

New thione chemistry

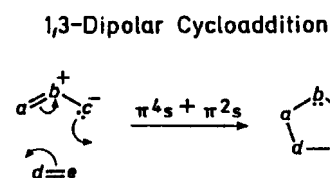
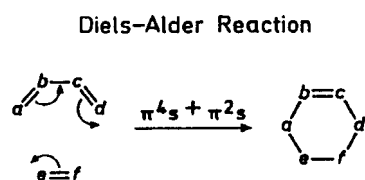
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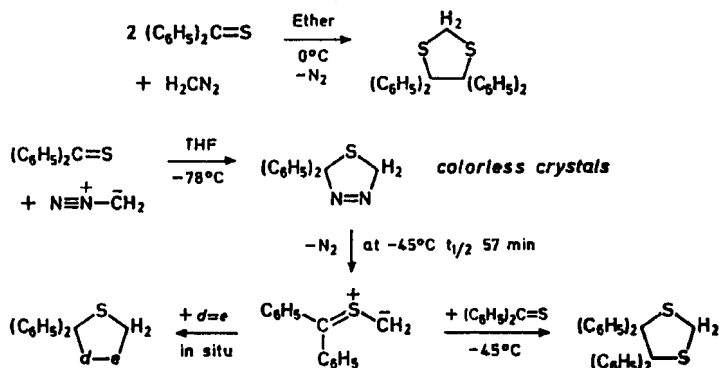
Abstract - Rate measurements reveal the superiority of C=S bonds over CC multiple bonds as dipolarophiles in cycloadditions of thiobenzophenone *S*-methylide, diphenyldiazomethane, and *N*-methyl-*C*-phenylnitrene. Thione *S*-oxides (sulfines) and thione *S*-sulfides likewise prefer thiones as cycloaddition partners. Many cycloadditions of thiones approach equilibria; the high reactivity is a kinetic phenomenon, the low HO-LU distance of the π -MOs being responsible. *Ab initio* calculations for $\text{H}_2\text{C}=\text{S} + \text{H}_2\text{C}=\text{NH}^+-\text{O}^-$ result in a *negative* activation energy. π Bonds with silicon, phosphorus etc. exhibit likewise low HO-LU gaps and increased reactivity.

Cycloaddition Rates with Thiones as Dipolarophiles

Diels-Alder reactions and 1,3-dipolar cycloadditions have the same π -electronic balance: $\pi^4_s + \pi^2_s$. The role of the diene as a 4π unit is taken over by the 1,3-dipole which harbors an *allyl anion type* MO with 4 π -electrons. The wide scope, the mild reaction conditions, and the stereospecificity suggested early that the two reactants interlock via *highly ordered* transition states. Orbital control allows these thermal reactions to be concerted (1).



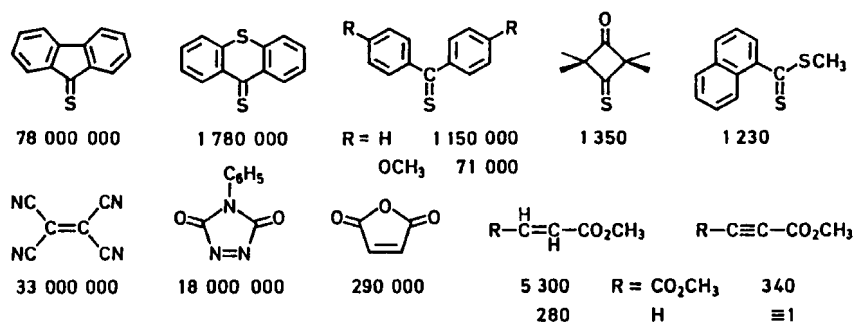
Scheme 1. Thiobenzophenone and Diazomethane



In 1981 we clarified the *Schönberg reaction* (2,3): two molecules of thiobenzophenone combine with diazomethane furnishing 4,4,5,5-tetraphenyl-1,3-dithiolane (*Scheme 1*). It was shown that the cycloaddition of diazomethane to the CS double bond is fast even at -78°C . The diphenyl-1,3,4-thiadiazoline eliminates nitrogen at -45°C in a cycloreversion (4). The resulting *thiobenzophenone S-methylide* is a 1,3-dipole with a sulfonium function in the middle. It is not isolable, but rather adds to the CS double bond of a second thiobenzophenone molecule giving Schönberg's 1,3-dithiolane. In the absence of an excess of thiobenzophenone, the thiocarbonyl ylide is capable of adding *in situ* to a variety of other dipolarophiles $d=e$ giving rise to five-membered cycloadducts (4,5).

As an *electron-rich* 1,3-dipole, thiobenzophenone *S*-methylide combined easily with *electron-deficient* dipolarophiles like α,β -unsaturated esters and nitriles. All the cycloadducts with the dipolarophiles of *Scheme 2* were isolated and characterized. Thiobenzophenone *S*-methylide was reacted *in situ* with *pairs of dipolarophiles* and the concentrations of cycloadducts were determined by HPLC. Quantitative evaluation of competition constants provided a set of relative rate constants, based on methyl propiolate ($k_{\text{rel}} \equiv 1$) (6). The rate constant increases dramatically with the introduction of further electron-attracting substituents and reaches 33 million for tetracyanoethylene (TCNE).

Scheme 2. Relative Rate Constants for Cycloadditions of Thiobenzophenone *S*-Methylide (k_{rel} by competition method, THF, -45°C)

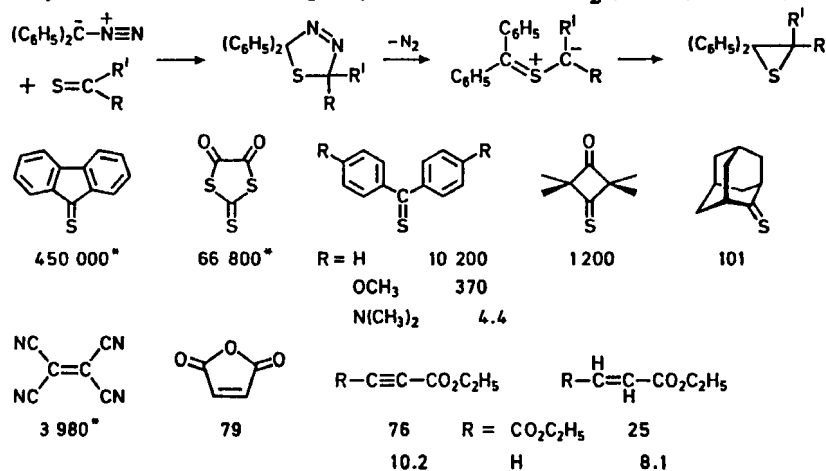


Thioketones were also active as dipolarophiles. The reason is not obvious, since sulfur has the same electronegativity as carbon; thus, the C=S double bond is neither *electron-poor* nor *polar*. However, thiofluorenone with 78 million exceeds even TCNE in its dipolarophilic activity. Thiobenzophenone reacts 3 000 times faster than dimethyl acetylenedicarboxylate (DMAD). The hindered tetramethyl-3-thioxocyclobutanone has still k_{rel} 1 350 (*Scheme 2*).

Thiobenzophenone can be titrated at -78°C with a solution of diazomethane in THF affording the thiadiazoline of *Scheme 1* (4). This suggests the same mystery here, a fabulously *high dipolarophilic activity* of the thioketone.

The reaction with *diphenyldiazomethane* was monitored by spectrophotometry (7). The first formula line of *Scheme 3* indicates the net course with the 1,3-cycloaddition being rate-determining. Diazoalkanes are notorious for their 1,3-cycloadditions to α,β -unsaturated esters or nitriles. In fact, these were the first 1,3-dipolar cycloadditions discovered by Eduard Buchner in 1888 (8). Rate constants of 8 and 25 at 40°C were measured for ethyl acrylate and diethyl fumarate versus diphenyldiazomethane (7); TCNE came out close to 4 000.

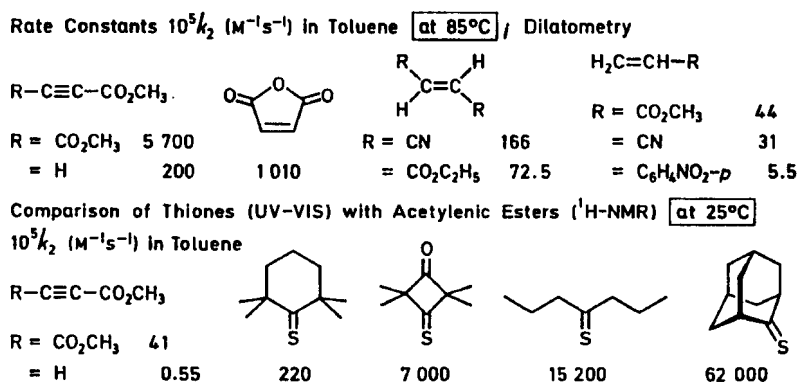
Scheme 3. Cycloaddition Rates of Diphenyldiazomethane; $10^3 k_2$ ($\text{M}^{-1}\text{s}^{-1}$), DMF ($^*\text{CHCl}_3$), 40°C



Again, thiones are super. Thiofluorenone beats TCNE by a factor of 115, and thiobenzophenone is 1 000 times more active than ethyl propiolate. The rate constant of thiobenzophenone is reduced 2 000 fold on planting electron-releasing substituents into the *p*-positions. This behavior is typical for *nucleophilic* 1,3-dipoles to which thiocarbonyl ylides and diazoalkanes belong (Scheme 3).

Nitrones are *nucleophilic-electrophilic* 1,3-dipoles; these *N*-oxides of imines react fast with electron-deficient dipolarophiles, slow with common alkenes, and again fast with the electron-rich enamines. In the 1960s, the 1,3-cycloadditions of nitrones were systematically developed in the Munich laboratory. Those to thioketones, missing in the first survey, were described in 1973 by Black et al. (9). In 1969 the cycloaddition rates of *N*-methyl-*C*-phenylnitronone, $C_6H_5-CH=N(CH_3)^+-O^-$, to CC double and triple bonds were measured dilatometrically at 85°C (10). According to Scheme 4, the second-order rate constant of acrylonitrile was found to be 31. Fumaronitrile exceeded 5-fold, and the triple bond of DMAD was at the top with 5 700.

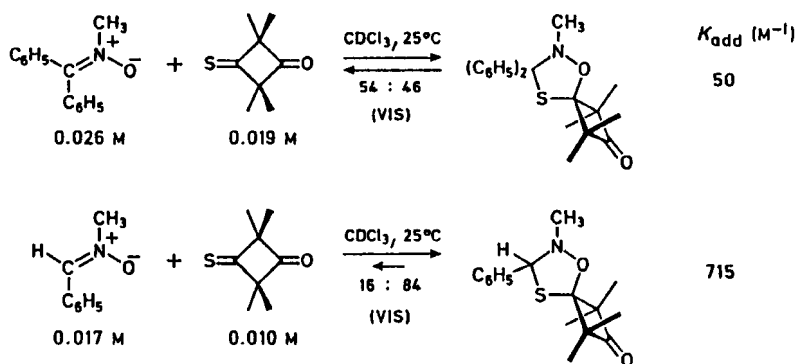
Scheme 4. Dipolarophilic Activity versus *N*-Methyl-*C*-phenylnitronone



Thiones combine at room temperature fast with *N*-methyl-*C*-phenylnitronone. The rate constants were measured spectrophotometrically at 25°C (Scheme 4). The value of $10^5 k_2$ now amounted to 41 for DMAD. Even the least active thione, the highly encumbered tetramethylcyclohexanethione, ranked higher; the backbending of the methyl groups in the thioxocyclobutanone derivative was rewarded by another 30-fold increase. 15 200 was found for the open-chain heptane-4-thione and was exceeded four-fold by adamantanethione (11). On building model molecules with *high steric hindrance*, chemists often choose an *adamantyl* residue. Here adamantanethione was 1 500 times more active than the fastest dipolarophile with carbon-carbon multiple bond.

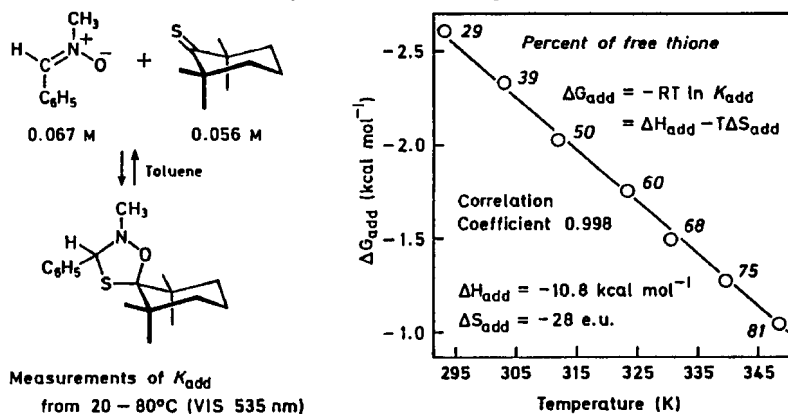
Many cycloadditions of nitrones and thiones reach equilibria (Scheme 5). *N*-Methyl-*C*,*C*-diphenylnitronone combines with tetramethyl-3-thioxocyclobutanone in dilute solution in $CDCl_3$ - the initial concentrations are given at the left; an equilibrium is established which contains 54% of the free

Scheme 5. Cycloaddition-Cycloreversion Equilibria of Nitronone Cycloadditions



thione and 46% bound in the cycloadduct. The lack of side reactions allows to determine the equilibrium constants of cycloaddition; K_{add} amounts to 50 M^{-1} and is exceeded 14-fold by that of *N*-methyl-*C*-phenylnitron. Thiobenzophenone would lose its conjugation energy in the 1,3-cycloaddition; no cycloaddition takes place, for thermodynamic reasons (11).

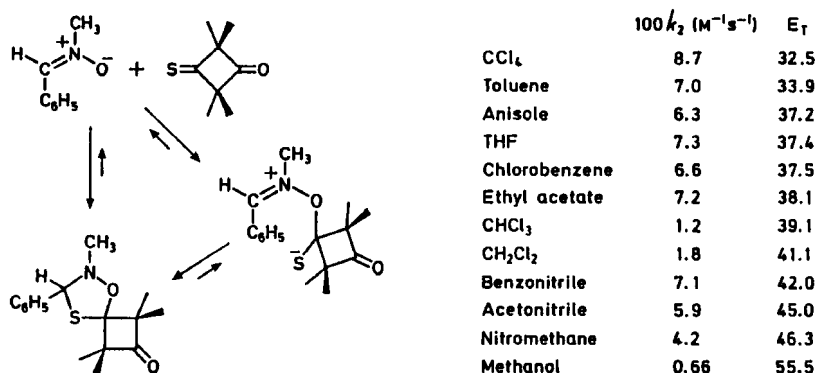
Scheme 6. Cycloaddition Enthalpy and Entropy



The equilibrium of *N*-methyl-*C*-phenylnitron and tetramethylcyclohexanethione with the oxathiazolidine in toluene was measured in its temperature dependence (Scheme 6). With the initial concentrations listed at the upper left, the fraction of the free thione in the equilibrium rises from 29% at 20°C to 81% at 76°C (11). A plot of the free energies of addition versus the absolute temperature furnished a cycloaddition enthalpy of $-11 \text{ kcal mol}^{-1}$ from the intercept of the straight line and a reaction entropy of -28 e.u. from the slope. The enthalpy value favors the addition, the negative entropy promotes the dissociation. With a reaction free energy of only -1 kcal mol^{-1} at 80°C, the addition of the nitron to the aliphatic thione is close to thermoneutral. Thus, the *high rate of equilibration* cannot be of thermodynamic origin. It must be a kinetic phenomenon.

Besides the concerted pathway, a twostep reaction is conceivable, initiated by a nucleophilic addition to the $\text{C}=\text{S}$ double bond. An increase of *charge separation* during activation would be expected. The more polar transition state of zwitterion formation should be better solvated than the ground state. The rate constant is expected to increase with rising solvent polarity.

Scheme 7. Rate Constant at 25°C and Solvent Polarity






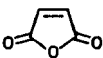
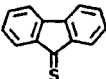
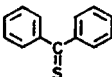


However, this was not borne out by the kinetic results of Scheme 7. The largest and the smallest rate constant differ by a factor of only 13. E_T is the Reichardt parameter, an empirical measure of solvent polarity (12). The data for CCl_4 and methanol at the lower and upper end of the E_T scale, 8.7 and 0.66, suggest a slightly inverse relation with solvent polarity. Thus, the rate constants do not confirm a mechanism with an increase of charge separation in the rate-determining step (11).

Fast Diels-Alder Reactions of Thiones

Thioaldehydes - apart from a few sterically hindered ones - are not isolable due to their high reactivity. Their occurrence was established just through interception by Diels-Alder reactions.

Scheme 8. Rate Constants of Diels-Alder Reactions with Thiones; $10^4 k_2$ ($M^{-1}s^{-1}$)

					
	920	3.4	2.3	1.5	0.68
	(Dioxane, 30°C)				
	51 000	870	2 900	320	85
	$(CH_2Cl_2, 20^\circ C)$				
	7.2	0.68	0.78	0.51	0.33
	$(CH_2Cl_2, 20^\circ C)$				

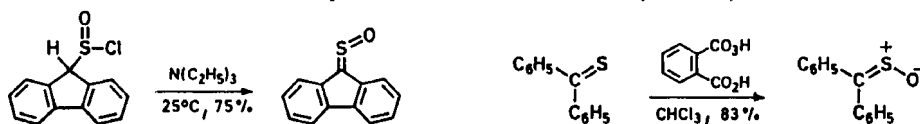
2,3-Dimethylbutadiene was used by Baldwin and Lopez for capturing thiobenzaldehyde (13). Photochemically generated cyanothioformaldehyde was intercepted by 2-ethoxybutadiene (14).

J. Sauer et al. contributed more to the kinetics of Diels-Alder reactions than any other group (15). Recently, they included thiofluorenone and thiobenzophenone as dienophiles (16). Thiofluorenone combines with cyclopentadiene 55 times faster than maleic anhydride (Scheme 8). Versus 1,3-pentadiene, the rate ratio reaches nearly 1300 despite a 10°C higher reaction temperature for maleic anhydride.

Thione S-Oxides and Thione S-Sulfides

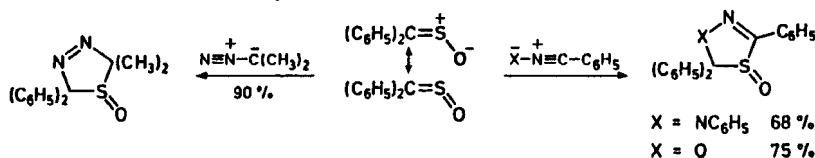
There are certain 1,3-dipoles which have a low tendency to add to dipolarophiles. Their foot-dragging may have thermodynamic or kinetic reasons; each case requires a critical investigation.

Scheme 9. Synthesis of Thione S-Oxides (Sulfines)

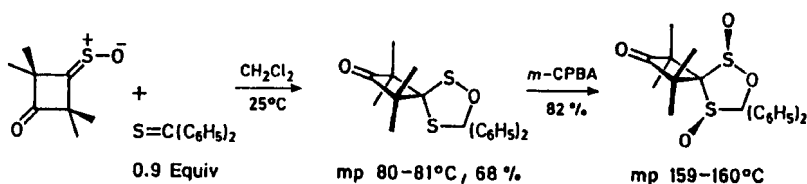


Sulfines are usually described by the cumulated system $C=S=O$. Although the first representative goes back to 1923, the chemistry of sulfines was essentially developed in the last 25 years. Sulfines are anhydrides of sulfinic acids and can be prepared by treating sulfinyl chlorides with triethylamine (17). Sulfines can also be regarded as *thione S-oxides*. A second method of preparation is based on the interaction of thiones with peracids, perphthalic acid in the example given in Scheme 9. Besides the cumulated bond system, zwitterionic structures of sulfines can be drawn. These are *octet structures* of the allyl anion type with a sulfonium cation in the middle. This representation as a 1,3-dipole appears to be superior to the description with tetravalent sulfur (18).

Scheme 10. 1,3-Cycloadditions of Thione S-Oxides (Sulfines)

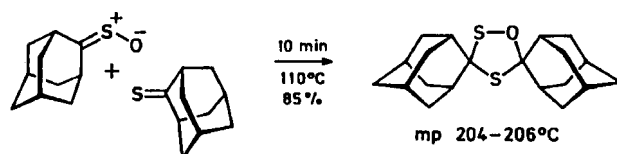


Thione S-oxides are *dienophiles* and accept 1,3-dienes at the CS double bond. These Diels-Alder reactions were studied by Zwanenburg at Nijmegen who made the deepest inroad into sulfine reactivity (17). The CS bond is likewise *dipolarophilic*. Additions of 2-diazopropane, diphenylnitrilimine, and benzonitrile oxide to diphenylsulfine are recorded in Scheme 10. Thus, the sulfine functi-

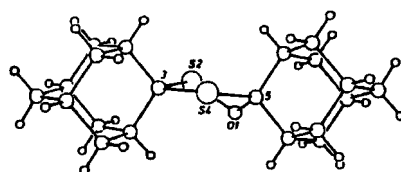
Scheme 11. 1,3-Cycloadditions of a Thione *S*-Oxide to Aromatic Thiones

ons as a 2π reactant in these cycloadditions. Thione *S*-oxides should also behave as 1,3-dipoles, but they refused to accept dipolarophiles like DMAD in 1,3-positions (19).

In 1991, our attempts of reacting thione *S*-oxides with *thiones* were successful right away. The tetramethyl-3-thioxo-cyclobutanone *S*-oxide and thiobenzophenone furnished a crystalline colorless 1,2,4-oxadithiolane (*Scheme 11*). It was converted to the *S,S*-dioxide; the X-ray structure indicated an envelope conformation of the five-membered heterocycle with *cis*-located oxide functions. The oxadithiolanes turn blue at the melting point suggesting a *cycloreversion* to the diarylthioiketone.

Scheme 12. 1,2,4-Oxadithiolane-3,5-dispiro-bis(adamantane)

Single Crystal X-Ray Analysis



Envelope conformation of the heteroring with O1 as the flap

Dihedral angles

C3-S2-O1-C5 54.5°

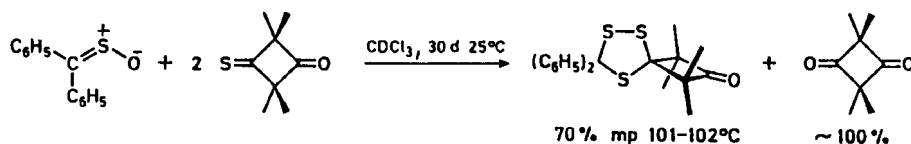
S2-C3-S4-C5 9.8°

Bond Lengths

S2-O1 166.7 pm

C3-S2 184.4

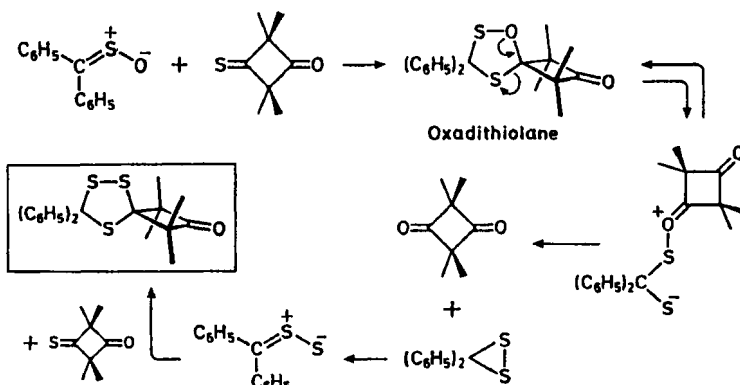
Aliphatic thiones are expected to afford *more stable* oxadithiolanes. That was the case, but the higher temperature points to a greater activation barrier. Adamantanethione *S*-oxide combined with adamantanethione producing the dispiro compound (*Scheme 12*). The X-ray structure determination revealed an envelope conformation of the heterocycle with 54.5° for S2-O1 as the largest torsion angle (20). Open-chain disulfides assume torsion angles of 90° resulting in orthogonal C-S bonds; the same repulsion of the lone-pair orbitals enforces here the largest dihedral angle at the S2-O1 bond.

Scheme 13. Thiobenzophenone *S*-oxide and 2,2,4,4-tetramethyl-3-thioxocyclobutanone

We are missing one more combination, that of an *aromatic* sulfine and an *aliphatic* thione. Monitoring the reaction of *Scheme 13* by NMR disclosed a slow conversion. Surprisingly, the cycloadduct was a *trithiolane* instead of the expected *oxadithiolane*. The stoichiometry had changed to 1 sulfine plus 2 thiones. The third sulfur must come from a second molecule of the thioxocyclobutanone which, in turn, was converted to the dione. An X-ray analysis of the 1,2,4-trithiolane confirmed the result of a deep-seated structural change (20).

In the probable reaction pathway of *Scheme 14*, the usual (3+2) cycloaddition of thiobenzophenone *S*-oxide as the first step is followed by an ionization of the *S,O*-acetal group. The ring-opened zwitterion is positioned so as to recognize the closure of the dithiirane ring as an *intramolecular* substitution; the cyclobutanedione is the leaving group. The first dithiirane has been described by

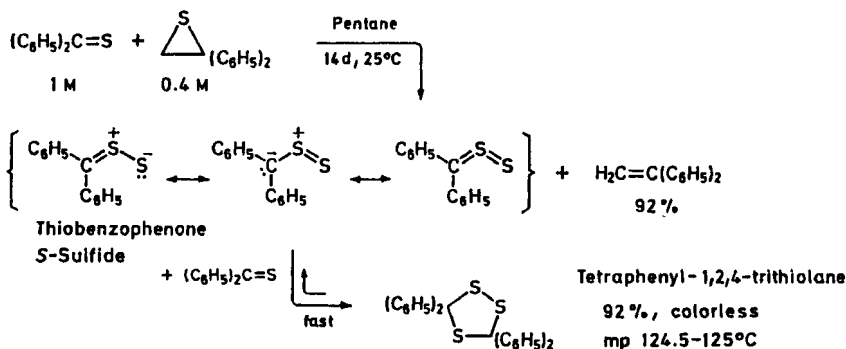
Scheme 14. Suggested Mechanism of Trithiolane Formation



Nakayama et al. (21) in 1994. The electrocyclic ring opening of the dithiirane to a resonance-stabilized 1,3-dipole appears probable here.

With the assumption of thiobenzophenone *S*-sulfide as an intermediate we are setting foot on territory, familiar in the Munich laboratory. The cycloaddition of thiobenzophenone *S*-sulfide, *independently prepared*, to the thioxocyclobutanone led indeed to the trithiolane under consideration.

Scheme 15. Access to Thiobenzophenone *S*-Sulfide



Thione *S*-oxides *alias* thiosulfines appeared sporadically in the literature. Claims were countered by refutations (22). Our paper of 1987 offered the first unequivocal evidence for the existence of thione *S*-sulfides (23). A donor which is capable of transferring a formal *sulfur atom* to the thione sulfur was found in thiiranes. Two moles of thiobenzophenone slowly reacted with 2,2-diphenylthiirane to give 92% each of diphenylethylene and tetraphenyl-1,2,4-trithiolane (*Scheme 15*). The thiirane transfers its sulfur atom to the thio ketone, thus furnishing olefin and thiobenzophenone *S*-sulfide. The thione *S*-sulfide adds to a second molecule of thiobenzophenone.

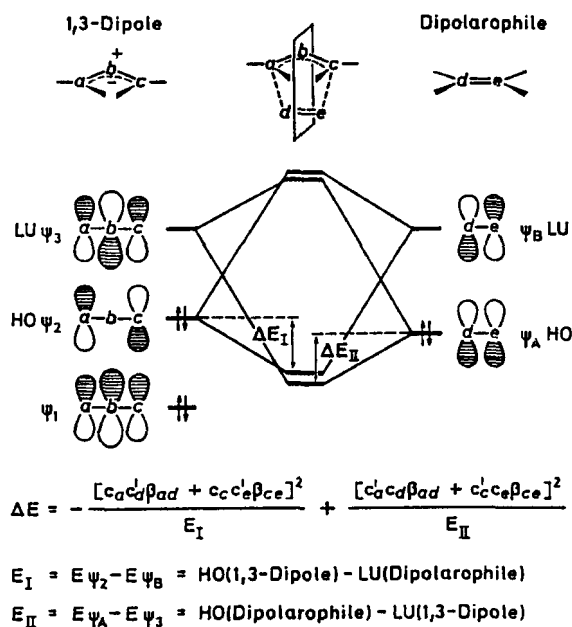
Solutions of the colorless trithiolane turn blue above 50°C, the color of thiobenzophenone. A *cycloreversion equilibrium* appears likely.

When the dissociation equilibrium of the trithiolane was established in the presence of DMAD, the intermediate thiobenzophenone *S*-sulfide was intercepted by 1,3-dipolar cycloaddition to yield the yellow crystalline 3,3-diphenyl-3*H*-1,2-dithiole-4,5-dicarboxylic ester in 83% yield; the structure was clarified (23). Thiones enjoy the privilege of very fast cycloadditions to thione *S*-sulfides. In recent years, several groups reported on other routes to thione *S*-sulfides (24-26).

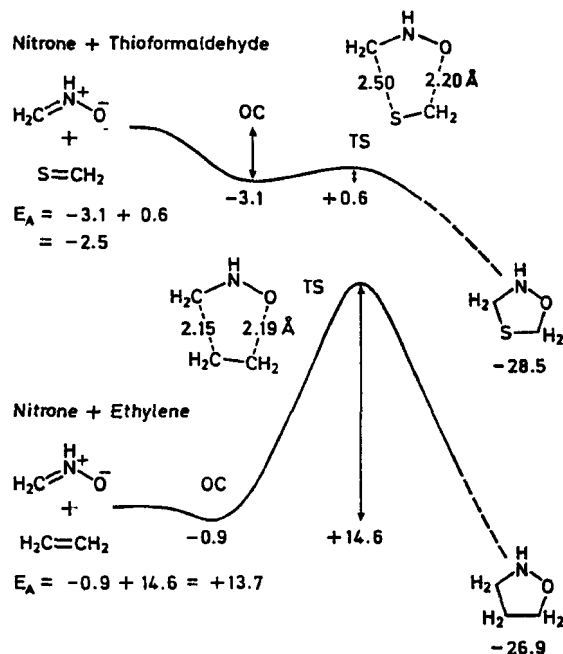
Ab Initio Calculations of Transition Structures

The central question is still open: Why are thiones *superdipolarophiles*? *Kinetic phenomena* are obviously more important than thermodynamic considerations. The MO theory offers the key to the high rate constants: a *low HO-LU energy distance* of the CS double bond compared with C=O. Calculations by Houk *et al.* revealed a π, π^* distance of 12.6 eV for thioformaldehyde in contrast to 18.4 eV for formaldehyde (27). The light absorption due to the $\pi \rightarrow \pi^*$ transition shows for thiobenzophenone (314.5 nm) a bathochromic shift compared with benzophenone (248 nm) (28).

Schemes 16. HO-LU Interaction in the Transition State of 1,3-Dipolar Cycloaddition



Scheme 17. *Ab Initio* Calculations of Orientation Complexes (OC) and Transition Structures (TS); Structures and Energies (kcal mol^{-1}) by Becke3LYP/6-31G*



How does a diminished HO-LU distance give rise to an enhanced rate of cycloaddition? MO perturbation theory allowed an elegant explanation of *reactivity sequences* in concerted cycloadditions in 1971 (29). The second-order term of the perturbation equation contains the attractive interactions. The frontier π -MOs of the 1,3-dipole are depicted in *Scheme 16* on the left, those of an ethylenic dipolarophile on the right; the *transition state* of cycloaddition is in the middle. ΔE_I and ΔE_{II} are the energy gains in the transition state which are the larger the smaller the energy distances between the interacting HO-LU pairs are. The energy separations E_I and E_{II} occur in the denominators of the fractions. When now the HO-LU distance *within* one reactant, say the dipolarophile, is reduced, E_I and/or E_{II} are diminished. A larger gain of ΔE means increased reaction rate.

The qualitative reasoning by perturbation theory finds support in quantumchemical *ab initio* calculations. The model is the cycloaddition of the unknown parent system of the nitrones with *thioformaldehyde*. The high-caliber computation (*Scheme 17*) was recently performed (30).

Interestingly, an orientation complex of the reactants occurs as a minimum on the energy hypersurface, $3.1 \text{ kcal mol}^{-1}$ below the ground state. The energy of the transition structure (TS) is $0.6 \text{ kcal mol}^{-1}$ above the complex OC, i.e., $2.5 \text{ kcal mol}^{-1}$ below the ground state of the reactants. Thus, we are facing the rare case of a *negative* activation energy.

The cycloaddition of the nitron parent with *ethylene* was calculated using the same programs.

The TS is more-balanced with respect to the length of the two new bonds. However, its energy is 13.7 kcal mol⁻¹ above the ground state (*Scheme 17*). With the assumption of similar activation entropies, the rate constant of the cycloaddition to thioformaldehyde should be 10¹¹ times faster than that to ethylene. The *substituted* nitrones and thiones which we studied experimentally are not amenable to such sophisticated calculations. However, semiempirical methods provided good agreement with the cycloaddition equilibria in those systems (30).

Conclusions

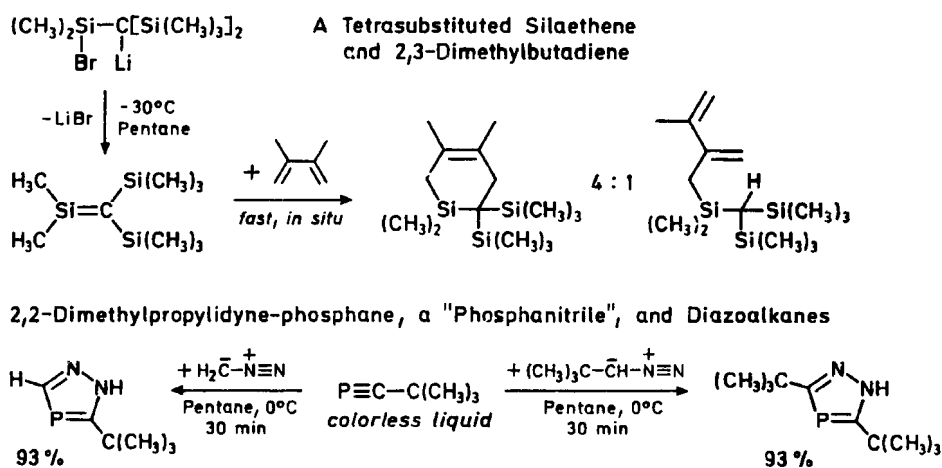
Thiones are super in cycloadditions. They belong to the most active dipolarophiles and dienophiles. The synthetic utilization of this fact has barely begun. Carbon-sulfur single bonds are easily split by hydrogen on nickel. It is conceivable that cycloadditions to thiones and subsequent hydrogenolytic removal of sulfur from the heterocycles might develop to a useful method for generating carbon-carbon single bonds.

The rate phenomenon should not be limited to the C=S double bond. π -Bonds of carbon with other elements of the higher long periods show likewise diminished HO-LU energy distances. High reactivities in cycloadditions have been reported, albeit no kinetic data are available for those systems.

A silaethylene was set free from a lithiated precursor at -30°C (*Scheme 18*). Despite its high degree of substitution, it smoothly accepted 2,3-dimethylbutadiene. Diels-Alder and ene reaction proceed concurrently, as observed by Wiberg et al. in the Munich laboratory (31). The corresponding CC double bond with the same voluminous substituents is not suspected to combine with 1,3-dienes.

An exciting achievement are nitriles in which the nitrogen has been replaced by phosphorus. The phosphanitride of trimethylacetic acid on the lower formula line of *Scheme 18* is even isolable.

Scheme 18. Cycloadditions to Some Carbon-Heteroatom Multiple Bonds



Regitz et al. described cycloadditions of diazomethane and its *tert*-butyl derivative (32). Aliphatic nitriles like acetonitrile or trimethylacetonitrile do not react with diazoalkanes at all.

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