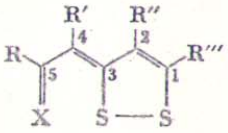
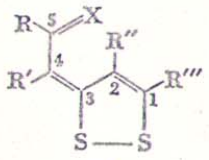
G. CALZAFERRI, R. GLEITER, R. GYGAX, K.-H. KNAUER, E. SCHMIDT and H. BEHRINGER (Physikalisch-Chemisches Institut der Universität Basel und Institut für Organische Chemie der Universität München) *Photochromism of Oxygen and Nitrogen Analogues of Thiathiophthenes*

Irradiation of Ia to If yields a transient intermediate which reverts thermally to the starting material[1].



I

	X	R	R′	R″	R‴
a	O	CH_3	H	H	CH_3
b	O	C_6H_5	H	H	C_6H_5
c	O	$-(CH_2)_4-$		H	$C_6H_4-CH_3(p)$
d	O	$-(CH_2)_3-$		H	$C_6H_4-CH_3(p)$
e	N–C_6H_5	CH_3	H	H	CH_3
f	S	CH_3	H	H	CH_3
g	O	C_2H_5	$-(CH_2)_3-$		C_2H_5
h	N–C_6H_5	C_2H_5	$-(CH_2)_3-$		C_2H_5
i	S	C_2H_5	$-(CH_2)_3-$		C_2H_5



II

The kinetics of this thermal back reaction in ethanol, toluene and acetonitrile has been investigated, using the flash photolysis[2]. The energies and entropies of activation were found to be 10 to 15 kcal/mol and −15 to −40 e.u. resp. The large negative entropy of activation and the observation that the thermal back reaction is catalyzed by acids point to a *cis-trans* isomerization reaction. This is supported by the fact that Ig to Ii do not undergo photoreaction under the same conditions.

In case of Ia to Id we were able to measure the nmr and ir spectra of the photoproduct. We find an increase in the ν_{CO} stretching frequency of 40 to 75 cm^{-1} and a downfield shift of the hydrogen in the dithiolic ring moiety ($R'' = H$) to 8.2 to 9 ppm[3]. Based on these measurements we were able to assign the structure of the photoproduct to II for X = O.

In case of Ie and If the kinetic data again suggest a *cis-trans* isomerism at the C_3–C_4 bond. For Ie this is supported by the similarity of the electronic spectra of Ia and Ie, and by an increase in $\nu_{C=N}$ of 30 cm^{-1}.[4]

Summarized by the authors

[1] R. GLEITER, D. WERTHEMANN and H. BEHRINGER, *J. Amer. Chem. Soc. 94* (1971) 651.
[2] G. CALZAFERRI, R. GLEITER, K.-H. KNAUER, E. ROMMEL, E. SCHMIDT and H. BEHRINGER, *Helv. Chim. Acta 56* (1973) 597.
[3] R. GLEITER, K.-H. KNAUER, E. SCHMIDT, Y. MOLLIER and R. PINEL, *Tetrahedron Letters 1973*, 1257.
[4] G. CALZAFERRI, R. GLEITER, R. GYGAX, K.-H. KNAUER, E. SCHMIDT and H. BEHRINGER, *Helv. Chim. Acta* submitted.