

of the other trimer (a liquid)⁶ suggests its structure is related to that of IV in a similar way.

(14) (a) Supported by National Science Foundation GP 7809; (b) supported by GM 12470 and a Sloan fellowship.

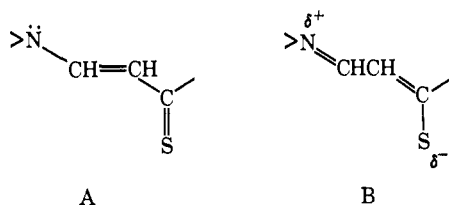
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New Synthesis of 2,5-Disubstituted Thiophenes

Sir:

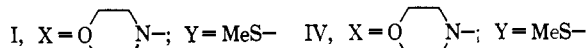
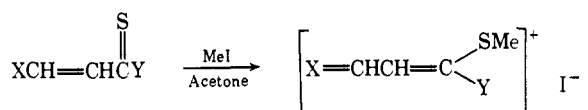
We have described recently an easy preparation of a new class of compounds, dithioacrylate esters and amides, from trithione.¹ All of the compounds described showed a prominent band or series of bands in the infrared between 1660 and 1570 cm^{-1} . This strong absorption was assigned to the polarized double bond which conjugates the electron-donating nitrogen and the electron-accepting sulfur ($A \leftrightarrow B$). If structure



B makes a significant contribution to the ground-state structure, then nucleophilic displacement reactions by sulfur would be expected.

In testing this hypothesis, a new synthesis for substituted thiophenes was discovered, which makes them readily available in two steps from trithione.

When the aminothioacrylates I, II, and III were dissolved in acetone and treated with methyl iodide, there was a rapid separation of colored crystalline



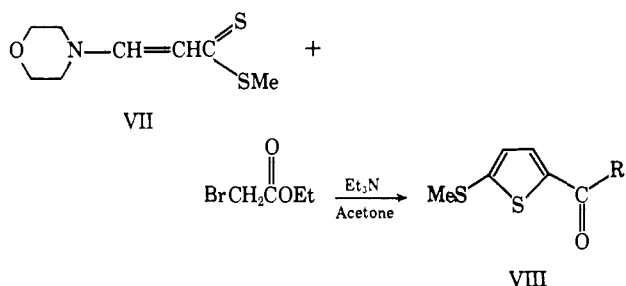
solids in high yields. These products proved to have the composition of starting material plus methyl iodide and were formulated as the thionium salts, IV, V, and VI. The structure proof for these compounds rests on the correct microanalytic result and infrared and nmr spectra.

The reaction, when extended to α -halocarbonyl compounds, led to 2,5-disubstituted thiophenes rather than the expected salt. The reaction was most simply run by dissolving the thioacrylate compound in acetone and adding excess α -halocarbonyl compound followed

(1) E. J. Smutny, W. V. Turner, E. D. Morgan, and R. Robinson, *Tetrahedron*, **23**, 3785 (1967).

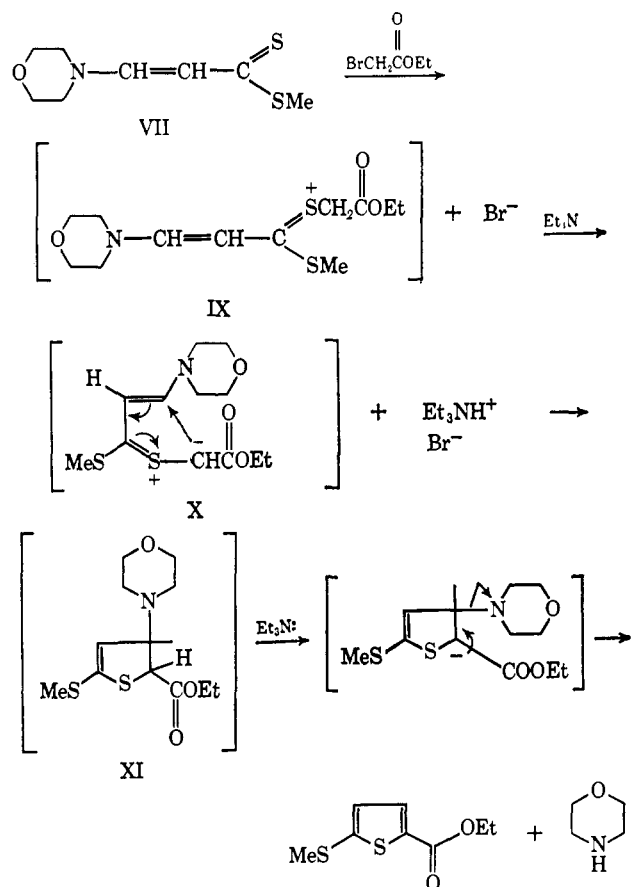
by excess triethylamine. A very simple work-up procedure gives the substituted thiophene in good to excellent yields.

For example, from methyl 3-morpholinodithioacrylate (VII) and ethyl α -bromoacetate, the 2-methylthio-5-carboethoxythiophene (VIII, R = OEt) was isolated in almost quantitative yield. Four by-products were isolated and identified: triethylammonium



hydrobromide, ethyl (α -triethylammonium)acetate bromide, ethyl (α -morpholino)acetate, and morpholine. The reaction can be run in the absence of triethylamine, but in this case the yield of substituted thiophene was substantially lower.

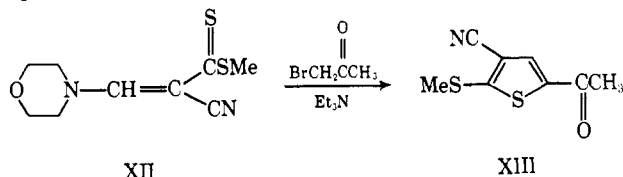
The reaction is a general one with α -halocarbonyl compounds. The thioacrylate ester most commonly used was compound VII, but is certainly not limited to it, as other esters work as well. Some of the thiophene derivatives prepared from methyl 3-morpholinodithioacrylate are: VIII, R = CH₃, 70% yield; VIII, R = C₆H₅, 70% yield; and VIII, R = C₆H₄-*p*-NO₂, 83% yield. The 3-morpholinodithioacrylamorpholide (II) reacts readily with α -bromo-*p*-nitroacetophenone to give 2-morpholino-5-*p*-nitrobenzoylthiophene (70%



yield). The anilide III does not give a thiophene product with ethyl α -bromoacetate.

The mechanism of this reaction we believe to proceed as follows: the dithioacrylate (VII) reacts with ethyl α -bromoacetate to form salt IX, but in the presence of base is immediately converted to the sulfur ylide X and triethylammonium bromide. The ylide reacts intramolecularly to compound XI, which in the presence of base loses morpholine to produce the 2,5-disubstituted thiophene. All by-products are explainable by this mechanism as is the requirement of excess ethyl α -bromoacetate and base.

The reaction was extended to the electronegatively substituted dithioacrylate ester XII. In this case, the expected 2-acetyl-4-cyano-5-thiomethylthiophene (XIII)



was isolated.

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Electrogenerated Chemiluminescence. IV. Magnetic Field Effects on the Electrogenerated Chemiluminescence of Some Anthracenes¹

Sir:

Reports have recently appeared describing a substantial group of "energy-deficient" chemiluminescent electron-transfer reactions involving the ion radicals of various aromatic hydrocarbons.^{2,3} The term "energy-

pounds of interest at a platinum electrode in DMF. The oxidation and reduction products are the ion radicals of the parent species, but the hydrocarbon cations are unstable in DMF.⁴⁻⁷ The electrogenerated chemiluminescence of the anthracene⁶ and DPA⁷ systems in DMF has been discussed recently. In addition, Table I displays the energies of the hydrocarbon triplet and first excited singlet levels. Following the reasoning previously employed,^{2,3} it is evident that the energy of the ion-radical annihilation between $WB^{\cdot+}$ (the Wurster's Blue cation) and a hydrocarbon anion radical is indeed insufficient to produce the hydrocarbon ion its first excited singlet. In contrast, this state is attainable in the reaction between $DPA^{\cdot+}$ and $DPA^{\cdot-}$. Since the emission spectrum is always identical with the fluorescence spectrum of the hydrocarbon, one must classify the hydrocarbon-WB systems as energy-deficient.

The reactants for the magnetic field experiments were produced electrolytically from DMF solutions which were about 10 mM in the organic solutes. A small ac cell containing two platinum electrodes⁶ was employed. The electrolysis source was a 10-cps square-wave generator whose output was adjusted to a value about midway between the voltage of maximum emission and the voltage for which emission was just detectable. This procedure assured that only the anion radical of the hydrocarbon and the cation radical of the most easily oxidized species in solution were formed at the electrodes. One then observes two light spikes per cycle. The emission intensity was recorded using an apparatus similar to that used in earlier experiments,³ except the photomultiplier tube was removed 90 cm from the magnet to ensure that the detection system was unaffected by the field. The detection system was tested for magnetic field dependence by positioning its components exactly in their

Table I. Electrochemical and Spectroscopic Data

Compound (A)	$E_p (A^+/A), V$ vs. sce	$E_p (A/A^-), V$ vs. sce	Lowest triplet, eV	First excited singlet, eV
WB	+0.24	(Not reduced)
Anthracene	+1.38	-1.96	1.8	3.2
DPA	+1.35	-1.89	1.6-1.8	3.0

deficient" denotes that the energy of the light produced is much greater than the enthalpy of the redox reaction for a single pair of reacting species producing ground-state products. We have examined the magnetic field dependence of the chemiluminescence intensity for two reactions in this category, *i.e.*, the reactions of the cation radical of *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (WB) with the anion radicals of anthracene and 9,10-diphenylanthracene (DPA) in *N,N*-dimethylformamide (DMF). For comparison, we have also studied the field effects on one reaction which is not energy deficient, the mutual annihilation of the anion and cation radicals of DPA.

Table I summarizes the cyclic voltammetric peak potentials for oxidation and reduction of all the com-

operating configuration and allowing a leak of room light to enter the photomultiplier tube. This system was completely unaffected by the applied field, even at the highest photomultiplier sensitivity.

The results of these experiments are summarized in Figure 1. For solutions containing WB, the emission intensity increases with the applied field. This behavior contrasts markedly with that of the solution containing only DPA, where the field had no effect upon the emission intensity. The points for Figure 1 were taken in a random order. A zero-field intensity reading was obtained after each set of three data points measured at higher field strengths. The zero-

(1) This research was supported by the Robert A. Welch Foundation and the National Science Foundation (GP 6688X).

(2) A. Weller and K. Zachariasse, *J. Chem. Phys.*, **46**, 4984 (1967).

(3) K. S. V. Santhanam and A. J. Bard, *J. Am. Chem. Soc.*, **87**, 139 (1965).

(4) M. E. Peover in "Electroanalytical Chemistry," Vol. II, A. J. Bard, Ed., Marcel Dekker, New York, N. Y., 1967, Chapter 1, and references contained therein.

(5) K. S. V. Santhanam and A. J. Bard, *J. Am. Chem. Soc.*, **88**, 2669 (1966).

(6) L. R. Faulkner and A. J. Bard, *ibid.*, **90**, 6284 (1968).

(7) S. A. Cruser and A. J. Bard, *ibid.*, in press.