[Contribution No. 688 from the Chemistry Laboratories of Indiana University]

Preparation and Absorption Spectra of Some β-Aryl-α-Mercaptoacrylic Acids and Related Disulfides[1, 2]

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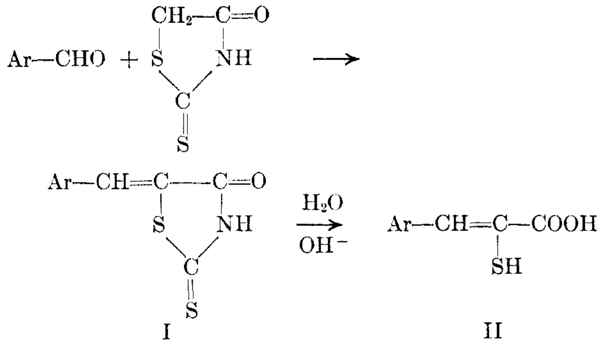
A series of seven 5-(arylmethylene)rhodanines, including the 1- and 2-naphthylidene derivatives not previously reported, have been prepared and hydrolyzed in dilute base to their respective β-aryl-α-mercaptoacrylic acids. The properties of these acids, including the new 1- and 2-naphthyl and 3-thienyl compounds, are reported. Each of the α-mercaptoacrylic acids was oxidized to its respective disulfide with iodine or benzoyl peroxide.

The principal peaks in the ultraviolet absorption spectra of both the β-aryl-α-mercaptoacrylic acids and the derived α,α'-dithiobis(β-arylacrylic) acids are reported. The close similarity in wave length, and intensity of the spectral peaks of the α-mercaptoacids, their disulfides and sulfides, indicate that the compounds are correctly represented as ene-thiols rather than thiones.

The hypsochromic shift observed when the α-mercaptoacids are converted to disulfides indicates that the disulfide link provides little, if any, additional conjugation to the system. The bathochromic spectral shifts observed when the α-mercaptoacrylic acids were dissolved in base are compared to the hypsochromic shifts observed when the corresponding disulfides and sulfides were similarly treated. These shifts are explained in terms of ionization of the carboxyl and thiol groups.

In connection with another problem,[5] it was necessary to prepare some α-mercaptoacrylic acids with unsaturated or aromatic groups in the *beta*-position, and to convert them to their respective disulfides. The most convenient sources of β-aryl-α-mercaptoacrylic acids are 5-(arylmethylene)rhodanines (I), which are obtained in excellent yield by condensation of the aromatic aldehydes with rhodanine, and can be hydrolyzed in alkaline solution to produce the desired unsaturated acids (II). Julian and Sturgis[6] have provided adequate directions for this sequence of reactions, and the properties of the α-mercaptoacids have been reviewed.[7]



The derivatives of type I are listed in Table I. With the exception of the naphthaldehyde derivatives they are not new, but some improvement in melting point was obtained for some of the compounds. The low yield of 5-(2-naphthylidene)rhodanine was expected, since it has been pointed out[8] that 2-naphthaldehyde gives a poorer yield of Perkin condensation products than does 1-naphthaldehyde.

The hydrolysis of 5-(arylmethylene)rhodanines is known to lead to amorphous products which are difficult to crystallize.[9] This is understandable in view of the fact that under the vigorous conditions usually used (15% sodium hydroxide at 100° for one-half hour) some reversal of the Perkin condensation may take place, as is shown by the distinct odor of the aromatic aldehydes which accompanies these hydrolyses. Furthermore, Granacher[10] has shown that α-mercaptocinnamic acid was completely hydrolyzed to phenylpyruvic acid in boiling ammonium hydroxide. The strong odor of hydrogen sulfide which arises when the alkaline hydrolysate is neutralized shows that this reaction has also occurred. The β-aryl-α-mercaptoacrylic acids themselves are capable of existing in several tautomeric and polymeric forms (see below). Indeed, Crowe and Nord[11] were unable to obtain satisfactory melting points for a series of β-2-thienyl-α-mercaptoacrylic acids prepared by this method, although analyses were satisfactory. They attribute the non-homogeneity of their products to the presence of tautomeric forms. The variety of melting points reported for the different products in Table II attests the difficulty of this preparation.

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(2) Taken in part from the thesis of Richard E. Cline, presented in partial fulfillment of the requirements for the degree Doctor of Philosophy at Indiana University, June, 1951. A portion of this work was presented before the Organic Division of the American Chemical Society at the 123rd meeting, Los Angeles, 1953.

(3) This author wishes to thank the Chemistry Department of the University of California at Los Angeles for the use of their excellent facilities during the completion of this work.

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(5) Campaigne and Cline, *J. Org. Chem.*, **21**, 39 (1956).

(6) Julian and Sturgis, *J. Am. Chem. Soc.*, **57**, 1126 (1935).

(7) Campaigne, *Chem. Revs.*, **39**, 20–22 (1946).

(8) Johnson, *Org. Reactions*, **1**, 220 (1942).

(9) Granacher, Gero, Ofner, Klopfenstein, and Schlatter, *Helv. Chim. Acta*, **6**, 458 (1923).

(10) Granacher, *Helv. Chim. Acta*, **5**, 610 (1922).

(11) Crowe and Nord, *J. Org. Chem.*, **15**, 81 (1950).

TABLE I

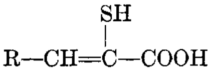
PROPERTIES OF THE 5-(ARYLMETHYLENE)RHODANINES

	Yield,[a]	M.P., °C.				Analyses N	
Prepared from	%	Found[b]	Lit.	Ref.	Formula	Calc'd	Found
Benzaldehyde	90	204–205	200	(10)	$C_{10}H_7NOS_2$	6.33	6.44
Cinnamaldehyde	91	223–224	220–221	(12)	$C_{12}H_9NOS_2$	5.66	5.79
			208–211	(13)			
Veratraldehyde	93	231–232	232	(6)	$C_{12}H_{11}NO_3S_2$	4.98	4.76
1-Naphthaldehyde	90	224–225			$C_{14}H_9NOS_2$	5.16	5.33
2-Naphthaldehyde	37	269–270			$C_{14}H_9NOS_2$	5.16	5.40
2-Furaldehyde	97	232–233	229–231	(14)	$C_8H_5NO_2S_2$	6.63	6.62
3-Thenaldehyde	93	213–214	212–213	(15)	$C_8H_5NOS_3$	6.17	6.05

[a] Crude product. [b] Uncorrected.

TABLE II

PROPERTIES OF THE β-ARYL-α-MERCAPTOACRYLIC ACIDS



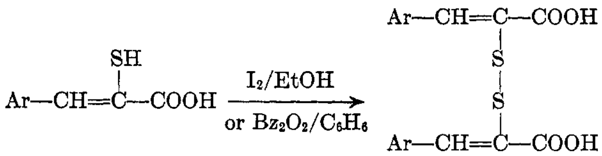
$R{-}CH{=}\overset{\overset{\displaystyle SH}{|}}{C}{-}COOH$

	Yield,[a]	M.p., °C.				Analyses S	
R	%	Found[b]	Lit.	Ref.	Formula	Calc'd	Found
Phenyl	83	133–134	125–129	(10)	$C_9H_8O_2S$	17.78	17.53
			115, 129	(16)			
Styryl	90	148–151	149	(13)	$C_{11}H_{10}O_2S$	15.54	15.51
Veratryl	61	171–172	182	(16)	$C_{11}H_{12}O_4S$	13.34	13.10
			179	(6)			
1-Naphthyl	76	177–178			$C_{13}H_{10}O_2S$[c]	13.92	13.93
2-Naphthyl	81	168–169			$C_{13}H_{10}O_2S$[d]	13.92	14.00
2-Furyl	89	115–117	114–115	(14)	$C_7H_6O_3S$	18.83	18.97
			110, 113	(16)			
			102	(17)			
3-Thienyl	70	157–158			$C_7H_6O_2S_2$[e]	34.44	34.50

[a] Crude product. [b] Uncorrected. [c] *Anal.* Calc'd: C, 67.74; H, 4.38. Found: C, 67.71; H, 4.45. [d] *Anal.* Calc'd: C, 67.74; H 4.38. Found: C, 67.80; H, 4.40. [e] *Anal.* Calc'd: C, 45.15; H, 3.24. Found: C, 45.91; H, 3.43.

α-Mercaptocinnamic acid was converted to α,α′-dithiobicinnamic acid (III, Ar = C_6H_5) by Bondzynski,[18] using iodine in moist carbon disulfide. Andreasch[17] was able to isolate 2,2′-dithiobis(3-α-furylacrylic) acid (III, Ar = *2*-C_4H_3O) by oxidation of β-2-furyl-α-mercaptoacrylic acid with iodine in alcohol. A product melting about 300° with decomposition was obtained on hydrolysis of 5-veratrylidenerhodanine which analyzed correctly for the disulfide [III, Ar = *3,4*-$(CH_3O)_2C_6H_3$] by Libermann, Himbert, and Hengl.[16] Reduction of this product produced the known β-veratryl-α-mercaptoacrylic acid, and therefore it was assigned the disulfide structure. However, the properties of this disulfide, reported in Table III, indicate that this product was something other than the disulfide.

Oxidation of the α-mercaptoacrylic acids by iodine in alcohol appeared to be the simplest method for preparing the desired disulfides. Experiment showed that satisfactory yields could be obtained in this way, provided no excess iodine was used. 5-Phenyl-2-mercapto-2,4-pentadienoic acid (II, Ar = $C_6H_5CH{=}CH{-}$) was exceptional, in that iodine in alcohol gave only tars. In the presence of strong acids or excess iodine, the disulfides reacted to form other products.[5] It was therefore desirable to use milder oxidizing conditions. Benzoyl peroxide in benzene at room temperature for seven to ten days in the dark produced very pure disulfides directly. The possibility of complicating free-radical addition or decomposition of the peroxide in other ways was ruled out by showing that benzoic acid was produced in roughly stoichiometric proportions to the mercaptan present. The properties of the various disulfides are reported in Table III.



$$\underset{\text{II}}{Ar{-}CH{=}\overset{\overset{\displaystyle SH}{|}}{C}{-}COOH} \xrightarrow[\text{or } Bz_2O_2/C_6H_6]{I_2/EtOH} \underset{\text{III}}{\begin{array}{c} Ar{-}CH{=}C{-}COOH \\ | \\ S \\ | \\ S \\ | \\ Ar{-}CH{=}C{-}COOH \end{array}}$$

Previous investigators have always classified the products of the alkaline hydrolysis of 5-(arylmethylene)rhodanines as thiopyruvic acids (IV),

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(12) Bargellini, *Gazz. chim. ital.*, **36**, II, 140; *Chem. Zent.*, II, 962 (1906).

(13) Zipser, *Monatsh.*, **23**, 958 (1902).

(14) Plucker and Amstutz, *J. Am. Chem. Soc.*, **62**, 1512 (1940).

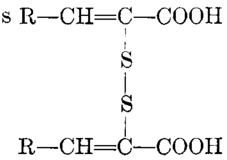
(15) Campaigne and LeSuer, *J. Am. Chem. Soc.*, **70**, 1555 (1948).

(16) Libermann, Himbert, and Hengl, *Bull. soc. chim.*, **15**, 1120 (1948).

(17) Andreasch, *Monatsh.*, **39**, 419 (1918).

TABLE III

PROPERTIES OF THE 2,2'-DITHIOBIS(3-ARYLACRYLIC) ACIDS

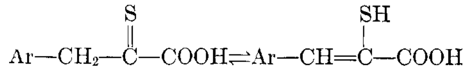


$$\mathrm{\underset{\underset{\underset{\underset{R{-}CH{=}C{-}COOH}{|}}{S}}{|}}{S}}{\overset{}{R{-}CH{=}\overset{}{C}{-}COOH}}}$$

R	Yield,[a] %	M.P., °C.		Ref.	Formula	Analyses S	
		Found[b]	Lit.			Calc'd	Found
Phenyl	62[c] 87[d]	186–187	179	(18)	$C_{18}H_{14}O_4S_2$	17.89	17.91
Styryl	58[d]	184–185			$C_{22}H_{18}O_4S_2$	15.62	15.68
Veratryl	75[d] 84[c]	206–207	300	(16)	$C_{22}H_{22}O_8S_2$	13.40	13.21
1-Naphthyl	66[c]	223–224			$C_{26}H_{18}O_4S_2$	13.98	13.78
2-Naphthyl	71[c]	214–215			$C_{26}H_{18}O_4S_2$	13.98	14.04
2-Furyl	75[c]	195–196	190–191	(17)	$C_{14}H_{10}O_6S_2$	18.95	18.98
3-Thienyl	49[c]	206–207			$C_{14}H_{10}O_4S_4$	34.61	34.32

[a] Crude product. [b] Uncorrected. [c] Oxidation by iodine in ethanol. [d] Oxidation by benzoyl peroxide in dry benzene.

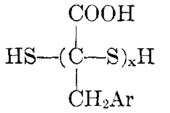
although they are usually regarded as in equilibrium with their ene-thiol forms in solution.[7] There



$$\mathrm{Ar{-}CH_2{-}\overset{\overset{S}{\|}}{C}{-}COOH \rightleftharpoons Ar{-}CH{=}\overset{\overset{SH}{|}}{C}{-}COOH}$$

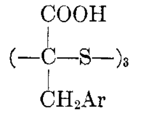
IV II

is little evidence for the existence of aliphatic thione forms such as IV. Granacher[10] claimed phenylthiopyruvic acid (IV, Ar = C_6H_5) existed because it gave the same oxime and phenylhydrazone as did phenylpyruvic acid. Such ketone derivatives may arise, however, from only a trace of the thione present in solution, or conceivably even directly from the ene-thiol, II. The isolation of amorphous, non-homogeneous products has also been regarded as evidence of the presence of tautomeric forms.[11] The known tendency of aliphatic thiones to polymerize or trimerize, however, would indicate that such forms as V or VI are the more likely impurities in these cases, even though such forms have not been isolated. The instability of the products render molecular weight determinations unsatisfactory.



$$\mathrm{HS{-}(\underset{\underset{CH_2Ar}{|}}{\overset{\overset{COOH}{|}}{C}}{-}S)_xH}$$

V



$$\mathrm{({-}\underset{\underset{CH_2Ar}{|}}{\overset{\overset{COOH}{|}}{C}}{-}S{-})_3}$$

VI

On the other hand, the chemical and physical properties of these products are quite consistent with structure II. For example, Zipser[13] found that they were easily alkylated with benzyl chloride to form the benzyl sulfides. We found that reaction of representative α-mercaptoacrylic acids with 2,4-dinitrochlorobenzene or ethyl iodide in alkaline solution gave nearly quantitative yields of the respective sulfides. The ready conversion to disulfides also indicates the thiol structure. Compounds in which the thione group is unequivocally present are known to be intensely colored.[7] This apparently is true even in aliphatic thiones, since di-*tert*-butyl thione was a deep red oil.[19] However, the so-called α-thiopyruvic acids are yellow or orange in color. Mercaptans characteristically give a red color in the nitroprusside test, and ene-thiols, like enols, give blue or green colors with dilute ferric chloride. Maimind and Berlin[20] reported that dimethyl-α-thiopyruvic acid gave a red color with nitroprusside and a blue color with ferric chloride.

Grote[21] describes a specially prepared nitroprusside reagent which he claimed would distinguish between thiol and thione forms, the first giving a red color and the second a green or blue color. The reagent also was reported to give a pink to purple color after about one-half hour with disulfides, although aromatic disulfides failed to react. Application of this color test to all of the thiols and disulfides listed in Tables II and III gave the following results. All the α-mercaptoacrylic acids gave green colors immediately. The disulfides failed to show any distinct color changes. These results might be interpreted in favor of structure IV for the compounds in Table II, except that Grote lists no unequivocal examples of thiones which give this test, whereas some of the compounds which do give it, such as thiourea and thioacetic acid, are undoubtedly ene-thiols. Ferric chloride also gave blue-green colors with the compounds in Table II.

It is apparent from the foregoing discussion that evidence for either structure II or IV is inconclusive. More information on the structure of the products listed in Tables II and III would be useful. In the equilibrium system, II ⇌ IV, structure II contains a carboxyl group conjugated to an aro-

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(18) Bondzynski, *Monatsh.*, **8**, 349 (1887).

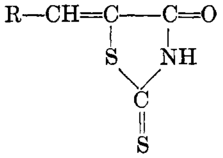
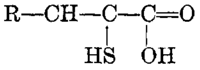
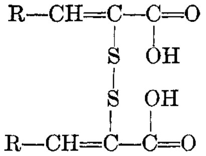
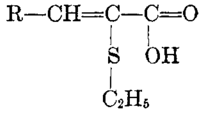
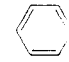
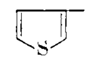
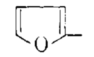
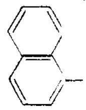
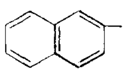
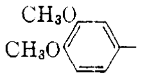
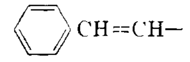
(19) Kretov and Komissarov, *J. Gen. Chem., U.S.S.R.*, **5**, 388 (1935).

(20) Maimind and Berlin, *J. Gen. Chem., U.S.S.R.*, **20**, 1628 (1950).

(21) Grote, *J. Biol. Chem.*, **93**, 25 (1931).

TABLE IV

ULTRAVIOLET ABSORPTION MAXIMA AND LOG MOLAR EXTINCTION COEFFICIENTS OF 5-(ARYLMETHYLENE)RHODANINES, α-MERCAPTOACRYLIC ACIDS, 2,2′-DITHIOBIS(3-ARYLACRYLIC) ACIDS AND 3-ARYL-2-ETHYLTHIOACRYLIC ACIDS IN 95% ETHANOL (OR 0.5 N SODIUM BICARBONATE)

R								
	$\lambda_{max.}^{m\mu}$	log ε	$\lambda_{max.}^{m\mu}$	log ε	$\lambda_{max.}^{m\mu}$	log ε	$\lambda_{max.}^{m\mu}$	log ε
	236	3.93	227	3.94	231^{a}	4.25		
			(240^{a}	4.05)^{b}	(c)^{b}			
	272	3.94						
	374	4.52	310	4.16	285	4.37		
			(325	4.08)^{b}	(275	4.32)^{b}		
			239	3.95	242^{a}	4.17		
			310	4.09	293	4.35		
			224	3.67	^{c}			
			(249^{a}	4.00)^{b}				
			324	4.25	318	4.41		
			(335	4.32)^{b}				
	213	4.58						
	267	3.96	223^{a}	4.44	220	4.90		
	292	3.89	275	3.66	260^{a}	4.25		
	390	4.41	327	4.02	327	4.19		
			225	4.47	220^{a}	4.68		
			(230^{a}	4.59)^{b}	(c)^{b}			
			273	4.17	268	4.61		
			(278	4.06)^{b}	(262	4.57)^{b}	(260	4.28)^{b}
			327	4.27	314	4.45		
			(344	4.18)^{b}	(310	4.28)^{b}	(313	4.13)^{b}
	260	3.92	238^{a}	3.95	239^{a}	4.32	^{c}	
			(c)^{b}		(c)^{b}		(c)^{b}	
			((253	4.00))^{d}				
	288	3.93						
	400	4.53	327	4.23	335	4.31	330	4.18
			(335	4.15)^{b}	(318	4.30)^{b}	(308	4.15)^{b}
			((370	4.25))^{d}				
			238	3.92	238	4.30		
			340	4.34	325	4.75		

[a] Shoulder. [b] Determination in 0.5 N sodium carbonate. [c] Strong absorption below 250 mμ, but no obvious peaks or shoulders. [d] Determination in 5% sodium hydroxide.

matic system, whereas this conjugation is lost in structure IV. It was felt that ultraviolet absorption spectra of these compounds would be strongly influenced by the presence or absence of this conjugation and thus provide some insight into the molecular structure.

DISCUSSION OF ABSORPTION SPECTRA

The ultraviolet absorption spectra of the β-aryl-α-mercaptoacrylic acids and 2,2′-dithiobis(3-arylacrylic) acids reported in Tables II and III were determined on freshly prepared solutions in ethanol or 0.5 N sodium carbonate solutions, at concentrations of approximately 0.1 mmol/l. using a Beckman model DU quartz spectrophotometer equipped with a hydrogen discharge tube and 1-cm. quartz cells. It was necessary to carry out the measurements as soon as possible after preparing the solutions, since marked changes in the spectra occurred on standing, especially in alkaline solution. For purposes of comparison, spectra of several of the 5-(arylmethylene)rhodanines and the two β-aryl-α-ethylmercaptoacrylic acids were also determined. The important maxima of all spectra are tabulated in Table IV.

It is apparent from the values presented in the table that the spectra are all closely related, and represent the characteristic absorption of the conjugated system, $\mathrm{Ar{-}CH{=}\underset{\underset{S-}{|}}{C}{-}\underset{|}{C}{=}O}$. Since the 5-arylidenerhodanines generally are more intensely colored than are the derived acids, they absorb at longer wave-lengths, and show an additional peak at about 272–292 mμ. The absorption in the near ultraviolet of the 5-(arylmethylene)rhodanines may be attributed to conjugation of the aromatic group to rhodanine by an exocyclic double bond.[22]

Two characteristic strong bands are shown by the β-aryl-α-mercaptoacrylic acids, one in the range 310–340 mμ, and the other at about 223–238 mμ. An interesting bathochromic shift is apparent in the 310–340 band, as the nature of the β-aryl group changes from highly aromatic, as in phenyl and thienyl, to the styryl analog. Increased conjugation would account for this shift.[23] The two naphthyl derivatives exhibit a third peak at 274 ± 1 mμ, not found in the other derivatives. This band is undoubtedly due to naphthalene absorption found in this region, which is relatively intense (log ϵ 4). The benzene absorption in the vicinity of 250 mμ, being weaker (log ϵ 2), is obscured by the stronger absorption of the α,β-unsaturated carbonyl system.

The 2,2′-dithiobis(3-arylacrylic) acids also have two characteristic peaks at about the same wavelengths as the β-aryl-α-mercaptoacrylic acids. The band at about 300 mμ exhibits the same correlation, roughly, with the nature of the aryl group, showing a bathochromic shift from phenyl (λ_{max} 285 mμ) to styryl (λ_{max} 325 mμ). The peaks at shorter wavelengths (220–242 mμ) correlate very closely with the peaks shown by the mercaptoacids, not differing by more than ± 5 mμ in any case, but always more intense. The two naphthyl derivatives again show a third peak, this time shifted toward shorter wavelengths.

The spectra of all the compounds measured show strong absorption in the far ultraviolet (below 210 mμ). This phenomenon is characteristic of aromatic compounds, carbonyl derivatives and sulfides, all functions present in the molecular species being examined.

The absorption characteristics of these substances are quite in accord with the predicted curves for β-arylacrylic acids containing an α-sulfur atom. Bowden, Braude, and Jones[23] have pointed out that addition of an unsaturated atom to an unsaturated system causes a bathochromic shift ($S > O$). Cinnamic acid has a strong band at 275 mμ,[24] and α-hydroxycinnamic acid a similar band at 285 mμ.[25] The absorption band at 310 mμ for α-mercaptocinnamic acid falls in the range predicted for the addition of —SH to the cinnamic acid system ($+\Delta\lambda$ of 33–75 mμ).[23] $\Delta\lambda$ has the smaller value because the α-SH is in effect a "crossed" conjugation. Bowden, Braude, and Jones[23] also predicted that RS— has a slightly greater bathochromic effect than —SH, which is confirmed by the value of 330 mμ for β-veratryl-α-ethylmercaptoacrylic acid, as compared to 327 mμ for β-veratryl-α-mercaptoacrylic acid.

The hypsochromic effect of converting the thiol group to disulfide, shown in all but one case, is somewhat surprising. The absence of a band at about 250 mμ characteristic of disulfides,[26] would be expected, since it is a weak band (log ϵ 2.6) and would be masked by the more intense absorption of the conjugated system being measured (log $\epsilon > 4.0$). It would seem reasonable to assume that cross-linking two conjugated systems by a disulfide bond would tend to increase conjugation, and therefore cause a bathochromic shift in the spectrum. The effect actually observed is in the opposite direction, and partially corresponds to cross-linking two identical chromophores (the α-thiocinnamic acids) by an insulating group, *i.e.*, doubling the intensity with no shift in maxima. For example, compare the absorption at 310 mμ for α-mercaptocinnamic acid (ϵ 14,500) with the band at 285 for its disulfide (ϵ 23,500). In the 2-naphthyl derivatives, compare the peak at 260 mμ (ϵ 19,000) for the ethylthio derivative with that at 262 (ϵ 37,300) for the disulfide. That the disulfide bond is not a pure insulator is indicated by the fact that there is some shift of absorption maxima, and although always higher, the intensities are usually less than double the value for the related mercaptan or alkylthio derivative.

The strong absorption of the α-mercaptoacids in the range of 310–340 mμ, and the close similarity in the curves of the respective disulfides, indicate that the α-mercaptoacrylic acids are present chiefly in that form, with little, if any, thione form in the fresh solutions. This is confirmed by the very nearly congruent curves of β-veratryl-α-mercaptoacrylic acid (λ_{max} 327 mμ, log ϵ 4.23) and β-veratryl-α-ethylmercaptoacrylic acid (λ_{max} 330 mμ, log ϵ 4.18).

The shifts in absorption spectra observed when the various sulfur-substituted acrylic acids were measured in alkaline solution are significant, and provide a satisfactory test for distinguishing mercaptan from disulfide in this series. Although ionization of the mercapto group was probably incomplete in 0.5 *N* sodium carbonate, the fact that stronger base could not be used was illustrated by one experiment, in which β-veratryl-α-mercaptoacrylic acid was measured in 5% sodium hydroxide. Decomposition was more rapid, making the determination less reliable, and it was apparent that in this strong base the peaks had shifted farther toward the red, indicating that new chromophores had appeared.

For all of the mercaptoacids measured, solution in 0.5 *N* sodium carbonate caused a bathochromic shift of all peaks from 5–25 mμ, whereas similar treatment of the disulfide acids caused a hypsochromic shift of 4–17 mμ. The two α-ethylmercaptoacids correspond quite closely to their related disulfides in this respect, showing a hypsochromic shift. These shifts are readily explained in terms of ionization of the carboxyl and mercapto groups. It

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[22] *Cf.* Woodward, *J. Am. Chem. Soc.*, **64**, 76 (1942).

[23] Bowden, Braude, and Jones, *J. Chem. Soc.*, 948 (1946).

[24] Bodforss, *Ann.*, **534**, 235 (1938).

[25] Boe and Gex, *Compt. rend.*, **204**, 770 (1937).

[26] Baer and Carmack, *J. Am. Chem. Soc.*, **71**, 1215 (1949).

is well known that conversion of a carboxylic acid to a carboxylate ion causes a small hypsochromic shift in the spectrum. For example, cinnamic acid (λ_{max} 275 mμ) in alkaline solution absorbs at 265 mμ[24] a $\Delta\lambda$ of -10 mμ. Therefore, hypsochromic shifts of 4–22 mμ observed when the sulfide and disulfide acids are dissolved in base are quite reasonable.

On the other hand, it has also been shown that conversion of a conjugated phenolic hydroxyl group to phenoxide ion causes a large bathochromic shift.[24] For example, Geissman and Harborne[27] found that *p*-hydroxycinnamic acid shows a bathochromic shift of 25 mμ (310 → 335) in changing from acid to basic solution, while the corresponding methyl ester exhibited a similar shift of 44 mμ (308 → 352) under the same conditions. These two values indicate a bathochromic shift of 44 mμ for conversion of —OH to —O$^-$, and by difference a hypsochromic shift of 19 mμ for conversion of —COOH to —COO$^-$. This has been confirmed by the observation that *p*-hydroxycinnamic acid absorbs strongly at 290 mμ in saturated alcoholic sodium acetate ($\Delta\lambda = -20$ mμ) in which only the carboxyl group is ionized.[28]

α-Mercaptocinnamic acid is analogous to *p*-hydroxycinnamic acid, in that it contains a vinyl —SH group in conjugation. Solution in 0.5 *N* sodium carbonate causes partial ionization of the thiol group, causing a bathochromic shift which is sufficiently large to overcome the simultaneous hypsochromic shift due to ionization of the carboxyl group, and resulting in a net $+\Delta\lambda$ of 15 mμ in the principal absorption peak. Similar shifts of 10–17 mμ are observed for other members of the series.

EXPERIMENTAL

Preparation of the rhodanine derivatives. The aldehydes listed in Table I were treated with an equimolar amount of rhodanine (B. F. Goodrich Co.) and 2.5–3.0 *molar* equivalents of anhydrous sodium acetate in boiling glacial acetic acid for approximately one-half hour, following the procedure of Julian and Sturgis.[6] The products were isolated by filtration after dilution of the reaction mixtures with water. Toluene appeared to be the best solvent for recrystallization but ethanol, butanol, and acetic acid could also be used. With the exception noted below, all of the 5-(arylmethylene)-rhodanines prepared here proved to be yellow to orange needles. The following preparation, not previously reported, is characteristic.

5-(1-Naphthylidene)rhodanine. A hot solution of 4.0 g. (0.03 mole) of rhodanine and 7.5 g. (0.09 mole) of fused sodium acetate in 20 ml. of glacial acetic acid was shaken while 5.0 g. (0.032 mole) of 1-naphthaldehyde was slowly added. The mixture then was refluxed for ten minutes, and poured into a liter of cold water. The red precipitate, when collected and dried, weighed 7.4 g. and melted from 205–220°. Two recrystallizations from absolute ethanol gave dark red needles melting sharply at 224–225°.

Sodium salts of the 5-(arylmethylene)rhodanines. Three of the rhodanine derivatives described in Table I formed insoluble sodium salts in cold sodium hydroxide solution. This offered a convenient means of purification, especially when the product was to be further hydrolyzed in alkaline solution, since the sodium salt could be used directly in the next step. When the rhodanine derivatives of 1-naphthaldehyde, 2-naphthaldehyde, or veratraldehyde were mechanically stirred into an ice-cold solution of 1% sodium hydroxide, containing a slight excess of 1 molar equivalent of base per mole of rhodanine, hard crystals of bright yellow precipitates were obtained in about ten minutes in each case. The weight of the dried precipitates indicated yields in the order of 90%, depending on the purity of the crude 5-(arylmethylene)-rhodanine. These yellow crystals charred above 300°, and left an alkaline ash on a red-hot spatula. On stirring these salts into cold dilute hydrochloric acid, gelatinous precipitates were formed, which upon digestion for a time on the steam-bath gave crystals of the original 5-(arylmethylene)-rhodanine.

Preparation of the α-mercaptoacrylic acids. A quantity of the desired rhodanine or its sodium salt was heated to approximately 75° for 20–30 minutes in excess dilute alkali. The odor of the original aldehyde was usually apparent at this point. The solution then was rapidly cooled, usually to room temperature, quickly neutralized with a slight excess of cold hydrochloric acid with vigorous stirring, and the precipitate was collected and washed with water immediately. The odor of hydrogen sulfide was distinct in the acid solution. Only in the case of the styryl and 3-thienyl derivatives were better yields obtained when the alkaline solution was cooled to 0° before neutralization. Most of the mercaptoacrylic acids were recrystallized from toluene or a mixture of toluene and ligroin, but chlorobenzene was used once (below) and anisole-kerosene proved to be an especially good solvent pair for the recrystallization of veratryl-α-mercaptoacrylic acid. The styryl derivative could not be recrystallized from any of a variety of solvents, and it was used in the crude form. Two specific examples of these preparations are given below, and the properties of all of the aryl-α-mercaptoacrylic acids prepared for this work are given in Table II.

β-1-Naphthyl-α-mercaptoacrylic acid. To a rapidly stirred, ice-cold solution of 26 ml. of 10% sodium hydroxide in 300 ml. of water was added 15 g. of crude 5-(1-naphthylidene)-rhodanine. After 10 minutes, the yellow precipitate of sodium salt was collected and stirred directly into a warm (60°) solution of 90 ml. of 10% sodium hydroxide in 1.2 l. of water. The mixture was heated to 60–65° for 20 minutes, cooled, and filtered through a Norit pad. The filtrate was stirred rapidly and 60 ml. of 6 *N* hydrochloric acid was added all at once. The yellow precipitate weighed 9.7 g. when dry, and melted at 169–171°. It recrystallized from toluene in yellow needles.

β-3-Thienyl-α-mercaptoacrylic acid. A solution of 6.0 g. of 5-(3-thenylidene)rhodanine and 53 ml. of 10% sodium hydroxide in 400 ml. of water was heated on a boiling water-bath for 20 minutes. The mixture then was set in an ice-salt bath, and crushed ice added with stirring until the solution was cooled to 0°, after which 13 ml. of conc'd hydrochloric acid was added. The yellow precipitate, which weighed 3.4 g. and melted at 156–158° when dry, was recrystallized from chlorobenzene as orange needles with little improvement in melting point.

Color tests on the mercaptoacrylic acids. Each of the mercaptoacrylic acids listed in Table II gave a color with the reduced nitroprusside solution prepared as described by Grote.[21] A few crystals of each compound were dissolved in 2–3 ml. of saturated sodium bicarbonate solution, and 0.5 ml. of the test solution was added. A light to dark green color developed immediately, but gradually faded. When a few drops of a 1% aqueous ferric chloride solution was added to an alcoholic solution of each of the mercaptoacrylic acids, light green to blue-green colors were obtained.

Preparation of the 2,2′-dithiobis(3-arylacrylic) acids. The disulfides listed in Table III were prepared by oxidation of

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(27) Geissman and Harborne, *Arch. Biochem. and Biophys.*, **50,** 447 (1955).

(28) Geissman and Jurd, unpublished data.

the mercaptoacrylic acids, using one or both of the following methods.

Oxidation by iodine in ethanol. The mercaptoacrylic acid (0.001 to 0.1 mole) was dissolved in slightly more than the minimum volume of absolute ethanol required to keep it in solution at 0°, and a slight excess of an equivalent of iodine added with stirring. After standing from one to two hours at 0°, the reaction mixture deposited yellow to orange crystals, which were collected and recrystallized from 95% ethanol.

Oxidation by benzoyl peroxide in dry benzene. The preparation of 2,2′-dithio-bis-3-phenylacrylic acid is typical. A solution of 1.2 g. (0.005 mole) of benzoyl peroxide in 30 ml. of dry benzene was added to 1.5 g. (0.0083 mole) of β-phenyl-α-mercaptoacrylic acid dissolved in 60 ml. of dry benzene. A small amount of tarry material which soon formed was removed by filtration, and the reaction mixture was allowed to stand in the dark at room temperature for seven days, during which time beautiful yellow needles of the disulfide formed. After filtration, the solution was concentrated under reduced pressure (water pump) and allowed to stand two more days, forming a second crop of yellow needles. The combined dry weight of product melting at 181–182° was 1.30 g. (0.0036 mole). Recrystallization from a mixture of tetrahydrofuran and petroleum ether gave 0.91 g. of yellow needles melting at 186–187°.

The benzene mother liquor from the above benzoyl peroxide oxidation was extracted several times with 0.1 *N* sodium carbonate; the alkaline solution was washed with chloroform, and acidified. The acidic solution was extracted twice with chloroform, and the chloroform layers were combined and dried. This solution then was concentrated, transferred to a sublimation tube, and evaporated to dryness. Sublimation of the residual tar at 25 mm. pressure and 130° (bath temperature) gave 0.545 g. of benzoic acid (53%) melting at 121–122°, undepressed when mixed with an authentic sample. When 1.2 g. of benzoyl peroxide was allowed to stand for 19 days in benzene in the dark, with a catalytic amount (50 mg.) of α-mercaptocinnamic acid added, only a trace (20 mg.) of benzoic acid could be found by the above procedure.

α-2,4-Dinitrophenylthio-β-veratrylacrylic acid. A solution of 0.3 g. of β-veratryl-α-mercaptoacrylic acid and 0.2 g. of 2,4-dinitrochlorobenzene in 11 ml. of absolute ethanol was treated with a few drops of aqueous saturated potassium hydroxide solution and heated for five minutes over a steam-bath. On cooling, a solid mass of yellow crystals formed. The product was stirred with dilute acetic acid, filtered, and recrystallized twice from ethanol as yellow needles, melting at 224–225°.

Anal. Calc'd for $C_{17}H_{14}N_2O_8S$: N, 6.89. Found: N, 6.82.

α-Ethylthio-β-veratrylacrylic acid. To a solution of 0.3 g. of β-veratryl-α-mercaptoacrylic acid in 10 ml. of 95% ethanol was added 3 ml. of 5% sodium hydroxide solution and 2 ml. of ethyl iodide, and the mixture was refluxed for ten minutes. The cooled solution was diluted with 10 ml. of water and acidified with 1 ml. of conc'd hydrochloric acid. After standing for several hours, the yellow crystals were collected and recrystallized twice from a mixture of ethanol and water, and melted at 125–126°.

Anal. Calc'd for $C_{13}H_{16}O_4S$: S, 11.93. Found: S, 11.85.

α-Ethylthio-β-2-naphthylacrylic acid. In a similar manner, treatment of 1.15 g. of β-(2-naphthyl)-α-mercaptoacrylic acid with ethyl iodide produced a heavy oily crystalline mass. After recrystallization, first from toluene and then from a benzene–petroleum ether mixture, brown platelets melting at 154–155° were obtained.

Anal. Calc'd for $C_{15}H_{14}O_2S$: S, 12.40. Found: S, 12.15.

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