51. *Organic Sulphur Compounds. Part XXVIII. Thiono-thiol Tautomerism manifested by Sulphur Analogues of Cyclic Acid Anhydrides.*

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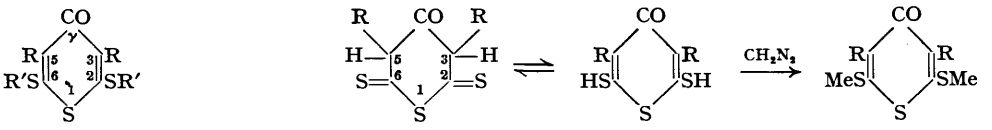
The tautomeric changes (II $\rightleftharpoons$ III) are discussed. Substances (II) are deep orange and form (*e.g.*, with diazomethane) colourless products of the general formula (I, R and R′ = univalent residue).

Apitzsch (*Ber.*, 1904, **37**, 1599; 1905, **38**, 2888; 1908, **41**, 4028) has stated that ketones of the general type $R{\cdot}CH_2{\cdot}CO{\cdot}CH_2R$ react with carbon disulphide in the presence of potassium hydroxide with the formation of orange-red substances of the general formula (III, R = univalent residue). He stated that compounds (III), when allowed to react with sodium methoxide, form the sodium salts, which, with methyl iodide, propyl chloride, benzyl chloride and so on, form colourless or almost colourless substances of the general formula (I, R = univalent residue).

According to modern views on the relationship between colour and constitution, it is very improbable that substances of constitution (III) are deeply coloured, whereas the derivatives, *e.g.*, the dimethyl ethers (IV), are colourless. Moreover, there is no reason why substances of constitution (III) should be deeply coloured.

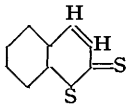
We believe that the orange substances mentioned above are derivatives of 2 : 6-dithio-1-thiopyranone (II, R = H) and that in their solutions a thiono-thiol equilibrium exists (II ⇌ III). The orange colour



(I.) (II.) (III.) (IV.)

attributed to substances of structure (II) is in accordance with the colour of substances of similar constitution (see Table), which all (except VI*a*) contain, as (II) does, the group $>C(=S)-C(=S)-SR$ (R = univalent residue). The lack of colour in (I) and the orange colour of (II) may be compared with the lack of colour in (VI*a*) and the orange colour of (V*a*) (Schönberg and co-workers, *Ber.*, 1931, **64**, 2582).

TABLE.

$Me-C(=S)-SH$	Red-yellow	$\alpha\text{-}C_{10}H_7-C(=S)-S\cdot S-C(=S)-C_{10}H_7(\alpha)$	Red
$Ph-C(=S)-SH$	Violet-red		Red

$CHPh_2-C(=S)-SPh$ (V*a*.)	Orange
$CPh_2=C(SH)\cdot SPh$ (VI*a*.)	Colourless

Very little is known about thiono-thiol tautomerism. The text books concerned with tautomerism hardly mention this type, as there is a great tendency for the substances in question to react in the thiol form only. The problem arises, why substances of the general formula (II) are stable. It seems quite possible that the stabilisation is due to resonance and that these substances have to be regarded as resonance hybrids involving the forms (II), (V), and (VI).

The supposed equilibrium (II ⇌ III) explains why colourless or light yellow substances are obtained from the orange-red substances, not only in the cases mentioned by Apitzsch and co-workers (see above) but also by the action of diazomethane, diphenyldiazomethane, and piperidine. For instance, we found that the orange compounds (II, R = Ph or CO_2Et) yield the colourless compounds (IV, R = Ph or CO_2Et). We obtained, by the action of piperidine on (II, R = Ph), a yellow crystalline substance soluble in cold water and decomposing on heating with the splitting of piperidine; we advance for this substance the formula of a salt [compare (VII)].

(V.) (VI.) (VII.)

EXPERIMENTAL.

Action of Diazomethane on 2 : 6-*Dithio*-3 : 5-*diphenyl*-1-*thio*-γ-*pryanone* (II, R = Ph).—An ethereal solution of diazomethane (*Org. Syn.*, Vol. XV, 3) was added to the deep red ethereal solution of (II, R = Ph). Vigorous evolution of gas was observed and the mixture was kept at 0° for 24 hours. The product was crystallised from ligroin (b. p. 100—150°) and proved to be the colourless 2 : 6-bismethylthio-3 : 5-diphenyl-1-thio-γ-pyrone (IV, R = Ph), m. p. not depressed by an authentic specimen (Apitzsch, *Ber.*, 1904, **37**, 1607).

Action of Diphenyldiazomethane on 2 : 6-*Dithio*-3 : 5-*diphenyl*-1-*thio*-γ-*pyranone* (II, R = Ph).—To a warm benzene solution (30 c.c.) of (II, R = Ph) (1 g.), a benzene solution of diphenyldiazomethane [prepared from benzophenonehyrazone (1·5 g.) (Staudinger and co-workers, *Ber.*, 1916, **49**, 1928)] was added. Vigorous evolution of gas took place and the mixture was kept for 1 day at room temperature, the solvent then being driven off and the residue crystallised from alcohol. Almost colourless crystals of 2 : 6-*bisbenzhydrylthio*-3 : 5-*diphenyl*-1-*thio*-γ-*pyrone* (I; R = Ph, R′ = $CHPh_2$), m. p. 162°, were obtained. The substance was freely soluble in benzene, and dissolved with difficulty in cold ether and cold ligroin (b. p. 100—110°) (Found: C, 77·8; H, 4·9. $C_{43}H_{32}OS_3$ requires C, 78·2; H, 4·8%).

Action of Piperidine on 2 : 6-*Dithio*-3 : 5-*diphenyl*-1-*thio*-γ-*pyranone* (II, R = Ph).—The pyranone derivative (1 g.) was dissolved in acetone (15 c.c.) and refluxed for 1 hour with piperidine (10 c.c.). After cooling, the crystals formed were collected and washed with acetone, in which (II, R = Ph) is freely soluble. The light yellow crystals of *dipiperidinium* 2 : 6-*disulphydryl*-3 : 5-*diphenyl*-1-*thio*-γ-*pyrone* (VII) dissolved with difficulty in ether, turned orange at about 180°, and melted at about 200° with the splitting of piperidine. They were soluble in cold water and on addition of dilute sulphuric acid an orange deposit was formed (Found: C, 65·0; H, 6·9; N, 5·2; S, 19·3. $C_{27}H_{34}ON_2S_3$ requires C, 65·0; H, 6·8; N, 5·6; S, 19·2%).

The thermal decomposition of the substance was accomplished in a closed apparatus which allowed the liberated piperidine to condense and the decomposition was carried out in a boiling nitrobenzene bath. The product was identified as piperidine by means of the picrate.

Action of Diazomethane on Ethyl 2 : 6-*Dithio*-1-*thio*-γ-*pyranone*-3 : 5-*dicarboxylate* (II, R = CO_2Et).—To the substance (2 g.), dissolved in ether, an ethereal solution of diazomethane was added, and the mixture kept at 0° for 24 hours. The product separated from alcohol in colourless crystals, m. p. 81—82°. It gave no depression with authentic ethyl 2 : 6-bismethylthio-1-thio-γ-pyrone-3 : 5-dicarboxylate (IV, R = CO_2Et) (Apitzsch, *Ber.*, 1908, **41**, 4033) (Found: C, 45·1; H, 4·8. Calc. for $C_{13}H_{16}O_5S_3$: C, 44·8; H, 4·6%).

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[*Received, October 21st*, 1944.]