Synthesis of Tripyridiniumylpropenyl Anions from Tripyridiniumylcyclopropanes and -cyclopropenes[1]

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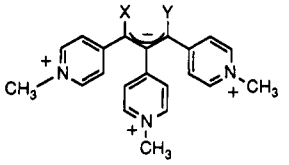
The syntheses of three stable, isolatable tripyridiniumylpropenyl anions are described. 1,2,3-Tris(4-(*N*-methylpyridiniumyl))propenyl anion and 1-(benzenesulfonyl)-1,2,3-tris(4-(*N*-methylpyridiniumyl))propenyl anion were prepared by treating the corresponding cyclopropane with a base. 1,3-Bis(benzenesulfonyl)-1,2,3-tris(4-(*N*-methylpyridiniumyl))propenyl anion was prepared by nucleophilic attack of benzenesulfinate anion on 3-(benzenesulfonyl)-1,2,3-tris(4-(*N*-methylpyridiniumyl))cyclopropene. Reduction of this cyclopropene gave either 1-(benzenesulfonyl)-1,2,3-tris(4-(*N*-methyl)pyridiniumyl))propenyl anion or hexakis(4-(*N*-methylpyridiniumyl))benzene depending on the solvent used.

Several years ago, Streitwieser reported the preparation of a stable pentapyridiniumylpropenyl anion produced when (dimethylamino)pyridine reacted with tetrachlorocyclopropene.[2] During the course of our work toward the preparation of an isolatable cyclopropenyl anion,[1] we also encountered several novel isolatable propenyl anions (actually dications!), in our case stabilized by the 4-(*N*-methylpyridiniumyl) group. Each one is highly colored and insensitive to both air and water.

Two of these tripyridiniumylpropenyl anions, **1** and **2**, were prepared by base-induced ring opening of the corresponding substituted cyclopropanes, which were easily prepared by conventional methods. The other anion, **3**, was prepared by reaction of a substituted cyclopropene with a nucleophile.



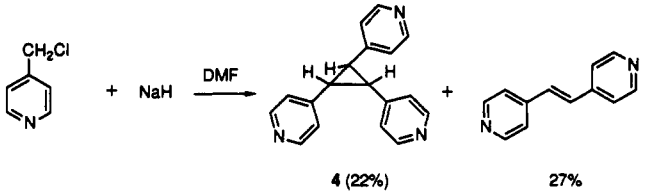
1 X=Y=H
2 X=SO_2Ph, Y=H
3 X=Y=SO_2Ph

Results and Discussion

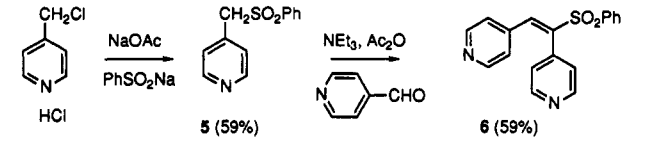
Simply stirring a solution of commercially available 4-(chloromethyl)pyridine with sodium hydride in dimethylformamide (DMF) gave a low yield of *trans*-1,2,3-tri(4-pyridyl)cyclopropane, **4**, accompanied by a fair amount of 1,2-di(4-pyridyl)ethylene (Scheme I). The ^1H NMR spectrum of **4** shows two different sets of pyridine signals in a ratio of 2:1, and the ^{13}C NMR shows two ring carbons appearing at 34.2 and 29.2 ppm, indicating that the molecule has the stereochemistry shown. The olefin is presumably formed first by reaction of the anion of 4-(chloromethyl)pyridine with an unionized molecule to yield a chloroethane, which loses HCl. Then, Michael addition of another anion of 4-(chloromethyl)pyridine with this olefin accompanied by cyclization with loss of chloride gives the cyclopropane. Not surprisingly, the yield of cyclopropane was substantially increased (to 44%) when commercially available di(4-pyridyl)ethylene was added to the reaction mixture.

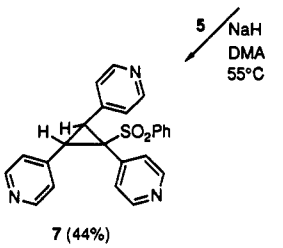
1-(Benzenesulfonyl)-1,2,3-tri(4-pyridyl)cyclopropane, **7**, was prepared in a similar fashion by heating a solution of 4-((benzenesulfonyl)methyl)pyridine (**5**) and 1-(benzenesulfonyl)-1,2-di(4-pyridyl)ethylene (**6**) with sodium hydride

Scheme I

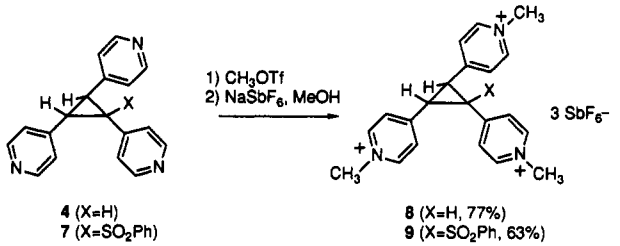


Scheme II





Scheme III



in dimethylacetamide (DMA) (Scheme II). Only one isomer was isolated; the ^1H NMR spectrum of **7** shows two doublets at 4.28 and 3.50 ppm (J = 8.6 Hz), indicating that the compound has trans hydrogens. Earlier attempts to do this reaction with 4-(chloromethyl)pyridine resulted in lower yields of the product (about 20%).

The required olefin **6** was simply prepared by reaction of commercially available 4-pyridinecarboxaldehyde with 4-((benzenesulfonyl)methyl)pyridine (**5**) in a solution of triethylamine and acetic anhydride. The stereochemistry of this olefin was determined by the use of NOE difference spectroscopy. As shown in Figure 1, when the β-proton of ring A was irradiated, a 7% NOE was observed on the vinylic proton. However, when the β-proton of ring B was irradiated, no NOE was observed on the vinylic proton.

(1) A preliminary communication of some of this work has appeared: Breslow, R.; Crispino, G. A. *Tetrahedron Lett.* **1991**, *32*, 601.
(2) Waterman, K. C.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 3874.

0022-3263/92/1957-1849$03.00/0

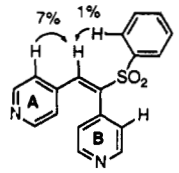


Figure 1. NOEs observed in 6.

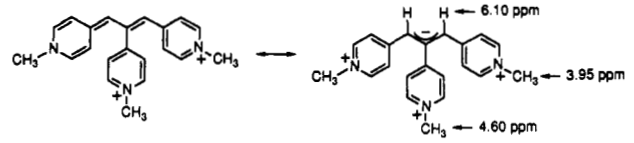
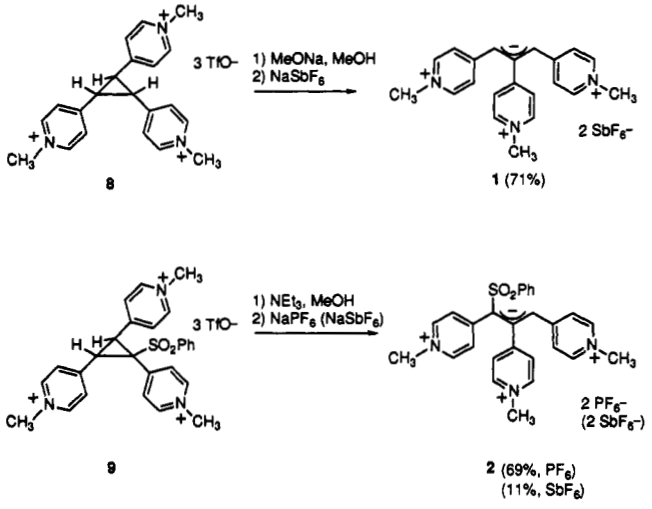


Figure 2.

Scheme IV



This result seems to suggest the *E* isomer with both pyridine rings on the same side. This assumption was confirmed when the phenyl proton α to the SO_2 was irradiated to give a 1% NOE on the vinylic proton, indicating that the benzenesulfonyl group and the vinylic proton must be on the same side.

Methylation of the cyclopropanes with methyl triflate gave the hygroscopic 4-(*N*-methylpyridinium) triflates **8** and **9**, which were converted to their hexafluoroantimonate salts for easier characterization (Scheme III). Treatment of these salts with base gave the highly colored propenyl anions which were isolated as the hexafluoroantimonate and/or hexafluorophosphate salts (Scheme IV).

Propenyl anion **1** was isolated as dark green crystals; it has a broad absorption in the visible region at 643 nm ($\epsilon = 2.1 \times 10^4$) and a weaker absorption at 458 nm ($\epsilon = 4.9 \times 10^3$). It has the expected 10-line ^{13}C NMR spectrum. The ^1H NMR spectrum shows the contribution of the neutral resonance form in the upfield shifts of the signals of the *N*-methyl groups of the two equivalent flanking pyridine rings (Figure 2).

Sulfone propenyl anion **2** was isolated as a dark violet powder; it has a very weak, broad UV absorption at 560 nm ($\epsilon = 2.3 \times 10^3$). The ^1H NMR spectrum has some structural similarity to that of the literature compound 1,4-dihydro-1-methyl-4-((benzenesulfonyl)methylene)-pyridine, **10**.[3] In this compound, the hydrogens on either side of the pyridine ring are not equivalent; this illustrates the contribution of the neutral resonance form (Figure 3). Anion **2** also shows the contribution of the resonance form with an anhydropyridine ring attached to the sulfone

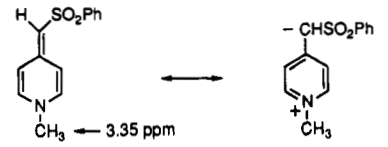


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Figure 3.

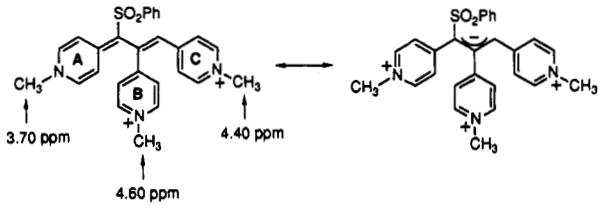
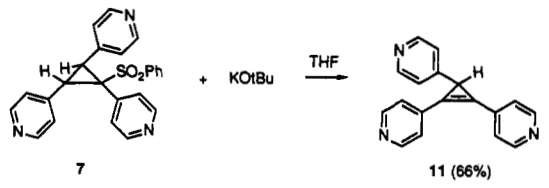
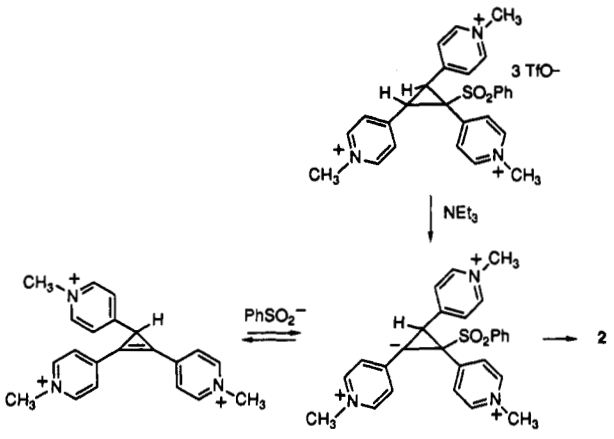


Figure 4.

Scheme V



Scheme VI

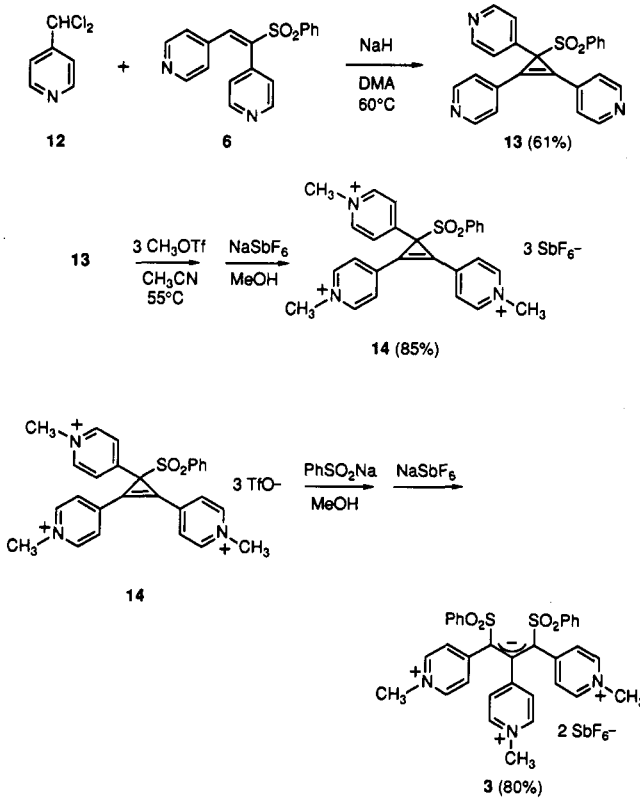


group, ring A (Figure 4). The hydrogens on either side of this anhydro pyridine ring are not equivalent; however, as expected, this asymmetry is not present in the two pyridine rings B and C. The contribution of this resonance form is also evident from the shifts of the methyl group protons, since the *N*-methyl group of the anhydro pyridine ring A is found upfield of the other two. In contrast, the propenyl anion **1** and the disulfone propenyl anion **3** (vide infra) do not show the above behavior; as expected, the protons of the *N*-methyl groups on either side of the flanking pyridine rings are equivalent in these molecules.

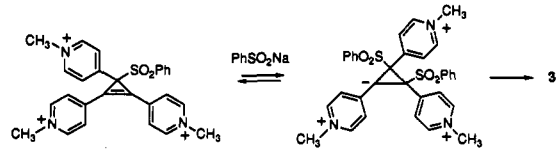
It is interesting to compare the marked difference in behavior between the sulfone tripyridiniumylcyclopropane salts and the corresponding free base, 1-(benzenesulfonyl)-1,2,3-tri(4-pyridyl)cyclopropane, **7**, with base. Reaction of this latter cyclopropane with potassium *tert*-butoxide gave only 1,2,3-tri(4-pyridyl)cyclopropene (**11**) (Scheme V); no evidence for the formation of ring-opened sulfone-containing products was found. This observation can be explained by noting that whereas elimination in the 4-pyridyl series is irreversible, elimination in the 4-pyridinium series is probably reversible, since the double bond in this series is much more activated toward nucleophilic attack than is the double bond in the pyridyl series. However, the ring opening reaction is irreversible,

(3) Golding, S.; Katritsky, A. R.; Zucharska, H. Z. *J. Chem. Soc.* **1965**, 3090.

Scheme VII



Scheme VIII

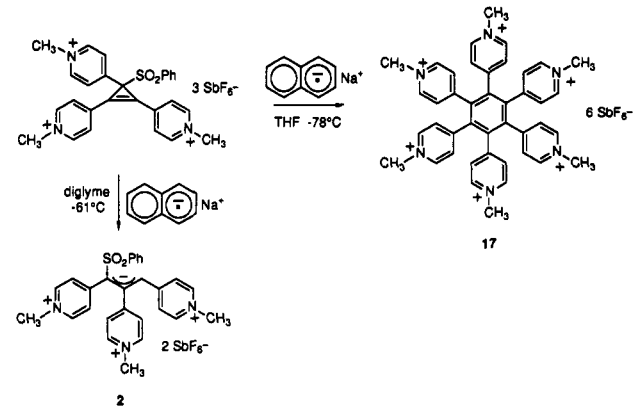


and the equilibrium is driven toward the propenyl anion (Scheme VI).

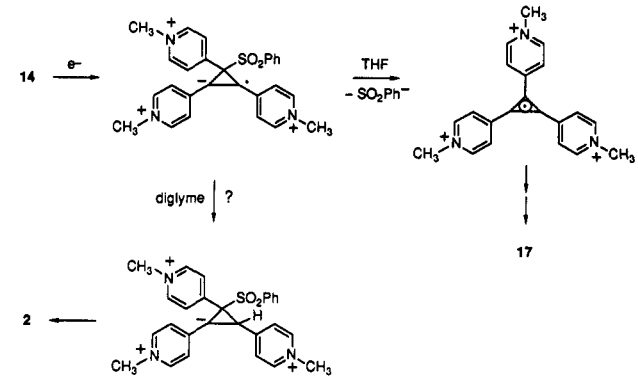
Finally, the synthesis of 1,3-bis(benzenesulfonyl)-1,2,3-tris(4-(*N*-methylpyridiniumyl)propenyl anion was accomplished in three steps (Scheme VII). Heating a solution of the olefin **6** with 4-(dichloromethyl)pyridine, prepared using a modification of the literature procedure,[4] in the presence of sodium hydride in DMA gave 3-(benzenesulfonyl)-1,2,3-tri(4-pyridyl)cyclopropene (**13**) in good yield. N-Methylation with methyl triflate gave the trimethylated triflate salt **14**, which was converted to the hexafluoroantimonate salt for easier characterization. This cyclopropene is stable for several weeks at room temperature, but is highly reactive to nucleophiles; addition of sodium benzenesulfinate gave an immediate deep red solution of the disulfone propenyl anion which could be isolated as the hexafluoroantimonate salt **3**. Two maxima appear in the visible region at 390 ($\epsilon = 1.7 \times 10^4$) and 556 ($\epsilon = 4.4 \times 10^3$) nm. The driving force for this ring opening is the formation of the highly stabilized anion (Scheme VIII). It was also observed that other nucleophiles such as iodide and chloride ions lead to ring-opened products.

The reduction of the tripyridiniumylcyclopropenyl sulfone **14** should also be mentioned, since it was found that the product was solvent dependent. In diglyme, reaction with sodium naphthalenide gave only the sulfone propenyl anion **2**; however, in tetrahydrofuran (THF), only hexakis(4-(*N*-methylpyridiniumyl))benzene (**17**) was isolated (Scheme IX). This latter result parallels the reduction of the free base, 3-(benzenesulfonyl)-1,2,3-tri(4-pyridyl)cyclopropene, **13**, which yielded only hexa(4-pyridyl)benzene, **16**. An identical sample of hexakis(4-(*N*-methylpyridiniumyl))benzene (**17**) was prepared by methylation of hexa(4-pyridyl)benzene with methyl triflate and conversion of the triflate to the hexafluoroantimonate counterion.

Scheme IX



Scheme X



Whereas the formation of benzene derivatives from the reduction of substituted cyclopropenes has been found to be a common reaction,[5] the isolation of the sulfone propenyl anion **2** is unusual. It is possible to rationalize the solvent effect by noting that the cyclopropenylsulfone **14** (SbF_6 salt) dissolves in diglyme but does not dissolve in THF, the latter reaction is run as a suspension. Presumably, in diglyme, the initial product of reduction, an anion radical, is stabilized by the solvent so that the relatively poor leaving group does not eliminate. Instead, we believe that a hydrogen abstraction occurs to give the cyclopropyl anion which electrocyclically ring opens to the propenyl anion (Scheme X). However, in THF, the anion radical is not stabilized by the solvent since the reaction occurs on the surface, so benzenesulfinate is lost to give the cyclopropenyl radical which dimerizes and rearranges to the benzene derivative. Since this explanation is speculative, further work needs to be done to elucidate the mechanisms of these reactions.

In conclusion, we have described the synthesis of several propenyl anions stabilized by the 4-(*N*-methylpyridiniumyl)group. These remarkable compounds are highly conjugated dications which have been isolated and

(4) Brown, B. R.; Hammick, D. L.; Thewlis, B. H. *J. Chem. Soc.* **1951**, 1145.

(5) Breslow, R.; Gal, P. *J. Am. Chem. Soc.* **1959**, *81*, 4747. Breslow, R.; Dowd, P. *J. Am. Chem. Soc.* **1963**, *85*, 2729. Breslow, R.; Gal, P.; Chang, H. W.; Altman, L. J. *J. Am. Chem. Soc.* **1965**, *87*, 5139. Breslow, R.; Cortes, D. A.; Jaun, B.; Mitchell, R. D. *Tetrahedron Lett.* **1982**, *23*, 795.

characterized under normal laboratory conditions. The results described in this paper suggest that the isolation of a trisubstituted cyclopropenyl anion should be possible, and further work is continuing in this area.

Experimental Section

^1H NMR spectra were taken on Varian VXR 200 and 300 spectrometers at 200 and 300 MHz, respectively. ^{13}C NMR spectra were taken on a Varian VXR 300 spectrometer at 75 MHz. All chemical shifts were measured relative to residual solvent resonances. Infrared spectra were recorded on either a Perkin-Elmer 983 IR spectrometer or a Perkin-Elmer 1600 FT-IR spectrometer with polystyrene as the reference. Electron impact (EI) or chemical ionization (CI) mass spectra were obtained on a Nermag R-10-10 quadrupole instrument. Fast atom bombardment mass spectra (FAB^+) were recorded on a JEOL DX303HF or a VG instruments 7070 EQ mass spectrometer. Visible and UV spectra were recorded on a Beckman DU-8 or DU-8B spectrometer using CH_3CN as solvent. Elemental analysis were performed either by Galbraith Laboratories (Gal) or by the author on a Perkin-Elmer 2400 CHN elemental analyzer (PE); reported results are averages. Melting and boiling points are uncorrected. All reagent chemicals were purchased from Aldrich Chemical Co. and used without further purification unless noted otherwise. Flash chromatography was performed by the method of Still.[6] Alumina gel chromatography was performed under gravity, wet packing the gel. Activity grades 2 and 4 were prepared by adding 3% or 10% water, respectively, to Brockman activity 1 neutral alumina gel purchased from Fisher. All reactions were performed under anhydrous conditions in an atmosphere of dry argon.

1,2,3-Tri(4-pyridyl)cyclopropane (4). A solution of 1.68 g (13.1 mmol) of 4-(chloromethyl)pyridine (from 2.15 g of the hydrochloride) in 5 mL of CH_2Cl_2 was added to a solution of 2.1 g (11.5 mmol) of di(4-pyridyl)ethylene and 639 mg (13.3 mmol) of NaH (50% in oil) in 40 mL of dry DMF at 0 °C. The solution was slowly warmed to room temperature and stirred for 2 days. After the addition of 1 mL of absolute ethanol, the solvent was removed in vacuo and the residue was partitioned between CH_2Cl_2 and H_2O. The aqueous layer was further extracted with CH_2Cl_2, the combined solutions were dried over $MgSO_4$, and the solvent was removed in vacuo to give a red-black oily solid. Flash chromatography on silica with acetone as eluent gave a clear, colorless oil (R_f = 0.13) which was triturated with ether to give 1.397 g (44%) of 4 as a white powder; 1.248 g of the olefin was recovered. Four recrystallizations from hexanes/ethyl acetate gave clear, colorless crystals: mp 122.5–123.5 °C; IR (KBr) 3020 (w), 1600 (s), 1410 (s), 1220 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.58 (d, J = 6.0 Hz, 2 H), 8.4 (d, J = 6.0 Hz, 4 H), 7.2 (d, J = 6.1 Hz, 2 H), 6.9 (d, J = 6.1 4 H), 2.85–2.95 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 150.3, 149.9, 149.2, 144.96, 123.96, 121.54, 34.2, 29.2; MS (CI, NH_3) 274 (M + 1). Anal. (Gal.) Calcd for $C_{18}H_{15}N_3$: C, 79.10; H, 5.53; N, 15.37. Found: C, 78.85; H, 5.50; N, 15.34.

4-((Benzenesulfonyl)methyl)pyridine (5). The literature procedure was followed.[3] Starting from 48 g of 4-(chloromethyl)pyridine hydrochloride, 40.19 g (59%) of 4-((benzenesulfonyl)methyl)pyridine (5) was obtained as tan flakes after one recrystallization from absolute ethanol (lit. yield 68%): mp 198–200 °C (lit.[3] mp 199–200.5 °C); ^1H NMR ($CDCl_3$) δ 8.52 (d, J = 5.9 Hz, 2 H), 7.6 (t, J = 8.0 Hz, 3 H), 7.48 (t, J = 7.4 Hz, 2 H), 7.0 (d, J = 6.0 Hz, 2 H), 4.28 (s, 3 H).

(*E*)-1-(Benzenesulfonyl)-1,2-di(4-pyridyl)ethylene (6). A suspension of 12.0 g (51.7 mmol) of 4-((benzenesulfonyl)methyl)pyridine (5) and 7.4 mL (77.5 mmol) of freshly distilled 4-pyridinecarboxaldehyde in 140 mL of Ac_2O and 140 mL of NEt_3 was heated in a 55 °C oil bath overnight. After ca. 1 h everything dissolved to give a black solution which became a suspension again a few hours later. The next day the suspension was poured into ice and made basic with Na_2CO_3. The aqueous layer was extracted with CH_2Cl_2 (about 2 L total). After drying over Na_2SO_4, the solvent was removed in vacuo to leave behind a gray solid which was taken up in about 800 mL of hot acetone, concentrated to 600 mL, and cooled to give 9.8 g (59%) of 6 as white crystals. An analytical sample was prepared by three such recrystallizations. The NOE difference spectra were taken on a Varian VXR 400 instrument at 400 MHz: mp 216–217 °C; ^1H NMR ($CDCl_3$) δ 8.57 (d, J = 6.0 Hz, 2 H), 8.48 (d, J = 6.1 Hz, 2 H), 7.9 (s, 1 H), 7.6 (t, J = 8.5 Hz, 3 H), 7.4 (t, J = 7.6 Hz, 2 H), 7.0 (d, J = 6.0 Hz, 2 H), 6.9 (d, J = 6.2 Hz, 2 H); MS (CI, NH_3) 323 (M + 1). Anal. (Gal.) Calcd for $C_{18}H_{14}N_2O_2S$: C, 67.06; H, 4.38; N, 8.69. S, 9.94; Found: C, 66.97; H, 4.34; N, 8.58; S, 9.97.

1-(Benzenesulfonyl)-1,2,3-tri(4-pyridyl)cyclopropane (7). To a solution of 3.417 g (14.7 mmol) of 4-((benzenesulfonyl)methyl)pyridine (5) and 3.136 g (9.7 mmol) of the unsaturated sulfone 6 in 100 mL of warm (60 °C) DMA was added 433 mg (10.8 mmol) of NaH (60% in oil) in small portions. After the addition was complete, the deep red solution was stirred at this temperature for 3 h and then at room temperature overnight. Absolute ethanol was added, and the solvents were removed in vacuo. The residue was partitioned between CH_2Cl_2 and H_2O, the layers were separated, and the aqueous layer was further extracted with CH_2Cl_2. The combined organics were dried over $MgSO_4$, and the solvent was removed in vacuo to give a dark red oil, which was flash chromatographed on silica with acetone as eluent. (The crude was applied to the column with CH_2Cl_2.) Fractions containing the desired product 7 (R_f = 0.18) were concentrated to yield an oil which was triturated with ether to give 1.485 g (37%) of a white powder; 487 mg of unsaturated sulfone 6 was also recovered. Therefore, a total yield of 44% was obtained based on recovered starting material. An analytical sample of the cyclopropane was prepared by three recrystallizations from ethyl acetate: mp 243–244.5 °C dec; IR (KBr) 3040 (w), 1600 (s), 1150 (m) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 8.66 (d, J = 5.9 Hz, 2 H), 8.40 (d, J = 6.0 Hz, 4 H), 7.60 (t, J = 7.3 Hz, 1 H), 7.43 (d, J = 5.7 Hz, 2 H), 7.33 (t, J = 8.3 Hz, 2 H), 7.00 (d, J = 8.4 Hz, 2 H), 6.88 (d, J = 6.2 Hz, 2 H), 6.83 (d, J = 6.0 Hz, 2 H), 4.28 (d, J = 8.6 Hz, 1 H), 3.50 (d, J = 8.6 Hz, 1 H); ^1H NMR ($CDCl_3$) δ 8.68 (d, J = 6.0 Hz, 2 H), 8.45 (d, J = 6.0 Hz, 4 H), 7.55 (t, J = 7.5 Hz, 1 H), 7.38 (d, J = 5.9 Hz, 2 H), 7.30 (t, J = 8.0 Hz, 2 H), 6.92 (d, J = 8.0 Hz, 2 H), 6.88 (d, J = 6.0 Hz, 4 H), 4.25 (d, J = 8.5 Hz, 1 H), 3.42 (d, J = 8.5 Hz, 1 H); MS (CI, NH_3) 414 (M + 1). Anal. (Gal.) Calcd for $C_{24}H_{19}N_3O_2S$ (Found): C, 69.71; H, 4.63; N, 10.16; S, 7.75. Found: C, 69.48; H, 4.77; N, 9.93; S, 7.93.

1,2,3-Tris(4-(*N*-methylpyridiniumyl))cyclopropane Triflate and Hexafluoroantimonate (8). To a solution of 356 mg (1.3 mmol) of the cyclopropane 4 in 15 mL of dry CH_2Cl_2 was added 0.60 mL (5.3 mmol) of freshly distilled methyl triflate. A clear, colorless oil precipitated. The solvent was removed by pipet, and the oil was triturated with ether to give 974 mg (98%) of 8 (triflate) as a hygroscopic white powder: mp 113–116 °C; ^1H NMR (CD_3OD) δ 8.89 (d, J = 6.8 Hz, 2 H), 8.71 (d, J = 6.8 Hz, 4 H), 8.17 (d, J = 6.9 Hz, 2 H), 7.9 (d, J = 6.8 Hz, 4 H), 4.4 (s, 3 H), 4.3 (s, 6 H), 4.2 (t, J = 6.3 Hz, 1 H), 3.94 (d, J = 6.2 Hz, 2 H).

A solution of 1.2 g (4.5 mmol) of sodium hexafluoroantimonate (Alfa) in 20 mL of MeOH was filtered through Celite into a solution of 345 mg (0.45 mmol) of the triflate salt in 50 mL of MeOH. A cloudy solution was obtained which was filtered to obtain a clear solution from which crystals grew. The white crystals were collected by filtration and washed with MeOH and dried; 365 mg (79%) of 8 (SbF_6) was obtained: mp 240–241.5 °C; ^1H NMR (CD_3CN) δ 8.6 (d, J = 6.7 Hz, 2 H), 8.43 (d, J = 6.7 Hz, 4 H), 7.97 (d, J = 6.8 Hz, 2 H), 7.68 (d, J = 6.8 Hz, 4 H), 4.3 (s, 3 H), 4.2 (s, 6 H), 3.86 (t, J = 6.0 Hz, 1 H), 3.73 (d, J = 6.1 Hz, 2 H); ^{13}C NMR (CD_3CN) δ 159.2, 154.8, 145.8, 128.7, 126.7, 48.8, 48.7, 37.4, 30.5. Anal. (PE) Calcd for $C_{21}H_{24}F_{18}N_3Sb_3$: C, 24.59; H, 2.36; N, 4.10. Found: C, 24.77; H, 2.34; N, 3.86.

1-(Benzenesulfonyl)-1,2,3-tris(4-(*N*-methylpyridiniumyl))cyclopropane Triflate and Hexafluoroantimonate (9). To a solution of 109 mg (0.26 mmol) of the cyclopropane 7 in 10 mL of dry CH_3CN at 55 °C was added 0.09 mL (0.79 mmol) of freshly distilled methyl triflate. After 5 min, the solution was cooled to room temperature, and the solvent was removed in vacuo to give a clear colorless oil which was triturated with ether to give 229 mg (97%) of 9 (triflate) as a hygroscopic white powder: ^1H NMR (acetone-d_6) δ 9.21 (d, J = 6.5 Hz, 2 H), 8.91 (d, J = 6.6 Hz, 2 H), 8.85 (d, J = 6.8 Hz, 2 H), 8.65 (d, J = 6.5 Hz, 2 H), 8.05 (d, J = 6.8 Hz, 2 H), 7.85 (d, J = 6.8 Hz, 2 H), 7.79 (t, J = 7.5 Hz, 1 H), 7.55 (t, J = 8.1 Hz, 2 H), 7.43 (d, J = 8.2 Hz, 2 H), 5.25 (d, J = 8.6 Hz, 1 H), 4.95 (d, J = 8.6 Hz, 1 H),

(6) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

4.70 (s, 3 H), 4.49 (s, 3 H), 4.44 (s, 3 H).

A solution of 321 mg (1.2 mmol) of sodium hexafluoroantimonate (Alfa) in 10 mL of MeOH was filtered through Celite into a solution of 72 mg (0.08 mmol) of the triflate salt in 10 mL of MeOH. A cloudy solution was obtained which was filtered to obtain a clear solution from which crystals grew. The white crystals were collected by filtration and washed with MeOH and dried; 60 mg (65%) of **9** (SbF_6) were obtained: mp 276–279.5 °C dec; ^1H NMR (acetone-d_6) δ 9.24 (d, J = 6.5 Hz, 2 H), 8.97 (d, J = 6.5 Hz, 2 H), 8.89 (d, J = 6.4 Hz, 2 H), 8.65 (d, J = 6.4 Hz, 2 H), 8.10 (d, J = 6.4 Hz, 2 H), 7.96 (d, J = 6.0 Hz, 2 H), 7.83 (t, J = 7.4 Hz, 1 H), 7.57 (t, J = 8.0 Hz, 2 H), 7.44 (d, J = 8.2 Hz, 2 H), 5.29 (d, J = 8.6 Hz, 1 H), 4.93 (d, J = 8.5 Hz, 1 H), 4.71 (s, 3 H), 4.52 (s, 3 H), 4.47 (s, 3 H); UV 233.8 ($\epsilon = 3.2 \times 10^4$), 261.3 ($\epsilon = 1.6 \times 10^4$) nm. Anal. (PE) Calcd for $C_{27}H_{28}F_{18}N_3O_2SSb_3$: C, 27.82; H, 2.42; N, 3.60. Found: C, 27.84; H, 2.48; N, 3.52.

1,2,3-Tris(4-(*N*-methylpyridiniumyl))propenyl Anion (1). A solution of sodium methoxide (2.7 mmol, from 63 mg Na) in 5 mL of MeOH was added to a solution of 463 mg (0.61 mmol) of the cyclopropane **8** (triflate) in 70 mL of MeOH to give a deep green solution. After 1 h, 1.67 g (6.4 mmol) of $NaSbF_6$ in 10 mL of MeOH (filtered first through Celite) was added. Dark green crystals of **1** grew slowly which were collected by filtration, washed with MeOH, and dried to give 343 mg (71%): mp 190–192 °C; ^1H NMR (acetone-d_6) δ 9.1 (d, J = 6.7 Hz, 2 H), 8.35 (d, J = 6.9 Hz, 2 H), 7.9 (d, J = 7.2 Hz, 4 H), 6.75 (d, J = 7.3 Hz, 4 H), 6.1 (s, 2 H), 4.6 (s, 3 H), 3.95 (s, 6 H); ^{13}C NMR (acetone-d_6), 161.5, 149.7, 146.8, 146.4, 141.1, 128.2, 121.1, 107.1, 48.6, 45.1; UV 266.3 ($\epsilon = 1.0 \times 10^4$), 320.9 ($\epsilon = 2.1 \times 10^4$), 458.4 ($\epsilon = 4.9 \times 10^3$), 643.4 ($\epsilon = 2.1 \times 10^4$) nm. Anal. (PE) Calcd for $C_{21}H_{23}F_{12}N_3Sb_2 \cdot H_2O$: C, 31.26; H, 3.00; N, 5.21; Found: C, 31.10; H, 2.79; N, 4.95.

1-(Benzenesulfonyl)-1,2,3-tris(4-(*N*-methylpyridiniumyl))propenyl Anion Hexafluorophosphate and Hexafluoroantimonate (2). To a solution of 208 mg (0.23 mmole) of the sulfone cyclopropane **9** (triflate) in 4 mL of MeOH was added 0.35 mL (2.5 mmol) of NEt_3 to give a deep violet solution. After about 5 min, a solution of 400 mg (2.38 mmol) of $NaPF_6$ in 2 mL of MeOH was added to give a violet precipitate. The solid was collected by filtration and washed with MeOH and ether. A total of 119 mg (69%) of **2** (PF_6) was obtained: mp 159–163 °C; IR (KBr) 3066 (m), 2923 (m), 1641 (s), 1509.9 (s), 840 (s) cm^{-1}; ^1H NMR (acetone-d_6) δ 8.97 (d, J = 6.7 Hz, 2 H), 8.68 (d, J = 6.7 Hz, 2 H), 8.20 (d, J = 6.8 Hz, 2 H), 7.89 (d, J = 6.8 Hz, 2 H), 7.85 (m, 1 H), 7.75–7.60 (m, 4 H), 7.51 (t, J = 6.9 Hz, 1 H), 7.41 (d, J = 7.6 Hz, 2 H) 7.3 (m, 1 H), 6.20 (m, 1 H), 4.60 (s, 3 H), 4.40 (s, 3 H), 3.70 (s, 3 H); UV 317.6 ($\epsilon = 2.9 \times 10^4$), 365.0 ($\epsilon = 2.1 \times 10^4$), 560 ($\epsilon = 2.3 \times 10^3$) nm. Anal. (PE) Calcd for $C_{27}H_{27}F_{12}N_3O_2P_2S \cdot H_2O$: C, 42.36; H, 3.82; N, 5.49. Found: C, 42.47; H, 3.62; N, 5.54.

To a solution of 223 mg (0.25 mmol) of the sulfone cyclopropane **9** (triflate) in 6 mL of MeOH was added 0.35 mL (2.5 mmol) of NEt_3 to give a deep violet solution. After about 10 min, a solution of 699 mg (2.7 mmol) of $NaSbF_6$ in 1 mL of MeOH was added (filtered this solution through Celite first) to give an oily violet precipitate. The solvent was removed by pipet, and ether was added to give a violet powder which was collected by filtration and washed with MeOH and ether. After drying, 25 mg (11%) of **2** (SbF_6) was obtained: mp 122–125 °C dec; ^1H NMR (acetone-d_6) δ 9.00 (d, J = 6.8 Hz, 2 H), 8.70 (d, J = 6.8 Hz, 2 H), 8.21 (d, J = 6.98 Hz, 2 H), 7.92 (d, J = 6.9 Hz, 2 H), 7.85 (m, 1 H), 7.75 (s, 1 H), 7.67 (t, J = 6.99 Hz, 2 H), 7.54 (t, J = 7.3 Hz, 1 H), 7.41 (d, J = 7.7 Hz, 2 H), 7.33 (m, 2 H) 6.20 (m, 1 H), 4.60 (s, 3 H), 4.40 (s, 3 H), 3.70 (s, 3 H). Anal. (PE) Calcd for $C_{27}H_{27}F_{12}N_3O_2SSb_2 \cdot H_2O$: C, 33.60; H, 3.24; N, 4.35. Found: C, 33.54; H, 2.86; N, 4.35.

1,4-Dihydro-1-methyl-4-((benzenesulfonyl)methylene)pyridine (10). The anhydro base was prepared in two steps following a literature procedure.[3] The methyl iodide salt of 4-((benzenesulfonyl)methyl)pyridine was prepared from 540 mg (2.3 mmol) of the sulfone **5** and 2 mL (32.1 mmol) of methyl iodide (freshly percolated through activity I neutral alumina). A total of 558 mg (65%) of fluffy yellow crystals were obtained. Addition of 5 mL of 0.5 N NaOH solution to 242 mg (0.65 mmol) of the iodide salt and extraction with CH_2Cl_2 provided 131 mg (81%) of brown crystals of the anhydro base **10**: mp 103–105 °C (lit.[3] mp 128–129 °C); ^1H NMR (CH_2Cl_2) δ 7.83 (m, 2 H), 7.40 (d, 3 H), 7.05 (d, J = 5.8 Hz, 1 H), 6.75 (d, J = 7.4 Hz, 1 H), 6.65 (d, J = 7.3 Hz, 1 H), 5.98 (d, J = 5.7 Hz, 1 H), 4.90 (s, 1 H), 3.35 (s, 3 H).

1,2,3-Tri(4-pyridyl)cyclopropene (11). To a solution of 501 mg (1.2 mmol) of recrystallized cyclopropanyl sulfone **7** in 75 mL of THF at 50 °C was added 1.2 mL (1.2 mmol) of potassium *tert*-butoxide (1.0 M in THF) to give a pink suspension. After stirring for 10 min, H_2O and saturated NaCl solution were added and the layers were separated; the aqueous layer was then extracted with CH_2Cl_2, and the combined organics were dried over Na_2SO_4. After the solvent was removed in vacuo, the yellow oil was chromatographed on activity 4 neutral alumina with 50:1 CH_2Cl_2/MeOH as eluent. Fractions containing the cyclopropene **11** (R_f = 0.33) were combined and concentrated to give 294 mg (90%) of a clear colorless oil from which white crystals grew. This was then recrystallized from ether/petroleum ether to give white crystals (66%): mp 127.5–129 °C; IR (KBr) 3010 (w), 2960 (w), 1833 (m, C=C of cyclopropene), 1590 (s), 1410 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.75 (d, J = 6.0 Hz, 4 H), 8.35 (d, J = 6.0 Hz, 2 H), 7.5 (d, J = 6.0 Hz, 4 H), 7.1 (d, J = 6.0 Hz, 2 H), 3.3 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 151.7, 150.7, 149.8, 133.7, 123.7, 121.0, 114.3, 23.8; MS (EI) 271; UV 308.8 ($\epsilon = 2.3 \times 10^4$), 330 ($\epsilon = 1.9 \times 10^4$) nm. Anal. (Gal.) Calcd for $C_{18}H_{13}N_3$: C, 79.68; H, 4.83; N, 15.49. Found: C, 79.34; H, 4.88; N, 15.37.

4-(Dichloromethyl)pyridine Hydrochloride (12). To a suspension of 45.97 g (344 mmole) of NCS in 200 mL of degassed CCl_4 was added 10 mL (103 mmol) of distilled 4-picoline and 610 mg of dibenzoyl peroxide. After refluxing for 3.5 h, TLC (2:1 hexanes/ethyl acetate, silica) showed that the reaction was complete. The suspension was filtered to remove the black solid, and the solvent was removed in vacuo to give a black oil which was dissolved in CH_2Cl_2, washed with saturated Na_2CO_3 solution, and then dried over $MgSO_4$. Removal of the CH_2Cl_2 gave a black oil which was distilled under vacuum; bp 88–92 °C (7 mmHg). A white solid came over with the clear colorless oil. The distilled fraction was then dissolved in CH_2Cl_2, washed with saturated Na_2CO_3 solution, and dried over $MgSO_4$. Removal of the solvent gave 7.0 g (35%) of 4-(trichloromethyl)pyridine as a clear colorless oil: ^1H NMR ($CDCl_3$) δ 8.75 (d, J = 5.9 Hz, 2 H), 7.80 (d, J = 6.0 Hz, 2 H).

The first part of this step is based on the literature procedure.[4] A solution of 4.26 g (35.8 mmol) of tin metal in 20 mL of concentrated HCl (waited several hours for the tin to completely react) was added to a solution of 6.98 g (35.8 mmol) of 4-(trichloromethyl)pyridine in 60 mL of acetone. This solution was heated at 60 °C in an oil bath for 1 h, the acetone was removed in vacuo, Na_2CO_3 and H_2O were added, and the aqueous solution extracted with CH_2Cl_2. After drying over $MgSO_4$, the solvent was removed in vacuo to give a clear colorless oil which was dissolved in 200 mL of ether and saturated with HCl gas. A white solid formed which was collected and dissolved in 200 mL of hot ethanol. After concentrating to 100 mL and cooling to room temperature, about 100 mL of ether was added to give white crystals. After collecting by filtration and drying, 7.31 g (70%) of **12** (HCl) were obtained: mp 138–140 °C; ^1H NMR (D_2O) δ 8.69 (d, J = 6.7 Hz, 2 H), 8.12 (d, J = 6.7 Hz, 2 H), 7.1 (s, 1 H). Anal. (PE) Calcd for $C_6H_6Cl_3N$: C, 36.32; H, 3.02; N, 6.91. Found: C, 36.31; H, 3.05; N, 7.06.

3-(Benzenesulfonyl)-1,2,3-tri(4-pyridyl)cyclopropene (13). To a solution of 2.95 g (18.2 mmol) of 4-(dichloromethyl)pyridine (from the hydrochloride salt) and 3.54 g (11.0 mmol) of the olefin **6** in 110 mL of DMA at 60 °C was added 521 mg (13.0 mmol) of NaH (60% in oil) in small portions. The orange solution was stirred at this temperature overnight, and then 1 mL of ethanol was added after cooling to room temperature. The solvents were removed in vacuo, and the residue was partitioned between H_2O and CH_2Cl_2. The aqueous layer was further extracted with CH_2Cl_2 and then the combined organics were dried over $MgSO_4$. The solvent was removed in vacuo to give a yellow solid which was flash chromatographed on silica with acetone as eluent. After concentrating down the fractions containing the cyclopropene **13** (R_f = 0.30), a yellow solid was obtained which was washed with ether to yield 1.65 g (36%) of a white powder which was recrystallized from ethyl acetate to give 1.395 g of clear, colorless crystals; 1.747 g of the olefin **6** (R_f = 0.49) was also recovered. Therefore, a total yield of 61% of recrystallized cyclopropene **13** was obtained based on recovered starting material. Five additional

recrystallizations from ethyl acetate provided an analytical sample: mp 203–205 °C dec; IR (KBr) 3050 (m), 1830 (w, C=C of cyclopropene), 1600 (s), 1310 (s, SO_2Ph), 1150 (s, SO_2Ph) cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.8 (d, J = 6.0 Hz, 4 H), 8.6 (d, J = 6.1 Hz, 2 H), 7.7–7.4 (m, 7 H), 7.5 (d, J = 6.0 Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ 151.1, 150.3, 143.3, 138.4, 134.3, 131.3, 129.2, 128.99, 123.8, 123.7, 115.2, 55.0; MS (EI) 270 (M – SO_2Ph) (cyclopropenyl cation); MS (FAB^+) 412 (M + 1), 270; UV 274.7 ($\epsilon = 1.1 \times 10^4$), 308.8 ($\epsilon = 1.9 \times 10^4$) nm. Anal. (Gal.) Calcd for $C_{24}H_{17}N_3O_2S$: C, 70.06; H, 4.16; N, 10.21; S, 7.79. Found: C, 70.25; H, 4.11; N, 10.28; S, 7.91.

3-(Benzenesulfonyl)-1,2,3-tris(4-(*N*-methylpyridiniumyl))cyclopropene Triflate and Hexafluoroantimonate (14). To a solution of 207 mg (0.50 mmol) of the sulfone cyclopropene **13** in 15 mL of dry CH_3CN at 55 °C was rapidly added 0.17 mL (1.5 mmol) of freshly distilled CH_3OTf to give a light orange solution. After stirring for 5 min, the solution was cooled and the solvent was removed in vacuo to give an orange oil which was triturated with ether to give 452 mg (100%) of **14** (triflate) as an orange powder: ^1H NMR (acetone-d_6) δ 9.25 (d, J = 6.8 Hz, 4 H), 9.02 (d, J = 6.7 Hz, 2 H), 8.62 (d, J = 6.9 Hz, 4 H), 8.52 (d, J = 6.8 Hz, 2 H), 7.88 (d, J = 7.3 Hz, 2 H), 7.75 (t, J = 7.8 Hz, 1 H), 7.58 (t, J = 8.0 Hz, 2 H), 4.70 (s, 6 H), 4.55 (s, 3 H).

To a solution of 366 mg (0.41 mmol) of the triflate salt dissolved in 15 mL of MeOH was added a solution of 803 mg (3.1 mmol) of $NaSbF_6$ in 5 mL of MeOH (filtered this solution through Celite before adding). A cloudy solution formed from which a yellow microcrystalline powder precipitated which was collected by filtration and washed with MeOH and ether to give 407 mg (85%) of **14** (SbF_6). White crystals could be obtained by filtering the cloudy solution through Celite: mp 222–224 °C dec; IR (KBr) 3128 (m), 1840 (w, C=C of cyclopropene), 1641 (s), 1149 (s), 662 (s) cm^{-1}; ^1H NMR (acetone-d_6) δ 9.32 (d, J = 6.6 Hz, 4 H), 9.05 (d, J = 6.8 Hz, 2 H), 8.65 (d, J = 6.89 Hz, 4 H), 8.55 (d, J = 7.1 Hz, 2 H), 7.88 (d, J = 7.2 Hz, 2 H), 7.80 (t, J = 7.6 Hz, 1 H), 7.58 (t, J = 8.1 Hz, 2 H), 4.7 (s, 6 H), 4.55 (s, 3 H); ^{13}C NMR (acetone-d_6) δ 152.4, 148.3, 147.3, 138.4, 137.9, 137.0, 131.7, 130.5, 130.4, 129.3, 117.8, 56.8, 50.2, 49.4; UV 227 nm ($\epsilon = 2.5 \times 10^4$), 260 ($\epsilon = 1.5 \times 10^4$), 336 ($\epsilon = 1.6 \times 10^4$) nm. Anal. (PE) Calcd for $C_{27}H_{26}F_{18}N_3O_2SSb_3$: C, 27.87; H, 2.25; N, 3.61. Found: C, 27.76; H, 2.19; N, 3.55.

1,3-Bis(benzenesulfonyl)-1,2,3-tris(4-(*N*-methylpyridiniumyl))propenyl Anion Hexafluoroantimonate (3). To a solution of 75 mg (0.08 mmol) of the sulfone cyclopropene **14** (triflate) in 15 mL of MeOH was added 49 mg (0.30 mmol) of solid sodium benzenesulfinate; a deep red solution formed. After several minutes, a solution of 233 mg (0.90 mmol) of $NaSbF_6$ in 5 mL of MeOH was added (filtered this solution through Celite first), and the resulting solution was allowed to sit at room temperature overnight. Dark red crystals of **3** slowly grew which were collected by filtration and washed with MeOH. A total of 69 mg (80%) was obtained: mp 253–254.5 °C; ^1H NMR (acetone-d_6) δ 8.95 (d, J = 6.5 Hz, 2 H), 8.27 (d, J = 7.2 Hz, 4 H), 8.12 (d, J = 6.8 Hz, 2 H), 7.64 (d, J = 7.2 Hz, 4 H), 7.52 (m, 10 H), 4.63 (s, 3 H), 4.11 (s, 6 H); UV 241.4 ($\epsilon = 2.4 \times 10^4$), 269.7 ($\epsilon = 2.3 \times 10^4$), 390.0 ($\epsilon = 1.7 \times 10^4$), 555.9 ($\epsilon = 4.4 \times 10^3$) nm. Anal. (PE) Calcd for $C_{33}H_{31}F_{12}N_3O_4S_2Sb_2$: C, 37.07; H, 2.92; N, 3.93. Found: C, 37.09; H, 2.85; N, 3.86.

Reduction of 3-(Benzenesulfonyl)-1,2,3-tris(4-(*N*-methylpyridiniumyl))cyclopropene Hexafluoroantimonate (14) in Diglyme. To a solution of 1.26 mmol of sodium naphthalenide (prepared from 29 mg (1.26 mmol) of clean Na and 177 mg (1.38 mmol) of naphthalene) in 10 mL of diglyme/4 mL of THF at –65 °C was added 130 mg (0.11 mmol) of a solution of 3-(benzenesulfonyl)-1,2,3-tris(4-(*N*-methylpyridiniumyl))-cyclopropene hexafluoroantimonate (**14**) in 10 mL of diglyme at –65 °C to give a deep red solution. After stirring for 15 min, 558 mg (1.3 mmol) of 2,6-di-*tert*-butylpyridine hydrohexafluoroantimonate (**15**) (vide infra) was added, and the solution was warmed to room temperature. The solvent was removed in vacuo to give a purple solid which was washed three times each with CH_2Cl_2, MeOH, and ether and dried to give 53 mg (52%) of a gray powder. Spectral data matched those of an authentic sample of the sulfone propenyl anion hexafluoroantimonate **2**.

2,6-Di-*tert*-butylpyridine Hydrotriflate and Hydrohexafluoroantimonate (15). To a solution of 1.7 g (8.9 mmol) of 2,6-di-*tert*-butylpyridine in 20 mL of CH_2Cl_2 was added 0.75 mL (8.5 mmol) of triflic acid (used a previously unopened vial) at 0 °C. After stirring the clear tinted yellow solution for 5 min, the solvent was removed in vacuo to give white crystals which were washed with ether and dried. A total of 2.7 g (90%) of **15** (triflate) was obtained: mp 137–139 °C; ^1H NMR ($CDCl_3$) δ 8.41 (t, J = 8.2 Hz, 1 H), 7.77 (d, J = 8.1 Hz, 2 H), 1.6 (s, 18 H). Anal. (PE) Calcd for $C_{14}H_{22}F_3NO_3S$: C, 49.26, H, 6.50; N, 4.10. Found: C, 49.21; H, 6.42; N, 4.18.

A solution of 782 mg (3.0 mmol) of $NaSbF_6$ in 2 mL of MeOH was filtered through Celite into a solution of 425 mg (1.25 mmol) of the triflate salt **15** in 6 mL of MeOH. White crystals grew which were collected by filtration and washed with MeOH and ether. After drying, 372 mg (70%) of **15** (SbF_6) were obtained: mp 214–216 °C; ^1H NMR (acetone-d_6) δ 8.70 (t, J = 8.2 Hz, 1 H), 8.17 (d, J = 8.1 Hz, 2 H), 1.62 (s, 18 H). Anal. (PE) Calcd for $C_{13}H_{22}F_6NSb$ (Found): C, 36.48; H, 5.18; N, 3.27. Found: C, 36.63; H, 5.06; N, 3.23.

Hexa(4-pyridyl)benzene (16). A solution of 172 mg (0.42 mmol) of the cyclopropenyl sulfone **13** in 15 mL of THF at –78 °C was added to a solution of 0.78 mmol of sodium naphthalenide (prepared from 18 mg (0.78 mmol) of clean Na and 118 mg (0.97 mmol) of naphthalene) in 10 mL of THF at –78 °C. The resulting deep purple solution was stirred for 5 min and then cannulated into 5 mL of D_2O at room temperature. Saturated NH_4Cl solution was added and the layers separated. The aqueous layer was further extracted with CH_2Cl_2, and the combined organics were dried over $MgSO_4$. Removal of the solvent in vacuo gave a yellow-white solid which was chromatographed on activity 2 neutral alumina with 20:1 CH_2Cl_2/MeOH as eluent; 91 mg (80%) of hexa(4-pyridyl)benzene **16** (R_f = 0.24) were obtained as fine white crystals. An analytical sample was prepared by two recrystallizations from $CHCl_3$: mp >360 °C; IR (KBr) 3030 (m), 1596 (s), 1406 (s), 833 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.22 (d, J = 6.0 Hz, 2 H), 6.75 (d, J = 6.1 Hz, 2 H); ^{13}C NMR (CD_3OD) δ 149.5, 148.7, 139.3, 127.7; MS (FAB^+) 541 (M + 1). Anal. (Gal.) Calcd for $C_{36}H_{24}N_6$: C, 79.98; H, 4.47; N, 15.54. Found: C, 79.68; H, 4.55; N, 15.43.

Reduction of 3-(Benzenesulfonyl)-1,2,3-tris(4-(*N*-methylpyridiniumyl))cyclopropene Hexafluoroantimonate (14) in THF. To a solution of 1.78 mmol of sodium naphthalenide (prepared from 41 mg (1.78 mmol) of clean Na and 280 mg (2.2 mmol) of naphthalene) in 6 mL of THF at –78 °C was added 183 mg (0.16 mmol) of solid 3-(benzenesulfonyl)-1,2,3-tris(4-(*N*-methylpyridiniumyl))cyclopropene hexafluoroantiomate (**14**) to give a deep red solution. After stirring for 40 min, 762 mg (1.78 mmol) of 2,6-di-*tert*-butylpyridine hydrohexafluoroantimonate **15** was added, and the solution was warmed to room temperature. A black suspension formed. The solvent was removed with a pipet, and the black solid was washed twice each with CH_2Cl_2, MeOH, and again with CH_2Cl_2 to give 300 mg of a black powder. The ^1H NMR (CD_3CN) spectrum showed that only hexa(4-pyridiniumyl)benzene **17** was present. The crude solid was washed twice with acetone and twice with ether to yield 89 mg (54%) of a light gray powder. Spectral data matched those of an authentic sample of **17** (SbF_6) prepared below.

Hexakis(4-(*N*-methylpyridiniumyl))benzene Triflate and Hexafluoroantimonate (17). To a solution of 119 mg (0.22 mmol) of recrystallized hexa(4-pyridyl)benzene (**16**) in 24 mL of dry CH_2Cl_2 at room temperature was added 0.17 mL (1.54 mmol) of distilled CH_3OTf. A white powder precipitated which was collected by filtration and washed with CH_2Cl_2 and ether. A total of 280 mg (83%) of hexakis(4-(*N*-methyl)pyridiniumyl)benzene triflate (**17**) was obtained. Recrystallization with CH_3CN/acetone gave white crystals: mp >360 °C; IR (KBr) 3062 (m), 1644 (m), 1264 (s), 1162 (s), 1032 (s), 639.5 (s) cm^{-1}; ^1H NMR (CD_3CN) δ 8.4 (d, J = 6.5 Hz, 2 H), 8.0 (d, J = 6.7 Hz, 2 H), 4.1 (s, 3 H); ^{13}C NMR (D_2O) δ 152.8, 147.2, 137.2, 130.3, (127.147, 122.9, 118.7, 114.5, CF_3SO_3, J = 317.5 Hz), 49.5; UV 260.5 ($\epsilon = 4.9 \times 10^4$) nm. Anal. (PE) Calcd for $C_{48}H_{42}F_{18}N_6O_{18}S_6 \cdot 1.5H_2O$: C, 37.14; H, 2.82; N, 5.41; Found: C, 37.12; H, 2.72; N, 5.58.

To a solution of 25 mg (0.016 mmol) of the triflate in 4 mL of MeOH/1 mL of H_2O was added 80 mg (0.16 mmol) of $NaSbF_6$ in 1 mL of H_2O (filtered this solution through Celite first). A

cloudy white precipitate formed which was collected by filtration, washed with H_2O, MeOH, and ether, and dried. A total of 14 mg (43%) of the hexafluoroantimonate **17** was obtained: mp >360 °C; IR (KBr) 3138 (m), 1644 (s), 1462 (m), 1276 (m), 662 (s) cm^{-1}; ^1H NMR (CD_3CN) δ 8.35 (d, J = 6.5 Hz, 2 H), 7.75 (d, J = 6.5 Hz, 2 H), 4.10 (s, 3 H). Anal. (PE) Calcd for $C_{42}H_{42}F_{36}N_6Sb_6$: C, 24.66; H, 2.25; N, 4.11. Found: C, 24.30; H, 2.07; N, 4.11.

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Photochemistry of 9,10-Dicyanoanthracene–1,2-Diarylcyclopropane Systems. Photocycloaddition and Photoisomerization

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The photochemical reactions of 9,10-dicyanoanthracene (DCA)–1,2-diarylcyclopropane (CP) systems have been investigated. In degassed acetonitrile solution, ($4\pi + 2\sigma$) photocycloaddition between DCA and CP occurred to give *cis*- and *trans*-2,4-diaryl-1,5-dicyano-6,7:8,9-dibenzobicyclo[3.2.2]nona-6,8-dienes in a 3:1 ratio in good chemical yields although the quantum yields were not high (Φ = 0.002–0.04). This photocycloaddition did not occur in benzene. The DCA-sensitized photoisomerization of *trans*- and *cis*-1,2-bis(4-methoxyphenyl)cyclopropanes (**1a** and **2a**) in acetonitrile efficiently occurred to afford a photostationary mixture containing **1a** and **2a** in a 95:5 ratio. The photoisomerization was remarkably accelerated by bubbling air, by adding metal salts such as $Mg(ClO_4)_2$ and $LiBF_4$, and also by aromatic hydrocarbons such as phenanthrene and biphenyl. The quantum yield for the photoisomerization of **2a** to **1a** exceeded unity, indicating that this photoisomerization involved a chain process. The DCA-sensitized photoisomerization of optically resolved (–)-**1a** afforded a racemic mixture of (+)-**1a** and (–)-**1a**. These photoreactions are initiated by a one-electron transfer from CP to the excited singlet of DCA. The photocycloaddition proceeds via radical ion pairs in solvent cage and the photoisomerization proceeds via solvent-separated radical cations of CP.

Introduction

Photoinduced electron transfer reactions from electron donors (D) to electron acceptors (A) in polar media have been a subject of considerable interest in recent years.[1] In these photoreactions, the separation of an initially produced radical ion pair [$D^{+\cdot}$···$A^{-\cdot}$] to dissociated radical ions $D^{+\cdot}$ and $A^{-\cdot}$ is crucial in determining the efficiency and selectivity of the photoreactions. Recently, Farid et al. have reported that the photodimerization of 1,1-diphenylethene in the presence of DCA proceeds via geminate radical ion pair and also via the free radical cation of 1,1-diphenylethene, and the extent of participation of these reactive species in the photoreaction can be determined by means of kinetic analysis.[2] However, ambiguity still exists about the distinction of these reactive species and their reactivity features. Previously, we proposed that the separation of a radical ion pair to dissociated free radical ions may be facilitated by the addition of certain additives such as aromatic hydrocarbons and metal salts into the reaction system (Scheme I).[3] On the basis of this view, we have studied the effects of metal salts and other additives on photoinduced electron-transfer reactions with the intention of developing highly efficient and selective photoreactions.

This paper deals with the ($4\pi + 2\sigma$) photocycloaddition between 9,10-dicyanoanthracene (DCA) and 1,2-diarylcyclopropanes and the DCA-sensitized photoisomerization of 1,2-diarylcyclopropanes.[3,4] The effects of additives and solvents on these photoreactions have been studied and their mechanistic features are discussed.

Results and Discussion

($4\pi + 2\sigma$) Photocycloaddition between DCA and 1,2-Diarylcyclopropanes. Irradiation of a degassed acetonitrile solution containing DCA and *trans*-1,2-bis(4-methoxyphenyl)cyclopropane (**1a**) with a 500-W high-pressure mercury lamp through an aqueous $CuSO_4$–NH_3 filter solution (≥400 nm) for 50–70 h gave the ($4\pi + 2\sigma$) cycloadducts **3a** and **4a** in 85% yield.[5] The photoreaction

Scheme I[a]

$$A + D \xrightarrow{h\nu} [A^{\delta-}D^{\delta+}] \longrightarrow [A^{-\cdot}\cdots D^{+\cdot}]$$

Exciplex — Radical ion pair

$$[A^{-\cdot}\cdots D^{+\cdot}] \xrightarrow{\text{Back-electron transfer}} A + D$$

$$[A^{-\cdot}\cdots D^{+\cdot}] \xrightarrow{\text{Dissociation}} A^{-\cdot} + D^{+\cdot}$$

$$[A^{-\cdot}\cdots D^{+\cdot}] + X \longrightarrow [A\cdots X]^{-\cdot} + D^{+\cdot}$$

$$[A^{-\cdot}\cdots D^{+\cdot}] + Y \longrightarrow A^{-\cdot} + [D\cdots Y]^{+\cdot}$$

$$[A^{-\cdot}\cdots D^{+\cdot}] + M^+Z^- \longrightarrow [A^{-\cdot}\cdots M^+] + [D^{+\cdot}\cdots Z^-]$$

[a] A, electron acceptor; D, electron donor; X, Y, M^+Z^-, additives.

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