Photochemistry of Sulfur Compounds Related to the 1,2-Dithiole System. Part VII. Photoisomerization of α-(1,2-Dithiol-3-ylidene)-cycloalkanones

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Dedicated to Professor K. A. Jensen on his 70th birthday

A series of α-(1,2-dithiol-3-ylidene)cycloalkanones are transformed upon irradiation into photoproducts which possess a *trans*-1,2-dithiolylidene ketone structure. The photoproducts revert to starting materials by a dark process obeying first order kinetics. The stability of the *trans* form has been shown to be controlled mainly by steric factors; it is strongly dependent on the ability of the carbonyl group to be coplanar with the dithiole ring. A parallel was observed between the variation of the rate constant for the back reaction with ring size, and the variation of the ^{13}C chemical shift of the carbonyl carbon in the *cis* form with ring size.

It has been shown in several cases that compounds of the general type *1* upon irradiation are transformed into photoproducts, which possess the *trans* configuration *2*.[1]


1   *2*   X = O or S
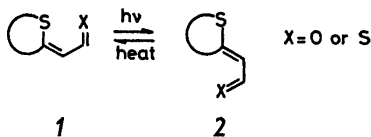
During a study of the photochemistry of 1,6,6aλ^4-trithiapentalenes[4] a great difference was observed in the rate constants for the thermal back reaction of the *trans* forms of the two compounds *3* and *4*.

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3   *4*

k = 5.17 S^{-1} k = 10500 S^{-1}
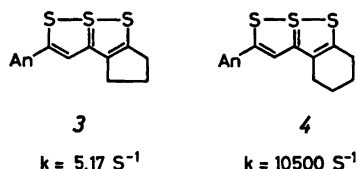
This difference can be explained by steric strain in the *trans* forms introduced by the condensed cycloalkane rings.

It was found of interest to study whether the same effect was operative in 1,2-dithiol-3-ylidene cycloalkanones *5*, and to study the influence of the ring size on the rate constants


An = 4 - CH$_3$OC$_6$H$_4$

5
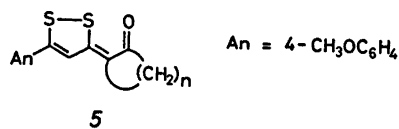
for the dark reaction. Therefore, a series of α-(1,2-dithiol-3-ylidene)cycloalkanones *5a − 5k* with *n* ranging from 3 to 13 were irradiated, and the rate constants for the thermal back reaction were measured.

RESULTS AND DISCUSSION

All compounds upon irradiation in ethanolic solution were transformed into photoproducts, which decayed to starting materials by a dark process obeying first-order kinetics. The rate

Table 1. Rate constants for thermal *cis-trans*-isomerization and ^{13}C chemical shift of carbonyl carbon of *5*.

5j   *5k*
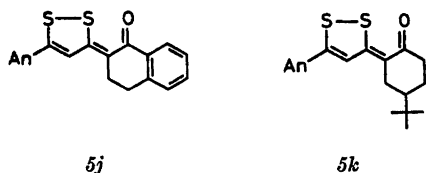
Com-pound	n	$k_{EtOH}/$ $10^{-5}s^{-1}$ [a]	$\delta\text{-}^{13}C(>CO)/$ ppm	M.p. [b] °C
5a	3	4.00	201.74	Ref. 9
5b	4	233	189.39	Ref. 8
5c	5	27.2	195.05	Ref. 9
5d	6	75.9	193.55	Ref. 9
5e	7	140	192.77	130—131
5f	8	173	191.35	137—138
5g	9	146	191.47	151—152
5h	10	149	191.61	153—154
5i	13	61.0	191.80	132—133
5j		42.8	179.85	172—173
5k		118	189.39	156—157

[a] Rate constants for the thermal back reaction obtained from 10^{-5} M solutions in 96 % ethanol. [b] All compounds show satisfactory elemental analyses (C, H, S).

constants for this reaction are given in Table 1.

When irradiations were carried out in poly-methacrylate matrices it was observed that the photoproducts formed were stable and reverted to starting materials by prolonged heating only. This supports the *trans* structure of the photoproducts in the same way as discussed for simple 1,2-dithiolylidene ketones.[2]

The difference in rate constants for *5a* and *5b* is substantial.

Models of the *trans* forms of the two compounds show that the carbonyl group in *5a*, Fig. 1, is forced by the cyclopentane ring to be coplanar with the dithiole ring. If the rate constant for *5a*, 4×10^{-5} s^{-1} is compared to the

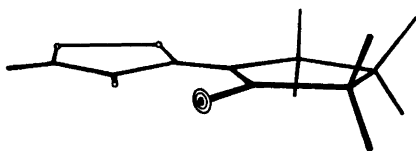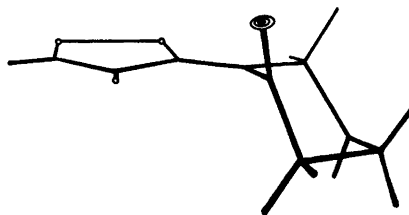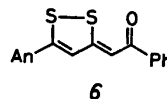*Fig. 1.* Model of the *trans* form of *5a*.

Fig. 2. Model of the *trans* form of *5b*.

rate constant of *6*,[2] 9.6×10^{-3} s^{-1} it is obvious that the coplanarity forced by the cyclopentane

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ring stabilizes the *trans* form. It has been shown that electronic factors only play a minor role in determining the rate constants of the back reaction.[2]

If we look at a model of the *trans* form of *5b* with the cyclohexane ring in a chair conformation, Fig. 2, it is seen that the carbonyl group in the *trans* form is forced out of the dithiole plane at an angle of *ca.* 60° which means that the *trans* form in this case loses resonance stabilization from the dithiole ring. This is reflected in the higher rate constant for the dark reaction.

With larger rings the system is less rigid and it is again possible for the carbonyl to come close to coplanarity with the dithiole ring, which is equivalent to a gain in stability of the *trans* form. However, with these larger rings a new destabilizing factor is introduced, *i.e.* the hydrogen-hydrogen interaction in the rings which may counteract the possibility of coplanarity of the carbonyl group. This is observed as an increase in the rate constant of the series *5c* to *5f*. The strain introduced by the hydrogen-hydrogen interaction reaches its maximum for the ten-membered ring and then decreases.

It is not possible to make a detailed analysis of the influence of this hydrogen-hydrogen interaction since, as far as we know, no studies of the conformation of such α-methylene substituted cyclic ketones have been published.

The variation in rate constants in the series *5c* to *5i* could be the result of small variations

in the polarization of the carbonyl group in the *trans* forms. This will give rise to forms such as *7* which lower the double bond character of

7
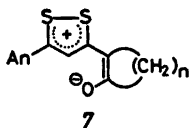
the bond between the dithiole ring and the side chain and thereby give a more free rotation round this bond.

If one considers the ^{13}C chemical shift of the carbonyl carbon atom in the *cis* α-(1,2-dithiol-3-ylidene)cycloalkanones,[3] it is observed that the ^{13}C chemical shift varies in the same manner with ring size as do the life times of the *trans* dithiolylidene cycloalkanones (cf. Fig. 3). On the other hand this variation finds a parallel in the variation of the ^{13}C chemical shift of the carbonyl carbon atom in the simple cycloalkanones,[4,5] where it is assumed that the variation is due to sterical interactions in the ring.

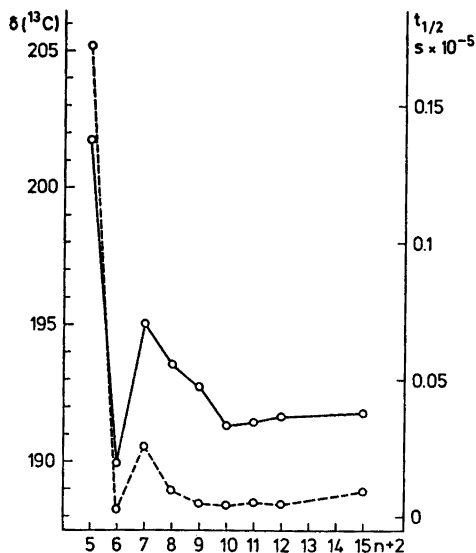The polarization in the carbonyl group o the *cis* form is probably very different from the polarization of the *trans* form due to the strong sulfur-oxygen interaction in the *cis* form.[6,7] We will therefore assume that the variation in rate constant for the dark reaction in the series *5c* to *5i* is caused by variations in the sterical interactions in the rings.

The low rate constant of *5j* (of the same magnitude as that of *6*) compared to *5b* can be explained by the stabilizing effect of the condensed benzene ring, which in the *trans* form is still planar with the carbonyl group.

For $n = 8$ and 9 it is observed that the decay of the photoproduct does not exactly obey first order kinetics. For these two compounds we are probably observing two decays, the decay mentioned in the table and a decay which is somewhat faster. The fast decay is for *5f* ca. 900×10^{-5} s^{-1} and for *5g* ca. 1000×10^{-5} s^{-1}. We have no explanation for these two fast decays, but it can be ruled out that they are caused by the presence of impurities.

EXPERIMENTAL

The ^{13}C NMR spectra were recorded on a Jeol FX60 Fourier Transform NMR spectrometer operating at 15.03 MHz with deuterium internal lock. Proton decoupled spectra were obtained using noise decoupling and 8K data points. The pulse length used was 6 μs corresponding to a flip angle of 60°. The chemical shifts are given an accuracy of 0.07 ppm. CDCl$_3$ was used as solvent with TMS as internal standard.

The rate constants for the *trans-cis*-isomerization were obtained from 10^{-5} M ethanolic solutions by a flash photolytic equipment described previously.[2] The rate constants were reproducible within 10 % except for *5f* and *5g* where the uncertainty was 20 %.

α-(1,2-Dithiol-3-ylidene)cycloalkanones were prepared from 3-(p-methoxyphenyl)-1,2-dithiolylium hydrogen sulfate and cycloalkanones as described.[8–10] All compounds were recrystallized from 2-methoxyethanol.

Fig. 3. Variation of half-life time of the *trans* form of *5* with ring size – – – and variation of ^{13}C chemical shift of carbonyl carbon of *5* with ring size ——.

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