1,3-Dipolar Cycloadditions, 116[‡]

The Formation of 1,3-Dithiolanes from Aromatic Thioketones and Diazomethane − The Mechanism of the Schönberg Reaction

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Dedicated to Christoph Rüchardt, Freiburg, on the occasion of his 70th birthday

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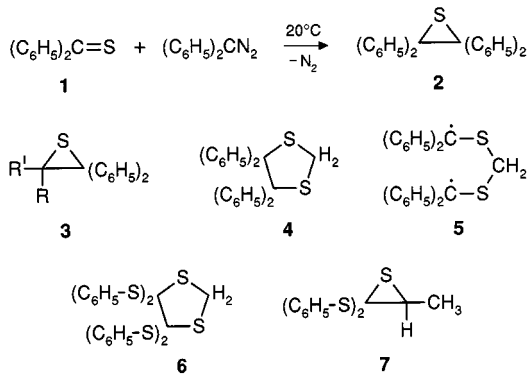
Reactions of diaryl thioketones with diazomethane at room temperature afford 4,4,5,5-tetraaryl-1,3-dithiolanes; the scope of this surprising 2:1 interaction has been studied for decades (*Schönberg Reaction*). The clue to the mechanism was our observation that the stoichiometry is 1:1 at –78 °C, and 2,5-dihydro-2,2-diaryl-1,3,4-thiadiazoles are formed as primary [2+3] cycloadducts. They lose N_2 at –45 °C in first-order reactions generating diaryl thioketone *S*-methylides which can be intercepted by thioketones (→1,3-dithiolanes), multiple CC bonds, or acids HX. In the absence of trapping reagents, the elusive intermediates either dimerize furnishing 2,2,3,3-tetraaryl-1,4-dithianes or give rise to 2,2-diarylthiiranes by electrocyclization. Beyond thiobenzophenone and diazomethane, our main model reaction, the studies involve fluorene-9-thione, 4,4-dimethoxy- and 4,4-dichlorothiobenzophenone. The ring of 2,5-dihydro-2,2-diphenyl-1,3,4-thiadiazole (**8**) is opened by LDA at –78 °C and derivatives of anion **12** are obtained. – *In summa*: The Schönberg reaction consists of two 1,3-dipolar cycloadditions, linked by a 1,3-dipolar cycloreversion.

Introduction

In 1920 Staudinger and Siegwart have studied the reaction of thiobenzophenone (**1**) with *diphenyldiazomethane*; tetraphenylthiirane (**2**) was obtained in high yield.[1] Thiophosgen, thiobenzoyl chloride, diphenyl trithiocarbonate and other thiocarbonyl compounds likewise reacted with diphenyldiazomethane furnishing the corresponding thiiranes **3** (Scheme 1).[1,2]

Surprisingly, the reaction of **1** with *diazomethane* at 0° − 20 °C follows another stoichiometry. The formation of 4,4,5,5-tetraphenyl-1,3-dithiolane (**4**) was independently reported in 1930/31 by Bergmann et al.[3] and Schönberg et al.;[4] the diradical **5** was assumed to be a common intermediate on the pathway to thiirane and 1,3-dithiolane.[4] The earlier proposals failed to consider that diazomethane is stable in ether at 0 °C; the brisk evolution of N_2 in the interaction with **1** indicates an induced decomposition.

On varying thione and diazoalkane, Schönberg's group observed that each pair produces either the thiirane or the dithiolane; the two were never found side by side. It was baffling that, e.g., diphenyl trithiocarbonate afforded **6** with diazomethane, and **7** with diazoethane.[5] Within four decades,[6] Schönberg returned repeatedly to the dichotomy of pathways and its causes. A paper of 1967 reviewed the reactions of 18 diazoalkanes with 32 thiocarbonyl compounds;[7] the mechanistic conclusion was not encouraging: "Regrettably, all attempts to elucidate the mechanism by the isolation of intermediates or otherwise were in vain".[8]



Scheme 1

In a preliminary report,[9] we found a sequence of two 1,3-dipolar cycloadditions, linked by a 1,3-dipolar cycloreversion, to be responsible for the formation of 1,3-dithiolanes from thiones and diazo compounds; we named this pathway to 1,3-dithiolanes the *Schönberg Reaction*.[10] We

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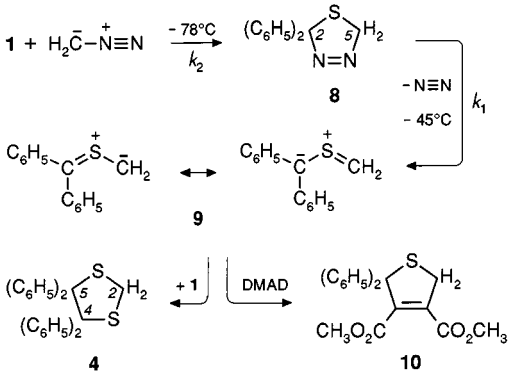
give here the detailed description, supplemented by new material and deeper insight.

2,5-Dihydro-2,2-diphenyl-1,3,4-thiadiazole (8) as an Intermediate

The reaction of thiobenzophenone (**1**) with diazomethane in THF or ether is remarkably fast even at −78 °C; in fact, the deep-blue solution of **1** at −78 °C can be titrated (delay by 2−3 s) by dropwise addition of a diazomethane solution until the deep color disappeared, and the slightly yellow color indicated the excess of diazomethane. The stoichiometry was 1:1 and no N_2 was evolved. When the reaction took place in *diethyl ether* at −78 °C, the mixture solidified to a crystalline mass of the cycloadduct **8** (Scheme 2). Isolated colorless crystals of the 2,5-dihydro-2,2-diphenyl-1,3,4-thiadiazole **(8)** are stable at −78 °C, but explode on warming at about −20 °C.



Scheme 2

Since the addition of diazomethane to **1** proceeds quantitatively, there is no necessity to handle the crystals of **8**. In a routine operation, gaseous diazomethane was passed into the solution of 10 mmol of **1** in THF at −78 °C, until the blue color vanished. The ^{1}H NMR spectrum of **8** ($CDCl_3$, −45 °C) shows the 5-H_2 at δ = 5.98, reflecting the shift to higher frequencies by sulfur and azo functions. In the isolable spiro[adamantane-2,2′-thiadiazoline] (**17**) the δ(5′-H_2) was observed at 5.75.[11]

When the solution of thiadiazoline **8** was warmed from −78 °C to −45 °C, one mol of N_2 is evolved, and the short-lived *thiobenzophenone S-methylide* (**9**) is set free. The N_2 elimination followed first-order kinetics, and the half-life of **8** at −45 °C was volumetrically determined: 56 min in THF and 57 min in $CHCl_3$ (Table 1).

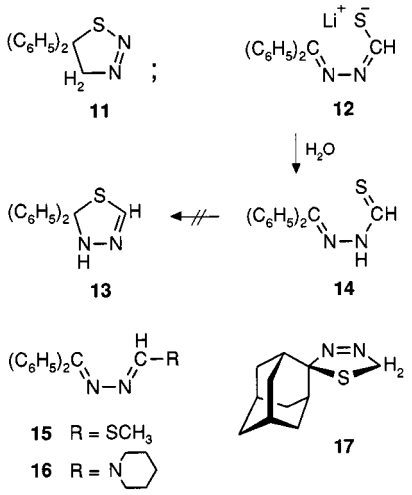
Table 1. First-order rate constants for N_2 evolution from 2,5-dihydro-2,2-diphenyl-1,3,4-thiadiazole (**8**) at −45 °C

8 (M)	Solvent and additives	$10^4\ k_1\ s^{-1}$
0.13	THF	2.03, 2.11
0.15	$CHCl_3$	2.02
0.15	THF, 0.3 M in ethyl acetate	1.99
0.12	THF, 0.3 M in DMAD	1.88
0.13	THF, 0.4 M in DMAD	1.80
0.11	THF, 5 M in methanol, 0.1 M in CF_3CO_2H	1.77

Reagents which intercept the short-lived **9** do not intervene in the rate-determining step, **8** → N_2 + **9**. Dimethyl acetylenedicarboxylate (DMAD), but not ethyl acetate, captures the 1,3-dipole affording the cycloadduct **10**.[12] The influence of these additives on the rate constant of N_2 evolution was unsignificant and reflects small effects of solvation. Furthermore, the rate process was undisturbed when methanol and trifluoroacetic acid was added to the THF solution of **8** (Table 1); the trapping of **9** with methanol and acid will be described below.

The high reactivity of diazomethane to thiobenzophenone requires brief comment. Diazomethane belongs to the nucleophilic 1,3-dipoles; the rate constant of its cycloaddition to ethyl acrylate has been measured between −20 °C and −50 °C.[13] Even at −78 °C, thiobenzophenone was found to react with diazomethane so fast, that the rate could not be measured by conventional techniques. A low LUMO energy is responsible for the *superdipolarophilic* character of thiones.[14] Diphenyldiazomethane reacts 1260 times faster with **1** than with ethyl acrylate (DMF, 40 °C).[15]

Two regioisomers can result from 1,3-cycloadditions of diazomethane to thiones − and they often do (see ref.[11] and the ref. quoted there). Sterically hindered thioketones prefer formation of the 2,5-dihydro-1,3,4-thiadiazoles, which supports structure **8**, not the 1,2,3-isomer **11** (Scheme 3).



Scheme 3

There is direct evidence for structure **8**. Deprotonation of **8** by 1.0 equiv. of LDA in THF at −78 °C and subsequent hydrolysis gave rise to the yellow benzophenone N^{β}-thioformylhydrazone (**14**, 44%), which is identical in melting point and ^{1}H NMR parameters with a specimen which Zelenin et al. obtained by thioformylation of benzophenone hydrazone.[16] The thioformyl group of **14** shows δ_H = 9.72 and δ_C = 189.6, in agreement with other thioformamides.[17] The interaction of **14** with piperidine at 20 °C produced the light-yellow azine **16** (83%). When the lithium salt, obtained from **8** and LDA, was treated with methyl iodide, the (methylthiomethylene)hydrazone **15** was isolated. The proton shift of N=CH appears at δ = 7.72 for

15 and at δ = 8.05 for **16**. Conceivably, the anion of **8** is already the ring-opened species **12**.

Thioacylhydrazones of ketones undergo a ring-chain tautomerism with 2,3-dihydro-1,3,4-thiadiazoles.[16,18] In accordance with the Russian authors,[16] we found no evidence for the appearance of **13**. It is worth mentioning that the analogous treatment of the spiro[adamantane-2,2′-thiadiazoline] (**17**)[11] with LDA and protonation of the lithium salt furnished the cyclic Δ^2-tautomer corresponding to **13**.[19]

Schönberg Reaction as Three-Step Procedure

1.2 Equiv. of thiobenzophenone (**1**) were added to the solution of thiadiazoline **8** in THF *at −78 °C*. After 3 h in a bath of *−40 °C*, the N_2 evolution was complete and workup furnished Schönberg′s tetraphenyl-1,3-dithiolane **4** in 95% yield. When diazomethane was slowly introduced into the solution of **1** in ether *at 20 °C*, a brisk evolution of nitrogen took place and likewise 95% of **4** was isolated; these are the reaction conditions, which led Bergmann et al.[4] and Schönberg et al.[4] to the discovery of **4**.

The cleavage of thiadiazoline **8** into thiobenzophenone *S*-methylide (**9**) and N_2 is a 1,3-dipolar cycloreversion. The two-step sequence, $CH_2N_2 + \mathbf{1} \rightarrow \mathbf{9} + N{\equiv}N$, can be regarded as a *1,3-dipole metathesis*. The short-lived 1,3-dipole **9** is intercepted by the second molecule of **1** in the concluding 1,3-cycloaddition. Thus, the Schönberg reaction consists of a sequence of three cyclic six-electron processes (*supra-supra*), which may be concerted in accord with the Woodward−Hoffmann rules.[20a] The process formally resembles the conversion of alkene + O_3 → ozonide, that also proceeds by two 1,3-dipolar cycloadditions, linked by a 1,3-dipolar cycloreversion.

The stationary concentration of intermediate **8** in the consecutive system is a function of the two rate constants, k_2 for the second-order cycloaddition and k_1 for the first-order cycloreversion (Scheme 2). Concerted cycloadditions usually have low activation enthalpies and large negative activation entropies.[21] The temperature coefficient, defined as the ratio of rate constants upon an increase of 10 °C, will be lower for k_2 than for k_1, the latter referring to a first-order process with small activation entropy. On rising the temperature, k_1 will grow much faster than k_2. As a general rule, cycloadditions furnishing labile adducts should be run at as low a temperature as feasible. This reasoning prompted the elucidation of the Schönberg reaction by the low-temperature experiment.

The mechanistic study opens up synthetic aspects. Subsequent to the 1:1 reaction of **1** with diazomethane at −78 °C, other thiocarbonyl compounds can be added as dipolarophiles. High yields of "mixed" 1,3-dithiolanes were obtained in this widely variable synthesis.[22] It is the same type of interception, which allowed the capture of **9** by DMAD furnishing the dihydrothiophene derivative **10** in 71% yield. It is chosen here as an example of the interaction with a multitude of electron-deficient ethylenes and acetylenes.[23]

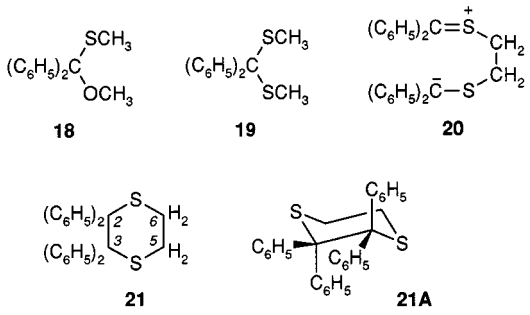
Thiocarbonyl ylides are not new. Plenty of push-pull-stabilized types are isolable,[24] but do not undergo cycloadditions. Short-lived representatives are intermediates (although not recognized previously) in Barton′s two-fold extrusion process leading to highly hindered olefins.[25] The most versatile access to thiocarbonyl ylides is the N_2 extrusion from 2,5-dihydro-1,3,4-thiadiazoles; those from *aliphatic* thioketones and diazoalkanes are isolable and have limited storage capacity. Why does **8** enter into the cycloreversion at as low a temperature as −45 °C? The transition state of the cycloreversion reflects the stabilization of the thiocarbonyl ylide **9** by phenyl conjugation.

1,3-Dipoles possess the π-MOs of the allyl anion. Since sulfur has the same electronegativity as carbon, thiocarbonyl ylides are expected to have MO energies not too far below those of the allyl anion; they are nucleophilic 1,3-dipoles in Sustmann′s PMO concept of concerted cycloadditions.[26]

Thiobenzophenone *S*-methylide (**9**) is a *weak* base. Neither piperidine, aniline, methanol, or phenol interacted with **9**. However, when **9** was set free in methanolic 0.1 M trifluoroacetic acid at −45 °C, the mixed *O,S*-dimethyl acetal **18** was isolated in 83% yield. Both δ_H values, 1.63 for SCH_3 and 3.18 for OCH_3, reveal some shielding by the phenyl groups. Thus, protonation of **9** initiates the reaction with methanol. An additional example is the reaction of **9** with benzoic acid, which furnished 22% of the dimethyl dithioacetal **19** and up to 71% of benzophenone; obviously, these are secondary products.

Head-Head Dimerization vs. Electrocyclization

In the absence of dipolarophiles, the N_2 extrusion from **8** in THF at −40 °C furnished 95% of 2,2,3,3-tetraphenyl-1,4-dithiane (**21**) and 1% of 1,1-diphenylethylene (Scheme 4). The concerted combination of two 4π-systems is forbidden by orbital control, but a twostep process renders the formation of the head-head dimer intelligible. Establishing of the first bond between the two methylene groups allows the intermediate **20** a charge stabilization by the phenyl groups; zwitterion and spin-coupled biradical are probably synonymous here.



Scheme 4

The typical AA′BB′ splitting pattern of 5-H_2 and 6-H_2 in the ^1H NMR spectrum of **21** at 25 °C indicates hindered ring inversion. Also the ^{13}C signals of the four phenyl substituents are pairwise different, whereas C-2/C-3 (δ = 64.5)

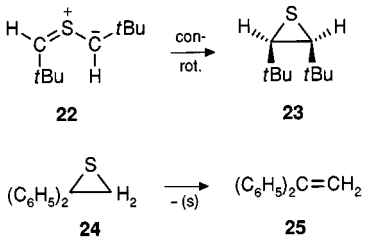
and C-5/C-6 (δ = 31.4) give one signal each. The X-ray analysis of the parent 1,4-dithiane disclosed a chair conformation;[27] assuming the same conformation for **21**, the point group C_2 (**21A**) concords with the symmetry properties displayed in the NMR spectra. Further 2,2,3,3-tetrasubstituted 1,4-dithianes were recently obtained from thiocarbonyl *S*-methylides, and confirmed by X-ray analyses.[28,29]

The ^{1}H NMR spectrum (60 MHz) of **21** in [D_5]bromobenzene was studied in its dependence on temperature. Coalescence of the CH_2 signals was reached at 74 °C, and a singlet at δ = 2.90 at 102 °C indicates the conversion of AA′BB′ to A_4. An approximate value of $\Delta G^{\neq} \approx 17.2 \pm 0.6$ kcal mol^{-1} at 74 °C was calculated.

Barriers to ring inversion of the parent 1,3-dithiane and 1,2-dithiane, determined at low temperature,[30,31] are slightly below that of cyclohexane ($\Delta G^{\neq}$ = 10.2 kcal mol^{-1}). For perfluoro-1,4-dithiane, $\Delta G^{\neq}$ = 10.1 kcal mol^{-1} (T_C at −33 °C) was measured by ^{19}F NMR.[32] Thus, we suppose that the slow process in the case of **21** comes from the hindrance, which the proximal *gem*-diphenyl groups exert on the ring inversion.

Thiocarbonyl ylides, when not intercepted, usually undergo an irreversible *electrocyclization* affording thiiranes. The example **22** → **23**, reported by Buter, Wassenaar, and Kellogg,[33] elegantly established the *conrotatory* ring closure, a steric course, which was predicted by Woodward and Hoffmann[20b] for the ring opening of cyclopropyl anions to allyl anions. The adamantanethione *S*-methylide, originating from **17**, cyclizes to the spirothiirane, and no dimer was observed.[11] Thiobenzophenone *S*-methylide (**9**), however, either dimerizes giving **21** or undergoes electrocyclization forming **24**, depending on stationary concentration and temperature.

When 0.26 M **8** in THF, kept at −78 °C, was slowly introduced into 1.5-fold the volume of THF at 20 °C, 55% of dithiane **21** was isolated; ^{1}H NMR analysis of the mother liquor indicated 13% of 2,2-diphenylthiirane (**24**) and 25% of 1,1-diphenylethylene (**25**) (Scheme 5). Repeated ^{1}H NMR recordings showed that the conversion **24** → **25** proceeded with a half-life of ≈16 h. Many reagents, especially thiolate anions,[34] catalyse the desulfurization of **24**. Thus, dimerization and electrocyclization of **9** took place in the proportion ≈ 60:40.



Scheme 5

Control by temperature alone was determining when 0.1 M **8** in THF was allowed to decompose at different temperatures. Since **24** is the precursor of **25**, the yields (in % of **8**) were combined:

Table 2

	−45 °C	−25 °C	0 °C	+20 °C
dithiane **21**	91	90	87	79
thiirane **24**	1.8	2.3	5.8	10.4

Since the two processes compete, the free energy changes must be of the same order of magnitude. The dithiane formation is burdened by the large negative $\Delta S^{\neq}$ of bimolecular processes. Therefore, $\Delta H^{\neq}$, which controls the temperature coefficient (see above) alone, must be greater for the unimolecular ring closure **9** → **24**. This is the reason for a 5.8-fold increase of the thiirane pathway between −45 °C and +20 °C.

Schönberg, König et al. emphasized that each system of thione and diazoalkane furnishes *either* the thiirane *or* the 1,3-dithiolane (2:1 product).[7] The statement needs revision. When the Schönberg procedure[4] was reversed, i.e., the solution of thiobenzophenone (**1**) slowly dropped into the ether solution of 1 equiv. of diazomethane at 20 °C, ^{1}H NMR analysis showed the presence of 50% of 1,3-dithiolane **4**, 18% of dimer **21**, and 22% of thiirane **24** (more precisely: 8% of **24** + 14% of **25**). Despite the low stationary concentration of **1,** still 50% of the *S*-methylide is intercepted, an impressive demonstration for the high rate of the cycloaddition, **9** + **1**.

Dithiolane **4** turns blue at the melting point, suggesting a cycloreversion. When **4** was heated in $CDCl_3$ for 35 h *at 135 °C*, conversion into diphenylethylene (**25**) amounted to 66%, i.e., the cycloreversion was followed by electrocyclization, **9** → **24**, and desulfurization.

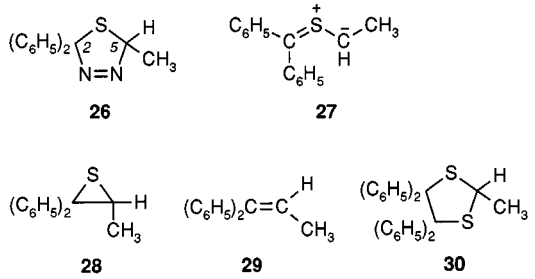
Is it astonishing that the bimolecular dimerization, 2 × **9** → **21**, beats the unimolecular electrocyclization, **9** → **24**? The latter process is not as simple, as it appears at first glance. The thiocarbonyl ylide **9** has a *quasi-planar* structure, and two 90° rotations about the CS bonds are required for generating the new σ-bond. Thus, the resonance energy of the thiocarbonyl ylide is sacrificed early on the energy profile.

Thiobenzophenone *S*-Ethylide

The cycloaddition of diazoethane to **1** in THF at −78 °C proceeded as smooth as that of the lower homolog. The thiadiazoline **26** could be isolated, but the solid exploded when the temperature rose above −40 °C. In the ^{1}H NMR spectrum at −65 °C, the 5-methyl appeared as doublet at δ_H 1.89 and 5-H as quadruplet at 6.03. The ^{13}C NMR spectrum reflects the diastereotopicity of the phenyl groups with two sets of 4 aromatic C-signals.

Thiadiazoline **26** in THF expels N_2 at −45 °C with a half-life of 18 min, i.e., shorter than that of **8** by a factor of 3. Thiobenzophenone *S*-ethylide (**27**) cyclized to give 93% of the thiirane **28** and 3% of 1,1-diphenylpropene (**29**); the

latter came from a partial desulfurization **28** → **29** (Scheme 6). Thus, compared with the behavior of **9**, the additional methyl group in the *S*-ethylide **27** is sufficient to thwart the dimerization leading to a 1,4-dithiane. This accords well with our interpretation of dithiane formation via the initial linkage by the methylene groups.



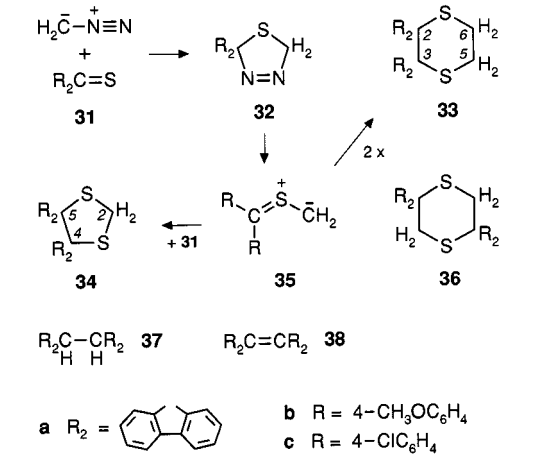
Scheme 6

In his 1931 report, Schönberg et al.[4] briefly mentioned that 1,3-dithiolane **30** was obtained when diazoethane was introduced into the solution of **1** at room temperature. This protocol provided us with 87% of **30**, accompanied by 5% each of **28** and **29**. The reverse procedure, i.e., the slow addition of **1** into the stirred solution of diazoethane at 20 °C, reduced the yield of **30** to 29%, but promoted the electrocyclization: 40% of **28** and 28% of **29**.

The C_{2v} symmetry of 1,3-dithiolane **4** is reduced to C_s in **30**. The phenyl groups located *cis* and *trans* to the 5-CH_3 are pairwise different, as revealed by the ^{13}C NMR parameters.

Fluorene-9-thione *S*-Methylide

Schönberg, König et al.[7] isolated 92% of the 1,3-dithiolane **34a**, when diazomethane was added to fluorene-9-thione (**31a**) in ether at room temperature; the reduction of **34a** with zinc and acid furnished 9,9′-bifluorenyl (**37a**). We confirmed the high yield of **34a** and used Raney nickel in methanol for the hydrogenolysis. The 2-H_2 of **34a** resonates at δ = 4.70. The ^{13}C NMR parameters accord with the point group C_{2v}; there are six aromatic C-signals (4d + 2s), and the s of C-4/C-5 appears at δ = 74.2.



Scheme 7

We observed a rapid fading of the dark-green THF solution of **31a** upon addition of 1 equiv. of diazomethane at −78 °C. N_2 (95%) was liberated from the clear solution of thiadiazoline **32a** at −45 °C, and the colorless dimer **33a** precipitated (Scheme 7). The N_2 evolution at −45 °C followed the first-order with $t_{1/2}$ = 9.1 min; the rate constant is 6 times greater than that of **8**.

The high-melting 1,4-dithiane **33a** has a low solubility. The ^1H NMR spectrum in [D_5]pyridine or $CDCl_3$ (dilute solution) essentially features an AB pattern for 5-H_2 and 6-H_2 with an apparent J = 10.5 Hz; small satellites are indistinct. The appearance of AA′BB′ spectra highly depends on the ratio of the four coupling constants.

There is no sufficient reason to assume the head-tail dimer **36a**. Hindered inversion of **36a** in the centrosymmetric chair conformation should indeed give rise to an AB spectrum for 3-H_2/6-H_2. However, with the separation of the voluminous aromatic substituents in **36a** the major reason for hindrance would be gone. In the ^{13}C NMR spectrum of **33a**, the triplet of C-5/6 at δ = 27.4 and the singlet of C-2/3 at 55.4 disclose a shift to lower frequencies, compared with the parameters of tetraphenyldithiane **21** (31.5, 64.5 ppm); the opposite would be expected for 36a, where the methylene groups are flanked by sulfur *and* fluorenyl. Some fragments in the MS are also better reconcilable with **33a** than with **36a**.

4,4′-Dimethoxy- and 4,4′-Dichlorothiobenzophenone *S*-Methylide

1,3-Dipoles **35b** and **35c** were only briefly studied. Both prefer head-head dimerization to the electrocyclic ring closure.

When ethereal diazomethane was added portionwise to 0.2 M 4,4′-dimethoxythiobenzophenone (**31b**) in ether at room temperature, the disappearance of the deep-blue color was markedly slower than observed for **1**. That is not unexpected. According to rate measurements for the cycloadditions of diphenyldiazomethane, the electron-releasing 4-methoxy groups in **31b** deactivate thiobenzophenone by a factor of 28 ($CHCl_3$, 40 °C).[15]

Bergmann et al.[3] reported in 1930 already on the formation of 1,3-dithiolane **34b** (49%) and established its regiochemistry by treatment with zinc and acid, producing tetraanisylethylene (**38b**). We isolated the crystalline **34b** in 93% yield; the desulfurization by Raney nickel in methanol likewise halted at **38b** (94%).

At −78 °C, the interaction of **31b** with diazomethane required 7 h; that is very slow compared with the titration of **1** with diazomethane. The N_2 loss from the thiadiazoline **32b** in THF at −45 °C was measured by volumetry ($t_{1/2}$ 36.8 min). Dimerization of the *S*-methylide **35b** was observed; the AA′BB′ spectrum for 5-H_2/6-H_2 of the 1,4-dithiane **33b** left no doubt about the structure element $-CH_2-CH_2-$ in the ring.

4,4′-Dichlorothiobenzophenone (**31c**) accepted diazomethane rapidly at −78 °C. Like the other 1,4-dithianes,

33c (82%) is slightly soluble. The NMR evidence for the structure is conclusive. Apart from the AA′BB′ spectrum of 5-H_2/6-H_2 which stretches over 0.5 ppm, the ^{13}C parameters reveal the equivalence of the pairs C-5/6 (t at δ = 31.2) and C-2/3 (s at δ = 63.1). The four 4-chlorophenyl groups are pairwise in different environments, in accordance with C_2 symmetry.

Experimental Section

General: IR: Perkin−Elmer 125. − NMR: Varian A60 for ^1H (60 MHz) and Varian XL 100 for ^1H (100 MHz) and ^{13}C (25.2 MHz); Bruker WP 80 for ^{13}C (20.2 MHz). TMS was used as internal standard and acid-free $CDCl_3$ (stored over dry K_2CO_3) as solvent, if not otherwise stated. − The MS are EI spectra with 70 eV, recorded with MS 902 of AEI, Manchester; some recent recordings with MAT 90 gave peak intensities (isotope peaks) with higher precision. Isotope peaks are given in the form, e.g., ^{13}C% calcd./found. − PLC is thick-layer (1 or 2 mm) chromatography on silica gel, usually Merck F_{254}. − Melting points are uncorrected.

Thioketones are subject to autoxidation; all operations were carried out under a nitrogen or argon atmosphere.

2,5-Dihydro-2,2-diphenyl-1,3,4-thiadiazole (8) and Thiobenzophenone *S*-Methylide (9)

Dimethyl 2,2-Diphenyl-2,5-dihydrothiophene-3,4-dicarboxylate (10): The magnetically stirred solution of 1.14 g (5.75 mmol) of thiobenzophenone (**1**)[35] in 20 mL of THF was cooled to −78 °C (acetone/CO_2 bath) under N_2; 6 mL of ≈ 1.0 M diazomethane[36] in THF was introduced slowly so as to diminish the increase of temperature. When the color of the dark-blue solution lightened, the residual diazomethane solution was added dropwise. The titration worked with a delay of 2−3 s per drop; the solution became colorless and then yellow-tinged by the excess of diazomethane. 1.63 g (11.5 mmol, 2 equiv) of dimethyl acetylenedicarboxylate (DMAD) in 8 mL of THF, precooled to −78 °C, was added, and the solution was kept in a bath at −40 °C (low-temp. thermostat) overnight. After removal of the solvent, the residue was triturated with little methanol, and 1.41 g of colorless crystals, m.p. 137−139.5 °C, were filtered. The mother liquor was brought to dryness by distilling solvent and excess of DMAD in vacuo. A second crop of **10** (38 mg, total yield 71%) was obtained from 1 mL of methanol. The analytical specimen was recrystallized from ether, m.p. 140−142 °C. − ^1H NMR: δ = 3.40, 3.73 (2 s, 2 OCH_3), 4.04 (s, 5-H_2), 7.2−7.6 (m, 2 C_6H_5). − ^{13}C NMR (20.2 MHz): δ = 36.2 (t, C-5), 52.2, 52.5 (2 q, 2 OCH_3), 74.9 (s, C-2), 127.3, 127.9, 128.6 (3 d, 10 arom. CH), 135.2, 143.2, 148.1 (3 s, C-3, C-4, 2 C-1′), 163.4, 165.1 (2 s, 2 C=O). − $C_{20}H_{18}O_4S$ (354.4): calcd. C 67.77, H 5.12, S 9.05; found C 68.04, H 5.19, S 9.01.

Isolation of Thiadiazoline 8: The reaction above could also be carried out by the inverse procedure, i.e., by adding the solution of **1** to the diazomethane solution which was magnetically stirred in a −78 °C bath. This "titration" was even more sensitive; a persistent blue indicated the passing of the point of equivalence. In an experiment in diethyl ether as solvent, **8** crystallized and was suctionfiltered on a precooled funnel. After washing with little precooled ether and pumping off the solvent, the colorless **8** was stable at −78 °C. When the cooling was shut off, the specimen rapidly decomposed with gas evolution at about −20 °C.

Gaseous diazomethane, diluted by N_2,[36] was passed into the solvent to prepare the solutions used above; the concentration was determined by reacting an aliquot with a weighed excess of benzoic acid in ether and back-titration with 0.1 N NaOH.[37] A still simpler access to **8** was the passing of gaseous diazomethane into the solution of 10 mmol of **1** in 30 mL of THF at −78 °C, until the deep-blue color turned to light-yellow. The slight excess of diazomethane can be removed by adding a small amount of **1**. The stock solution was divided into aliquots to study the reactions of **8**.

Kinetic Measurement of the N_2 Extrusion by Nitrometry: The magnetically stirred solution of about 3 mmol of **8** in 20 mL of THF, prepared at −78 °C, was placed into a bath of −44.8 ± 1 °C (thermostat) and connected with a 100 mL nitrometer. The reading of the N_2 volume after 20 min defined V_o, and V_∞ was determined after 10 h (and corrected when necessary). The first-order law, $k\,t = \ln (V_\infty/V_\infty\text{-}V_t)$, was strictly followed, at least for two half-lives. Two runs (0.14 and 0.13 M **8**) provided $10^4\,k_2$: 2.11, 2.03 s^{-1}; linear regression of 25 readings up to 105 min gave a correlation with $r = 0.999$. In the same way, the other experiments of Table 1 were performed.

Deprotonation of 8: 3.0 mmol of **8** in 50 mL of abs. THF were flushed with argon at −78 °C and treated portionwise with 3.1 mmol of LDA in 25 mL of THF, freshly prepared from diisopropylamine and butyllithium. After allowing the solution to come to room temp., the solvent was evaporated, and the lithium salt **12** treated with 50 mL of water and 25 mL of CH_2Cl_2. Workup of the organic phase furnished 315 mg (44%) of *benzophenone N-thioformylhydrazone* (**14**); the yellow prisms were recrystallized from ethanol, m.p. 122−123 °C (122−124 °C).[16] − UV (CH_2Cl_2): λ_{max} (log ε) = 3.31 (4.57), 241 (4.04). − IR (KBr): $\tilde{\nu}$ = 691, 699, 779 st (C_6H_5 out-of-plane deform.), 1279, 1302, 1328 st; 1492 st, 1510 vst (arom. ring vibr., C=N), 3135 m, 3290 w (N−H); ($CHCl_3$): 3290 m (N−H). − ^1H NMR: δ = 7.05−7.92 (m, 2 C_6H_5). 9.72 (s, HC=S; 9.66[16]). − ^{13}C NMR: δ = 128.0, 128.4, 128.5 (3 d, 10 arom. CH), 135.9 (s, 2 C-1 of C_6H_5), 155.2 (s, C=N; 155.5[16]), 189.6 (d, CHS). − MS (70 °C); *m/z* (%): 240 (30) [M^+], 180 (100) [no ^{34}S peak, probably $C_6H_5{-}C{\equiv}N^+{-}C_6H_5$), 163 (90) [$M^+ - C_6H_5$]. − $C_{14}H_{12}N_2S$ (240.3): calcd. C 69.97, H 5.03, N 11.66, S 13.34; found C 69.92, H 5.11, N 11.50, S 13.24.

Lithium Salt 12 and Methyl Iodide: 12, prepared from 3.0 mmol of **8**, as described above, was refluxed with 5 mL of methyl iodide for 1.5 h. Workup with 5% aqueous ammonia/CH_2Cl_2 and PLC (acetone/petroleum ether, 3:7) furnished 365 mg (48%) of *benzophenone N$^\beta$-(methylthiomethylene)hydrazone* (**15**), m.p. 80−82 °C (ethanol). − UV (CH_2Cl_2): λ = 302 (4.14), 238 (4.27). − IR (KBr): $\tilde{\nu}$ = 692, 702, 764, 779 st (C_6H_5 out-of-plane deform.), 1446, 1495 m, 1556 st br (arom. ring vibr., C=N). − ^1H NMR: δ = 2.40 (s, SCH_3), 7.07−7.47 (m, 8 arom. CH), 7.52−7.70 (m, 2 arom. CH), 7.72 (s, HC=N). − MS (70 °C); *m/z* (%): 254 (30) [M^+], 180 (90) [$C_6H_5{-}C{\equiv}N^+{-}C_6H_5$)], 77 (100) [$C_6H_5^+$]. − $C_{15}H_{14}N_2S$ (254.3): calcd. C 70.83, H 5.55, N 11.02, S 12.61; found C 71.20, H 5.65, N 10.90, S 12.71.

Benzophenone N$^\beta$-(Piperidinomethylene)hydrazone (16): 240 mg (1.00 mmol) of **14** was dissolved in 5 mL of piperidine (10 h, 20 °C). Workup with water/CH_2Cl_2 and PLC (CH_2Cl_2/ethanol 99:1) afforded 241 mg (83%) of **16** as a light-yellow oil. − IR (film): $\tilde{\nu}$ = 694, 732, 769, 777 st (C_6H_5 out-of-plane deform.), 1450 st br, 1494 st, 1544 st br, 1618 vst br (C_6H_5 ring vibr., C=N). − ^1H NMR: δ = 1.42−1.75 (m, 3 CH_2), 3.15−3.40 (m, 2 NCH_2), 7.12−7.42 (m, 8 arom. H), 7.42−7.65 (m, 2 arom. H), 8.05 (s, HC=N). − MS (70 °C); *m/z* (%): 291 (43) [M^+], 182 (81), 111 (60), 84 (90) [$C_5H_{10}N^+$],

83 (100) [$C_5H_9N^+$], 77 (48) [$C_6H_5^+$]. − $C_{19}H_{21}N_3$ (291.4): calcd. C 78.31, H 7.26, N 14.42; found C 78.30, H 7.37, N 14.16.

4,4,5,5-Tetraphenyl-1,3-dithiolane (4). − (a): 3.96 g (20.0 mmol) of **1** in 20 mL of ether was treated portionwise with 14 mmol of diazomethane in 20 mL of ether at room temp. When the N_2 evolution ceased and the dark-blue color turned yellow, the excess of diazomethane was destroyed by some drops of acetic acid; on concentration to ≈ 10 mL, 3.90 g (95%) of colorless **4** deposited, m.p. 205−207 °C (blue melt; 199−200 °C[4]). − **(b):** 654 mg (3.30 mmol) of **1** in 10 mL of THF was "titrated" at −78 °C with diazomethane in THF, and 800 mg (4.03 mmol) of **1** in 5 mL of THF was added. After 4 h at −40 °C and several h at room temp., workup furnished 1281 mg (95%) of **4**, m.p. 203−204 °C (dec., blue). − ^{1}H NMR: δ = 3.66 (s, 2-H_2), 6.45−7.49 (m, 2 C_6H_5). − $C_{27}H_{22}S_2$ (410.6): calcd. C 78.98, H 5.40, S 15.62; found C 79.17, H 5.65, S 15.63. − **(c) Hydrogenolysis:** 800 mg (1.95 mmol) of **4** were refluxed in 50 mL of methanol with 15 g of Raney nickel for 4 d. Hot filtering, washing with 200 mL of $CHCl_3$, and evaporation of the solvent furnished 580 mg (90%) of *tetraphenylethylene*, m.p. 222−223 °C.

α-Methoxy-α-(methylthio)diphenylmethane (18). − (a): 4.32 mmol of thiadiazoline **8** in 14 mL of THF at −78 °C was added to 0.2 mL (2.7 mmol) of trifluoroacetic acid in 10 mL of methanol, precooled to −78 °C. After 6 h at −45 °C, the solution was neutralized by dropwise addition of methanolic KOH. The solvent was removed at the rotary evaporator at room temp. and the residue triturated with 10 mL of pentane and filtered. Distillation of the pentane, finally at high vacuum, left 877 mg (83%) of a colorless oil which was almost pure **18** according to the NMR spectra. The analytical specimen was purified by PLC ($CHCl_3$/petroleum ether 1:1). − ^{1}H NMR: δ = 1.63 (s, SCH_3), 3.18 (s, OCH_3), 7.0−7.6 (m, 2 C_6H_5). − ^{13}C NMR: δ = 10.4 (q, SCH_3), 50.4 (q, OCH_3), 94.1 (s, C_q), 127.0 (d, C-2/6 + C-3/5 of 2 C_6H_5), 127.7 (d, C-4 of 2 C_6H_5), 143.6 (s, C-1 of 2 C_6H_5). − MS (30 °C); *m/z* (%): 213 (0.5) [$M^+ - OCH_3$], 197 (6) [$M^+ - SCH_3$], 182 (41) [$(C_6H_5)_2CO^+$], 167 (5) [$M^+ - C_6H_5$], 105 (100) [$C_6H_5-C\equiv O^+$], 77 (53) [$C_6H_5^+$]. − $C_{15}H_{16}OS$ (244.3): calcd. C 73.73, H 6.60, S 13.12; found C 73.66, H 6.35, S 13.13.

(b) Disproportionation of 18: When the ^{1}H NMR spectrum of the above sample was recorded again after 1 and 2 weeks, the signals of α,α-*bis(methoxy)diphenylmethane* (δ = 3.08, s, 2 OCH_3) and α,α-*bis(methylthio)diphenylmethane* (**19**, δ = 1.80, 2 SCH_3) appeared, indicating a partial disproportionation.

(c) 8 and Methanol Without Acid: 500 mg (2.52 mmol) of **1** in 5 mL of THF at −78 °C was converted into **8** and mixed with 20 mL of precooled methanol. The 1,4-dithiane **21** precipitated during the reaction at −40 °C: 450 mg (84%), m.p. 166−169 °C.

8 and Benzoic Acid: 4.04 mmol of **8** in 15 mL of THF at −78 °C was reacted with 541 mg (4.43 mmol) of benzoic acid for 5 h at −40 °C. Evaporation of the solvent left a foul-smelling oil which was subjected to PLC ($CHCl_3$). The first fraction furnished 115 mg (22%) of **19** as light-yellow crystals, m.p. 68−70 °C (pentane). − IR (KBr): ṽ = 694, 736 st (C_6H_5 out-of-plane deform.), 1445, 1496 m, 1592 w (C_6H_5 ring vibr.). − ^{1}H NMR: δ = 1.81 (s, 2 SCH_3), 7.05−7.56 (m, 2 C_6H_5). − ^{13}C NMR: δ = 13.3 (q, 2 CH_3), 69.5 (s, C_q), 127.0 (d, 2 C-4), 127.8. 128.4 (2 d, 2 C-3/5, 2 C-2/6), 143.5 (s, 2 C-1). − MS (30 °C); *m/z* (%): 260 (3) [M^+], 213 (100) [$M^+ - SCH_3$], 165 (31) [9-fluorenyl$^+$], 121 (26) [$C_6H_5-C\equiv S^+$], 77 (7) [$C_6H_5^+$]. − $C_{15}H_{16}S_2$ (260.4): calcd. C 69.18, H 6.19, S 24.63; found C 69.57, H 6.23, S 24.62. − The second PLC fraction afforded 258 mg (35%) of *benzophenone*, m.p. 47.5−48.5 °C (pentane), and the third fraction (eluted by methanol) consisted of 237 mg of benzoic acid. − In a second experiment with 2.50 mmol of **8** and 3.0 mmol of benzoic acid, the reaction solution was neutralized with 0.1 N NaOH. Workup with water/ether afforded 322 mg (71%) of benzophenone, m.p. 47−48 °C (pentane).

2,2,3,3-Tetraphenyl-1,4-dithiane (21). − (a): 11.1 mmol of **8** in 25 mL of THF was prepared at −78 °C; **8** partially crystallized and dissolved with rising temperature. On warming to −40 °C (1 h) and keeping at −30 °C over night, N_2 was evolved, and the crystallization of the colorless **21** took place; in two fractions 2.24 g (95%) was obtained, m.p. 145−150 °C (dec.) and, recrystallized from $CHCl_3$, m.p. 166−169 °C (dec.); the mother liquor contained 1.2% of *1,1-diphenylethylene* (**25**, NMR analysis see below). Crystalline **21** turns violet in sunlight. − ^{1}H NMR ($CDCl_3$): δ = 2.44−3.70 (AA′BB′, 12 lines visible at 25 °C, 5-H_2, 6-H_2), 6.7−7.8 (m, 20 arom. H); ([D_5]bromobenzene, 60 MHz): 2.32−3.46 (AA′BB′ at +35 °C); broadens on increase of temp. and reaches coalescence at +74 °C; at 102 °C s δ = 2.90 (A_4); (400 MHz): δ = 2.56, 3.14 (2 d + satellites, AA′XX′, $J_{appar.}$ = 9.8 Hz). − ^{13}C NMR ($CDCl_3$, 20.2 MHz): δ = 31.4 (t, C-5/6), 64.5 (s, C-2/3), 125.2, 126.4, 126.8, 131.9, 134.5 (5 d, 20 arom. CH for 2 pairs of diastereotopic C_6H_5), 144.7, 146.3 (2 s, 2 C-1′ of 4 C_6H_5). − MS (70 °C); *m/z* (%): 424 (1.6) [M^+], 332 (11) [$M^+ - 92$, $C_{26}H_{20}^+$; ^{13}C 3.3/3.1], 230 (6) [$C_{13}H_{10}S_2^+$?], 229 (7), 198 (90) [**1**$^+$; ^{13}C 13/14, (^{34}S+$^{13}C_2$) 4.9/4.7], 165 (100) [9-fluorenyl$^+$, ^{13}C 14.5/14.6], 121 (61) [$C_6H_5-C\equiv S^+$; ^{13}C 4.8/5.1; (^{34}S+$^{13}C_2$) 2.9/2.9], 105 (11) [$C_8H_9^+$, α-phenylethyl$^+$?], 77 (22) [$C_6H_5^+$]. − $C_{28}H_{24}S_2$ (424.6): calcd. C 79.20, H 5.70, S 15.10; found C 79.32, H 5.60, S 15.11.

(b) Determination of the Barrier to Ring Inversion: Based on 9 visible lines, due to 5-H_2/6-H_2, in the ^{1}H NMR spectrum (60 MHz) of **21** in [D_5]bromobenzene, the AA′BB′ pattern was simulated by the program *Numarit*[38] (in Hz); ν_A = 156.6, ν_B = 190.0, J_{gem} = −13.0 Hz, and J_{vic} = 12.6, 2.8, 1.9 Hz; Δν = 33.4 Hz. In the 400 MHz spectrum, T_C is expected around 100 °C; massive decomposition of **21** started even earlier. Therefore, we used the 400 MHz parameters only to determine the temperature dependence of Δν (transformed to 60 MHz) in Hz (°C): 34.9 (25), 34.6 (45), 34.2 (65). The rate constant of ring inversion was calculated with $\Delta\nu$ = 34.0 Hz at T_C = 74 °C by the expression for AB spectra:[39] $k_C = \pi[0.5\ (\Delta\nu^2 + 6\ J_{AB}^2)]^{1/2} = 103\ s^{-1}$.

The free energy change amounts to 17.2 ± 0.6 kcal mol^{-1}.

(c): 3.8 equiv. of piperidine was added to the THF solution of **8** at −78 °C. The N_2 expulsion took place at −40 °C, and workup afforded 84% of dithiane **21**. Corresponding experiments with 2 equiv. of phenol or aniline yielded 71% and 72% of **21**, respectively.

Competition of Dimerization and Electrocyclization for 10. − (a): From a double-jacketed dropping funnel, cooled to −78 °C, the solution of **8** (3.16 mmol) in 12 mL of THF was introduced within 20 min into 20 mL of THF, magnetically stirred. After concentration at the rotary evaporator, 5 mL of petroleum ether was added and 366 mg (55%) of **21** was filtered. The residue of the mother liquor was ^{1}H NMR analyzed ($CDCl_3$) with stilbene (δ_H = 6.47) as weight standard: 91 mg (14%) of *2,2-diphenylthiirane* (**24**, δ_H = 2.98) and 143 mg (25%) of *1,1-diphenylethylene* (**25**, δ_H = 5.38). − **(b):** The solution of 4.0 mmol of **8** in 11 mL of THF, prepared at −78 °C, was mixed under stirring with 29 mL of THF, thermostated in a −45° bath. After 5 h at −45 °C the THF was evaporated at room temp., and the residue triturated with 10 mL of ether/petroleum ether (1:1). **21** (772 mg) remained undissolved; a second fraction of 15 mg included, the yield ot **21** was 91%. The ^{1}H NMR analysis ($CDCl_3$) of the mother liquor indicated 0.07 mmol of (**24** + **25**, 1.8%). Three analogous experiments at −25 °C (2 h), 0 °C

(1 h), and 20 °C (30 min) afforded the yields listed in Table 2. – **(c):** 758 mg (3.82 mmol) of **1** in 10 mL of ether was dropped into the stirred solution of 3.8 mmol of diazomethane in 20 mL of ether at room temp. within 30 min. The residue after evaporation was triturated with ether/petroleum ether as above; 537 mg of colorless powder consisted of 390 mg (50%) of **4** and 140 mg (17%) of **21**, as the ^{1}H NMR analysis ($CDCl_3$, 2-methylnaphthalene as weight standard, δ = 2.42) of the CH_2 signals indicated. The oily residue of the mother liquor contained 8% of **24** and 14% of **25** (all yields based on **1**). – **(d):** 42.4 mg (103 μmol) of **4** in 0.5 mL of $CDCl_3$ was heated in a closed NMR tube to 135 °C for 35 h. The CH_2 signal of **4** had disappeared, and 66% of **25** was formed; the deep-blue color comes from the liberated **1**.[40]

5-Methyl-2,2-diphenyl-2,5-dihydro-1,3,4-thiadiazol (26)

1 and Diazoethane. – (a): **1** (752 mg, 3.79 mmol) in 7 mL of CH_2Cl_2 was cooled to −78 °C and mixed with the precooled solution of 1 equiv. of diazoethane in 5.6 mL of CH_2Cl_2. The dark-blue color vanished within several s, and thiadiazoline **26** partially precipitated. N_2 evolution took place at −40 °C. After warming to room temp., the solvent was removed, and the oil subjected to ^{1}H NMR analysis: 93% of *3-methyl-2,2-diphenylthiirane* (**28**) and 3% of *1,1-diphenylpropene* (**29**). The desulfurization **28** → **29** (catalysts unknown) was slow at room temp.; $t_{1/2} \approx 400$ h was estimated from repeated ^{1}H NMR measurements. – ^{1}H NMR of **28**: δ = 1.24 (d, *J* = 6.0 Hz, CH_3), 3.62 (q, *J* = 6.0 Hz, 3-H), 6.9−7.4 (m, 2 C_6H_5). – ^{13}C NMR of **28**: δ = 18.8 (q, CH_3), 42.9 (d, C-3), 59.6 (s, C-2), 126.8, 127.1, 2 × 127.7, 128.0, 130.2 (6 d, 10 arom. CH; 2 diastereotopic C_6H_5), 138.8, 144.6 (2 s, 2 C-1′ of 2 C_6H_5). – ^{1}H NMR of **29**: δ = 1.68 (d, *J* = 7.0 Hz, CH_3), 6.10 (q, *J* = 7.0 Hz, 2-H), 7.0−7.6 (m, 2 C_6H_5).

(b) NMR spectra of 26: A solution of **26** in $CDCl_3$ was prepared at −78 °C. – ^{1}H NMR (100 MHz, −65 °C): δ = 1.89 (d, *J* = 7.0 Hz, 5-CH_3), 6.03 (q, *J* = 7.0 Hz, 5-H), 7.2−7.6 (m, 2 C_6H_5). – ^{13}C NMR (25 MHz, −60 °C, signals of **28** deducted): δ = 20.3 (q, CH_3), 95.7 (d, C-5), 116.0 (s, C-2), 126.9, 127.0, 127.1, 128.1, 128.2 (5 d, 10 arom. CH of 2 diastereotopic C_6H_5), 139.6, 142.3 (2 s, 2 C-1′ of 2 C_6H_5).

Kinetics of N_2 Evolution: The volumetric rate measurement at −45 °C was carried out as described above for **8**. 0.15 M **26** in THF afforded $k_1 = 6.34\ 10^{-4}\ s^{-1}$.

2-Methyl-4,4,5,5-tetraphenyl-1,3-dithiolane (30). – (a): The orange 0.5 M solution of diazoethane in ether was dropwise added to the stirred solution of 995 mg (5.02 mmol) of **1** in 7 mL of THF at room temp., until the dark-blue color had faded. After removal of the solvent, the residue crystallized from ether/pentane (1:1): 924 mg (87%) of colorless **30**, m.p. 172−174 °C (dec., blue); ref.[4]: no yield given, m.p. 170−172 °C. – ^{1}H NMR: δ = 1.65 (d, *J* = 6.3 Hz, CH_3), 4.09 (q, 2-H), 6.9−7.6 (m, 10 arom. H). – ^{13}C NMR (20 MHz): δ = 18.4 (q, CH_3), 42.7 (d, C-2), 79.6 (s, C-4/5), 126.1, 126.2, 126.4, 126.6, 131.3, 132.0 (6 d, 2 diastereotopic pairs of C_6H_5), 142.9, 143.9 (2 s, 4 C-1′ of C_6H_5). – MS (80 °C); *m/z* (%): 424 (1.3) [M^+], 332 (17) [$M^+ - CH_2S_2$, $(C_6H_5)_2C{=}C(C_6H_5)_2^+$ or isomer; ^{13}C 5.0/4.8, $^{13}C_2$ 0.7/0.6], 255 (4) [332 − C_6H_5; ^{13}C 0.8/0.7], 254 (4), 253 (7), 252 (5), 226 (94) [**27**$^+$, $C_{15}H_{14}S^+$; ^{13}C 16/17, (^{34}S+$^{13}C_2$) 5.4/5.6], 225 (56) [$C_{15}H_{13}S^+$, (**27**$^+$- H)], 211 (30) [$C_{14}H_{11}S^+$; ^{13}C 4.6/5.0, (^{34}S+$^{13}C_2$) 1.7/1.7], 198 (64) [**1**$^+$; ^{13}C 9/10, (^{34}S+$^{13}C_2$) 3.5/3.5], 197 (21) [$C_{13}H_9S^+$], 194 (33) [$C_{15}H_{14}^+$; ^{13}C 5.5/5.8], 193 (26) [$C_{15}H_{13}^+$, 9-ethylfluorenyl$^+$], 179 (12) [$C_{14}H_{11}^+$, 9-methylfluorenyl$^+$], 178 (21) [$C_{14}H_{10}^+$], 165 (100) [$C_{13}H_9^+$, 9-fluorenyl$^+$; ^{13}C 15/16], 152 (9) [$C_{12}H_8^+$, biphenylene$^+$], 121 (48) [$C_6H_5{-}C{\equiv}S^+$; ^{13}C 3.8/4.1, (^{34}S+$^{13}C_2$) 2.3/2.4], 77 (12) [$C_6H_5^+$]. – The mother liquor was evaporated. ^{1}H NMR analysis ($CDCl_3$) with *N,N*-dimethylaniline as weight standard indicated 5% of 28 and 5% of **29**. – **(b):** Ethereal 0.35 M **1** was dropped into the stirred solution of 2.04 mmol of diazoethane in 10 mL of ether at room temp., until the color had changed to light-blue. Workup as above gave 247 mg (29%) of **30** and the ^{1}H NMR analysis revealed 40% of **28** and 28% of **29** (all yields based on diazoethane).

Fluorene-9-thione *S*-Methylide (35a)

Dispiro[1,3-dithiolane-4,9′;5,9′′-bis(fluorene)] (34a). – (a): Fluorene-9-thione (**31a**, 1.96 g, 10.0 mmol) in 25 mL of ether at room temp. was treated portionwise with an excess of ethereal diazomethane, until the dark-green color turned yellow, and became colorless, when a few drops of acetic acid were added. After concentration to ≈ 10 mL, 1.90 g (94%) of colorless **34a** deposited, m.p. 259−262 °C (dec., red melt; 253−256 °C[7]) after recrystallization from toluene. – ^{1}H NMR: δ = 4.70 (s, 2-H_2), 6.9−7.6 (m, 16 arom. H). – ^{13}C NMR (25 MHz): δ = 32.4 (t, C-2), 74.2 (s, C-4/5), 119.1, 126.4, 126.5, 128.3 (4 d, 16 arom. CH), 140.0, 144.5 (2 s, 8 arom. C_q).

(b) Hydrogenolysis: 1.02 g (2.51 mmol) of **34a** and 20 g of Raney nickel (Merck, activated) were refluxed in 100 mL of methanol for 4 d. Hot filtration, washing with $CHCl_3$, and evaporation of the solvent gave 580 mg (70%) of 9,9′-bifluorenyl (**37a**), colorless crystals, m.p. 248−249 °C ($CHCl_3$), 246−247 °C.[7] – ^{1}H NMR: δ = 4.83 (s, 2 benzylic H), 6.83−7.75 (m, 16 arom. H). – MS (90 °C); *m/z* (%): 330 (15) [M^+], 165 (100) [$C_{13}H_9^+$, 9-fluorenyl$^+$; ^{13}C 15/13].

Dispiro[1,4-dithiane-2,9′;3,9′′-bis(fluorene)] (33a). – (a): 655 mg (3.34 mmol) of **31a** in 10 mL of THF was cooled to −78 °C. The dark-green color faded upon slow addition of 1 equiv. of diazomethane in ≈ 1 min. No N_2 evolution was observed at −78 °C; when the clear solution was placed in a −45 °C bath, 79.5 mL of N_2 (3.14 mmol, 95%) were liberated within 2 h, and a colorless powder precipitated. Removal of the solvent at the rotary evaporator left 625 mg (89%) of **33a**, m.p > 250 °C (dec.), which has a low solubility in the usual solvents. Recrystallization from benzene furnished colorless platelets, m.p. > 260 (dark-red black). – ^{1}H NMR ([D_5]pyridine): δ = 3.13, 4.16 (nearly AB, *J* = 10.5 Hz, 5-H_2/6-H_2), 6.1−7.6 (16 arom. H); ($CDCl_3$, 100 MHz): 3.07, 4.07 (AB, *J* = 10.4 Hz, 5-H_2/6-H_2), 6.05−7.56 (m, 16 arom. H); due to the low solubility, the satellites expected for AA′BB′ are not very distinct. – ^{13}C NMR ($CDCl_3$, 20 MHz): δ = 27.4 (t, C-5/6), 55.4 (s, C-2/3), 119.0, 120.2, 125.2, 126.3, 126.5, 127.7, 2 × 128.3 (8 d, 16 arom. CH), 139.7, 140.2, 144.0, 149.5 (4 s, 8 arom. C_q). – MS (140 °C); *m/z* (%): 420 (26) [M^+; ^{13}C 8.2/8.1, (^{34}S+$^{13}C_2$) 3.6/3.5], 360 (2) [$M^+ - SC_2H_4$, $C_{26}H_{16}S^+$; ^{13}C 0.54/0.56, (^{34}S+$^{13}C_2$) 0.16/0.13], 328 (16) [$C_{26}H_{16}^+$, 9,9′-bifluorenylidene$^+$; ^{13}C 4.5/4.1, no ^{34}S peak], 327 (16), 326 (12), 210 (6) [$C_{14}H_{10}S^+$, **35a**$^+$ or M^{++}; ^{13}C 0.88/0.79], 196 (100) [**31a**$^+$; ^{13}C 14.5/13.7; (^{34}S+$^{13}C_2$) 5.4/4.9], 165 (1) [$C_{13}H_9^+$], 152 (6) [$C_{12}H_8^+$; ^{13}C 0.86/0.85]. – $C_{28}H_{20}S_2$ (420.6): calcd. C 79.96, H 4.79, S 15.25; found C 80.26, H 4.67, S 15.26.

(b) Rate of N_2 Evolution from 32a: The N_2 extrusion (nitrometry) of 20 mL 0.167 M **32a** in THF at −45 °C followed the first order; with $k_1 = 1.27\ 10^{-3}\ s^{-1}$, the rate constant is 6.2 times higher than that of **8**.

4,4′-Dimethoxythiobenzophenone *S*-Methylide (35b)

2,2,3,3-Tetrakis(4-methoxyphenyl)-1,4-dithiane (33b). – (a): The reaction of thione **31b** with 1 equiv. of diazomethane in THF at −78 °C required 7 h and afforded a clear solution of **32b**. Nitrometry of the N_2 extrusion from 20 mL of 0.15 M **32b** in THF at −45 °C

furnished $k_1 = 3.14 \cdot 10^{-4}\ s^{-1}$. The unstable colorless dimer **33b** was isolated. – ^{1}H NMR: δ = 2.77–3.35 (symmetric AA′BB′, 5-H_2/6-H_2), 3.68, 3.77 (2 s, 4 OCH_3), 6.07–7.53 (m, 16 arom. H). – $C_{32}H_{32}O_4S_2$ (544.7): calcd. C 70.56, H 5.92; found C 71.18, H 5.80.

(b): When the same reaction was carried out in ether at −78 °C overnight, the *2,5-dihydro-2,2-bis(4-methoxyphenyl)-1,3,4-thiadiazole* (**32b**) deposited in crystals which were suction-filtered. On warming, decomposition occurred < 0 °C.

4,4,5,5-Tetrakis(4-methoxyphenyl)-1,3-dithiolane (34a). – (a): The reaction of 2.58 g (10.0 mmol) of **31b** in 50 mL of ether with ethereal diazomethane at room temp. required 20–30 min for the disappearance of the blue color, and some drops of acetic acid removed the yellow color of the excess of diazomethane. **34a** was obtained in colorless crystals (2.60 g, 93%), m.p. 161–162 °C (cyclohexane/benzene); ref.[3]: 49% yield, m.p. 161–162 °C. – ^{1}H NMR: δ = 3.66 (s, 2-H_2), 3.75 (s, 4 OCH_3), 6.58, 7.53 (AA′BB′ of 16 arom. H). – **(b):** *Hydrogenolysis of* **34a** was achieved by Raney nickel in refluxing methanol, as described above for **4**. *Tetrakis(4-methoxyphenyl)ethylene* (**37b**) was obtained in 94% yield, m.p. 185–186.5 °C[3] after recrystallization from toluene. – ^{1}H NMR: δ = 3.70 (s, 4 OCH_3), 6.5–7.1 (AA′BB′, 16 arom. H). – $C_{30}H_{28}O_4$ (452.5): calcd. C 79.62, H 6.24; found C 79.61, H 6.27.

4,4′-Dichlorothiobenzophenone *S*-Methylide (35c)

2,2,3,3-Tetrakis(4-chlorophenyl)-1,4-dithiane (33c):[41] 1.06 (3.97 mmol) of 4,4′-dichlorothiobenzophenone (**31c**)[35,42] in 10 mL of THF was cooled to −78 °C and stirred; 3.5 mL of 1.14 M diazomethane in THF was added within 10 min. The color turned from blue to light-yellow, and some colorless **32c** deposited. The mixture was removed from the cold bath and diluted with 200 mL of pentane (20 °C). After the N_2 evolution was finished, the solvent was evaporated and the crystalline residue triturated with 15 mL of methanol: 920 mg (82%) of **33c**; recrystallized from $CHCl_3$/pentane, the m.p. was 154–156 °C (dec.). – ^{1}H NMR: δ = 2.84–3.30 (AA′BB′, 5-H_2/6-H_2), 6.88–7.45 (m, 16 arom. H). – ^{13}C NMR: δ = 31.2 (t, C-5/6), 63.1 (s, C-2/3), 125.7, 127.0, 132.9, 135.6 (4 d, 2 × 8 arom. CH), 132.7, 133.4, 142.3, 143.9 (4 s, 2 × 4 arom. C_q). – MS (120 °C): *m/z* of most populous isotope peak (%): 562 (1) [M^+], 470 (5) [$C_{26}H_{16}Cl_4^+$; the intensities of the six isotope peaks correspond to natural abundances], 266 (100) [**31c**$^+$], 231 (63) [**31c**$^+$ − Cl], 155 (33) [$ClC_6H_4–C{\equiv}S^+$]. – $C_{28}H_{20}Cl_4S_2$ (562.4): calcd. C 59.79, H 3.58, S 11.40; found C 59.63, H 3.72, S 11.38.

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