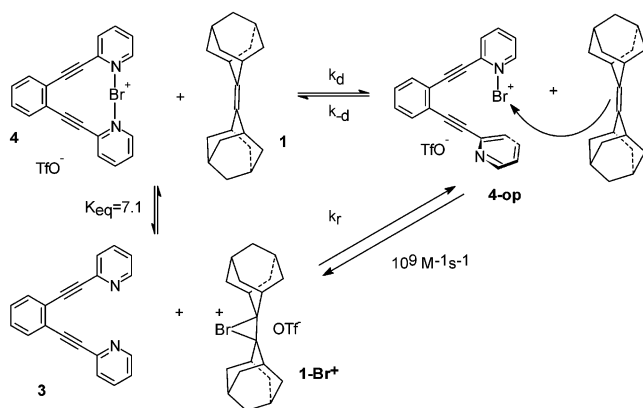
(ii) Kinetics of Br<sup>+</sup>-Transfer from **4** to Various Acceptors. Shown in Table 1 are the observed second-order rate constants ( $k_2$ ) for the transfer of Br<sup>+</sup> from **4** to acceptors. There are two points of note. First, all neutral acceptors (alkenes and collidine) react with a very similar rate constant thus indicating a general lack of selectivity. Second, the anionic acceptor Br<sup>-</sup> reacts at least 1000 times faster than the neutral species, suggesting different overall mechanisms for these two categories of acceptors.

The lack of selectivity for the alkene acceptors is at variance with the generally observed behavior of these alkenes toward other brominating and electrophilic reactions.<sup>2,15</sup> The only acceptable rationale for lack of selectivity in a process that is clearly dependent on [acceptor], as shown in Figure 1 for five of the alkenes, is that the actual Br<sup>+</sup>-transfer step proceeds without a substantial chemical barrier at or near the diffusion limit, which is known to be  $\sim 10^{10}$  M<sup>-1</sup> s<sup>-1</sup> at room temperature in a variety of solvents.<sup>16</sup> Collidine reacts some 5–10-fold faster with **4** than any of the alkenes, and so we set its rate constant at  $10^{10}$  M<sup>-1</sup> s<sup>-1</sup>, and those for the remaining alkenes an order of magnitude lower. Although the Br<sup>+</sup>-transfers to these acceptors is very fast, the overall  $k_2$

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## SCHEME 4



constants in Table 2 are between 1 and  $10 \text{ M}^{-1} \text{ s}^{-1}$ . This suggests a process that involves a highly unfavorable preequilibrium as shown in Schemes 4 and 5 which respectively portray the detailed mechanisms for reaction of **4** with Ad=Ad and collidine.

The location of the triflate counterions included in the schemes is not specified, but these are likely to be ion-paired with the various bromonium ions. At present we have no evidence that these influence the kinetics in a meaningful way. We deal with the kinetic details of these two schemes in turn.

(iii) Kinetic Details of the  $\text{Br}^+$ -Transfer Process.

Steady-state kinetic analysis of the process depicted in Scheme 4 gives the expression in eq 5. Since the rate for intramolecular capture of the open form (**4-op** in Schemes

$$k_{\text{obs}} = k_d(10^9[\text{Ad}=\text{Ad}])/(k_{-d} + 10^9[\text{Ad}=\text{Ad}]) \quad (5)$$

4 and 5) to reform **4** is larger than that for intermolecular capture by Ad=Ad at the concentrations employed, eq 5 reduces to  $k_{\text{obs}} = k_d/(k_{-d}(10^9[\text{Ad}=\text{Ad}]))$  and from the plots of  $k_{\text{obs}}$  vs [Ad=Ad] one determines that the ratio of  $k_d/k_{-d}$  is  $10^{-9}$ . For the cycle given in Scheme 5,  $K_{\text{eq}} = k_d/k_{-d}(10^9/k_r) = 7.1$ , so  $k_r$ , the rate constant for  $\text{Br}^+$ -transfer from **1-Br**<sup>+</sup> to free ligand **3** giving **4-op**, can be computed as  $0.14 \text{ M}^{-1} \text{ s}^{-1}$ .

Two interesting facts emerge from the above analysis. First, the equilibrium constant for  $\text{Br}^+$ -transfer from **4-op** to Ad=Ad can be computed to be  $\sim 7 \times 10^9$ , pointing to an equilibrium free energy difference of  $\sim 13.5 \text{ kcal/mol}$  for **4-op** relative to **1-Br**<sup>+</sup>. The high energy of **4-op** is the main reason this species reacts with all the neutral acceptors with rate constants at or approaching the diffusion limit. Thus, the small  $K_{\text{eq}} = 7.1$  for the overall transfer from **4** to Ad=Ad stems from the fact that reformation of **4** from **4-op** benefits from a very efficient intramolecular process leading to a large stabilization when the  $\text{Br}^+$  is bound between two pyridine rings.

For the process shown in Scheme 5, the experimental  $K'_{\text{eq}}$  is  $56 \text{ M}^{-1}$  in dichloromethane, a solvent that we assume has very similar properties to the dichloroethane we used for kinetic studies. In a previous study<sup>2</sup> we determined that the dissociation and reformation rate constants for **2** are  $205 \text{ s}^{-1}$  and  $3 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ , respectively (numbers added to Scheme 5). Using these values and the equilibrium expression for the cycle given in eq 6, one can compute that the rate constant for  $\text{Br}^+$ -

transfer from collidine to ligand **3** is  $2600 \text{ M}^{-1} \text{ s}^{-1}$ . This

$$K'_{\text{eq}} = k_d/k_{-d}k_{\text{diff}}/K_r(3 \times 10^6)/205 = 56 \text{ M}^{-1} \quad (6)$$

in turn indicates that the equilibrium constant for  $\text{Br}^+$ -transfer from **4-op** to collidine is  $4 \times 10^6$ .

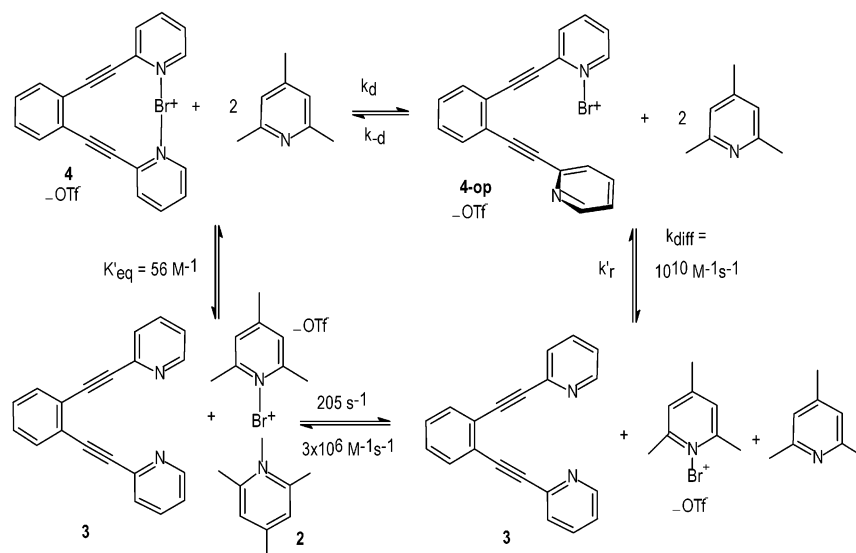
For both equilibria discussed above, the reclosure of **4-op** is a highly effective process. While we have no structural information about either **4** or **4-op**, it is likely that the rigid carbon framework identified in the X-ray structures for the  $\text{Ag}^+$  and  $\text{PdCl}_2$  salts<sup>7</sup> only allows dissociation via a rotation of either or both the pyridine and pyridine- $\text{Br}^+$ , such as we have shown in Schemes 4 and 5. Conversely, the reverse reaction of reclosure of **4-op** must involve only low-energy rotations leading to a very large rate constant for that process.

(iv) Reaction of  $\text{Br}^-$  with **4**. The reaction of **4** with  $\text{Br}^-$  proceeds much more quickly ( $>10^3$ -fold) than with any of the neutral acceptors we have investigated and cannot be explained involving any mechanism in which the first step is the unfavorable preequilibrium opening to form **4-op**. The likely mechanism must avoid the formation of the high-energy **4-op** intermediate and involves direct nucleophilic attack of  $\text{Br}^-$  on **4** as shown in Scheme 6 to yield a species such as **12** that may be considered an intermediate or a transition state having a hypervalent bromine covalently bonded to both the nitrogens, or as a complex where one of the bromines is coordinated to the two nitrogen lone pairs. In any event **12** probably decomposes by a two-step process involving sequential dissociation of first one and then the second  $\text{Br}$ -pyridine bond. It is not likely that **12** proceeds directly to  $\text{Br}_2$  and free ligand **3** in a single step since, due to the principle of microscopic reversibility, attack of  $\text{Br}_2$  on **3** would necessarily involve both pyridines attacking the halogen simultaneously.

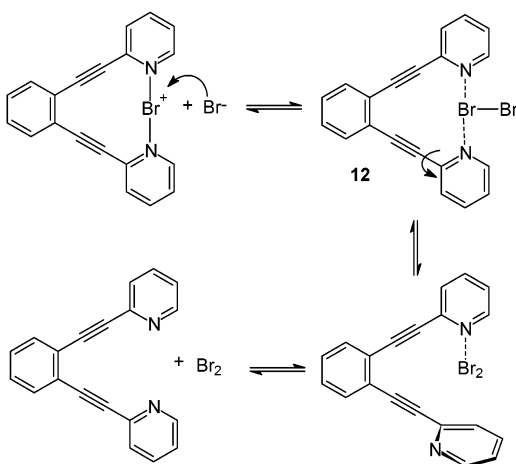
The direct nucleophilic attack mechanism proposed for the  $\text{Br}^-$  anion probably results from its greater nucleophilicity in chlorinated hydrocarbon relative to that of neutral alkenes or collidine.  $\text{Br}^-$  is also far less encumbered than alkenes such as Ad=Ad, where it is difficult to envision how a crowded double bond can directly attack the hindered  $\text{Br}^+$  without severe steric buttressing thus enforcing the **4-op** mechanism.

(v) Reaction of Bis(pyridine)bromonium Triflate (**5**) with Olefin Acceptors Ad=Ad (**1**), Cyclohexene (**6f**), 4-Penten-1-ol (**6a**), and 4-Pentenoic Acid (**6c**). The observed high reactivity of **4-op** relative to that of collidine- $\text{Br}^+$  results from the former's higher energy, which is additionally confirmed by the value of the equilibrium constant  $K = [\text{coll-Br}^+][\mathbf{3}]/[\mathbf{4-op}][\text{coll}] = 4 \times 10^6$ . The higher stability of the collidine complex is attributable to the presence of the three electron-donating methyl groups which are absent in ligand **3**. Since electronic effects and possibly substitution pattern play an important role in determining the stabilities and reactivities of the bromonium ion complexes, we decided to investigate the kinetic behavior of the parent complex **5**. The  $k_{\text{obs}}$  values for the reaction of **5** with the above alkenes show a common species rate depression in the presence of added pyridine, and a saturation behavior in the presence of increasing [olefin] as illustrated in Figure 2. This behavior is consistent with the process given in Scheme 1 and is analogous to the mechanism of

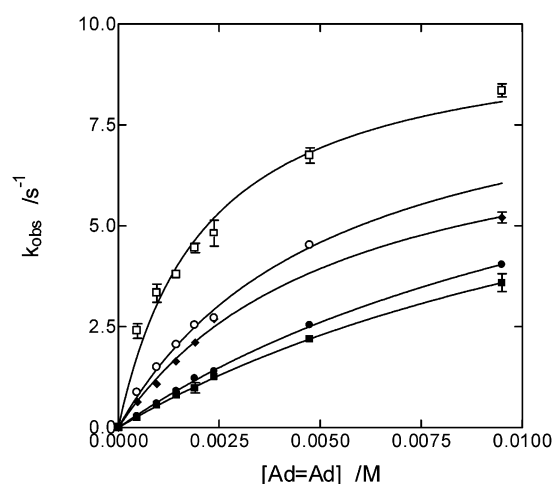
## SCHEME 5



## SCHEME 6



$\text{Br}^+$ -transfer from **2-OTf** that we investigated previously.<sup>2</sup> Using the analyses described in the Results Section (ii) the dissociation rate constant ( $k_1$ ) and partitioning ratio  $k_{-1}/k_2$  were determined (see Table 2) and there are two points of note in these data. First, the  $k_1$  dissociation rate constant for these alkenes is, within experimental uncertainty, constant at  $\sim 12.8 \text{ s}^{-1}$  as one would expect for a mechanism where the dissociation step does not involve the acceptor alkene. This value is some 20 times slower than that for dissociation of the bis(collidinium)bromonium complex ( $205 \text{ s}^{-1}$ ),<sup>2</sup> indicating that the generation of pyridine- $\text{Br}^+$  species from **5** requires a higher overall activation energy than the dissociation of **2** to generate coll- $\text{Br}^+$  due to the latter's rings having an increased ability to accommodate (+) charge. The second point of note is the relative insensitivity of the partitioning ratio,  $k_{-1}/k_2$ , to the nature of the alkene, which varies by only a factor of 4 in the Ad=Ad, cyclohexene, 4-penten-1-ol, and 4-pentenoic acid series. This contrasts the behavior of the bis(2,4,6-collidine)bromonium<sup>2</sup> system, where the relative reactivity of Ad=Ad, cyclohexene, and 4-penten-1-ol toward coll- $\text{Br}^+$  is 24, 3, and 1, and even more so the situation for transfer of  $\text{Br}^+$  from the Ad=Ad bromonium ion to Ad=Ad, cyclohexene, 4-penten-1-ol, and 4-pen-



**FIGURE 2.** Plot of the observed rate constant for the reaction of **5** ( $4.9 \times 10^{-5} \text{ M}$ ) at  $T = 25 \text{ }^\circ\text{C}$ , in dichloroethane, with Ad=Ad at various fixed concentrations of pyridine:  $4.75 \times 10^{-4} \text{ M}$  ( $\square$ ),  $9.5 \times 10^{-4} \text{ M}$  ( $\circ$ ),  $1.42 \times 10^{-3} \text{ M}$  ( $\blacklozenge$ ),  $1.90 \times 10^{-3} \text{ M}$  ( $\bullet$ ),  $2.38 \times 10^{-3} \text{ M}$  ( $\blacksquare$ ).

tenoic acid where the respective reactivities are  $2 \times 10^7$ , 1.1, 3.4, and  $7.6 \times 10^{-2}$ .<sup>1c</sup> We earlier attributed<sup>2</sup> the reactivity difference between the coll- $\text{Br}^+$  and **1-Br**<sup>+</sup> ions to the fact that the transfer from coll- $\text{Br}^+$  to the alkene is largely exothermic, having an early TS with little charge development on the alkene. Conversely, the transfer from **1-Br**<sup>+</sup> to the alkene is thermoneutral (in the case of Ad=Ad) or largely endothermic with other olefins, and in the latter cases must proceed through a late TS with a large degree of charge on the alkene. The same explanation applies for pyr- $\text{Br}^+$ , which must be even higher in energy and more reactive than coll- $\text{Br}^+$  and therefore less selective in its reaction with alkenes. This points to an interesting dilemma in designing pyridine-based  $\text{Br}^+$ -transfer agents that will discriminate between alkenes with a possible eye to chiral or diastereoselective synthesis: any appropriate transfer agent cannot produce an intermediate so reactive that it reacts with all alkenes at similar rates.

(vi) **X-ray Crystal Structures of Bis(collidine)-bromonium Perchlorate (2-ClO<sub>4</sub>) and Bis(pyridine)-bromonium Triflate (5).** The structure of compound **2-ClO<sub>4</sub>** is comprised of *C2/c* arranged unit cells. Each unit cell has eight asymmetric units, each consisting of one and a half molecules, meaning that two types of molecules exist in the unit cell. One of them is an independent bromonium ion complex with almost linear N–Br–N arrangement with one N–Br bond longer (2.143 Å) than the other (2.086 Å), and with the two collidine planes twisted around the N–Br–N axis at a dihedral angle of 33.2°. In this molecule, the separation between the *o*-methyl groups on opposing pyridines is 4.220 and 4.188 Å. The other molecule is completely flat with two coplanar collidine groups with its Br<sup>+</sup> ion positioned at the inversion center with a C<sub>2</sub> symmetric perchlorate ion. The N–Br bond length is 2.11 Å and the separation of the *o*-methyls on opposing pyridines is 3.991 Å, essentially the sum of the van der Waals radii of the two groups.<sup>17</sup> Correspondingly, the twisted conformation of the second molecule arises not from methyl–methyl steric repulsion but from crystal packing forces. The two independent bromonium ion complexes overlap with an angle of 15.5° between the two collidine rings of the separate (collidine)<sub>2</sub>Br<sup>+</sup> units and with a distance of 3.10 to 3.76 Å between the carbon skeletons of those aromatic rings. Interestingly, the average separation between the rings at 3.43 Å is less than twice the half-thickness of an aromatic ring (2 × 1.84 Å),<sup>17</sup> suggesting that there is some attraction between the two rings bringing them closer together. The perchlorate groups fill interstices in the cation framework.

The structure of **5** comprises *P1* unit cells containing two molecules in each. The N–Br<sup>+</sup> bond lengths are 2.075 and 2.107 Å, while the N–Br<sup>+</sup>–N bond angles are 178.4°. The dihedral angle between the two pyridine rings in a given molecule is between 10.3 and 13.0°, indicating that one or both of the rings are slightly nonplanar. The packing diagram indicates two interleaved stacked arrays of nearly flat parallel pyr–Br<sup>+</sup>–pyr units repeated in such a way that the 1,2-bond of a pyridine in one array lies nearly over top the 3,4-bond of the pyridine below, creating a situation where planes 1,3,5,7... and 2,4,6,8... are repeated. The triflate counterions are situated in channels perpendicular to the planes of the pyridine rings. The distance between C<sub>3</sub> (of pyridine in the top plane) and N<sub>1</sub>' (of the plane beneath) is 3.47 Å while that between C<sub>4</sub> and C<sub>2</sub>' is 3.68 Å. Thus the average separation between the planes of the aromatic rings in **5** is less than the van der Waals thickness, again suggesting a favorable interaction between them.

To our knowledge there are only two reported N–Br<sup>+</sup>–N type structures, bis(quinoline)bromonium perchlorate **10**<sup>8</sup> and bis(quinuclidine) bromonium tetrafluoroborate **11**,<sup>9</sup> and the bond lengths and angles for those are compared with those found for **2-ClO<sub>4</sub>** and **5** in Table 3. The N–Br–N angle is almost linear for all four compounds, consistent with the description of Robertson et al.<sup>8</sup> for the hybridization of the Br in such complexes as sp<sup>3</sup>d<sub>z</sub>. In all four compounds one of the N–Br bonds is longer than the other in the near-linear N–Br–N arrangement

(except the second independent molecule found in the structure of **2-ClO<sub>4</sub>** where the bonds are equal at 2.115 Å). Nevertheless, the average value for the two bonds in each molecule varies only slightly in the range of 2.09–2.14 Å, in all cases being larger than the sum of the covalent radii of N and Br (1.84 Å).<sup>18</sup> It is also interesting to note that the N–Br bond lengths in *N*-bromoacetamide<sup>19</sup> and *N*-bromosuccinimide complex<sup>20</sup> are considerably shorter at 1.82 and 1.896 Å, respectively, perhaps suggesting that the bonding exhibited by the N–Br<sup>+</sup>–N complexes is less covalent and more indicative of that extant in metal–N complexes.

It is important also to note that while the two independent molecules found in the **2-ClO<sub>4</sub>** crystal have different N–Br<sup>+</sup> bond lengths, the sum of the N–Br<sup>+</sup> lengths in each molecule is exactly the same at 4.230 Å, indicating the Br<sup>+</sup> can be positioned variously along the N–N axis with little molecular and presumably energetic distortion. Blair et al.<sup>9</sup> suggested that the asymmetry between the two N–Br bond lengths is common in such 10-Br-2<sup>21</sup> systems, and based on prior evidence that the pyridines are not equivalent in the Nujol mull IR spectra for bis(pyridine)bromonium perchlorate and tribromide salts,<sup>22</sup> but are equivalent for bis(pyridine)bromonium PF<sub>6</sub><sup>−</sup> salt.<sup>22,23</sup> Blair et al. concluded that the symmetric and asymmetric structures have very similar energies and the degree of asymmetry found in the crystal might be determined by crystal packing considerations and the location of the counterions.

## Conclusions

The above study reveals several interesting points concerning the synthesis, reactivity, and structure of certain pyr–Br<sup>+</sup>–pyr complexes. Among these is the synthesis of the first intramolecularly *N*-complexed bromonium ion, **4**, which this work shows reacts with a variety of different acceptors including several alkenes, collidine, and Br<sup>−</sup>. The reaction of **4** with neutral acceptors involves an initial unfavorable equilibrium formation of a high-energy open form that is suggested to react with all acceptors at or near the diffusion limit. However, due to unfavorable preequilibrium opening, the overall second-order rate constants are only between 1 and 10 M<sup>−1</sup> s<sup>−1</sup>. The reaction of **4** with the anionic acceptor Br<sup>−</sup> is very much faster and proceeds by a different mechanism involving direct nucleophilic attack on the Br.

While the reaction of the parent bis(pyridine)bromonium species **5** with alkenes follows the general process that we have observed previously for the reactions of the bis(2,4,6-collidine)bromonium ion, discrimination of the pyr–Br<sup>+</sup> intermediate between alkenes in terms of their relative rates of reaction with pyr–Br<sup>+</sup> is poor relative to their reaction with coll–Br<sup>+</sup>, suggesting that pyr–Br<sup>+</sup> is a higher energy intermediate that is far less selective.

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Finally, the structures of the collidine and pyridine bromonium ions determined by X-ray diffraction indicate a general asymmetry in the N–Br<sup>+</sup>–N bond lengths, although the average bond length for these and the other two known N–Br<sup>+</sup>–N complexes is quite invariant at 2.09–2.14 Å and significantly longer than the sum of the N and Br covalent radii (1.94 Å). The longer bond lengths are consistent with a weak N–Br–N linkage and account for the high dissociation rate of these species during their reactions with neutral acceptors.

**Acknowledgment.** The authors gratefully acknowledge the financial assistance of the Natural Sciences and Engineering Research Council (NSERC) of Canada and Queen's University. In addition they are grateful

to Dr. Yousheng Zhang and Dr. Ruiyao Wang for determination of the X-ray structures of **2-ClO<sub>4</sub>** and **5**. K.H. thanks NSERC for the award of a Summer Undergraduate Research Fellowship.

**Supporting Information Available:** Tables of kinetic data for the reaction of **4** and **5** with various acceptors (Tables S1–S14), tables of crystal data, structure refinement parameters, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for **2-ClO<sub>4</sub>** and **5** (Tables S15–S25); Figures S1, S3, and S2, S4 giving ORTEP diagrams for **2-ClO<sub>4</sub>** and **5** as well as their crystal packing diagrams. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JO020750M