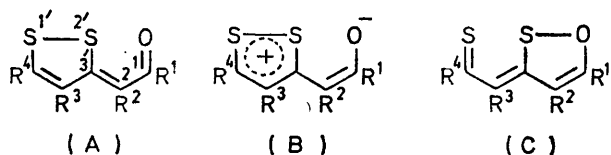


Thermal Reversal of the Photochemically Induced *cis*-*trans*-Isomerisation of α -(3*H*-1,2-Dithiol-3-ylidene) Ketones and Aldehydes. Substituent Effects

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Sixteen substituted α -(3*H*-1,2-dithiol-3-ylidene) ketones and aldehydes have been shown to give *trans*-isomers and not O-S bonded valence tautomers upon photolysis. The *cis*-*trans*-isomerization was found to be a photochemical process whereas the *trans*-*cis*-isomerization was a thermal process. The rate constants for the *trans*-*cis*-isomerization were found to be controlled mainly by steric factors.

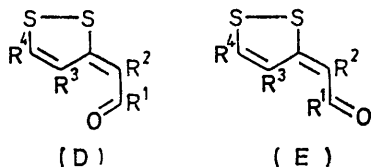
THE structure of dithiolylidene ketones and aldehydes has been the subject of numerous, recent studies. The main structures that have been considered are (A)—(C),¹



(I) — (XVI)

which can be regarded as valence tautomers. It has been shown by ESCA spectroscopy that the oxygen atom has some negative charge. There is no evidence for the presence of an O-S bond² although the S-O distance in these compounds is smaller than the sum of the van der Waals radii.¹ This does not exclude the possibility that such O-S bonded tautomers can be formed *via* an excited state.

Gleiter *et al.*³ have reported that dithiolylidene ketones are transformed into O-S bonded tautomers upon irradiation. We have recently reported that the compounds actually formed are the *trans*-isomers (D) of the dithiolylidene ketones.⁴ This was substantiated by the

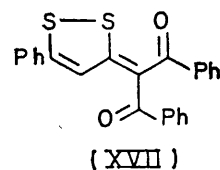


fact that dithiolylidene ketones irradiated in ethanolic solution were converted into a photoproduct which reverted to starting material *via* a process which obeyed first-order kinetics. If the same ketones were irradiated in polymethacrylate matrices they were converted into the photoproducts, but these only reverted to starting material by prolonged heating at 110 °C for 24 h.⁴ 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, possible in the matrix only at high temperature.

¹ E. Klingsberg, *Quart. Rev.*, 1970, **23**, 537; N. Lozac'h, *Adv. Heterocyclic Chem.*, 1971, **13**, 161.

² 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, *Chemica Scripta*, 1971, **1**, 183.

The assumption that we are dealing with a *cis*-*trans*-isomerisation was further supported by the observation that compound (XVII) was photostable in ethanolic solution in the region 400–500 nm. The *trans*-form of



this compound is, if the oxygen atoms are not labelled, identical with the *cis* form.

Our theory of *cis*-*trans*-isomerization in these compounds has recently been further substantiated by Calzaferri *et al.*⁵ by means of a study of the ¹H n.m.r. and i.r. spectra at low temperature of the photoproduct derived from some selected dithiolylidene ketones. Calzaferri *et al.* suggested that substituents which lower the overlap population between C-2 and -3' will augment the rate of the thermal back process. We have found only small changes when phenyl groups were exchanged for *p*-methoxyphenyl groups, whereas substituent variation supports the operation of a considerable steric effect.

The photoreaction of compounds (I)—(XVI) (Table) were studied in a polymethacrylate matrix as well as in ethanolic solution. In the matrix experiments a stable photoproduct was formed for all the compounds studied. This photoproduct could in all cases be converted into the starting material by prolonged heating of the matrix at 110 °C. Thus the photoreaction seems in all cases to be a *cis*-*trans*-isomerization. The influence of substituents in the dithiolylidene ketone system was studied in ethanolic solution. The results in the Table likewise support the assumption of a *cis*-*trans*-isomerization.

The compounds studied can be divided into three classes according to the magnitude of the rate constant for the thermal reaction. (a) Compounds (I)—(V) in this class have rate constants of the order $3-9 \times 10^{-3} \text{ s}^{-1}$. The class consists of compounds with substituents at C-2 and -4' and no bulky substituents at C-2 and -4'. (b) Compounds (VI)—(IX) in this class have rate

³ R. Geiter, D. Werthemann, and H. Behringer, *J. Amer. Chem. Soc.*, 1972, **94**, 651.

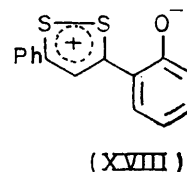
⁴ C. Th. Pedersen and C. Lohse, *J.C.S. Chem. Comm.*, 1973, 123.

⁵ G. Calzaferri, R. Gleiter, K.-H. Knauer, E. Rommel, E. Schmidt, and H. Behringer, *Helv. Chim. Acta*, 1973, **56**, 597.

constants of the order $3-10 \times 10^2 \text{ s}^{-1}$. All have 1- and 4'-phenyl substituents. (c) Compounds (X)—(XIII) in this class have rate constants of the order $0.3-10 \text{ s}^{-1}$. All have 1-, 2-, and 4'-phenyl substituents.

From considerations of models of the *trans*-form (D) it can be seen, that introduction of bulky substituents such as phenyl groups at C-4' will lead to high steric hindrance and thereby diminish the stability of the *trans*-isomer. Thus the photoproduct reverts faster to starting material. A methyl group does not give rise to such steric hindrance. Accordingly the rate constant for the back process of (IV) is the same as that of (I).

These results are in agreement with the observations of Gleiter *et al.*⁶ that the back reaction for (XVIII) is



extremely fast since the double-bond character of the bond between the two rings of the zwitterion is practically zero.

Rate constants for thermal *trans-cis*-isomerization of compounds (I)—(XVI)

| Compound | R ¹ | R ² | R ³ | R ⁴ | $k_{\text{EtOH}}/\text{s}^{-1}$ ^a |
|----------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|--|
| (I) | Ph | H | H | Ph | 3.1×10^{-3} |
| (II) | Ph | H | H | 4-MeOC ₆ H ₄ | 9.6×10^{-3} |
| (III) | Me | H | H | Ph | 5.7×10^{-3} |
| (IV) | Ph | H | Me | Me | 3.1×10^{-3} |
| (V) | Me | H | H | Me | 9.5×10^{-3} |
| (VI) | Ph | H | Ph | H | 3.6×10^2 |
| (VII) | Ph | H | Ph | Ph | 5.0×10^2 |
| (VIII) | 4-MeC ₆ H ₄ | H | Ph | Ph | 2.9×10^2 |
| (IX) | 4-BrC ₆ H ₄ | H | Ph | Ph | 10.6×10^2 |
| (X) | Ph | Ph | Ph | Ph | 2.6 |
| (XI) | Ph | Ph | Ph | H | 2.5 |
| (XII) | Ph | Ph | 4-MeOC ₆ H ₄ | 4-MeOC ₆ H ₄ | 10.3 |
| (XIII) | 4-MeOC ₆ H ₄ | 4-MeOC ₆ H ₄ | Ph | Ph | 0.35 |
| (XIV) | H | Ph | Ph | Ph | 45 |
| (XV) | H | H | Ph | Ph | 4.3 |
| (XVI) | H | Ph | H | Ph | 2×10^{-2} |

^a Rate constants for the thermal back reaction obtained from 10^{-5}M solutions in absolute ethanol.

Introduction of one additional phenyl substituent at C-2 causes the back process to slow down. Although this does not diminish steric hindrance in the *trans*-form, it introduces steric hindrance in the *cis*-form and consequent destabilization; thus the *trans*- becomes more stable relative to the *cis*-form.

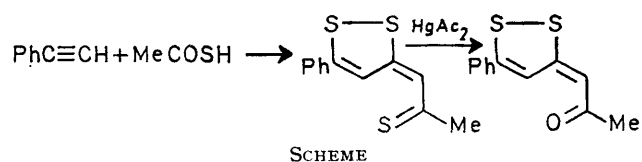
The *trans*-form may exist in the two configurations (D) and (E). The latter is less favourable for the following reasons. A 1-phenyl group in configuration (E) will give rise to severe interactions with the dithiol nucleus whereas such interactions are not present in configuration (D). This will destabilize (E) which means that the back process should be faster for a 1-phenyl substituent [*e.g.* (I)] than for a 1-methyl substituent [*e.g.* (III)]. However, as seen from the Table the opposite effect is observed.

As mentioned earlier substituents which diminish the overlap population between C-2 and -3' will probably destabilize the *trans*-form. That the electronic effect, however, is small compared with the steric effect is supported by the fact that there are no great differences in the rate constants in group (a).

Introduction of electron-donating groups such as *p*-methoxyphenyl at C-5' gives a small increase in the rate constant for the back reaction, *e.g.* $k_{\text{(X)}} 2.6$ and $k_{\text{(XII)}} 10.3 \text{ s}^{-1}$. Compound (XIII) with a 1-*p*-methoxyphenyl group has $k 0.35 \text{ s}^{-1}$. This is in accord with the ability of 1-*p*-methoxyphenyl group to stabilize the double bond between C-2 and -3'.

The rate of the *trans-cis*-reaction is not affected by irradiation of the *trans*-isomer. The life-time of the *trans*-isomer was found to be independent of the light intensity over three orders of magnitude. Thus our observations support a mechanism in which the forward reaction is photochemical only, and the back reaction is thermal only.

It has been reported by Behringer,⁷ that the reaction of arylacetylenes with thioacetic acid gives rise to '*trans*-trithiapentalenes' which can be desulphurized by mercury acetate to give stable '*trans*-dithiolylydene ketones' (Scheme). This seems not to be in accord



with our observations and the observations of Gleiter *et al.* that all dithiolylydene ketones on irradiation are converted into products which revert to the starting material by a dark process. We have found the rate constant for the back reaction of (5-phenyl-3*H*-1,2-dithiol-3-ylidene)acetone (III) to be in the same order as other 1,5'-disubstituted dithiolylydene ketones. This indicates that the structure of the irradiation product

⁶ R. Gleiter, K.-H. Knauer, E. Schmidt, Y. Mollier, and R. Pinel, *Tetrahedron Letters*, 1973, 1257.

⁷ H. Behringer, *Chimia (Switz.)*, 1965, 19, 132.

derived from (III) cannot be the same as Behringers 'trans-dithiolylidene ketone.'

We have also studied some dithiolylidene aldehydes (XIV)—(XVI). Although the photochemistry qualitatively resembles that of dithiolylidene ketones the reactions are less clean, probably because of some secondary photoprocesses involving the aldehyde group. Furthermore the influence of substitution does not follow the general scheme depicted above.

EXPERIMENTAL

The rate constants for the *trans-cis*-isomerization were obtained by a flash photolytic equipment designed for this study. The flash lamps were filled with air, and quartz copper(II) sulphate filters were used. The flash energies were between 300 and 600 J. The monitoring light source was passed into a monochromator, through the reaction cell, and into a second monochromator with a photomultiplier on the exit slit. This optical system prevented photoisomerization by the 100 W quartz iodine monitoring lamp. If the first monochromator was omitted life-times were changed by an order of magnitude. The rate con-

stants were obtained where possible by measurements at wavelengths where only the *trans*-form absorbed light. The life-times were reproducible within 10%.

Dithiolylidene ketones and aldehydes were prepared by conventional methods.⁸

2-(4,5-Diphenyl-3H-1,2-dithiol-3-ylidene)-4'-methoxy-2-(4-methoxyphenyl)acetophenone (XIII).—This was prepared from 4,5-diphenyl-3H-1,2-dithiolylium perchlorate and 4-methoxybenzyl 4-methoxyphenyl ketone in 44% yield, m.p. 195—196° (from 2-methoxyethanol) (Found: C, 73.4; H, 4.8; S, 12.5. C₃₁H₂₄OS₂ requires C, 73.2; H, 4.8; S, 12.6%).

2-[4,5-Bis-(4-methoxyphenyl)-3H-1,2-dithiol-3-ylidene]-2-phenylacetophenone (XII).—This was prepared from 4,5-bis-(*p*-methoxyphenyl)-3H-1,2-dithiolylium perchlorate and benzyl phenyl ketone in 50% yield, m.p. 218—219° (from 2-methoxyethanol) (Found: C, 73.1; H, 4.8; S, 12.5. C₃₁H₂₄OS₂ requires C, 73.2; H, 4.8; S, 12.6%).

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⁸ F. Arndt, P. Natchway, and P. Push, *Ber.*, 1928, **58**, 1633; E. Klingsberg, *J. Amer. Chem. Soc.*, 1963, **85**, 3244; *J. Org. Chem.*, 1966, **31**, 3489; 1968, **33**, 2915; G. Cailloud and Y. Mollier, *Bull. Soc. chim. France*, 1972, 151.