Photolysis of Tetraalkyl-1-pyrazoline-4-thiones. – Diastereoselective Formation of (*E*)/(*Z*)-Alkylidenethiiranes from *cis*- and *trans*-Tetraalkyl-1-pyrazoline-4-thiones[1,2)]

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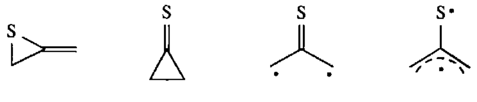
The tetraalkyl-1-pyrazolin-4-ones **5** react with hydrazine to afford the hydrazones **6** which are transformed into the thiones **7** in high yields by treatment with disulphur dichloride in the presence of triethylamine. Selective excitation of the azo chromophor of **7a** with 350-nm light gives rise to the isopropylidenethiirane **8**, besides molecular nitrogen, in a very clean reaction; at almost quantitative conversions, less than 2% of byproducts are observed, and about 10% of **8** have isomerized to the pentadienethiol **9**. Photolysis of the stereoisomers *cis*- and *trans*-**7b** yields mixtures of the alkylidenethiiranes (*E*)- and (*Z*)-**10** with (*E*)/(*Z*) ratios of 35:65 and 49:51. The results are interpreted in terms of diastereomeric bis-orthogonal (*cis*- and *trans*-**21**) and mono-orthogonal thioxyallyl diradicals (*E*)- and (*Z*)-**23** which cyclize to furnish (*E*)- and (*Z*)-**10**. There seems to be a qualitative resemblance between the photochemical and thermal stabilities in the series of 4-substituted tetramethyl-1-pyrazolines, viz. **7a** < **12** < **5a**, **13**, similar to that suggested by Engel for 2,3-diazabicyclo[2.2.2]oct-2-ene derivatives.

Since the discovery of the first example by Middleton more than two decades ago[3)], alkylidenethiiranes (allene episulphides) have been the topic of numerous experimental and some theoretical studies[4)]. The parent methylenethiirane **1**[5,6)] is a sulphur analogue of methylenecyclopropane and coexists on the C_3H_4S potential energy surface together with other intriguing species such as the elusive cyclopropanethione **2** and the hypothetical thioxyallyl diradicals **3** and **4**[4–7)]. The latter may be related to the non-Kekulé molecules[8)] trimethylenemethane[9)] and oxyallyl[10)] as well.

The parent methylenethiirane **1** has been produced by flash vacuum pyrolysis from several spirocyclic precursors[5,6)] and by rearrangement of 3-thietanylidene, which was generated by thermolysis of the sodium salt of 3-thietanone tosylhydrazone[6)]. The latter method had been applied previously to the synthesis of the alkylidenethiirane **8**[11)] and was later employed for bis(alkylidene)thiiranes[12)]. The *thermal* extrusion of molecular nitrogen from 2-alkylidene-Δ^3-1,3,4-thiadiazolines[3,13)] and tetramethyl-1-pyrazoline-4-thione (**7a**)[14,15)] yielded 3,3-disubstituted alkylidenethiiranes. Special methods of formation involved the thermal rearrangement of a 2-alkylidene-1,3-thioxolene[16)], thionation of a sterically protected methylenecyclopropanone[17)] and [2 + 1] cycloaddition reactions to cumulenes, viz. the formal addition of a sulphur atom to donor-acceptor-substituted allenes[18)] and of alkenylidene carbenes to thioketones and thioketenes[19)].

Several years ago, we have devised the only *photochemical* approach to alkylidenethiiranes, i.e. the photoextrusion of molecular nitrogen from 1-pyrazoline-4-thiones[20)], and now want to present our results in detail. Some hints concerning the nature of hypothetical thioxyallyl intermediates are obtained from *cis*- and *trans*-tetraalkyl-1-pyrazoline-4-thiones which are converted into (*E*)- and (*Z*)-alkylidenethiiranes in different proportions, depending on whether the *cis* or *trans* isomer is photolyzed.



1 **2** **3** ($^1A_1$) **4** ($^1B_1$)

C_{2v} symmetry

Synthesis of Tetraalkyl-1-pyrazoline-4-thiones

The pyrazolinone **5a**[21–24)], already known for a long time, is the most reasonable precursor of the pyrazolinethione **7a** though a compound of this general structure has been obtained by reduction of a thioketone *S*-oxide[25)] which results from a 1,3-dipolar cycloaddition of a thioketene *S*-oxide and 2-diazopropane[26)]. Of the many reagents recommended for the conversion of a ketone into a thioketone[27)], diphosphorus pentasulphide in pyridine was applied to **5a** by Bushby and co-workers with moderate success[23)]. As this reagent failed to yield better results under a variety of conditions[14)], we turned to the two-step method by Okazaki et al.[28)] which involves formation of a hydrazone and subsequent reaction with disulphur dichloride in the presence of triethylamine[20)]. This route to **5a** was also adopted by Bushby and co-workers[24)].

Mock[21)] and Bushby et al.[23)] converted the pyrazolinone **5a** into the hydrazone **6a** by heating with hydrazine *hydrate* in ethanol for several *hours*. The more encumbered pyrazolinone *cis*-**5b**, on the other hand, was reported to require heating with *anhydrous* hydrazine in ethanol for several *days*[29)]. When *cis*- and *trans*-**5b** were

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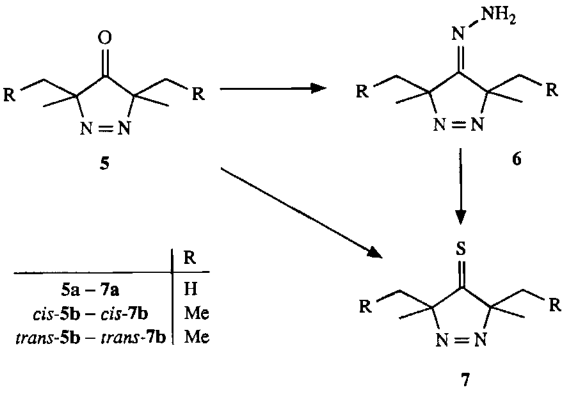
heated with an excess of hydrazine hydrate in boiling 1-propanol in the presence of catalytic amounts of acetic acid, the hydrazones *cis*- and *trans*-**6b** formed slowly as monitored by gas chromatography (93% conversion after five days, yield 69%). Surprisingly, the hydrazones reacted further to afford products which were not identified, however. Suspecting that oxidation by air had produced diimine[30] which would reduce the 1-pyrazolinone hydrazones to the pyrazolidinone hydrazones, we carried out the reaction under argon. This procedure raised the yield to 89% at 98% conversion after nine days. Eventually, the best results were obtained with rigorous exclusion of oxygen, when the reactions were performed in methanol at 110°C in evacuated (10^{-5} Torr) sealed tubes. Thus, the hydrazones *cis*- and *trans*-**6b** resulted in 90 and 87% yield as colourless low-melting crystals (Table 1).



	R
5a – **7a**	H
cis-**5b** – *cis*-**7b**	Me
trans-**5b** – *trans*-**7b**	Me

Table 1. Yields, physical and spectroscopic characteristics of some tetraalkyl-1-pyrazolines; values reported in the literature are given in square brackets

Cpd.	Yield [%]	m. p. [°C] (b. p. [°C/ 0.03 Torr])	IR [cm^{-1}] N=N	C=N	(nujol) NH$_2$
6a	97	115 - 116	1535	1610	3405[a)]
	[63	120.5 - 121.5		1610	3200,3280, 3380][23)]
	[62	118 - 119			3442[b)]][21)]
cis-**6b**	90	38 - 39 (72)	1538	1620[c)]	3415[a)]
			[1550	1630	3450 3350][29)]
trans-**6b**	87	38 - 39 (72)	1538	1620[c)]	3415[a)]
7a	82[d)] [82[d)]][24)] [47[e)]	45 - 46 44 - 45.5][23)]	1542[a)]		
cis-**7b**	80[d)]	(25)	1538[c)]		
trans-**7b**	81[d)]	(25)	1538[c)]		

[a)] Solvent tetrachloromethane, 10-mm Infrasil quartz cuvette. — [b)] Solvent trichloromethane. — [c)] Neat liquid. — [d)] From the corresponding hydrazone **6** and disulphur dichloride in the presence of triethylamine. — [e)] From the ketone **5a** and phosphorus pentasulphide.

The pyrazolinone hydrazones **6** reacted smoothly with disulphur dichloride in the presence of triethylamine to furnish the thiones **7** in high yields. The tetramethyl compound **7a** formed volatile purple low-melting crystals[23)] while both *cis*- and *trans*-**7b** remained as deep red oils. All new compounds were characterized by analytical and spectroscopic techniques (Tables 1, 4, 5).

The pyrazolinethione **7a** exhibits several absorption maxima in the UV and visible spectrum which have been assigned with the help of CNDO/S-CI calculations[31)]. The bands at long wavelengths (600, 554, 529 nm, in hexane) result from the (n_s) → ($\pi^*_{C=S}$) transition of the thiocarbonyl group. They are responsible for the purple colour. The absorption at 341 nm has been assigned to the (n_-) → (π^*_{NN}) and the band at 304 nm to the (n_+) → (π^*_{NN}) transition of the azo group. The high intensity of the maximum at 235 nm is indicative of a $\pi \rightarrow \pi^*$ transition[27,32)].

The electron-impact-induced decomposition of the pyrazolinethiones **7** in the mass spectrometer produced molecular nitrogen and radical cations which may be regarded as sulphur analogues of the intriguing trimethylenemethane radical cation discovered recently[33)]. The radical cation formed by extrusion of nitrogen from the molecular ion of **7a** showed a fragmentation pattern which was very similar to that of the molecular ion of the isopropylidenethiirane **8**. It was characterized by the loss of either alkyl radicals (CH_3, C_3H_7), a sulphur atom, or an SH radical.

Methods

The diastereomeric purity of *cis*- and *trans*-**7b** and of the photolysis products was investigated by NMR spectroscopy (400 MHz) and gas chromatography on a very efficient column. When the retention times nevertheless differed too little to allow detection of traces of the minor diastereomer, a singlet of the latter in the ^{1}H-NMR spectrum was compared to the ^{13}C satellites of the singlet of the major diastereomer. Thus, the limits of detection (<0.5%) approached that of gas chromatography. For example, a diastereomeric excess of at least 99% was confirmed for both diastereomers *cis*- and *trans*-**7b**, which corresponded to the diastereomeric purity of the starting ketones *cis*- and *trans*-**5b** as expected.

Carefully degassed solutions of the 1-pyrazolinethiones **7** in [D$_6$]benzene or [D$_{12}$]cyclohexane, sealed in NMR sample tubes, were irradiated with the 333.6- and 335.5-nm light of an argon ion laser or with a focussed 500-W high-pressure mercury lamp through a cobalt dichloride solution used as a filter. Thus, only the azo chromophor was excited. Selective excitation of the thiocarbonyl chromophor was accomplished with the 589-nm light of a sodium lamp. The course of the photolyses was monitored by ^{1}H-NMR spectra which were complemented by ^{13}C-NMR spectra and gas chromatograms after termination of the irradiation. Both techniques furnished virtually identical results (Table 2). The signals in the ^{13}C-NMR spectra were assigned on the basis of DEPT spectra. When several components were present in similar proportions, as in the case of irradiated samples, ^{1}H,^{1}H decoupling experiments and ^{1}H,^{13}C-COSY spectra allowed an unequivocal assignment of the signals to a particular compound.

Results

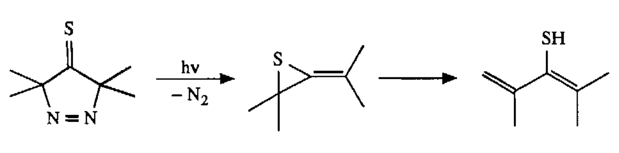
When solutions of the pyrazolinethione **7a** in hydrocarbon solvents were irradiated in a way that *only the azo chromophor was excited,* the characteristic pink colour faded rapidly, and the samples remained clear and colourless up to almost quantitative conversion. The very clean photolysis afforded only a single product until about half of the pyrazolinethione **7a** had reacted. About 10% of a second product emerged, besides the primary compound, while the rest of **7a** was photolyzed (Table 2, Figure 1). If there were any unidentified byproducts they totalled less than 2%. Similar results were obtained in [D$_{14}$]methylcyclohexane in the temperature range between −60 and +90°C. In a [D$_{14}$]methylcyclohexane matrix at the temperature of liquid nitrogen, however, **7a** exhibited only a strong pink fluorescence but no decomposition even during extended periods of irradiation.

Table 2. Experimental conditions and results of the direct irradiation at 20°C of 0.6−0.7 M solutions of the tetraalkyl-1-pyrazoline-4-thiones **7**

Cpd.	Solvent	λ [nm]	Period of Irradiation [h]	Conversion [%]	**8** : **9**	Method of Analysis
7a	C_6D_6	333.6, 335.5[a)]	1.0	57	>99 :< 1	NMR
			2.0	98	90 : 10	NMR
	C_6D_{12}	333.6, 335.5[a)]	1.5	46	>99.5 :< 0.5	NMR
	C_6D_6	330−410[b)]	1.0	57	>99 :< 1	NMR
			2.0	93	88 : 12	NMR
	C_6D_6	589[c)]	28.0	18	ca. 80 : 20	NMR
					(*E*)-**10** : (*Z*)-**10**	
cis-**7b**	C_6D_6	330−410[b)]	3.0	63	35 : 65	NMR
				66	36 : 64	GC
trans-**7b**	C_6D_6	330−410[b)]	3.0	57	49 : 51	NMR
				59	49 : 51	GC

[a)] The 333.6- and 335.5-nm lines of an argon ion laser were used. — [b)] The light of a focussed 500-W mercury high-pressure lamp passed a 10-cm water filter and a solution of cobalt dichloride in dimethylformamide/aqueous hydrochloric acid contained in a 5-cm Duran cuvette. — [c)] A 400-W sodium lamp was used; besides **8** and **9**, unidentified products were formed to a large extent.

When *only the thiocarbonyl chromophor was excited,* only small amounts of the products of nitrogen extrusion, viz. **8** and **9**, were formed; other products predominated which were not identified, however.



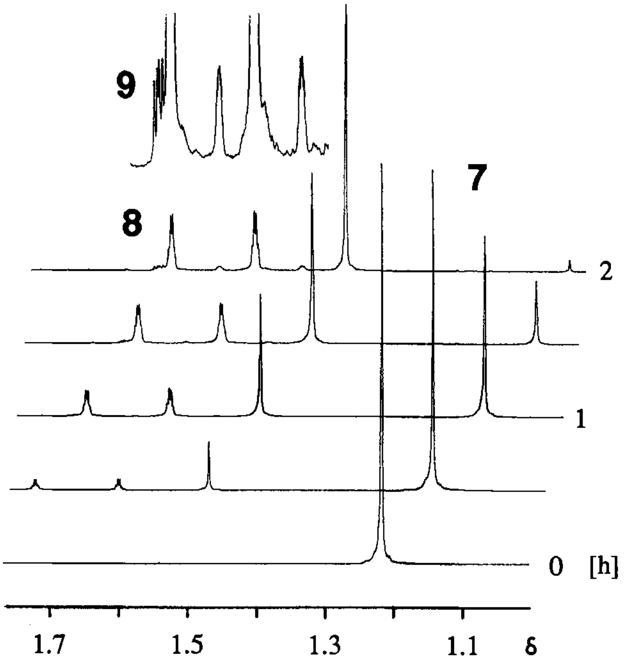


Figure 1. Methyl signals in the ^{1}H-NMR spectra (200 MHz) recorded after a [D$_6$]benzene solution of the pyrazolinethione **7a** had been irradiated with 333.6- and 335.5-nm light for the given period; the expanded ^{1}H-NMR spectra of the isopropylidenethiirane **8** and the pentadienethiol **9** are reproduced in Figure 2

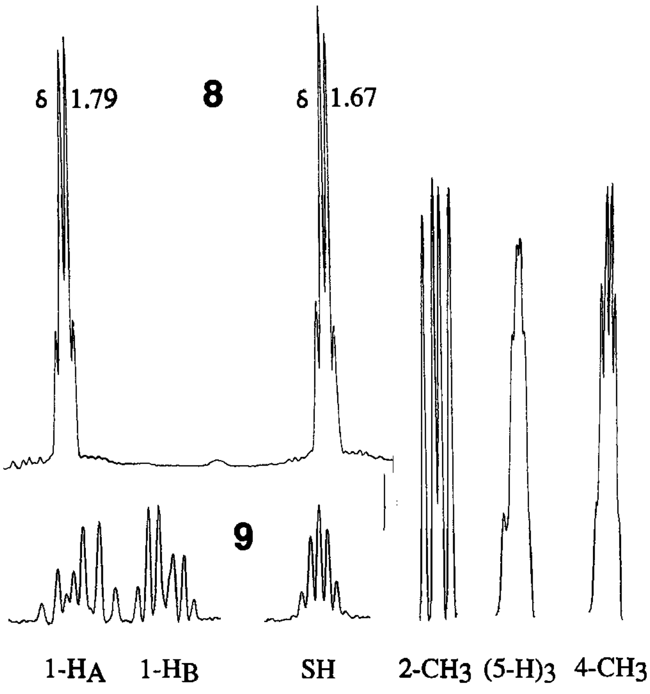


Figure 2. Expanded multiplets (4 Hz/cm) of the ^{1}H-NMR spectra (200 MHz, 0.077 Hz/point) of the isopropylidenethiirane **8** (top) and the pentadienethiol **9** (bottom) both obtained from [D$_6$]benzene solutions; for spectral parameters of **9** see Table 3

The photoproduct of **7a** was readily identified as the isopropylidenethiirane **8** by a comparison of the ^{1}H- and ^{13}C-NMR spectra with those of an authentic sample prepared by the method of Hortmann and Bhattacharjya[11)]. In the high-resolution spectra now available from degassed samples of **8**, it was possible to resolve the isopropylidene coupling ^4J = 0.5 Hz (Figure 2) which had hitherto gone unnoticed[7,11)]. The second product, obviously being formed from **8**, was assigned the pentadienethiol structure **9** on the

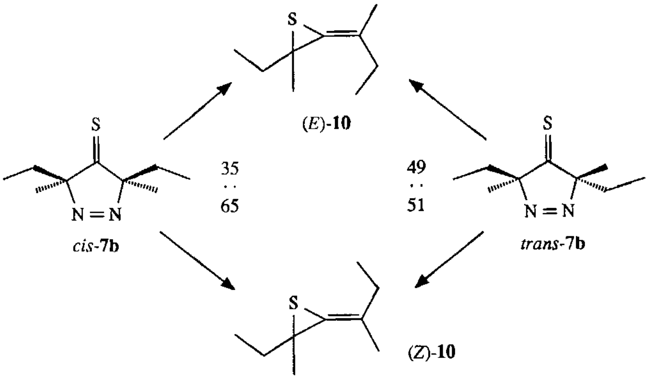
Table 3. Chemical shifts (δ values; main diagonal) and absolute values of the coupling constants (Hz; other data) in the ^{1}H-NMR spectrum of the pentadienethiol **9** recorded in [D$_6$]benzene solution; values in *italics* may be reversed

	1-H$_A$	1-H$_B$	2-CH$_3$	SH	4-CH$_3$	(5-H)$_3$
1-H$_A$	4.791	2.3	1.5			
1-H$_B$		4.752	0.9			
2-CH$_3$			1.809			
SH				2.374	0.8[a]	0.8[a]
4-CH$_3$					*1.602*	0.4
(5-H)$_3$						*1.720*

[a] $1/2\,|\,^5J_{AX} + {}^5J_{BX}\,|$.

basis of an analysis of the ^{1}H-NMR spectrum (Figure 2) which yielded the shift and coupling parameters compiled in Table 3. Data from a poorly resolved 60-MHz ^{1}H-NMR spectrum of **9** obtained by thermolysis of **8** have been reported recently[7].

As in the case of **7a**, the photolyses of *cis*- and *trans*-**7b** proceeded very cleanly producing less than 2% of unidentified compounds. During the decay of *cis*- and *trans*-**7b**, the diastereomeric purity was not diminished. Direct excitation of the azo chromophor in *cis*-**7b** gave rise to the formation of molecular nitrogen and the alkylidenethiiranes (*E*)- and (*Z*)-**10** in a ratio 35:65. On the other hand, *trans*-**7b** yielded the same alkylidenethiiranes but in a *different* ratio, e.g. 49:51. The proportions of the photoproducts remained unaltered. Thus, the configurations of substrates and products as well were invariable upon irradiation.



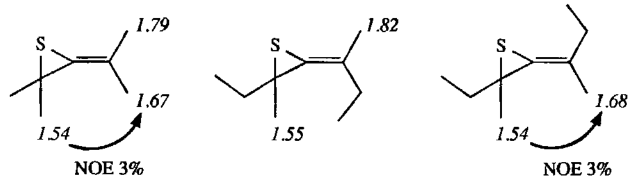
Though separation of the photoproducts was not attempted, the signals in the NMR spectra could be assigned to a particular diastereomer, (*E*)- or (*Z*)-**10**, and to individual groups in a certain chemical environment as well, by a combination of gas chromatography and NMR spectroscopy including ^{1}H,^{1}H decoupling and ^{1}H,^{13}C-COSY experiments. Inspection of the NMR data (Tables 4 and 5) leads immediately to the gross structure **10** for both products. Assignment of their configurations was not trivial, however. In the event, it was accomplished by means of retention times in the gas chromatography, nuclear Overhauser experiments[34], asymmetric solvent induced shifts (ASIS)[35] and a comparison of ^{13}C-NMR data with those of similar alkylidenecyclopropanes, viz. (*E*)- and (*Z*)-**11**[36].

In contrast to the pyrazolinethiones *cis*- and *trans*-**7b** (separation factor α = 1.004), the alkylidenethiiranes (*E*)- and (*Z*)-**10** exhibited a substantial difference between the retention times (α = 1.077). Because the sulphur atom is somewhat more shielded in (*Z*)-**10** than in (*E*)-**10** the former configuration was assigned to the faster isomer.

Irradiation of the ring methyl protons of the isopropylidenethiirane **8**, which served as a standard of reference, caused a nuclear Overhauser enhancement of 3% for the high-field quadruplet of the isopropylidene group. Therefore, this quadruplet stems from the methyl group *trans* to the sulphur atom. An analogous experiment allowed the relative position of the allylic methyl protons in the major photoproduct to be recognized which, accordingly, has the (*Z*) configuration (*Z*)-**10**. This assignment is corroborated by the chemical shifts of the allylic methyl protons in (*E*)- and (*Z*)-**10** which are very similar to those of the *cis* and *trans* methyl groups (relative to the sulphur atom) of the isopropylidenethiirane **8**.

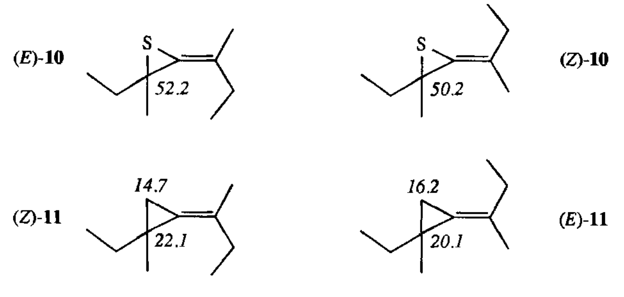
The structurally equivalent allylic protons of the alkylidenethiiranes **8**, (*E*)- and (*Z*)-**10** resonate at close frequencies *in [D$_{12}$]cyclohexane solution* irrespective of their position relative to the sulphur atom. *In [D$_6$]benzene solution*, on the other hand, one set of allylic protons experiences a significant high-field shift. This shift can be traced back to an asymmetric solvation resulting from a repulsion between the electron pairs of the sulphur atom and the π electrons of the [D$_6$]benzene molecules. As a result, the allylic protons *trans* to the sulphur atom come into the shielding cone of the solvent molecules. The observed asymmetric solvent induced shifts (ASIS), therefore, confirm the configurations assigned on the basis of the experiments described above. The present application of the ASIS method is just another example for the usefulness of a stereochemical tool known for a long time[35].

The configuration of the photoproducts were substantiated in yet another way. Differences in the long-range effects between allylic methyl and ethyl groups are reflected in the chemical shifts of the ring ^{13}C atoms as revealed by a com-



8 (*E*)-**10** (*Z*)-**10**

Chemical shifts and nuclear Overhauser enhancements in ^{1}H-NMR spectra (400 MHz, [D$_6$]benzene solution)



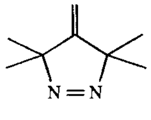
Chemical shifts in ^{13}C-NMR spectra reflecting different long-range effects of methyl and ethyl groups (100 MHz, [D$_6$]benzene solution) parison of the alkylidenecyclopropanes (*E*)- and (*Z*)-**11**[36]. Such ^{13}C atoms resonate at higher field when located at the same side of the double bond as the methyl group. Application of this stereochemical correlation to the alkylidenethiiranes **10** leads once again to the conclusion that the major product from both precursors is (*Z*)-**10**.

Discussion

The photochemical approach to 3,3-disubstituted alkylidenethiiranes described here proceeds under very mild conditions and furnishes the final products in high yields. Although scope and limitations have not yet been explored, only minor obstacles – if any – are to be expected towards extensions to other alkylidenethiiranes of this type. Furthermore, the experimental procedure may be modified by the use of low-boiling solvents in such a way as to allow isolation of pure compounds. Thus, the photochemical route compares favourably with existing methods[3,11,13,16].

The efficiency of the photolysis of **7** at room temperature and the observation, that molecular nitrogen is still extruded from **7a** at temperatures as low as −60°C, suggest the absence of a substantial barrier to loss of nitrogen. This contrasts with the photolysis of similar 4-alkylidene-[37,38] and 4-imino-1-pyrazolines[39,40], and 1-pyrazolin-4-ones[20,41] as well, which do exhibit sizable energy barriers to photocleavage. Engel and co-workers have studied the photolysis of many reluctant azoalkanes derived from the parent compound 2,3-diazabicyclo[2.2.2]oct-2-ene and arrived at the following conclusion: "The main factor controlling quantum yields of nitrogen is a 6–11 kcal mol^{-1} activation barrier that differs for the singlet and triplet states and that seems to mimic the barrier to ground-state deazatization"[42]. Though the heights of the barriers to thermal loss of nitrogen are known only for 4-alkylidene-1-pyrazolines, e.g. **12**[22], and the 1-pyrazoline-4-thione **7a**[14,15], the latter is certainly the least thermally stable, and **5a** and **13** are the most stable members of the tetramethyl-1-pyrazoline series **5a, 7a, 12** and **13**. As **5a**[41] and **13**[39,40] are particularly reluctant towards photoextrusion of nitrogen while **7a** is photochemically most labile, it is hard to escape the conclusion that Engel's statement holds also in the series of 4-substituted tetraalkyl-1-pyrazolines.

We have postulated recently that, particularly in hydrogen donor solvents, photoreduction may compete with photoextrusion of molecular nitrogen from *reluctant* azoalkanes. In view of the efficiency of nitrogen extrusion from the pyrazolinethiones **7** it comes as no surprise, that photoreduction products – if there are any – amount to less than 2% in the present study.

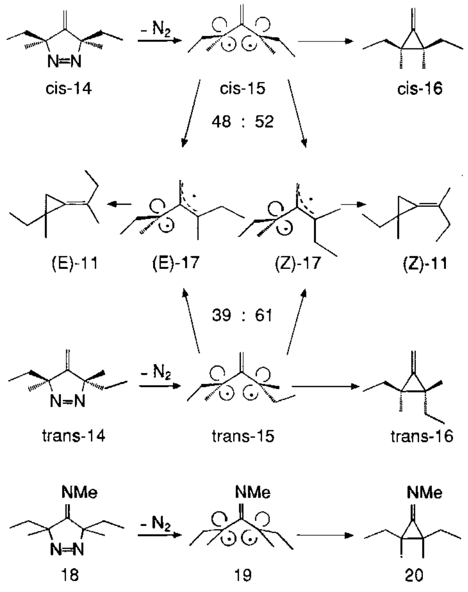


	X	ΔH$^{\neq}$ [kJ mol^{-1}]	ΔS$^{\neq}_{150°C}$ [J K^{-1} mol^{-1}]	ΔG$^{\neq}_{141°C}$ [kJ mol^{-1}]
5a	O[a]			
7a	S[b]			139
12	CH_2[c]	166.5 ± 1.7	41 ± 4	150
13	NMe[d]			

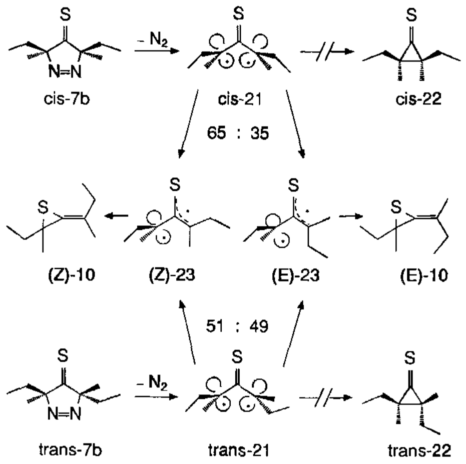
[a] Heating of **5a** for 4.5 h at 205°C gave only ca. 35% decomposition[41]. – [b] In benzene solution[14,15]. – [c] Decomposition in the gas phase at 165–200°C[22]. – [d] The synthesis of **13** and **18** involves prolonged heating of the ketones and methylamine in the presence of an acidic catalyst, e.g. 24 d at 150°C for **18**[39,40].

Because the hypothetical cyclopropanethiones which would originate on the least-motion path are considerably less stable than methylenethiiranes[5], the exclusive formation of the latter is not at all surprising. As a matter of fact, the regioselectivity of cyclization observed in the present study corroborates the general pattern derived from similar systems. Accordingly, it does not matter whether the least-motion path or a non-least-motion path is followed when intermediates may cyclize to yield heteromethylenecyclopropanes derived from *different skeletons*. It is the relative stability of the latter which determines the direction of ring closure[43].

The stereochemical label tagged to the pyrazolinethiones *cis*- and *trans*-**7b** allows some conclusions to be drawn concerning the mechanism of the alkylidenethiirane formation. Very similar stereochemical criteria have already helped to elucidate the pathways followed in the photolysis of 4-methylene-[36] and 4-imino-1-pyrazolines[40]. Therefore, those pathways offer a frame of reference to compare the present results and hence will be outlined below.



Irrespective of the configuration of the substrates, the photolyses of *cis*- and *trans*-**7b** yield more (*Z*)-**10** than (*E*)-**10**, but the *extent* of stereoselectivity depends on that configuration. This difference in the (*Z*) selectivities is not compatible with equilibrated intermediates nor with thermodynamic product control. An explanation seems possible, however, in terms of the mechanistic features which have emerged from the stereochemistry of the photolyses of the 4-methylene-1-pyrazolines *cis*- and *trans*-**14**[36] as well as the 4-imino-1-pyrazolines *cis*- and *trans*-**18**[40]. The retention of configuration in the least-motion products **16** and **20** strongly suggests the formation of diastereomeric bis-orthogonal diradicals, i.e. **15** and **19**, in the first step. Similar bis-orthogonal thioxyallyl diradicals, viz. *cis*- and *trans*-**21** may be invoked in the photolysis of the thiones *cis*- and *trans*-**7b**. The ratios of the non-least-motion products (*E*)- and (*Z*)-**11** have been rationalized in terms of the relative stability of the mono-orthogonal trimethylenemethane diradicals (*E*)- and (*Z*)-**17**, due to subtle differences in the 1,3-interactions, and the propensity of the ethyl groups in *cis*-**15** to rotate away from each other[36]. The explanations for the observed ratios of the non-least-motion products (*E*)- and (*Z*)-**10** follow similar lines. Thus, the mono-orthogonal thioxyallyl diradicals (*E*)- and (*Z*)-**23** are formed with almost equal probability by 90° bond rotations from *trans*-**21**, which possesses C_2 symmetry and, accordingly, identical 1,3-interactions on both sides of the molecular plane. On the other hand, the 90° bond rotation in *cis*-**21** affording (*Z*)-**23** is the one which increases the distance between the ethyl groups and, therefore, somewhat preferred over the other bond rotation giving rise to (*E*)-**23**.



In summary, the stereochemical results of the present study fit well to a most concise mechanistic picture from the photolysis of 4-substituted 3,3,5,5-tetraalkyl-1-pyrazoline derivatives involving product formation via nonplanar trimethylenemethane and heterotrimethylenemethane diradicals.

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Experimental

Yields, physical and spectroscopic characteristics: Table 1; results of the photolysis experiments: Table 2; ^{1}H NMR: Tables 3, 4; ^{13}C NMR: Table 5. – Melting points were taken in sealed capillary tubes on an apparatus from Büchi, Flawil, Switzerland. – NMR: Bruker AC 200 or WM 400 NMR spectrometer in the PFT mode (pulse angle: 20–35°). The deuterium solvent signal was used as an internal lock. The spectral windows were carefully chosen to ensure that folding did not obscure the spectral region of interest, while at the same time giving a digital resolution in the frequency domain of better than 0.08 Hz. Zero-filling to 64 K data points was carried out before the Fourier transformation[44]. In order to achieve resolution of very close signals and of small long-range couplings, we carried out a Lorentzian-to-Gaussian line-shape transformation[44]. Spectra of higher order were analysed by standard methods[45] and simulated with the help of the program RACOON[46]. The samples used in the NOE experiments were carefully degassed by several freeze-pump-thaw cycles and sealed under high vacuum (10^{-5} Torr). – IR: Perkin-Elmer 1420 spectrometer. – UV/Vis: Cary 17 from Varian or U 3200 Hitachi spectrometer. – MS (70 eV): Finnigan MAT 8200 mass spectrometer connected to an SS 200 data system. – A Varian 1400 gas chromatograph equipped with a Shimadzu Chromatopac C-R6A integrator was applied to GLC analyses on 1.5- × 0.002-m glass columns packed with 3% silicon oil SE 30 on Volaspher A_2 (0.18–0.25 mm, Merck, Darmstadt); carrier gas 35 ml/min nitrogen, column temperature C = 50°C with 6°C/min to 150°C, detector temperature D = 250°C, injector temperature I = 205°C, retention times t_R [min] = 5.6 (*cis*- and *trans*-**5b**), 11.4 (*cis*- and *trans*-**6b**). – Capillary gas chromatography: Packard model 436 from Chrompack, Frankfurt am Main, equipped with a Shimadzu Chromatopac C-R6A integrator. A 50- × 0.0001-m fused-silica column having 425500 theoretical plates was employed which was coated with 0.12-μm silicon oil CP Sil 5CB; 4.0 bar nitrogen pressure, split injection 1:50; C = 100, D = 300, I = 200°C, t_R [min] = 13.13 (**8**), 18.54 (**7a**), 24.61 [(*Z*)-**10**], 26.50 [(*E*)-**10**], separation factor α = 1.077, 50.59 (*cis*-**7b**), 50.79 (*trans*-**7b**), α = 1.004. – Preparative gas chromatography: Varian 920 equipped with a 1.5- × 0.01-m glass column packed with 20% silicon oil SE 30 on Chromosorb P AW/DMCS; carrier gas 190 ml/min hydrogen, C = 120°C, t_R [min] = 1.25 (**8**).

Toluene, benzene, ether and tetrahydrofuran were distilled under argon (99.998%) from sodium hydride. Triethylamine was distilled under argon from lithium aluminium hydride and pyridine from powdery potassium hydroxide. The pyrazolin-4-ones **5a**[22], *cis*-**5b** and *trans*-**5b**[47] were prepared as described previously. The latter had a diastereomeric excess of at least 99%. Disulphur dichloride was distilled shortly before used.

2,2,4,4-Tetramethylthietan-3-one was synthesized according to the known procedure[48] from 2,4-dibromo-2,4-dimethylpentan-3-one[49] (272 g, 1.00 mol) and hydrogen sulphide in a solution of sodium methoxide (2.00 mol) in methanol (1 l). The crude product contained 17% 3,3,5,5-tetramethyl-1,2-dithiolan-4-one. – ^{1}H NMR ($CDCl_3$): δ = 1.50. – Recrystallization from 100 ml of methanol afforded 106 g (74%) of colourless malodorous needles, m.p. 105–106°C. – IR (CCl_4): $\tilde{\nu}$ = 1770 cm^{-1} (C=O). – ^{1}H NMR ($CDCl_3$): δ = 1.63.

2,2,4,4-Tetramethylthietan-3-one Hydrazone: A mixture of 2,2,4,4-tetramethylthietan-3-one (3.60 g, 25 mmol), hydrazine hydrate (3.75 g, 75 mmol), acetic acid (0.30 g, 5.0 mmol) and methanol (25 ml) was prepared under nitrogen, sealed in an evacuated thick-walled glass tube and heated to 100°C for 93 h. The mixture was filtered through a pad of potassium carbonate which was rinsed with dichloromethane. The solvent was distilled in vacuo, and the excess hydrazine hydrate was removed by azeotropic distillation after addition of benzene (50 ml). Sublimation of the residue at 40°C/10^{-3} Torr, followed by recrystallization of the sublimate from methanol (3 ml) at –20°C, afforded 3.85 g (97%) of colourless crystals, m.p. 66°C. – IR (nujol): = 3340 cm^{-1}, 3260, 3220 (NH), 1670, 1640. – ^{1}H NMR ($CDCl_3$): δ = 1.65 (2 Me), 1.83 (2 Me), 4.95 (br., NH_2). – MS: *m/z* (%) = 158 (24) [M^+], 143 (5) [M^+ – Me],

Table 4. Chemical shifts (δ values relative to internal tetramethylsilane) and coupling constants [Hz] in ^{1}H-NMR spectra (400 MHz) of some tetraalkyl-1-pyrazolines and 3,3-dialkyl-2-alkylidenethiiranes; data reported in the literature are given in square brackets

Cpd.	CH_3	(dq)CH_2—CH_3(t)		^2J	^3J	NH_2[a)]				[b)]
6a	1.32,1.40					4.67				B
	[1.42,1.62					5.2				T][23)]
	[1.36,1.56					5				T][21)]
cis-**6b**	1.211 1.328	1.641 1.842 1.916 2.154	0.704 1.064	14.3[c)]	7.5[c)]	4.464				B
	[1.33,1.49	2.00	0.87			5.38				T][29)]
trans-**6b**	1.303 1.405	1.716 1.791 1.944 2.121	0.607 0.821	14.2[c)]	7.5[c)]	4.631				B
7a	1.213									B
	1.397									C
	[1.48									T][23)]
cis-**7b**	1.179	1.644 1.925	0.803	14.0	7.5					B
	1.337	1.735 2.039	0.919	13.9	7.5					C
trans-**7b**	1.239	1.651 1.969	0.602	13.9	7.5					B
	1.352	1.782 2.113	0.746	13.8	7.5					C
	CH_3 —C—CH_2—CH_3(t)			^3J	^4J	$CH_3-\overset{\|}{C}-CH_2-CH_3(t)$[d)]			^3J	
8	1.537				0.5 0.5	1.668 (q) 1.790 (q)				B
	1.653				0.5 0.5	1.800 (q) 1.831 (q)				C
	[1.70					1.85 (broad s)				T][11,7)]
	[1.52					1.65 1.75				B][11)]
(*Z*)-**10**[e)]	1.543	1.57 - 1.67 1.78 - 1.92	0.914	7.4	0.4[f)]	1.680 (m)	2.195[g)] 2.220	1.038	7.6	B
	1.628	1.66 - 1.73 1.95 - 2.07	0.977	7.4	0.4[f)]	1.803 (m)	2.15 - 2.22	1.062	7.6	C
(*E*)-**10**[e)]	1.549	1.57 - 1.62 1.78 - 1.92	0.928	7.3	0.4[f)]	1.815 (m)	2.052[h)]	0.930	7.6	B
	1.637	1.66 - 1.73 1.95 - 2.07	0.983	7.4	0.4[f)]	1.803 (m)	2.15 - 2.22	1.051	7.5	C

[a)] Broad singlet. — [b)] Solvent B: [D_6]benzene; C: [D_{12}]cyclohexane; T = [D]trichloromethane. — [c)] Average of the values from both ABX_3 spectra. — [d)] The AB part of the spectrum exhibits further splittings by small, unresolved long-range couplings. — [e)] Because mixtures of (*E*)- and (*Z*)-**10** were investigated, a complete analysis of the ABX_3 spectra of the ethyl groups was frustrated in some cases by the overlap of the AB parts. — [f)] $1/2\ |\ ^4J_{AX} + {}^4J_{BX}\ |$. — [g)] The AB part of the spectrum appears as a doublet of quadruplets (^2J = 14.1 Hz). — [h)] The diastereotopic methylene protons resonate fortuitously at exactly the same frequency.

Table 5. Chemical shifts (δ values relative to internal tetramethylsilane) in ^{13}C-NMR spectra (100 MHz) of some tetraalkyl-1-pyrazolines and 3,3-dialkyl-2-alkylidenethiiranes recorded in [D_6]benzene solutions; data reported in the literature for [D]trichloromethane solutions are given in square brackets; the chemical shift of carbon atoms equivalent by virtue of symmetry is given only once

Cpd.	C(4)	CH_3 —	C —	CH_2 —	CH_3	CH_3 —	$\overset{\|}{C}$ —	CH_2 —	CH_3
6a	157.70	21.16 26.11	82.46 87.73						
cis-**6b**	156.32	20.39 24.49	87.27 90.45	28.13 31.29	8.96 9.82				
trans-**6b**	155.32	19.46 23.16	87.66 91.33	28.04 32.92	9.12 9.82				
7a	270.44	26.56	99.18						
	[269.0	26.8	99.1][23)]						
cis-**7b**	270.62	25.74	102.74	32.28	8.96				
trans-**7b**	270.32	24.06	103.41	34.07	8.96				
	C(2)								
8	132.0	28.17	45.97			21.07 21.19	113.7		
	[130.9	28.1	46.2			21.0 21.1	114.2][7)]		
(*Z*)-**10**[a)]	130.28	25.85	50.22	33.49	11.36	18.88	119.02	28.99	12.23
(*E*)-**10**[a)]	131.51	26.32	52.17	33.72	11.36	19.18	119.66	29.49	13.12

[a)] The data stem from mixtures of the diastereomers (*E*)- and (*Z*)-**10**; spectra of mixtures having different (*E*)/(*Z*) ratios and a ^{1}H,^{13}C-COSY experiment allowed assignment of the signals to a particular stereoisomer.

129 (23) [M^+ − N_2H], 96 (12) [M^+ − N_2H_2 − S], 84 (100), 68 (42), 59 (34).

$C_7H_{14}N_2S$ (158.3)	Calcd.	C 53.12	H 8.92	N 17.70	S 20.26
	Found	C 52.56	H 8.92	N 17.40	S 19.75

2,2,4,4-Tetramethylthietan-3-one Tosylhydrazone: Since the reaction of 2,2,4,4-tetramethylthietan-3-one with tosylhydrazine[7,11)] furnished poor yields (⩽30%) in our hands, the tosylhydrazone was prepared from the hydrazone: A solution of tosyl chloride (20.2 g, 106 mmol) in ether (50 ml) was slowly added dropwise to a stirred solution of 2,2,4,4-tetramethylthietan-3-one hydrazone (15.2 g, 96 mmol) in pyridine (75 ml) under nitrogen. The mixture turned yellow immediately. Stirring was continued for 0.5 h. The solvent was distilled in vacuo. The orange-coloured residue was triturated with water (100 ml). The pale yellow crystals were filtered and washed with water. Recrystallization from methanol (200 ml) followed by recrystallization from toluene (120 ml) yielded 15.4 g (51%) of colourless crystals, m.p. 176−178°C (ref.[11)] 173−174.5°C). — IR (nujol): ṽ = 3300 cm^{-1}, 3240 (NH), 1655 (C=N). — ^{1}H NMR ($CDCl_3$): δ = 1.55 (2 Me), 1.66 (2 Me), 2.45 (Me), 7.25 (NH), 7.60 (m_c, 4 ArH). — MS: m/z (%) = 312 (28) [M^+], 246 (25), 214 (27), 157 (64) [M^+ − $C_7H_7SO_2$], 155 (21), 140 (95), 139 (100), 128 (27), 124 (24), 91 (51) [C_7H_7].

3,3-Dimethyl-2-(methylethylidene)thiirane (**8**): Under nitrogen, sodium hydride (290 mg, 12 mmol) was added to a stirred solution of 2,2,4,4-tetramethylthietan-3-one tosylhydrazone (1.88 g, 6.0 mmol) in tetrahydrofuran (30 ml). Stirring was continued for 2 h. The solvent was distilled in vacuo, and the residue was dried for 12 h at 60°C/10^{-3} Torr over diphosphorus pentoxide. The solid was slowly heated (1−2°C/min) to 150°C under a vacuum of 1 Torr and kept for 2 h at that temperature whilst **8** was condensed in an efficient cold trap (−78°C) to yield 0.52 g (68%) of a colourless liquid. Further purification was accomplished by preparative gas chromatography and transfer by means of vacuum-line techniques (10^{-5} Torr). — IR (CCl_4): ṽ = 1775 cm^{-1} (w), 1740 (w, C=C). — MS: *m/z* (%) = 128 (100) [M^+], 113 (58) [M^+ − Me], 95 (47) [M^+ − C_3H_7], 85 (50), 81 (31), 79 (50), 77 (26), 71 (18), 69 (13), 67 (26), 59 (21), 55 (26), 53 (24).

3,3,5,5-Tetramethyl-3,5-dihydro-4H-pyrazol-4-one Hydrazone (**6a**): A solution of **5a** (14.0 g, 0.10 mol), hydrazine hydrate (15.0 g, 0.30 mol) and acetic acid (1.0 g, 17 mmol) in 1-propanol (50 ml) was heated under nitrogen for 20 h. The solution was filtered through a pad of potassium carbonate which was rinsed with dichloromethane (100 ml). The solvent was distilled in vacuo by means of a rotary evaporator. After addition of benzene (100 ml), the excess of hydrazine hydrate was removed by azeotropic distillation. Sublimation of the residue at 50°C/10^{-3} Torr yielded 15.0 g (97%) of a colourless solid, m.p. 115–116°C. – MS (12 eV): m/z (%) = 155 (17) [M^+ + 1], 126 (34) [$M^+ - N_2$], 111 (13) [$M^+ - N_2 - Me$], 109 (100) [$M^+ - N_2 - NH_3$], 97 (10), 94 (11), 84 (40), 68 (50), 58 (71).

3,3,5,5-Tetramethyl-3,5-dihydro-4H-pyrazole-4-thione (**7a**): A solution of triethylamine (11.1 g, 0.11 mol) in benzene (200 ml) was stirred at 0°C under nitrogen. A solution of **6a** (7.71 g, 50 mmol) in benzene (200 ml) and a solution of disulphur dichloride (6.75 g, 50 mmol) in benzene (100 ml) were added simultaneously from two dropping funnels within 0.5 h. Stirring was continued for 16 h at 25°C. The triethylammonium chloride was filtered and washed with benzene (50 ml). The solution was extracted with water (4 × 50 ml) and dried with potassium carbonate. The solvent was distilled on a 1-m spinning-band column until ca. 100 ml remained in the flask. Flash chromatography of the deep red solution on silica gel (40- × 3.5-cm column, 0.063–0.20 mesh) with pentane and sublimation at 30°C/1 Torr yielded 6.38 g (82%) of purple crystals, m.p. 45–46°C. – UV/Vis (hexane): λ_{max} (lg ε) = 600 nm (sh, 0.022), 554 (1.015), 529 (0.978), 341 (2.362), 304 (2.117), 235 (3.947). – MS: m/z (%) = 156 (59) [M^+], 128 (100) [$M^+ - N_2$], 113 (46) [$M^+ - N_2 - Me$], 96 (13), 95 (23), 86 (8), 85 (32), 84 (7), 81 (33), 79 (44), 77 (22), 71 (21), 69 (21), 67 (36), 59 (29).

r-3,c-5-Diethyl-t-3,t-5-dimethyl-3,5-dihydro-4H-pyrazol-4-one Hydrazone (*cis*-**6b**): A solution of *cis*-**5b** (840 mg, 5.0 mmol), hydrazine hydrate (880 mg, 17.5 mmol) and acetic acid (60 mg, 1.0 mmol) in methanol (2.5 ml) was carefully degassed by means of several freeze-pump-thaw cycles and sealed under vacuum (10^{-5} Torr) in a thick-walled glass tube which was kept at 110°C for 12 d. Ether (30 ml) was added, and the mixture was extracted twice with saturated aqueous sodium carbonate (30-ml portions) and dried with potassium carbonate. Distillation of the solvent and the residue in vacuo yielded a colourless oil (830 mg, 90%), b.p. 72°C/0.03 Torr which slowly crystallized to afford colourless crystals, m.p. 38–39°C. – MS: m/z (%) = 182 (0.2) [M^+], 154 (16) [$M^+ - N_2$], 139 (8) [$M^+ - N_2 - Me$], 122 (73) [$M^+ - N_2 - Me - NH_3$], 108 (17), 83 (54), 82 (100), 55 (76).

r-3,t-5-Diethyl-t-3,c-5-dimethyl-3,5-dihydro-4H-pyrazol-4-one Hydrazone (*trans*-**6b**): The procedure given for *cis*-**6b** was followed exactly yielding a colourless oil (800 mg, 87%) which slowly crystallized to afford colourless crystals, m.p. 38–39°C. – MS: m/z (%) = 182 (0.3) [M^+], 154 (15) [$M^+ - N_2$], 139 (7) [$M^+ - N_2 - Me$], 122 (68) [$M^+ - N_2 - Me - NH_3$], 108 (16), 83 (53), 82 (100), 55 (78).

$C_9H_{18}N_4$ (182.2)	Calcd.	C 59.31	H 9.95	N 30.74
cis-**6b**:	Found	C 59.12	H 9.87	N 30.79
trans-**6b**:	Found	C 59.19	H 10.00	N 30.71

r-3,c-5-Diethyl-t-3,t-5-dimethyl-3,5-dihydro-4H-pyrazole-4-thione (*cis*-**7b**): A solution of triethylamine (670 mg, 6.6 mmol) in toluene (15 ml) was stirred under argon (99.998%). A solution of *cis*-**6b** (550 mg, 3.0 mmol) in toluene (15 ml) and a solution of disulphur dichloride (410 mg, 3.0 mmol) in toluene (10 ml) were added slowly and simultaneously from two dropping funnels. Stirring was continued for 12 h. The mixture was extracted with water (4 × 20 ml) and dried with potassium carbonate. Distillation of the solvent and the residue in vacuo yielded a purple oil (440 mg, 80%), b.p. 25°C/0.03 Torr. – MS: m/z (%) = 184 (19) [M^+], 156 (43), 141 (36), 123 (42), 107 (85), 99 (100), 85 (53), 81 (80).

r-3,t-5-Diethyl-t-3,c-5-dimethyl-3,5-dihydro-4H-pyrazole-4-thione (*trans*-**7b**): The procedure given for *cis*-**7b** was followed exactly yielding a purple oil (450 mg, 81%), b.p. 25°C/0.03 Torr. – MS: m/z (%) = 184 (32) [M^+], 156 (43), 141 (31), 107 (84), 100 (28), 99 (100), 85 (56), 81 (84).

$C_9H_{16}N_2S$ (184.1)	Calcd.	C 58.65	H 8.75	N 15.20
cis-**7b**:	Found	C 58.43	H 8.50	N 15.47
trans-**7b**:	Found	C 58.60	H 8.99	N 15.33

Photolysis Experiments: Solutions of the thiones 7 (0.3 mmol) in [D_6]benzene or [D_{12}]cyclohexane (0.5 ml) were made up in NMR sample tubes which were carefully degassed by means of several freeze-pump-thaw cycles and sealed under vacuum (10^{-5} Torr).

a) The samples were irradiated with the 333.6- and 335.5-nm light of an argon ion laser Innova 100 from Coherent Ltd., Palo Alto, California, USA, equipped with quartz optics. The output in the near UV totalled 2.5 W (at 363.8, 351.4, 351.1, 335.5, 333.6 nm). The sample tubes were shaken frequently.

b) The samples were kept at 20°C and irradiated with a focussed (quartz optics) 500-W high-pressure mercury lamp HBO 500 W/2 from Osram. The light passed through a 10-cm water filter and a stirred solution of cobalt dichloride kept at 10–20°C in a 5-cm Duran cuvette. The filter solution[50] was prepared by dissolving cobalt dichloride hexahydrate (40 g, 0.17 mol) in a mixture of water (266 ml) and concd. hydrochloric acid (84 ml, 1 mol); dimethylformamide was added up to a total volume of 1 l. A 5-cm layer of the filter solution transmitted more than 80% of the light between 330 and 410 nm.

c) The sample was directly attached to the cooling jacket of a 400-W sodium lamp Vialox NAV-TS from Osram and kept at 20°C.

CAS Registry Numbers

5a: 30467-62-0 / (*cis*)-**5b**: 74097-99-7 / (*trans*)-**5b**: 74097-35-1 / **6a**: 16642-47-0 / (*cis*)-**6b**: 132855-97-1 / (*trans*)-**6b**: 132855-98-2 / **7a**: 65927-08-4 / (*cis*)-**7b**: 132855-99-3 / (*trans*)-**7b**: 132856-00-9 / **8**: 61097-65-2 / (*E*)-**10**: 132856-01-0 / (*Z*)-**10**: 132856-02-1 / 2,2,4,4-tetramethylthietan-3-one: 58721-01-0 / 3,3,5,5-tetramethyl-1,2-dithiolan-4-one: 92350-67-9 / 2,2,4,4-tetramethylthietan-3-one hydrazone: 89050-85-1 / 2,2,4,4-tetramethylthietan-3-one tosylhydrazone: 109142-68-9

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[1] Dedicated to Professor *Marianne Baudler* on the occasion of her 70th birthday.

[2] Photochemical formation of heteromethylenecyclopropanes, 23. – For part 22 of this series see H. Quast, H. Jakobi, *Chem. Ber.* **124** (1991) 1619. The results are taken from the *Dissertations* by A. Fuß (1981) and H. Jakobi (1991), University of Würzburg.

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