

Photochemistry of Sulphur Compounds Related to the 1,2-Dithiole System. Part IV.† Photoisomerization of α -[7-(5-Aryl or -Alkyl-1,2-dithiol-3-ylidene)]-4,5,6,7-tetrahydro-1,2-benzodithiol-3-ylidene Ketones

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The photochemistry of a series of higher polysulphur analogues of 1,2-dithiol-3-ylidene ketones has been studied. The normal *cis* form is converted into the *trans* on irradiation of an ethanolic solution containing catalytic amounts of hydrogen chloride. The photoproduct reverts to starting material by a dark process, which obeys first-order kinetics. The rate constants are only slightly affected by variation of substituents.

It has recently been shown that α -(1,2-dithiol-3-ylidene) ketones and aldehydes (I) upon irradiation are transformed into the *trans*-isomers (II), which revert to the starting compound *via* a thermal process.¹⁻⁴

The 1,2-dithiol-3-ylidene ketone system can be extended to include one more 1,2-dithiole nucleus⁵ in compounds of type (III). (The cyclohexane ring has

hitherto been an absolute prerequisite for the synthesis of this type of compound.)

The geometry of the ketonic portion of compounds (III) has been shown to be closely related to that of the 1,2-dithiol-3-ylidene ketones (I). The geometry for compound (IIIb) determined by X-ray crystallography is as shown.⁶

† Refs. 1 and 2 are considered to be Parts II and III, respectively, of this series.

¹ C. Th. Pedersen and C. Lohse, *J.C.S. Perkin I*, 1973, 2837.

² C. Th. Pedersen and C. Lohse, *J.C.S. Chem. Comm.*, 1973, 123.

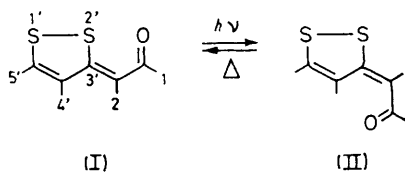
³ G. Calzaferri, R. Gleiter, K.-H. Knauer, E. Rommel, E. Schmidt, and H. Behringer, *Helv. Chem. Acta*, 1973, **56**, 597.

⁴ R. Gleiter, K.-H. Knauer, E. Schmidt, Y. Mollier, and R. Pinel, *Tetrahedron Letters*, 1973, 1257.

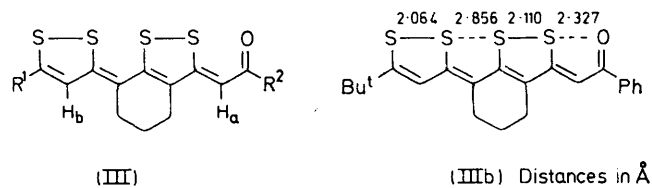
⁵ M. Stavaux, *Bull. Soc. chim. France*, 1971, 4429.

⁶ J. Sletten and M. Velsvik, *Acta Chem. Scand.*, 1973, **27**, 3881.

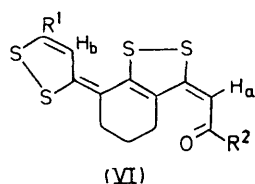
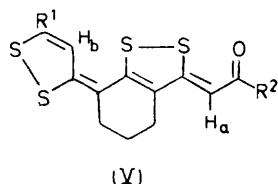
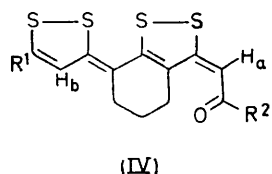
In the 1,2-dithiol-3-ylidene ketone series, S-O distances in the range 2.184–2.443 Å and S(1')–S(2') distances



in the range 2.101–2.137 Å have been observed, depending on the substitution (*cf.* ref. 6). The same type of *cis-trans*-photoisomerization as is observed for



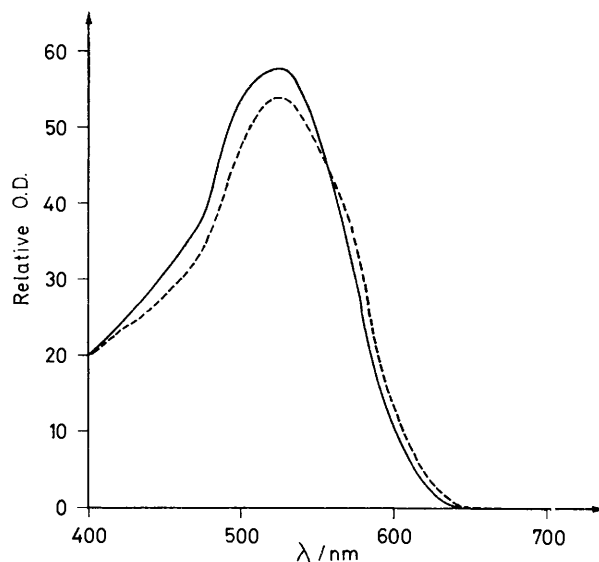
the 1,2-dithiol-3-ylidene ketones should therefore be possible for compounds of type (III), giving rise to isomers such as (IV). However, isomerization around the other double bond or around both double bonds is also possible and will lead to isomers such as (V) and (VI), respectively.



RESULTS AND DISCUSSION

Gleiter *et al.* originally claimed that the photoproduct obtained from 1,2-dithiol-3-ylidene ketones was an O-S-bonded valence tautomer.⁷ The formation of such isomers from the irradiation of (III) can be excluded on the basis of the following observation. When a compound of type (III) was irradiated in a polymethacrylate matrix it was converted into a photoproduct with an absorption spectrum slightly different from that of the starting material (Figure). The photoproduct only reverted to starting material on heating at 120 °C for 24 h. If O-S-bonded tautomers were formed only small geometrical changes in the molecule would be necessary during the reversion, whereas the change from *trans* to *cis* requires a large modification in geometry, which is only possible in the matrix at high temperature.

Flash-photolysis of (III) in neutral 10⁻⁶M-ethanolic solution converted it into the same photoproduct, which reverted so slowly to the starting material that it was not possible to study accurately the kinetics of the back reaction owing to the long term instability of the equipment used. However, Calzaferri *et al.*³ observed that the reversion of the photoproducts from 1,2-dithiol-3-ylidene ketones was catalysed by acids. We have observed that if the photolysis of (III) was carried out in a 10⁻⁶M solution containing 10⁻⁴M-hydrogen chloride, reasonable rate constants for the back



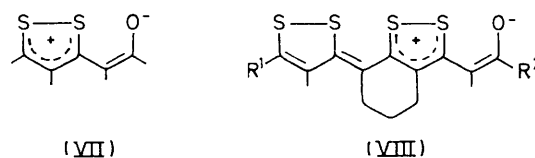
Visible spectrum of (IIIa) in a polymethacrylate matrix: full line before irradiation, dotted line after irradiation

reaction were obtained at 25 °C, and the process was found to obey first-order kinetics. The rate constants for various substituted compounds are given in the Table.

Rate constants for thermal back reaction of photoproducts from (III) at 25 °C obtained from 10⁻⁶M solutions in absolute ethanol containing 10⁻⁴M-hydrogen chloride

Compound	R ¹	R ²	k/s ⁻¹
(IIIa)	Bu ^t	4-MeOC ₆ H ₄	0.65
(IIIb)	Bu ^t	Ph	0.90
(IIIc)	Bu ^t	Bu ^t	0.43
(IIId)	Ph	4-MeOC ₆ H ₄	0.26
(IIIe)	Ph	Ph	0.28
(IIIf)	Ph	Bu ^t	0.19
(IIIg)	4-MeOC ₆ H ₄	Ph	1.83
(IIIh)	4-MeOC ₆ H ₄	Bu ^t	0.88

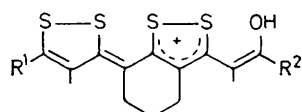
Both compounds of type (III) and dithiolylidene ketones can be regarded as resonance hybrids of forms such as (III) and (VIII) and (I) and (VII), respectively.



⁷ R. Gleiter, D. Werthemann, and H. Behringer, *J. Amer. Chem. Soc.*, 1972, **94**, 651.

It has been shown for the dithiolylidene ketones by comparison of i.r. spectra with those of ^{18}O enriched compounds that the contribution of the ketonic forms in some cases is as low as 27%.⁸ As O-S-bonded structures can be excluded by means of ESCA spectra⁹, this means that it is the polar forms which dominate.

These polar forms which lower the double-bond character between C(2) and C(3') in the dithiolylidene ketones and that of the corresponding bond in compounds (III) will probably give rise to a shortening of the O-S distance. The relatively long O-S distance in (III) may thus indicate a strong contribution of the ketonic form, which means that the bond to the dithiole nucleus has high double-bond character. Catalysis is therefore necessary in these compounds. Protonation of the oxygen will give rise to structures such as (IX) which lower the double-bond character, and therefore give a faster back reaction.



(IX)

Rate measurements at several concentrations of hydrogen chloride were performed. It is to be noted that the isomerization reactions are very strongly catalysed by acid, and moreover, a plot of $\log k_{\text{obs}}$ vs. $-H_0$ is linear with a slope of 1.00. The same slope was found for 1,2-dithiol-3-ylidene ketones. Thus a similar process seems to be operative in both isomerizations. In the u.v. spectrum a shift of the carbonyl absorption towards longer wavelengths was observed on addition of acid.

The results discussed hitherto are consistent with the presence of isomer (IV) but do not exclude isomers (V) and (VI). The 90 MHz ^1H n.m.r. spectrum of (IIIh) shows two singlets at δ 6.88 and 6.52 in carbon tetrachloride, consistent with the previously reported values in carbon disulphide by Stavaux,⁵ who assigned the signal at δ 6.88 to H_b and that at 6.52 to H_a . These signals were not shifted on addition of 10^{-5}M trifluoroacetic acid.

When the photolysis experiments were carried out in 10^{-5}M -trifluoroacetic acid in carbon tetrachloride the photoproduct had a lifetime of *ca.* 20 min, which was long enough to obtain its n.m.r. spectrum. Owing to the low solubility of the product and its relatively short lifetime, ^1H Fourier transform spectra were found most suitable for the study.

After irradiation of a 0.2% solution with a mercury lamp without a filter in a Pyrex n.m.r. tube for 60 s, the signal at δ 6.52 had disappeared and a new signal had appeared at 6.25, whereas the signal at 6.88 was not shifted. Thus the signal corresponding to H_a was shifted to higher field whereas that corresponding to H_b was not shifted, which is consistent only with structure (IV) for the photoproduct. If isomer (V) were formed, the H_b signal should be shifted and that of H_a not, and if (VI) were formed both signals should be shifted. The shift observed is in accordance with the observations of Calzaferri *et al.* of the analogous shift in the case of 1,2-dithiolylidene ketones.

If the concentration of trifluoroacetic acid was increased to 10^{-1}M the compounds were photostable and the colour was shifted from red or red-violet to blue. At this concentration of acid the compounds are probably entirely in the salt form and there is free rotation around the former double bond, as is observed for (1,2-dithiol-3-ylideno)phenolates.⁴

As shown in the Table, the influence of changing the substituents on the rate constants is only slight, in accord with the observations for the 1,2-dithiol-3-ylidene ketones.² It was found for these compounds that the rate constants for the thermal back reaction are only weakly dependent on the substituents in positions 1 and 5', but strongly dependent on those in position 4'. All the compounds studied here have the same substituent, *viz.* part of the cyclohexane ring, in the position corresponding to the 4' position of the 1,2-dithiolylidene ketones.

EXPERIMENTAL

The rate constants for the *trans-cis*-isomerization were obtained by using the flash photolytic equipment described previously.¹ The kinetics were extremely sensitive to the presence of water.

The ^1H n.m.r. spectra were recorded on a Bruker WH 90 Fourier transform n.m.r. spectrometer.

Compounds (IIIa-h) were prepared as previously described.⁵

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⁸ D. Festal and Y. Mollier, *Tetrahedron Letters*, 1970, 1259.

⁹ B. J. Lindberg, S. Högberg, G. Malmsten, J.-E. Bergmark, Ö. Nilsson, S.-E. Karlsson, A. Fahlman, U. Gelius, R. Pinel, M. Stavaux, Y. Mollier, and N. Lozac'h, *Chimica Scripta*, 1971, 1, 183.