

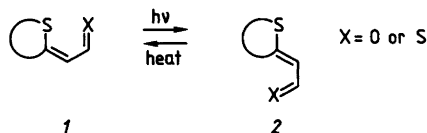
# Photochemistry of Sulfur Compounds Related to the 1,2-Dithiole System. Part 8.\* Photoisomerization of 1',2'-Dithiol-3':4-ylidene-2-cyano-2-butene Nitriles

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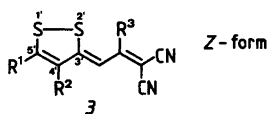
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A series of twelve 1',2'-dithiol-3':4-ylidene-2-cyano-2-butene nitriles has been prepared and its photochemistry studied. The stable *Z*-form is converted into the *E*-form on irradiation of ethanolic solutions. The photoproducts revert to starting material by a thermal process which obeys first-order kinetics. The influence of substituents is studied.

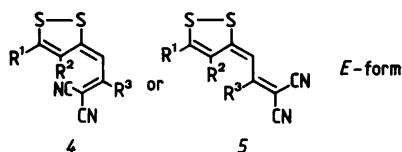
It has been shown in several series of compounds of type 1, that they are transformed into photoproducts of type 2 upon irradiation.<sup>1</sup>



It is general for all compounds studied hitherto that a strong interaction is present in the stable *Z*-forms 1 between X and the sulfur atom of the ring. It was, therefore, of interest to study compounds of analogous structure but without possibility for this interaction. As models for such substances the 1',2'-dithiol-3':4-ylidene-2-cyano-2-butenenitriles 3 were chosen.



As two identical groups are present at the terminal double bond, we need not consider isomerization round this double bond; *i.e.* the two isomers we have to consider are the two rotamers 4 and 5.

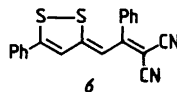


## RESULTS AND DISCUSSION

Flash photolysis of 3 in neutral  $10^{-4}$  M ethanolic solution converted it into photoproducts which reverted to starting material by a dark process obeying first-order kinetics.

The rate constants for various substituted compounds are given in Table 1, 2 and 3.

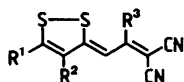
It has been shown by *x*-ray crystallographic structure determination that compound 6 has the geometry given below.<sup>2</sup>



Catel and Mollier<sup>3</sup> have shown that compounds 3 with  $R^3 = H$  are present as mixtures of *Z*- and *E*-forms in solutions. This conclusion is based on dipole moments measurements and <sup>1</sup>H NMR data. Due to this observation we are not able to say with certainty whether the process we observe during

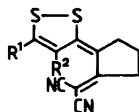
\* Part 7. Lohse, C. and Pedersen, C. Th. *Acta Chem. Scand. B* 31 (1977) 683.

Table 1. Rate constant for the dark reaction 2 → 1. 1 kcal = 4.184 kJ.



Compound	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	k/s <sup>-1</sup> in EtOH	E <sub>A</sub> /kcal mol <sup>-1</sup>
6	Ph	H	Ph	5.79	12.2
7	4-MeOC <sub>6</sub> H <sub>4</sub>	H	Ph	19.50	12.1
8	<i>t</i> -Bu	H	Ph	10.80	10.4
9	Me	H	H	1.90	14.4
10	<i>t</i> -Bu	H	H	1.74	13.3

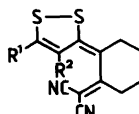
Table 2. Rate constants for the dark reaction 2 → 1.



Compound	R <sup>1</sup>	R <sup>2</sup>	k/s <sup>-1</sup> in EtOH	E <sub>A</sub> /kcal mol <sup>-1</sup>
11	Ph	H	512	12.2
12	4-MeOC <sub>6</sub> H <sub>4</sub>	H	2900	13.0
13	Ph	Me	1000	11.1 <sup>a</sup>

<sup>a</sup> In cyclohexane.

Table 3. Rate constants for the dark reaction 2 → 1.



Compound	R <sup>1</sup>	R <sup>2</sup>	k/s <sup>-1</sup> in EtOH	E <sub>A</sub> /kcal mol <sup>-1</sup>
14	Ph	H	3 860	9.1
15	4-MeOC <sub>6</sub> H <sub>4</sub>	H	11 900	5.0
16	<i>t</i> -Bu	H	17 300	<sup>b</sup>
17	Ph	Me	<sup>b</sup>	

<sup>b</sup> Too fast to be measured.

irradiation is *E* → *Z* or *Z* → *E* in the case of compounds 9 and 10.

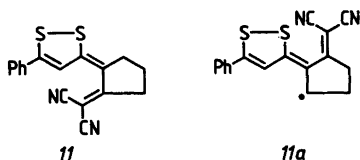
The variation in rate constants seen in Table 1 is probably due to electronic factors. It has been

observed during studies of the photoisomerization of α(1,2-dithiol-3-ylidene)ketones<sup>4</sup> that introduction of electron donating substituents in the position corresponding to C-5' gives rise to a small increase

in the rate constant for the back reaction. This is in agreement with the variation observed in going from 6 to 7. If we assume that we observe  $E \rightarrow Z$  the difference in rate constants between, e.g., 8 and 10 can be explained by sterical interaction between the phenyl group in position 3 and the hydrogen atom at C-4' in the *E*-form of 8, which destabilizes the *E*-form. In the case of  $\alpha$ -(1,2-dithiole-3-ylidene)ketones it has been shown that sterical interactions at the position corresponding to C-4' has strong influence on the rate of the back reaction.<sup>4</sup>

The structure of compounds where the side chain is incorporated in a cycloalkane ring, has not been determined by X-ray crystallography. From <sup>1</sup>H NMR studies, however, it is evident that only one isomer is present in solution.<sup>5</sup>

From model considerations it is not possible unambiguously to see which of the forms 11 or 11a is the most strained.

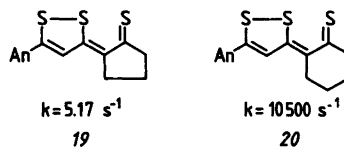


Studies by means of paramagnetic shift reagents as well as dipole moment measurements are in accordance with the assumption that the stable compounds have a structure corresponding to 11. This hypothesis is further substantiated by studies of the Nuclear Overhauser effect in the case of 13. Irradiation of the methyl group in position 4' does not give rise to an increase in the intensity of the proton signal from the CH<sub>2</sub> group marked with an asterisk in 11a.<sup>6</sup> This would have been expected if the geometry had been as in 11a.

From the rate constants in both Tables 2 and 3, it can be seen that the electronic influence of the substituents on the back reaction is the same as that found for the open chain compounds in Table 1.

Introduction of a substituent in position 4' in these compounds also gives rise to strong increase in the rate constants. In the case of 13, the reaction was too fast in ethanolic solution for the rate constant to be measured. In a less polar solvent such as cyclohexane, the rate was sufficiently slow to allow the rate constant to be determined. This solvent effect is in accordance with what has been found for analogous compounds.<sup>1</sup>

If the difference in rate constants for 12 and 15 is compared to the difference in rate constants for



19 and 20,<sup>7</sup> it is obvious that the great stability of the photoproduct with a five-membered ring in the case of 1,6,6a $\lambda^4$ -trithiapentalenes was not observed here. The *E*-form of the trithiapentalenes was stabilized because the thiocarbonyl group was forced by the five-membered ring in the case of 19 to be coplanar with the rest of the molecule. In the corresponding compound 12, a strong interaction is present in the *E*-form between the sulfur atom of the 1,2-dithiole cycle and the cyano groups, thus the *E*-form is destabilized by this interaction.

The results obtained for the compounds in Table 3 with a six-membered ring can be explained in the same way.

From these experiments we will conclude that the photoisomerizations which are observed in these compounds are of the same nature as that in compounds of type 1.

## EXPERIMENTAL

The rate constants for the *E* and *Z* isomerizations were obtained by using the flash photolysis equipment described previously.<sup>4</sup>

Compounds 6–17 were prepared as described.<sup>8,9</sup>

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