with a reaction time of 30 min at −40° and overnight at −78°. Addition of 95% ethanol (15 ml) and work-up as above gave 2.13 g (99%) of crude benzyl sulfoxide, mp 115–120°. The crude product was free of benzyl sulfide and benzyl sulfone by nmr analysis and when the solid was washed with some hexane gave 1.88 g (88%) of pure benzyl sulfoxide: mp 133–134° (lit.[11] mp 135–136°); nmr ($CDCl_3$) δ 7.34 (s, 10, aromatic H's), 3.87 (s, 4, $-CH_2-$). The nmr spectrum was identical with that of an authentic sample.

Phenyl Sulfoxide.—Reaction of phenyl sulfide (1.0 g, 5.4 mmol) and sulfuryl chloride (0.80 g, 5.9 mmol) in CH_2Cl_2 (9 ml) at −30 to −40° for 90 min produced a yellow precipitate, hydrolysis of which, with 95% ethanol (10 ml) and usual work-up, gave 1.04 g (95%) of crude phenyl sulfoxide, mp 63–67°. The crude material was washed with a small amount of hexane and provided 0.57 g (53%) of pure phenyl sulfoxide: mp 68–70° (lit.[11] mp 69–71°); ir ($CHCl_3$) 1033 cm^{-1} (>S=O) [lit.[11] 1033 cm^{-1} (>S=O)].

Phenyl Methyl Sulfoxide.—Thioanisole (1.0 g, 8.1 mmol) in CH_2Cl_2 (1 ml) and sulfuryl chloride (1.09 g, 8.0 mmol) in CH_2Cl_2 (10 ml) were mixed and kept at −70° for 2 hr. Hydrolysis of the resulting yellow solution with 95% ethanol (15 ml) followed by the usual work-up gave 1.09 g (96%) of phenyl methyl sulfoxide: mp 29–30° (lit.[11] mp 29–30°); ir (CCl_4) 1050 cm^{-1} (>S=O) [lit.[11] 1050 cm^{-1} (>S=O)]; nmr ($CDCl_3$) δ 7.70–7.33 (m, 5, aromatic H's), 2.73 (s, 3, $-SOCH_3$). Nmr analysis showed that the product was free of thioanisole and phenyl methyl sulfone.

Ethyl *n*-Octadecyl Sulfoxide.—Employing the general oxidation procedure, ethyl *n*-octadecyl sulfide (603 mg, 1.92 mmol) and sulfuryl chloride in CH_2Cl_2 (15 ml) were allowed to react at −60° for 24 hr. The reaction mixture was treated with 95% ethanol (10 ml) and standard work-up gave 0.50 g (80%) of ethyl *n*-octadecyl sulfoxide, mp 75–76° (dried by azeotropic distillation of H_2O with benzene), ir ($CHCl_3$) 1010 cm^{-1} (>S=O). An analytical sample, mp 78.5–79.5°, was prepared by recrystallization from ether and dried over P_2O_5 at 65° for 2 days. The sulfoxide is hygroscopic.

Anal. Calcd for $C_{20}H_{42}OS$: C, 72.66; H, 12.81. Found: C, 72.88; H, 12.79.

Ethyl *n*-Octadecyl Sulfone.—A mixture of *m*-chloroperbenzoic acid (0.80 g, 4.6 mmol) and ethyl *n*-octadecyl sulfoxide prepared from ethyl *n*-octadecyl sulfide (1.21 g, 3.8 mmol) and sulfuryl chloride (0.59 g, 4.4 mmol) was stirred in $CHCl_3$ (5 ml) at room temperature for 1 day. After the reaction mixture was filtered and the solvent removed from the filtrate, the residual oil was chromatographed on alumina (A-540) and upon elution with benzene gave 1.2 g (90%) of ethyl *n*-octadecyl sulfone, mp 85–86°, ir ($CHCl_3$) 1300 and 1130 cm^{-1} (>SO_2).

Anal. Calcd for $C_{20}H_{42}O_2S$: C, 69.30; H, 12.22. Found: C, 69.11; H, 12.18.

Tetramethylene Sulfoxide.—Sulfuryl chloride (15.8 g, 0.117 mol) in CH_2Cl_2 (5 ml) was added to a solution of tetramethylene sulfide (10 g, 0.114 mol) in CH_2Cl_2 (20 ml) and the mixture was allowed to stand at −70° for 3 days. The reaction mixture was treated with 80% ethanol (20 ml) and allowed to warm up to room temperature. The aqueous solution after neutralization of the reaction mixture with potassium carbonate was concentrated prior to extraction with $CHCl_3$. After the $CHCl_3$ extract was dried and the solvent was removed, distillation of the residue (7.1 g) gave 6.0 g (50%) of tetramethylene sulfoxide, bp 48–53° (0.15–0.20 Torr). The product was identified by comparison of nmr and ir spectra with those of an authentic sample.

Low-Temperature Nmr Measurements.—The nmr spectra of 2,3-dihydro-1-benzothiepin,[28] 1-methoxy-2,3-dihydro-1-benzothiepinium fluoroborate (**12**), and the intermediate from the reaction of sulfuryl chloride and 2,3-dihydro-1-benzothiepin were obtained at −50° on a Varian HA-60 nmr spectrometer equipped with a variable temperature probe. The chemical shifts were measured using TMS as an internal standard.

A 0.2-ml aliquot of a 2.5 *M* 2,3-dihydro-1-benzothiepin (**10**)[28] stock solution in $CDCl_3$ was mixed with 0.1 ml of $CDCl_3$ and cooled to −50°. To this solution was added a 0.2-ml aliquot of 2.5 *M* sulfuryl chloride in $CDCl_3$ mixed with 0.1 ml of $CDCl_3$ precooled to −50°. The resulting yellow solution was shaken vigorously with cooling and placed in the nmr probe at −50°.

The chemical shifts for these compounds are summarized in Table II.

Registry No.—**2**, 41947-71-1; **4**, 21609-60-9; **5**, 41947-73-3; **6**, 41947-74-4; **8**, 26524-92-5; **8** 2,4-dinitrophenylhydrazone, 41947-76-6; **10**, 21609-62-1; **11**, 41947-78-8; **12**, 41947-79-9; **14**, 41947-80-2; 3,4-dihydro-1-benzothiepin-5(2*H*)-one, 21609-70-1; 5-hydroxy-2,3,4,5-tetrahydro-1-benzothiepin, 20500-27-0; ethyl *n*-octadecyl sulfoxide, 41947-83-5; ethyl *n*-octadecyl sulfide, 41947-84-6; sulfuryl chloride, 7791-25-5; ethyl *n*-octadecyl sulfone, 41947-85-7; *m*-chloroperbenzoic acid, 937-14-4.

Reactions of Thiopyrylium Cations with Amines

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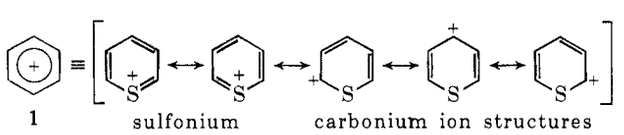
The reactions of parent thiopyrylium cation (**1**) with various primary amines under mild conditions give ring-opening products, 5- (alkyl- or arylamino-) *N*-alkyl- or -aryl-2,4-pentadienylideniminium salts (**4**) in good yield. Secondary amines also react with **1** to afford the same type of products. No reaction of 2,4,6-triphenylthiopyrylium cation with aromatic amines took place.

As recently reported[1] SCF MO calculations show that the positive charge in thiopyrylium cation (**1**) is largest at the sulfur atom (+0.854), but still considerable at the carbon atoms of the α and the γ positions (+0.080 and +0.039, respectively), indicating that **1** can be expressed as a resonance hybrid of sulfonium structures (Kekulé structures) and carbonium ion structures.



Little work has been carried out on the reaction of the parent thiopyrylium cation (**1**) with nucleophilic reagents. Price, *et al.*,[2] reported that the reaction of **1** and 2,4,6-triphenylthiopyrylium cation (**2**) with phenyllithium gave thiabenzene derivatives by nucleophilic attack at the sulfur atom. In the case of phosphopyridinium salt, water also reacts preferentially at the heteroatom, rather than carbon.[3] In contrast, we found[4] that the reaction of **2** with a variety of active methylene compounds in the presence of a base yielded substituted benzenes by nucleophilic attack of the carbanions at the α carbon atom. Attempts to isolate

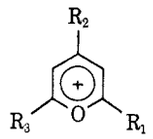
(1) Z. Yoshida, H. Sugimoto, and S. Yoneda, *Tetrahedron*, **28**, 5873 (1972).

(2) (a) M. Polk, M. Siskin, and C. C. Price, *J. Amer. Chem. Soc.*, **91**, 1206 (1969); (b) G. Suld and C. C. Price, *ibid.*, **83**, 1770 (1961); (c) *ibid.*, **84**, 2090 (1962); (d) *ibid.*, **84**, 2094 (1962).

(3) C. C. Price, T. Parasaran, and T. V. Lakshminarayan, *J. Amer. Chem. Soc.*, **88**, 1034 (1966).

(4) Z. Yoshida, S. Yoneda, H. Sugimoto, and T. Sugimoto, *Tetrahedron*, **27**, 6083 (1971).

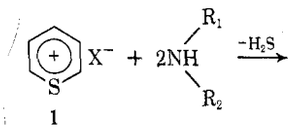
the product in a similar reaction of **1** with active methylene compounds were unsuccessful. A substituted pyrylium cation (**3**) where R_1, R_2, and R_3 denote sub-



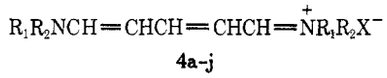
3

stituents, reacts with ammonia to give pyridine derivatives[5] while the reaction with primary amines affords pyridinium salts.[6] Generally, **3** does not react with secondary amines. This paper deals with the reactions of **1** and **2** toward a variety of amines.

When **1** was treated with aromatic amines in acetonitrile under gentle warming or aliphatic amines in methanol with cooling, the reaction mixture immediately became red or yellow, respectively, with evolution of hydrogen sulfide. The product (**4a**) obtained by the



1



4a-j

reaction of thiopyrylium fluoroborate with aniline showed a uv absorption maximum at 486 nm (log ϵ 4.85) in methanol, suggesting that the product is a highly conjugated one. Elemental analysis ($C_{17}H_{17}N_2BF_4$) indicated that 1 mol of the cation reacted with 2 mol of aniline and hydrogen sulfide was eliminated. The nmr spectrum of **4a** in DMSO-d_6 showed two triplets centered at δ 6.43 (2 H) and 8.03 (1 H) and a broad doublet at δ 8.65 (2 H) besides the phenyl proton signal (δ 7.5, 10 H). From comparison of these spectral data with those of the authentic sample prepared by another procedure,[7] the product **4a** was identified as 5-(anilino)-*N*-phenyl-2,4-pentadienylideniminium fluoroborate. The results of the reactions shown below are summarized in Table I. As is seen in Table I, secondary amines as well as primary amines reacted with **1** to afford cyanine-type products (**4**), except *p*-nitroaniline and sulfanilic acid, which did not react with **1** even under vigorous conditions. It is evident that the reactivity of amines with **1** depends upon their basicity. In no cases were pyridinium salts obtained.

TABLE I

RESULTS OF THE REACTION OF **1** WITH AMINES (R_1R_2NH)[a]

4	R_1	R_2	X	Yield, %	Mp (dec), °C
a	H	Ph	BF_4	90	157–169
b	H	Ph	ClO_4	71	190–192
c	H	*p*-CH_3Ph	BF_4	63	138–140
d	H	*p*-CH_3OPh	BF_4	62	165–166
e	H	*p*-HOPh	BF_4	64	180
f	H	*p*-ClPh	BF_4	54	167–170
g	Me	Ph	BF_4	32	84–86
h	H	Me	BF_4	66	mp 79
i	Me	Me	BF_4	65	mp 128
j	Morpholino		BF_4	52	mp 184–186

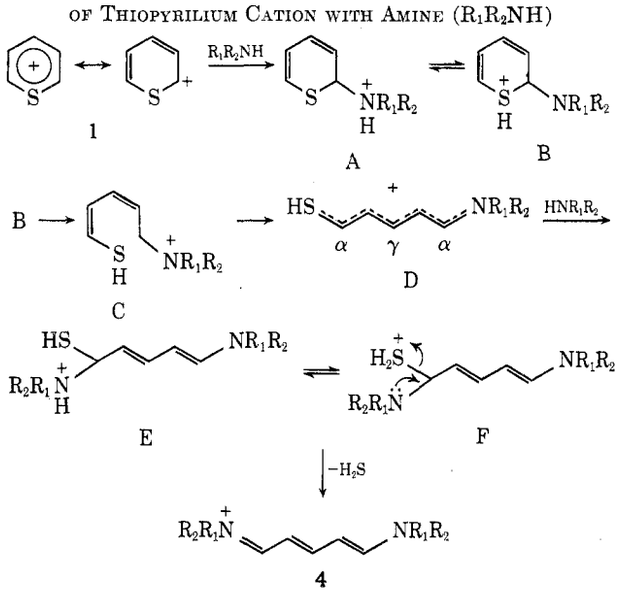
[a] Satisfactory analytical values (±0.4%) for C, H, and N were reported for all compounds except **4d** (calcd, C, 57.55; found, C, 56.88): Ed.

Each product (**4**) has three double bonds and the stereochemistry was ascertained from the spectral data. For example, in the spectrum of **4i**, two kinds of equivalent protons (α and β protons) revealed a symmetrical structure and all the J_{H-H} values of 12 Hz indicated an all-trans configuration. Further evidence for the trans configuration was obtained by the out-of-plane bending vibrations of vinyl C–H bonds which were observed at 859 and 869 cm^{-1}, the latter being shoulder, for **4i**. Similar spectral data for the all-trans configuration of 2,8-dimethylnonatrienyl cation have been reported by Sorensen.[8]

The formation of the ring-opening product **4** might be explained by the reaction course shown in Scheme I.

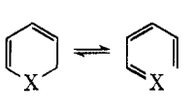
SCHEME I

A PROBABLE MECHANISM OF THE REACTION OF THIOPYRILIUM CATION WITH AMINE (R_1R_2NH)



The initial nucleophilic attack by amine takes place at the α carbon atom, in accord with the reaction indices obtained by the HMO method.[4]

Recently, attention has been focused on the ring opening of α-pyrans or α-thiopyrans to dienones or dienothiones, respectively, or on their equilibrium as shown below. For α-pyran derivatives, Marvell and



collaborators[9] observed that the rate constant for the ring opening to *cis*-β-ionone (a cis dienone) from 1-oxa-2,5,5,8a-tetramethyl-5,6,7,8-tetrahydronaphthalene (as a model α-pyran) is around one-tenth as large as that for the reverse reaction. Furthermore, Becker and Kolk have found that the ring opening of 2,2-diphenyl-

(5) (a) A. Bayer and J. Piccard, *Justus Liebigs Ann. Chem.*, **384**, 208 (1911); (b) *ibid.*, **407**, 332 (1914); (c) A. T. Balaban, *Tetrahedron, Suppl.*, **7**, 1 (1966).

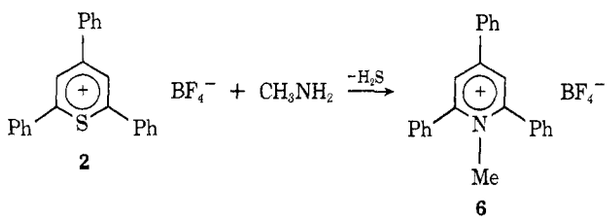
(6) C. Toma and A. T. Balaban, *Tetrahedron, Suppl.*, **7**, 9 (1966).

(7) T. Zincke, *Justus Liebigs Ann. Chem.*, **330**, 361 (1903).

(8) T. S. Sorensen, *J. Amer. Chem. Soc.*, **87**, 5075 (1965).

(9) E. N. Marvell, T. Chadwick, G. Caple, T. Gosink, and G. Zimmer, *J. Org. Chem.*, **37**, 2992 (1972).

2*H*-benzothiopyran is affected only by a photochemical process.[10] In both cases the molecules in question have no polar substituent. However, in the ring opening of the initial adduct (A) of **1** with amines, the ammonium group permits an ionic path rather than a retroelectrocyclic process. This is experimentally suggested from the fact that the reaction proceeds very rapidly and even in the dark. In view of these arguments, the ring opening of the adduct is considered to occur *via* the sulfonium type isomer (B), in which the driving force of the ring opening should come from the electron-withdrawing sulfonium group. The ring opening intermediate might, then, be isomerized from the cis form (C) to the trans form (D). The intermolecular attack of amine at the α carbon adjacent to the sulfur atom followed by the elimination of hydrogen sulfide gives the final cyanine-type product. A marked contrast was found in the reaction of **2** with methylamine, which gives exclusively pyridinium salt and no ring opening product.



The bulky substituents (phenyl groups) may prevent isomerization of the ring opening intermediate for **2**. In addition to this, since the positive charge can delocalize on the phenyl groups, the Coulomb repulsion in the nontrans configuration is considered to be sufficiently lowered.

It is established that **3** ($R_1 = R_2 = R_3 = Ph$) reacts both with aromatic and aliphatic primary amines; on the other hand, **2** has been found to react only with aliphatic amines. These results indicate that **2** is less reactive toward nucleophilic reagents than **3** ($R_1 = R_2 = R_3 = Ph$). It is generally accepted that the electron-releasing conjugative effect of oxygen is larger than that of sulfur. For instance, the rate constant of the hydrolysis of α-chloromethyl ether was reported to be about 1600 times as large as that of α-chloromethyl sulfide.[11] If the nature of the heteroatom plays a major role in the stability and reactivity of **2** and **3** ($R_1 = R_2 = R_3 = Ph$), then the pyrylium cation should be more stable and less reactive toward nucleophiles than thiopyrylium cation, but this is not the case. These differences must be ascribed to the double bond character of the carbon–heteroatom bond, or, in other words, delocalization of the positive charge. The contribution of carbonium ion structure to a resonance hybrid of pyrylium cation is larger than that of thiopyrylium cation,[1] and this difference may be responsible for the difference in the reactivities of both cations.

Experimental Section

Ultraviolet spectra were run on a Hitachi EPS-3T recording photometer. Infrared spectra were recorded on a Hitachi grating infrared spectrophotometer. Nmr spectra were determined on a Jeolco C-60H with TMS as an internal standard. Melting points were not corrected.

(10) R. S. Becker, and J. Kolk, *J. Phys. Chem.*, **72**, 997 (1968).

(11) C. C. Price and S. Oae, "Sulfur Bonding," Ronald Press, New York, N. Y., 1962, Chapter 2.

Thiopyrylium Fluoroborate (1).—**1** was prepared according to Degani, Fochi, and Vincenzi[12] and purified by reprecipitation from acetonitrile–ether.

2,4,6-Triphenylthiopyrylium Fluoroborate (2).—**2** was prepared by the method of Wizinger and Ultrich.[13]

5-(Substituted amino)-N-Substituted 2,4-Pentadienylideniminium Salts (4a–j).—These were prepared by the following procedure. The yields and elemental analyses are listed in Table I.

General Procedure.—To a solution of 5.0 mmol of **1** in 10 ml of acetonitrile for arylamines or methanol for alkylamines was added a solution of 20 mmol of arylamine in 10 ml of acetonitrile at 40–50° or a solution of 20 mmol of alkylamine in 10 ml of methanol at ice-cooled temperature. The reaction mixture was immediately colored red or yellow and the evolution of hydrogen sulfide was observed. After stirring was continued for about 1 hr, the dark-red colored reaction mixture was filtered and an excess of ether was added to the filtrate. The precipitate was filtered and recrystallized from methanol to give the product salts. The products were shown to be 5-(substituted amino)-N-substituted 2,4-pentadienyldienylideniminium fluoroborate or perchlorate by their elemental analyses and spectral data. Some of them were identified by the spectral data of the authentic sample.[7,14]

5-(Phenylamino)-*N*-phenyl-2,4-pentadienylideniminium fluoroborate (4a) had mp 157–159° dec; λ_{max} (MeOH) 486 nm (log ϵ 4.85); ir (KBr) 1625, 1610, 1545, 1325, 1175, 1015, 880, 855, 765, and 685 cm^{-1}; nmr (DMSO-d_6) 8.65 (d, 2 H, the protons at the α positions of the pentamethine system), 8.03 (t, 1 H, the proton at the γ position), 7.5 (m, 10 H, phenyl protons), and 6.43 (t, 2 H, the protons at the β positions).

5-(Phenylamino)-*N*-phenyl-2,4-pentadienylideniminium perchlorate (4b) had mp 190–192° dec. The electronic and nmr spectra were entirely the same as those of **4a**. The ir spectrum is also identical with that of **4a** except for the absorption due to the counteranion.

5-(*p*-Toluidino)-*N*-(*p*-tolyl)-2,4-pentadienylideniminium fluoroborate (4c) had mp 138–140° dec; λ_{max} (EtOH) 490 nm (log ϵ 4.91) [lit.[8] λ_{max} (MeOH) 489 nm (log ϵ 5.00)]; ir (KBr) 1625, 1560, 1505, 1330, 875, 863, and 816 cm^{-1}.

5-(*p*-Anisidino)-*N*-(*p*-anisyl)-2,4-pentadienylideniminium fluoroborate (4d) had mp 165–166° dec; λ_{max} (EtOH) 498 nm (log ϵ 4.86) [lit.[8] λ_{max} (MeOH) 498 nm (log ϵ 4.87)]; ir (KBr) 1615, 1560, 1505, 880, 865, and 825 cm^{-1}; nmr (DMSO-d_6) δ 8.3 (d, 2 H, α protons), 7.4 (t, 1 H, γ proton), 7.2 (m, phenyl protons), and 3.8 (s, 6 H, methyl protons). The protons at the β position were not observed, probably because of being included in the aromatic proton region.

5-(*p*-Chloroanilino)-*N*-(*p*-chlorophenyl)-2,4-pentadienylideniminium fluoroborate (4f) had mp 167–170° dec; λ_{max} (EtOH) 492 nm (log ϵ 5.05) [lit.[8] λ_{max} (MeOH) 492 nm (log ϵ 5.13)]; ir (KBr) 1625, 1610, 1565, 1495, 1330, 880, 760, 825, and 730 cm^{-1}; nmr (DMSO-d_6) δ-8.3 (d, 2 H, α protons), 7.4 (m, phenyl protons), and 6.3 (t, 2 H, β protons).

5-(*N*,*N*-Methylphenylanilino)-*N*′,*N*′-methylphenyl-2,4-pentadienylideniminium fluoroborate (4g) had mp 84–86°; dec; λ_{max} (EtOH) 449 nm (log ϵ 4.88); ir (KBr) 1603, 1530, 1375, 886, 867, 800, 764, and 696 cm^{-1}; nmr (DMSO d_6) δ 8.4 (d, 2 H, α protons), 7.5 (m, phenyl protons), 6.5 (t, 2 H β protons), 3.6 (s, 3 H, methyl protons), and 3.8 (s, 3 H, methyl protons).[15]

5-(Methylamino)-*N*-methyl-2,4-pentadienylideniminium fluoroborate (4h) had mp 79°; ir (KBr) 1600, 1550, 1414, 1350, 1265, 865, 765, and 682 cm^{-1}; nmr (DMSO-d_6) δ 7.75 (d, 2 H, α protons), 7.50 (s, 1 H, γ proton), 5.70 (t, 2 H, β protons), and 3.00 (s, 6 H, methyl protons).

5-(Dimethylamino)-*N*-dimethyl-2,4-pentadienylideniminium fluoroborate (4i) had mp 128°; ir (KBr) 1603, 1560, 1393, 1180, 869, and 859 cm^{-1}; nmr (DMSO-d_6) δ 7.70 (d, 2 H, α protons), 7.44 (t, 1 H, γ proton), 5.91 (t, 2 H, β protons), 3.26 (s, 6 H, methyl protons), and 3.09 (s, 6 H, methyl protons).[15]

(12) I. Degani, R. Fochi, and C. Vincenzi, *Gazz. Chim. Ital.*, **94**, 203 (1964).

(13) P. Wizinger and P. Ultrich, *Helv. Chim. Acta*, **39**, 207 (1956).

(14) (a) A. T. Balaban, *Tetrahedron, Suppl.*, **7**, 1 (1966); (b) C. Toma and A. T. Balaban, *ibid.*, **7**, 9 (1966); (c) B. E. Grigor'eva, I. K. Ginste, and A. P. Severina, *Zh. Obshch. Khim.*, **26**, 3447 (1956).

(15) That the nmr signals for the methyl groups of **4g** and **4i** appear with differing chemical shifts might be explained as follows. Fluoroborate anion poorly solvated with DMSO-d_6 is probably not located at the central position of the cyanine-type cation (**4g** and **4i**) in DMSO-d_6 solution. As a result, the small difference (around 0.17–0.20 ppm) in the chemical shift for methyl protons could arise from the effect of the electric field of BF_4^-.

5-Morpholino-*N*,*N*-γ-oxapentamethylene-2,4-pentadienylideniminium fluoroborate (4j) had mp 184–186°; ir (KBr) 1560, 1435, 1295, 1240, 1200, 855, and 805 cm^{-1}; nmr (DMSO-d_6) δ 7.85 (d, 2 H, α protons), 7.67 (t, 1 H, γ proton), 6.10 (t, 2 H, β protons), and 3.7 (b, 16 H, ethylene).

Reaction of 2 with Methylamine.—To an ice-cooled solution of 0.82 g (2.0 mmol) of **2** in 10 ml of methanol was added a solution of 0.62 g (20 mmol) of methylamine in 5.0 ml of methanol. After addition of amine the reaction mixture was refluxed for about 1 hr. The hot reaction mixture was rapidly filtered and the filtrate was allowed to stand at room temperature to give 0.08 g of **6** as white needles: mp 215–216°; yield 10%; nmr (DMSO-d_6) δ 8.44 (s, 2 H, β protons), 7.50 (m, 15 H, phenyl), and 3.70 (s, 3 H), methyl protons). The product **6** was determined to be *N*-methyl-2,4,6-triphenylpyridinium fluoroborate by mixture melting point with an authentic sample.[16]

Registry No.—1 BF_4, 41656-11-5; 1 ClO_4, 2567-16-0; **2**, 1582-78-1; **4a**, 41656-13-7; **4b**, 41737-40-0; **4c**, 41656-14-8; **4d**, 41724-27-0; **4e**, 41656-15-9; **4f**, 41656-16-0; **4g**, 41656-17-1; **4h**, 41656-18-2; **4i**, 41656-19-3; **4j**, 41656-20-6; **6**, 2355-56-8; aniline, 62-53-3; *p*-toluidine, 106-49-0; *p*-anisidine, 104-94-9; *p*-hydroxyaniline, 123-30-8; *p*-chloroaniline, 106-47-8; *N*-methylaniline, 100-61-8; methylamine, 74-89-5; dimethylamine, 124-40-3; morpholine, 110-91-8.

(16) A. Baeyer and J. Pickard, *Justus Liebigs Ann. Chem.*, **384**, 208 (1911).

Cyanide-Induced Dimerization of (4-Pyridyl)pyridinium Chloride. Synthesis of 4,4′-Bipyridine and (4-Pyridyl)viologen Salts[1a]

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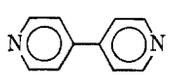
Warming solutions of the title compound (**2**) and sodium cyanide produces 1,1′-di(4-pyridyl)-1,1′-dihydro-4,4′-bipyridine (**3**). After oxidizing **3** in aqueous acid, the resulting solution is heated to afford 4,4′-bipyridine (**1**). This sequence provides a convenient procedure for the synthesis of **1** without simultaneous formation of isomeric side products. The formation of stable (4-pyridyl)viologen cation radicals (**7**) and salts (**6**) from oxidation of **3** is described.

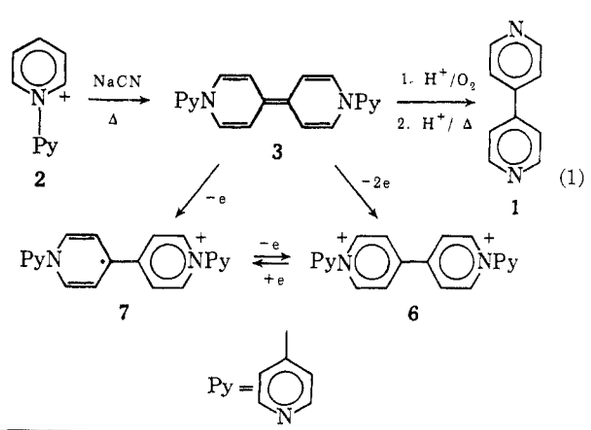
In recent years 4,4′-bipyridine (**1**) has found increasing importance in both organic and organometallic



1

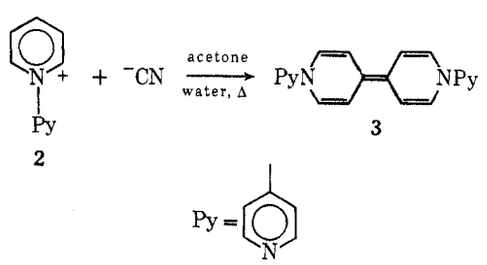
chemistry.[2-4] The synthesis of **1** is usually accomplished by the dimerization of pyridine by metals in inert solvents.[5a] Unfortunately, this procedure suffers from either low yields[5b] or formation of 2,4′- and 2,2′-bipyridine as side products.[5c] In our studies of the cyanide ion induced dimerization of pyridinium salts,[6] we have developed a new, convenient synthesis of **1** which avoids the problem of isomeric side products.

When 1-(4-pyridyl)pyridinium chloride (**2**) and sodium cyanide were heated in aqueous acetone (eq 1),

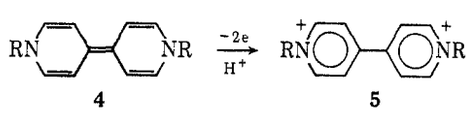


(1)

a 53% yield of 1,1′-di(4-pyridyl)-1,1′-dihydro-$\Delta^{4,4'}$-bipyridine (**3**) was obtained. Previous work[7] had



shown that related dihydrobipyridines (**4**) are readily oxidized to 4,4′-bipyridinium (viologen) salts (**5**) in



R = alkyl, Ph

acidic solution (*vide infra*). Since it is known that acidic solutions of **2** are susceptible to hydrolysis to afford 4-pyridone and pyridine,[8] it was probable that a similar reaction of (4-pyridyl)viologen (**6**) would give **1**.

(1) (a) Abstracted from the Ph.D. dissertation of R. H. Reuss, Drexel University, 1972. (b) NSF Predoctoral Fellow, 1968–1971. (c) Address all correspondence to this author at Department of Chemistry, Virginia Commonwealth University, Academic Center, Richmond, Va. 23220.

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