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Registry No.—Thianthrene, 92-85-3.

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Synthesis of 4,5-Dicyano-2-methylthio-1,3-dithiolylium Salts: A Supposedly Impossible Alkylation

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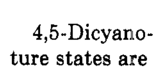
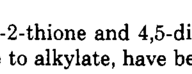
4,5-Dicyano-1,3-dithiol-2-thione and 4,5-dicarbomethoxy-1,3-dithiol-2-thione, two compounds that the literature states are impossible to alkylate, have been successfully alkylated with methyl fluorosulfonate in high yield. The alkylated salts undergo dye formation with both activated aromatic amines and methylene reagents.

Theoretical calculations and recent experimental data have shown quite conclusively that the C-2 carbon atom of a 1,3-dithiolylium cation is very electron deficient.[1,2] In our search for dye molecules that are easily reduced (reduction potential approaching zero), we prepared and measured the electrochemical reduction potentials of several 1,3-dithiolylium dyes. For this class of dyes (Table I) we found a range of reduction potentials of −0.9 to −0.5 V; however, a range of −0.5 to −0.2 V was desired. We therefore anticipated that placing electronegative groups such as cyano or carboxyl at the 4 and 5 positions of the dithiolylium ring would shift the reduction potentials of the corresponding dyes toward 0 V. A search of the literature quickly revealed that, although compounds such as 1 or 2 are easily synthesized, the alkylated derivatives 3 and 4, which would be derived from 1 and 2 and



1, R = $-CO_2CH_3$
2, R = CN-



3, R = $-CO_2CH_3$
4, R = CN-

would be necessary for dye formation, were by normal methods "impossible to prepare by alkylation".[2] Our problem thus became the synthesis of dithiolylium salts 3 and 4.

We found that thiones 1 and 2 are alkylated rapidly and exothermally by methyl fluorosulfonate.[3] Thione 1 reacts readily in refluxing methylene chloride. However, thione 2 requires elevated temperatures for alkylation to proceed; in fact, alkylation occurs readily only in refluxing methyl fluorosulfonate (92 °C). The reaction becomes exothermic at about 90 °C and gives 4 in 96% yield within a few minutes.

4,5-Dicyano-2-methylthio-1,3-dithiolylium fluorosulfonate (4) and to a lesser extent the diester 3 react readily with nucleophilic reagents. The salts appear hygroscopic but are in fact reacting with atmosphere moisture. The 2-methylthio group is rapidly hydrolyzed, yielding 4,5-cyano- (or carbomethoxy) 1,3-dithiol-2-ones.[4] The hydrolysis of 4 can be monitored by either IR or NMR spectroscopy. The increase in absorption due to a carbonyl group at 1660 cm^{-1} in a sample of 4 in KBr is virtually complete in 30 min. Displacement of the $-SCH_3$ group in 4 by D_2O is complete within 5 min in acetonitrile/D_2O (followed by the disappearance of $^+SCH_3$ absorption and the appearance of CH_3SD in NMR).

Reactions of methylthio salts 3 and 4 with active methylene reagents yield the dithiolylium dyes shown in Table I. Dye formation proceeds readily in acetic anhydride (minimizes hydrolysis) without the necessity of added base. In fact, addition of external nitrogen bases results in either the formation of a charge-transfer complex between the dye and base (R_3N) or an addition compound (with RNH_2).[5] Apparently, the dyes (Table I) are extremely electron deficient (as indicated by their reduction potentials) and are active as electron acceptors with the nitrogen bases acting as the donors.

As expected, the dithiolylium dyes with electronegative groups in the 4 and 5 positions are more easily reduced electrochemically than the unsubstituted dyes. They exhibited reduction potentials in a range of −0.2 to −0.5 V. The increased (less negative) reduction potential was accompanied generally by a hyposochromic shift of the long-wavelength absorption maxima and a decrease in extinction coefficient.[6] It is unclear at this time whether this is a general phenomenon or a fortuitous correlation.

Experimental Section

All melting points are uncorrected. IR spectra were obtained with a Perkin-Elmer 137 spectrophotometer and NMR spectra with a Varian T-60 spectrometer using Me_4Si as an internal standard. UV

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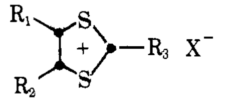
Table I. Electrochemical Reduction Potential of 1,3-Dithiolylium Dyes



Registry no.	R_1	R_2	R_3	X^-	$-\epsilon^0$, V[a]	λ_{max}[b]	mp, °C[c]	%[d]
64457-14-3	H	H	9-Julolidinyl	BF_4	0.76	554	225 (dec)	96
64457-16-5	C_6H_5	H	9-Julolidinyl	BF_4	0.73	568	234	90
64457-18-7	C_6H_5	C_6H_5	9-Julolidinyl	BF_4	0.71	567	214	55
64457-20-1	CO_2CH_3	CO_2CH_3	9-Julolidinyl	FSO_3	0.51	552	165 (dec)	82
64457-22-3	CN	CN	9-Julolidinyl	BF_4	0.36	547	208 (dec)	78
64457-24-5	H	H	3-(1,2,5-Trimethylpyrrole)	BF_4	0.94	423	264 (dec)	97
64457-26-7	H	H	2-(2,4-Dimethyl-3-ethylpyrrole)	BF_4	0.91	446	241	83
64457-43-8	C_6H_5	C_6H_5	α-(4-Methylene-2,6-diphenylpyran)	ClO_4	0.55	555	248	68
64457-41-6	CN	CN	*p*-(*N*,*N*-Dimethylaniline)	FSO_3		540	142 (dec)	76
64457-39-2	CN	CN	3-(1,2-Dimethylindole)	FSO_3		443	251 (dec)	76
64457-37-0	CN	CN	α-(4-Methylene-2,6-diphenylpyran)	ClO_4	0.23	493	245 (dec)	78
64457-35-8	CN	CN	α-(2-Methylene-4-phenyl-1,3-dithiole)	ClO_4	0.24	492	238 (dec)	86
64457-49-5	C_6H_5	H	α-(2-Methylene-4-phenyl-1,3-dithiole)	ClO_4		520	242	75
64457-33-6	H	H	3-(1,2-Dimethylindole)	BF_4		436	>300	96

[a] Measured in 2×10^{-4} M CH_3CN using cyclic voltammetry with 0.1 M tetra-*n*-butylammonium tetrafluoroborate as supporting electrolyte at a platinum electrode and SCE as reference electrode. Scan rate, 0.1 V/s. [b] Measured in acetonitrile unless otherwise noted. [c] Satisfactory combustion and spectral analyses were obtained for all new compounds. [d] Yields are not optimized.

spectra were taken with a Cary 17 spectrophotometer.

4,5-Dicyano-2-methylthio-1,3-dithiolylium Fluorosulfonate (4). 4,5-Dicyano-1,3-dithiol-2-thione[7] (1.8 g, 0.01 mol) and methyl fluorosulfonate[3] (10 mL) were slowly heated to reflux on a steam bath with stirring. At about 90 °C an exothermic reaction ensued and the solution refluxed gently. After 10 min, the mixture was cooled to ambient temperature, diluted with ethyl acetate (25 mL), and filtered. The pale-yellow solid was washed quickly with ethyl acetate and dried in a dry nitrogen atmosphere, giving 4,5-dicyano-2-methylthio-1,3-dithiolylium fluorosulfonate (2.8 g, 96%): NMR (CD_3CN) δ 3.0 (s), addition of D_2O caused the peak at 3.0 to disappear and a singlet to appear at δ 2.4 (CH_3SD); IR (KBr) 2220 (w, $C{\equiv}N$), 1307, 1282 (FSO_3), 1081, 1020, and 740 cm^{-1}. Exposure of the KBr pellet to air caused a peak at 1660 cm^{-1} to appear rapidly.[8]

4,5-Dicarbomethoxy-2-methylthio-1,3-dithiolylium Fluorosulfonate (3). 4,5-Dicarbomethoxy-1,3-dithiol-2-thione (1)[5] (2.5 g, 0.01 mol) and methyl fluorosulfonate (1.1 g, 0.1 mol) were refluxed in methylene chloride (20 mL) for 2 h. The addition of diethyl ether (20 mL) and cooling caused yellow crystals to precipitate. Filtration and drying under nitrogen gave 3.0 g (83%) of yellow crystals: NMR (CD_3CN) δ 3.9 (s, 6 H, OCH_3), 3.1 (s, 3 H, $-SCH_3$); IR (KBr) 1724 (C=O), 1563, 1280 (FSO_3) cm^{-1}.

Anal. Calcd for $C_8H_9FO_7S_4$: C, 26.4; H, 2.5; S, 35.2. Found: C, 26.0; H, 2.1; S, 34.8.

General Method for the Synthesis of Dithiolylium Dyes (Table I). A 2-methylthio-1,3-dithiolylium salt (0.01 mol) and the appropriate aromatic amine or methylene reagent (0.01 mol) were refluxed gently for 15–20 min in acetic anhydride (15 mL). Cooling and dilution with ethyl acetate (50 mL) gave the crystalline dye. The fluorosulfonate anion was exchanged for perchlorate or tetrafluoroborate anion by dissolving the dye in the minimum amount of ethanol at reflux, adding 70% perchloric or 47% tetrafluoroboric acid (3–5 mL), and cooling to give the crystalline dye as the perchlorate or tetrafluoroborate salt.

1:1 Addition Complex of 4,5-Dicyano-2-(9-julolidinyl)-1,3-dithiolylium Fluorosulfonate with *p*-Anisidine. 4,5-Dicyano-2-(9-julolidinyl)-1,3-dithiolylium fluorosulfonate (423 mg, 1.1 mmol) and *p*-anisidine (135 mg, 1.1 mmol) were dissolved in acetonitrile (20 mL) and refluxed for 5 min. Cooling followed by filtration gave green crystals which were washed with 50% ethyl acetate–acetonitrile and air dried: yield 280 mg (51%); mp 180 °C (dec); UV–vis (CH_3CN) (log ϵ) 610 (4.66), 520 (4.15) nm; IR (KBr) 2210 ($C{\equiv}N$), 1640, 1610, 1370, 1290 cm^{-1}; NMR (F_3AcOH) δ 7.4 (m, 6 H), 4.0–3.8 (2 s, 3 H), 3.8 (m, 4 H), 3.0 (m, 4 H), 2.4 (m, 4 H).

Anal. Calcd for $C_{24}H_{23}FN_4O_4S_3$ (1:1 adduct): C, 52.7; H, 4.2; N, 10.2; S, 17.6. Found: C, 52.5; H, 4.4; N, 9.9, S, 17.4.

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Registry No.—**1**, 7396-41-0; **2**, 1005-10-3; **3**, 64457-31-4; **4**, 64508-86-7; methyl fluorosulfonate, 421-20-5; perchloric acid, 7601-90-3; tetrafluoroboric acid, 16872-11-0; 4,5-dicyano-2-(9-julolidinyl)-1,3-dithiolylium fluorosulfonate 1:1 complex with *p*-anisidine, 64457-29-0; *p*-anisidine, 104-94-9; julolidine, 479-59-4; 1,2,5-trimethylpyrrole, 930-87-0; 2,4-dimethyl-3-ethylpyrrole, 517-22-6; 4-methylene-2,6-diphenylpyran, 15899-02-2; *N*,*N*-dimethylaniline, 121-69-7; 1,2-dimethylindole, 875-79-6; 2-methylene-4-phenyl-1,3-dithiole, 64457-27-8.

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(3) **Caution:** a death has occurred due to improper handling of this reagent. See *Chem. Eng. News*, **54 (36)**, 5 (1976).
(4) Some hydrolysis of the nitriles occurs also under these conditions.
(5) A bathochromic shift of the visible absorption spectrum is noted when a tertiary amine such as *N,N*-dimethylaniline is added to the dyes. No attempt was made to isolate the complexes.
(6) Extinction coefficients for the first, fourth, and fifth dyes in Table I are 6.7, 5.8, and 3.3 × 10^4 L/mol-cm.
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(8) Due to the hygroscopic nature of **4**, satisfactory elemental analysis could not be obtained.