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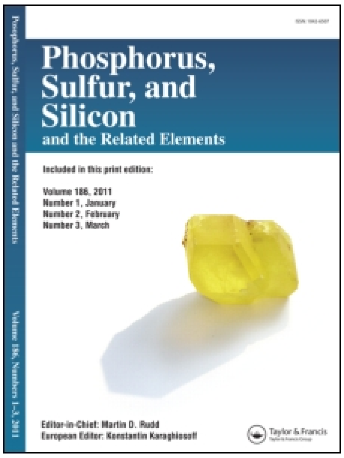

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From Thiiranes to Thiocarbonyl *S*-Sulfides; Recent Results

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To cite this Article Huisgen, Rolf(1989) 'From Thiiranes to Thiocarbonyl *S*-Sulfides; Recent Results', Phosphorus, Sulfur, and Silicon and the Related Elements, 43: 1, 63 — 94

To link to this Article: DOI: 10.1080/10426508908040279

URL: http://dx.doi.org/10.1080/10426508908040279

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Phosphorus, Sulfur and Silica, Vol. 43/1-2, pp. 63–94
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FROM THIIRANES TO THIOCARBONYL *S*-SULFIDES; RECENT RESULTS

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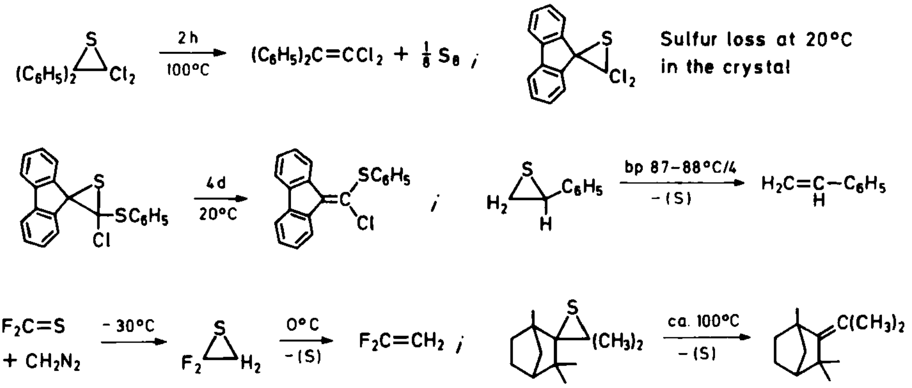
Abstract A novel nucleophilic catalysis for the desulfurization of thiiranes is described. Triphenylthiirane is quantitatively converted to triphenylethylene by some mol% sodium thiophenoxide or other thiolates in DMSO at 35°C. A rapid initial reaction is retarded by the eliminated sulfur leading to a pseudo-first-order reaction under quasi-stationary conditions. The suggested mechanism is based on structure-rate relationships. - The thiolate-catalyzed reaction of cis-2,3-diphenylthiirane is exceptional in furnishing equimolar quantities of cis-stilbene and 3,4,6,7-tetraphenyl-1,2,5-trithiepane (2 diastereoisomers with bilateral symmetry); mechanistic implications - thiolate attack on sulfur or C-atom of thiirane - are discussed. - Desulfurization of 2,2-diphenylthiirane by thiobenzophenone or other thioketones gives access to thiocarbonyl *S*-sulfides ("thiosulfines") which are intercepted by 1,3-cycloadditions to activated acetylenes or to thiones.

A FORGOTTEN REACTION PATHWAY ?

Thiirane constitutes the smallest sulfur heterocycle. Recent studies in the Munich Laboratory do not deal with the *con*struction, but rather with the *de*struction of thiiranes. The elimination of sulfur converts thiiranes into olefins. This reaction is not without importance. Barton's pathway to overcrowded ethylenes [1] may be remembered; its final step is the desulfurization of a thiirane by one equivalent of tertiary phosphine. Eschenmoser's "sulfide contraction via alkylative coupling" [2] offers another synthetic application. It is again an episulfide intermediate which is freed of sulfur by triphenylphosphine.

SCHEME 1

Spontaneous Desulfurization of Substituted Thiiranes

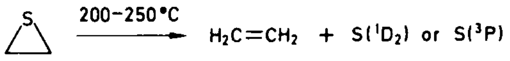


A *spontaneous* loss of sulfur from thiiranes, substituted by aryl or halogen, has sporadically been reported since 1920. Among few examples, observations by Staudinger and Siegwart [3] are quoted on the first line of Scheme 1. Schönberg and his school contributed further cases.[4] Styrene episulfide was described to suffer "occasional decomposition" on vacuum distillation.[5] 2,2-Difluorothiirane lost sulfur at 0°C.[6] Even aliphatic thiiranes such as fenchane-spiro-thiirane of Scheme 1 extruded sulfur at moderately elevated temperatures.[7]

The lack of a systematic or mechanistic study justifies speaking of a forgotten reaction pathway. Is it conceivable that thiiranes eliminate *atomic sulfur* ?

The standard heats of formation are known for thiirane and ethylene as well as for the singlet and triplet sulfur atom.[8,9] The splitting of thiirane into ethylene + sulfur atom should be endothermic by as much as 85 or 59 kcal mol^{-1} depending on which of the two sulfur species is formed (Scheme 2). The thermolysis rate of

SCHEME 2



$\Delta H_f^\circ(g)$ kcal mol^{-1} 19.3 12.5 92.0 65.6

$\Delta H_{calcd.} = +85$ or 59 kcal mol^{-1}

$\Delta H^{\ddagger}_{exp} = 40.2$ kcal mol^{-1}; $\Delta S^{\ddagger}_{exp} = 2.5$ e.u.

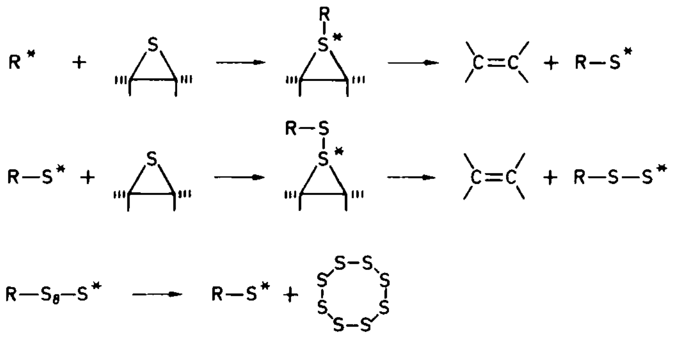
Sulfur extrusion is of *first order*, $k_{225°C} = 3.7\ 10^{-5}\,s^{-1}$, $t_{1/2} = 5.2$ h

thiirane in the gas phase at 200-250°C was measured by O.P. Strausz et al.;[10] the first order reaction showed only $E_a = 40.2$ kcal mol^{-1} and $\Delta S^{\ddagger} = -2.5$ e.u. Thus, energetic considerations rule out the thermal loss of a *sulfur atom* in thiiranes.

How did we chance upon the problem ? Li X., a Chinese guest in Munich, observed in 1980 that 2,2-diphenylthiirane freshly prepared lost sulfur with a half-life of 16 h at room temperature. With each stage of purification the half-life grew until it reached 53 days in DMSO at 35°C. This suggested *catalysis*.

SCHEME 3

Proposed Scheme for Sulfur Extrusion at Low Temperature



R*: Radical R· or Anion R⁻ ?

A conceivable pathway is delineated in Scheme 3. A catalyst R^* adds to the thiirane sulfur, and a cheletropic elimination furnishes alkene + RS^*. The latter attacks the next thiirane molecule, attaching another sulfur to the catalyst. When the sulfur chain has reached a sufficient length, it rolls around and eliminates cyclooctasulfur, thus regenerating the active RS^*. Does the asterisk mark radical or anion ?

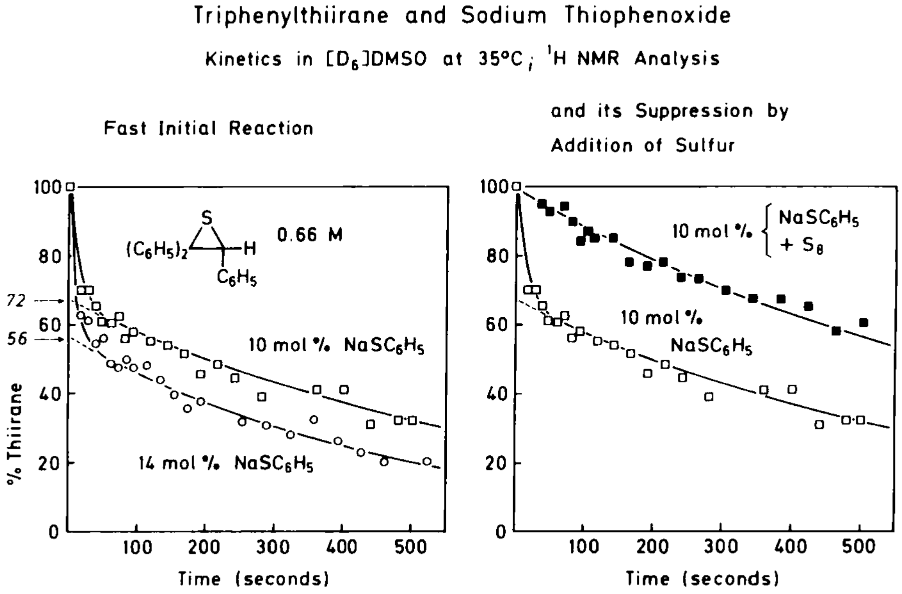
In 1983 Albert Pröbstl in the Munich Laboratory confirmed the catalytic scheme right away; nucleophilic reagents as well as radicals were effective as catalysts.[11]

Now we are confronted with the problem of choosing a good model. In historical retrospect, the clarification of reaction mechanisms was often tied to unique models. It is advisable to tailor a model to fit the particular measures of an experiment. Even harder to satisfy is the following requirement: the model should readily lend itself to generalizations. Many generations of chemists have trapped themselves in the delusion that all these wishes can be met.

THIOLATE-CATALYZED DESULFURIZATION OF TRIPHENYLTHIIRANE

Triphenylthiirane was chosen, and ^1H NMR spectroscopy allowed to follow the sulfur extrusion in $[D_6]$DMSO at 35°C by concentration measurements against a standard. At an early stage of the investigation we resorted to the *kinetic method* which can be more easily applied to nucleophilic catalysis than to short-lived radicals as initiators. According to Scheme 3, the initial nucleophile R^- is converted to oligothiolates of variable chain length. Only the S-S bond and not the C-S bond is broken in the formation of S_8. Thus, sodium thiophenoxide as a monothiolate was our choice. The desulfurization of triphenylthiirane proceeded quantitatively in the presence of a few mol% of $NaSC_6H_5$.

SCHEME 4



Triphenylthiirane and Sodium Thiophenoxide

Kinetics in $[D_6]DMSO$ at 35°C; ^1H NMR Analysis

Fast Initial Reaction

and its Suppression by Addition of Sulfur

A. Pröbstl, München 1986

On combining 0.66 M triphenylthiirane in $[D_6]DMSO$ with as much as 10 or 14 mol% of $NaSC_6H_5$, a rapid initial desulfurization was observed: 28 and 44% of the thiirane were consumed in less than a minute, i.e., roughly three times the quantity of the thiophenoxide applied (Scheme 4). Subsequently, the reaction followed the first order. In fact, pseudo-first order, because the concentration of the catalyst can obviously be regarded as constant.[12]

This experiment reveals that the very fast desulfurization of triphenylthiirane by $NaSC_6H_5$ is slowed down by the interaction with the eliminated sulfur. The right-hand diagram of Scheme 4 offers the crucial test. The conversion curve for 10 mol% of $NaSC_6H_5$ is compared with an experiment in which elementary sulfur (S_8) was dissolved in the DMSO solution of $NaSC_6H_5$ prior to the addition of the thiirane. Now the rapid initial phase of the thiirane consumption has vanished.

The explanation we favor regards the thiophenoxide anion as the preferred carrier of activity. In the presence of the extruded sulfur, benzene*poly*thiolate anions are formed, and the equilibrium concentration of the active thiophenoxide is diminished.

A special NMR technique permitted concentration measurements at intervals of 11 seconds; this was much too slow for obtaining the rate profile of the fast initial phase.

The story of the man may be recalled who searched at night for his front-door key on the sidewalk, next to a lantern. A passer-by came to his aid. He was unsuccessful as well and asked where exactly the key was lost. The answer was: probably on the other side of the street, but it's pitch-dark over there.

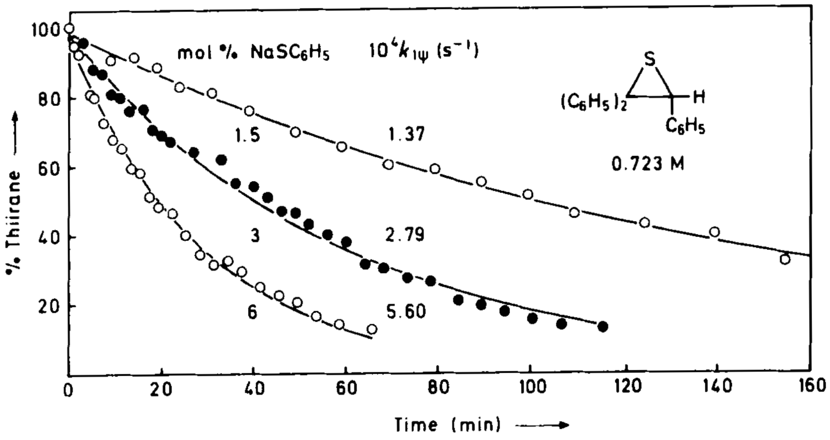
Being stuck in a similar predicament, we decided to learn more about the slower part of the desulfurization curve of Scheme 4. The first measurement of the triphenylthiirane concentration was done 1 or 2 minutes after addition of the catalyst; this reading defined a new starting point as to reaction time and concentration.

Scheme 5 shows such conversion functions in which the fast initial phase was cut off. The solid curves were computer-calculated and -drawn for the first reaction order with a least-square program. The time is given in minutes, no longer in seconds. The thiirane concentrations fit the curve up to high conversions. The $k_{1\psi}$ values are proportional to the concentration of $NaSC_6H_5$. The half-life of triphenylthiirane amounts to 20 min in

SCHEME 5

Triphenylthiirane and Sodium Thiophenoxide

Quasi-Stationary Conditions in [D_6]DMSO at 35°C



the run with 6 mol% catalyst.[11]

The solubility of S_8 in DMSO is rather low. The precipitation of S_8 starts early during the catalyzed desulfurization of the thiirane. *Quasi-stationary* conditions are reached: the sulfur of the thiirane adds onto the growing sulfide chain of the catalyst, whereas at the other end crystalline S_8 leaves the system.

The table in Scheme 6 lists $k_{1\psi}$ values for double measurements as a function of the thiophenoxide concentration. Division by the molar concentration of the catalyst provided the second-order rate constants k_2 which show fair agreement. The spontaneous loss of sulfur from triphenylthiirane is slow at 35°C; 1 M sodium thiophenoxide effects a 700,000-fold rate acceleration.

Sodium thiophenoxide is subject to autoxidation. It was stored under argon and titrated before use. The thiirane solution was flushed with argon. A control test indicated that diphenyl disulfide, the main product of oxidation, did not influence the rate of desulfurization.

SCHEME 6

Kinetics of Desulfurization of Triphenylthiirane (0.72 M)
Quasi-Stationary Conditions in [D_6]DMSO at 35°C (NMR Analysis)

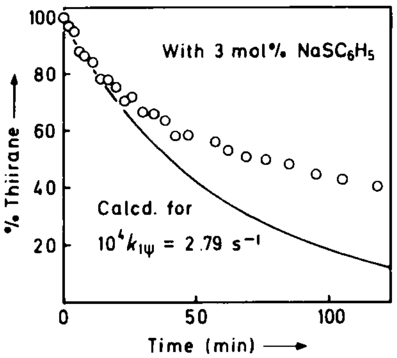
Under Argon

[$NaSC_6H_5$] mol %	$10^4 k_{1\psi}$ s^{-1}	$100 k_2$ $M^{-1}s^{-1}$
6.0	5.60, 5.43	1.27
4.5	4.28, 4.30	1.32
3.0	2.92, 2.79	1.32
3.0*	2.81, 2.92	1.33
1.5	1.56, 1.37	1.24
none	1.92 10^{-4}	

* + 5 mol % $C_6H_5SSC_6H_5$

A. Pröbstl, München 1984/85

Under Oxygen



In the experiment presented on the right side of Scheme 6, oxygen was bubbled through the solution of triphenylthiirane, before 3 mol% sodium thiophenoxide was added. The solid curve illustrates the decrease of thiirane concentration which was expected under argon. The desulfurization lagged behind and came to a stop due to the oxidative destruction of the catalyst.

An important piece of information has been withheld so far. When the thiophenoxide solution was admixed to the triphenylthiirane, a yellow and then blue-green color appeared which, after a few seconds, gave way to a deep red-brown color which persisted when the desulfurization of the thiirane was completed. The same color occurred when the solution of $NaSC_6H_5$ in DMSO - without thiirane - was stirred with elementary sulfur.

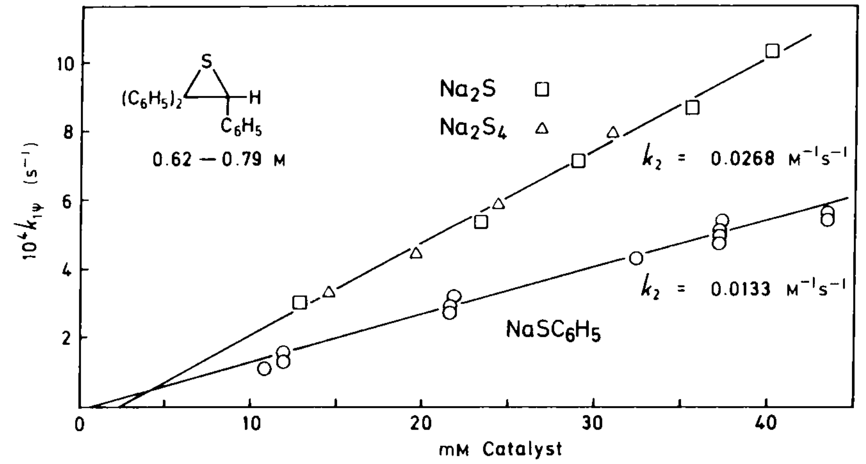
Color phenomena in basic solutions of sulfur have kept chemists busy since 1864.[13] According to studies by F. Seel and others in the 1970s, the green-blue color is ascribed to the S_3 radical anion, the deep red-brown color to the S_4 ;[14,15] both species occur in dissociation equilibria of the dimeric dianions. It is well-known that the blue S_3 is responsible for the color of the mineral ultramarin.[16]

For a while, we suspected the sulfur radical anions to be the true catalysts in the stripping of sulfur from thiiranes.

SCHEME 7

Desulfurization of Triphenylthiirane; Quasi-Stationary Conditions

Dependence of $k_{1\psi}$ on Catalyst Concentration in [D_6]DMSO at 35°C



A. Pröbstl, P. Vorstheim, München 1984, 1988

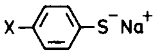
Indeed, disodium sulfide and disodium tetrasulfide are likewise active in converting phenylated thiiranes into olefins; again, first-order reaction curves were obtained in the quasi-stationary phase. The $k_{1\psi}$ values of five kinetic runs with Na_2S and four runs with Na_2S_4 define a straight line when plotted versus the molar concentration of the catalyst (Scheme 7). The line is expected to go through the origin and does so within some error limits. The even better function for catalysis by sodium thiophenoxide is based on twelve determinations of $k_{1\psi}$.

The slopes of the lines are identical with k_2, the second-order rate constants. It should be noticed that k_2 of the sulfide *dianion* is twice as large as that of the thiophenoxide *monoanion*. The question arises: What is the catalytically active species under the quasi-stationary conditions, i.e., after the first initial phase?

SCHEME 8

Thiolate-Catalyzed Desulfurization of Triphenylthiirane

Rate Constants 100 k_2 ($M^{-1}s^{-1}$) under Quasi-Stationary Conditions in [D_6]DMSO at 35°C



X =	CH_3O	CH_3	H	Cl	NO_2
	1.50	1.84	1.32	1.80	1.12

$C_6H_5-CH_2-S^-Na^+$	$(CH_3)_3C-S^-Na^+$	$Na^+S^{--}Na^+$	$Na^+\bar{S}-S-S-\bar{S}\ Na^+$
1.34	1.53	2.66	2.80

Why is the influence of R in $R-S^-Na^+$ so small ?

$$R-S^- + (x-1)\ S \rightleftharpoons R-S_x^-$$

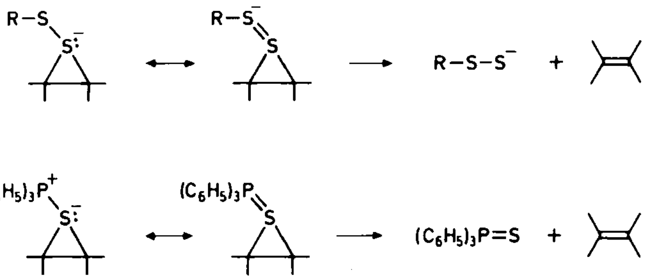
$$2\ R-S^- + S_8 \rightleftharpoons R-S-S-R + S_8^{--}$$

Peter Vorstheim varied the nature of the thiolate catalyst. Values of $k_{1\psi}$ were determined for 4-5 different concentrations of each new thiolate, and the slope of the straight lines, similar to those of Scheme 7, provided the k_2 values of Scheme 8. The range was surprisingly small: 0.011 - 0.018 for four p-substituted thiophenoxides. Sodium benzyl sulfide gave nearly the same value as $NaSC_6H_5$ and sodium *tert*-butyl sulfide is only insignificantly more active.

Several interpretations are possible. The influence of the substituent on the catalytic activity of the monothiolate and on the equilibrium of polythiolate formation compensate each other. A second explanation: polythiolates are the weak catalysts under quasi-stationary conditions, and the nature of the distant R in $R{-}S_x^-$ hardly matters. The polysulfide dianion, S_x^{--}, disposes of two reactive centers and, therefore, shows double the k_2 value of monoanions, $R{-}S_x^-$. The last formula line of Scheme 8 suggests a third possibility: the arene- or alkanethiolate is oxidized by elementary sulfur to the disulfide; the open-chain S_8^{--} equilibrates with the lower polysulfide dianions including the highly active S^{--}. However, sodium benzyl sulfide was not converted to dibenzyl disulfide by S_8 in DMSO, thus ruling out this pathway.

When Na_2S serves as catalyst, one reaches the stage of Na_2S_4 after three sulfur transfers from triphenylthiirane. No wonder the k_2 values are virtually the same in the quasi-stationary phase.

SCHEME 9



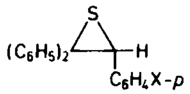
The tentative mechanism in Scheme 9 postulates an intermediate formed additively from thiiranes and thiophenoxide or other anionic sulfur functions.[12] The charge-delocalized intermediate undergoes cheletropic elimination, and the dithiolate regenerates the active catalyst by equilibration. The well-known desulfurization of thiiranes by triphenylphosphine could pass an analogous intermediate, now free of net charge. This reaction is not catalytic; the phosphine sulfide is the final product.

Thus, we cancelled our conjecture that the colored radical anions play a dominant role in the desulfurization of thiiranes. The thiolate catalysis can be stopped by electrophiles blocking the anionic sulfur function, e.g., acids, methyl iodide, trimethylsilyl chloride, lead nitrate, or 2,4-dinitrochlorobenzene. Tetramethylpiperidinoxyl, hydroquinone, and tetramethyl-p-phenylenediamine were without effect.

SCHEME 10

Variation of Thiirane in Catalytic Desulfurization
by $NaSC_6H_5$; Quasi-Stationary Conditions, $[D_6]DMSO$, 35°C

Thiirane	$1000\,k_2\,(M^{-1}s^{-1})$
cis-2,3-Diphenyl-	(3 160)
2,2-Diphenyl-	1 070
trans-2,3-Diphenyl-	162
Triphenyl-	13.3
Tris(*p*-chlorophenyl)-	280
Triphenyl-	13.3
Tris(*p*-methoxyphenyl)-	3.6



X	$1000\,k_2\,(M^{-1}s^{-1})$
OCH_3	9.1
H	13.3
Cl	33
CN	390
NO_2	10 700

A. Pröbstl, München 1985/86

In standard experiments with sodium thiophenoxide as catalyst, a series of phenylated thiiranes was compared in the rate of sulfur extrusion in the quasi-stationary phase (Scheme 10). cis-Stilbene episulfide ranks at the top, reacting 240 times faster than triphenylthiirane.[12]

Does electron release or electron withdrawal promote the desulfurization of thiiranes ? Tris(p-chlorophenyl)-thiirane reacts 20 times faster than triphenylthiirane, whereas the tris(p-methoxyphenyl) compound is 4 times slower. This is not surprising for a reaction with an anion as partner. A somewhat larger series of p-substituents was introduced into the 3-phenyl (Scheme 10).

The conversion of thiiranes into olefins proceeds quantitatively in the examples discussed - with one exception: cis-2,3-diphenylthiirane. This exception will acquaint us with a delightful new reaction.

CIS-STILBENE AND TRITHIEPANES FROM CIS-2,3-DIPHENYLTHIIRANE

SCHEME 11

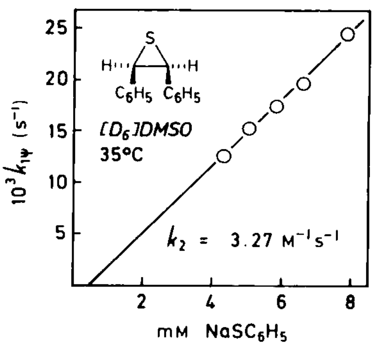
cis-2,3-Diphenylthiirane and Thiolate Catalysts

0.86 M Thiirane in [D_6]DMSO at 35°C
Product Analysis by ^{1}H-NMR (Standard)

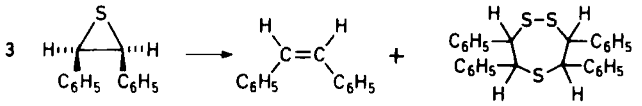
mol%	Catalyst	*cis*-Stilbene	$C_{28}H_{24}S_3$
0.50	$NaSC_6H_5$	32%	61%
0.54	Na_2S_4	32	70
0.40	$NaSCH_2C_6H_5$	33	60

$2\ C_{14}H_{12}S + S \longrightarrow C_{28}H_{24}S_4$

Two Diastereoisomers in 3 : 1 Ratio,
mp 209-211°C and mp 197-198°C



Stoichiometry



No S_8 is formed (tlc test)

The reaction, observed by Albert Pröbstl, was induced by 0.5 mol% of sodium thiophenoxide or other thiolates and required a half-life of less than a minute. It afforded only one third of cis-stilbene, the desulfurization product; the remaining two thirds of cis-stilbene sulfide emerged as a compound $C_{28}H_{24}S_3$ (Scheme 11). The molecular formula corresponds to two molecules of the thiirane + one sulfur. The new compound was a 3:1 mixture of two crystalline diastereoisomers which were separated by thick-layer chromatography.[11]

The stoichiometry did not depend on the nature of the catalyst: Three molecules of cis-stilbene sulfide gave rise to one molecule each of cis-stilbene and the compound $C_{28}H_{24}S_3$. *Elementary sulfur did not occur.* Even small amounts of S_8 would generate the deep color in the thiolate-containing medium. The solution stayed pale yellow up to the end.

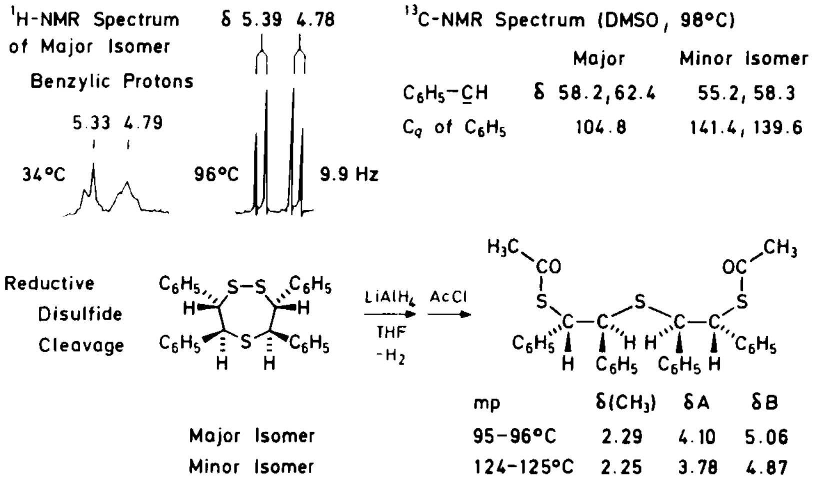
The conversion follows the first order from the beginning and the $k_{1\psi}$ values are proportional to the concentration of the catalyst $NaSC_6H_5$ as indicated by the graph in Scheme 11.[12] The high rate constant k_2 may well correspond to the rapid initial phase in the desulfurization of triphenylthiirane. The subsequent retardation by the sulfur eliminated in the process is missing here, because the formal sulfur atom of one molecule of cis-diphenylthiirane is consumed by two more molecules of the substrate.

The NMR spectrum of the major C_{28} compound, in the region of the benzylic protons, resembles a cross-section through a mountain-range. Warming to 96°C led to an impeccable AB spectrum (Scheme 12). More correctly, to two identical AB spectra, since we are dealing with a 4H signal. The minor isomer exhibited the same bilateral symmetry; however, its AB spectrum was different from that of the major component. The ^{13}C shifts at 98°C corroborated the symmetry; only two doublets appeared for four aliphatic CH groups.

The 1,2,5-trithiepane structure proposed in Scheme 12 finds confirmation in the reductive cleavage of the disulfide bond. Treatment with $LiAlH_4$ was accompanied

SCHEME 12

Structure of the Trithiepanes



^{13}C-NMR Spectrum (DMSO, 98°C)

	Major	Minor Isomer
$C_6H_5-\underline{C}H$	δ 58.2, 62.4	55.2, 58.3
C_q of C_6H_5	104.8	141.4, 139.6

	mp	δ(CH$_3$)	δA	δB
Major Isomer	95-96°C	2.29	4.10	5.06
Minor Isomer	124-125°C	2.25	3.78	4.87

A. Pröbstl, München 1983

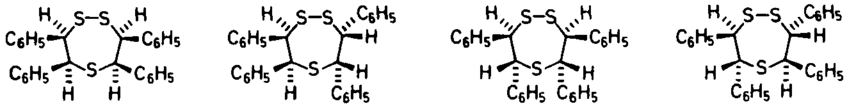
by evolution of one mole of hydrogen. In situ acetylation furnished crystalline diacetyl derivatives still containing all three *S*-atoms. The open-chain diacetyl compounds likewise reveal bilateral symmetry in their ^{1}H NMR spectra.[11]

Four structures fulfilling the symmetry requirements are conceivable for tetraphenyltrithiepane. The first pair of formulae in Scheme 13 is built by *cis*-diphenyl units. The 7-membered ring in the second pair harbors two *trans*-diphenyl units. The first and third structure are characterized by a symmetry plane, the second and fourth by a twofold axis.

What are the correct structures of the isolated trithiepanes ? The starting material is cis-2,3-diphenylthiirane; the trans isomer did not give rise to trithiepanes under the same conditions. Nevertheless, we preferred the third and fourth formulae with trans-diphe-

SCHEME 13

3,4,6,7-Tetraphenyl-1,2,5-trithiepanes with Bilateral Symmetry



C_s cis,cis,cis — C_2 cis,trans,cis — C_s trans,cis,trans — C_2 trans,trans,trans

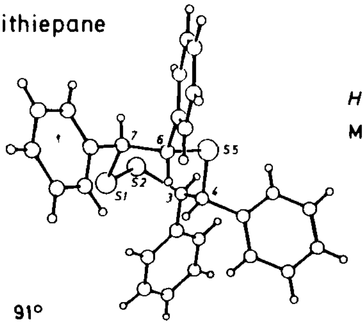
X-Ray Analysis of Major Trithiepane

C7—S1—S2—C3
184 204 185 pm

C4—S5—C6
184 184

∢ S1–S2–C3 104°
S2–S1–C7 107°
C4–S5–C6 104°

Dihedral Angle C7-S1-S2-C3 91°



H. Nöth, München 1986

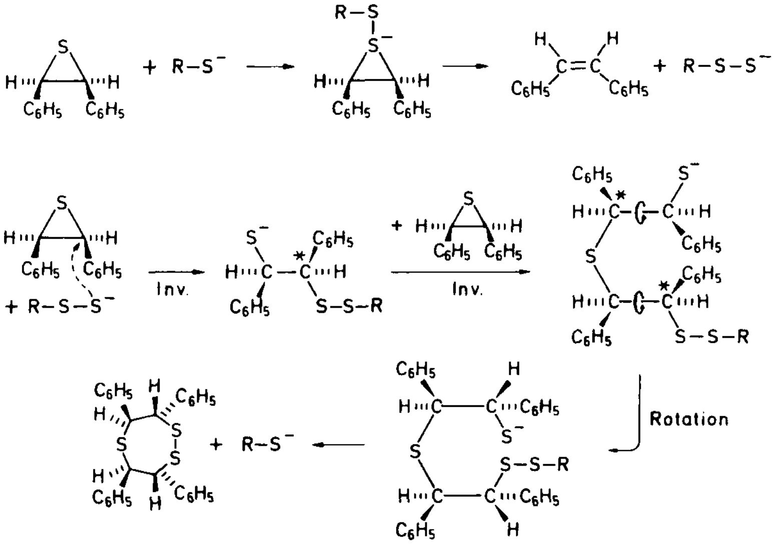
nyl blocks on the basis of the mechanistic considerations delineated below.

In 1986 my colleague Heinrich Nöth was kind enough to carry out a single crystal X-ray analysis of the major trithiepane and established the trans,cis,trans configuration (Scheme 13). A dihedral angle of 91° at the S-S bond signals freedom of angle strain. Similar proton coupling constants of 9.9 and 9.2 Hz suggest that both trithiepanes contain trans-vicinal benzylic proton pairs.

In the mechanism of Scheme 14, the monothiolate attacks cis-diphenylthiirane at the sulfur and triggers a cheletropic elimination with retention of configuration. Now the dithiolate anion, $R\text{-}S_2^-$, is supposed to approach the C-atom of the 3-membered ring; the nucleophilic ring opening is associated with inversion. The new thiolate function reacts with a second thiirane molecule by the same S_N2 type of ring opening. A second inversion occurs;

SCHEME 14

Tentative Mechanism of Trithiepane Formation



the two inverted centers are marked by asterisks. In a rotamer depicted at the lower right of Scheme 14, the thiolate anion cleaves the S-S bond with formation of a cyclic disulfide. This type of substitution is well-known from intermolecular analogues.

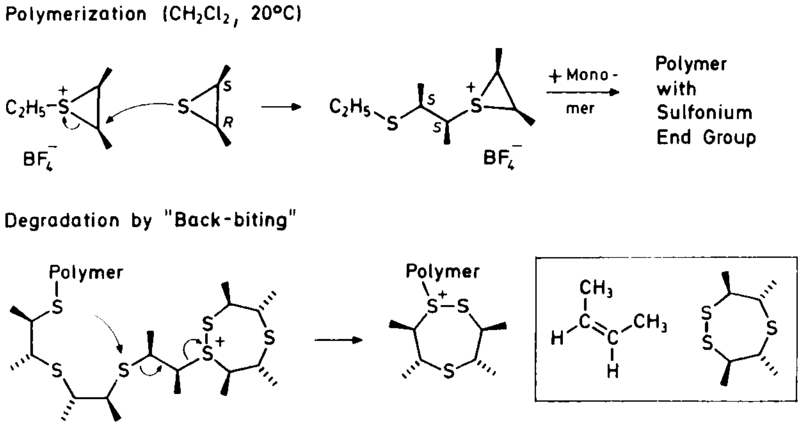
One inversion at each *cis*-diphenylthiirane unit furnishes *trans*-diphenyl building blocks. The meso form is illustrated; a similar pathway provides the racemic structure (trans,trans,trans).

The experimentally established stoichiometry - 1:1 for cis-stilbene and trithiepane - puts stringent conditions on the mechanism. The exclusive attack of the *mono*-thiolate on the thiirane sulfur and that of the *di*thiolate at the C-atom is improbable, but does not violate basic principles. There is no general activity sequence of nucleophiles. The nucleophilicity scales may well be different versus thiirane sulfur and thiirane carbon.

The real stumbling block is the assumption that the ring-opened monothiolate formed by dithiolate attack at the thiirane carbon again reacts at S and not at C of the next thiirane unit. Our initial guess that the reaction of a benzyl type monothiolate might differ from that of thiophenoxide, was not supported by experiment. The crumbling of a single cornerstone can cause an entire vault to collapse.

SCHEME 15

cis-2,3-Dimethylthiirane and Triethyloxonium Fluoroborate



A paper published in 1976 by Van Craeynest and Goethals in the European Polymer Journal [17] may be pertinent. cis-2,3-Dimethylthiirane polymerized under catalysis by triethyloxonium fluoroborate, and subsequently the polymer degraded to give cis-2-butene and tetramethyl-1,2,5-trithiepane. By the way, the major degradative pathway afforded a cyclic tetramer of the thiirane, harboring a 12-membered ring. Polymerization goes along with inversion at the C-atom attacked (Scheme 15).

The Belgian authors assumed the occurrence of a trithiepanium ion as end group in the polymer, shown on the lower formula line of Scheme 15. The essence of the degradation process is a trans elimination of the E2 type. Leaving group is the terminal tetramethyltrithiepane; the loss of the sulfonium charge probably contributes most of the driving force. The electron release towards the incipient double bond is assumed to come from the 1,7 interaction of two sulfide functions. This "back-biting" process establishes a new trithiepanium ion which is ready for the next degradation step. The authors obtained two diastereoisomeric trithiepanes, both with bilateral symmetry.[17] It should be noticed that the *(SS)* or *(RR)* configuration of the recurring C_4 unit of the polymer necessarily affords *cis*-butene and *trans*,*cis*, *trans*- or *trans*,*trans*,*trans*-tetramethyl-1,2,5-trithiepane.

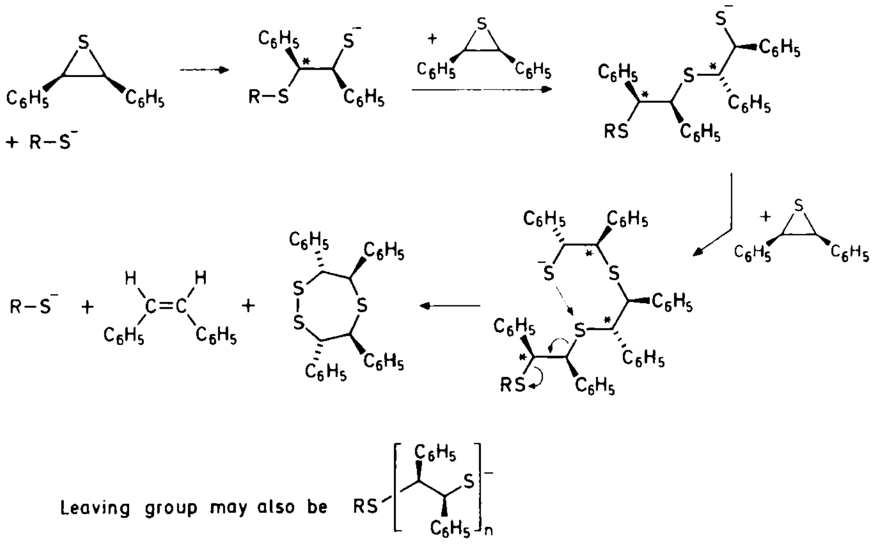
Our inconsistent Scheme 14 for the formation of tetra*phenyl*trithiepane likewise comprises a 1,7 sulfur-sulfur back-biting. However, in the elegant mechanism proposed by Van Craeynest and Goethals,[17] cis-butene and trithiepane emerge from one and the same concerted process and, therefore, occur in equimolar quantities.

Tentative acceptance of this idea assigns the key step of desulfurization to the thiolate attack on the *C-atom* of cis-stilbene sulfide (Scheme 16). Three successive nucleophilic ring openings provide the open-chain trimer; the asterisks denote the inverted centers. Now the scenario is set up for the concerted trans elimination yielding cis-stilbene and the trithiepanes. It is the 1,7 sulfur-sulfur interaction which supplies the push,whereas the thiolate anion is a poor leaving group.

Independent of the nature of the nucleophilic catalyst, we observed equimolar quantities of cis-stilbene and tetraphenyltrithiepane in almost quantitative yield;

SCHEME 16

Simultaneous Formation of *cis*-Stilbene and Trithiepane



the concertedness guarantees equimolarity. The rate constant k_2 did not change much when different thiolates were applied. It is conceivable that not the open-chain trimer of Scheme 16, but rather a higher oligomer is subject to the back-biting process. This modification would shield the leaving group in the E2 reaction from the influence of the varying catalyst $R-S^-$.

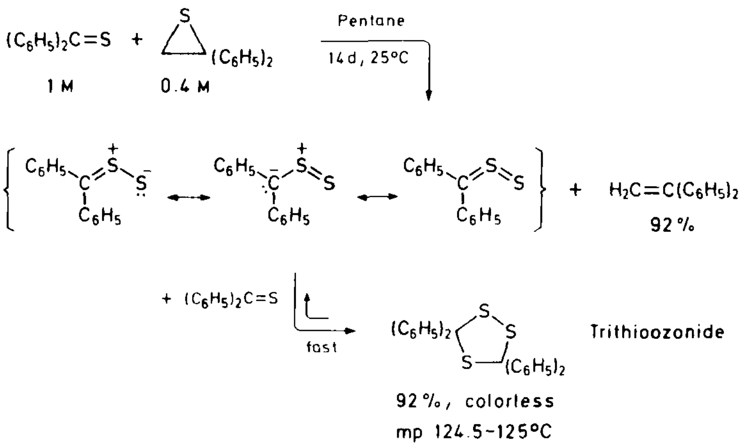
Not all scruples concerning this mechanism are dispelled, and we are looking for further confirmation. The retention of configuration in the desulfurization of cis-2,3-diphenylthiirane no longer requires an attack of the thiolate catalyst on the thiirane sulfur in the framework of Scheme 16. Do we have to revise, as a consequence, the mechanistic Scheme 9 for the quantitative desulfurization of triphenylthiirane or 2,2-diphenylthiirane proceeding without concomitant trithiepane formation ? We are actively pursuing the idea that the *thiirane carbon* is the attacked party in all cases. However, at this point we cannot yet make ends meet.

Doubts as to whether nucleophilic sulfur functions can interact with the *sulfur* of thiiranes will be swept aside by the next Chapter.

THIOCARBONYL *S*-SULFIDES AND THEIR CHEMISTRY

SCHEME 17

Thiobenzophenone *S*-Sulfide
from Thiobenzophenone and 2,2-Diphenylthiirane

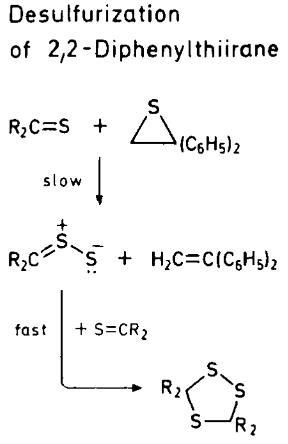


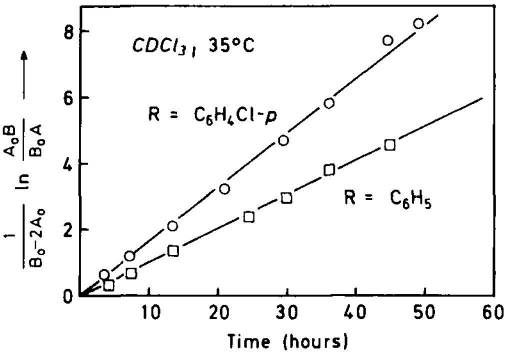
Jochen Rapp found in thioketones a new reagent capable of abstracting sulfur from thiiranes. Two moles of thiobenzophenone slowly reacted with 2,2-diphenylthiirane in pentane at room temperature to give 92% each of 1,1-diphenylethylene and of a 5-membered ring with three sulfurs, the 3,3,5,5-tetraphenyl-1,2,4-trithiolane.[18]

An adventurous pathway is suggested in Scheme 17. The thiirane donates sulfur to the thioketone, thus furnishing olefin and thiobenzophenone *S*-sulfide. Its zwitterionic structures of the allyl anion type characterize a 1,3-dipole; a cumulated structure is free of formal charges. The thione *S*-sulfide is not isolable, but adds to the CS double bond of a second molecule of thiobenzophenone. The "trithioozonide" is not only a formal analogue of ozonides; 1,2,4-trioxolanes arise from the cycloaddition of carbonyl oxides to carbonyl compounds.

Why patiently wait two weeks for the reaction to occur ? Heating is counterproductive. Solutions of the colorless trithiolane turn blue above 50°C, the color of thiobenzophenone; a cycloreversion equilibrium seems likely. The trithiolane is virtually insoluble in pentane and precipitates.[18]

SCHEME 18





	$10^5 k_2$ M^{-1} s^{-1}
Triphenylphosphine	139
4,4-Dichlorothiobenzophenone	4.5
Thiobenzophenone	2.8
Adamantanethione	0.18

A kinetic study is consistent with this pathway. The rate plots in Scheme 18 reveal the first order for each of the two reactants. One thiobenzophenone and one diphenylthiirane enter the rate-determining step. The second molecule of thiobenzophenone is consumed in a fast subsequent cycloaddition. Triphenylphosphine is

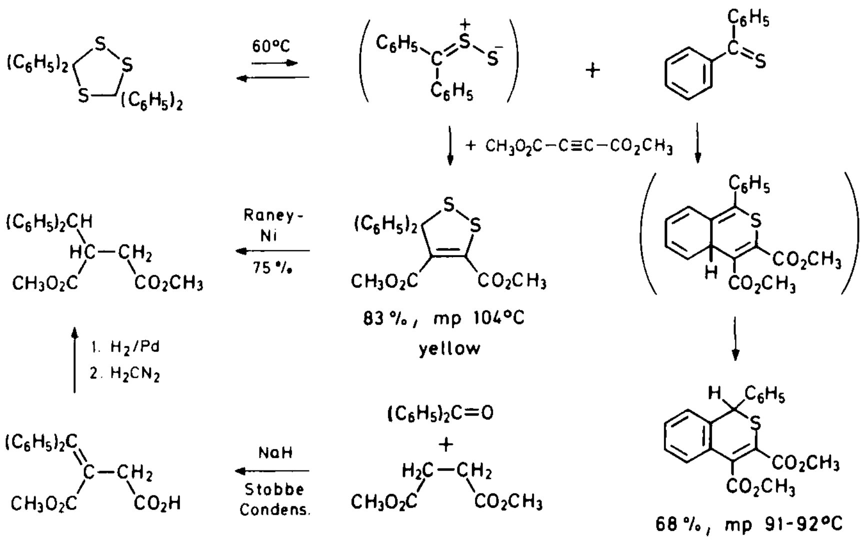
50 times more active than thiobenzophenone in the desulfurization of the thiirane. Adamantanethione as an aliphatic thioketone is likewise capable of abstracting the thiirane sulfur, although at a 15-fold diminished rate.

Thiocarbonyl *S*-ylides have been under investigation in the Munich Laboratory for 9 years.[19] The wish to make thiocarbonyl *S*-sulfides accessible motivated the experiments described here. We were looking for a donor transferring a formal sulfur atom to the thione sulfur, and phenylated thiiranes were our first try.[20]

The postulated thione *S*-sulfides belong to the so-called thiosulfines which sporadically appeared in the literature since 1921.[21] Claims were countered by refutations; thiosulfines were mainly assumed to satisfy stoichiometric equations. A. Senning gave an excellent summary [22] and contributed to the field.[23] However, the evidence for the existence of thiosulfines is not unequivo-

SCHEME 19

Thiobenzophenone *S*-Sulfide
1,3-Cycloaddition to Dimethyl Acetylenedicarboxylate



cal so far.

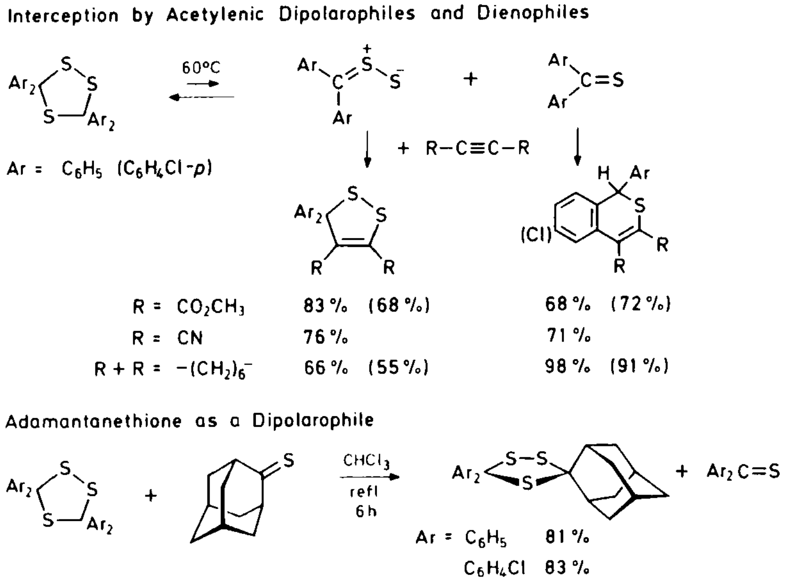
This evidence is no presented. It was mentioned that solutions of tetraphenyl-1,2,4-trithiolane assume a blue color at temperatures above 50°C. Jochen Rapp established the dissociation equilibrium of the trithiolane at 60°C in chloroform in the presence of dimethyl acetylenedicarboxylate. Thiobenzophenone *S*-sulfide was intercepted by 1,3-dipolar cycloaddition to yield the crystalline dimethyl 3,3-diphenyl-3*H*-1,2-dithiolane-4,5-dicarboxylate (Scheme 19). The structure was clarified by treatment with Raney nickel; the 2-benzhydrylsuccinic ester was independently synthesized.[18] Stobbe condensation of benzophenone with dimethyl succinate, treatment with diazomethane, and catalytic hydrogenation provided an identical sample.

The second dissociation product, thiobenzophenone, likewise combined with acetylenedicarboxylic ester, now in a Diels-Alder reaction. The C=S double bond plus an aromatic bond function as a 1,3-diene. Rearomatization is achieved by 1,3-prototropy and a benzothiopyran derivative resulted (Scheme 19). This Diels-Alder adduct of thiobenzophenone was described by H. Gotthardt in 1980.[24]

Dicyanoacetylene and the strained cyclooctyne were also suitable trapping reagents. They act as dipolarophiles versus thiobenzophenone *S*-sulfide and as dienophiles towards thiobenzophenone (Scheme 20). The tetrakis(4-chlorophenyl)-1,2,4-trithiolane was analogously prepared and subjected to the conditions of cycloreversion; the yields of products obtained by in situ interception of 4,4'-dichlorothiobenzophenone *S*-sulfide are shown in brackets in Scheme 20.[18]

Aliphatic thiones only play the role of the dipolarophile. When our trithiolanes and adamantanethione were refluxed in chloroform, the intermediate thione *S*-sulfi-

SCHEME 20

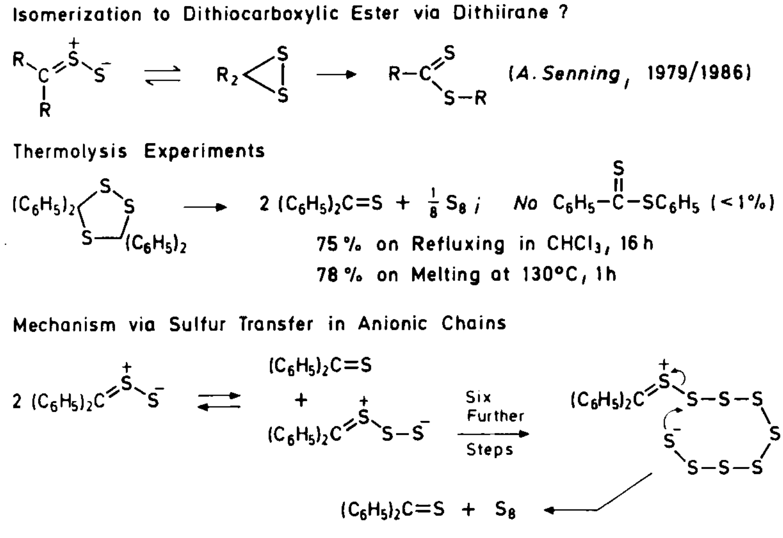


des added onto the aliphatic C=S bond furnishing mixed trithiolanes; the aromatic thioketones were set free (Scheme 20).[18] In the overall process, the aromatic thione is displaced by adamantanethione. It is probably the conjugation energy of thiobenzophenone and its dichloro derivative which shifts the equilibrium to the right side.

What happens to thiobenzophenone *S*-sulfide in the absence of intercepting dipolarophiles ? Senning supposed an electrocyclic equilibration of thiosulfines with dithiiranes and subsequent rearrangement to dithiocarboxylic esters (Scheme 21).[23] We subjected tetraphenyl-1,2,4-trithiolane to thermolysis in boiling chloroform or to brief heating of the melt to 130°C; high-vacuum distillation afforded 75% or 78% of thiobenzophenone. The red phenyl dithiobenzoate was *not* found in the distillate. In artificial mixtures, specific infrared absorptions

SCHEME 21

Thermolysis of Thiobenzophenone *S*-Sulfide



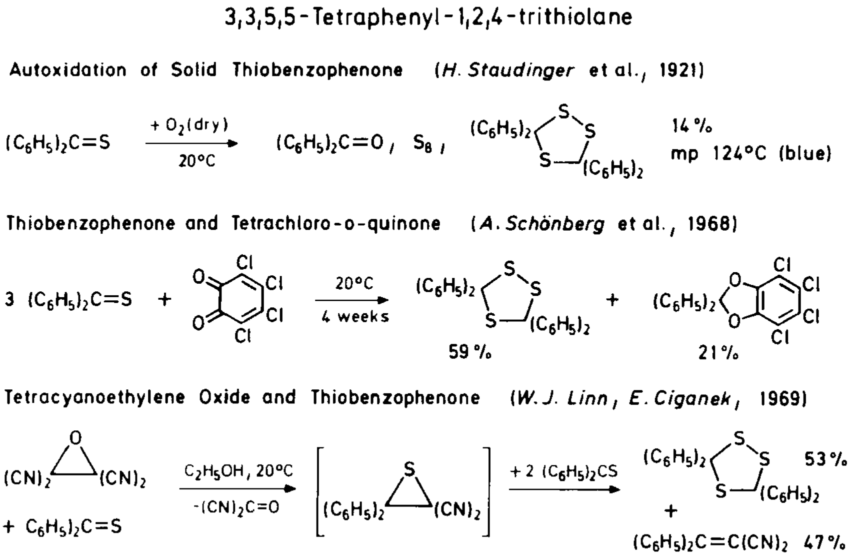
allowed to recognize as little as 1% of the dithioester along with thiobenzophenone.[18]

How is S_8 formed in the decomposition of thiobenzophenone *S*-sulfide ? We can imagine rapid sulfur transfers in anionic chains. Long sulfur chains are built up which shed cyclooctasulfur (Scheme 21) as described before.

By the way, the tetraphenyl-1,2,4-trithiolane is not new; it emerged in rather obscure reactions. In 1928 Staudinger et al. stored crystalline thiobenzophenone in an atmosphere of dry nitrogen; they isolated 14% of the trithiolane and noticed the regeneration of thiobenzophenone at the melting point (Scheme 22).[25]

Schönberg and König interacted thiobenzophenone with tetrachloro-o-benzoquinone and obtained the trithiolane in higher yield.[26] A diphenylmethylene unit is transferred to the quinone; the mechanism is unknown. No less complex is the reaction of tetracyanoethylene oxide with thiobenzophenone; Linn and Ciganek suggested a thiirane,

SCHEME 22



3,3,5,5-Tetraphenyl-1,2,4-trithiolane

Autoxidation of Solid Thiobenzophenone (*H. Staudinger* et al., 1921)

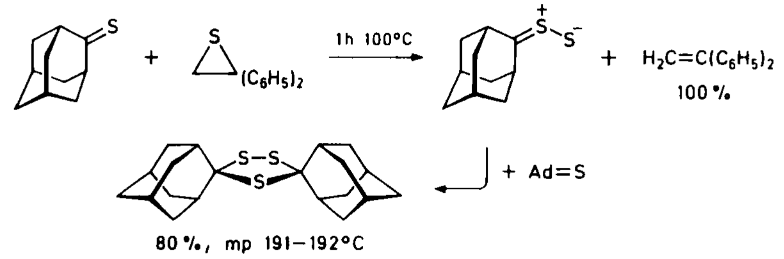
Thiobenzophenone and Tetrachloro-o-quinone (*A. Schönberg* et al., 1968)

Tetracyanoethylene Oxide and Thiobenzophenone (*W. J. Linn*, *E. Ciganek*, 1969)

substituted by phenyl and cyano groups, as an intermediate (Scheme 22).[27] The present knowledge allows the reconstruction of an extended sequence of electrocyclic ring opening, 1,3-cycloaddition, and cycloreversion steps.

SCHEME 23

Adamantanethione and 2,2-Diphenylthiirane



J. Rapp, München 1986

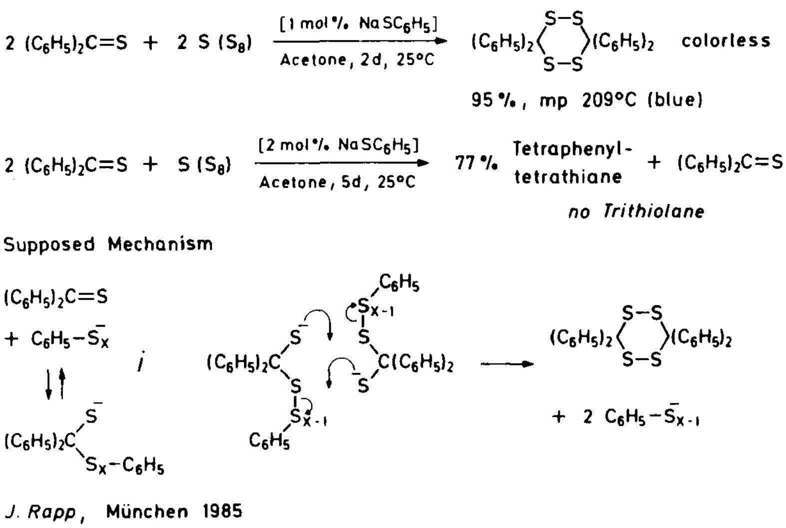
Aliphatic thiones are likewise capable of desulfurizing thiiranes. Adamantanethione and diphenylthiirane afforded diphenylethylene and an aliphatic thione *S*-sulfide; the latter, again, was intercepted by a second molecule of the thione (Scheme 23).[18] The bis-adamantane-spiro-trithiolane does not dissociate at 100°C, unlike the tetraphenyl-1,2,4-trithiolane; therefore, heating was allowed, and the reaction was completed in 1 hour at 100°C.

Admittedly, the use of phenylated thiiranes as sulfur donor in the synthesis of thione *S*-sulfides is inconvenient. Is there a more handy sulfur donor ? Although we have not yet accomplished it, the experience is amusing.

THE REACTION OF THIONES WITH ELEMENTARY SULFUR

SCHEME 24

S_8 + $NaSC_6H_5$ as S Donor for Thiones



J. Rapp, München 1985

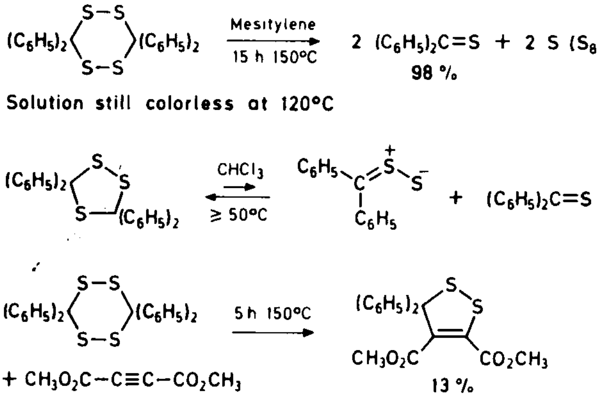
Elementary sulfur, S_8, does not interact with thiones. However, in the presence of 1 mol% of sodium thiophenoxide, thiobenzophenone and sulfur smoothly combined in a 1:1 ratio affording 95% of 3,3,6,6-tetraphenyl-1,2,4,5-tetrathiane (Scheme 24).[28]

At first glance, one might suppose that the tetrathiane emerges from the dimerization of thiobenzophenone *S*-sulfide. This is not the case. On reducing the amount of sulfur to half, the material balance would just be right for the interception of the *S*-sulfide by a second mole of thiobenzophenone according to Scheme 17. The expected tetraphenyl-1,2,4-trithiolane was not found, however; instead, the tetrathiane was isolated in 77% yield, based on the 1:1 stoichiometry. This result excludes thiobenzophenone *S*-sulfide as an intermediate.

In the mechanism conjectured in Scheme 24, a polysulfide anion attacks the *C-atom* of the thione. Now nucleophilic substitution of a sulfur in the polysulfide chain by the anionic thiolate of a second molecule finally gives rise to the tetrathiane. The schematic illustration is not intended to suggest concertedness of the two substitution events. It is the thermodynamically favored tetrathiane which in the end results from "trans-disul-

SCHEME 25

Does Tetraphenyl-1,2,4,5-tetrathiane Dissociate into Thiobenzophenone *S*-Sulfide ?



fidization" equilibria. Thus, $NaSC_6H_5$ acts as a sulfur carrier, but - regrettably - does not deliver it to the right place, the double-bonded sulfur of the thione.

The blue melt obtained from tetraphenyl-tetrathiane at 200°C again suggests thiobenzophenone as product of decomposition.

In solution, the tetraphenyltetrathiane is colorless up to 120°C. It requires heating at 150°C for 15 hours to effect cleavage into thiobenzophenone + sulfur (Scheme 25).[28] The thermal cycloreversion to two molecules of thiobenzophenone *S*-sulfide is forbidden by orbital symmetry to be concerted ($_{\sigma}4_{s}+_{\sigma}4_{s}$). On the other hand, tetraphenyl-1,2,4-trithiolane establishes at 50°C the 1,3-dipolar cycloreversion equilibrium. This is a powerful demonstration of orbital control.

However, some thiobenzophenone *S*-sulfide appears to occur in the polystep decomposition of the tetrathiane. Heating with dimethyl acetylenedicarboxylate at 150°C furnished a modest amount of the 3*H*-1,2-dithiole derivative.

ACKNOWLEDGMENT

The experiments described are parts of the Ph.D. Theses of Albert Pröbstl and Jochen Rapp. Some results of the current studies by Peter Vorstheim were likewise included. The author expresses his sincere thanks to these capable young associates for their successful cooperation. An important X-ray analysis by Professor Heinrich Nöth, München, is noted with gratitude. Thanks are going to the Fonds der Chemischen Industrie, Frankfurt, for financial support.

This article is dedicated to Sir Derek Barton on the occasion of his seventieth birthday.

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