of anhydrous dimethoxyethane was refluxed for 12 hr. Ethyl iodide (10 ml) was added and the mixture was refluxed for an additional 18 hr. Water (25 ml) was added; the solution was extracted with two 25-ml portions of ether. The ether solution was dried over magnesium sulfate, filtered, and evaporated to give 0.030 g of yellow oil. Vpc on a 7.5% Carbowax 20 M column at 150° showed only one major peak (retention time, 9.75 min) which was collected. This vpc-purified **7** had λ_{max} 2.95 μ in an infrared spectrum markedly different from that of **5**; $\delta_{TMS}^{CCl_4}$ 1.26 (t, CH_3CH_2O–), 1.64 (s, $-CH_2-$), and 3.50 ppm (q, CH_3CH_2O–). Note that in contrast to the methylene protons of **5**, which appear as a multiplet from 1.2 to 2.2 ppm, those of **7** appear as a broad singlet at 1.64 ppm, most likely as a result of rapid conformational flipping in the *trans* isomer. The methylene regions in the nmr spectra of the dibenzoate derivatives of *cis*- and *trans*-cyclohexane-1,3-diol show an analogous difference.

Registry No.—**1**, 5323-87-5; **4**, 13619-73-3; **5**, 13618-81-0; **7**, 13618-82-1; **8**, 13618-83-2.

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Heterocyclic Syntheses Involving Acetylenedicarboxylate Adducts of Thiosalicylic Acid Derivatives

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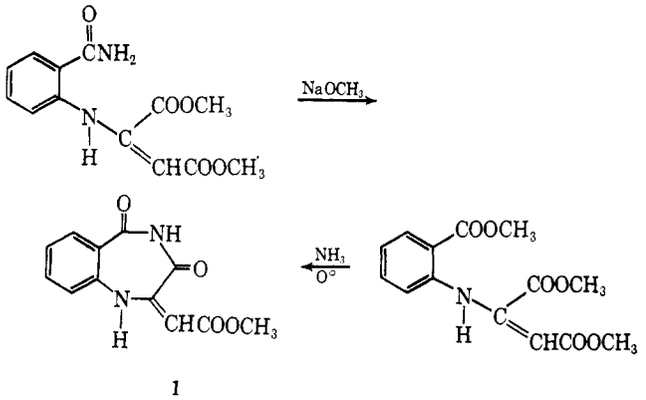
Adducts prepared by the nonanionic addition of thiosalicylates or mercaptobenzamide to dimethyl acetylenedicarboxylate have been shown to possess fumarate geometry. These adducts undergo facile cyclization to 3-hydroxybenzo[*b*]thiophenecarboxylate and benzothiazinone derivatives, respectively.

Recent reports of the utility of dimethyl acetylenedicarboxylate as a heterocyclic ring-forming reagent with amino, mercapto, and hydroxyl groups adjacent to electrophilic centers[1,2] prompt us to report our results in some related thiophenol derivatives. One of us has demonstrated the facile synthesis of benzodiazepinediones (**1**) by base-catalyzed cyclization of the Michael adducts of dimethyl acetylenedicarboxylate (**2**) and *o*-aminobenzamides and by controlled ammonolysis of similar adducts of **2** with methyl anthranilates.[3] In



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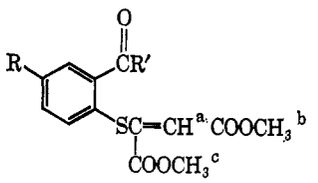
the event that an analogous reaction course is attained with *o*-mercaptobenzamide adducts and methyl thiosalicylate adducts of **2**, a new and direct route to the benzothiazepine ring system would be achieved. Members of both the benzodiazepine[4] and the benzothiazepine[5] systems have come under recent scrutiny for their tranquilizer and muscle-relaxant potential.

TABLE I[a]



	H[a]	CH_3[b]	CH_3[c]	R′ = OCH_3	R′ = OH
6a (R′ = OCH_3; R = H)					
Maleate	6.05	3.68	3.68	3.90	...
Fumarate	6.80	3.45	3.80	3.90	...
6b (R′ = OCH_3; R = Cl)	6.81	3.46	3.78	3.92	...
6c (R′ = OCH_3; R = Br)	6.83	3.46	3.75	3.93	...
6d (R′ = OH; R = H)	6.84	3.48	3.80	...	10.95
6e (R′ = NH_2; R = H[b])	6.74	3.43	3.80	...	...

[a] All spectra were run in $CDCl_3$ against tetramethylsilane (TMS) and are reported in parts per million. [b] Run in dimethyl sulfoxide-d_6 owing to lack of solubility in $CDCl_3$.

The *o*-mercaptobenzamide (**3**) underwent a spontaneous and mildly exothermic reaction with **2** which resulted in formation of the adduct **6e**. Absence of SH absorption in the infrared and nmr spectra of the product and the retention of the amide NH_2 bands clearly defined the adduct as an S-substituted species. Furthermore, benzamide was inert to reaction with **2** under these conditions, but thiophenol formed an adduct. The nmr spectrum of **6e** (see Table I) allowed the structural assignment of fumarate geometry to the diester portion. This adduct required a catalytic quantity of sodium methoxide to effect ring closure and the resulting product was not the expected benzothiazepinedione but 2-carbomethoxymethyl-2-carbomethoxy-1,3-

(1) J. B. Hendrickson, R. Rees, and J. F. Templeton, *J. Am. Chem. Soc.*, **86**, 107 (1964).

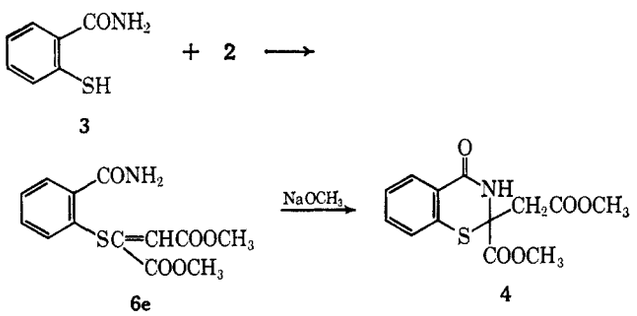
(2) E. C. Taylor and N. D. Heindel, *J. Org. Chem.*, **32**, 1666 (1967).

(3) N. D. Heindel and T. F. Lemke, *J. Heterocyclic Chem.*, **3**, 389 (1966), and Abstracts, South Eastern and South Western Regional Meeting of the American Chemical Society, Memphis, Tenn., Dec 1965, p 58.

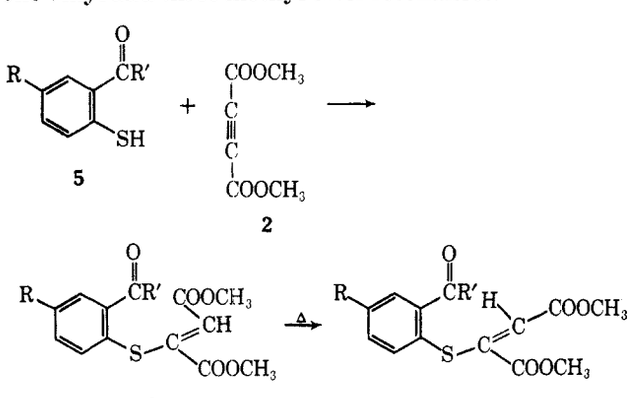
(4) L. H. Sternbach, L. O. Randall, and S. R. Gustafson in "Psychopharmacological Agents," M. Gordon, Ed., Academic Press Inc., New York, N. Y., 1964, pp 137–224.

(5) F. Hunziker, F. Kuenzle, and J. Schmutz, *Helv. Chim. Acta*, **49**, 244 (1965).

benzothiazin-4-one (**4**). This assignment was consistent with elemental analysis and nmr spectral data which located two methyl ester resonances at 3.75 and 3.81 ppm, an unsplit methylene at 3.35 ppm, a broad NH at 8.23 ppm, and an aromatic complex centered at 7.32 ppm.



Preparation of the requisite thiol adducts **6** needed for investigation of the partial ammonolysis synthesis projected for the benzothiazepinediones was made possible by the facile, uncatalyzed addition of methyl thiosalicylates (**5a**, **b**, and **c**) to **2**. Although Truce has investigated the base-catalyzed *trans* additions of thiols to numerous acetylenes[6] including acetylenedicarboxylate and its disodio salt,[7] the uncatalyzed reaction has received almost no attention in the mercaptan additions and only recent consideration in the nonanionic addition of amine nucleophiles to acetylenes.[8] When generated at temperatures from ambient to the boiling point of methanol, thiol adducts were of exclusively *trans* (fumarate) geometry. The nmr spectra, Table I, demonstrated the presence of only one vinyl and three methyl ester resonances.



a, R′ = OCH_3; R = H
b, R′ = OCH_3; R = Cl
c, R′ = OCH_3; R = Br
d, R′ = OH; R = H
e, R′ = NH_2; R = H

The parent methyl thiosalicylate adduct (**6a**) was a viscous oil which could be vacuum distilled without decomposition. The distilled material gave evidence of a thermal isomerization of the olefinic linkage, a new peak in the vinyl region (6.05 ppm), and two new methyl ester resonances for the pendant butanedioate portion (3.68 ppm). It was possible to heat the initially *trans* adduct for 0.5 hr at 190° and to produce 35% isomerization to *cis* (maleate) material. Further conversion to 45% *cis* adduct was obtained after 0.5 hr at 210°. It was not verified whether equilibrium had been reached in the latter isomerization. Thermal isomerization of thiol–acetylene adducts has been reported by Kohler[9] and Truce.[10]

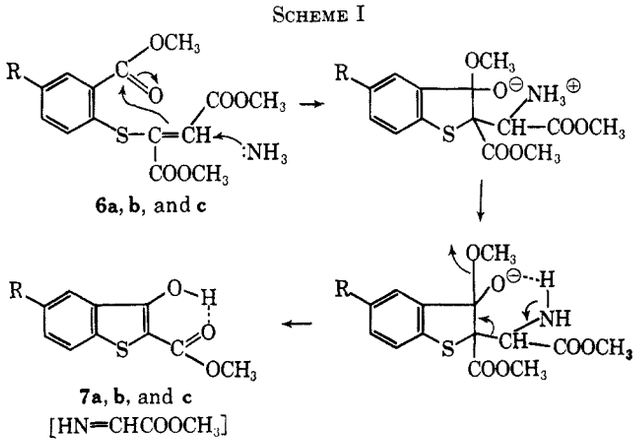
Dolfini's[11] method for relating the chemical shifts of the vinyl protons in the isomeric amine–acetylenedicarboxylate adducts to the stereochemistry of the system can be applied to the thiol adducts. The initially produced isomer (**6a**) displayed vinyl resonance at 6.08 ppm and the ester methyls at 3.45 and 3.80 ppm, characteristic of the fumarate geometry. This more highly deshielded vinyl proton experiences the greater diamagnetic anisotropy of the two flanking ester carbonyls. Likewise, the esters themselves are in slightly different electronic environments and hence are less equivalent than those of the maleate which appear under the same peak at 3.68 ppm.[12]

Verification of the assignment of the fumarate esters as 3.45 and 3.80 ppm and of the ring-attached carbomethoxy at 3.90 ppm (in **6a**) was obtained from adducts **6d** and **6e** which bear only the butenedioate esters. Comparison of the vinyl resonance positions in the four nonisomerized adducts allows the assignment of fumarate geometry to them. No trace of *cis* adduct was evident at ambient temperatures.

The ammonolysis of the thiosalicylate–acetylenedicarboxylate adducts (**6a**, **b**, and **c**) did not lead to the seven-membered benzothiazepinediones but instead resulted in formation of 3-hydroxybenzo[*b*]-thiophene-2-carboxylates (**7a**, **b**, and **c**). Methylamine also catalyzed the reaction, but attempted catalysis by sodium methoxide or piperidine led to high-melting, insoluble products which could not be adequately purified or characterized. A low yield (18%) of the diadduct of piperidine and methyl thiosalicylate to **2**, *i.e.*, dimethyl α-(1-piperidinyl)-α′-(2-carbomethoxyphenylthio)succinate, was isolated from the piperidine treatment of **6a**.

A plausible mechanism for the formation of the 3 hydroxybenzo[*b*]thiophene-2-carboxylates, whose structure was confirmed by nmr and by independent synthesis of the parent member, is shown in Scheme I.

SCHEME I



(6) W. E. Truce in "Organic Sulfur Compounds," Vol. 1, N. Kharasch, Ed., Pergamon Press Inc., New York, N. Y., 1961, pp 112–120.
(7) W. E. Truce and R. B. Kruse, *J. Am. Chem. Soc.*, **81**, 5372 (1959).
(8) W. E. Truce and D. G. Brady, *J. Org. Chem.*, **31**, 3543 (1966).
(9) E. P. Kohler and H. Potter, *J. Am. Chem. Soc.*, **57**, 1316 (1935).
(10) W. E. Truce and R. J. McManimie, *ibid.*, **76**, 5745 (1954).
(11) J. E. Dolfini, *J. Org. Chem.*, **30**, 1298 (1965).
(12) See also R. Husigen, K. Herbig, A. Siegl, and H. Huber, *Chem. Ber.*, **99**, 2526 (1966), and E. Winterfeldt and H. Preuss, *ibid.*, **99**, 450 (1966), where similar arguments have been employed in amine–acetylene adducts.

This mechanism and other alternatives which can be proposed all require the elimination of a three-carbon moiety, possibly as methyl iminoacetate. Numerous attempts to isolate the remaining fragment from the reaction mixtures have been fruitless. After filtration of the precipitated benzothiophenes (**7a**, **b**, and **c**) from the reaction mixture, the highly colored mother liquors yielded only red tars on concentration. Small quantities of thioindigo could be isolated from these gums.[13] Apparently the stereochemistry of the thiol adducts **6a**, **b**, and **c** is of little importance in the amine-catalyzed cyclization. Product yields of **7a** exceeded 75% from thermally isomerized mixtures of fumarate and maleate forms of **6a** containing 45% maleate isomer.

While in general 3-hydroxybenzo[*b*]thiophenes have been found to exist almost exclusively in their keto tautomers,[14] it appears obvious from the spectral evidence that these products more closely parallel β-keto esters and, at least in solution, exist almost entirely as their hydroxy forms. The solution infrared spectra of **7a**, **b**, and **c** in CCl_4 all display strongly bonded hydroxyls at 3155 ± 15 cm^{-1} and bonded ester carbonyls at 1664 ± 5 cm^{-1}. The resonance for the enolic proton in the nmr was extremely difficult to locate and was found to be temperature and solvent dependent. In deuteriobenzene at ambient temperatures, it could be identified at 10.32 ppm in **7a**. This low-field position virtually dictates that the proton is in the hydroxyl form. In deuteriodimethyl sulfoxide or deuteriochloroform, the enolic proton was not detected.

Experimental Section

Infrared spectra of **7a**, **b**, and **c** were obtained as dilute solutions in spectral grade CCl_4 on a Perkin-Elmer 21 calibrated against polystyrene standard. All other were obtained as Nujol mulls on a Perkin-Elmer 237.

Dimethyl (2-carboxamidophenylthio)fumarate (6e) was prepared by mixing equimolar quantities (3.0 mmoles) of dimethyl acetylenedicarboxylate and *o*-mercaptobenzamide[15] in 20 ml of anhydrous methanol. The solution was refluxed for 0.5 hr and allowed to stand overnight. Distillation of the solvent produced a deep yellow oil which deposited colorless prisms on standing. A 55% yield, mp 143.5–144.5°, was obtained on recrystallization from methanol.

Anal. Calcd for $C_{13}H_{13}NO_5S$: C, 52.87; H, 4.44; N, 4.74. Found: C, 53.05; H, 4.62; N, 4.79.

In addition to the pertinent nmr data reported in Table I, this compound also displayed two NH stretching bands at 3280 and 3096 cm^{-1} and carbonyls at 1724 and 1686 cm^{-1} in the infrared.

2-Carbomethoxymethyl-2-carbomethoxy-1,3-benzothiazin-4-one (4) could be prepared either by the direct reaction of *o*-mercaptobenzamide and **2** in methanolic methoxide or by methoxide treatment of the adduct **6e**. Comparable conversions were obtained in either method and a typical procedure is described for the former route. Sodium methoxide (0.1 g) was added to a refluxing solution of 5.2 mmoles of *o*-mercaptobenzamide and 5.2 mmoles of dimethyl acetylenedicarboxylate in 30 ml of methanol. The reaction was refluxed for 1 hr, the solvent removed under vacuum, and the product crystallized as white microneedles (59% yield), mp 168–169°, from methanol.

Anal. Calcd for $C_{13}H_{13}NO_5S$: C, 52.87; H, 4.44; N, 4.74. Found: C, 52.93; H, 4.53; N, 4.34.

Dimethyl (2-Carbomethoxyphenylthio)fumarate (6a).—Equimolar quantities (0.03 moles) of dimethyl acetylenedicarboxylate and methyl thiosalicylate[16] were refluxed for 0.5 hr in 80 ml of methanol. The solution was evaporated to a viscous oil and examined in the nmr (see Table I for **6a**, fumarate). The oil was fractionated under vacuum and the portion boiling at 178–180° (0.90 mm) (75% yield) was taken as product.

Anal. Calcd for $C_{14}H_{14}O_6S$: C, 54.19; H, 4.54. Found: C, 53.99; H, 4.83.

The nmr spectrum of the distilled material showed that extensive thermal isomerization (to maleate) had occurred on heating.

Dimethyl (5-chloro-2-carbomethoxyphenylthio)fumarate (6b) was synthesized by reaction of 0.016 moles of **2** and methyl 5-chlorothiosalicylate[16] according to the above method. The product (76% yield) was a pale yellow solid, mp 103–104° from benzene.

Anal. Calcd for $C_{14}H_{13}ClO_6S$: C, 48.78; H, 3.77. Found: C, 48.69; H, 4.03.

Dimethyl (5-Bromo-2-carbomethoxyphenylthio)fumarate (6c).—According to the procedure of Katz,[16] 0.027 moles of 5-bromoanthranilic acid were diazotized, treated with potassium ethyl xanthate, and esterified. The crude methyl 5-bromothiosalicylate was treated directly in dry ether with 0.022 moles of dimethyl acetylenedicarboxylate dissolved in 5.0 ml of methanol. The reaction mixture was refluxed for 0.5 hr and evaporated *in vacuo* to an oil which crystallized on standing. The uncrystallized portion of the product was examined in the infrared and showed the presence of unreacted dimethyl acetylenedicarboxylate but no unreacted thiol groups (absorption at 2510 cm^{-1}). The light yellow crystals (69% based on starting 5-bromoanthranilic acid) were recrystallized from 1:1 benzene–methanol, mp 96–98°.

Anal. Calcd for $C_{14}H_{13}BrSO_6$: C, 43.20; H, 3.37. Found: C, 43.50; H, 3.19.

Dimethyl (2-carboxyphenylthio)fumarate (6d) was prepared for nmr comparison with **6a**, **b**, and **c** by condensing 0.035 moles each of **2** and thiosalicylic acid in 100 ml of methanol. Evaporation, after 1 hr reflux of the solution, produced a dark yellow syrup which was triturated with benzene and chilled to produce white crystals (58%), mp 127° from benzene.

Anal. Calcd for $C_{13}H_{12}O_6S$: C, 52.69; H, 4.08. Found: C, 52.47; H, 4.18.

Methyl 3-hydroxy-5-R-benzo[*b*]thiophene-2-carboxylates (7a, b, and c) were prepared in an identical manner from the adducts **6a**, **b**, and **c**. The preparation of **7a** is cited as an example. A solution of 0.013 moles of **6a** in 50 ml of methanol was treated with anhydrous ammonia passed through the medium at a rapid rate for 10 min. A deep red color developed almost at once and an exothermic reaction ensued. After approximately 5 min, pinkish white crystals began to precipitate. These were removed by filtration and concentration of the mother liquors produced additional crops. The product (76% yield) was purified by recrystallization from methanol or by sublimation *in vacuo*, mp 107–108°.

Anal. Calcd for $C_{10}H_8O_3S$: C, 57.68; H, 3.87. Found: C, 57.66; H, 4.05.

Further concentration of the mother liquors yielded a red tarry resin which deposited small amounts of thioindigo (5–15%), identified by spectral comparison with an authentic sample. By the above procedure, methyl 5-chloro-3-hydroxybenzo[*b*]-thiophene-2-carboxylate (**7b**), mp 154–155° (from N,N-dimethylformamide), was prepared in 82% yield.

Anal. Calcd for $C_{10}H_7ClO_3S$: C, 49.49; H, 2.91. Found: C, 49.48; H, 3.09.

The bromo isomer (**7c**) was obtained in 80% yield, mp 174.5–176°. It was recrystallized from methanol (sparingly soluble) and sublimed *in vacuo* at 140° (0.05 mm).

Anal. Calcd for $C_{10}H_7BrO_3S$: C, 41.83; H, 2.46. Found: C, 41.87; H, 2.29.

Methyl 3-hydroxybenzo[*b*]thiophene-2-carboxylate (7a) was prepared by a modification of Friedlander's procedure[13b] as an independent confirmation of structure of the product isolated from the ammonolysis of **6a**. A solution of 0.010 moles of methyl thiosalicylate and 0.010 moles of sodium methoxide in 15 ml of methanol was chilled to 0° and mixed rapidly with 0.010 moles of methyl α-chloroacetate in 5.0 ml of methanol, also cooled to 0°. After standing at room temperature for 1 hr, the reaction

(13) (a) Thioindigo is an established air oxidation product of the hydroxybenzothiophenecarboxylate system; (b) see P. Friedlander, *Chem. Ber.*, **39**, 1060 (1906).

(14) A. R. Katritzky and J. M. Lagowski, *Advan. Heterocyclic Chem.*, **2**, 10 (1963).

(15) R. Boudet, *Bull. Soc. Chim. France*, 322 (1956).

(16) L. Katz, L. S. Karger, W. Schroeder, and M. S. Cohen, *J. Org. Chem.*, **18**, 1394 (1953).

mixture was refluxed for 1 hr, cooled to room temperature, filtered to remove precipitated salt, and concentrated *in vacuo*. Chilling and scratching with a glass rod caused the oil to crystallize and a 77% yield, mp 51–54° from methanol (lit.[13b] mp 52°), of methyl (S-carbomethoxymethyl)thiosalicylate was obtained.

The crystals were redissolved in 18 ml of methanol containing 0.60 g of sodium methoxide and refluxed for 10 hr. Cold water was added dropwise and the organic precipitate filtered off, washed with cold water, and recrystallized from methanol. A 76% yield of white needles, mp 106.5–108° (lit.[17] mp 107–108°), was obtained. Mixture melting point and infrared spectrum were identical with those of the ammonolysis product.

Attempted Piperidine Catalysis of Cyclization of 6a.—To 0.029 moles of **6a** was added a solution of 0.029 moles of piperidine in 100 ml of methanol. The mixture was refluxed for 1 hr and became progressively more yellow and a white precipitate appeared. The solid was filtered off and recrystallized from N,N-dimethylformamide. After several recrystallizations, the melting range, 170–220° dec, of the crystals (30% yield) was still not precisely defined. Although the material was of insufficient solubility to obtain an nmr spectrum, the infrared spectrum revealed intense carbonyl absorptions centered at 1710 cm^{-1}. The crystals did not appear to contain nitrogen and analyzed for the approximate loss of one molecule of methanol from the adduct **6a**.

Anal. Calcd for $C_{13}H_{10}O_5S$: C, 56.11; H, 3.62. Found: C, 56.19; H, 4.05.

Concentration of the mother liquors from the original reaction precipitate a highly soluble, pinkish white compound, mp 85–88° from methanol, in 18% yield. The elemental and nmr analyses were consistent with an assignment as dimethyl α-(1-piperidinyl)-α′-(2-carbomethoxyphenylthio)succinate.

Anal. Calcd for $C_{19}H_{25}NO_6S$: C, 57.70; H, 6.37. Found: C, 57.67; H, 6.40.

The nmr spectrum displayed proton complexes characteristic of piperidine moieties centered at 2.50 ppm (four protons adjacent to nitrogen) and at 1.41 ppm (six protons of C-3 and C-4). Two mutually coupled doublets at 4.30 and 3.52 ppm (one proton each) were assigned to the methines. Three ester methyls at 3.65, 3.69, and 3.86 ppm and an aromatic complex at 7.0–8.0 ppm (four protons) were also in agreement with the assignment.

(17) K. V. Auwers, *Ann. Chem.*, **393**, 373 (1912).

Registry No.—**4**, 13134-72-0; **6a** maleate, 13134-73-1; **6a** fumarate, 13134-74-2; **6b** fumarate, 13134-75-3; **6c** fumarate, 13127-30-5; **6d** fumarate, 13127-31-6; **6e** fumarate, 13127-32-7; **7a**, 13134-76-4; **7b**, 13134-77-5; **7c**, 13134-78-6; dimethyl α-(1-piperidinyl)-α′-(2-carbomethoxyphenylthio)succinate, 13134-79-7.

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One-Step Synthesis of Fused Pyrimidinethiones from *o*-Aminonitriles and Thioamides

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Substituted quinazoline-4(3H)-thiones were prepared in one step from 2-aminobenzonitriles and aliphatic or aromatic thioamides in acetic acid–hydrogen bromide or N,N-dimethylformamide–hydrogen bromide solvent. Competing reaction between aminobenzonitrile and solvent leads to the formation of quinazolin-4(3H)-one side products. Cyclization of aminonitrile to quinazolinone is the major reaction in the acidic solvents in the absence of thioamide. Alcoholic solutions of quinazolinethiones spontaneously form diquinazolinyl disulfides.

Quinazoline-4(3H)-thiones, examples of fused-ring pyrimidinethiones, frequently have been prepared by multistage syntheses which often involve drastic conditions.[1] Among the more convenient preparations, however, are four one-step routes; each of these starts with a 2-aminobenzonitrile. The first of these is the most general preparation in that a variety of 2-substituted quinazoline-4(3H)-thiones may be synthesized when a mixture of an inorganic sulfide and an acid anhydride are employed as additional reactants.[2] Since the anhydride is encorporated into the 2 position of the heterocyclic ring during the cyclization, a change in the structure of this reactant provides a method for the preparation of a variety of substituted compounds. This method, however, is limited by the accessibility of the acid anhydrides. In a second approach, a thiol acid is employed to introduce sulfur into the aminonitrile and to act as the cyclizing agent.[2] A third synthesis utilizes ethyl orthoformate and inorganic sulfide to effect cyclization to quinazoline-4(3H)-thione unsubstituted at position 2.[3] When pyridine and carbon disulfide are employed in a fourth method of cyclizing 2-aminobenzonitriles, quinazoline-2,4(1H,3H)-dithiones are prepared.[4]

Our report deals with a new, one-step synthesis of quinazoline-4(3H)-thiones from 2-aminobenzonitriles.[5] This simple, convenient method may be employed for the preparation of quinazoline-4(3H)-thiones having a hydrogen, an aliphatic, or an aromatic group at C-2. Thioamides are employed to effect cyclization of the aminonitrile. In the preparation, reactants are heated in a strongly acidic solution and then concentrated; the residue is taken up in aqueous alkali and quinazolinethione is precipitated on acidification, Scheme I. The 2-aminobenzonitrile reactants employed in this study include those with a methoxyl group at C-4 (R_3) and a methoxyl, methyl, or nitro group at C-5 (R_2).

(1) For reviews of reactions, see (a) T. A. Williamson in "Heterocyclic Compounds," Vol. 6, R. C. Elderfield, Ed., John Wiley and Sons, Inc., New York, N. Y., 1957, pp 369–372; (b) W. L. F. Armarego, *Advan. Heterocyclic Chem.*, **1**, 253 (1963); (c) H. M. Blatter and H. Lukaszewski, *Tetrahedron Letters*, 855 (1964); (d) H. M. Blatter, H. Lukaszewski, and G. de Stevens, *J. Org. Chem.*, **30**, 1020 (1965).

(2) M. T. Bogert, H. C. Breneman, and W. F. Hand, *J. Am. Chem. Soc.*, **25**, 372 (1903).

(3) E. C. Taylor, A. McKillop, and S. Vromen, *Tetrahedron*, **23**, 885 (1967).

(4) E. C. Taylor, A. McKillop, and R. N. Warrener, *ibid.*, **23**, 891 (1967).

(5) For a preliminary account of this method, see E. C. Taylor and J. A. Zoltewicz, *J. Am. Chem. Soc.*, **83**, 248 (1961).