Mechanism of Oxidative Ring Closure of Compounds of the Buta-1,3-diene-1-thiol Type with Halogens to give Thiophen Derivatives

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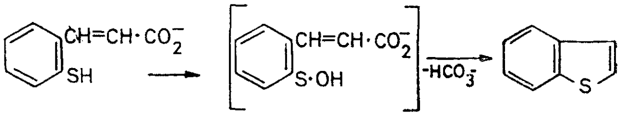
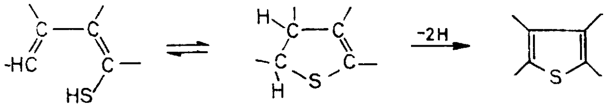
The mechanism of oxidative ring closure of compounds of the above type to thiophen derivatives has been studied in detail. It is suggested that in aprotic solvents a sulphenyl halide is formed, rather than the disulphide postulated by Campaigne and Cline, as a reactive intermediate, which then cyclises to the thiophen derivative, probably by a polar mechanism. A free-radical mechanism is not, however, completely ruled out, and is indeed proposed for the cyclisation under other reaction conditions.

ISOLATED examples of oxidative ring closure of compounds of the buta-1,3-diene-1-thiol type to give thiophen derivatives have been known for a long time.[1-3] Mechanistic schemes have also been suggested for such cyclisations but they are usually speculative and without much experimental support. Thus Chmelewsky and Friedländer[1] believed that alkaline oxidation of *o*-mercaptocinnamate (I) to give benzo[*b*]thiophen (III), involved an intermediate sulphenic acid (II), and Campaigne and Cline[2,3] suggested a tautomeric equilibrium of the buta-1,3-diene-1-thiol structure (IV) with the corresponding 2,3-dihydrothiophen structure (V) to explain the ready dehydrogenation of (IV) to a thiophen structure (VI).

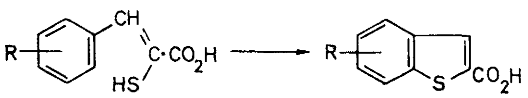
Of great preparative importance, however, has been the oxidative cyclisation of the readily accessible β-aryl-α-mercaptoacrylic acids (VII), particularly those with electron-releasing groups in their aromatic ring, to give benzo[*b*]thiophen-2-carboxylic acids, first reported by Campaigne and Cline.[3] The reaction is usually carried out by heating the mercapto-acid for 12—24 hr. with a large excess of iodine in dry dioxan or dry benzene. Campaigne and Cline[3] asserted that the reaction proceeds through the disulphides derived from the mercapto-acids, and proposed a rate-limiting acid-catalysed electrophilic ring closure of the former to the benzo[*b*]thiophen derivatives as shown in Scheme 1. Recently, we have improved[4] this cyclisation by using 1 mol. of



(I) (II) (III)



(IV) (V) (VI)



(VII) (VIII)

[R = Electron-releasing group]

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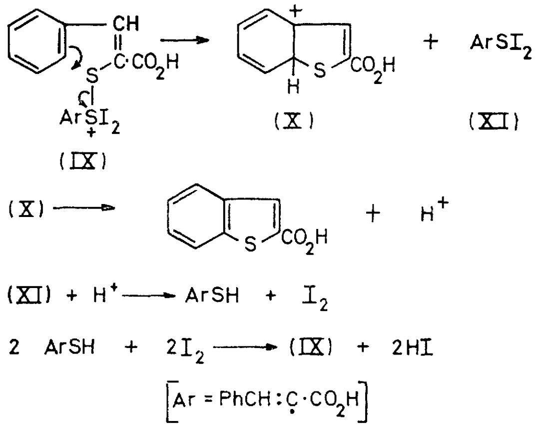
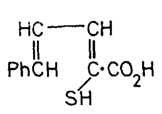
[1] C. Chmelewsky and P. Friedländer, *Ber.*, 1913, **46**, 1903.
[2] E. Campaigne, *J. Amer. Chem. Soc.*, 1944, **66**, 684.
[3] E. Campaigne and R. E. Cline, *J. Org. Chem.*, 1956, **21**, 39.
[4] P. M. Chakrabarti, N. B. Chapman, and K. Clarke, *Tetrahedron*, 1969, **25**, 2781.

chlorine, instead of an excess of iodine, in an aprotic solvent at room temperature. With chlorine the reaction occurred within a few min., and the product was obtained in much better yield and purity than by cyclisation with iodine. Our observations did not fit well into the mechanistic scheme (Scheme 1) proposed by Campaigne and Cline,[3] and this prompted us to re-investigate the mechanism.

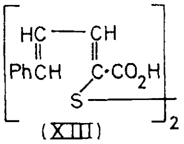
When α-mercapto-β-styrylacrylic acid (XII) is used in these reactions, 5-phenylthiophen-2-carboxylic acid (XIV) is obtained.[3,4] Most of Campaigne and Cline's mechanistic work was based on observations on this particular reaction. In order to use their findings and for the sake of comparability with our findings, we chose the same acid (XII) for our studies. Campaigne and Cline based their mechanism on the following observations. (*a*) The disulphide (XIII) and other disulphides[5] derived from β-aryl-α-mercaptoacrylic acids (VII), on oxidation with iodine, gave (XIV) and (VIII) respectively, (*b*) on treatment with an excess of iodine in ethanol the mercapto-acid (XII) immediately consumed 0·5 mol. of iodine, and took about 18 hr. to consume another 0·5 mol.,* (*c*) the disulphide (XIII), when similarly treated, took 18 hr. to consume † 1 mol. of iodine, and (*d*) the disulphide (XIII), when heated under reflux in dry benzene with boron trifluoride for 5 hr., gave *ca.* 40% yield of (XIV). They attributed the initial consumption of 0·5 mol. of iodine in (*b*) to the formation of the disulphide (XIII), but when they tried to prepare the latter by the action of 0·5 mol. of iodine on (XII) in ethanol, they obtained only an intractable tar.‡ In our hands, however, the reaction went smoothly; 0·5 mol. of iodine was consumed instantaneously by (XII) in ethanolic solution and by diluting the solution with water we were able to isolate the disulphide (XIII) in 97% yield. In this respect, therefore, (XII) is no different from other β-aryl-α-mercaptoacrylic acids (VII), which are also oxidised to the corresponding disulphides almost instantaneously and quantitatively by 0·5 mol. of iodine in ethanol.[4,5] In this connection Campaigne and Cline [3] failed to obtain the mercapto-acid (XII) in a crystalline form, but when prepared by our different method, it crystallised very well from benzene in thick orange needles, which appeared yellow when powdered.



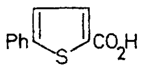
SCHEME 1 This scheme is represented exactly as in the report of Campaigne and Cline.[3] It seems that a negative charge is missing in structures (IX) and (XI).



(XII)



(XIII)



(XIV)

Although disulphide formation is the primary process in an amphiprotic solvent such as ethanol, this might not be the case in aprotic solvents such as dry benzene or dry dioxan, which were usually used by Campaigne and Cline. We found that in these solvents, when used dry [$<$0·01% H_2O (w/w)] the consumption of iodine was sluggish, but became rapid when traces of water were added; in this case the corresponding disulphides were isolated as products. Similarly, α-mercaptocinnamic acid was converted into the αα′-dithiobiscinnamic acid with iodine in moist carbon disulphide by Bondzynsky,[6] although iodine in dry carbon disulphide apparently had no effect.

When a solution of the mercapto-acid (XII) in dry benzene was added to 0·5 mol. of iodine in the same solvent, the violet iodine solution immediately turned brown (*cf.* p. 916). This solution, when heated under reflux in the dark under dry carbon dioxide, required about 8 hr. for all its iodine to be consumed. From the mixture we isolated 5-phenylthiophen-2-carboxylic acid (XIV) (*ca.* 40%), and the residual material when subjected to mass spectrometric analysis showed molecular ion peaks at *m*/*e* 204 and 206 due to (XIV) and (XII) respectively, in addition to a small peak at *m*/*e* 222, the significance of which will be discussed later. There was, however, no sign of a peak at *m*/*e* 410 which could be attributed to the disulphide (XIII). The mass spectrum of the disulphide (XIII) itself showed the peak at *m*/*e* 410. When 1 mol. of iodine was used in this experiment (9 hr. under reflux), 5-phenylthiophen-2-carboxylic acid (75%) was obtained, but here again the mass spectrum of the residue had a small but distinct peak at *m*/*e* 222, but none at *m*/*e* 410. We further found that the reaction times could be reduced from 8—9 hr. to 20—25 min. if the hydriodic acid formed in the reaction were removed by constant distillation of benzene from the reaction vessel with addition of dry benzene at the same rate. Here again no disulphide formation could be detected and the product was (XIV) in the same yield as

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* The final compound isolated was (XIV), in 61% yield.

† The product isolated was (XIV), in 68% yield.

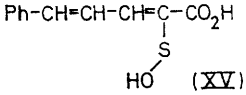
‡ However, they prepared the disulphide (XIII) by oxidising a solution of (XII) in benzene with dibenzoyl peroxide for 7 days in the dark.[5]

[5] E. Campaigne and R. E. Cline, *J. Org. Chem.*, 1956, **21**, 32.

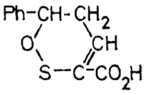
[6] S. Bondzynski, *Monatsh.*, 1887, **8**, 349.

before. If the disulphide were the rapidly formed preliminary product in this reaction, and if this then underwent cyclisation to (XIV) by a slow rate-limiting process as suggested by Campaigne and Cline [3] (Scheme 1), then in the last experiments where the reaction times were reduced to about 1/25th of the usual period, one would expect the presence of some of the disulphide in the product. Since no disulphide could be detected in any of the experiments, we concluded that this was unlikely to be the intermediate in the cyclisation.

In the mass spectra of the products we invariably found a small peak at *m/e* 222; the accurate mass was found to be 222·03506. This corresponds to a formula $C_{11}H_{10}O_3S$, which contains one oxygen atom more than the mercapto-acid (XII). This peak was absent from the spectra of pure (XII), (XIII), and (XIV). The reasonable explanation seems to be that this peak is due to a sulphenic acid derivative (XV) or its tautomer (XVI).* Formation of a sulphenic acid as by-product suggests that in the cyclisation under study the active intermediate was a sulphenyl iodide, and a trace of it that escaped the cyclisation was hydrolysed by water during the work-up. As mentioned before a sulphenic acid intermediate was also postulated by Chmelewsky and Friedländer [1] in their mechanism for alkaline ferricyanide oxidation of *o*-mercaptocinnamic acid to benzo[*b*]thiophen.



$Ph{-}CH{=}CH{-}CH{=}C(S{-}OH){-}CO_2H$ (XV)



(XVI)

When solutions of the mercapto-acid (XII) and of iodine in dry benzene were mixed, the violet iodine colour turned brown. This we attribute to the formation of a complex involving the sulphur atom of the mercapto-compound and an iodine molecule. We also observed similar behaviour with carbon tetrachloride as solvent. Organic sulphur compounds are well known for *n*-complex formation [8a] with halogens, and several such complexes, R^1R^2S,X_2 (X = Cl, Br, or I) have been isolated as solids.[9–11] The most direct proof of such complex formation in solution, however, is the appearance of a charge-transfer band in the u.v. spectrum, which is absent from the spectra of the components.[8b,12] For complexes of iodine with various substances this appears as a relatively intense band in the neighbourhood of 350 nm. in addition to the normal but slightly shifted iodine band around 520 nm.[8b] Since the mercapto-acids under study themselves absorbed very strongly in the neighbourhood of 350 nm. the u.v. method of detecting such complexes was uncertain. We found that the behaviour of benzenethiol in dry benzene or dry carbon tetrachloride was similar to that of our mercapto-acids, in that here also, with iodine a brown solution was obtained with apparently no consumption of iodine, as shown by the intensity of the free iodine band at *ca.* 520 nm., and on treating the solutions with water diphenyl disulphide was immediately formed. Further, in the dry solutions there was apparently no chemical reaction between the benzenethiol and the iodine, since the i.r. spectra of the benzenethiol solutions in the presence or absence of iodine were virtually identical. Similarly, i.r. spectra of the mercapto-acids under study were also virtually unaffected by addition of iodine in dry benzene or dry carbon tetrachloride. This would be expected of charge-transfer complexes since very little distortion of bonds of the components occurs in such loose complexes.[13–15] However, the u.v. spectrum of benzenethiol, in the presence of iodine in carbon tetrachloride, showed a relatively strong charge-transfer band at 355 nm., a region in which both iodine and benzenethiol are transparent. Since the cases are comparable, it is reasonable that for the mercapto-acids also a charge-transfer complex is formed with iodine.

The foregoing discussion implies that in the presence of iodine, equilibria (1) and (2) of Scheme 2 are established, involving a small concentration of the sulphenyl iodide. In dry aprotic solvents the sulphenyl iodide then undergoes intramolecular cyclisation in a crucial rate-limiting step (3), as represented in part (*A*) of Scheme 2. The hydrogen iodide formed forces the position of the equilibrium (2) to the left, thus decreasing the concentration of the sulphenyl iodide. Removal of hydrogen iodide, as we have observed, increases the rate of formation of the final product by favouring the formation of the sulphenyl iodide. The large excess of iodine used by Campaigne and Cline [3] in their cyclisation probably has a similar effect, by forcing equilibrium (1) to the right.

We next turned our attention to the disulphide (XIII). By boiling the disulphide in dry benzene with a catalytic amount of iodine in the dark for 2 hr. we could obtain the 5-phenylthiophen-2-carboxylic acid (XIV) (*ca.* 40%). A fast reaction between the small quantity of iodine in this experiment and the mercapto-compound (XII) as it is formed, if Campaigne and Cline's suggestions were correct, would soon form the disulphide (XIII) and eventually stop the reaction as soon as a quantity of the acid (XIV) equivalent to the iodine used was formed (Scheme 1). Here again it seemed probable that the iodine first reacted with the disulphide, presumably according to equation (4), to give the sulphenyl iodide, which then underwent ring closure according to equation

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* Although to our knowledge there is but one instance of the isolation of a free sulphenic acid (anthraquinone-1-sulphenic acid [7]) their esters have been well characterised.

[7] K. Fries, *Ber.*, 1912, **45**, 2965.

[8] L. J. Andrews and R. M. Keefer, 'Molecular Complexes in Organic Chemistry,' Holden-Day, San Francisco, 1964, (*a*) pp. 96—97; (*b*) pp. 16—19.

[9] E. Fromm and G. Raizigs, *Annalen*, 1910, **374**, 90.

[10] E. Bourgeois and A. Abraham, *Rec. Trav. chim.*, 1911, **30**, 414.

[11] K. Fries and W. Vogt, *Annalen*, 1911, **381**, 337.

[12] R. S. Mulliken, *J. Amer. Chem. Soc.*, 1952, **74**, 811.

[13] H. Kainer and W. Otting, *Chem. Ber.*, 1955, **88**, 1921.

[14] W. R. Burton and R. E. Richards, *J. Chem. Soc.*, 1950, 1316.

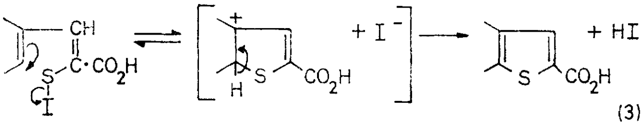
[15] R. E. Gibson and O. H. Loeffler, *J. Amer. Chem. Soc.*, 1940, **62**, 1324.

(3), with the elimination of hydrogen iodide. The hydrogen iodide now reversibly reduces the rest of the sulphenyl iodide to the mercapto-compound with the liberation of iodine according to the reverse of equations (2) and (1) as shown in part (*B*) of Scheme 2.

(*A*) Reaction of β-aryl-α-mercaptoacrylic acids with iodine in an aprotic medium:

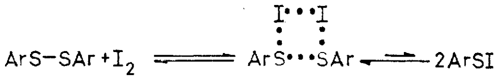
$$\mathrm{ArSH + I_2 \rightleftharpoons ArSH{,}I_2} \qquad (1)$$

$$\mathrm{ArSH{,}I_2 \rightleftharpoons ArSI + HI} \qquad (2)$$



(3)

(*B*) Reaction of αα′-dithiobis-(β-arylacrylic) acids with iodine in an aprotic medium:



$$\mathrm{ArS{-}SAr + I_2 \rightleftharpoons ArS\overset{\overset{I\cdots I}{\vdots\quad\vdots}}{\cdots}SAr \rightleftharpoons 2ArSI} \qquad (4)$$

Plus equation (3)
Plus reverse of equations (2) and (1)

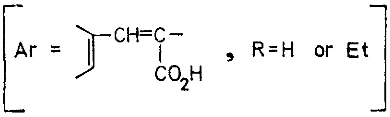
(*C*) Reaction of β-aryl-α-mercaptoacrylic acids with iodine in an amphiprotic medium:

Equations (1) and (2) plus

$$\mathrm{ArSH + ROH \rightleftharpoons ArS^- + ROH_2^+} \qquad (5)$$

$$\mathrm{\overset{\delta+}{ArS}{-}\overset{\delta-}{I} + ArS^- \longrightarrow ArS{-}SAr + I^-} \qquad (6)$$

Plus equations (4) and (5)



Scheme 2

If this view is correct, hydrogen iodide in the presence of a catalytic amount of iodine would liberate more iodine by interaction with the disulphide. We observed, by running two parallel experiments in the dark with anhydrous hydrogen iodide in dry benzene, but one with added disulphide (XIII) and the other without, that the one with the disulphide liberated much more iodine than the other, after 30 min. under reflux, as shown by the relative intensities of the iodine band at *ca.* 525 nm. in the u.v. spectra. In the second case liberation of iodine was due solely to decomposition of hydrogen iodide.

When the mercapto-acids under study are treated with iodine in an amphiprotic medium, *viz.* ethanol or moist aprotic solvents, the situation may be represented as in part (*C*) of Scheme 2. In addition to equilibria (1) and (2) an acid-base equilibrium (5) would also be established. Since $\mathrm{ArS^-}$ would be a very strong nucleophile,[16] it would react rapidly with a sulphenyl iodide leading to the disulphide according to equation (6). In the presence of an excess of iodine, the comparatively slow processes (4) and (3) would ultimately lead to the thiophen derivative. In an amphiprotic medium our picture [Scheme 2, part (*C*)] therefore differs from that of Campaigne and Cline (Scheme 1) in that here also we believe that a sulphenyl iodide is the active intermediate in the formation of the thiophen derivative.

Our observation[4] that the buta-1,3-diene-1-thiol structure is converted into a thiophen structure by chlorine in dry aprotic solvents within a few min. in much better yield than by iodine, is also better explained on the basis of the sulphenyl halide mechanism. Since hydrogen chloride has a negligible reducing power in comparison with hydrogen iodide, equilibria (1) and (2) in our mechanism will lie far to the right. The great ease of transformation of thiols by chlorine into sulphenyl chlorides is well known.[17] It is also known that chlorine and bromine react with disulphides in inert solvents[18,19] to produce sulphenyl halides, but there is little evidence concerning preparation of sulphenyl iodides. However, sulphenyl iodides have been suggested as reaction intermediates in a number of cases.[20,21] Katz and Schroeder[20] showed that disulphides immediately consume 1 mol. of iodine in methanol solution in the presence of piperidine to give a sulphenyl piperidide and suggested that the iodine first breaks down the disulphide into the corresponding sulphenyl iodide, and that this then reacts with piperidine to give the sulphenyl piperidide. Since piperidine is not only a relatively strong base but also an excellent nucleophile[16] it will indeed react very rapidly with the electrophilic sulphenyl iodide, shifting equilibrium (4) of Scheme 2 completely to the right. We also found that our disulphide (XIII) reacted immediately and quantitatively with 1 mol. of iodine in methanol, in the presence of piperidine. The superiority of chlorine over iodine in our cyclisation[4] may also be ascribed to the fact that the S–Cl bond would be more polar than the S–I bond and as such would be more prone to generate the electrophilic reagent in the actual ring closure through the sulphur atom [*cf.* equation (3)]. The great reactivities of sulphenyl chlorides towards alkenes and alkynes are well known[22] and a polar mechanism for such reactions has been demonstrated.[23]

Though Scheme 2 depicts the entire process as polar, the possibility of a homolytic reaction cannot be altogether ruled out. Homolytic reactions of sulphenyl chlorides have been suggested,[24,25] and Lecher[26] has shown that the diaryl disulphides when boiled with sodium in dry xylene form sodium salts of benzenethiols;

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[16] E. S. Gould, 'Mechanism and Structure in Organic Chemistry,' Holt, Rineheart, and Winston, New York, 1969, p. 260.

[17] Th. Zincke, *Ber.*, 1911, **44**, 769.

[18] Th. Zincke and J. Baeumer, *Annalen*, 1918, **416**, 86.

[19] H. Rheinboldt and E. Motzkus, *Ber.*, 1939, **72**, 657.

[20] L. Katz and W. Schroeder, *J. Org. Chem.*, 1954, **19**, 103.

[21] C. J. Miller and S. Smiles, *J. Chem. Soc.*, 1925, **127**, 224.

[22] I. B. Douglas in 'Organic Sulphur Compounds,' vol. 1, ed. N. Kharasch, Pergamon, Oxford, 1961, p. 350.

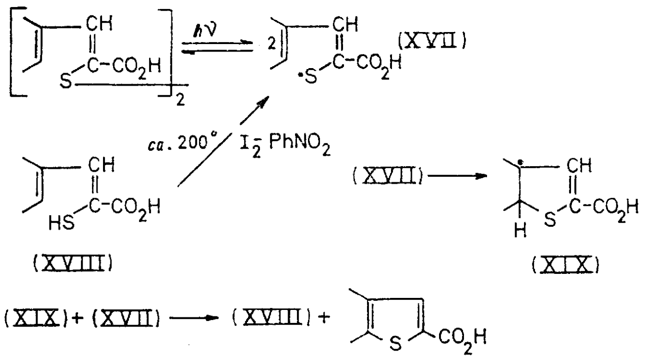
[23] K. E. Russell and A. V. Tobolsky, *J. Amer. Chem. Soc.*, 1954, **76**, 395.

[24] N. Kharasch, S. J. Potempa, and H. L. Wehrmeister, *Chem. Rev.*, 1946, **39**, 291.

[25] G. H. Williams, *Adv. Free-radical Chem.*, 1967, **2**, 32.

[26] H. Lecher, *Ber.*, 1915, **48**, 524.

homolytic dissociations of disulphides by photo-initiation[23] or radical initiation[25] are well known. Campaigne and Cline[3] found that in the absence of electron-releasing groups in the aromatic nucleus, β-aryl-α-mercaptoacrylic acids, such as α-mercapto-β-phenylacrylic acid, did not undergo cyclisation with iodine in benzene or dioxan, but by heating this acid with an excess of iodine in nitrobenzene at *ca.* 200° for 1—2 min., they obtained the benzo[*b*]thiophen-2-carboxylic acid in good yield. Hughes[27] also found that β-(*o*-chlorophenyl)- and β-(*p*-chlorophenyl)-α-mercaptoacrylic acid could not be cyclised by the normal procedure of Campaigne and Cline, but these compounds were cyclised when heated at *ca.* 200° in nitrobenzene with an excess of iodine for 1—2 min. A similar observation has been made by Faller[28] with β-(*o*-bromophenyl)-α-mercaptoacrylic acid. It appears reasonable that these high temperature cyclisations of the deactivated systems involve a free-radical mechanism and we have found that when a xylene solution of the disulphide (XIII) is boiled, with irradiation by two 500 w lamps, (XIII) is converted into the 5-phenylthiophen-2-carboxylic acid (XIV) in *ca.* 40% yield in 30 min. Since no oxidising agent was used in this reaction, the 40% yield actually corresponds to an 80% yield. This situation is represented in Scheme 3.



SCHEME 3

EXPERIMENTAL

I.r. spectra were recorded with a Perkin-Elmer 457 spectrophotometer. U.v. spectra were measured with a Unicam SP 700 spectrophotometer. Mass spectra were determined with an AEI MS 902 machine. M.p.s were determined for samples in open capillary tubes. Solutions were dried with anhydrous sodium sulphate. Light petroleum refers to the fraction of boiling range 60—80°.

Materials.—Reagent grade benzene, xylene, and dioxan were further dried and purified by refluxing over and distillation from sodium. Carbon tetrachloride was purified and dried by a standard procedure.[29] The dried and purified solvents were found to contain less than 0·01% of water (w/w) by the Karl Fischer titration.[30] Benzenethiol and piperidine were distilled before use, and resublimed iodine was used. Standard solutions of ethanolic iodine (0·2N), methanolic iodine (0·1N), and aqueous sodium thiosulphate (0·1M) were prepared by the usual procedure.[31] α-Mercapto-β-styrylacrylic acid (XII) was prepared as described previously[4] from cinnamaldehyde *via* the 5-cinnamylidenerhodanine, by a variation of a known procedure.[5] It gave thick orange needles, m.p. 155—156° (from benzene) (lit.,[4] 155—156°; lit.,[5] 148—151°) [Found: C, 64·0; H, 4·6; S, 15·3%; *M* (mass spectrum), 206. Calc. for $C_{11}H_{10}O_2S$: C, 64·1; H, 4·9; S, 15·5%; *M*, 206], $\nu_{max.}$ (2% in CCl_4) 2580 (SH) and 1680 (C=O) cm.$^{-1}$.

Action of Iodine on α-Mercapto-β-styrylacrylic Acid (XII) *in Ethanol. Preparation of 2,2′-Dithiobis-3-styrylacrylic Acid* (XIII).—Compound (XIII) was obtained in *ca.* 97% yield by oxidation of (XII) with 0·5 mol. of iodine in ethanol. When an excess of iodine was used only 0·5 mol. of iodine was consumed immediately. To a solution of (XII) (2·06 g., 10 mmoles) in ethanol (30 ml.) was added a solution of iodine (0·64 g., 5 mmoles) in ethanol (30 ml.). The brown colour of the iodine solution was discharged within a few seconds and a bright yellow solution resulted. After 5 min. the solution was diluted with water (*ca.* 200 ml.) and the 2,2′-dithiobis-3-styrylacrylic acid (XIII) that separated as a yellow solid (2 g., *ca.* 97%) was filtered off and crystallised from tetrahydrofuran–light petroleum. It had m.p. 185—186° (lit.,[5] 186—187°) [Found: C, 64·2; H, 4·5; S, 15·5%; *M* (mass spectrum), 410. Calc. for $C_{22}H_{18}O_4S_2$: C, 64·4; H, 4·4; S, 15·6%; *M*, 410), and an i.r. spectrum identical with that of an authentic sample prepared[5] by oxidation of (XII) with di-benzoyl peroxide in benzene.

To a solution of (XII) (0·206 g., 1 mmole) in ethanol (20 ml.) was added ethanolic 0·2N-iodine (20 ml., 2 mmoles of iodine); a brown solution resulted. This solution (20 ml.), when titrated for unchanged iodine, required 9·95 ml. of aqueous 0·1M-sodium thiosulphate. The remaining 20 ml. of the same solution was treated with 10 ml. of the same thiosulphate solution without the addition of starch solution, and the resulting yellow solution on dilution with water gave 2,2′-dithiobis-3-styrylacrylic acid (XIII) (0·1 g., *ca.* 97%), which after recrystallisation from tetrahydrofuran–light petroleum showed an i.r. spectrum identical with that of (XIII), and did not depress the m.p. of pure (XIII).

Absorption Spectra of Solutions of α-Mercapto-β-styrylacrylic Acid (XII) *and of Benzenethiol in Dry Aprotic Solvents*.—(i) *I.r. spectra*. A solution of iodine (0·6% w/v) in dry benzene or dry carbon tetrachloride did not absorb in the i.r. (4000—800 cm.$^{-1}$); compensating cells containing dry solvent were used. I.r. spectra of solutions of α-mercapto-β-styrylacrylic acid (XII) (0·25% w/v) in dry benzene and in dry carbon tetrachloride were unaffected by addition of iodine (0·6% w/v). Similarly, i.r. spectra of solutions of benzenethiol (0·3% w/v) in dry benzene and in dry carbon tetrachloride, were identical with those of fresh solutions containing a mixture of iodine (0·6% w/v) and benzenethiol (0·3% w/v) in dry benzene and dry carbon tetrachloride respectively.

(ii) *U.v. and visible spectra*. Solutions (*a*)—(*e*) were prepared by dissolving the appropriate materials in dry carbon tetrachloride (100 ml.) and their spectra were recorded between 330 and 600 nm.: (*a*) α-mercapto-β-styrylacrylic acid (XII) (0·1 g.), transparent above 440 nm. but absorbed very strongly below 440 nm.; (*b*) benzenethiol (1·7 g.), transparent; (*c*) iodine (5 mg.), $\lambda_{max.}$ 525 nm. (absorbance 0·1);

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(*d*) iodine (5 mg.) and α-mercapto-β-styrylacrylic acid (0·1 g.), $\lambda_{max.}$ 525 nm. (absorbance 0·1), very strong absorption below 440 nm; (*e*) iodine (5 mg.) and benzenethiol (1·7 g.), $\lambda_{max.}$ 525 nm. (absorbance 0·1) and 355 nm. (absorbance 0·61). The band with $\lambda_{max.}$ 355 nm. in the last case corresponds to the charge-transfer absorption of a complex between benzenethiol and iodine.

Action of Iodine on α*-Mercapto-*β*-styrylacrylic Acid* (XII) *in Moist Aprotic Solvents.*—To a solution of (XII) (1·03 g., 5 mmoles) in dry benzene (150 ml.), a solution of iodine (0·32 g., 2·5 mmoles) in dry benzene (30 ml.) was added. The solution was then shaken with a little water; the brown iodine colour was immediately discharged. The same behaviour was observed when dry dioxan or dry carbon tetrachloride was used in place of dry benzene. In each case a yellow solid [*ca.* 1 g., 97% of crude (XIII)] was obtained by removing the solvent under reduced pressure. The solid, after recrystallisation from tetrahydrofuran–light petroleum, showed an i.r. spectrum identical with that of pure (XIII) and did not depress its m.p.

Benzenethiol behaved in the same way. From benzenethiol (0·55 g., 5 mmoles) and iodine (0·32 g., 2·5 mmoles), a white solid (0·5 g.) was obtained, m.p. 62° (needles from ethanol), which did not depress the m.p. of pure diphenyl disulphide (lit.,[32] m.p. 62°) (Found: C, 66·0; H, 4·4; S, 29·2. Calc. for $C_{12}H_{10}S_2$: C, 66·1; H, 4·6; S, 29·4%).

Action of Iodine on α*-Mercapto-*β*-styrylacrylic Acid* (XII) *in Boiling Dry Benzene.*—A solution of (XII) (1 g., *ca.* 5 mmoles) and iodine (0·32 g., 2·5 mmoles) in dry benzene (150 ml.) was boiled in the dark under an atmosphere of dry carbon dioxide. After 8 hr. the brown iodine colour was discharged. The solution was evaporated and the residue gave 5-phenylthiophen-2-carboxylic acid (XIV) (0·4 g., *ca.* 40%) in shining colourless needles, m.p. 187° (from benzene) (lit.,[3] 187—188°) [Found: C, 64·5; H, 4·2; S, 15·6%; *M* (mass spectrum), 204. Calc. for $C_{11}H_8O_2S$: C, 64·7; H, 3·9; S, 15·7%; *M*, 204]. The mass spectrum showed no sign of a peak at *m*/*e* 222. The mother liquor was evaporated; the mass spectrum of the residue showed *m*/*e* 222 (small), 206, 204, *etc.*, but no sign of a peak at *m*/*e* 410. The accurate mass for the *m*/*e* 222 peak was 222·03506 ($C_{11}H_{10}O_3S$).

A solution of α-mercapto-β-styrylacrylic acid (1 g., *ca.* 5 mmoles) and iodine (0·32 g., 2·5 mmoles) in dry benzene (150 ml.) was heated to boiling in a distillation flask fitted with a dropping funnel and a downward condenser for distillation. Pure benzene was added from the funnel at the rate at which benzene containing hydrogen iodide was distilled out from the flask. Within 20 min. the brown iodine colour was discharged. The solution was evaporated and the residue was crystallised from benzene as before to give 5-phenylthiophen-2-carboxylic acid (XIV) (0·4 g., *ca.* 40%), mixed m.p. 187°, i.r. spectrum identical with that of pure (XIV). The benzene mother liquor from the crystallisation was evaporated and gave a residue; the mass spectrum of this showed, as before, peaks at *m*/*e* 222 (small, accurate value 222·0350), 206, 204, *etc.*, but no sign of a peak at *m*/*e* 410.

The two experiments just described were repeated with double the quantity of iodine (0·64 g., 5 mmoles) in each case. In the first experiment, it took 9 hr. for the brown iodine colour of the solution to be discharged. In the second case, where hydrogen iodide was constantly removed as it was formed, it took *ca.* 25 min. for the brown colour to be discharged. In both cases pure 5-phenylthiophen-2-carboxylic acid (XIV) (0·75 g., *ca.* 75%) was isolated after crystallisation, and the residual matter showed mass spectral peaks at *m*/*e* 222 (small, accurate mass 222·0350), 206, 204, *etc.*, but no peak at *m*/*e* 410.

Action of a Catalytic Amount of Iodine on 2,2′*-Dithiobis-*3*-styrylacrylic Acid* (XIII) *in Boiling Benzene.*—A solution of (XIII) (0·5 g.) in hot dry benzene (400 ml.) was treated with a minute crystal of iodine and boiled in the dark under an atmosphere of dry carbon dioxide. The light pink colour of the solution was discharged after 2 hr. The solution was evaporated and the residue gave 5-phenylthiophen-2-carboxylic acid (XIV) (0·2 g., *ca.* 40%) as shining colourless needles, m.p. 187° (from benzene), i.r. spectrum identical with that of pure (XIV).

Action of Hydrogen Iodide on 2,2′*-Dithiobis-*3*-styrylacrylic Acid* (XIII) *in Boiling Benzene.*—Two portions (each 150 ml.) of a saturated solution of dry hydrogen iodide in dry benzene, one containing (XIII) (0·25 g.), were boiled under reflux in the dark for 30 min. Iodine was liberated in both cases, but to different extents as shown by the relative intensity of the band at $\lambda_{max.}$ 525 nm.; the measurements were made after diluting each solution to three times its original volume with dry benzene. The solution containing (XIII) had $\lambda_{max.}$ 525 nm. (absorbance 0·66); the other had $\lambda_{max.}$ 525 nm. (absorbance 0·25).

Action of Iodine on 2,2′*-Dithiobis-*3*-styrylacrylic Acid* (XIII) *in Methanol in the Presence of Piperidine.*—A solution of (XIII) (0·82 g., 2 mmoles) and piperidine (2·0 ml.) in methanol (50 ml.) was titrated with a standard methanolic solution of iodine (0·1N). The iodine solution was instantaneously decolourised during the addition until 40 ml. (2 mmoles of iodine) had been consumed. In the absence of piperidine no iodine was apparently absorbed within a short period.

Action of Light on 2,2′*-Dithiobis-*3*-styrylacrylic Acid* (XIII) *in Boiling Xylene.*—2,2′-Dithiobis-3-styrylacrylic acid (0·4 g.) was boiled in dry xylene with irradiation by two 500 w bulbs. After about 30 min. the yellow solution had turned almost colourless, and was cooled and shaken with 5% aqueous sodium hydrogen carbonate. The aqueous layer was acidified with hydrochloric acid, the acidic solution was shaken with ether, and the ether extract was dried and evaporated. The residue gave 5-phenylthiophen-2-carboxylic acid (XIV) (0·16 g., 40%), m.p. 187° (from benzene), i.r. spectrum identical with that of pure (XIV).

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