spiro[4.11]hexadecan-6-ol as a white solid: mp 105–110 °C; IR (CCl_4) 2.86, 3.42, 6.80, 6.94, 7.19 (w), 7.41 (w), 9.9 μm; NMR (CCl_4) δ 1.14–1.75 (br s, 19 H), 2.05–2.18 (m, 2 H), 3.05–3.36 (m, 4 H), 3.70–3.82 (m, 1 H); mass spectrum, *m/e* (relative intensity) 274 (M^+, 31), 213 (16), 131 (19), 105 (100), 92 (16), 61 (11), 55 (12), 41 (17); exact mass calcd for $C_{14}H_{26}OS_2$ 274.14252, found 274.14206.

1,4-Dithiaspiro[4.12]heptadecan-6-one (22a) was prepared from 2.61 g (11.7 mmol) of α-(hydroxymethylene)cyclotridecanone, 4.82 g (12.0 mmol) of ethylene dithiotosylate,[37] and 3.43 g (35.0 mmol) of anhydrous potassium acetate in 100 mL of refluxing absolute methanol for 15 h by a method similar to the preparation of **5**. Chromatography on silica gel (5% ether–pentane) and recrystallization from ethanol yielded 1.12 g (33%) of **22a** as pale yellow needles: mp 71.0–72.5 °C; IR (KBr) 3.40, 5.87, 6.86, 7.16, 7.40, 7.65, 7.90, 8.58, 9.10, 9.25, 9.75, 10.51, 11.31, 13.32, 14.00, 14.62 μm; NMR (CCl_4) δ 1.18–1.36 (br s, 16 H), 1.57–1.73 (m, 2 H), 2.10–2.22 (m, 2 H), 2.73 (t, 2 H, J = 6 Hz), 3.07–3.26 (m, 4 H); mass spectrum, *m/e* (relative intensity) 286 (M^+, 17), 258 (12), 230 (17), 197 (34), 131 (100), 118 (21), 105 (15), 55 (30), 41 (44); exact mass calcd for $C_{15}H_{26}OS_2$ 286.14252, found 286.14240.

***cis*- and *trans*-6-Propenyl-1,4-dithiaspiro[4.12]heptadecan-6-ols (23a)** were prepared by a single treatment of 370 mg (1.29 mmol) of ketone **22a** with 8.3 mL (0.18 M in ether, 1.5 mmol) of 1-lithio-1-propene[29] in ether solution as described for the preparation of **21a**. VPC analysis (OV-101, 230 °C) showed the alcohol:ketone ratio as 88:12. Purification by preparative TLC (10% ether–pentane) yielded 295 mg (70%) of **23a** as a colorless oil: IR (film) 2.75, 3.35, 5.95 (w), 6.80, 6.89, 10.25 μm; NMR (CCl_4) δ 1.18–1.39 (br s, 20 H), 1.41–1.55 (m, 2 H), 1.61 (d, 3 H, J = 5 Hz), 2.30 (s, 1 H), 3.09 (s, 4 H), 5.45–5.86 (m, 2 H); mass spectrum, *m/e* (relative intensity) 328 (M^+, 10), 300 (5), 267 (12), 250 (9), 137 (10), 131 (31), 105 (100), 97 (19), 69 (52), 55 (32); exact mass calcd for $C_{18}H_{32}OS_2$ 328.18945, found 328.18982.

Attempted Rearrangement of 23a. From 230 mg (0.70 mmol) of **23a** and 210 mg (20% in oil, 1.0 mmol) of potassium hydride by the rearrangement procedure described for **6** was obtained a yellow oil. VPC, TLC, and NMR analysis showed no detectable rearranged product or starting material.

1-(Butylthio)-2-butylcyclotridecene (27). To a solution of 200 mg (0.70 mmol) of ketone **21a** in 10 mL of ether was added 1 mL (2.4 M in hexane, 2.4 mmol) of *n*-butyllithium at room temperature. The reaction mixture was stirred for 5 h and then poured into 20 mL of water. The organic layer was separated, dried ($MgSO_4$), and concentrated to yield 210 mg of a yellow oil. The UV-active band at highest R_f was isolated by preparative TLC (hexane) to yield 124 mg (55%) of **27** as a colorless oil: IR (film) 3.42, 6.87, 7.30 (w), 7.43 (w), 9.26 (w), 14.10 μm; NMR (CCl_4) δ 0.91 (t, 6 H), 1.18–1.57 (br, 26 H), 1.91 (m, 2 H), 2.09 (m, 2 H), 2.25 (m, 2 H), 2.45 (t, J = 7 Hz, 2 H); mass spectrum, *m/e* (relative intensity) 324 (M^+, 44), 281 (17), 267 (100), 211 (5), 186 (4), 95 (32), 81 (41), 67 (51), 55 (81), 41 (95); exact mass calcd for $C_{21}H_{40}S$ 324.28506, found: 324.285.

Acknowledgment. We gratefully acknowledge the National Institutes of Health (GM-26039) for support of this work. We thank the MSU–NIH Regional Mass Spectrometry Facility, East Lansing, MI, for mass spectra of some of the samples used in this study.

Registry No. *trans*-1, 40615-41-6; *cis*-1, 40615-42-7; **2a**, 15040-92-3; **2b**, 68984-50-9; **2c**, 68984-49-6; **2d**, 53178-46-4; **2e**, 62163-03-5; **2f**, 68984-53-2; **2g**, 73397-69-0; **3a**, 68984-52-1; **3c**, 68984-51-0; **3f**, 73397-70-3; **4**, 4883-01-6; **5**, 68984-55-4; (±)-*cis*-**6**, 73397-71-4; (±)-*trans*-**6**, 73397-72-5; (±)-**7**, 68984-58-7; (±)-**8**, 73397-73-6; (±)-**9**, 73453-96-0; (±)-**10**, 73453-97-1; **12**, 68914-27-2; (±)-**13**, 68984-60-1; **14**, 52190-43-9; **15**, 73397-74-7; **16**, 73465-26-6; **17**, 53601-11-9; **18a**, 51310-03-3; **18b**, 51310-07-7; **18c**, 73194-43-1; **20a**, 73454-01-0; **20b**, 73194-44-2; *cis*-**21a**, 73397-75-8; *trans*-**21a**, 73397-76-9; **22a**, 73397-77-0; **22b**, 68984-55-4; *cis*-**23a**, 73397-78-1; *trans*-**23a**, 73397-79-2; **23b**, 73397-80-5; **27**, 73397-81-6; 4-*tert*-butylcyclohexanone, 98-53-3; 1,3-dithiane, 505-23-7; vinyl bromide, 593-60-2; (α-bromovinyl)trimethylsilane, 13683-41-5; 2-methyl-1,3-dithiane, 6007-26-7; α-(hydroxymethylene)cyclotridecanone, 73397-82-7; ethyl formate, 109-94-4; trimethylene dithiotosylate, 3866-79-3; 1-lithio-1-propene, 29283-76-9; 2-lithiopropene, 3052-45-7; 1,5-dithiaspiro[5.12]-octadecan-7-ol, 73397-83-8; TPPA, 6415-07-2; phosphorus oxychloride, 10025-87-3; 2-(thiophenyl)cyclododecanone, 52190-43-9; vinyllithium, 917-57-7; cyclododecanone, 830-13-7; α-(hydroxymethylene)cyclododecanone, 949-07-5; ethylene dithiotosylate, 2225-23-2; pyrrolidine, 123-75-1.

Synthesis of the First Crystalline Thiaanthracenes, 9-Cyano- and 9-(Ethoxycarbonyl)-10-methyl-10-thiaanthracenes, and Their Reactions with Electrophiles[1]

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Received September 17, 1979

The isolable and crystalline thiaanthracene derivatives 9-cyano- (**9**) and 9-(ethoxycarbonyl)-10-methyl-10-thiaanthracene (**12**) were synthesized in high yield for the first time by proton abstraction from the corresponding thioxanthenium salts (**8a** or **8b** and **11**) with sodium hydride in THF under a nitrogen atmosphere. Upon standing in THF at 50 °C, thiaanthracenes **9** and **12** underwent thermal 1,4-rearrangement to give the corresponding thioxanthenes **13** and **14**, respectively. The ylidic property of the thiaanthracenes was manifested by spectral and chemical evidences. Reactions of the thiaanthracenes with electrophiles such as dimethyl acetylenedicarboxylate and tetracyanoethylene are also described together with the course of the reactions.

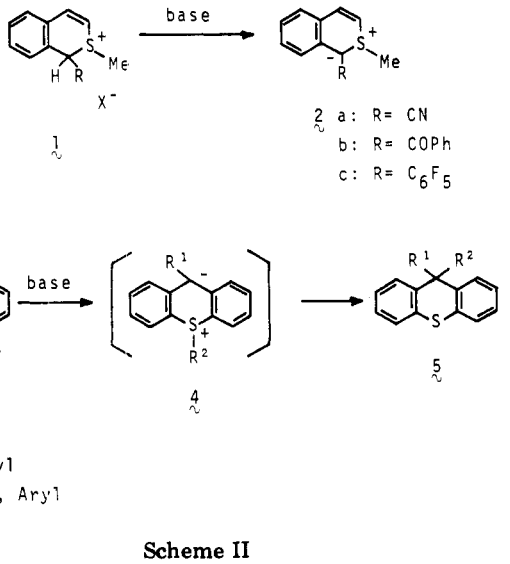
The chemistry of thiabenzenes[2] has attracted interest since Price et al. reported the synthesis of 1,2,4,6-tetraphenylthiabenzene from the reaction of 2,4,6-triphenylthiopyrylium perchlorate and phenyllithium.[3] In recent

(1) Preliminary communications of part of this work have been published: (a) M. Hori, T. Kataoka, H. Shimizu, S. Ohno, and K. Narita, *Tetrahedron Lett.*, 251 (1978); (b) M. Hori, T. Kataoka, H. Shimizu, and S. Ohno, *Heterocycles*, **7**, 863 (1977).

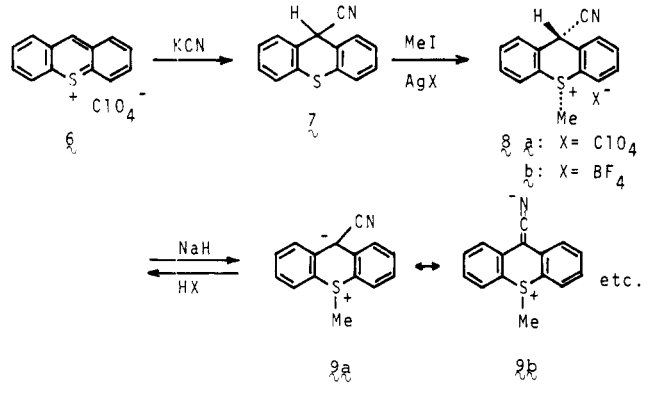
(2) For recent reviews, see (a) G. H. Senkler, Jr., B. E. Maryanoff, J. Stackhouse, J. D. Andose, and K. Mislow, "Organic Sulphur Chemistry—Structure, Mechanism and Synthesis", C. J. M. Stirling, Ed., Butterworths, London, 1975, p 157; (b) M. Hori and H. Shimizu, *Farumashia*, **12**, 468 (1976).

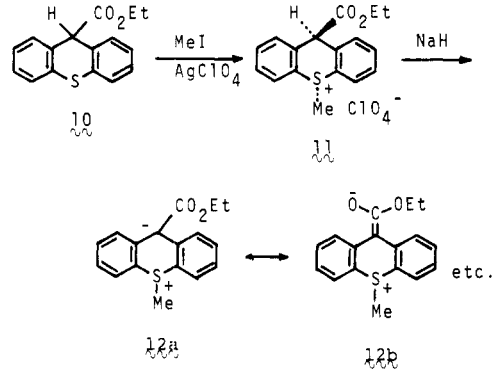
0022-3263/80/1945-2468$01.00/0

Scheme I



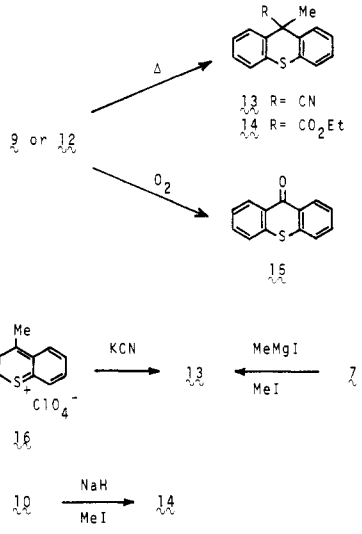
Scheme II





years, much interest has centered on the preparation and properties of stable thiabenzene derivatives. Thus, 1-cyano- (**2a**),[4] 1-benzoyl- (**2b**),[4] and 1-(pentafluorophenyl)-2-methyl-2-thianaphthalene (**2c**)[5] have been isolated as stable compounds from the corresponding 2-thiochromenium salts (**1**) (see Scheme I). Most recently, we reported an X-ray analysis of **2b** which revealed its ylidic structure.[6] However, 10-alkyl- or 10-aryl-10-thiaanthracenes (**4**) generated by the treatment of 10-alkyl- or 10-aryl-10-thioxanthenium salts (**3**) with strong bases are quite unstable compounds which undergo thermal six-electron 1,4-sigmatropic rearrangement to afford the corresponding 9-substituted thioxanthenes (**5**).[7] The isolation of a stable thiaanthracene derivative has not been described.[8]

Scheme III



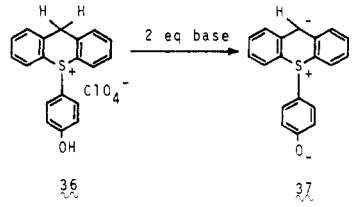
This paper presents the first synthesis of isolable and crystalline thiaanthracene derivatives 9-cyano- (**9**) and 9-(ethoxycarbonyl)-10-methyl-10-thiaanthracene (**12**) by treatment of the corresponding 10-methylthioxanthenium salts with sodium hydride and their novel reactions with electrophiles.

Results and Discussion

Synthesis of 10-Thiaanthracenes 9 and 12. Treatment of thioxanthylium perchlorate (**6**)[9] with potassium cyanide in water–methylene chloride afforded 9-cyanothioxanthene (**7**)[10] in 95% yield, which was methylated with methyl iodide in the presence of silver perchlorate or silver tetrafluoroborate to give 9-cyano-10-methylthioxanthenium perchlorate (**8a**),[11] or tetrafluoroborate (**8b**),[11]

(3) G. Suld and C. C. Price, *J. Am. Chem. Soc.*, **83**, 1770 (1961).
(4) M. Hori, T. Kataoka, H. Shimizu, K. Narita, S. Ohno, and H. Aoki, *Chem. Lett.*, 1101 (1974).
(5) J. Stackhouse, B. E. Maryanoff, G. H. Senkler, Jr., and K. Mislow, *J. Am. Chem. Soc.*, **96**, 5650 (1974); B. E. Maryanoff, J. Stackhouse, G. H. Senkler, Jr., and K. Mislow, *ibid.*, **97**, 2718 (1975).
(6) M. Hori, T. Kataoka, H. Shimizu, S. Ohno, K. Narita, H. Takayanagi, H. Ogura, and Y. Iitaka, *Tetrahedron Lett.*, 4315 (1979).

(7) (a) M. Hori, T. Kataoka, H. Shimizu, and C. F. Hsü, *Chem. Lett.*, 391 (1973); (b) M. Hori, T. Kataoka, and H. Shimizu, *ibid.*, 1117 (1974); (c) G. H. Senkler, Jr., J. Stackhouse, B. E. Maryanoff, and K. Mislow, *J. Am. Chem. Soc.*, **96**, 5648 (1974); (d) F. Ogura, W. D. Hounshell, C. A. Maryanoff, W. J. Richter, and K. Mislow, *ibid.*, **98**, 3615 (1976); (e) H. Pirelahi, Y. Abdoh, and A. Afzali, *Tetrahedron Lett.*, 4609 (1976); (f) C. A. Maryanoff, K. S. Hayes, and K. Mislow, *J. Am. Chem. Soc.*, **99**, 4412 (1977).
(8) Mislow and co-workers generated an anion (**37**) of 10-(*p*-hydroxyphenyl)thiaanthracene with remarkable stability in solution by the treatment of 10-(*p*-hydroxyphenyl)thioxanthenium perchlorate (**36**) with 2 equiv of dimsyl sodium in Me_2SO, but they could not isolate it.[7d]

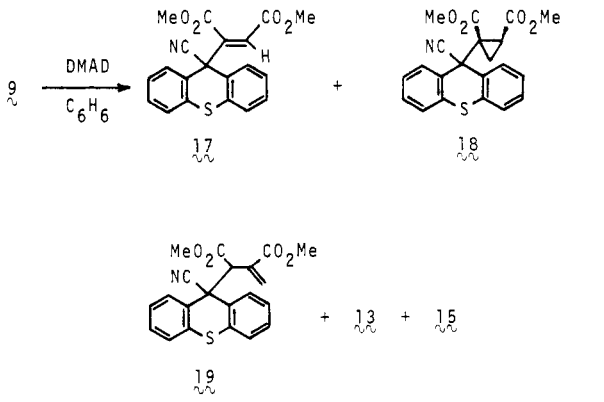


(9) C. C. Price, M. Hori, T. Parasaran, and M. Polk, *J. Am. Chem. Soc.*, **85**, 2278 (1963).
(10) J. F. Muren, *J. Med. Chem.*, **13**, 140 (1970).

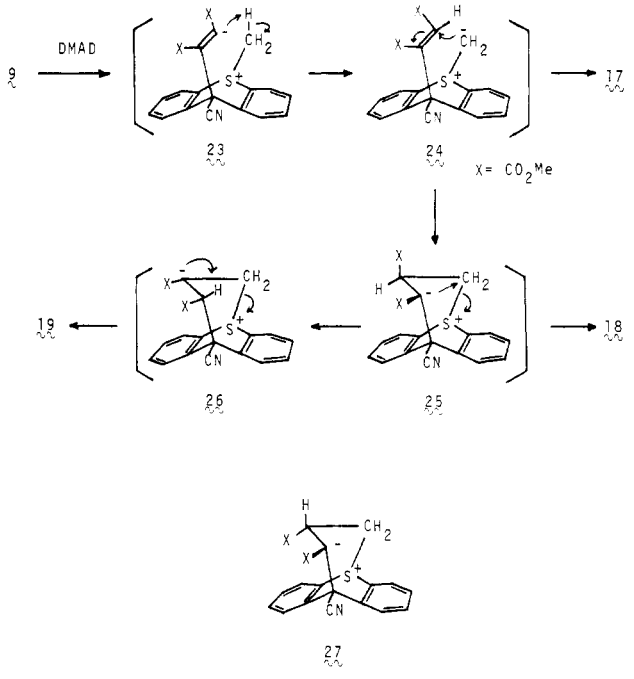
in yields of 54 or 64%, respectively. Deprotonation of **8a** or **8b** using sodium hydride in THF under a nitrogen atmosphere yielded 9-cyano-10-methyl-10-thiaanthracene (**9**) as orange-yellow needles, mp 115–116 °C, in 94% yield. A field-desorption (FD) mass spectrum showed a molecular ion peak at m/e 237. In the NMR spectrum of **9**, a singlet signal of the *S*-methyl group appeared at δ 2.22.

The synthesis of 9-(ethoxycarbonyl)-10-methyl-10-thiaanthracene (**12**) was performed as shown in Scheme II. Reaction of 9-(ethoxycarbonyl)thioxanthene (**10**)[16] with methyl iodide in the presence of silver perchlorate afforded 9-(ethoxycarbonyl)-10-methylthioxanthenium perchlorate (**11**)[11] in 94% yield. Perchlorate **11** was treated with sodium hydride in THF under nitrogen to yield a 10-thiaanthracene (**12**) as yellow needles, mp 117–119 °C, in 73% yield. The NMR spectrum of **12** showed a singlet at δ 2.29 assigned to the *S*-methyl group. The absorption bands of the cyano and carbonyl group in the IR spectra of **9** and **12** are stronger and shift to lower wavenumber (2170 cm^{-1} for CN, 1618 cm^{-1} for CO_2Et) than those of ordinary cyano or ester carbonyl groups, indicating delocalization of the carbanion electron of **9** and **12** by the cyano and carbonyl group, respectively. Thiaanthracene **9** was acidified with perchloric acid or tetrafluoroboric acid to give the corresponding thioxanthenium salt **8a** or **8b**, respectively. The above spectral and chemical observations reveal the ylidic property of the thiaanthracenes whose electronic structures can be depicted as **9a**, **9b**, **12a**, and **12b** (Scheme II). Further support for the ylidic property of **9** and **12** was also obtained by their thermal rearrangement. On standing in THF at 50 °C for 5 h under a nitrogen atmosphere, **9** gave the 1,4-rearrangement product, 9-cyano-9-methylthioxanthene (**13**), in 82% yield. Similarly, thiaanthracene **12** underwent conversion to 9-(ethoxycarbonyl)-9-methylthioxanthene (**14**) in 80% yield under the same conditions (see Scheme III). When air was introduced into the THF solution until the yellow color disappeared, **9** and **12** underwent autoxidation to give thioxanthone (**15**) in 88 and 85% yields, respectively. Identification of the structures of **13** and **14** was established

Scheme IV



Scheme V



by alternative synthesis of these compounds as described below. Authentic **13** was synthesized in quantitative yield by the reaction of 9-methylthioxanthylium perchlorate (**16**)[9] with potassium cyanide in water–methylene chloride or by the treatment of **7** with methylmagnesium iodide and methyl iodide. **14** was prepared by deprotonation of 9-(ethoxycarbonyl)thioxanthene (**10**) by sodium hydride in Me_2SO followed by the addition of methyl iodide.

Reactions of Thiaanthracenes with Electrophiles. It was expected that the thiaanthracenes would provide interesting reactions based on their ylidic properties. Thus, we investigated the reactions of them with some electrophiles such as dimethyl acetylenedicarboxylate (DMAD) and tetracyanoethylene (TCNE).

A solution of **9** and DMAD in benzene was stirred at room temperature under a nitrogen stream for 40 h. After evaporation of the solvent, the reaction mixture was purified by preparative thin-layer chromatography on silica gel to isolate dimethyl (9-cyanothioxanthen-9-yl)maleate (**17**, 28%), dimethyl 1-(9-cyanothioxanthen-9-yl)cyclopropane-*cis*-1,2-dicarboxylate (**18**, 4%), dimethyl 1-(9-cyanothioxanthen-9-yl)-2-propene-1,2-dicarboxylate (**19**, 9%), **13** (18%), and **15** (9%) (see Scheme IV). The structures of these new compounds were established mainly on the basis of spectral evidence. The mass spectra of **17**, **18**, and **19** showed ion peaks at m/e 222, corresponding to 9-cyanothioxanthylium (**20**), and at m/e 190,

(11) In Scheme II, dotted and thick lines drawn in **8a**, **8b**, and **11** indicate pseudo-equatorial and pseudo-axial bonds, respectively. The configuration of **8a** and **8b** is cis, but on standing in CF_3CO_2H solution a part of **8b** changed to the trans isomer **37**. The configuration of **11** is trans, and a part also changed to the cis isomer **39** in CF_3CO_2H solution. The assignment of the stereochemistry of the thioxanthenium salts was carried out by NMR spectroscopy. It has been established that two stereoisomers are present on the basis of the configuration in thioxanthene 10-oxide[12,13] and thioxanthenium salt systems[13] and that the signal of the pseudo-axial proton at the 9-position is broader than that of the pseudo-equatorial proton in thioxanthene,[14] thioxanthene 10-oxide,[12,13,15] and thioxanthenium salt systems.[13] In the NMR spectrum (CF_3CO_2H), the half-height widths ($w_{1/2}$) of the 9-proton signals of **8b** and **38** are 3.0 (δ 6.22) and 1.3 Hz (δ 6.07), respectively. Therefore, the 9-proton of **8b** is in a pseudo-axial position and the cyano group is in a pseudo-equatorial position. The 9-proton of **38** is in a pseudo-equatorial position and the cyano group is in a pseudo-axial position. Since $w_{1/2}$ of the 9-proton of **11** is 1.5 Hz (δ 5.75), the 9-proton is in a pseudo-equatorial position and the ethoxycarbonyl group is in a pseudo-axial position. On the other hand, the signals of the 10-methyl groups of **8b**, **38**, **11**, and **39** were observed at low field (δ 3.46–3.79, see Experimental Section), which is consistent with the 10-methyl groups occupying pseudo-equatorial positions in many thioxanthenium salt systems.[13] Consequently, the configuration of the thioxanthenium salts might be cis for **8b** and **39**, and trans for **11** and **38**. Since the spectrum of **8a** is similar to that of **8b**, the configuration of **8a** might be cis.

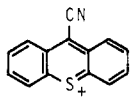
(12) (a) A. L. Ternay, Jr., L. Ens, J. Herrmann, and S. Evans, *J. Org. Chem.*, **34**, 940 (1969); (b) S. A. Evans and A. L. Ternay, Jr., *ibid.*, **40**, 2993 (1975).

(13) M. Hori, T Kataoka, H. Shimizu, and S. Ohno, *Heterocycles*, **12**, 1417, 1555 (1979).

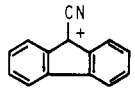
(14) A. L. Ternay, Jr., and D. W. Chasar, *J. Org. Chem.*, **33**, 2237 (1968).

(15) D. W. Chasar, *J. Org. Chem.*, **41**, 3111 (1976).

(16) I. Okabayashi, F. Miyoshi, and M. Arimoto, *Yakugaku Zasshi*, **92**, 1390 (1972).

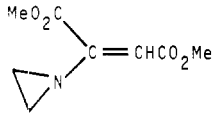


20 (m/e 222)



21 (m/e 190)

due to the 9-cyanofluorenyl cation (21), in addition to their molecular ion peaks at m/e 365, 379, and 379, respectively. These fragmentations indicate that these molecules contain the 9-cyanothioxanthene skeleton. Further, because of the low δ value (5.30) of the vinyl proton signal in the NMR spectrum of **17**, the ester groups are assumed to be cis, since the corresponding signals for the protons of the maleate and fumarate isomers of **22** appear at δ 5.31 and

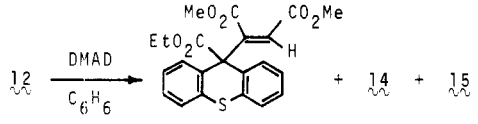


22

6.15, respectively.[17] The NMR spectrum of **18** showed absorptions at δ 1.57–1.95 (2 H, m) and 0.57–0.99 (1 H, m) which were consistent with the general cyclopropane ring protons having cis configurational ester groups.[18] The preference for the cis configuration of the ester groups in **18** may be ascribed to the intermediacy of betaine **25** (Scheme V). Although the terminal methylene protons' signal in **19** appeared at δ 6.57 as a singlet in $CDCl_3$, the signal was separated into two singlets at δ 6.40 and 6.49 in Me_2SO-d_6.

A plausible mechanism for the formation of **17**, **18**, and **19** is presented in Scheme V. The initial step of the reaction undoubtedly gives the first intermediate **23**, followed by an intramolecular proton abstraction from the proximate *S*-methyl group to form the second intermediate, methylide **24**, which affords the product **17** after loss of methylene. This type of methylene cleavage from methylides has been observed in other reactions.[7a,19] Furthermore, the well-known Michael-type addition[20] of the anionic site of **24** to the double bond forms the third intermediate **25**, which gives the product **18** with cis ester substituents via an S_N reaction at the sulfonium group. The intermediate **25**, in which the two ester groups take the trans configuration to avoid mutual steric repulsion and that with the thioxanthene ring, is more stable than the possible isomeric intermediate **27**, having such steric repulsions. **19** is formed via an E1cb reaction of the fourth intermediate (**26**) generated by a 1,2-proton shift in **25**.

Similarly, the reaction of thiaanthracene **12** and DMAD gave dimethyl (9-(ethoxycarbonyl)thioxanthen-9-yl)maleate (**28**), mp 107–109 °C, in 30% yield in addition to **14**



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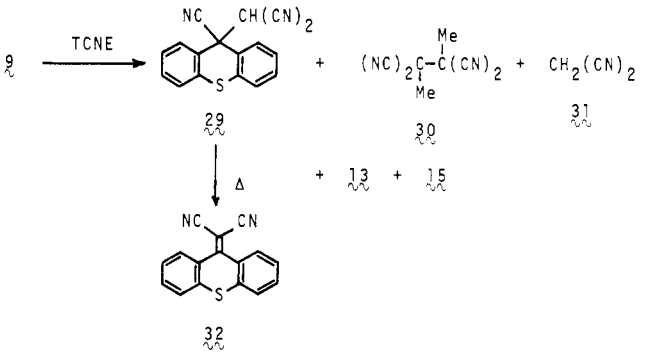
(17) J. E. Dolfini, *J. Org. Chem.*, **30**, 1298 (1965). It is apparent from the use of Dreiding models that there is great steric repulsion with the thioxanthene ring when the ester groups are trans. The good agreement of the chemical shift (δ 5.30) of the vinyl proton of **17** with that (δ 5.31) of the maleate isomer of **22** indicates no significant anisotropic effects of the thioxanthene ring system.

(18) N. F. Chamberlain, "The Practice of NMR Spectroscopy with Spectra-Structure Correlations for Hydrogen-1", Plenum Press, New York, 1974, p 223.

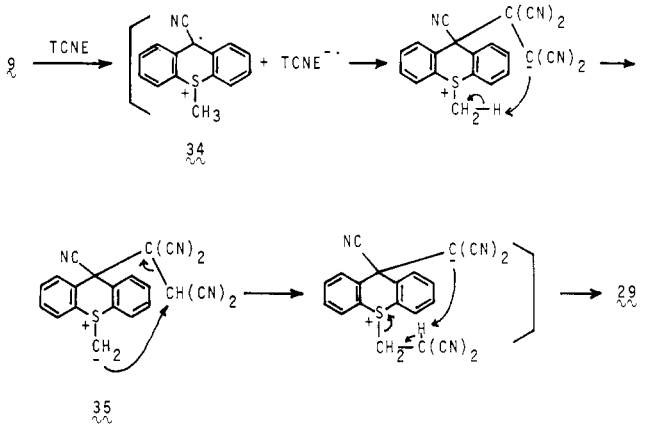
(19) V. Franzen, H. J. Schmidt, and C. Merz, *Chem. Ber.*, **94**, 2942 (1961).

(20) B. M. Trost and L. S. Mervin, Jr., "Sulfur Ylides", Academic Press, New York, 1975, p 77.

Scheme VI

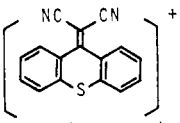


Scheme VII



(10%) and **15** (13%). The δ value (5.41) of the vinyl proton signal in **28** is assigned to the structure having cis ester groups as in the case of **17**. The formation of **28** could be explained by the same mechanism as described above in the reaction of **9**.

Next, we examined the reaction with TCNE as an electrophile. Treatment of **9** in THF with TCNE at room temperature under a nitrogen stream for 24 h yielded 9-cyano-9-(dicyanomethyl)thioxanthene (**29**, 11%), 2,2,3,3-tetracyanobutane (**30**, 24%), and malononitrile (**31**, 47% from TCNE), with the formation of **13** (8.5%) and **15** (13%) after separation by column chromatography on silica gel (see Scheme VI). The structure of **29** was elucidated by the spectral data which showed a singlet due to a methine proton at δ 4.98 in the NMR spectrum and mass spectral peaks at m/e 287 (M^+) and m/e 260 (**33**)



33 (m/e 260)

together with ion peaks of **20** and **21**. **29** was also chemically confirmed by heating at 150 °C for 3 h to lead to the known 9-(dicyanomethylene)thioxanthene (**32**),[21] mp 300–303 °C, in 80% yield with loss of hydrogen cyanide (Scheme VI).

On the basis of the observation of the TCNE radical anion in the ESR spectrum[22] in the reaction of **9** with TCNE, the formation of **29** may be viewed via the formation of intermediate methylide **35**, derived from the

(21) M. M. Hafez, N. Latif, and I. F. Zeid, *J. Org. Chem.*, **26**, 3988 (1961).

(22) The ESR spectrum was quite consistent with that observed in the reaction of TCNE and NaH in THF.

coupling of initially formed radical ion **34** and TCNE radical anion, with subsequent attack of the methylide carbanion and elimination of 1,1-dicyanoethylene as shown in Scheme VII.[23]

Experimental Section

Melting points were taken on a Yanagimoto micro-melting-point apparatus and are uncorrected. Microanalyses were performed at the Microanalytical Laboratory of our college. Nuclear magnetic resonance spectra were determined on a Hitachi R-20B spectrometer and chemical shifts are given in parts per million relative to tetramethylsilane as an internal standard. Infrared spectra were determined on a JASCO Model IRA-1. The EI and FD mass spectra were taken on a Hitachi RMU-6E spectrometer at an ionizing voltage of 70 eV and a JEOL JMS 01SG-2 double-focussing spectrometer at an emitter current of 15–18 mA, respectively. ESR spectra were determined on a JEOL JES-FE1X spectrometer.

9-Cyanothioxanthene (7). To a mixture of potassium cyanide (3.5 g), water (4 mL), and methylene chloride (30 mL) was added thioxanthylium perchlorate (**6**, 8.0 g) in limited amounts with stirring under a nitrogen atmosphere. The mixture was further stirred for 1 h, dried over anhydrous K_2CO_3, and evaporated in vacuo to afford 5.9 g (98%) of **7**. Recrystallization from 2-propanol gave colorless needles: mp 101–102 °C (lit.[10] mp 97–98 °C); IR (KBr) 2240 cm^{-1} (CN); NMR ($CDCl_3$) δ 4.74 (1 H, s, C_9-H), 7.15–7.92 (8 H, m, Ar H).

***cis*-9-Cyano-10-methylthioxanthenium Perchlorate (8a).** To a solution of **7** (2.1 g) and methyl iodide (14 g) in 1,2-dichloroethane (60 mL) was added silver perchlorate (2.1 g), and the mixture was stirred overnight. The precipitate was filtered off and extracted with a Soxhlet extractor using acetone. Removal of the solvent in vacuo gave 1.7 g (54%) of **8a**. Recrystallization from acetone gave colorless prisms: mp 181–183 °C dec; IR (KBr) 2240 (CN), 1147–1082 cm^{-1} (ClO_4^-); NMR (CF_3CO_2H) δ 3.48 (3 H, s, SMe), 6.25 (1 H, s, C_9-H), 7.72–8.50 (8 H, m, Ar H). Anal. Calcd for $C_{15}H_{12}ClNO_4S$: C, 53.34; H, 3.58; N, 4.15. Found: C, 53.31; H, 3.59; N, 4.04.

***cis*-9-Cyano-10-methylthioxanthenium Tetrafluoroborate (8b).** This compound (**8b**) was prepared from **7** (4.0 g), methyl iodide (25 g), $AgBF_4$ (3.9 g), and 1,2-dichloroethane (40 mL) in a similar manner as above. Recrystallization from acetone–ether gave 3.7 g (64%) of **8b** as colorless scales: mp 186–189 °C dec; IR (KBr) 2240 (CN), 1062 (BF_4^-), 1033 cm^{-1} (BF_4^-); NMR (CF_3CO_2H) δ 3.46 (3 H, s, SMe), 6.22 (1 H, br s, C_9-H), 7.73–8.52 (8 H, m, Ar H). Anal. Calcd for $C_{15}H_{12}BF_4NS$: C, 55.58; H, 3.42; N, 4.32. Found: C, 55.45; H, 3.69; N, 4.12. In a CF_3CO_2H solution, a part of **8b** changed to the trans isomer (**38**)[11] whose spectrum showed two singlet signals at δ 3.67 (SMe) and 6.07 (C_9-H); the cis:trans ratio was 2.6 (after 15 h) and 1.55 (after 24 h).

9-Cyano-10-methyl-10-thiaanthracene (9). All operations were carried out in an atmosphere of nitrogen.

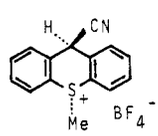
A. To a mixture of **8a** (1.0 g) and THF (25 mL) was added sodium hydride (90 mg) with stirring in an ice bath. The mixture was stirred for 3 h. The reaction mixture was evaporated at room temperature in vacuo, and the residue was dissolved in methylene chloride and filtered. The filtrate was concentrated to give a yellow oil which was crystallized by adding ether to afford 664 mg (94%) of **9** as orange-yellow needles. An analytical sample was prepared by recrystallization from methylene chloride–ether: mp 115–116 °C; IR (KBr) 2170 cm^{-1} (CN); NMR ($CDCl_3$) δ 2.22 (3 H, s, Me), 6.73–7.06 (2 H, m, C_3- and C_6-H), 7.19–7.77 (6 H, m, Ar H); FD mass spectrum, m/e 237 (M^+). Anal. Calcd for $C_{15}H_{11}NS$: C, 75.92; H, 4.67; N, 5.90. Found: C, 75.46; H, 4.40; N, 5.67.

B. In a similar manner as above, **9** was prepared from **8b** (3.0 g), THF (30 mL), and sodium hydride (80 mg) in 92% yield (2.0 g) with stirring for 5 h.

Treatment of 9 with Strong Acids. A. To a mixture of 70% perchloric acid (3 drops) and ether (5 mL) was added dropwise a solution of **9** (20 mg) in methylene chloride (1 mL), and the separated crystals were filtered off, washed with acetic acid and water, and recrystallized from acetone to yield 23 mg (81%) of **8a** as colorless prisms, mp 181–183 °C dec.

B. In a similar manner as above, **8b** was obtained from 42% tetrafluoroboric acid (5 drops), ether (5 mL), **9** (20 mg), and methylene chloride (1 mL). Recrystallization from acetone–ether gave 21 mg (77%) of **8b** as colorless scales, mp 186–189 °C dec.

***trans*-9-(Ethoxycarbonyl)-10-methylthioxanthenium Perchlorate (11).** To a solution of 9-(ethoxycarbonyl)thioxanthene (**10**, 2.7 g) and methyl iodide (14 g) in 1,2-dichloroethane (50 mL) was added $AgClO_4$ (2.4 g), and the mixture was stirred overnight. The filtrate was concentrated to ca. 15 mL in vacuo and diluted with ether to precipitate 3.6 g (94%) of **11**. Recrystallization from acetone–ether afforded colorless needles: mp 180–181 °C dec; IR (KBr) 1726 (CO), 1173–1090 cm^{-1} (ClO_4^-); NMR (CF_3CO_2H) δ 1.38 (3 H, t, J = 7.2 Hz, CH_2CH_3), 3.59 (3 H, s, SMe), 4.42 (2 H, q, J = 7.2 Hz, CH_2CH_3), 5.75 (1 H, s, C_9-H), 7.68–8.30 (8 H, m, Ar H). Anal. Calcd for $C_{17}H_{17}ClO_6S$: C, 53.06; H, 4.45. Found: C, 53.28; H, 4.44. During measurement of the NMR spectrum, a part of **11** changed to the cis isomer (**39**)[11] whose



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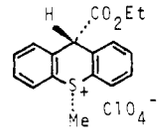

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NMR was δ 1.28 (3 H, t, J = 7.2 Hz, CH_2CH_3), 3.79 (3 H, s, SMe), 5.69 (1 H, s, C_9-H).

9-(Ethoxycarbonyl)-10-methyl-10-thiaanthracene (12). In a similar manner as with **9**, **12** (803 mg, 73%) was prepared from **11** (1.5 g), sodium hydride (120 mg), and THF (20 mL) with stirring for 4 h. Recrystallization from methylene chloride–ether gave yellow needles: mp 117–119 °C; IR (KBr) 1618 cm^{-1} (CO); NMR ($CDCl_3$) δ 1.42 (3 H, t, J = 7.2 Hz, CH_2CH_3), 2.29 (3 H, s, SMe), 4.36 (2 H, q, J = 7.2 Hz, CH_2CH_3), 6.70–7.05 (2 H, m, C_3- and C_6-H), 7.18–7.50 (4 H, m, Ar H), 8.48–8.70 (2 H, m, C_1- and C_8-H). Anal. Calcd for $C_{17}H_{16}O_2S$: C, 71.80; H, 5.67. Found: C, 71.68; H, 5.79.

Thermal Rearrangement of 9. A solution of **9** (670 mg) in THF (20 mL) was kept at 50 °C for 5 h under a nitrogen atmosphere. The solvent was evaporated off and the residue was purified by preparative thin-layer chromatography on silica gel with benzene–petroleum ether (3:1) to give 36 mg (5.7%) of thioxanthone (**15**) as colorless needles (from benzene), mp 218–220 °C, and 580 mg (82%) of 9-cyano-9-methylthioxanthene (**13**) as colorless prisms (from ethanol): mp 68–69 °C; IR (KBr) 2250 cm^{-1} (CN); NMR ($CDCl_3$) δ 1.78 (3 H, s, Me), 7.19–7.60 (6 H, m, Ar H), 7.78–8.11 (2 H, m, C_1- and C_8-H). Anal. Calcd for $C_{15}H_{11}NS$: C, 75.92; H, 4.67; N, 5.90. Found: C, 76.20; H, 4.69; N, 5.80.

Thermal Rearrangement of 12. A solution of **12** (340 mg) in THF (15 mL) was kept at 50 °C for 5 h under a nitrogen atmosphere and worked up as above except with ether–petroleum ether (1:1) as eluant for preparative thin-layer chromatography to give 22 mg (9%) of **15** and 270 mg (80%) of 9-(ethoxycarbonyl)-9-methylthioxanthene (**14**) as colorless prisms (from ethanol): mp 89–90 °C; IR (KBr) 1728 and 1720 cm^{-1} (CO); NMR ($CDCl_3$) δ 1.11 (3 H, t, J = 7.2 Hz, CH_2CH_3), 1.99 (3 H, s, Me), 4.15 (2 H, q, J = 7.2 Hz, CH_2CH_3), 7.08–7.63 (8 H, m, Ar H). Anal. Calcd for $C_{17}H_{16}O_2S$: C, 71.80; H, 5.67. Found: C, 71.78; H, 5.87.

Autoxidation of 9. Air was introduced into a solution of **9** (670 mg) in THF (30 mL) until the yellow color disappeared. Removal of the solvent gave a residue which was purified by column chromatography on silica gel with benzene to afford 530 mg (88%) of **15** and 25 mg (4%) of **13**.

Autoxidation of 12. Air was introduced into a solution of **12** (200 mg) in THF (10 mL) until the yellow color disappeared. Evaporation of the solvent afforded a solid residue which was recrystallized from benzene to give 127 mg (85%) of **15**.

9-Cyano-9-methylthioxanthene (13). Method A. To a mixture of potassium cyanide (2.0 g), water (2 mL), and methylene chloride (30 mL) was added 9-methylthioxanthylium perchlorate (**16**, 2.0 g)[9] in limited amounts with stirring. The mixture was

(23) The mechanism for the formation of **30** and **31** is not clear now, but may be viewed as the abstraction of the methyl group of **9** by the TCNE radical anion and self-decomposition of the TCNE radical anion, respectively.

further stirred for 1 h, dried over anhydrous K_2CO_3, and evaporated in vacuo to afford an oil which soon solidified to give 1.5 g (98%) of **13**. Recrystallization from ethanol gave colorless prisms, mp 68–69 °C.

Method B. To an ethereal solution of methylmagnesium iodide prepared from methyl iodide (4 g), Mg (0.3 g), ether (30 mL), and catalytic amounts of iodine was added dropwise a solution of **7** (2.2 g) in ether (20 mL). The mixture was refluxed for 5 h and treated with aqueous NH_4Cl solution. The organic layer was separated, washed with water, and dried over $MgSO_4$. Removal of the solvent gave 2.0 g (86%) of **13**.

9-(Ethoxycarbonyl)-9-methylthioxanthene (14). To a solution of sodium hydride (57 mg, 50% oil) in Me_2SO (6 mL) was added **10** (209 mg), and the mixture was stirred for 1 h. After addition of methyl iodide (300 mg), the mixture was further stirred for 1 h, then diluted with water, and extracted with ether. The extract was washed with water and dried over $MgSO_4$. Removal of the solvent gave a solid residue which was recrystallized from ethanol to afford 174 mg (79%) of **14** as colorless prisms, mp 89–90 °C.

Reaction of 9 with Dimethyl Acetylenedicarboxylate. To a solution of **9** (680 mg) in benzene (20 mL) was added dimethyl acetylenedicarboxylate (450 mg), and the mixture was stirred for 40 h under a nitrogen atmosphere. Removal of the solvent gave an oil, which was purified by preparative thin-layer chromatography on silica gel using methylene chloride as an eluant. The first fraction was concentrated to give an oil which was crystallized with ethanol to afford 120 mg (18%) of **13**. **15** was obtained from the second fraction in 9% yield (55 mg). The third fraction gave a colorless oil which was found to be a mixture of two compounds and then further subjected to preparative thin-layer chromatography on silica gel using CCl_4–ether (5:1). The first fraction was concentrated to afford an oil which soon solidified and was recrystallized from ether–petroleum ether to give 95 mg (9%) of dimethyl 1-(9-cyanothioxanthen-9-yl)-2-propene-1,2-dicarboxylate (**19**) as colorless prisms: mp 112–114 °C; IR (KBr) 2260 (CN), 1735 and 1721 (CO_2), 1618 cm^{-1} (C=C); NMR ($CDCl_3$) δ 3.33 (3 H, s, OMe), 3.39 (3 H, s, OMe), 5.06 (1 H, s, CH), 6.57 (2 H, s, $=CH_2$), 7.09–7.78 (7 H, m, Ar H), 7.90–8.18 (1 H, m, Ar H); NMR (Me_2SO-d_6) δ 3.28 (3 H, s, OMe), 3.36 (3 H, s, OMe), 4.94 (1 H, s, CH), 6.40 (1 H, s, $=CH_2$), 6.49 (1 H, s, $=CH_2$), 7.27–8.00 (8 H, m, Ar H); mass spectrum, m/e (relative intensity) 379 (5, M^+), 223 (18), 222 (100, **20**), 190 (19, **21**), 59 (7), 39 (7). Anal. Calcd for $C_{21}H_{17}NO_4S$: C, 66.48; H, 4.52; N, 3.69. Found: C, 66.53; H, 4.44; N, 3.60. Another fraction gave a colorless solid which was recrystallized from methylene chloride–petroleum ether to afford 288 mg (28%) of dimethyl (9-cyanothioxanthen-9-yl)maleate (**17**) as colorless needles: mp 149–151 °C; IR (KBr) 2260 (CN), 1727 (CO), 1633 cm^{-1} (C=C); NMR ($CDCl_3$) δ 3.48 (3 H, s, OMe), 3.63 (3 H, s, OMe), 5.30 (1 H, s, CH=), 7.25–7.66 (6 H, m, Ar H), 7.80–8.12 (2 H, m, C_1- and C_8-H); mass spectrum, m/e (relative intensity) 365 (13, M^+), 224 (7), 223 (17), 222 (100, **20**), 190 (10, **21**). Anal. Calcd for $C_{20}H_{15}NO_4S$: C, 65.74; H, 4.14; N, 3.83. Found: C, 65.74; H, 4.12; N, 3.68.

The last fraction was concentrated to give a solid which was recrystallized from methylene chloride–ether to yield 45 mg (4%) of dimethyl 1-(9-cyanothioxanthen-9-yl)cyclopropane-*cis*-1,2-dicarboxylate (**18**) as colorless plates: mp 183–184 °C; IR (KBr) 2260 (CN), 1746 and 1728 cm^{-1} (CO_2); NMR ($CDCl_3$) δ 0.57–0.99 (1 H, m, cyclopropane H), 1.57–1.95 (2 H, m, cyclopropane H), 3.39 (3 H, s, OMe), 3.67 (3 H, s, OMe), 7.20–7.63 (6 H, m, Ar H), 7.75–8.08 (2 H, m, C_1- and C_8-H); mass spectrum, m/e (relative intensity) 379 (0.5, M^+), 224 (7), 223 (23), 222 (100, **20**), 190 (19, **21**). Anal. Calcd for $C_{21}H_{17}NO_4S$: C, 66.48; H, 4.52; N, 3.69. Found: C, 66.46; H, 4.37; N, 3.61.

Reaction of 12 with Dimethyl Acetylenedicarboxylate. To a solution of **12** (890 mg) in benzene (20 mL) was added dimethyl acetylenedicarboxylate (600 mg), and the mixture was stirred for 12 h under a nitrogen atmosphere. Removal of the solvent afforded an oil which was separated by preparative thin-layer chromatography on silica gel using methylene chloride. The first fraction was further purified by preparative thin-layer chromatography on silica gel using ether–petroleum ether (1:1) to afford 89 mg (10%) of **14**. The second fraction gave 75 mg (13%) of **15**. The last fraction gave an oil which was again purified by preparative thin-layer chromatography on silica gel using ether–petroleum ether (1:1) to afford 390 mg (30%) of dimethyl (9-(ethoxycarbonyl)thioxanthen-9-yl)maleate (**28**). Recrystallization from ether–petroleum ether gave colorless needles: mp 107–109 °C; IR (KBr) 1729 (CO), 1642 cm^{-1} (C=C); NMR ($CDCl_3$) δ 1.32 (3 H, t, J = 7.2 Hz, CH_2CH_3), 3.46 (3 H, s, OMe), 3.66 (3 H, s, OMe), 4.44 (2 H, q, J = 7.2 Hz, CH_2CH_3), 5.41 (1 H, s, =CH), 7.16–7.59 (8 H, m, Ar H). Anal. Calcd for $C_{22}H_{20}O_6S$: C, 64.06; H, 4.89. Found: C, 64.11; H, 4.94.

Reaction of 9 with Tetracyanoethylene. To a solution of **9** (820 mg) in THF (10 mL) was added tetracyanoethylene (500 mg) in limited amounts with stirring at −15 °C under a nitrogen atmosphere. The mixture was stirred for 3 h at −15 °C and then at room temperature for 24 h. The reaction mixture was concentrated and the residue was purified by column chromatography on silica gel using chloroform. The first fraction gave 70 mg (8.5%) of **13**. The second fraction was concentrated to afford 105 mg (11%) of 9-cyano-9-(dicyanomethyl)thioxanthene (**29**) which was recrystallized from methylene chloride–cyclohexane to form colorless needles: mp >130 °C dec; IR (KBr) 2260 cm^{-1} (CN); NMR ($CDCl_3$) δ 4.98 (1 H, s, CH), 7.45–7.81 (6 H, m, Ar H), 8.00–8.32 (2 H, m, C_1- and C_8-H); mass spectrum, m/e (relative intensity) 287 (1.5, M^+), 261 (13), 260 (58, **33**), 233 (9), 228 (7), 224 (7), 223 (22), 222 (100, **20**), 190 (17, **21**), 149 (10), 111 (7). Anal. Calcd for $C_{20}H_9N_5S$: C, 71.06; H, 3.16; N, 14.62. Found: C, 70.97; H, 3.16; N, 14.62. The third fraction gave 95 mg (13%) of **15**. The fourth fraction gave 130 mg (24%) of 2,2,3,3-tetracyanobutane (**30**). Recrystallization from methylene chloride–chloroform formed colorless plates: mp 190–192 °C (sealed tube); NMR (Me_2SO-d_6) δ 2.23 (s, Me); mass spectrum, m/e (relative intensity) 158 (10, M^+), 142 (9), 80 (10), 79 (100, $MeC^+(CN)_2$), 78 (100, $CH_2{=}C(CN)_2^{+\cdot}$), 76 (10), 52 (24), 51 (59), 50 (18). Anal. Calcd for $C_8H_6N_4$: C, 60.75; H, 3.82; N, 35.42. Found: C, 60.67; H, 3.76; N, 35.12. The last fraction gave an oil which was distilled in vacuo to afford 120 mg of malononitrile (**31**).

Elimination of Hydrogen Cyanide from 29. **29** (25 mg) was heated at 150 °C for 3 h. The crude product was purified by column chromatography on silica gel using methylene chloride. Recrystallization from methylene chloride gave 19 mg (80%) of 9-(dicyanomethylene)thioxanthene (**32**) as yellow needles: mp 300–303 °C (lit.[21] mp 300–301 °C); IR (KBr) 2230 cm^{-1} (CN).

Acknowledgment. We thank Professor M. Sogami, Department of Physiology, School of Medicine, Gifu University, for determination of the ESR spectra.

Registry No. **6**, 2567-20-6; **7**, 25559-83-5; **8a**, 59181-75-8; **8b**, 59181-76-9; **9**, 59181-71-4; **10**, 17915-46-7; **11**, 59181-73-6; **12**, 59351-62-1; **13**, 59181-21-4; **14**, 59181-22-5; **15**, 492-22-8; **16**, 32348-57-5; **17**, 59215-69-9; **18**, 66223-42-5; **19**, 59181-23-6; **28**, 73398-11-5; **29**, 59215-71-3; **30**, 66223-43-6; **31**, 109-77-3; **32**, 6788-63-2; **38**, 59181-78-1; **39**, 59215-73-5; dimethyl acetylenedicarboxylate, 762-42-5; tetracyanoethylene, 670-54-2.