(80 g., "Alcoa F-20"). The column was washed with petroleum ether and 15-ml. fractions were collected. Each fraction was examined by infrared. The desired product (V) was detected in fractions 7–11, inclusive, free of starting material (I). These fractions were then distilled to yield 3.1 g., b.p. 72° at 11 mm., n_D^{25} 1.5229. Redistillation gave 1.04 g. of cyclohexylidenevinyl chloride (V), 86% pure by VPC, b.p. 72° at 11 mm., n_D^{25} 1.5235, d^{25} 1.025. The contaminents proved to be III (5.2%), II (1.4%), and VI (7.2%). Infrared bands (μ) at 3.40 (vs), 5.12 (vs), 6.93 (vs), 7.23 (s), 8.15 (vs), 10.28 (vs), 11.17 (s), 11.70 (s), 13.10–13.50 (vs), and 13.90–14.10 (vs). Notably significant are the bands at 5.12 and 13.10–13.50 μ, characteristic of the group $C{=}C{=}CHCl$.[5]

Anal.[9] Calcd. for $C_8H_{11}Cl$: Cl, 24.86. Found: Cl, 24.46. After redistillation, Cl found: 24.70.

Reaction of thionyl chloride with 1-ethynylcyclohexanol in pyridine. The procedure is essentially that of Hurd and Jones.[4] Purified[12] thionyl chloride (108 g., 0.9 mole) was added dropwise to a stirred mixture of 99 g. (0.81 mole) of 1-ethynylcyclohexanol and 78 g. (0.99 mole) of dry pyridine at 50–60°. After addition was complete the mixture was heated at 50–60° for 3 hr. and then cooled to room temperature. Water and petroleum ether (100 ml. of each) were added and the organic layer was separated. After washing and drying with anhydrous potassium carbonate, distillation gave 72 g., b.p. 39–75° at 12 mm., n_D^{25} 1.5178. Analysis of the total distillate by VPC (see Table I, line 1) showed that it contained 0.86 g. of recovered I, 5.98 g. of II, 4.04 g. of III, 7.14 g. of VI, and 54.0 g. (47% yield) of 1-(α-chlorovinyl)cyclohexene (IV).

Reaction of thionyl chloride with 1-ethynylcyclohexanol in ether. The procedure is essentially that of Bhatia, Landor, and Landor.[5] A solution of 37.2 g. (0.3 mole) of ethynylcyclohexanol and 39.3 g. (0.33 mole) of purified[12] thionyl chloride in 300 ml. of anhydrous ether was stirred for 1 hr. Most of the ether was then removed by distillation and the residue was heated on the steam bath for 3 hr. After cooling, the mixture was stirred with 100 ml. of saturated sodium bicarbonate solution, dried with anhydrous potassium carbonate, and distilled to give 30 g. of crude product, b.p. 34–82° at 11 mm., n_D^{25} 1.4992. Analysis of the total distillate by VPC (see Table I, line 4) indicated the composition to be 9.27 g. of I, 1.92 g. of II, 5.40 g. of III, 3.93 g. of VI, and 9.45 g. of a mixture of IV and V. The infrared spectrum revealed absorption bands for each of these substances.

Acknowledgment. The authors express their thanks to Air Reduction Company, New York, for generous gifts of 1-ethynylcyclohexanol and to the Dow Chemical Company, Midland, Michigan, for financial assistance. The gas chromatography unit used in this work was acquired under National Science Foundation Grant G-4058.

NOTRE DAME, IND.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, FACULTY OF SCIENCE, A'IN SHAMS UNIVERSITY]

Studies on 3-Acylcatechols. II.[1] A New Synthesis of 8-Hydroxyflavone

W. I. AWAD, M. F. EL-NEWEIHY, AND S. F. SELIM

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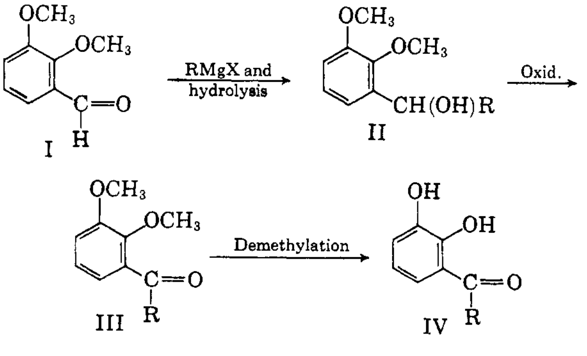
Some 3-acylcatechols are synthesized by an orthodox method. Their infrared spectra are recorded. 2,3-Dihydroxyacetophenone is utilized in the preparation of some chalcones, flavanones, and 8-hydroxyflavone. The latter has also been prepared *via* Claisen condensation of 2,3-dimethoxyacetophenone with ethyl benzoate followed by demethylation and cyclization.

In a previous publication,[1] we used the method described by Krannichfeldt,[2] for the preparation of some 3-acylcatechols[2], according to the following scheme:



In the present work we have prepared 2,3-dihydroxyisovalerophenone (IV. R = —$CH_2CH(CH_3)_2$) 2,3-dihydroxybenzophenone (IV. R = C_6H_5), 2,3,4′-trihydroxybenzophenone (IV. R = p-OHC_6H_4), and 2,3-dihydroxy-4′-chlorobenzophenone (IV. R = p-ClC_6H_4). The first of these compounds (m.p. 48°) is not identical with that reported by Miller, Hartung, Rock, and Crossley[3] (m.p. 93–95°) which they obtained as a by-product of a Fries rearrangement. The structure of our product cannot be questioned on account of the unambiguous method used in its preparation. Furthermore, our product gives a green color with ferric chloride that changes to red by the addition of sodium carbonate solution, a characteristic color test for catechols.[4,5] Moreover, the infrared data (*inter alia*) provides additional proof for the structure of 3-acylcatechols described here. The second

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[1] W. I. Awad, M. F. El-Neweihy, and S. F. Selim, *J. Org. Chem.* **23,** 1783 (1958).

[2] H. V. Krannchfeldt, *Ber.,* **46,** 4017-4018 (1913).

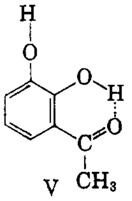
[3] Ellis Miller, Walter H. Hartung, Henry J. Rock and Frank S. Crossley, *J. Am. Chem. Soc.,* **60,** 7 (1938).

[4] Compare Paul Karrer, *Organic Chemistry,* Fourth English Edition, Elsevier Publ. Co., Inc., New York, N. Y., p. 435.

[5] A. Schönberg, W. I. Awad, and G. A. Mousa, *J. Am. Chem. Soc.,* **77,** 3850 (1955).

and third compounds have been prepared by Baker, *et al.*[6]

A comparative study of the infrared spectra of these acylcatechols has been carried out (*c.f.* Table I). 2,3-Dihydroxyacetophenone (IV. R = $-CH_3$) shows in solution a free OH stretching frequency (at 3717 cm.$^{-1}$) and a chelated OH stretching frequency (at 3106 cm.$^{-1}$). It has been previously[7] stated that this compound shows no free OH stretching frequency in the solid state, which led to the conclusion that it exhibits double chelation like that observed with 1,2-dihydroxy-3-aceto-4-cyanonaphthalene.[7] The present measurements show that this conclusion does not hold for 2,3-dihydroxyacetophenone, which in the solid state must possess an intramolecular and intermolecular hydrogen bridge,[8] the latter being destroyed in solution (*cf.* V).



V

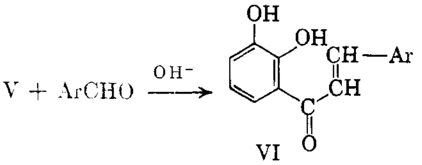
TABLE I[a]

INFRARED SPECTRA OF SOME ACYLCATECHOLS

Name of Compound	Stretching Frequency cm.$^{-1}$ Free OH	Chelated OH	Chelated C=O
2,3-Dihydroxyacetophenone[b]	3717	3106	1633
2,3-Dihydroxypropiophenone[c]	3759	3096	1656
2,3-Dihydroxy-*n*-butyrophenone[c]	3623	3333	1637
2,3-Dihydroxyisovalerophenone[d]	3703	3174	1647
2,3-Dihydroxybenzophenone[d]	3703	3174	1647
2,3-Dihydroxy-4′-chlorobenzophenone[d]	3583	3096	1619

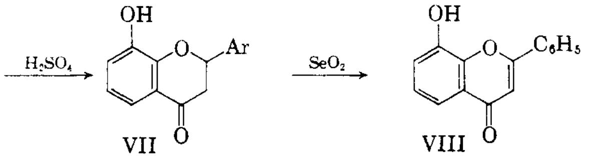
[a] The infrared measurements are carried out in carbon tetrachloride solution using Perkin Elmer Infracord model 137. Cell thickness 1 mm. [b] See ref. 2. [c] See ref. 1. [d] Prepared in this publication.

2,3-Dihydroxyacetophenone has been utilized to prepare some 8-hydroxyflavanones and 8-hydroxyflavones by known method,[9] according to the following scheme:



VI

VIa. Ar = C_6H_5
VIb. Ar = p-$CH_3OC_6H_4$
VIc. Ar = p-ClC_6H_4

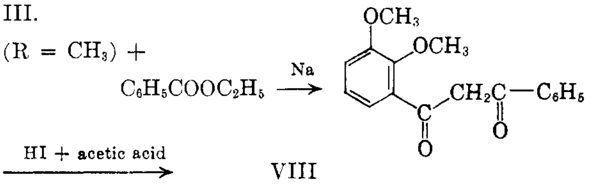


VII VIII

VIIa. Ar = C_6H_5
VIIb. Ar = p-$CH_3OC_6H_4$
VIIc. Ar = p-ClC_6H_4

VIII was prepared previously by Ruhemann[10] from β-(2-methoxyphenoxy)cinnamic acid and aluminium chloride in benzene, followed by demethylation of the product by hydriodic acid, a method which cannot be easily generalized for the preparation of 8-hydroxyflavones.

8-Hydroxyflavone (VIII) has also been prepared by the Claisen condensation of 2,3-dimethoxyacetophenone and ethyl benzoate in the presence of finely divided sodium metal followed by demethylation and cyclization using hydriodic acid and acetic acid according to the following scheme:



A study of the ultraviolet spectra of flavone and 8-hydroxyflavone (*cf.* Experimental) shows that they absorb at similar wave lengths but the molecular extinction coefficients of the latter are more pronounced in the first two maxima (hyperchrome effect).

EXPERIMENTAL

Microanalyses were carried out by Alfred Bernhardt, Max-Planck Institute; Mülheim (Ruhr), Germany. Melting points are not corrected.

Preparation of 2,3-dihydroxyisovalerophenone (IV. R= C_4H_9). a) *Action of isobutylmagnesium iodide on 2,3-dimethoxybenzaldehyde.* A solution of the aldehyde (I) (10 g.) in anhydrous ether was added dropwise to the isobutylmagnesium iodide (from 13.4 g. isobutyl iodide and 1.8 g. magnesium) while cooling in ice. When the addition was complete, the reaction mixture was treated as described previously[1] and the remaining oil distilled to give II (R = C_4H_9) as a pale-yellow oil b.p. 118–120°/0.5 mm., (yield 9.7 g.).

b) *Preparation of 2,3-dimethoxyisovalerophenone.* The previously described carbinol (9 g.) was added to a mixture of potassium dichromate (18 g.), water (90 ml.) and concd.

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(6) Wilson Baker and A. R. Smith, *J. Chem. Soc.*, 346–348 (1936).

(7) W. I. Awad and M. S. Hafez, *J. Am. Chem. Soc.*, **80**, 6057 (1958).

(8) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, First Edition, reprinted 1956, London Methuen Co., Ltd., p. 124.

(9) L. E. Fieser and M. Fieser, *Organic Chemistry*, 3rd edition D. C. Heath and Co., Boston, 1956, p. 822. This reference was added by one of the referees.

(10) Ruhemann, B., **46**, 2196 (1913). (*cf.* Beilst. **18** I, 323).

sulfuric acid (8.2 ml.). The reaction mixture was immediately steam-distilled, the distillate extracted with ether, dried (sodium sulfate), and then the ether driven off. III ($R = C_4H_9$) was obtained as a pale-yellow oil b.p. 130°/3 mm., (yield 5.3 g.).

c) *Demethylation of 2,3-dimethoxyisovalerophenone* (III. $R = C_4H_9$). The previously described ketone (III. $R = C_4H_9$) (6 g.) was refluxed with hydriodic acid (sp. gr. 1.71) (25 g.) and an equal volume of glacial acetic acid for 6 hr. The reaction mixture was worked out as described previously.[1] The viscous oil soon solidified on cooling and scratching. It was recrystallized from petroleum ether (b.p. 30–50°) as yellow flakes, m.p. 48°, (yield 4.6 g.). Miller, *et al.* gave m.p. 93–95°.

Anal. Calcd. for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27. Found: C, 68.23; H, 7.25. It gave bluish-green color with alcoholic ferric chloride solution which turned red by adding sodium carbonate solution.[4,5] It also gave a buff coloration with concd. sulfuric acid.

Preparation of 2,3-dihydroxy-4′-chlorobenzophenone (IV. $R = p\text{-}ClC_6H_4$). i) *Action of p-chlorophenylmagnesium bromide on 2,3-dimethoxybenzaldehyde.* A solution of the aldehyde (I) (10 g.) in anhydrous ether was added dropwise, to *p*-chlorophenylmagnesium bromide (from 13.8 g. *p*-chlorobromobenzene, and 1.8 g. magnesium) while cooling in ice. The reaction mixture was treated as in (a) and the carbinol (II. $R = p\text{-}ClC_6H_4$) was obtained as a viscous oil b.p. 220–225°/7–8 mm., (yield 18.1 g.).

Anal. Calcd. for $C_{15}H_{15}O_3Cl$: Cl, 12.71. Found: Cl, 12.22.

ii) *Preparation of 2,3-dimethoxy-4′-chlorobenzophenone.* (III. $R = p\text{-}ClC_6H_4$). The above carbinol (II. $R = p\text{-}ClC_6H_4$) (5 g.) was mixed with the dichromate solution [from potassium dichromate (10 g.), water (50 ml.) and sulfuric acid (4.8 ml.)]. The reaction mixture was treated as in (b). A lemon-yellow oil was obtained, (yield 4.2 g.); b.p. 130–132°/3 mm.

iii) *Demethylation of 2,3-dimethoxy-4′-chlorobenzophenone.* The above ketone (4 g.) was treated as in (c) to give 2,3-dihydroxy-4′-chlorobenzophenone (IV. $R = p\text{-}ClC_6H_4$) in dark-yellow long needles from petroleum ether (b.p. 60–80°) m.p. 115°, (yield 2.9 g.). It gave a dark-green color with alcoholic ferric chloride solution which turned red on adding sodium carbonate solution. It gave an orange-red color with concd. sulfuric acid.

Anal. Calcd. for $C_{13}H_9O_3Cl$: C, 62.78; H, 3.63; Cl, 14.24. Found: C, 62.86; H, 3.87; Cl, 13.96.

Preparation of 8-hydroxyflavone. a) *Preparation of the chalcone* (VIa). To a warm solution of 2,3-dihydroxyacetophenone[2] (IV. $R = CH_3$) (1 g.) and benzaldehyde (0.5 g.) in ethyl alcohol (12.5 ml.) was added dropwise a solution of sodium hydroxide (30%; 12.5 ml.). The reaction mixture was shaken vigorously for 10 to 15 min. and then diluted with ice-cold dilute acid. It was extracted with ether and the ethereal layer was washed with water, sodium bisulfite solution, and finally with water, dried (sodium sulfate), and the ether was driven off leaving reddish-brown material. This was triturated with a little methanol and filtered. It was recrystallized from ethyl alcohol m.p. 192°, (yield 0.6 g.). It gave no color with alcoholic ferric chloride solution. This proved to be the 8-hydroxyflavanone (VIIa) by melting and mixture melting point (see below).

The methanol mother-liquor contained the chalcone (VIa). It was treated with a little water and left for 48 hr. at 0° where red crystals separated. It was recrystallized from petroleum ether (b.p. 60–80°) as red needles, m.p. 151°, 0.4 g.). It gave a dark-green color with alcoholic ferric chloride solution which turned red by adding sodium carbonate solution.

Anal. Calcd. for $C_{15}H_{12}O_3$: C, 74.99; H, 5.03. Found: C, 75.28; H, 5.20.

Preparation of 8-hydroxyflavanone from the corresponding chalcone (VIa). The chalcone (0.2 g.) was dissolved in ethyl alcohol (15 ml.) and sulfuric acid was added. The reaction mixture was refluxed for 8 hr. on a water bath. On removal of the ethanol, a yellow crystalline substance was obtained. It was recrystallized from ethyl alcohol, m.p. 192°, (yield 0.16 g.).

Anal. Calcd. for $C_{15}H_{12}O_3$: C, 74.99; H, 5.03. Found: C, 75.25; H, 5.17.

c) *Oxidation of 8-hydroxyflavanone by selenium dioxide.* 8-Hydroxyflavanone (VIIa) (1 g.) was mixed with selenium dioxide (1 g.) and freshly distilled isoamyl alcohol (30 ml.). The reaction mixture was refluxed for 12 hr. on an oil bath (160–170°). After refluxing was complete, the reaction mixture was filtered while hot to remove selenium and the filtrate (dark-brown) was subjected to steam-distillation to remove isoamyl alcohol leaving an orange aqueous solution with a solid substance and a sticky mass. It was filtered, dissolved in benzene (charcoal), concentrated, and left to cool. An amorphous solid separated (yield 0.9 g.). It was sublimed to give colorless needles, m.p. 245°; (Ruhemann,[10] m.p. 249–250°). It gave no color with alcoholic ferric chloride solution, (yield 0.35 g.).

Ultraviolet measurements for VIII were: λ_{max} 211, mμ, ϵ_{max} 25,700; λ_{max} 267, ϵ_{max} 31,620; λ_{max} 300, ϵ_{max} 16,600. The ultraviolet measurements for flavone[11] were: λ_{max} 211 mμ, ϵ_{max} 18,840; λ_{max} 252, ϵ_{max} 19,140; λ_{max} 295, ϵ_{max} 24,024. Ultraviolet measurements were carried out in a Beckmann spectrophotometer model D.U. in ethyl alcohol.

Anal. Calcd. for $C_{15}H_{10}O_3$: C, 75.62; H, 4.23. Found: C, 74.97; H, 4.18.

Preparation of 8-hydroxy-4′-methoxyflavanone (VIIb). i) *Preparation of the chalcone* (VIb). To a warm solution of 2,3-dihydroxyacetophenone (1 g.) and *p*-anisaldehyde (0.5 g.) in ethyl alcohol (12.5 ml.) was added dropwise a solution of sodium hydroxide (30%, 12.5 ml.). The reaction mixture was treated as in (a). The methoxychalcone was recrystallized from petroleum ether (b.p. 60–80°) as reddish-brown crystals, m.p. 171°, (yield 0.7 g.). It gave a green color with alcoholic ferric chloride solution which turned red by adding sodium carbonate solution.

Anal. Calcd. for $C_{16}H_{14}O_4$: C, 71.11; H, 5.18. Found: C, 71.41; H, 5.38. ii) *Preparation of 8-hydroxy-4′-methoxyflavanone* (VIIb). The corresponding chalcone (VIb) (0.2 g.) was treated as in (b). The 8-hydroxy-4′-methoxyflavanone (VIIb) was recrystallized from petroleum ether (b.p. 60–80°) as fine yellow needles m.p. 183°, (yield 0.15 g.).

Anal. Calcd. for $C_{16}H_{14}O_4$: C, 71.11; H, 5.18. Found: C, 70.89; H, 5.33.

Preparation of 8-hydroxy-4′-chloroflavanone (VIIc). i) *Preparation of the chalcone* (VIc). To a warm solution of 2,3-dihydroxyacetophenone (1 g.) and *p*-chlorobenzaldehyde (0.5 g.) in ethyl alcohol (12.5 ml.) was added dropwise a solution of sodium hydroxide (30%, 12.5 ml.). The reaction mixture was treated as in (a). The chlorochalcone was recrystallized from petroleum ether (b.p. 60–80°) as brick-red needles, m.p. 141°, (yield 0.6 g.). It gave a red color with concd. sulfuric acid and a dirty green color with alcoholic ferric chloride solution which changed to red by adding sodium carbonate solution.

Anal. Calcd. for $C_{15}H_{11}O_3Cl$: C, 65.57; H, 4.01; Cl, 12.92. Found: C, 65.27; H, 4.35; Cl, 12.85.

ii) *Preparation of 8-hydroxy-4′-chloroflavanone* (VIIc). The corresponding chalcone (VIc) (0.2 g.) was treated as described in (b). The 8-hydroxy-4′-chloroflavanone (VIIc) was recrystallized from petroleum ether (b.p. 60–80°) as fine yellow needles, m.p. 178°, (yield 0.19 g.). It gave no color with alcoholic ferric chloride solution and an orange-red color with concd. sulfuric acid.

Anal. Calcd. for $C_{15}H_{11}O_3Cl$: C, 65.57; H, 4.01; Cl, 12.92 Found: C, 65.04; H, 3.98; Cl, 12.90.

Preparation of VIII *via the Claisen condensation.* 2,3-Dimethoxyacetophenone (5 g.) was mixed with ethyl

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(11) T. S. Wheeler, R. L. Shriner, and D. A. Scott, *Org. Syntheses*, **32**, 72 (1952).

benzoate (100 ml.) and finely divided sodium metal (5 g.). The reaction mixture was refluxed on an oil bath (180–200°) for 6 hr. The reaction mixture was then cooled and treated with methyl alcohol (10 ml.) to remove any unchanged sodium, acidified with acetic acid, and left overnight. It was steam-distilled until all the ethyl benzoate was removed and the reaction mixture assumed a yellow color. It was then extracted with ether and worked up as usual. The ether was driven off and a yellow oil was obtained, b.p. 220–225°/2 mm., (yield 8 g.).

The above condensation product (3 g.) was mixed with hydriodic acid (sp. gr. 1.71, 30 ml.) and glacial acetic acid (30 ml.). The reaction mixture was refluxed for 10 hr. It was then poured on ice, extracted with ether, and the ethereal layer was dried (sodium sulfate). The ether was driven off and the remaining oil was triturated with petroleum ether (b.p. 60–80°) until it solidified to an amorphous powder. It was sublimed to give VIII, m.p. 245°, (yield 2.2 g.).

Anal. Calcd. for $C_{15}H_{10}O_3$: C, 75.62; H, 4.23. Found: C, 75.28; H, 4.22.

ABBASSIA, CAIRO, U.A.R.

[CONTRIBUTION FROM THE ORGANIC CHEMICALS DIVISION, NITRO RESEARCH DEPARTMENT, MONSANTO CHEMICAL CO.]

Thiazolethiols and Their Derivatives

JOHN J. D'AMICO AND THOMAS W. BARTRAM

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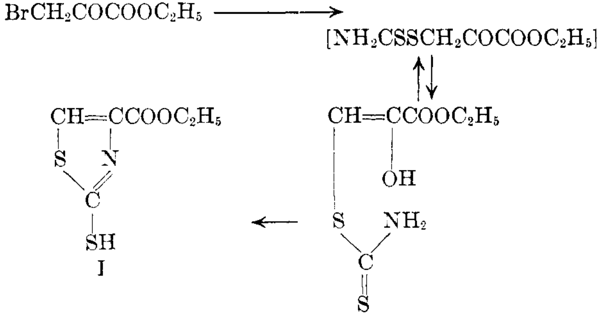
Ammonium dithiocarbamate and ethyl bromopyruvate reacted to give ethyl 2-mercapto-4-thiazolecarboxylate (I). Saponification of I gave 2-mercapto-4-thiazolecarboxylic acid. Thirty-four derivatives of I and related thiazolethiols were prepared. Oxidation of I, ethyl-2-mercapto-4-methyl-5-thiazolecarboxylate, or 2-mercapto-4-methyl-5-thiazolecarboxylic acid with hydrogen peroxide under acidic conditions gave the corresponding 4- or 5-substituted thiazoles.

Thiazolethiols and their derivatives have long been established as fundamentally important accelerators for the vlucanization of rubber with sulfur. Among the many derivatives prepared and screened, the thiazolesulfenamides, in particular, 2-(2,6-dimethylmorpholinothio)benzothiazole,[1] *N*-cyclohexyl-2-benzothiazolesulfenamide[2] and *N*-tert-butyl-2-benzothiazolesulfenamide,[3] have shown merit because of their delayed action. As thiazolethiols and their derivatives containing substituents, other than hydrocarbon radicals, in the 4-position have been prepared only in a limited number of examples,[4] it was desirable to prepare the unknown ethyl 2-mercapto-4-thiazolecarboxylate (I) and its derivatives. In addition, our objectives were: 1) the preparation of new derivatives of 5-substituted thiazolethiols and 2-mercaptobenzothiazole and 2) the synthesis of the 4- and 5-substituted thiazoles from the corresponding thiazolethiols. The accelerator activity for these new compounds will be reported in forthcoming patents.

Ammonium dithiocarbamate reacted with ethyl bromopyruvate to give I. The reaction may be represented as:



Saponification of I gave 2-mercapto-4-thiazolecarboxylic acid.

Diethyl 2,2′-dithiobis(4-thiazolecarboxylate) and 2,2′-dithiobis(4-thiazolecarboxylic acid) were prepared by the reaction of I or 2-mercapto-4-thiazolecarboxylic acid with an aqueous solution of ammonium persulfate.

The thiazolesulfenamides II, III, and IV were prepared by the oxidative condensation of I with *tert*-butylamine, cyclohexylamine, or morpholine.

The reaction of an aqueous solution of the sodium salt of I with zinc chloride or cadmium sulfate furnished the corresponding zinc and cadmium salt of I.

The reaction of an acetone solution of the potassium salt of I with β-dimethylaminoethyl chloride gave the desired ethyl 2-(2-dimethylaminoethylthio)-4-thiazolecarboxylate.

4-Ethoxycarbonyl-2-thiazolyl diethyldithiocarbamate was prepared by the reaction of the potassium salt of I with *N*,*N*-diethylthiocarbamoyl chloride.

The reaction of the potassium salt of I with 3-chloro-2,4-pentanedione, ethyl α-chloroacetoacetate, or chloroacetone gave ethyl 2-(1-acetyl acetonylthio)-4-thiazolecarboxylate (V), ethyl 2-(1-ethoxycarbonylacetonylthio)-4-thiazolecarboxylate (VI), and ethyl 2-acetonylthio-4-thiazolecarboxylate (VI), and ethyl 2-acetonylthio-4-thiazolecarboxylate (VII), respectively.

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(1) J. J. D'Amico, M. W. Harman, and R. H. Cooper, *J. Am. Chem. Soc.*, **79**, 5270 (1957); U. S. Patent **2,871,239**.

(2) M. W. Harman, *Ind. Eng. Chem.* **29**, 205 (1937); U. S. Patent **2,191,656**.

(3) R. H. Cooper and J. J. D'Amico, U. S. Patent **2,807,620**.

(4) J. J. D'Amico, *J. Am. Chem. Soc.*, **77**, 476 (1955).