cyclopropylacetonitrile. The mass spectra and ir were identical.[22,23]

Decomposition of Nitrosoacetylamino Alcohols in Cyclohexene.—In a typical experiment a solution at 10–15° of 0.74 (0.004 mol) of **18** in 10 ml each of pentane and cyclohexene containing 0.2 g of Aliquat 336[24] was treated slowly with a solution of 1 g of sodium hydroxide in 1 ml of water.[15] After 15 min the theoretical amount of nitrogen had been collected and the mixture was allowed to come to room temperature. The mixture was washed with water. The organic layer was filtered through a cone of anhydrous magnesium sulfate and concentrated to about 4 ml by fractionation through a small packed column. There was no evidence (glpc) for the presence of **9c** in the distillate or the concentrate. Further fractionation afforded 0.33 g (52%) of **5c**, bp 48° (0.4 mm), identical with the sample prepared from **8**.

In a similar experiment a 64% yield of **5b**, bp 74° (0.4 mm), was obtained from **17**.

Registry No.—**5b**, 35200-94-3; **5c**, 35200-95-4; **6**, 35200-96-5; **7**, 35200-97-6; **8**, 35200-98-7; **9a**, 21777-85-5; **9b**, 27998-49-8; **9c**, 35201-01-5; **10b**, 34189-07-6; **10b** 2,4-DNP, 35200-78-3; (*Z*)-**10c**, 35200-79-4; (*E*)-**10c**, 35200-80-7; **10c** 2,4-DNP, 35200-81-8; **13**, 35200-82-9; **14**, 35200-83-0; **15**, 35200-84-1; **16**, 35249-60-6; **17**, 35200-85-2; **18**, 35200-86-3; methyl 3-cyclopropyl-3-phenyl-3-hydroxypropionate, 35200-87-4; methyl 3,3-dicyclopropyl-3-hydroxypropionate, 35200-88-5; methyl 3-cyclopropyl-3-hydroxybutyrate, 35200-89-6; 5-cyclopropyl-5-phenyl-2-oxazolidinone, 35200-90-9; 5,5-dicyclopropyl-2-oxazolidinone, 35200-91-0; 5-cyclopropyl-5-methyl-2-oxazolidinone, 35200-92-1; cyclopropyl cyclopropylmethyl ketone, 14113-96-3.

(22) L. Michiels, *Bull. Cl. Sci., Acad. Roy. Belg.*, **10**, (1912) [C 1105 (1912)], report mp 82–83° for the semicarbazone of the ketone prepared by reaction of cyclopropyl cyanide with cyclopropylmethylmagnesium bromide. We believe their ketone was not the expected one.

(23) The nmr spectrum for cyclopropylmethyl ketone, reported by M. Hanack and H. M. Ensslin, *Ann.*, **697**, 100 (1966), has a quartet at τ 7.5 which is not present in the pure sample that we obtained.

(24) Methyl tricaprylammonium chloride obtained from General Mills Chemicals, Kankakee, Ill.

A Direct Synthesis of Benzo[*b*]thiophene-2-carboxylate Esters Involving Nitro Displacement

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Facile, one-step synthesis of methyl benzo[*b*]thiophene-2-carboxylates from *o*-nitrobenzaldehydes and methyl 3-aminobenzo[*b*]thiophene-2-carboxylates from *o*-nitrobenzonitriles are described. Both reactions involve nucleophilic displacement of activated nitro functions followed by base-catalyzed ring closures.

The first synthesis of benzo[*b*]thiophene-2-carboxylic acid was reported by Friedländer and Lenk.[1] The acid was formed by a series of reactions involving alkylation of *o*-mercaptobenzaldehyde with chloroacetic acid followed by ring closure in fused alkali. Modifications of this procedure were used in the preparation of 5-nitrobenzo[*b*]thiophene-2-carboxylic acid[2–4] and 5,6-dimethoxybenzo[*b*]thiophene-2-carboxylic acid.[5,6] A further modification of this general ring-closure principle, but starting with *o*-methylmercaptoacetophenone, has been reported recently by Ruwet and Renson.[7] The disadvantages of these approaches have been the inaccessibility of the starting materials and the low overall yields obtained. A second method, reported by Campaigne and Cline[8] and improved upon by Chakrabarti and coworkers,[9] involved oxidative cyclization of β-aryl-α-mercaptoacrylic acids and gave high yields especially in aryl systems containing methoxyl functions. A related synthesis was reported by Ruwet and Renson.[10]

An even less accessible group of compounds has been the 3-aminobenzo[*b*]thiophene-2-carboxylic acids. Friedländer and Laske[11] reported the synthesis of the parent compound by a sequence involving alkylation of *o*-mercaptoaniline with chloroacetic acid, diazotization, displacement by cyanide ion, and, finally, fusion with alkali. More recently, a synthesis of ethyl 3-aminobenzo[*b*]thiophene-2-carboxylate was reported by Carrington and coworkers.[12] This compound was prepared by a ring-opening rearrangement of 3-chloro-1,2-benzisothiazole.[13] The generality of these methods again suffers from inaccessibility of starting materials.

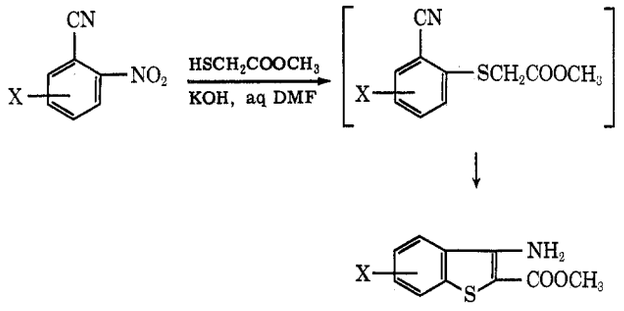
The author wishes to report facile, one-step syntheses of both methyl 3-aminobenzo[*b*]thiophene-2-carboxylates from *o*-nitrobenzonitriles and methyl benzo[*b*]-thiophene-2-carboxylates from *o*-nitrobenzaldehydes. The ease of nucleophilic displacement of activated nitro functions in aromatic systems has been known for some time, and scattered examples of its utility occur throughout the chemical literature. Bunnett and coworkers[14] studied the relative displacement rates by piperidine in substituted 2,4-dinitrobenzenes. They found the rate of nitro displacement was more than 200 times that of chlorine and was nearly equal to fluorine. In similar studies, Bolto and Miller,[15] using methoxide ion as the nucleophile, established the following order of ease of displacement: $SMe_2^+ > NMe_3^+ > F > NO_2 > Cl$. In the reactions to be discussed, advantage is taken of this

(1) P. Friedländer and E. Lenk, *Ber.*, **45**, 2083 (1912).
(2) L. F. Fieser and R. G. Kennelly, *J. Amer. Chem. Soc.*, **57**, 1611 (1935).
(3) K. Fries, H. Heering, E. Hemmecke, and G. Siebert, *Ann.*, **527**, 83 (1937).
(4) F. G. Bordwell and C. J. Albisetti, Jr., *J. Amer. Chem. Soc.*, **70**, 1955 (1948).
(5) J. Sićе and M. Mednick, *ibid.*, **75**, 1628 (1953).
(6) D. G. Bew and G. R. Clemo, *J. Chem. Soc.*, 1314 (1953).
(7) A. Ruwet and M. Renson, *Bull. Soc. Chim. Belg.*, **79**, 75 (1970).
(8) E. Campaigne and R. E. Cline, *J. Org. Chem.*, **21**, 39 (1956).
(9) R. M. Chakrabarti, N. B. Chapman, and K. Clarke, *Tetrahedron*, **25**, 2781 (1969).
(10) A. Ruwet and M. Renson, *Bull. Soc. Chim. Belg.*, **79**, 593 (1970).
(11) P. Friedländer and A. Laske, *Ann.*, **351**, 412 (1907).
(12) D. E. L. Carrington, K. Clarke, and R. M. Scrowston, *Tetrahedron Lett.*, 1075 (1971).
(13) A. Reissert, *Ber.*, **61**, 1680 (1928).
(14) J. F. Bunnett, E. W. Garbisch, Jr., and K. M. Pruitt, *J. Amer. Chem. Soc.*, **79**, 385 (1957).
(15) B. A. Bolto and J. Miller, *Aust. J. Chem.*, **9**, 74 (1956).

displacement lability of a nitro function, which is ortho to either a cyano or carboxaldehyde function.

When an *o*-nitrobenzonitrile[16] was allowed to react with an equivalent amount of methyl thioglycolate and excess potassium hydroxide in aqueous DMF at ice-bath temperature, the product obtained was the corresponding methyl 3-aminobenzo[*b*]thiophene-2-carboxylate (Scheme I). The product was formed by thiol

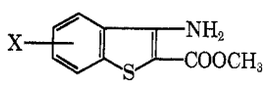
SCHEME I



anion displacement of the activated nitro function followed by base-catalyzed cyclization of the type earlier discussed. The reaction conditions and yields are summarized in Table I. When *o*-chlorobenzonitrile was utilized as starting material in the reaction, it was recovered unchanged even after two days at room temperature.

TABLE I

METHYL 3-AMINOBENZO[*b*]THIOPHENE-2-CARBOXYLATES[a]



X[b]	Mp, °C	Yield, %	Crystn solvent[c]	Temp, °C	Time, hr
H	110–111	72	A	0	0.5
4-Cl	111–112	84	B	0	1
6-Cl	151–152	72	B	0	1
4-OCH_3	147–148	35	B	0	0.5
4-NO_2	132–133	67	B	0	0.5
6-NO_2	229–231	47	B	0	0.5
6-CF_3	126–127	69	C	0	0.5
4-NO_2, 6-CF_3	189–191	80	B	0	5 min
4-NO_2, 6-CH_3	148–149	55	B	0	0.5

[a] Satisfactory analytical data (±0.3% for C, H, and N) were reported for all compounds: Ed. [b] Registry numbers are, respectively, 35212-85-2, 35212-86-3, 35212-87-4, 35212-88-5, 35212-89-6, 35212-90-9, 35212-91-0, 35212-92-1, and 35212-93-2. [c] A, alcohol–water; B, alcohol; C, methylcyclohexane.

Similarly, when an *o*-nitrobenzaldehyde was allowed to react with an equivalent amount of methyl thioglycolate and excess potassium carbonate in DMF at various temperatures, the product obtained was the corresponding methyl benzo[*b*]thiophene-2-carboxylate (Scheme II). The reaction conditions and yields are summarized in Table II. Yields of both tables are based on crystallized products.

These reactions represent but two examples wherein activated nitro functions can be utilized in the synthesis of heterocycles and uniquely substituted benzenes.

(16) *o*-Nitrobenzonitriles are readily prepared from 1-chloro-2-nitrobenzenes by reaction with cuprous cyanide and from *o*-nitroanilines by diazotization and displacement with cyanide ion.

SCHEME II

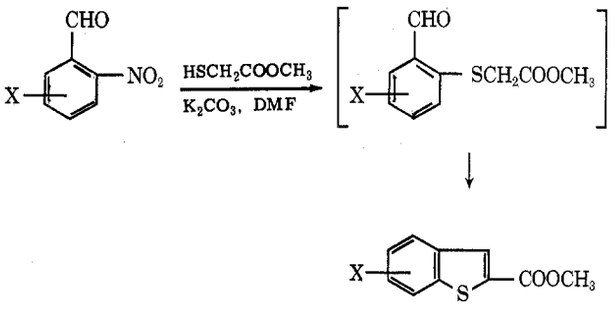
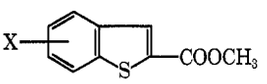


TABLE II

METHYL BENZO[*b*]THIOPHENE-2-CARBOXYLATES[a]



X[b]	Mp, °C	Yield, %	Crystn solvent[c]	Temp, °C; time, hr
H	72–73[d]	52	A	0, 0.5; 25, 20
4-Cl	89–90	70	B	0, 0.5; 25, 16
5-Cl	109–110	49	B	0, 0.5; 25, 21
4-NO_2	152–154	16	B	0, 3.5
6-NO_2	207–209	16	B	0, 2; 25, 1
5,6-diOMe	158–159	16	B	100, 18

[a] Satisfactory analytical values (±0.3% for C, H and N, S or Cl) were reported for all compounds: Ed. [b] Registry numbers are, respectively, 22913-24-2, 35212-95-4, 35212-96-5, 34084-87-2, 34084-88-3, 35212-99-8. [c] A, alcohol–H_2O; B, alcohol. [d] Lit. mp 72–73°: R. Weissgerber and O. Kruber, *Ber.*, **53**, 1551 (1920).

Further examples will be the subject of future communications from this laboratory.

Experimental Section[17]

Materials.—*o*-Nitrobenzonitrile, 6-chloro-2-nitrobenzonitrile, 4-chloro-2-nitrobenzonitrile, and all substituted *o*-nitrobenzaldehydes were obtained from the Aldrich Chemical Co. 2-Nitro-6-methoxybenzonitrile,[18] α,α,α-trifluoro-2-nitro-*p*-tolunitrile,[19] and 2,4-dinitrobenzonitrile[20] were prepared by procedures described in the literature.

General Procedure for Methyl 3-Aminobenzo[*b*]thiophene-2-carboxylates.—To a cold solution (ice bath) containing 30 mmol of the substituted *o*-nitrobenzonitrile and 30 mmol of methyl thioglycolate in 60 ml of DMF was added dropwise a solution of 3 g of potassium hydroxide in 15 ml of water. The mixture was stirred in the cold for the time shown in Table I and poured into ice water. The solid crude product was collected and crystallized from the appropriate solvent (Table I).

General Procedure for Methyl Benzo[*b*]thiophene-2-carboxylates.—To a cold solution (ice bath) containing 30 mmol of the substituted *o*-nitrobenzaldehyde and 5 g of anhydrous potassium carbonate in 60 ml of DMF was slowly added 30 mmol of methyl thioglycolate. The mixture was stirred in the cold for 0.5 hr and at the temperature and for the time period shown in Table II. The mixture was then poured into ice water, and the solid was collected and crystallized from the appropriate solvent (Table II).

2,6-Dinitrobenzonitrile.—A solution containing 25 g of 1-chloro-2,6-dinitrobenzene (0.123 mol) and 20 g of cuprous cyanide (0.222 mol) in 150 ml of *N*,*N*-dimethylacetamide was stirred and heated at 140° for 1 hr. The mixture was cooled and poured into ice water. The solid product was collected, dried, and triturated twice with 400 ml of hot ethyl acetate.

(17) Melting points were determined on a Mel-Temp apparatus and are uncorrected.

(18) A. Russell and W. G. Tebbens, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 293.

(19) M. Hauptschein, E. A. Nodiff, and A. J. Saggiomo, *J. Amer. Chem. Soc.*, **76**, 1051 (1954).

(20) P. Cohn and P. Friedländer, *Ber.*, **35**, 1265 (1902).

Filtration, removal of the solvent, and crystallization from alcohol yielded 12.7 g of product, mp 149–151° (lit.[21] 145°).

Anal. Calcd for $C_7H_3N_3O_4$: C, 43.54; H, 1.57; N, 21.76. Found: C, 43.46; H, 1.50; N, 21.74.

2,6-Dinitro-*p*-tolunitrile.—A solution containing 18 g of 4-chloro-3,5-dinitrotoluene (0.083 mol) and 15 g of cuprous cyanide (0.167 mol) in 150 ml of *N*,*N*-dimethylacetamide was stirred and heated at 130–135° for 1 hr. The mixture was cooled and poured into ice water. The crude product was collected by filtration, dried, and triturated with 500 ml of hot ethyl acetate. Filtration, removal of the solvent, and crystallization from alcohol yielded 10.9 g of product, mp 105–107° (lit.[22] 103°).

Anal. Calcd for $C_8H_5N_3O_4$: C, 46.39; H, 2.43; N, 20.29. Found: C, 46.32; H, 2.39; N, 20.01.

α,α,α-Trifluoro-2,6-dinitro-*p*-tolunitrile.—A solution containing 95 g of 4-chloro-3,5-dinitrobenzotrifluoride[23] (0.35 mol) and 35 g of cuprous cyanide (0.39 mol) in 200 ml of DMF was heated at 100° for 3.5 hr. The mixture was cooled and poured into ice water. The crude product was collected, dried, and triturated with hot ethyl acetate. Filtration, removal of the solvent, and crystallization from benzene yielded 60 g of product, mp 94–96°.

Anal. Calcd for $C_8H_2F_3N_3O_4$: C, 36.80; H, 0.77; N, 16.09. Found: C, 37.02; H, 0.91; N, 16.37.

(21) S. Reich, *Ber.*, **45**, 804 (1912).
(22) A. Claus and C. Beysen, *Ann.*, **266**, 223 (1891).
(23) L. M. Yagupol'skii and V. S. Mospan, *Ukr. Khim. Zh.*, **21**, 81 (1955); *Chem. Abstr.*, **49**, 8866 (1955).

Registry No.—2,6-Dinitrobenzonitrile, 35213-00-4; 2,6-dinitro-*p*-tolunitrile, 35213-01-5; α,α,α-trifluoro-2,6-dinitro-*p*-tolunitrile, 35213-02-6.

Acknowledgments.—The author wishes to thank Mr. Paul Unger and associates for spectral measurements and Mr. George Maciak and associates for microanalytical data.

The 1,2-Dithiolium Cation. XI.[1a] Polycyclic Dithiole and "No-Bond Resonance" Compounds[1b]

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The first known tricyclic 1,2-dithiolium salts **11**, **12**, and **13** have been prepared. The preparation of polycyclic thiothiophthene derivatives from these and related compounds is discussed.

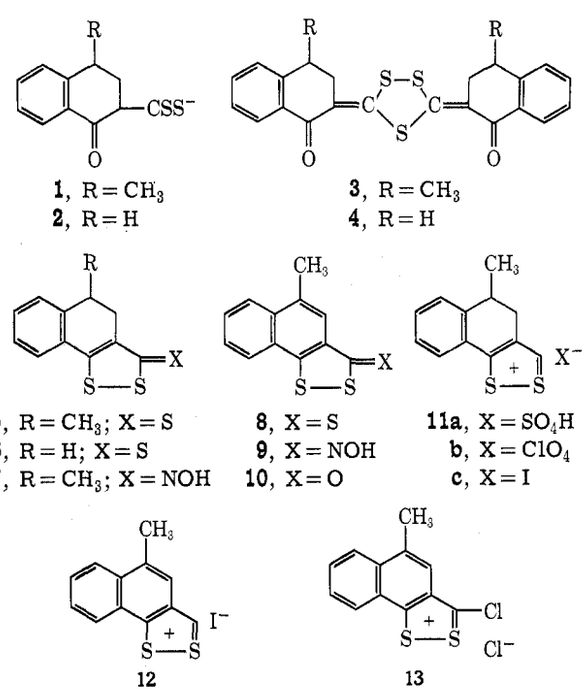
Recent investigations on the thiothiophthene "no-bond resonance" system have been facilitated by discoveries of attractive preparative methods based on condensation reactions of 1,2-dithiolium salts or other dithioles.[2] The present paper describes the preparation of certain bicyclic and tricyclic dithioles and the conversion of some of them to polycyclic thiothiophthene derivatives.

The investigation began with the application to 4-methyl-1-tetralone of the Thuillier–Vialle synthesis[3] of 1,2-dithiole-3-thiones. After base-catalyzed addition of carbon disulfide to give the dithiocarboxylic acid salt **1**, isolation from solution was effected by hypoiodite oxidation rather than the more usual procedures of acidification or alkylation. Analysis and molecular weight determination showed that the product thus obtained was the trithiolane **3**; it reacted smoothly with phosphorus pentasulfide to give the 1,2-dithiole-3-thione **5**, which was aromatized to **8** by sulfur at 190°.

Tetralone reacted similarly to give **2**, **4**, and **6**, but in somewhat lower yield; these were not investigated further.

Although **5** and **8** are of course closely related, they belong to different families of dithiolethiones ("trithiones"), the aryl and benzo substituted, which differ in their behavior toward peracetic acid. The former are rapidly converted to high yields of aryl-1,2-dithiolium salts,[4] while the latter give poorly defined oxidation products which are not saltlike. Benzo-1,2-dithiolium salts are, in fact, obtainable only by an entirely different and circuitous method.[5] It is therefore of some interest that peracetic acid converts both **5** and **8** to the tricyclic dithiolium salts **11** and **12**, respectively. The latter was, to be sure, obtained in only modest yield and an impure state.

Hydroxylamine reacts with both **5** and **8**, giving oximes **7** and **9**, respectively, but mercuric acetate desulfuration succeeded only with **8**, giving **10**.



(1) (a) For paper IX, see E. Klingsberg, *Syn.*, 29 (1972). (b) Presented in part at the 163rd National Meeting of the American Chemical Society, Boston, Mass., April 1972.
(2) E. Klingsberg, *Quart. Rev.*, **23**, 537 (1969).
(3) A. Thuillier and J. Vialle, *Bull. Soc. Chim. Fr.*, 1398 (1959).
(4) E. Klingsberg, *J. Amer. Chem. Soc.*, **83**, 2934 (1961).
(5) A. Lüttringhaus, M. Mohr, and N. Engelhard, *Ann.*, **661**, 84 (1963).