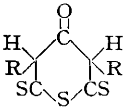
123. *Organic Sulphur Compounds. Part XXIX. Experiments with 1-Thia-γ-pyrones. Thermal Rearrangement of 1-Thia-γ-pyrone Derivatives into the Isomeric 1-Thia-α-pyrone Derivatives.*

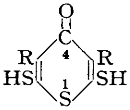
By Alexander Schönberg and (Miss) Wafia Asker.

2 : 6-Bisalkylthio-1-thia-γ-pyrones are stable towards acids, but yield on alkaline hydrolysis thio-ethers containing one triple and one double bond (see scheme A). Some 1-thia-γ-pyrones were converted into the corresponding 4-thio-1-thia-γ-pyrones by the action of thionyl chloride followed by that of thioacetic acid (see scheme B). 2 : 6-Dithio-3 : 5-diphenyl-1-thia-γ-pyranone (I, R = Ph) on heating yields the thionaphthen derivative (IX); in addition, another product of pyrolysis was formed for which formulæ (X) and (XII) are discussed. A thermal rearrangement by which 4-thio-1-thia-γ-pyrone derivatives were irreversibly transformed into the isomeric 2-thio-1-thia-α-pyrone derivatives was observed (see scheme C) and its mechanism is discussed. It was found that some 4-thio-1-thia-γ-pyrone derivatives (*e.g.*, XIV) and also thiobenzophenone and its derivatives are easily converted into the corresponding ketones (*e.g.*, benzophenone) by the action of thionyl chloride followed by hydrolysis (see scheme D). 3 : 5-Diphenyl-1-thia-γ-pyrone (XIX) was obtained by a dehydrogenating process using phorphorus pentachloride as the agent.

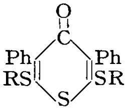
The orange substances obtained by the action of carbon disulphide on ketones of the general type $CH_2R{\cdot}CO{\cdot}CH_2R$ in the presence of alkali have the constitution (I); they exhibit thiono–thiol tautomerism and form colourless or almost colourless compounds which are derivatives of 2 : 6-dithiol-1-thia-γ-pyrone (II) (Schönberg and Asker, J., 1945, 198). Both groups of substances are easily available and have been investigated in some detail.



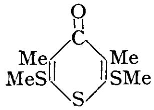
(I.)



(II.)

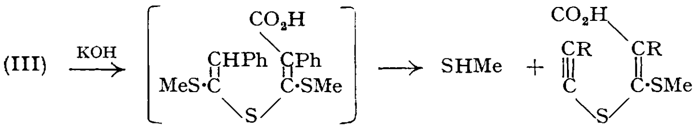


(III, R = Me.)
(IV, R = Et.)



(V.)

(a) *Action of Acids and of Alkalis on Derivatives of* (II).—Substances (III) and (V), heated under reflux with acetic acid saturated with hydrogen chloride, were recovered unchanged, but on treatment with aqueous-alcoholic potassium hydroxide the ring was opened, the acids (VI) and (VII), respectively, being obtained :



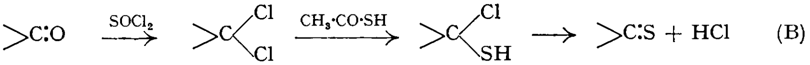
(A)

(VI, R = Ph.)
(VII, R = Me.)

The *acid* (VI) is bright yellow; it is soluble in aqueous alkalis and is reprecipitated unchanged on acidification. It reacts with diazomethane to form a *methyl* ester, insoluble in alkalis but readily hydrolysed to the acid by boiling alkalis or acids. The *acid* (VII) is similar.

This ring scission is of value in that it affords thio-ethers containing a triple and a double bond which are not otherwise readily available.

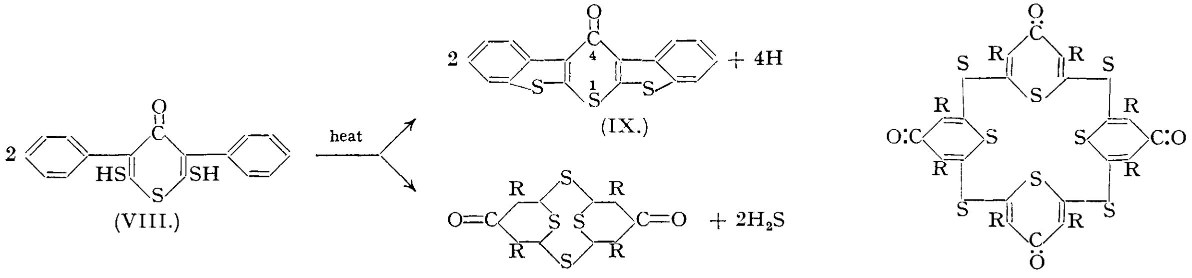
(b) *Action of Thionyl Chloride followed by Thioacetic Acid on* (III) *and* (IV).—When ketones which are not capable of forming enols (*e.g.*, benzophenone and xanthone) are treated with thionyl chloride followed by thioacetic acid, the corresponding thioketones are formed (Schönberg, *Ber.*, 1928, **61**, 1375) : *



$$>C{:}O \xrightarrow{SOCl_2} >C\begin{smallmatrix}Cl\\Cl\end{smallmatrix} \xrightarrow{CH_3{\cdot}CO{\cdot}SH} >C\begin{smallmatrix}Cl\\SH\end{smallmatrix} \longrightarrow >C{:}S + HCl \qquad (B)$$

By this means we have converted the ketones (III) and (IV) into the corresponding *thioketones* (XIV) and (XV). These substances are brilliantly coloured, showing the dichroism characteristic of substances of similar constitution, *e.g.*, 2 : 6-diphenyldithiopyrone (Arndt *et al.*, *Ber.*, 1925, **58**, 1644). With solid mercuric chloride both (XIV) and (XV) show the colour reaction described for xanthione and 2 : 6-dimethyl-4-thiopyrone (Schönberg, *Ber.*, 1925, **58**, 1794).

(c) *Pyrolysis of* 2 : 6-*Dithio*-3 : 5-*diphenyl- and* -3 : 5-*dimethyl*-1-*thia-γ-pyranone* (I, R = Ph or Me).—The ketone (I, R = Ph), or its thiol form (VIII), on pyrolysis yields two substances. One of these, namely, 2 : 3-6 : 5-*dithionaphtheno*-1-*thia-γ-pyrone* (IX) is a result of dehydrogenation (possibly under the influence of the elementary sulphur formed during pyrolysis); owing to its low solubility its molecular weight could not be determined, but it is nevertheless beyond doubt, since that of one of its derivatives, namely, 4 : 4-di-*m*-tolyl-2 : 3-6 : 5-dithionaphtheno-1-thia-γ-pyran (see following paper), has been established. The second *product* of pyrolysis, probably (X) or (XII), is formed with elimination of hydrogen sulphide; as it is very difficultly soluble in all the usual solvents, its molecular weight could not be ascertained.



(VIII.)

(IX.)

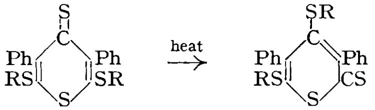
(X, R = Ph.) (XI, R = Me.)

(XII, R = Ph.) (XIII, R = Me.)

The methyl analogue of (I, R = Ph) yields on pyrolysis only one organic *product*, probably (XI) or (XIII).

(d) *Thermal Rearrangements of γ-Thiopyrones to α-Thiopyrones.*—Such rearrangements were observed when 2 : 6-*bismethylthio*-4-*thio*-3 : 5-*diphenyl*-1-*thiapyrone* (XIV) and its *ethyl* analogue (XV) were heated above their m. p., either alone or in the presence of solvents :

(XIV, R = CH_3.)
(XV, R = C_2H_5.)



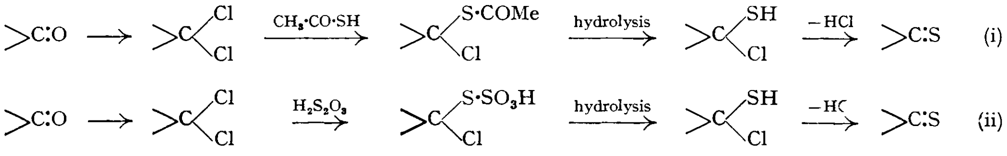
(XVI, R = Me.)
(XVII, R = Et.) (C)

The structure of the *products* (XVI) and (XVII) follows from their properties and method of formation.

4-Thio-1-thiapyrones dissolve with a blue or green colour in benzene (see Arndt *et al.*, *loc. cit.*; Schönberg *et al.*, *Ber.*, 1928, **61**, 1382), but (XVI) and (XVII) form red solutions in benzene. As many substances containing, as do (XVI) and (XVII), the grouping A–S–CS–C (A = univalent group) (see p. 606) also give red solutions, this is evidence in support of the constitutions assigned to (XVI) and (XVII). In accordance with

---

* Gleu and Schaarschmidt (*Ber.*, 1939, **72**, 1251) have published a method (cf. ii) of converting the carbonyl into the thiocarbonyl group remarking that it shows " eine offensichtliche Parallele zu einer Methode von Schönberg (*Ber.*, 1928, **61**, 1375)." According to them, Schönberg's method is represented by (i), but since the action of water is

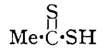
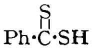
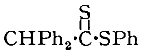
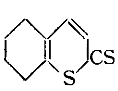
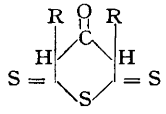


$$>C{:}O \longrightarrow >C\begin{smallmatrix}Cl\\Cl\end{smallmatrix} \xrightarrow{CH_3{\cdot}CO{\cdot}SH} >C\begin{smallmatrix}S{\cdot}COMe\\Cl\end{smallmatrix} \xrightarrow{\text{hydrolysis}} >C\begin{smallmatrix}SH\\Cl\end{smallmatrix} \xrightarrow{-HCl} >C{:}S \qquad (i)$$

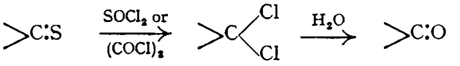
$$>C{:}O \longrightarrow >C\begin{smallmatrix}Cl\\Cl\end{smallmatrix} \xrightarrow{H_2S_2O_3} >C\begin{smallmatrix}S{\cdot}SO_3H\\Cl\end{smallmatrix} \xrightarrow{\text{hydrolysis}} >C\begin{smallmatrix}SH\\Cl\end{smallmatrix} \xrightarrow{-HC} >C{:}S \qquad (ii)$$

not necessary, it is correctly represented by (B). When thioketones are prepared by a method using hydrolysis (see ii), there is always the possibility that some of the corresponding ketone is formed in addition. Ketones and the corresponding thioketones are extremely difficult to separate by crystallisation, and for this reason the above method (B) was developed to avoid the use of a hydrolysing agent.

these structures, (XVI) and (XVII) do not show the behaviour of thioketones, for they are practically unchanged when treated with oxalyl chloride or thionyl chloride followed by water. If these substances,

 $\mathrm{Me{\cdot}\overset{S}{\overset{\|}{C}}{\cdot}SH}$	Red-yellow	 $\mathrm{Ph{\cdot}\overset{S}{\overset{\|}{C}}{\cdot}SH}$	Violet-red
$[(\alpha)C_{10}H_7{\cdot}CS{\cdot}S{\cdot}]_2$	Red	 $\mathrm{CHPh_2{\cdot}\overset{S}{\overset{\|}{C}}{\cdot}SPh}$	Orange
	Red	 (R = Me or Ph.)	Orange-red

like their progenitors, were thioketones, replacement of one sulphur atom by oxygen would have taken place:



$$>\!C{:}S \xrightarrow[(COCl)_2]{SOCl_2\text{ or}} >\!CCl_2 \xrightarrow{H_2O} >\!C{:}O \qquad \text{(D)}$$

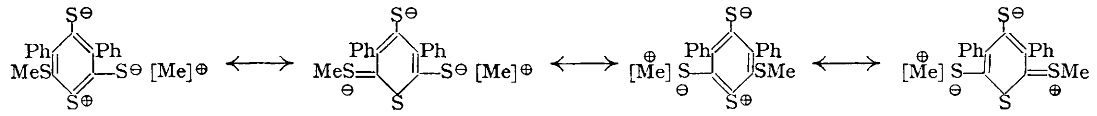
The ready replacement of the :CS group in thioketones according to (D) seems to be a general reaction; thiobenzophenone, *pp'*-dimethoxythiobenzophenone, xanthione, dithioflavone, 2 : 6-bisethylthio- (XV) and 2 : 6-bismethylthio-4-thio-3 : 5-diphenyl-1-thiapyrone (XIV) were found to react according to (D).

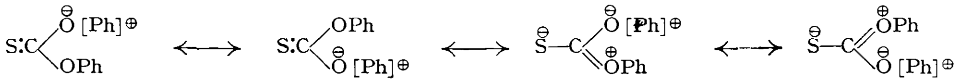
The rearrangement $R'{\cdot}CS{\cdot}CR''{:}CR'''{\cdot}SR \xrightarrow{\text{heat}} R'{\cdot}C(SR){:}CR''{\cdot}CR'''{:}S$ (cf. C) (R = alkyl; R', R'', R''' are univalent groups) is that of a pentad system, but resembles that of the triad system (Schönberg *et al.*, *Ber.*, 1930, **63**, 178; *Annalen*, 1930, **483**, 107):

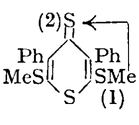
$$CO(SR)_2 \xrightarrow{\text{heat}} C(OR)(SR)S \qquad \text{(E)}$$

where R is an alkyl group. In both cases, (C) and (E), the rearrangements are irreversible and are brought about by heat, the migrating group before the rearrangement being attached to the sulphur atom. All the reactions of the types (C) and (E) yet investigated yield substances of lower m. p. from those of higher m. p.

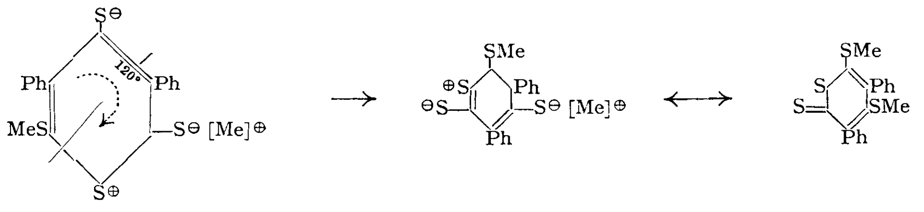
Mechanism of the Thermal Rearrangement of γ- to α-Thiopyrones (C) *and of Thioncarbonic Acids to Esters of Thiolcarbonic Acids* (E).—These thermal isomerisations may be explained by assuming that at high temperatures ionic structures make a definite contribution to the mesomeric state. In both cases, the unusual stability of the organic anion may be explained by resonance stabilisation. Only a few of the possible structures are shown below:



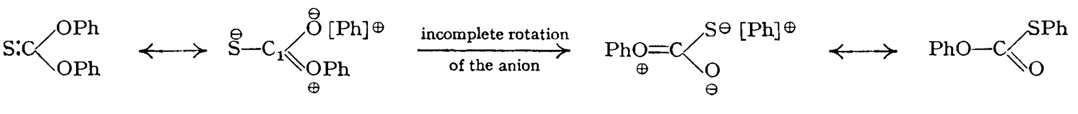




The migration of Me from S(1) to S(2) (see inset) is not believed to be a migration in the proper meaning of the word, *i.e.*, we believe that the Me group does not move an appreciable distance as indicated by the arrow, but we assume that the anion rotates about 120° in the plane of the paper as indicated below. According to this hypothesis, it is not necessary to assume that the ions have the independent existence which is necessary for a short time if the old conception of migration be true.

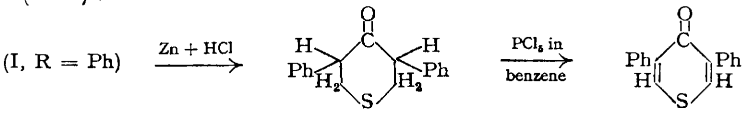


The thermal isomerisation of the aryl esters of the thioncarbonic acids on the basis of the " rotation theory " as contrasted with the old " migration theory " is pictured below. The rotation of the anion (about 120°) is effected round the axis going through the central atom C_1 perpendicular to the plane of the paper.



On the basis of the migration theory, it is difficult to explain why anions and cations, which are generally regarded as reactive, should not react with a solvent, and special theories have been advanced to explain this. When the rearrangement takes place in consequence of rotation, no reaction would be expected with the molecules of the solvent, as the electrically charged groups do not migrate in space and therefore do not collide with the molecules of the solvent; the concept of rotation has also led to the discovery of the reversible thermal rearrangement oxalyl dibenzyl ketone $\rightleftharpoons$ *iso*oxalyl dibenzyl ketone (Schönberg and Aly Sina, this vol., p. 601).

(e) We have treated (XVIII) with phosphorus pentachloride in benzene solution and obtained 3 : 5-*di*-*phenyl*-1-*thia*-γ-*pyrone* (XIX) :



(XVIII.) (XIX.)

By a similar process Arndt, Nachtwey, and Pusch (*Ber.*, 1925, **58**, 1639) prepared 2 : 6-diphenyl-1-thia-γ-pyrone.

EXPERIMENTAL.

Action of Alcoholic Potassium Hydroxide on 2 : 6-*Bismethylthio*-2 : 6-*diphenyl*-1-*thia*-γ-*pyrone* (III).—The pyrone (1 g.) (Apitzsch, *Ber.*, 1904, **37**, 1607; 1905, **38**, 2891) was refluxed with alcoholic potash (1·5 g. KOH in 30 c.c. alcohol) for one hour. The solution was filtered when cold and acidified with dilute hydrochloric acid; a yellow amorphous substance was obtained, and a foul pungent odour evolved. After standing for 24 hours the substance was collected, washed with water, and dried on a porous plate; β-(*phenylacetylenylthio*)-β-*methylthio*-α-*phenylacrylic acid* (VI) then crystallised from toluene in light yellow crystals, m. p. 200° (Found : C, 66·45; H, 4·55; S, 19·2. $C_{18}H_{14}O_2S_2$ requires C, 66·3; H, 4·3; S, 19·6%). It gave an almost colourless solution with concentrated sulphuric acid and dissolved in cold aqueous potassium hydroxide; it was recovered unchanged after 6 hours' refluxing with a mixture of acetic acid (20 c.c.) and concentrated hydrochloric acid (10 c.c.).

Action of diazomethane on (VI). Diazomethane in ethereal solution, added to (VI), dissolved with a vigorous evolution of gases; the solution was kept at 0° for 24 hours, and the solvent then evaporated. The residue was crystallised from ligroin (b. p. 80—90°), and the *methyl* ester obtained in yellow plates, m. p. 153° (Found : C, 67·1; H, 4·5; S, 18·4. $C_{19}H_{16}O_2S_2$ requires C, 67·1; H, 4·7; S, 18·8%), soluble in concentrated sulphuric acid with a yellow colour, and insoluble in aqueous potassium hydroxide. The ester (1 g.), when dissolved in acetic acid (30 c.c.) and refluxed for 4 hours with hydrochloric acid (10 c.c.), gave light yellow crystals of the acid.

Action of Alcoholic Potassium Hydroxide on 2 : 6-*Bismethylthio*-3 : 5-*dimethyl*-1-*thia*-γ-*pyrone* (V).—The pyrone (1 g.) (Apitzsch, *loc. cit.*, 1905), when treated with alcoholic potash as for (III), afforded ultimately pale yellow crystals, m. p. 155° (from benzene). This *acid* (VII) (Found : C, 47·8; H, 5·3; S, 31·3. $C_8H_{10}O_2S_2$ requires C, 47·5; H, 4·9; S, 31·6%) behaved exactly like its analogue (VI). Its *methyl* ester, prepared by means of diazomethane, crystallised from ligroin (b. p. 60—70°) in colourless crystals, m. p. 81° (Found : C, 49·8; H, 5·51; S, 30·0. $C_9H_{12}O_2S_2$ requires C, 50·0; H, 5·6; S, 29·6%), insoluble in aqueous potassium hydroxide. Hydrolysis as above afforded the acid (VII).

Non-action of Alcoholic Potassium Hydroxide on 2 : 6-*Dithio*-3 : 5-*diphenyl*-1-*thia*-γ-*pyranone* (I, R = Ph).—The pyranone (2 g.) (Apitzsch, *locc. cit.*), refluxed with alcoholic potash (3 g. KOH; 40 c.c. alcohol) for 4 hours, afforded a red-brown solution with much yellow deposit. The mixture was cooled, filtered, and the filtrate acidified with dilute hydrochloric acid, giving unchanged (I, R = Ph). The solid was dissolved in water (easily soluble) and acidified, but the red crystalline deposit, after crystallisation from chloroform, proved to be (I, R = Ph); m. p. of both samples 163°, not depressed by admixture with an authentic specimen.

2 : 6-*Bismethylthio*-4-*thio*-3 : 5-*diphenyl*-1-*thiapyrone* (XIV).—2 : 6-Bismethylthio-3 : 5-diphenyl-1-thia-γ-pyrone (III) Apitzsch, *loc. cit.*) (3 g.) was refluxed with thionyl chloride (30 c.c.) for 10 hours. The excess of thionyl chloride was distilled off by aid of the pump, and the residual red oil was dissolved in dry benzene (40 c.c.) and refluxed for 6 hours with thioacetic acid (8 c.c.). The excess of benzene and thioacetic acid was distilled off, and on addition of ligroin (b. p. 30—50°) to the residue, the *thioketone* (XIV) was deposited in violet-green crystals; recrystallised from xylene, it had m. p. 252° (red melt) [Found : C, 61·0; H, 4·4; S, 34·9; *M* (Rast's method), 384. $C_{19}H_{16}S_4$ requires C, 61·2; H, 4·3; S, 34·4%; *M*, 372]. It dissolved in hot benzene with a green colour, was difficultly soluble in ether and very sparingly soluble in acetone; the crystals when pressed gave a green powder. It was insoluble in aqueous potassium hydroxide and did not react with diazomethane; it was recovered unchanged when refluxed (1 g.) with copper bronze (4 g.) for 5 hours in xylene solution (30 c.c.). When mercuric chloride crystals were added to a dilute solution of the thioketone (XIV) in benzene, they at once become yellow on the surface and the green colour of the solution faded strongly; the yellow product was collected and shaken with an aqueous solution of potassium iodide in the presence of benzene. The benzene layer was isolated and on evaporation gave unchanged (XIV).

2 : 6-*Bisethylthio*-4-*thio*-3 : 5-*diphenyl*-1-*thiapyrone* (XV).—2 : 6-Bisethylthio-3 : 5-diphenyl-1-thia-γ-pyrone (IV) (Apitzsch, *locc. cit.*) (3 g.) was treated with thionyl chloride (40 c.c.) and thioacetic acid (8 c.c.) as described for (III). The *thioketone* (XV) was obtained after cooling the benzene solution and adding ligroin (b. p. 30—50°); it recrystallised from chloroform in green crystals, m. p. 206° (green melt) (Found : C, 63·0; H, 5·1; S, 32·2. $C_{21}H_{20}S_4$ requires C, 63·0; H, 5·0; S, 32·0%). This thioketone is difficultly soluble in cold ether, and soluble in concentrated sulphuric acid with a yellow colour. When the green solution of the substance in benzene was treated with mercuric chloride crystals, their colour changed immediately to orange and the colour of the solution faded.

Thermal Decomposition of 2 : 6-*Dithio*-3 : 5-*diphenyl*-1-*thia*-γ-*pyranone* (I, R = Ph).—(*a*) The substance (1 g.) was placed in a Pyrex tube through which a stream of dry carbon dioxide was passed for 10 minutes. The tube was then placed in a metal-bath at 120° while the gas was passing, and the temperature of the bath raised to 250° during 6 minutes and kept at 250—260° for 30 minutes. During the experiment white vapours passed over. The contents of the tube when cooled were powdered and washed well with acetone. 2 : 3-6 : 5-*Dithionaphtheno*-1-*thia*-γ-*pyrone* (IX) crystallised from tetralin in light yellow crystals, m. p. 263° (Found : C, 62·65; H, 2·55; S, 29·0. $C_{17}H_8OS_3$ requires C, 62·9; H, 2·5; S, 29·5%). It dissolves with great difficulty in hot benzene, xylene, acetone and chloroform, is soluble in hot nitrobenzene, and dissolves in concentrated sulphuric acid with a yellow colour. When heated at ordinary pressure, it sublimes in long yellow crystals. It is insoluble in cold or hot aqueous alcoholic potash and is not attacked by diazomethane or by boiling with a mixture of acetic acid and concentrated hydrochloric acid (3 : 1).

(*b*) Similar treatment of (I, R = Ph) (2 g.), the temperature being raised to 200° within 2 minutes and kept there for 30 minutes, caused vigorous evolution of hydrogen sulphide, and working up of the solid as in (*a*) afforded (X) or (XII); this crystallised from tetralin and then from nitrobenzene in light yellow crystals, m. p. above 350° [Found: C, 69·1; H, 3·4; S, 21·8. $(C_{17}H_{10}OS_2)_n$ requires C, 69·3; H, 3·4; S, 21·7%]. This *substance* dissolves with great difficulty in the ordinary solvents and gives a yellow colour with concentrated sulphuric acid. It does not react with diazomethane, and is unaffected by 6 hours' refluxing with a mixture of acetic acid and concentrated hydrochloric acid. It (0·5 g.) did not react with sulphur (1 g.) when the mixture was heated in a boiling ethyl phthalate bath for 30 minutes in a stream of carbon dioxide.

(*c*) *Thermal decomposition of* (I, R = Ph) *in nitrobenzene.* The substance was heated under reflux with nitrobenzene (15 c.c.) for 6 hours. The solution when cooled gave light yellow crystals of (X) or (XII) in good yield (Found: C, 69·3; H, 3·64; S, 21·2%).

Action of alcoholic potash on (X) *or* (XII). The substance (0·5 g.) was refluxed with alcoholic potash (3 g. KOH; 50 c.c. alcohol) for ½ hour. The solution was cooled, filtered, and acidified with dilute hydrochloric acid; an orange solid separated on the surface. It was filtered off, dried, crystallised from chloroform, and identified (mixed m. p.) as 2 : 6-dithio-3 : 5-diphenyl-1-thia-γ-pyranone (Apitzsch, *loc. cit.*).

Thermal Decomposition of 2 : 6-*Dithio*-3 : 5-*dimethyl*-1-*thia*-γ-*pyranone* (I, R = CH_3).—(*a*) *Without solvents.* Under conditions similar to those in (*b*) above, this substance decomposed with evolution of hydrogen sulphide, and after 30 minutes at 200—220° the *product* (XI) or (XIII) was worked up as before; it crystallised from tetralin or from benzonitrile in yellowish-white crystals, m. p. above 310° [Found: C, 50·0; H, 3·7; S, 37·8. $(C_7H_6OS_2)_n$ requires C, 49·4; H, 3·5; S, 37·6%]. It is very difficultly soluble in the ordinary organic solvents and dissolves in concentrated sulphuric acid with a yellow colour. It does not react with diazomethane or with acetic and hydrochloric acids as above.

(*b*) *In tetralin.* The substance (1 g.) was dissolved in boiling tetralin (15 c.c.) and refluxed for 4 hours. The solution on cooling gave yellow crystals of (XI) or (XIII) in good yield (Found: C, 49·3; H, 3·8; S, 37·7%).

Action of alcoholic potash on (XI) *or* (XIII). The substance (1 g.) was refluxed with alcoholic potash (alcohol, 40 c.c.; KOH, 2 g.) for 30 minutes. The solution was filtered and acidified with dilute hydrochloric acid, giving an orange semi-solid that solidified on standing. It was filtered off, dried, crystallised from chloroform (m. p. 155°), and identified (mixed m. p.) as (I, R = CH_3) (Apitzsch, *loc. cit.*).

Thermal Rearrangement of 2 : 6-*Bismethylthio*-4-*thio*-3 : 5-*diphenyl*-1-*thia*-γ-*pyrone* (XIV).—0·5 G. was heated in a Monax tube to 240—250° (bath temp.) for 10 minutes. The chloroform solution of the product was evaporated and the residue crystallised from chloroform–light petroleum (b. p. 30—50°). 4 : 6-*Bismethylthio*-2-*thio*-3 : 5-*diphenyl*-1-*thia*-α-*pyrone* (XVI) was obtained in red crystals, m. p. 209° (Found: C, 60·9; H, 4·3; S, 34·7. $C_{19}H_{16}S_4$ requires C, 61·2; H, 4·3; S, 34·4%); it is difficultly soluble in cold ether, insoluble in aqueous potassium hydroxide, and does not react with diazomethane. When mercuric chloride crystals are added to its red solution in benzene, they become orange on the surface. (XVI) (0·5 g.) was recovered unchanged after refluxing for 6 hours with thionyl chloride (15 c.c.). The isomeric change of (XIV) to (XVI) was also effected by dissolving (XIV) in ethyl phthalate and boiling the solution for about 15 minutes.

Thermal Rearrangement of 2 : 6-*Bisethylthio*-4-*thio*-3 : 5-*diphenyl*-1-*thia*-γ-*pyrone* (XV).—0·5 G. was heated in a Monax tube at 220—230° (bath temp.) for 10 minutes. The contents of the tube crystallised from petrol (b. p. 100—150°) in red-brown crystals, m. p. 200° (Found: C, 62·7; H, 5·2; S, 32·2. $C_{21}H_{20}S_4$ requires C, 63·0; H, 5·0; S, 32·0%). 4 : 6-*Bisethylthio*-2-*thio*-3 : 5-*diphenyl*-1-*thia*-α-*pyrone* (XVII) is readily soluble in chloroform and dissolves in concentrated sulphuric acid with a yellowish-brown colour. When mercuric chloride crystals are added to the red benzene solution of (XVII), they acquire an orange-yellow colour. (XVII) (0·5 g.) was recovered unchanged after refluxing for 3 hours with oxalyl chloride (8 g.).

The isomeric change of (XV) to (XVII) can also be effected by dissolving (XV) in ethyl phthalate and boiling the green solution for 10 minutes; after 2 minutes' boiling, the solution becomes red.

Action of Thionyl Chloride or Oxalyl Chloride followed by Water on Thioketones.—2 : 6-*Bisethylthio*-4-*thio*-3 : 5-*diphenyl*-1-*thia*-γ-*pyrone* (XV). 0·5 G. of the pyrone was added to oxalyl chloride (5 g.) (it dissolved immediately, giving a bright red colour) and heated under reflux for 2 hours. The solution was then poured into ice-cold water; the dirty yellow solid which separated was isolated, dried, and crystallised from petrol (b. p. 80—90°); it formed yellowish-white crystals, m. p. 140°, undepressed on admixture with the 1-thia-γ-pyrone (IV) (Apitzsch, *loc. cit.*).

When the bismethylthio-analogue (0·5 g.) was dissolved in thionyl chloride (10 c.c.) (red solution) and refluxed for 4 hours, the excess of thionyl chloride distilled off, and the remaining oil dissolved in benzene (10 c.c.) and shaken with water (20 c.c.), working up of the benzene layer afforded a yellow oil; on being washed with petrol (b. p. 30—50°), this solidified, and crystallisation from petrol (b. p. 90—100°) afforded colourless crystals of (III).

Xanthione, 4-thio-1-thiaflavone (Arndt, Nachtwey, and Pusch, *Ber.*, 1925, **58**, 1644), thiobenzophenone, or 4 : 4′-dimethoxythiobenzophenone (1 g.), similarly treated with thionyl chloride (15 c.c.) for 2 hours, each yielded the corresponding ketone.

3 : 5-*Diphenyl*-1-*thia*-γ-*pyranone* (XVIII).—Apitzsch's preparation (*Ber.*, 1904, **37**, 1609) of (XVIII) was modified as follows. 2 : 6-Dithio-3 : 5-diphenyl-1-thia-γ-pyranone (I, R = Ph) (5 g.) was dissolved in boiling acetic acid (200 c.c.). To this solution, zinc dust (20 g.) was added and then concentrated hydrochloric acid (25 c.c.) in small portions. After ½ hour's boiling, similar additions were made, and the solution was then boiled till the colour became pale yellow (2½ hours in all). The hot solution was filtered, and when cold it was poured into water (250 c.c.). The deposit obtained was collected after 2 hours and separated from alcohol (charcoal) in colourless crystals, m. p. 137° (2 g.).

3 : 5-*Diphenyl*-1-*thia*-γ-*pyrone* (XIX).—The pyranone (XVIII) (1 g.) was dissolved in dry benzene (15 c.c.) and refluxed for 2 hours with phosphorus pentachloride (2 g.); the yellow product which separated was filtered off after cooling, washed with benzene, and then dissolved in alcohol (20 c.c.) (vigorous reaction). The alcoholic solution was poured into ice-cold water (about 200 c.c.) and 3 : 5-*diphenyl*-1-*thia*-γ-*pyrone* (XIX) separated; after 2 hours, it was filtered off and then crystallised from alcohol in light yellow crystals, m. p. 167° (Found: C, 77·4; H, 4·6; S, 12·1. $C_{17}H_{12}OS$ requires C, 77·3; H, 4·5; S, 12·1%).

FOUAD 1ST UNIVERSITY, CAIRO, EGYPT.

[*Received, November* 14*th*, 1945.]