

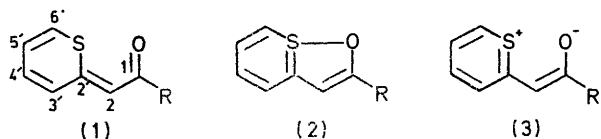
Photoisomerisation of α -(Thiopyran-2-ylidene) Ketones; Substituent Effects

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In a series of ten substituted α -(thiopyran-2-ylidene) ketones, the stable *Z*-form is transformed into the *E*-isomer upon irradiation. The photoproduct reverts to the starting material by a dark process, which obeys first-order kinetics. The rate constants for the *EZ*-isomerization are controlled mainly by steric factors. The activation energy for the thermal reversion is *ca.* 10 kcal mol⁻¹.

COMPARISON of the carbonyl absorptions in the i.r. spectra of α -thiopyranylidene ketones with those of ¹⁸O-enriched compounds shows that an interaction exists between sulphur and oxygen in these compounds.^{1,2} This can be explained in terms of contributions by the canonical structures (1)–(3). Analogous resonance



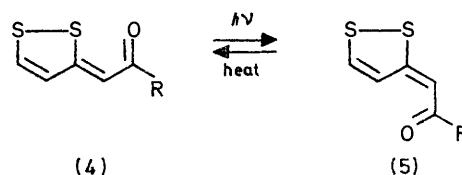
forms have been assumed to describe the corresponding α -(1,2-dithiol-3-ylidene) ketones (4).^{3,4}

¹ J.-P. Sauvé and N. Lozac'h, *Bull. Soc. chim. France*, 1974, 1196.

² R. Pinel, N. K. Son, and Y. Mollier, *Compt. rend.*, 1974, 278, 729.

³ N. Lozac'h, *Adv. Heterocyclic Chem.*, 1971, 13, 161.

It has been shown (*cf.* ref. 5) that α -(1,2-dithiol-3-ylidene) ketones and analogous multisulphur ketones⁶



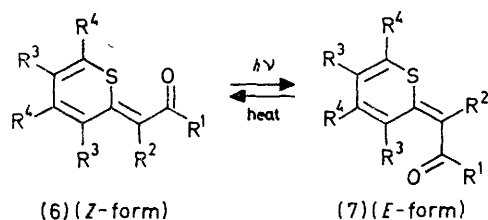
upon irradiation undergo geometrical isomerization. The thiopyranylidene ketones are structurally closely related to these compounds (although no *X*-ray structure determination of the former has yet been carried

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

⁵ C. Th. Pedersen and C. Lohse, *J.C.S. Perkin I*, 1973, 2837, and references therein.

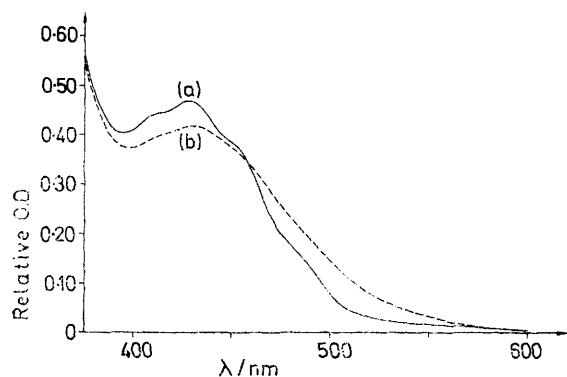
⁶ C. Th. Pedersen, C. Lohse, and M. Stavaux, *J.C.S. Perkin I*, 1974, 2722.

out). We therefore expected to observe the same type of isomerization as for the corresponding 1,2-dithiole derivatives, *i.e.* (6) \rightleftharpoons (7).



RESULTS AND DISCUSSION

If an α -(thiopyran-2-ylidene) ketone is irradiated in a polymethacrylate matrix it is converted into a photoproduct which is stable in the matrix and reverts to the starting material only when heated at 110 °C for 24 h. The visible spectrum of the photoproduct is only slightly different from that of the starting material (see Figure).



Visible spectra of (a) (IV) and (b) its photoproduct in a polymethacrylate matrix

By irradiation in ethanolic solution the same photoproduct was formed, but the lifetime in this case varied from microseconds to minutes. These observations are consistent with the assumption that the photoproduct is the *E*-isomer of the thiopyran-2-ylidene ketone. The thermal change from the *E*- to the *Z*-form requires a large modification in geometry, possible in the matrix only at elevated temperature, whereas only small geometrical changes in the molecule would be necessary during the reversion if the photoproduct had an O-S bonded structure analogous to (2).

The influence of substituents on the rate constants was studied for the thermal reversal in 96% ethanol at 25 °C. The results (Table 1) support the *ZE*-isomerization hypothesis.

The compounds studied can be divided into three classes according to the magnitude of the rate constant for the thermal back reaction: (a) compounds (I)–(IV), k $1\text{--}6 \times 10^{-2} \text{ s}^{-1}$, with no substituents in positions 2 and 3'; (b) compounds (V)–(VIII), k $30\text{--}110 \text{ s}^{-1}$, having a cyano-group in the 2-position and a hydrogen atom in position 3'; and (c) compounds (IX) and (X), k $10^4\text{--}10^5 \text{ s}^{-1}$, having a methyl group in the 3'-position.

Electron-attracting groups in position 2 will lower

the overlap population between C-2 and C-2' and thus accelerate the thermal back reaction. This explains the rise in rate in going from class (a) to class (b). Models indicate that the cyano-group introduces no steric strain in the *E*-form.

TABLE I

Rate constants for the dark reaction (7) \rightarrow (6)						
Compd.	R ¹	R ²	R ³	R ⁴	$k^* \text{ EtOH/s}^{-1}$	$k^* \text{ Ch/s}^{-1}$
(I)	Ph	H	H	Ph	1.81×10^{-2}	
(II)	Ph	H	H	4-ClC ₆ H ₄	6.53×10^{-3}	
(III)	4-MeC ₆ H ₄	H	H	Ph	9.94×10^{-3}	
(IV)	Ph	H	H	H	9.52×10^{-3}	
(V)	Ph	CN	H	Ph	74.0	
(VI)	4-ClC ₆ H ₄	CN	H	Ph	110.0	
(VII)	4-MeC ₆ H ₄	CN	H	Ph	43.0	1.62×10^{-2}
(VIII)	Ph	CN	H	4-ClC ₆ H ₄	32.2	
(IX)	Ph	H	Me	H	1.13×10^4	
(X)	Ph	CN	Me	H	5×10^5 ^a	186.0

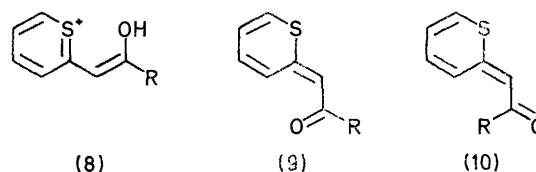
^a Estimated value.

* 10^{-5}-M -Solutions at 25 °C; Ch = cyclohexane.

Introduction of a substituent into the 3'-position gives rise to strong steric strain in the *E*-form. If such a substituent is present, the carbonyl group and the phenyl substituent in position 1 cannot be coplanar with the thiopyran part of the molecule in the *E*-form. This accounts for the great increase in rate constant in going from class (b) to class (c). If a cyano-group is further introduced into position 2, its electron-attracting effect and the steric hindrance of the methyl group destabilize the *E*-form to such an extent that it is not possible to observe the decay in ethanol. In cyclohexane, where the stability of the *E*-form is higher (see later), it is possible to observe the decay of the *E*- to the *Z*-form. From the rate constant obtained in this solvent it can be estimated that the rate constant must be *ca.* 5×10^5 in 96% ethanol.

p-Chloro-substitution in the phenyl group [*cf.* compounds (II), (VI), and (VIII)] results in only a small change (an increase) in the rate constant. The same was observed in the case of 1,2-dithiol-3-ylidene ketones,⁵ whereas introduction of a *p*-methyl group gives rise to a small decrease in both series.

The observation that the rate constants are much lower in cyclohexane is in accord with the postulate that non-polar solvents will favour true ketonic structures such as (1) which have a high degree of 2,2'-double-bond character.

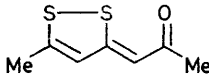
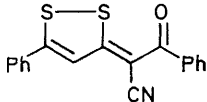


The thermal back reaction is strongly catalysed by acid. For example in ethanolic 10^{-3}M -hydrogen chloride, $k_{(IV)}$ is 1580 s^{-1} (*cf.* 9.52×10^{-3} in 96% ethanol). This is probably due to protonation of the carbonyl group, which gives rise to forms such as (8) where there is little 2,2'-double-bond character.

Two different conformations are possible for the *E*-forms (9) and (10). For steric reasons we will assume that (9) is preferred except where substituents are present in the 3'-position, in which case the carbonyl and the phenyl group in position 1 are twisted out of plane.

From the Arrhenius plots for a compound from group (a) and one from group (b) the energy of activation E_a and the entropy of activation ΔS^\ddagger have been calculated. The values (Table 2) fit well with those reported by

TABLE 2

				
k_{EtOH}	$4.68 \times 10^{-3} \text{ s}^{-1}$	k_{EtOH}	5.79 s^{-1}	
E_a	$11.6 \text{ kcal mol}^{-1}$	E_a	$12.3 \text{ kcal mol}^{-1}$	
ΔS^\ddagger	$-32.3 \text{ cal mol}^{-1} \text{ K}^{-1}$	ΔS^\ddagger	$-15.9 \text{ cal mol}^{-1} \text{ K}^{-1}$	
	(IV)		(V)	
k_{EtOH}	$9.52 \times 10^{-3} \text{ s}^{-1}$	k_{EtOH}	74.0 s^{-1}	
E_a	$10.4 \text{ kcal mol}^{-1}$	E_a	$11.4 \text{ kcal mol}^{-1}$	
ΔS^\ddagger	$-34.1 \text{ cal mol}^{-1} \text{ K}^{-1}$	ΔS^\ddagger	$-13.3 \text{ cal mol}^{-1} \text{ K}^{-1}$	

Gleiter and his co-workers for the corresponding dithiol-ylidene ketones.⁷ The correlation strongly supports the

⁷ G. Calzaferrri, R. Gleiter, K.-H. Knauer, E. Rommel, E. Schmidt, and H. Behringer, *Helv. Chim. Acta*, 1973, **56**, 597.

hypothesis that the same mechanism is operative in the two cases. The highly negative ΔS^\ddagger values further support a polar transition state with a high degree of orientation of the solvent molecules. The high ΔS^\ddagger values also rule out the possibility that the photoproduct is an O-S bonded isomer, since the reaction (3) \rightarrow (1) will probably have only a small entropy of activation.

The observed energies of activation are also in agreement with CNDO/2 calculations of the energy difference between the *E*- and the *Z*-form of α -(1,2-dithiol-3-ylidene)-acetaldehyde (a value of 20 kcal mol^{-1} has been found by inclusion of *d* orbitals on sulphur^{8,9}).

EXPERIMENTAL

The compounds used were prepared as described in ref. 1: (a) compounds (I)—(IV) and (IX) by rearrangement, with loss of sulphur, of 2-(phenacylmethylthio)thiopyrylium bromides; (b) compounds (V)—(VIII) and (X) by condensing 2-cyanoacetophenone with a 2-(methylthio)-thiopyrylium iodide.

The rate constants for the *EZ*-isomerization were obtained by using the flash photolytic equipment described previously.⁵

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⁸ R. Pinel, Y. Mollier, J.-P. de Barbeyrac, and G. Pfister-Guillouzo, *Compt. rend.*, 1972, **275**, 909.

⁹ J.-P. de Barbeyrac, D. Conbeau, and G. Pfister-Guillouzo, *J. Mol. Structure*, 1973, **16**, 103.