59. Photochromism of O-Analogs of Thiathiophthenes[1])

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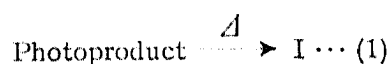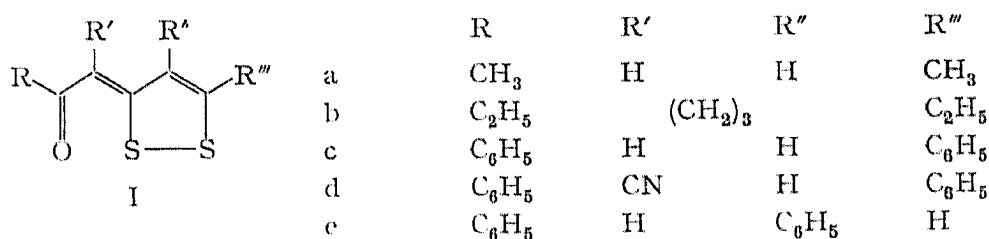
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Summary. Irradiation of O-analogs of thiathiophthenes yield a photoproduct which reverts thermally to the starting material. Kinetic measurements for this thermal reaction yield E_a values in the range of 10–15 kcal/mol and ΔS^* values between -16 and -41 eu. Based on NMR. and IR. results the structure of the photoproduct is established. The electronic spectra of the starting material and of the photoproduct are discussed. The experimental results are compared with MO-calculations.

Because their structures are still open to debate, the thiathiophthenes are among the most interesting systems in organic sulfur chemistry[2]. In our investigations and discussions of the electronic spectrum of thiathiophthene [3] the question of the shape of the potential surface in the first excited state arose [4]. Compounds I a, I c–I e yield photoproducts which revert to their starting material both in the presence and in the absence of light. These compounds have been investigated [4] in order to gain further information about this reaction and to establish the structure of their photoproducts.

The kinetics of the thermal back reaction were followed by UV.-spectroscopy in the 300–500 nm wave length range. The change in optical density accompanying the reaction (1) fits the first order kinetic law [4].

		R	R′	R″	R‴
	a	CH_3	H	H	CH_3
	b	C_2H_5	$(CH_2)_3$		C_2H_5
	c	C_6H_5	H	H	C_6H_5
	d	C_6H_5	CN	H	C_6H_5
	e	C_6H_5	H	C_6H_5	H

$$\text{Photoproduct} \xrightarrow{\Delta} I \cdots (1)$$

In Fig. 1 the *Arrhenius* plots for the thermal formation of I a and I d from their photoproducts are shown. The measurements were carried out in ethanol and toluene. The results are summarized in Table 1 (for a detailed description see the experimental part).

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[1]) The electronic structure of thiathiophthenes VI; part V see [1]. Presented at the I. IUPAC-Conference on Physical Organic Chemistry, Crans (Switzerland), Sept. 4–8, 1972.

[2]) For recent reviews see [2].

Additionally, the rates were not affected by the presence of oxygen. This and the lifetime of the photoproducts in non-deaerated solvents suggest a singlet ground state for the photoproduct. Further we observed that traces of acid accelerate the reaction (1) by a factor of 100–1000.

On the basis of these results we assume that the photoproduct is an isomer of I. Seven possible structures (II–VIII) can be derived for the photoproduct I and its valence isomer II by rotations about formal double and/or single bonds. (For the crystal structure of I a see Ref. [5]).
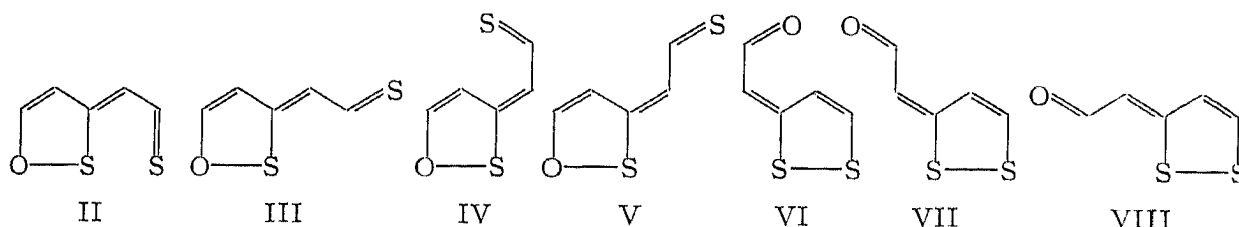

Table 1. *Kinetic data for the thermal back reaction (1)*

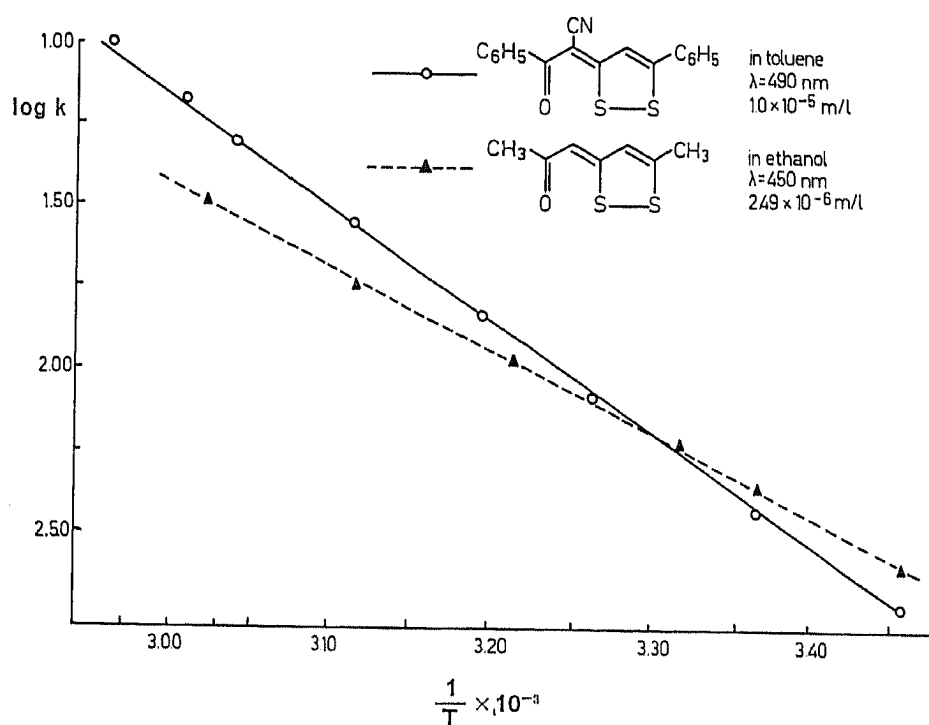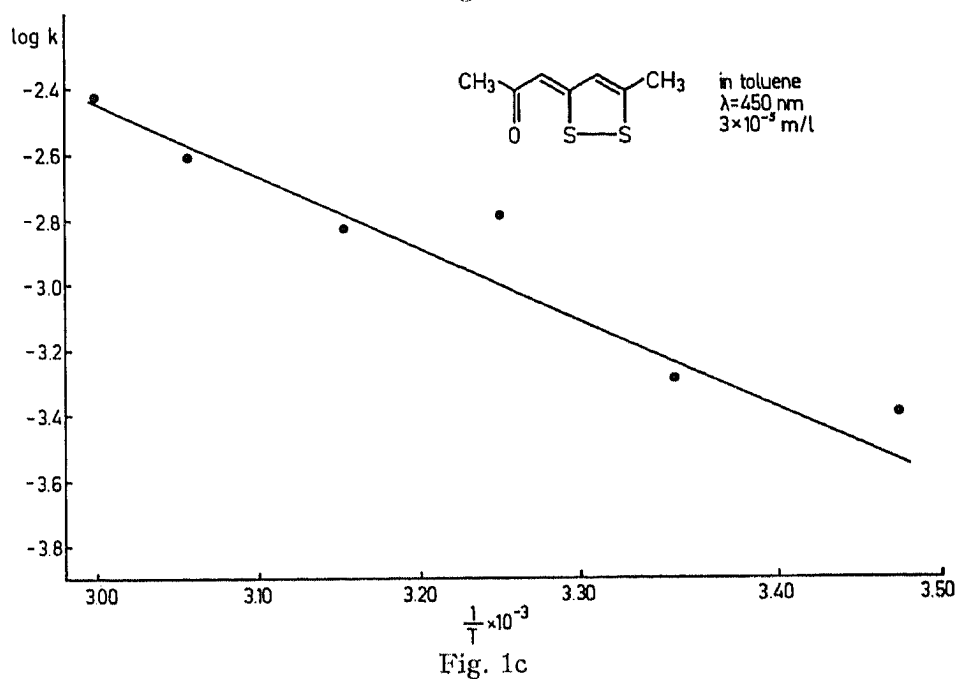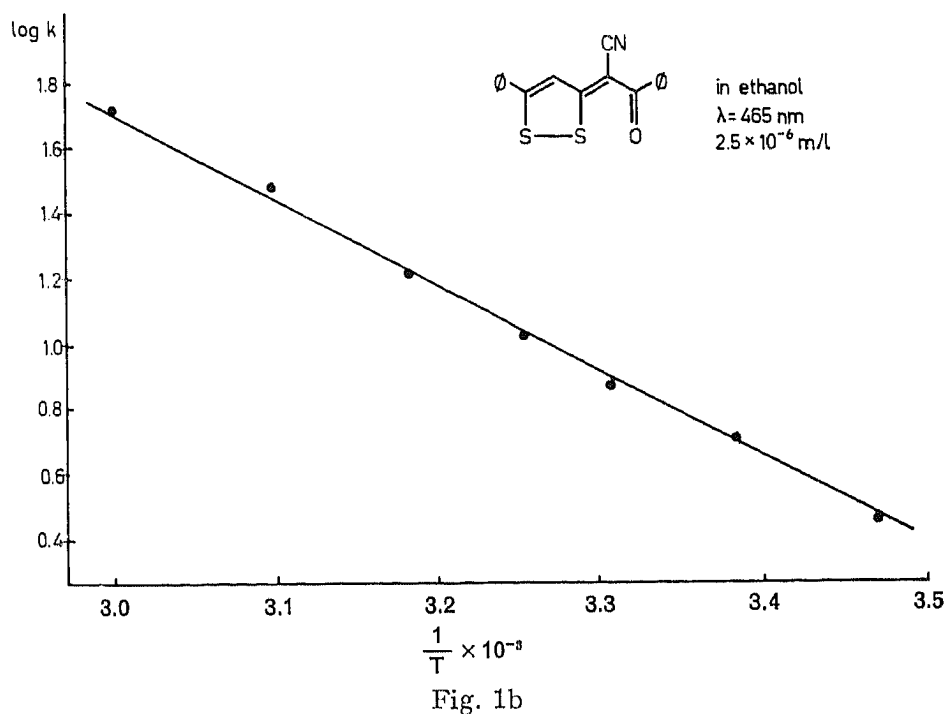|	solvent	temp. °C	k s^{-1}	$\tau_{1/2}$ s	E$_a$ kcal · mol^{-1}	ΔG^* kcal · mol^{-1}	ΔS^* e.u.
I a	ethanol	25.0	4.68 · 10^{-3}	148	11.6	20.6	– 32.3
I a	toluene	25.0	5.89 · 10^{-4}	1176	10.1	21.9	– 41.5
I d	ethanol	25.0	5.79	0.12	12.3	16.4	– 15.9
I d	toluene	25.0	2.78 · 10^{-3}	248	15.7	20.9	– 19.6
I c	toluene	26.5	1.14 · 10^{-3}	608	–	–	–
I e	cyclohexane	26.5	3.03 · 10^{-2}	23	–	–	–

Fig. 1a

Fig. 1b

Fig. 1c

Fig. 1. Arrhenius *plots for the thermal formation of 1a and 1d in ethanol and toluene according to (1)*. Solvents, wavelengths and concentrations are as indicated.

The techniques employed in this work do not distinguish between the rotamers IV and V resp. VI and VII. Therefore, in the following discussion equilibria IV ⇌ V and VI ⇌ VII are assumed which lie to the left for our compounds for steric reasons [6] [11]. The data in Table 1 especially the highly negative ΔS^* values can be rationalized by assuming a polar transition state with a high degree of orientation of solvent molecules. This interpretation argues against structure II for the photoproduct[3] since for the reaction II ⇌ I a small ΔS^* value is expected [21]. The large

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[3]   As the observed properties (electronic spectrum in the visible region and lifetimes) of the photoproducts were not compatible with those of a *trans* isomer reported in the literature [7], structure II was tentatively assigned to the photoproduct in a preliminary publication [4].

negative entropy of activation and the fact that reaction (1) is catalyzed by acids point to a *cis-trans* isomerization. In fact, similar values for ΔS^* and acid catalysis are observed in photochromic reactions of polar stilbenes [8]. The E_a and ΔS^* values obtained for the barrier of rotation around the C–N-bond in N, N-dialkyl-1,2-dithiol-3-imonium compounds [9] are also comparable to the values reported in this paper. A further observation which indicates a *cis-trans* isomerization is the absence of any photoreaction of I b under the conditions employed for I a, c–e. Here rotation around bonds 3–4 and 4–5 is prevented by the trimethylene bridge whereas rotation around

I b
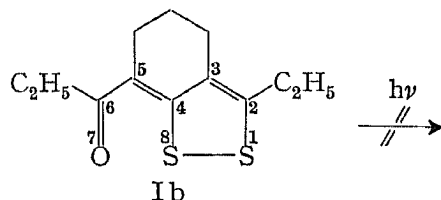
bonds 5–6 or 2–3 as well as the formation of a valence tautomer II should be possible. This makes the structures II, III and VIII for the photoproduct unlikely. The photoproducts of I a and I c were found to be rather stable in acetonitrile, carbon-disulfide and tetrachloroethylene ($\tau_{1/2} \approx 6\,h$ in acetonitrile for I a). This allows their NMR. and IR. spectra to be measured.

From these spectra and from the finding that the rates for the thermal back reaction measured at different wave lengths are identical we conclude that there is one single photoproduct formed in each case, with the restrictions imposed by the rapid equilibrium mentioned above.

Spectroscopic Investigations

NMR. spectra. – In Fig. 2 the NMR. spectrum of a mixture of I a with its photoproduct in CS_2 at $-50°$ is shown. The interpretation of the spectrum of I a is straightforward [2] [10]. The signal at 2.5 ppm is attributed to the methyl hydrogens at the dithiolring and the broadening is due to a long range coupling with the ring hydrogen atom at 6.8 ppm.

Irradiation of I a in CS_2 and tetrachloroethylene or I b in CS_2 yields one photoproduct (30% conversion) which is characterized by the data summarized in Table 2.

By comparing the NMR. spectrum of I a with that of its photoproduct one notices a small upfield shift of the signals corresponding to the methyl groups but a rather large shift of the signals ascribed to the olefinic hydrogens between 6 and 9 ppm. A slightly broadened signal appears at 8.15 ppm and a sharp one at 5.98 ppm. A similar observation is made upon irradiation of I c. Two sharp signals at 6.9 and 9.07 ppm emerge out of the phenyl multiplets.

Which of the possible isomeric structures are compatible with these experimental facts? If the olefinic protons of structures II, III and VIII are considered we should
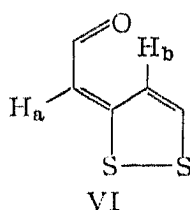

VI

Table 2. *NMR. results for Ia and Ic and their photoproducts. All values in ppm with TMS as internal standard*

	solvent	temp.	vinylic protons		methyl protons		phenyl protons	
			starting compound	photo-product	starting compound	photo-product	starting compound	photo-product
Ia	CS_2	−50°	6.58; 6.81	5.98; 8.15	2.21; 2.55	2.05; 2.46	—	—
Ia	C_2Cl_4	25°	6.56; 6.75	6.02; 8.21	2.22; 2.47	2.07; 2.38	—	—
Ic	C_2Cl_4	25°	7.4–7.6	6.9 ; 9.07	—	—	7.5–8.1 [a]	7.5–8.1 [a]

[a] multiplet

Table 3. *Electronic spectra of Ia–e in cyclohexane (c) and ethanol (e). All values are given in nm. The log ε values are included in brackets.*

| Compound	Ia		Ib		Ic		Id		Ie	
band \ solvent	c	e	c	e	c	e	c	e	c	e
1	418 (4.11) 399 (4.11) 380 s (3.85) 360 s (3.46)	419 (4.11) 400 (4.20) 380 s (3.90)	434 (4.12) 414 (4.12) 395 s (3.87) 375 s (3.46)	436 (4.18) 417 (4.15) 394 s (3.84) 375 s (3.40)	465 s (4.35) 450 (4.44) 430 s (4.32)	470 s (4.33) 451 (4.42) 426 s (4.20)	444 (4.37)	440 (4.44)	447 (4.38) 424 (4.27) 405 s (3.89)	448 (4.45) 428 (4.32) 405 (3.92)
2	260 s (3.40)	260 s (3.60)	280 s (3.08) 265 s (3.42)	280 s (3.23) 265 s (3.46)	322 s (3.85) 304 s (4.15) 295 s (4.20)	320 s (3.93) 305 s (4.10)	292 (4.19)	300 (4.17)	305 s (3.55)	290 (3.80)
3		245 s	245 s (3.99)	242 s (4.01)	285 s (4.27) 264 (4.40)	265 (4.20)			285 s (3.77) 265 s (4.01)	270 (3.96)
4	229 (4.28)	227 (4.28)	228 (4.25)	226 (4.22)	236 s (4.53) 230 (4.54)	230 (4.43)	232 (4.52)	229 (4.50)	245 s (4.28) 229 (4.42)	245 (4.22) 225 (4.40)
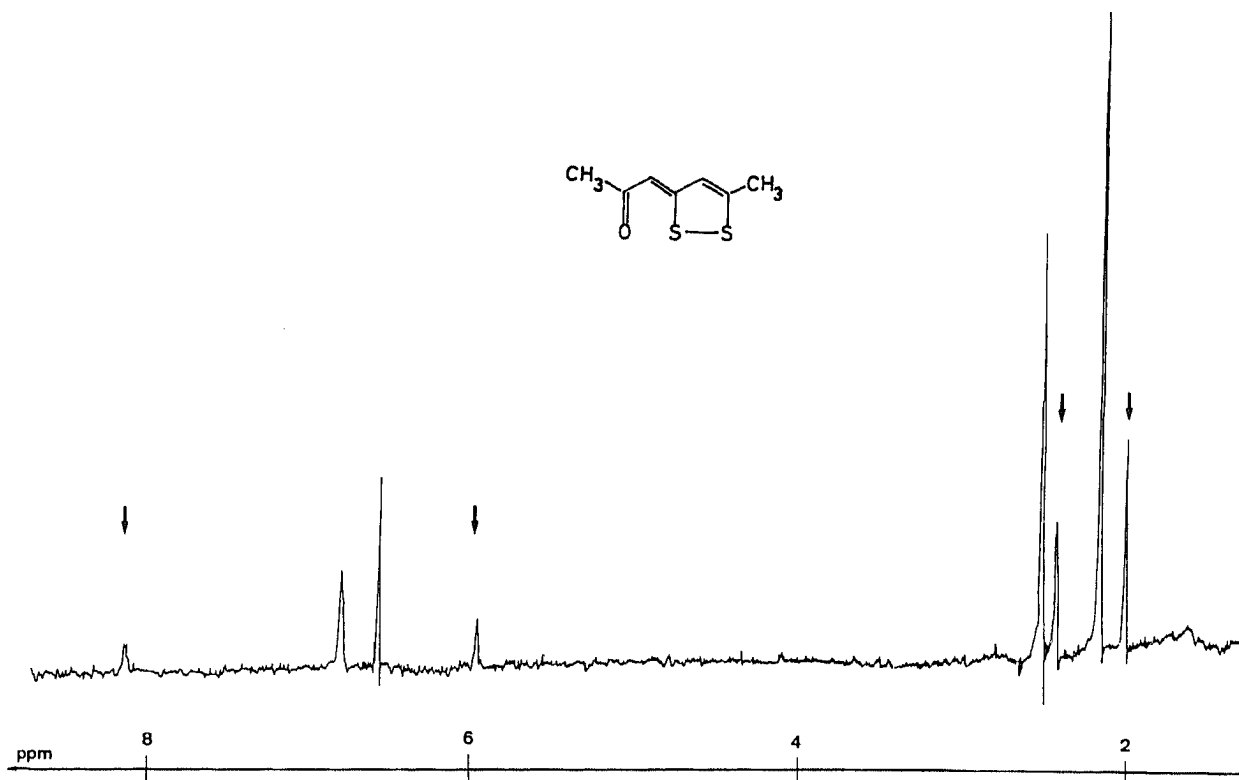
Fig. 2. *NMR. spectra of I a and its photoproduct in CS_2 at* $-50°$
The signals of the photoproduct are indicated by arrows

expect chemical shifts similar to those of the starting material. These isomers are therefore ruled out as photoproducts. For VI and for the equilibrium VI $\rightleftharpoons$ VII resp. we expect the signal of the olefinic proton H_b to be strongly shifted downfield due to the anisotropy effect of the carbonyl group. Model compounds of unsaturated ketones are available [11] which demonstrate this effect. Some results are shown below (all values in ppm). In going from the *trans* to the *cis* configuration the H_b signal is shifted strongly towards lower field. This is very similar to our results.
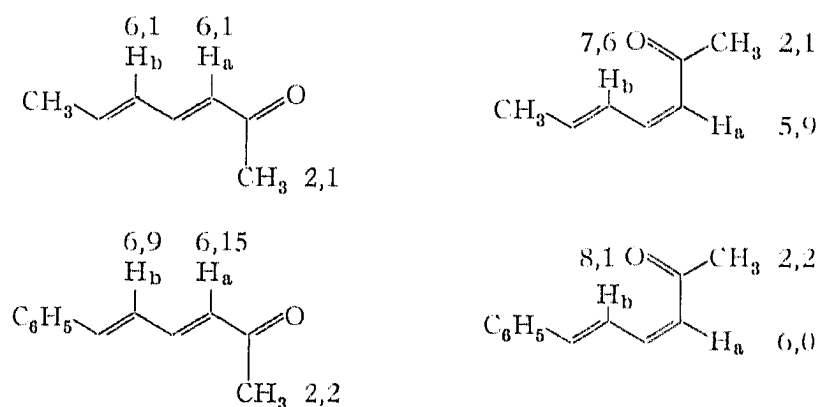
Though the fit between model compounds and VI $\rightleftharpoons$ VII is very good we are unable to eliminate IV $\rightleftharpoons$ V by the NMR. data, since model compounds are not available.

IR. spectra. – The ν_{CO} bands in I a and I c have been assigned by *Mollier* & *Pinei* [12] with the help of isotope effects. Their data are collected in Table 4. The main

feature in the spectrum of the photoproduct of I a (Fig. 3 a) is the appearance of a new band at 1645 cm^{-1}, whereas I a did not show any absorption above 1600 cm^{-1}.

The integrated intensity of the band at 1645 cm^{-1} of the photoproduct of I a was found to be 0.30 l · mol^{-1} · cm^2 which is the same order of magnitude as that of s-cis α, β-unsaturated ketones [13]. A similar band appears at 1635 cm^{-1} for the photoproduct of I c. Based on the models shown below [14] we assign this new band to the ν_{CO} stretching frequency. This assignment is fully confirmed by isotopic substitution.
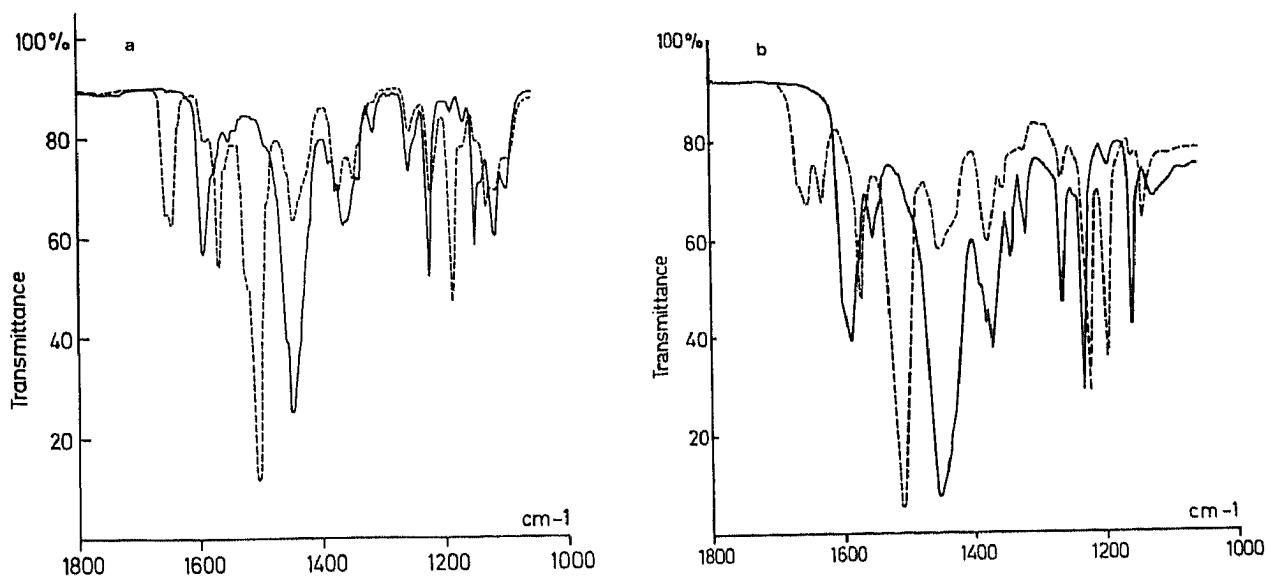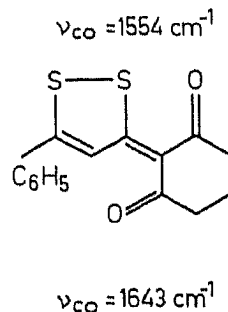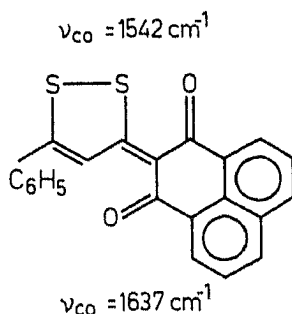

Fig. 3. a) IR. spectrum of I a (—) and its photoproduct contaminated with I a (———) in C_2Cl_4 at 25°
b) Same as in a) but with the starting material enriched 40% in ^{18}O

Table 4. C = O Stretching vibrations of I a and I c and their photoproducts

	ν_{CO}[cm^{-1}] of starting material		ν_{CO}[cm^{-1}] of photoproduct
	K Br	C_2Cl_4	C_2Cl_4
I a	1578	1595	1645
I c	1544	1552	1635

Replacing ^{16}O in part (40%) by ^{18}O in I a yields two bands in the IR.-spectrum of the photoproduct (see Fig. 3b), i.e. one at 1645 cm^{-1} for $\nu_{C^{16}O}$ and one at 1622 cm^{-1} for $\nu_{C^{18}O}$. In the starting material an isotopic shift of the ν_{CO} band was found to be 9 cm^{-1} [12]. This reveals that the group vibration contributes only 20% to the band

observed at 1595 cm^{-1} of the starting material. This is primarily due to the partial bond between S and O. In the photoproduct of Ia the contribution of the C–O-group vibration of the band at 1645 cm^{-1} is 57%. This is best understood by assuming a free carbonyl group in the photoproduct, which is compatible only with VI or the equilibrium VI $\rightleftharpoons$ VII, but not with the other structures II, III, IV and V.

The isotopic labeling experiment shows that the bands at 1568 cm^{-1} and 1504 cm^{-1} are not altered by the introduction of ^{18}O. This makes the assignment of the band at 1568 cm^{-1} to a C-C-stretching frequency and the broad band at 1504 cm^{-1} to a ν_{C-C} and a δ_{CH_3} frequency likely [12].

Electronic spectra. – The electronic spectra of I are related to that of dimethyl-thiathiophthene which has been studied in detail [3]. All bands of I between 500 and 250 nm show the anticipated hypsochromic shift due to the replacement of one sulfur atom by an oxygen atom. In the region from 500 to 350 nm compounds I have an intense band with fine structure which for Id is resolved only at lower temperature. Between 350 and 200 nm there is a system of overlapping transitions which is further complicated in compounds Ic–e by the absorption of substituents. These data are compiled in Table 3.

From Table 1 it is evident that at room temperature the thermal back reaction in ethanol and toluene is too fast for recording the spectrum of the photoproduct by conventional means. The spectra could however be obtained by performing the irradiation at low temperature where thermal stability is sufficient. Experimental data such as solvents used and temperatures are included in Table 5.

Table 5. *Electronic spectra of the photoproducts of Ia, Ic, Id and Ie*

All values are given in nm. The spectra were recorded in 2,2-dimethylbutane/n-pentane (r) ethanol/methanol (me) and ether (a)

Compound band	Ia		Ic	Id		Ie
\solvent	r −100°	me −150°	r −50°	a −120°	me −150°	r −50°
1	422 401 *382* 365	435 *413* 393 s 375 s	490 s 460 s *448* 415 s	485 s *453* 440 s	480 s *451* 435 s	500 s *446* 422 405 s
2	285 s		322 s 304 s	320 s	*320*	305 s
3	264 s *247*	275 s *225*	285 s *264*	*304* 278 s	300 s 255 s	285 s 265 s

To obtain the spectra of the photoproducts it is necessary to know the degree of conversion of I into VI. Because the photoproducts absorb in the same region as the starting materials we used the method elaborated by *Fischer* [15] to determine the concentration of the photoproduct. This technique approximates the ratio of the concentrations C_{VI}/C_I by the ratio $\varphi_I \cdot \varepsilon_I/\varphi_{VI} \cdot \varepsilon_{VI}$ where φ is the quantum yield and ε the molar extinction coefficient.

The photoreaction was carried out at $-100°$ by irradiation with light in the isosbestic region ($\varepsilon_I = \varepsilon_{VI}$) and with light in the region where the difference in absorbance of I and VI was a maximum ($\varepsilon_I > \varepsilon_{VI}$ and $\varepsilon_{VI} > \varepsilon_I$). Irradiation 'to completion' at these wavelengths yielded spectra which were identical. Additionally irradiation into the long wavelength shifted onset of the first band of the photoproducts VI showed that the back reaction VI $\rightarrow$ I can be initiated by light, as compounds I do not absorb in this region.

These results lead to the conclusion that the quantum yields for the photochemical forward and back reactions are very different and that the reaction I $\rightarrow$ VI is the faster one. In the photostationary state the concentration of I may be assumed to be negligible. The recorded spectra are therefore essentially those of the photoproducts.

The band at longest wavelength in the spectra of the photoproducts of compounds Ia, Ic–Ie is well separated and shows fine structure between 500 and 350 nm and a region of complex absorption between 330 and 200 nm.

The first band is broader in all cases and the total intensity is greater than that of the corresponding band of the starting material. The onset is shifted towards longer wavelength but the most intense maximum shows a hypsochromic shift. As is evident from Table 5 and Fig. 4 a bathochromic shift of the first band is observed upon increasing the polarity of the solvent.

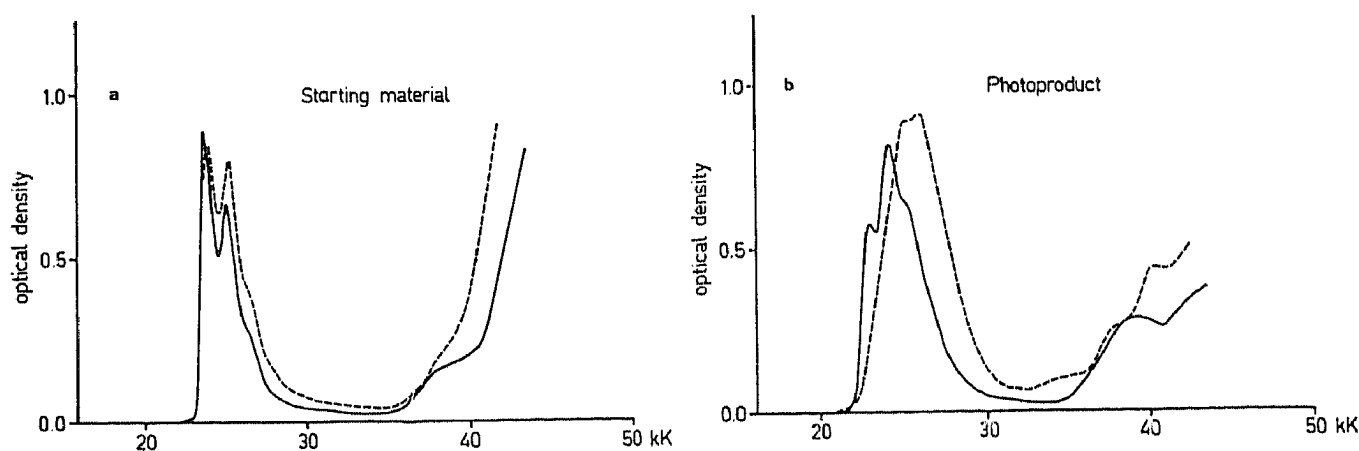In the region between 330 and 200 nm the spectra of the starting material and the photoproduct are very similar.

Fig. 4. a) *Electronic spectrum of* I a *at* $-100°$ *in 2,2-dimethylbutane/n-pentane 8:3* (– – –) *and in ethanol/ methanol 9:1* (—)

b) *Electronic spectrum of* VI a *at* $-100°$ *in 2,2-dimethylbutane/n-pentane 8:3* (– – –) *and in ethanol/ methanol 9:1* (—)

To rationalize the electronic spectral data LCAO-CI calculations of the PPP type have been carried out for the π-electron systems of I and VI, the following bond distances and angles being assumed: C–C = 1,41 Å, C–O = 1,27 Å, C–S = 1,75 Å, S–S = 2,15 Å, $\angle$ CCC, CCS, CCO = 120°. The parameters used were: $U_S = -9,0$ eV, $\gamma_{SS} = 10,84$ eV, $\beta_{C-S} = -1,62$ eV, $U_C = -11,42$ eV, $\gamma_{CC} = 10,84$ eV, $\beta_{CC} = -2,318$ eV, [16]. The two center integrals were calculated according to *Mataga-Nishimoto* [17]. All singly excited configurations were used for the CI treatment.

The results of the model calculations are listed in Table 6.

Table 6. *Calculated electronic transition energies and intensities for I and VI*

band	I		VI	
	λ(nm)	$\log \varepsilon$	λ(nm)	$\log \varepsilon$
1	419	4.47	402	4.62
2	276	3.41	284	2.14
3	267	4.02	260	4.11
4	234	4.45	238	2.75

As can be seen by comparing the experimental and calculated values energies and intensities are reproduced satisfactorily. Moreover, the observed solvent shifts of 163 cm^{-1} for I a and 715 cm^{-1} for VI a in going from an unpolar solvent (2,2 dimethyl-butane/n-pentane 8:3) to a polar solvent (ethanol/methanol 9:1) are explained by the differences of the calculated dipole moments between the first excited state and the ground state which is 0.2 D for I a and 2.3 D for VI a.

A comparison of the observed solvent shifts and intensity changes with results of all valence electron calculations of the extended *Hückel* and CNDO/2 type suggests that the first band is due to an π^* ← π transition in all the O-analogues of thiathiophthenes discussed in this paper. In Fig. 5 the differences in the π-bond order $\delta p_{\mu\nu}$ between the first excited singlet state $p_{\mu\nu}^*$ and the ground state $p_{\mu\nu}^o$, $\delta p_{\mu\nu} = p_{\mu\nu}^* - p_{\mu\nu}^o$, are shown for I and VI. They are obtained from a PPP-CI calculation. For both molecules a lowering of the barrier of rotation in the first excited singlet state as compared to the ground state is predicted.
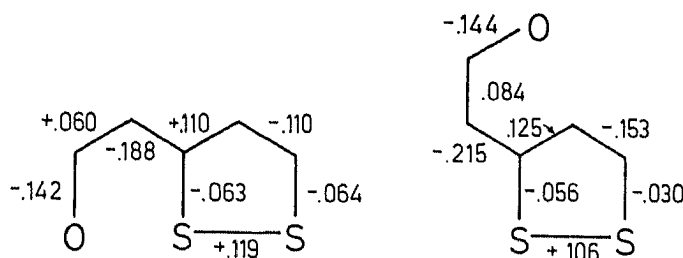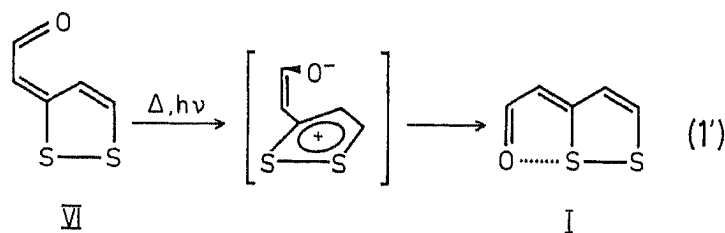

Fig. 5. *Calculated changes in π-bond order $\delta\,p_{\mu\nu} = p_{\mu\nu}^* - p_{\mu\nu}^o$ for I and VI according to a PPP-calculation*

For the meaning of p* and p° see text.

Concluding remarks

From the reported data we infer that VI is the structure of the photoproduct. This is corroborated by the observation that the photoproduct I c reverts to the
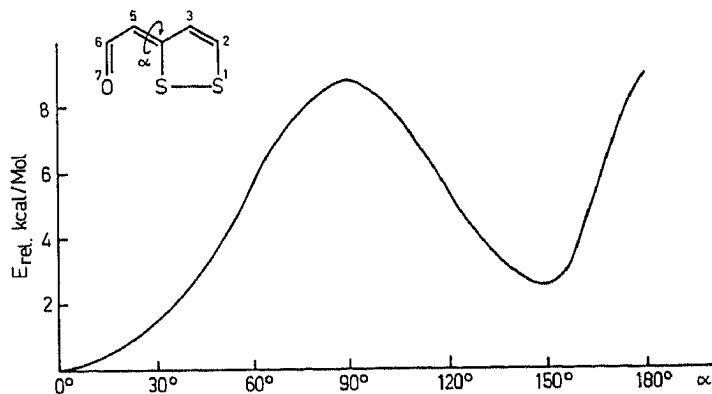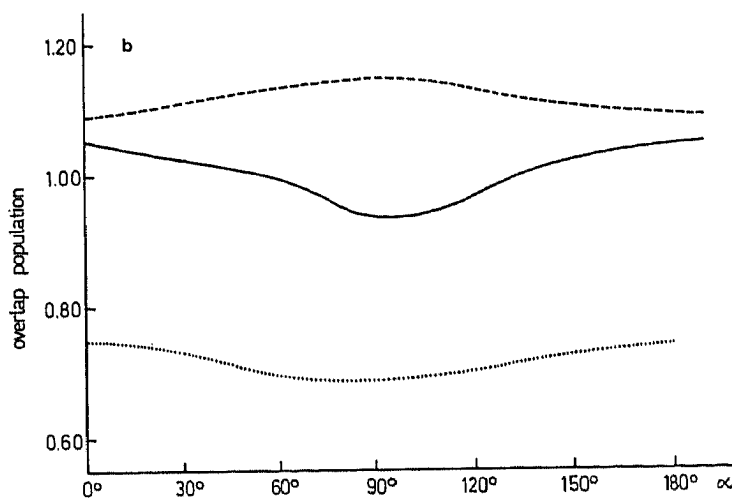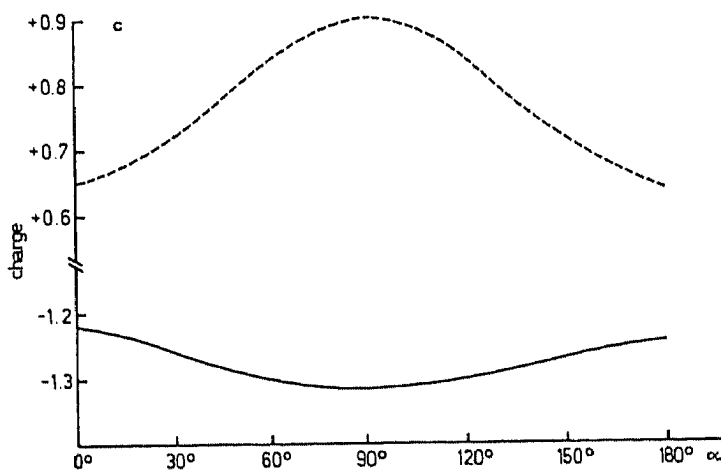
Fig. 6a

Fig. 6b

Fig. 6c

Fig. 6. a) *Energy profile as a function of* α *obtained from an extended* Hückel *calculation*

b) Mulliken *overlap population for the bonds* C_4-C_5 (——) C_5-C_6 (————) *and* C_6-O_7 (...) *as a function of* α

c) *Charge at the oxygen atom* (——) *and the sum of the charges at the centers 1, 2, 3, 4 and 8* (————) *as a function of* α

starting material faster than I c by a factor of 30. This fact can be attributed to steric interactions between the carbonyl group and the phenyl substituent at the dithiol ring; Eq. (1) can now be rewritten as (1′).

The polar transition state would account for the acid catalysis observed in this reaction as well as for the large negative ΔS^* values.

Semiempirical calculations of the CNDO/2 [18] and extended *Hückel* type have been carried out on I, varying the angle α from $0°$ to $180°$. The geometric parameters used for I ($\alpha = 0°$) and VI($\alpha = 180°$) were those reported in the literature [5] for I a.
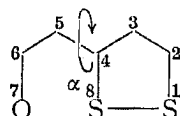
The activation energy for the reaction 1′ obtained by the CNDO/2 method[4]) was 73.59 kcal/mol, which is far from the experimental results listed in Table 1. This value did not change considerably when the following bond lengths were varied independantly for $\alpha = 90°$: $C_4 - C_5$, $C_5 - C_6$ and $C_6 - O$.

The extended *Hückel* method[5]) predicts an activation energy of 6,2 kcal/mol for reaction 1′. Energy minima were found for $\alpha = 0°$ (I) and $\alpha = 150°$ (VI non planar). The latter is probably due to the steric interaction between oxygen and the hydrogen attached to position 3. The energy difference between VI and I was found to be 2,5 kcal/mol (see Fig. 6a) and is essentially due to the interaction of the 2p lone pair of the oxygen and the $3d_{x^2-y^2}$ orbital of the central sulfur in I. If we exclude the 3d orbitals from our basis set the energy difference between I and VI is found to be zero, which is not supported by experiment.

Both semiempirical methods showed similar changes of the overlap population between $C_4 - C_5$, $C_5 - C_6$ and $C_6 - O$ (see Fig. 6b) and an increase of the polarity of the molecule (see Fig. 6c) between $\alpha = 0°$ and $\alpha = 90°$. These results suggest that a substituent on position 5 and 6 which increases the overlap population of this bond should lower the energy of the transition state.

Experimental Part

Compounds I a–I e were prepared as reported in the literature [2] [22]. The kinetic measurements were carried out with a 900 J (30 KV, 2 μ F) flash. A WG-1 *Schott* filter which absorbs below 350 nm was used. Since light from the spectrometer could initiate a photoreaction in the case of a slow thermal reaction the light source was filtered. The temperature in the 10 cm quartz cell was kept constant to $\pm 0,5°$[6]) by a thermostat. The kinetics of the thermal back reaction were studied at two different wavelengths between 15 and 70° for each compound. All reactions were found to be first order. E_a was calculated from the slope of the *Arrhenius* plot (see Fig. 1),

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[4]) For the CNDO/2 calculation we used the parameters suggested by *Pople, Santry* & *Segal* [18]. The parameters used for sulfur in the CNDO/2 calculations were the basis sets sp and spd referred by *Santry* & *Segal* [18].

[5]) For the extended *Hückel* calculations the *Slater* exponents and ionization potentials for H,O and C were those used by *Hoffmann* [19] except for a *Slater* exponent of 1.3 for H. The *Slater* exponents for sulfur were taken from *Clementi* & *Raimondi* [20] except for the sulfur 3d orbitals which were estimated as 1.6. The valence state ionization potentials of sulfur were estimated as H_{11} (3 s) $= -20.0$ eV, H_{11} (3p) $= -13.3$ eV and H_{11} (3d) $= -6.0$ eV.

[6]) This value takes into consideration that the temperature in the cell is raised after each flash.

ΔG^*, ΔH^* and ΔS^* were determined assuming the transition state theory [21]. The solvents used were *Merck* Uvasols.

The ^{18}O enriched product of Ia was synthesized according to *Pinel* [12] by acid catalyzed solvolysis of dimethyl thiathiophthene with $H_2^{18}O$. The fraction of ^{18}O in the isolated crystalline product was 40% as determined by mass spectrometry.

The electronic spectra were measured on a *Cary* 14 spectrometer. For the measurements below room temperature a quartz cell cooled with liquid nitrogen was used, the irradiation being carried out in the instrument.

The IR. spectra were recorded on a *Perkin Elmer* instrument (model 457) in tetrachloroethylene, the NMR. spectra on a *Varian* instrument (model XL 100) in carbon disulfide or tetrachloroethylene with TMS as internal standard. The samples were irradiated for 30 min. with a mercury HBO-200 lamp from *Osram* using K-filters from *Balzers*.

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