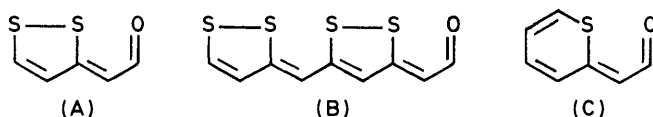


Photochemistry of Sulphur Compounds related to the 1,2-Dithiole System. Part 6.† Photoisomerization of 1,6,6aλ⁴-Trithiapentalenes

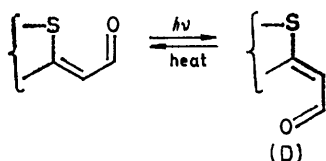
By Carl Th. Pedersen and Christian Lohse,* Department of Chemistry, Odense University, DK-5000 Odense, Denmark

A series of 1,6,6aλ⁴-trithiapentalenes are transformed upon irradiation into photoproducts which revert to starting materials by a dark process obeying first-order kinetics. The photoproducts have been assigned a *trans*-1,2-dithiol-3-ylidene thione structure. The stability of the *trans*-forms has been shown to be controlled mainly by steric factors; it is strongly dependent on the ability of the thiocarbonyl group to be coplanar with the dithiole ring. The rate constants and energy and entropy of activation for the thermal back reactions are reported.

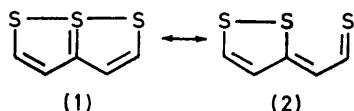
THE photoisomerization of a series of ketones of types (A)—(C) has recently been studied by flash photolysis



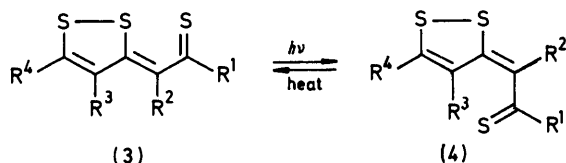
(references 1—3 and references therein). The products have in all cases been shown to have the *trans*-structure (D), which reverts to the starting material by a dark process.



1,6,6aλ⁴-Trithiapentalenes [*e.g.* (1)] may be considered as 1,2-dithiol-3-ylidene thiones [*e.g.* (2)]. Although a



bicyclic representation is the more correct for the ground state,⁴ the compounds may exist as 1,2-dithiol-3-ylidene thiones in the excited state, and an isomerization (3) \rightleftharpoons (4) analogous to that observed for 1,2-dithiol-3-ylidene ketones might be expected.

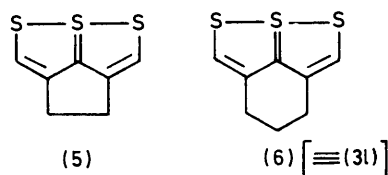


RESULTS AND DISCUSSION

When 1,6,6aλ⁴-trithiapentalenes were irradiated in ethanolic solution they were transformed into photoproducts which decayed to the starting materials by a dark process obeying first-order kinetics. The rate

constants of the back reaction are given in Table 1. The lifetimes of the photoproducts were independent of the presence or absence of oxygen, but were much shorter in the presence of acids.

Compounds (5) and (6), which should not be able to undergo *cis-trans* photoisomerization, were transformed by irradiation into photoproducts which also decayed



by a first-order dark reaction; this reaction, however, was not catalysed by acids.

In a steady state photolysis experiment compounds (5) and (6) were found to undergo an irreversible photochemical reaction as observed for other trithiapentalenes. If, however, a filter which cut out light of wavelength <400 nm was used, all trithiapentalenes were found to be stable in the steady state experiment. When the same filter was used in the flash photolysis experiment, (5) and (6) were found to be photostable under the conditions used.

On the basis of these observations we conclude that the photoproducts formed from 1,6,6aλ⁴-trithiapentalenes upon irradiation with light of wavelengths >400 nm revert to the starting material by a dark process.

Two different modes of *cis-trans* isomerization should be open to unsymmetrically substituted trithiapentalenes, *e.g.* (7) could be transformed into both (8) and (9). In accordance with this, two decay rates are observed for nearly all unsymmetrically substituted trithiapentalenes, the difference in rate constants depending on the degree of asymmetry and steric hindrance in the *trans*-form. In some cases only one decay rate is observed for an unsymmetrically substituted compound; this is probably because one photoproduct decays too fast for the rate to be measured. Two decay rates have never been observed for symmetrically substituted trithiapentalenes.

In the photolysis of 1,2-dithiol-3-ylidene ketones,¹ a substituent in the position corresponding to position 4 in 1,6,6aλ⁴-trithiapentalenes markedly destabilizes the

³ C. Th. Pedersen, C. Lohse, N. Lozac'h, and J.-P. Sauvé, *J.C.S. Perkin I*, 1976, 166.

⁴ C. Th. Pedersen in 'Nonbenzenoid Aromatics,' vol. 3, ed. J. P. Snyder, Academic Press, New York, in the press.

† Part 5, C. Th. Pedersen and C. Lohse, *Acta Chem. Scand.*, 1975, **B29**, 831.

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

² C. Th. Pedersen, M. Stavaux, and C. Lohse, *J.C.S. Perkin I*, 1974, 2722.

photoproduct, owing to steric hindrance in the *trans*-form. As the geometry of the trithiapentalenes is much the same as that of 1,2-dithiol-3-ylidene ketones, the same type of steric hindrance would be expected. Table 1 supports this idea. Owing to the greater size of the sulphur atom one would expect even greater steric

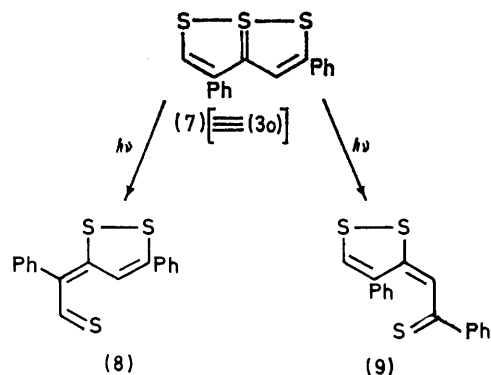
(13) being too fast to be observed. The steric interaction between the thiocarbonyl group and the cyclohexane ring thus appears to be even stronger than the interaction between the thiocarbonyl group and the phenyl group. The instability of (14), reflected in the high rate constant observed for the dark reaction, is

TABLE 1

Rate constants for the dark reaction (4) \rightarrow (3)						
	R ¹	R ²	R ³	R ⁴	k* (EtOH)/s ⁻¹	k*(Ch)/s ⁻¹
a;	H	H	H	H	2 090	
b;	Me	H	H	H	82 (s), 2 000 (f)	
c;	Ph	H	H	H	46 (s), 690 (f)	
d;	H	Me	H	H	800 (s), 9 800 (f)	
e;	H	Ph	H	H	530 (s), 11 500 (f)	
f;	Me	H	H	Me	1 030	
g;	Ph	H	H	Ph	360	
h;	4-MeO·C ₆ H ₄	H	H	4-MeO·C ₆ H ₄	400	
i;	4-MeO·C ₆ H ₄	H	H	Ph	290	
j;	Ph	H	H	Me	360	
k;	H	Me	Me	H	1 480	
l;	H	CH ₂ ·CH ₂ ·CH ₂	H	H	Stable	
m;	Ph	Me	H	H	570	
n;	Ph	Ph	H	H	950	
o;	Ph	H	Ph	H	250 (s), 8 500 (f)	
p;	α -Thienyl	H	Ph	H	330 (s), 11 500 (f)	
q;	Ph	Ph	H	Ph	260	
r;	4-MeO·C ₆ H ₄	4-MeO·C ₆ H ₄	H	4-MeO·C ₆ H ₄	210	
s;	Ph	Ph	H	4-MeO·C ₆ H ₄	320	
t;	CH ₂ ·CH ₂ ·CH ₂ ·CH ₂	H	H	4-MeO·C ₆ H ₄	10 500	
u;	CH ₂ ·CH ₂ ·CH ₂	H	H	4-MeO·C ₆ H ₄	5.17	
v;	Ph	Ph	Ph	H	20 000	0.047
w;	Ph	Ph	Ph	Ph		54
x;	4-MeO·C ₆ H ₄	4-MeO·C ₆ H ₄	4-MeO·C ₆ H ₄	4-MeO·C ₆ H ₄		19 300
y;	Me	CH ₂ ·CH ₂	Me	Me	Stable	8 500
z;	Me	CH ₂ ·CH ₂ ·CH ₂	Me	Me	Stable	
aa;	Ph	CH ₂ ·CH ₂ ·CH ₂	Ph	Ph	Stable	

* 10⁻³M-Solutions in 96% EtOH at 25 °C [or in cyclohexane (Ch)]; s = slow; f = fast.

hindrance in the trithiapentalenes, in accord with observation [(11) k 3.6 \times 10² s⁻¹; (7) k 86 \times 10² s⁻¹].

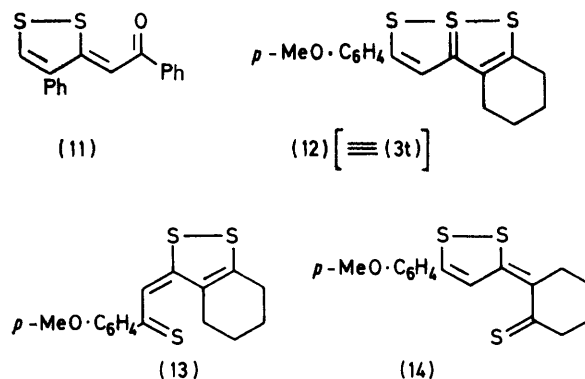


On the basis of these observations, in cases where two decay rates are observed, we assign the fast decay to the product of type (9) and the slow one to that of type (8). In unsymmetrical cases with only one decay rate we consider this to be a 'slow' decay; we were not able to observe decays with rate constants greater than *ca.* 2 \times 10⁴ s⁻¹. In systems such as (3i) \rightleftharpoons (4i) the two rate constants differ too little to allow us to observe the two decays separately.

Only one decay (k 10⁴ s⁻¹) is observed for (12); this is presumably the 'slow' decay, the back reaction of

presumably due to the thiocarbonyl group being forced out of the plane of the 1,2-dithiolen ring (by an angle of *ca.* 60°); as the stability of the *trans*-form is strongly dependent on the coplanarity of the system, the *trans*-form is destabilized in this case.

The opposite is found to be the case for the *trans*-form of (15). In this case also we only observed one decay, the 'slow' one, with k 5.6 s⁻¹, *i.e.* the *trans*-form is surprisingly stable. Models show that the cyclopentane ring forces the thiocarbonyl group to be coplanar with



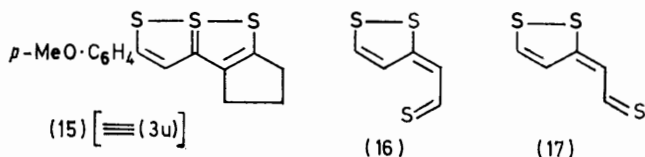
the rest of the molecule; this is the only possible conformation of the *trans*-form in this case.

Table 1 shows that electronic factors only play a minor

role in controlling the rate of the back reaction, *e.g.* there is not much difference in the rate constants in the series (g—j). The steric factor is dominant in determining the stability of the *trans*-form.

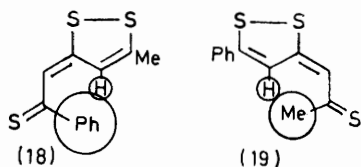
The same solvent dependence on the rate of the decay as observed for 1,2-dithiol-3-ylidene ketones¹ was also observed in this case, *i.e.* the decay rates are higher in polar solvents such as ethanol than in nonpolar solvents such as cyclohexane.

Two different conformations are possible for the *trans*-



forms with the thiocarbonyl group coplanar with the dithiole ring, (16) and (17). If (17) were the preferred conformation, introduction of a phenyl group in position 2 would lead to higher steric hindrance in the *trans*-form than introduction of a methyl group. This means that in case j in Table 1 the decay of (18) should be faster than the decay of (19) and we should therefore be able to observe two decay rates. However two decay rates were not observed, and as we were able to observe the decays in cases f and g we consider the conformation (16) more likely.

Energies of activation (Table 2) were estimated for a representative series of compounds. Values in the



range 5–13 kcal mol⁻¹ were found, and entropies of activation were in the range -6 to -30 cal mol⁻¹ K⁻¹. These are the same ranges as found for 1,2-dithiol-3-ylidene ketones,⁵ thiopyran-2-ylidene ketones,³ and nitrogen analogues of trithiapentalenes.⁶ This further confirms that we are dealing with the same type of reaction in all four cases, a *cis-trans* isomerization.

The results in Table 1 agree with the data given by Calzaferri *et al.*⁶ for the photolysis of 2,5-dimethyl-1,6,6aλ⁴-trithiapentalene.

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

⁶ G. Calzaferri, R. Gleiter, R. Gygas, K.-H. Knauer, and H. Behringer, *Helv. Chim. Acta*, 1973, **56**, 2584.

We have no definite conclusion concerning the short wavelength photoreaction, which we believe is irreversible. As the trithiapentalenes corresponding to (3y)

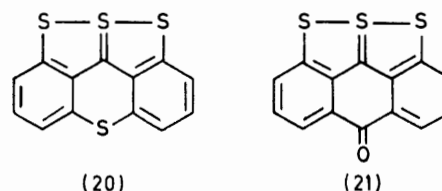
TABLE 2

Energies and entropies of activation for the dark reaction (4) → (3) *

	E_a /kcal mol ⁻¹	ΔS^\ddagger /cal mol ⁻¹ K ⁻¹
a;	15.1	+4.8
c;	13.0 (s)	-9.4
	9.5 (f)	-14.7
d;	13.3 (s)	-2.8
	3.7 (f)	-29.7
e;	9.9 (s)	-14.6
	3.1 (f)	-30.7
f;	7.6	-21.0
g;	8.3	-20.3
j;	10.0	-15.4
o;	13.1 (s)	-6.1
v;	10.1	-7.1

* 10⁻⁵M-Solutions in 96% EtOH.

and (3z) as well as (20) and (21), in contrast to (6), are photostable, we assume that the hydrogen atoms in



positions 2 and 5 are involved in this secondary photoreaction. If a hydrogen atom is present in position 2 or 5, the monocyclic form (3) is a thioaldehyde, expected to be far more unstable than a thioketone.

EXPERIMENTAL

The compounds studied were prepared by conventional methods (see refs. 7–9).

The rate constants for the *trans-cis* isomerization were obtained by using the flash photolysis equipment described previously.¹ A 400 nm cut-off filter (NiCl₂-CuSO₄-HCl) was used. The life-times were reproducible within 10%.

Compounds which showed two rates of decay were studied in two separate experiments, one with a fast and the other with a comparatively slow sweep rate.

We thank Professor D. Leaver, University of Edinburgh, for samples of compounds (20) and (21), and Dr. M. Stavaux, Département de chimie, Université de Caen, for samples of the trithiapentalenes corresponding to (3y) and (3z).

[6/1696 Received, 6th September, 1976]

⁷ E. Klingsberg, *Quart. Rev.*, 1970, **23**, 537.

⁸ N. Lozac'h, *Adv. Heterocyclic Chem.*, 1971, **13**, 161.

⁹ R. Gleiter and R. Gygas, *Topics Current Chem.*, 1976, **63**, 49.