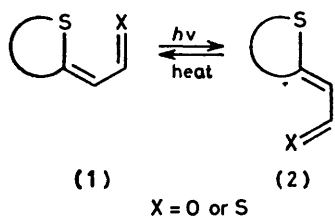


Photochemical Induced *cis*-*trans*-Isomerization of Substituted α -(4*H*-3,1-Benzothiazin-4-ylidene) Ketones and Esters

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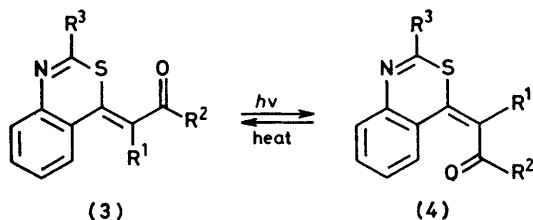
A series of α -(4*H*-3,1-benzothiazin-4-ylidene) ketones has been prepared and their photochemistry studied. The normal *cis*-form is converted into the *trans*-form on irradiation of ethanolic solutions. The photoproducts revert to starting materials by a thermal process which obeys first-order kinetics. The rate constants are slightly affected by variation of substituents on the benzothiazine nucleus.

THE reversible photoisomerization of a series of compounds of type (1) has been studied by flash photolysis.¹⁻⁶ In all cases compounds (1) were transformed into photoproducts of structure (2) which reverted to



starting materials by a dark process obeying first-order kinetics.

The 4*H*-3,1-benzothiazine system (3) is structurally related to the thiopyran system studied previously.⁴ The same type of *cis*-*trans*-photoisomerization leading to (4) should therefore be possible in these compounds, and we have studied the photoreactions of compounds of type (3).



RESULTS AND DISCUSSION

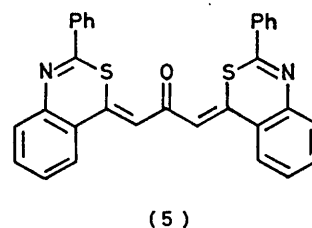
Flash photolysis of (3) in neutral 10^{-4} M ethanolic solution converted it into a photoproduct, which reverted to starting material in a slow ($t_{1/2}$ ca. 200 days) first-order process. It was, however, not possible to obtain reproducible rate constants for this process owing to traces of acids on the silica surface of the reaction vessel. We have earlier observed a similar effect for higher analogues of α -(1,2-dithiol-3-ylidene) ketones.³ In that case the problem was solved by addition of a known amount of hydrogen chloride to the reaction

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

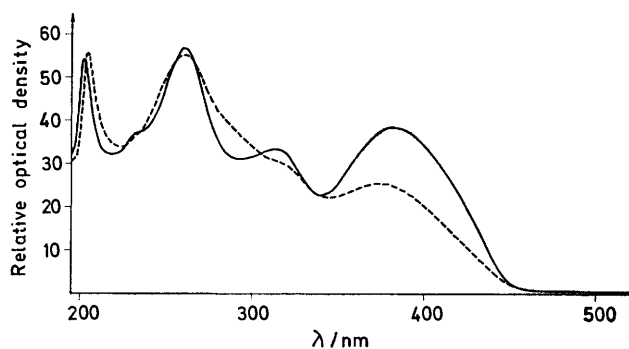
² G. Calzaferri, R. Gleiter, K.-H. Knauer, E. Rommel, E. Schmidt, and H. Behringer, *Helv. Chim. Acta*, 1973, **56**, 597.

³ C. Th. Pedersen, C. Lohse, and M. Stavaux, *J.C.S. Perkin I*, 1974, 2722.

mixture. In the present case, if the photolysis of (3) was carried out in 10^{-4} M solution containing 10^{-4} M hydrogen chloride, reproducible rate constants for the back reaction were obtained at 25 °C, and the process was found to obey first-order kinetics. The rate constants for various substituted compounds are given in the



Table, and the u.v.-visible spectrum of a representative compound and its photoproducts in ethanol is given in the Figure.



U.v. and visible spectra of (3d) — and its photoproduct
---- in absolute ethanol ($c \times 10^{-5}$ M)

The process observed could be bond switching with formation of the hypervalent sulphur compounds (6) as photoproducts. This possibility can be excluded, however, owing to the photostability of (3f); bond switching in this case would give rise to compound (6f) which is different from the starting (3f), whereas *cis*-*trans*-isomerization would result in a compound identical

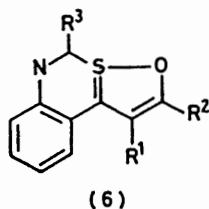
⁴ C. Th. Pedersen, C. Lohse, N. Lozac'h, and J.-P. Sauvé, *J.C.S. Perkin I*, 1976, 166.

⁵ G. Calzaferri, R. Gleiter, R. Gyax, K.-H. Knauer, and H. Behringer, *Helv. Chim. Acta*, 1973, **56**, 2584.

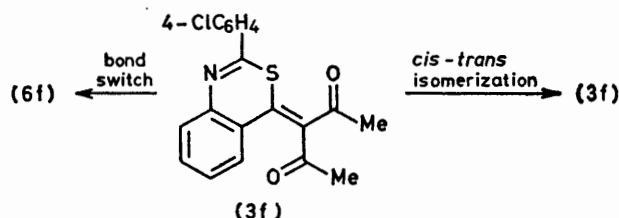
⁶ C. Th. Pedersen and C. Lohse, *J.C.S. Perkin I*, 1977, 994.

with (3f). The photostability of (3f) is in accordance with the process being a *cis-trans*-isomerization.

It is obvious from the rate constants for compounds

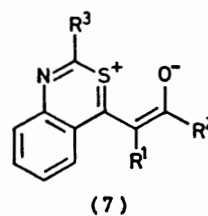


(3a—d) that the rate of the back reaction is only slightly dependent on small changes in the electron-donating

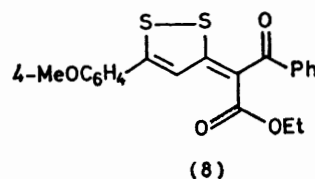


ability of the substituents R^2 and R^3 . From studies of the effect of substituents on the dark reaction of α -(1,2-dithiol-3-ylidene) ketones¹ it is known that substituents which lower the double bond character of the exocyclic

For an analogous 1,2-dithiolylidene ester (8) the kinetic data shown have been found. These data show



that the original double bond is less disturbed in this compound by the electron-withdrawing substituent.



$$k(\text{EtOH} + \text{H}^+) = 1.30 \text{ s}^{-1}; k(\text{EtOH}) = 0.46 \text{ s}^{-1}$$

Callendret⁷ has shown that, according to the ¹H n.m.r. spectra of solutions prepared without precautions to exclude light, compounds (3g) and (3h) exist as a mixture of *cis*- and *trans*-forms. This is in agree-

Rate constants for the dark reaction (4) \rightarrow (3)

Compd.	R^1	R^2	R^3	$k^a(\text{EtOH} + \text{H}^+)/\text{s}^{-1}$	$k^b(\text{EtOH})/\text{s}^{-1}$
(3a)	H	4-ClC ₆ H ₄	Ph	7.3×10^{-2}	
(3b)	H	4-ClC ₆ H ₄	4-ClC ₆ H ₄	3.6×10^{-2}	
(3c)	H	Ph	4-ClC ₆ H ₄	4.3×10^{-2}	
(3d)	H	4-MeOC ₆ H ₄	Ph	1.9×10^{-2}	5.7×10^{-7}
(3e)	H	Me	Ph	40.0×10^{-2}	
(3f)	MeCO	Me	4-ClC ₆ H ₄	Stable	
(3g)	CO ₂ Me	Me	Ph	29.3	22.1
(3h)	MeCO	OH	Ph	Too fast to be measured	572
(5)				3.2×10^{-2}	

^a 10^{-4} M Solution in 96% EtOH containing 10^{-4} M HCl at 25 °C. ^b 10^{-4} M Solution in abs. EtOH at 25 °C.

double bond decrease the stability of the *trans* form. This is in agreement with the change in rate constant in going from (3c) ($R^2 = \text{Ph}$) to (3e) ($R^2 = \text{Me}$). The effect is even more drastic when more electronegative substituents such as ethoxycarbonyl [compound (3g)] or carboxy [compound (3h)] are introduced. In compound (3h) the rate of the back reaction was extremely high even in absolute neutral ethanol, probably owing to a combination of the catalytic effect of the proton on the carboxy-group and the electronegativity of the substituent.

It is interesting that the rate of the dark reaction of (3g) (Table) is only slightly dependent on the addition of hydrogen chloride. The catalytic effect of the protons is probably due to a promotion of polar forms such as (7) which lowers the double bond character of the exocyclic double bond. The lack of a catalytic effect of protons on the kinetics of (3g) may be explained by an extreme lowering of the double bond character caused by the electron-withdrawing substituent.

⁷ R. Callendret, Thesis, University of Caen, France, 1975.

ment with the low double bond character of the exocyclic double bond already mentioned. A similar low energy barrier has not been reported in the case of α -(1,2-dithiolylidene) ketones or α -(thiopyranylidene) ketones.

EXPERIMENTAL

The rate constants for the *trans-cis*-isomerizations were obtained by using the flash photolysis equipment described previously.¹ The rate constants were reproducible within $\pm 10\%$.

The compounds were prepared by the route in the Scheme.⁷

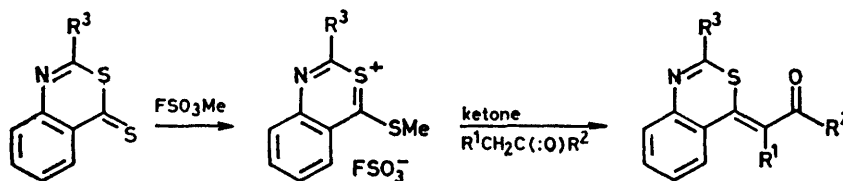
2-Aryl-4-methylthio-3,1-benzothiazinium Fluorosulphate.—To a refluxing solution of the appropriate 3,1-benzothiazine-4-thione (1 g) in 50 ml of 1,2-dichloroethane (purified by distillation from phosphorus pentoxide) was added a slight excess of methyl fluorosulphate. The mixture was heated under reflux until the colour had changed. On cooling crystals separated, which were not isolated: the suspension was used directly in the next step.

2-Aryl-4H-3,1-benzothiazin-4-ylidene Ketones.—To the sus-

pension of the fluorosulphate from the foregoing preparation was added the appropriate ketone (0.5 g) and the mixture was heated under reflux for 30 min after the salt had dissolved. After some minutes the colour turned deep red. Solvent was then evaporated off and a mixture of benzene and triethylamine was added, followed by water to

which was prepared by the procedure in the next section.

Preparation of 2-Phenyl-4H-3,1-benzothiazin-4-ylideneacetone (3e).—To a well stirred refluxing solution of 3,1-benzothiazine-4-thione (1.5 g) in light petroleum (b.p. 155–160 °C; 50 cm³) was added diazoacetone (*ca.* 1.5 g) during 30 min, and the stirred mixture was heated for a further 30



dissolve the triethylammonium fluorosulphate. The benzene solution was washed with water to neutrality, dried over sodium sulphate, and concentrated. The products were separated by chromatography on neutral alumina. On elution with light petroleum (b.p. 70–78 °C) the benzothiazinethione and benzothiazinone were eluted first followed by the required benzothiazinylidenemethyl ketones (3a–d) and (3f–h), which were recrystallized from ethanol. This reaction with acetone ($R^1 = H$, $R^2 = Me$) gives the double condensation product (5) and not compound (3e),

min. After partial cooling, solvent was removed *in vacuo*, and a solution of the residue in light petroleum (b.p. 70–80 °C) was chromatographed on alumina. Unchanged 3,1-benzothiazine-4-thione was eluted first, followed by the ketone (3e), in 60% yield.

Full details of the preparation and chemistry of compounds (3a–h) and (5) will be published elsewhere.⁸

We thank Professor Y. Mollier, Département de Chimie, Université de Caen, France, for a sample of compound (8).

⁸ R. Callendret and M. Ebel, to be published.