Bis(dimesitylmethylene)-1,3-dithietane, -1,2,4-trithiane, and -1,2,4,5-tetrathiane. Conformation and DNMR Study. Observable Dimesityl Thioketene

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The reaction of dimesityl ketene with P_2S_5 and pyridine gives 2,4-bis(dimesitylmethylene)-1,3-dithietane (**3**), 3,6-bis(dimesitylmethylene)-1,2,4,5-tetrathiane (**4**), 3,5-bis(dimesitylmethylene)-1,2,4-trithiane (**5**), and dimesityl thioketene **2** as a transient. The structures of **3** and **4** were determined by X-ray crystallography. The dimesitylmethylene moieties in **3** and **4** have a propeller conformation, and the tetrathiane ring in **4** has a twist-boat conformation. Static NMR data are consistent with the presence of two enantiomers and one meso form for **3** and of three pairs of enantiomers for **4**. The several aromatic signals observed for **3** and **4** at slow exchange at 160 K coalesce to a single signal at higher temperatures. The threshold barriers for these dynamic processes are 12.7 (**3**) and 13.3 (**4**) kcal mol^{-1}, and the dynamic behavior was analyzed in terms of flip processes. On standing, a solution of **3** develops a blue color which is attributed to formation of **2**, by retro-dimerization of **3**. Diphenylacetyl chloride gives with P_2S_5 the analog of **5** and its one-double bond reduction product. Ditipylketene forms a product identified tentatively as the analog of **3**.

Introduction

Thioketenes **1** ($R^1R^2C{=}C{=}S$) are mostly reactive, short-lived species which dimerize rapidly,[1] similarly to their ketene analogs.[2] Bulky substituents reduce the reactivities of ketenes,[3] and crystal structures of dimesityl[4] and ditipyl[5] ketenes (mesityl = Mes = 2,4,6-$Me_3C_6H_2$; tipyl = Tip = 2,4,6-i-$Pr_3C_6H_2$) were determined by X-ray diffraction,[5,6] and both are stable to thermal dimerization. The structure of 2,6-di-*tert*-butylcyclohexyl thioketene was determined by X-ray diffraction,[7a] and di-*tert*-butyl thioketene is isolable and stable to dimerization.[7b] However, in attempts to apply a known method for a C=O → C=S transformation[1,8] for preparing dimesityl thioketene **2** and analogs from the corresponding ketene and P_2S_5 in pyridine, the dimer of **2** and trithiane- and tetrathiane-substituted compounds were formed. Fewer analogs were also obtained from ditipyl ketene and diphenylacetyl chloride. These compounds contain two 2,2-diarylmethylene groups, and since the dynamic behavior of dimesityl and related vinyl propellers were extensively studied by us,[9,10] we investigated by DNMR the rotational behavior of two of the compounds obtained. Also, although **2** is apparently formed but not accumulated in the C=O → C=S transformation, it is apparently generated by retro-dimerization of its dimer.

Results

Synthesis: (a) Mesityl-Substituted Derivatives. In the reaction of dimesityl ketene and P_2S_5 in pyridine, a blue color ascribed to dimesityl thioketene **2** was initially formed at the beginning of the reaction, but it disappeared after a few minutes. Instead, three *exo*-bis-(2,2-dimesitylmethylene) heterocycles **3**−**5** were formed (eq 1 in Scheme 1).

2,4-Bis(dimesitylmethylene)-1,3-dithietane, **3**, the dimer of **2**, was isolated in 7% yield and identified by microanalysis, X-ray diffraction, and spectral properties. In $CDCl_3$ at rt its ^1H NMR spectrum displays only two signals in a 4.5:1 ratio: at 2.17 ppm, ascribed to the *o*- and *p*-Me-H and at 6.77 ppm, ascribed to the *m*-mesityl-H. Its ^{13}C spectrum displays eight signals: at 20.8 and 21.2 ppm (2:1 ratio) ascribed to the *o*- and *p*-Me groups, at 121.1 and 137.1 ppm, ascribed to the Mes_2*C*=C and the C=*C*(S-)$_2$ carbons, respectively, and four mesityl-C signals at 128.2−136.8 ppm. The mass spectrum shows a molecular peak at m/z 588 and a peak at m/z 294 ascribed to $Mes_2C{=}C{=}S^+$.

3,6-Bis(dimesitylmethylene)-1,2,4,5-tetrathiane, **4**, was obtained in 17% yield and identified by microanalysis, X-ray crystallography, and spectral properties. At 400 K its ^1H NMR spectrum in $Cl_2CDCDCl_2$ displayed 3:1.5:1 signals at 2.21, 2.25, and 6.79 ppm ascribed to the 24 *o*-Me, 12 *p*-Me, and 8 Ar-H protons. The ^{13}C NMR spectrum (330 K, $Cl_2CDCDCl_2$) displayed eight signals at 22.2, 22.5 (in a 2:1 ratio) ascribed to the *o*- and *p*-Me-C, and at 130.8−141.1 ppm ascribed to the C=C and Ar-C. In the MS the molecular peak is at m/z 652 and peaks showing consecutive loss of sulfur atoms [620 (($Mes_2C{=}C)_2S_3^+$), 588 (($Mes_2C{=}C)_2S_2^+$)] or cleavage [294 ($Mes_2C{=}C{=}S^+$)] were also observed.

The formation of **5** was deduced from the NMR study (see below).

[⊗] Abstract published in *Advance ACS Abstracts,* September 15, 1996.

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[4] Fuson, R. C.; Rowland, S. P. *J. Am. Chem. Soc.* **1943**, *65*, 992.

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[10] (a) Rappoport, Z.; Biali, S. E. *Acc. Chem. Res.* **1988**, *21*, 442. (b) Hart, H.; Rappoport, Z.; Biali, S. E. In *The Chemistry of Enols*; Rappoport, Z., Ed.; Wiley: Chichester, 1990; Chapter 8, pp 481−590.

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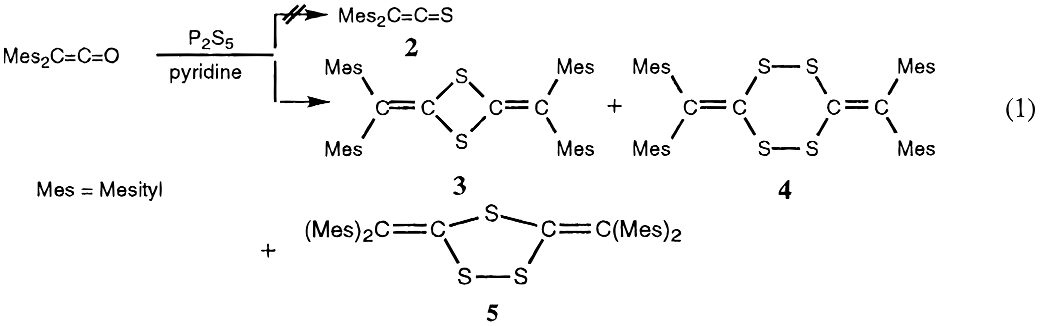
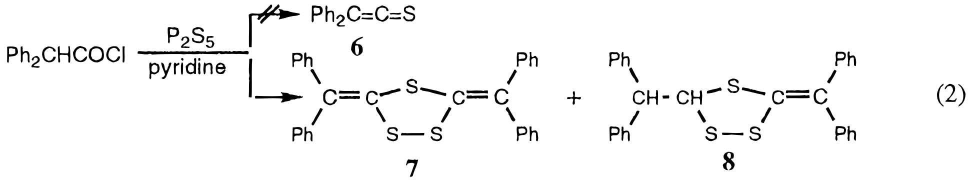
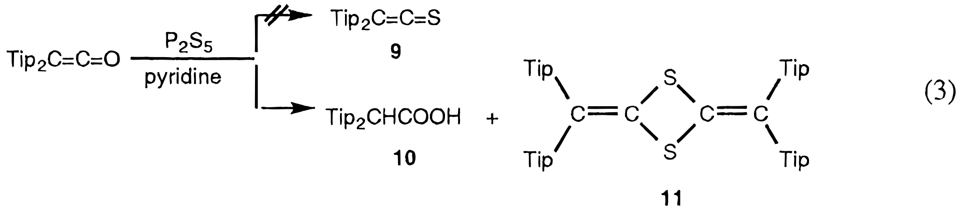
Scheme 1



Scheme 2



Scheme 3



(b) Phenyl-Substituted Derivatives. Reaction of diphenylacetyl chloride and P_2S_5 in pyridine did not give diphenyl thioketene, **6**. Instead, 14% of 3,5-bis(diphenylmethylene)-1,2,4-trithiane (**7**) and 5% of 3-(diphenylmethylene)-5-(diphenylmethyl)-1,2,4-trithiane (**8**) were obtained (eq 2 in Scheme 2).

The known **7**[11] shows a molecular peak at m/z 452 and a fragment at 210 ($Ph_2C{=}C{=}S^+$). The ^1H NMR ($CDCl_3$, rt) displays an aromatic multiplet at δ 7.24–7.39. The ^{13}C spectrum ($CDCl_3$, rt) displays 10 signals at the 127.9–142.0 region.

Compound **8**, the reduction product of one C═C of **7** displays peaks at m/z 454 (M^+), 242 ($Ph_2C{=}CS_2^+$), 212 (Ph_2CHCHS^+), and 210 (B, $Ph_2C{=}C{=}S^+$). The ^1H NMR spectrum ($CDCl_3$, rt) display two vicinal aliphatic ^1H doublets at 4.56 and 5.75 ppm and an Ar-H multiplet at δ 7.16–7.37. The ^{13}C NMR ($CDCl_3$, rt) displays signals at 55.2 ($Ph_2\mathit{C}$), and at 69.0 ppm (saturated ring C), twelve *C*-Ph signals at 127.3–129.4 ppm, two signals at 132.5 and 140.9 ppm (C═C), and four *ipso* signals at 141.7–142.6 ppm.

(c) Tipyl-Substituted Derivatives. Ditipyl thioketene (**9**) was not obtained from ditipyl ketene[5] and P_2S_5. Instead, ditipylacetic acid (**10**)[5] (24%) and 40% of a compound, *tentatively* identified as **11**, the dimer of **9**, were obtained (eq 3 in Scheme 3). The $^+$DCI mass spectrum of **11** showed signals at m/z 725 ($MH_3^+ - Tip$), 521 ($MH_3^+ - 2Tip$), 464 ($Tip_2C{=}C{=}SH_2^+$, 100%); −DCI: m/z 927 (MH_3, 100%), 463 ($Tip_2C{=}C{=}SH$, 7%).

In the ^1H NMR spectrum ($CDCl_3$, rt) only tipyl rings were observed as judged by the 18:3:2 ratio of three groups of signals: (i) i-Pr-Me overlapping doublets at 0.87–1.35 ppm, (ii) a multiplet at 2.65–3.20 (i-Pr-H), and (iii) three 1:1:2 Ar-H signals at 6.90, 6.97, and 7.06 ppm. The latter observation suggests the presence of two enantiomers and one meso form in analogy with **3** (see below). We did not have enough material for a detailed study.

Dimesityl Thioketene. When the reaction mixture from dimesityl ketene was chromatographed, the fraction identified as **3** was initially light yellow, but on standing at rt it reproducibly developed a deep blue color. At 0 °C, pale yellow crystals of **3** precipitated, and TLC of the blue filtrate displayed only the two spots corresponding to **3** and the blue compound. Yellow solutions of **3** in $CDCl_3$ or CD_2Cl_2 did not change color during several months at 0 °C, but turned blue when brought to rt.

A UV-vis spectrum of the blue solution in CD_2Cl_2 showed λ_{max} at 582 nm. The IR spectrum displayed absorptions at 1608 and 1742 cm^{-1}. Mass spectra of the blue solution without attempted separation gave signals once at m/z 588 (100%, B of **3**) and 295 (100%, $Mes_2C{=}C{=}SH^+$), but after a different reaction time, no signal at m/z 588 was observed, indicating the possibility that the mixture contains two compounds.

A ^1H NMR spectrum (CD_2Cl_2, rt) display five signals at 2.16, 2.19, 2.27, 6.78 and 6.89 in a 6:2:3:0.6:2 ratio, respectively. Two of these belong to **3** and three to the blue species. In nitrobenzene, signals at 2.25 (*o*-Me), 2.28 (*p*-Me), 6.84 (Ar-H) for **3** and 2.03 (*o*-Me), 2.40 (*p*-Me), and 6.75 (Ar-H) for the blue compound were observed. The ^{13}C NMR spectrum of the mixture at CD_2Cl_2 (rt) displayed 15 signals at 20.7, 20.7, 21.0, 21.1, 86.3, 121.0, 126.1, 128.2, 129.4, 129.8, 132.2, 136.8, 137.2, 137.7, and *257.0* ppm.

From the separate signals in $C_6D_5NO_2$ the monomer:dimer ratio after it reached a constant value was 3.3:1 at rt starting with ca. 0.03 M of the dimer. It is unknown if this is the equilibrium ratio, but if this is the case the $[\mathbf{2}]^2/[\mathbf{3}]$ ratio is ca. 0.12.

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[11] Kyi, H. J.; Praefcke, K. *Tetrahedron Lett.* **1975**, 555.

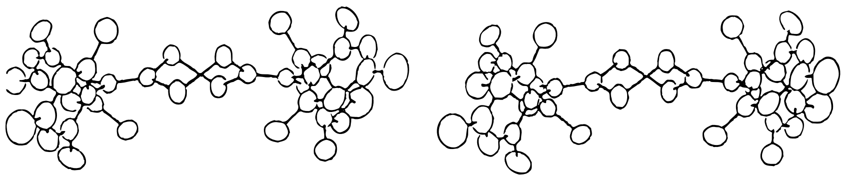
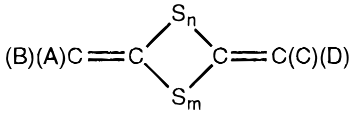


Figure 1. Stereoview of **4**.

The λ_{max}, the ν_{max} = 1742 cm^{-1}, and $\delta^{13}C$ = 257.0 ppm identify convincingly the new species as a thioketene; e.g., λ_{max} (nm) for **1**, $R^1 = R^2$ = *t*-Bu, *p*-ClC_6H_4, Ph are 570,[7b] 627,[12a] 624,[12a] respectively, and for R^1= H, R^2= *t*-Bu, 575 nm.[12a] Diaryl and dialkyl thioketenes display a strong IR stretching around ν_{max} = 1750 cm^{-1}[11b] (e.g., 1725−1758 cm^{-1} for the ketenes above)[7b,12a] due to a ν_{asym} of the C=C=S group,[1b] and a very low field *C*=S signal at 215−285 ppm.[1b,12b] The blue compound is therefore probably dimesityl thioketene **2**, and the phenomenon observed is a dimer (**3**) ⇌ monomer (**2**) retro-dimerization. On this basis we can extract the signals for **2** from the spectra of the **2**/**3** mixtures. They are ^1H NMR δ: 2.16(*o*-Me), 2.27(*p*-Me), and 6.89(Ar-H) ppm;^{13}C NMR δ: 86.3(allenic C) and 257.0(C=S) ppm.

Solid State Structures of 3 and 4. X-ray diffraction structures of both **3** and **4** have been determined. That of **3** is the first 1,3-dithietane structure having two exo diarylmethylene groups, i.e., **12**, *m* = *n* = 1.[13] The central ring is planar having an inversion center in the middle of the ring exchanging the two pairs of the mesityl groups on its both sides. A C_2 axis passing through the double bonds, exchanges two geminal mesityl rings. The Mes-C=C dihedral angles are 59.8°. The double bond torsional angle is 8.7°.



12 A, B, C, D = hydrogen, alkyl, aryl

Several 1,2,4,5-tetrathiane crystal structures are available and that of **4** is the second structure **12**, *n* = *m* = 2, determined by X-ray diffraction. The tetrathiane ring exists in a twist boat conformation as shown by its stereoview in Figure 1.[13] The four Mes-C=C torsional angles are nearly the same, being 58.7°, 59.5°, 61.2° and 62.1°. The two double bonds are appreciably twisted, their torsional angles being 15.1° and 13.5°.

Dynamic NMR Study of 3. When a solution of **3** in CD_2Cl_2 is cooled to 160 K, the ^1H NMR aromatic singlet at 6.77 ppm split to four signals at 6.59, 6.62, 6.75 and 6.84 ppm (1:2:2:1 intensities, respectively) and the aliphatic signal at 2.17 ppm split to four singlets at 1.70, 2.07, 2.41 and 2.52 ppm with 3:3:2:1 intensities, respectively (Figure 2A).

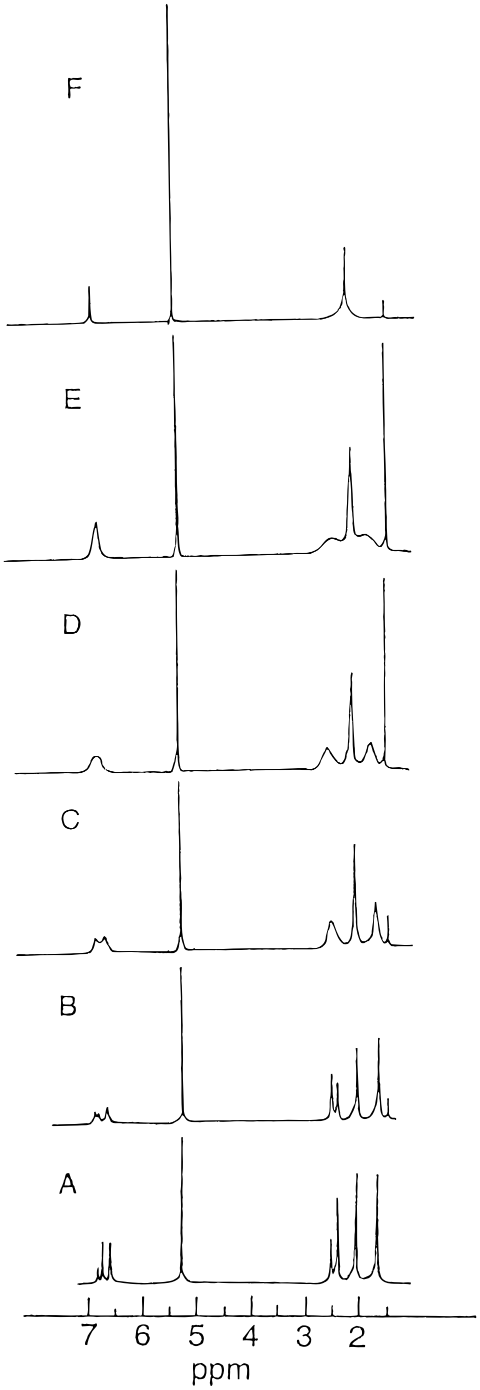


Figure 2. A dynamic NMR experiment for **3** in CD_2Cl_2. A: At 160 K; B: at 235 K; C: at 255 K; D: at 263 K; E: at 273 K; F: at 295 K.

Since the two dimesitylvinyl moieties are chiral due to their helicity, three stereoisomers should be present at equilibrium at the low temperature: two enantiomers **13a** and **13b** for which we assign two pairs of signals and a meso isomer **13c** to which we assign the other two pairs of signals. The three isomers with letters a−f labeling the *ortho*- and *para*-positions and letters with bars $\bar{a}$−$\bar{f}$ designating the corresponding enantiotopic sites are shown in Figure 3. Similar designations apply for the aromatic hydrogens.

In each enantiomer the four rings are twisted in the same sense and they have opposite right and left helicities and a D_2 symmetry. The meso isomer **13c** has C_{2h}

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(12) (a) Seybold, G.; Heibl, C. *Angew. Chem.* **1975**, *87*, 171. (b) Okazaki, R.; Ishii, A.; Fukuda, N.; Oyama, H.; Inamoto, N. *J. Chem. Soc., Chem. Commun.* **1982**, 1187.

(13) The author has deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

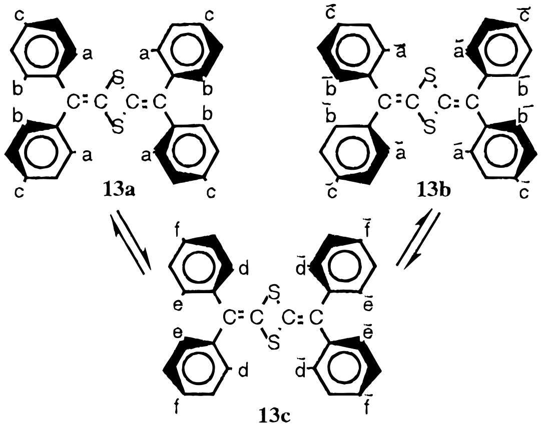

Figure 3. The two enantiomers **13a** and **13b** and the meso form **13c** of **3**.

Table 1. DNMR Data for 3 and 4 in CD_2Cl_2

compound	signals/ ppm^a	$\Delta\nu$/Hz^a	T_c/K	δ^b	k_c/s$^{-1\,c}$	$\Delta G^{\#}_c$/kcal mol^{-1}
3	6.62, 6.75	52.6	263	6.77	117	12.8
	6.59, 6.84	99.2	263	6.77	220.5	12.5
	1.70, 2.52	327.5	287	2.17	727.5	13.0
4	6.58, 6.80	88.8	278	6.79	197.2	13.3
	6.65, 6.87	90.7	278	6.79	201.5	13.3
	1.60, 2.31	285	252	2.21^d	633.1	13.3

^{a} At slow exchange at 160 K. ^{b} δ of the average signal obtained after coalescence. ^{c} At T_c. ^{d} In $Cl_2CDCDCl_2$.

symmetry, with a symmetry plane passing through the two sulfur atoms and bisecting the central ring plane. Mesityl rings on one side of the plane have the same helicity, opposite to that of the other rings.

The two $Mes_2C=$ groups are remote from one another and assuming that they exert a negligible mutual influence, the three forms should have a similar enthalpy. Statistically, the meso:*d,l* ratio should then be 1:1. However, the observed ratio is strongly temperature-dependent, before broadening due to coalescence interferes with its determination (cf. A and B in Figure 2). At 160 K the ratio is either ca. 1:2 or ca. 2:1 since we are unable to assign a certain signal to a certain isomer.

Six methyl signals are expected at slow exchange: one for the *p*-Me and two for the *o*-Me groups of **13a**,**b** and similarly for **13c**. However, all the *p*-Me groups appear accidentally isochronous at 2.07 ppm with one-third of the intensity. This is corroborated by the nearly constant δ and shape during the dynamic process. The signal at 1.70 ppm with one-third of the intensity is again ascribed to accidental isochrony of one *o*-Me group of **13c** and one *o*-Me in **13a,b**. The 2:1 signals at 2.41 and 2.52 ppm are assigned to the second *o*-Me in **13a,b** and in **13c**, respectively.

When the temperature was raised, signal broadening, coalescence, and then sharpening of both the aliphatic and aromatic signals took place (Figure 2). The pair of Ar-H signals at 6.62 and 6.75 ppm and the other pair of Ar-H signals at 6.59 and 6.84 ppm coalesce at the same temperature (T_c = 263 K) giving an average signal at rt at 6.77 ppm. The $\Delta G^{\#}_c$ values for the two processes which lead to interconversion of stereoisomers were calculated from the Gutowsky–Holm[14] and the Eyring equations (Table 1). The average $\Delta G^{\#}_c$ is 12.7 ± 0.2 kcal mol^{-1}.

The three singlets at 1.70, 2.41, and 2.52 ppm coalesce at 287 K. At rt, the average signal appears at 2.17 ppm. Based on the data in Table 1 and the Gutowsky–Holm equation, $\Delta G^{\#}_c$ = 13.0 kcal mol^{-1}. Overlap of the *p*-Me signal with the average *o*-Me signal increase the error in T_c, and the estimated error in $\Delta G^{\#}_c$ is ±0.3–0.4 kcal mol^{-1}. The average $\Delta G^{\#}_c$ value from all probes is 12.7 kcal mol^{-1}. Since the Gutowsky–Holm equation is strictly applicable for an exchange of two signals with identical intensities and our processes involve exchange at four sites (the Ar-H or the *o*-Me of **13c** with those in **13a,b**), its use is not necessarily correct. However, we believe that the equation gives an approximate barrier, although its error is higher than the quoted ±0.2 kcal mol^{-1}.

Dynamic NMR Study of 4. When a solution of **4** in CD_2Cl_2 is cooled to 160 K the ^1H NMR rt aromatic singlet at 6.77 ppm split to five signals. Partial overlap interferes with exact relative integration but the two slightly <1:1 signals at 6.58 and 6.80 ppm consist ca. 85% of the intensity, and three 1:1:1 signals at δ 6.65, 6.83, and 6.87 ppm have ca. 15% intensity. An additional small signal (of 5% intensity) may be hidden below the δ 6.58 signal. The aliphatic signal appearing at fast exchange at 400 K at δ 2.21 split on cooling to ca. 1:1:1 signals at 1.60, 2.09, and 2.31 ppm (80% intensity) and to two 1:1 signals at 1.75 and 2.46 ppm (20% intensity).

These signals are ascribed to eight groups of hydrogens belonging to three enantiomeric pairs. The central ring of **4** has in the crystal a twist-boat (TB) conformation, and since 1,2,4,5-tetrathianes probably have a similar conformation in solution,[15] we assume it also for **4** in solution. Since a TB conformation is chiral and each pair of mesityl rings can have either a right handed or a left handed helicity, the maximum possible number of stereoisomers is six (**14a–16a, 14b–16b**) as drawn in Figure 4, with labeling similar to that for **13a–c**. Assuming a negligible mutual influence of the two $Mes_2C=C$ groups, and identical enthalpies, statistics suggest a 1:2:1 ratio of **14a,b:15a,b:16a,b**.

There are several alternative assignments based on the relative intensities of the observed five signals, plus the hidden one at 6.58 ppm to the six isomers. (i) The four 1:1:1:1 signals at (6.58), 6.65, 6.83, and 6.87 ppm belong to the two enantiomers **15a,b** having C_2 symmetry, where each pair of geminal mesityl rings have a different helicity and the two large signals to the **14a,b, 16a,b** with D_2 symmetry, assuming that they appear at the same δ value due to accidental isochrony. The **15a,b/14a,b** + **16a,b** equilibrium ratio is then 1:2. (ii) The two large signals belong each to **14a,b** or **16a,b**, and one of these isomers has a lower population. Isomers **15a,b** and **14a,b** or **16a,b** are then at equilibrium ratio of 1:4, respectively. (iii) The four small signals belong to **14a,b** and **16a,b** and the two large signals to **15a,b**, assuming that due to accidental isochrony the signals for protons c, d, e, and f appear as two signals only. The ratio **14a,b: 15a,b:16a,b** is then ca. 1:9:1. The two pairs with different intensities were assigned to the other two pairs (**14a,b; 16a,b**). We cannot decide between the alternatives but possibility i seems most likely.

On raising the temperature, the usual broadening, coalescence, and resharpening of signals of the DNMR experiments were observed (Figure 3). In CD_2Cl_2 for the large signals at 6.58 and 6.80 ppm, T_c = 278 K, $\Delta G^{\#}_c$ = 13.3 kcal mol^{-1}. The average signal of all four signals

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(14) Gutowsky, S. H.; Holm, C. H. *J. Chem. Phys.* **1956**, *25*, 1228.

(15) For a recent review see *Conformational Behavior of Six-Membered Rings. Analysis, Dynamics and Stereoelectronic Effects*; Juaristi, E., Ed.; VCH: New York, 1995; pp 202–209.

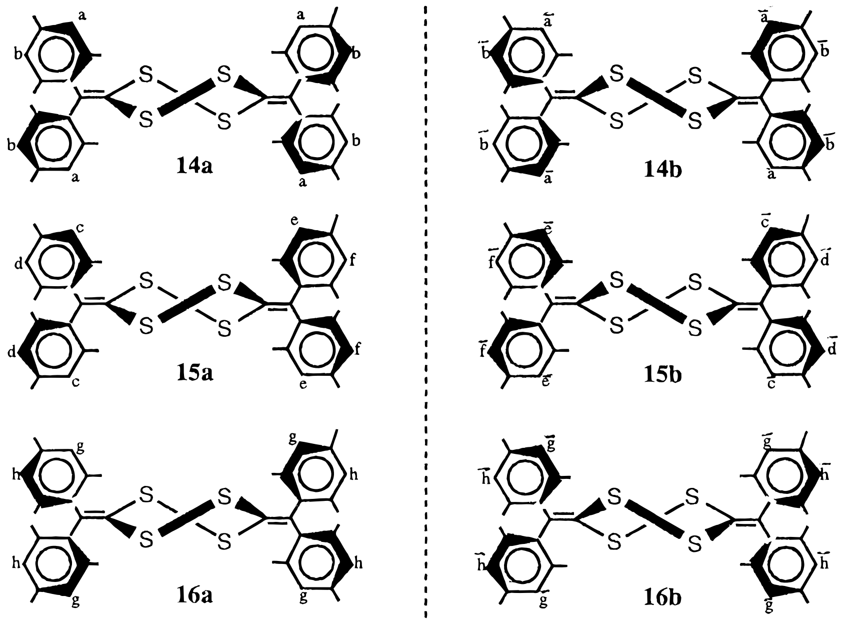

Figure 4. The six stereoisomers of **4**.

appear at 6.79 ppm at 400 K in $Cl_2CDCDCl_2$. The two small aromatic signals at 6.65 and 6.87 ppm give T_c = 278 K, $\Delta G^{\#}_c$ = 13.3 kcal mol^{-1} (Table 1).

The two aliphatic signals at δ 1.60 and 2.31 ascribed to the two types of *o*-Me signals in one or two of the isomeric pairs coalesce in CD_2Cl_2 at 252K, $\Delta G^{\#}_c$ = 13.3 kcal mol^{-1}. The average signal appears in $Cl_2CDCDCl_2$ at 400 K at 2.21 ppm (Table 1). The $\Delta G^{\#}_c$ value for the exchange between several sites was calculated by the Gutowsky–Holm equation[14] and the reservation raised above concerning its accuracy applies here too.

Discussion

Formation of the Cyclic Compounds. One of our goals was to obtain thioketenes **2**, **6**, and **9** by thionation of the corresponding diaryl ketenes with P_2S_5. Although they may be transiently formed as observed for **2**, none of them was accumulated during the reaction. The reaction gave instead heterocyclic compounds containing *n* atoms with $n - 2$ sulfur atoms ($n = 4-6$) with two exo diarylmethylene groups or their derivatives. 1,3-Dithietanes, 1,2,4-trithianes, and 1,2,4,5-tetrathianes are well known, but we are unaware of their formation by thionation of ketenes. The formation of the various rings can be accounted for by an initial formation of the diarylthioketene, as demonstrated with **2**.

Initially **2** is formed by thionation (eq 4 in Scheme 4), as a short-lived intermediate which may dimerize by a reversible [2 + 2] cycloaddition to **3** (eq 5 in Scheme 4). An additional P_2S_5 molecule or the species $^-SPS_2$ derived from it and suggested as the reactive thionation species with P_2S_5[16] traps **2** rapidly to give anion **17**. Nucleophilic attack of **17** on the sulfur of another anion **17** with expulsion of PS_2^- and an intramolecular displacement in the resulting anion gives tetrathiane **4** (eq 6 in Scheme 5). Likewise, addition of **17** to **2** leads to an anionic product which by an intramolecular displacement of PS_2^- gives trithiane **5** (eq 7 in Scheme 5).

Alternatively, loss of sulfur from the ring of **4** can give the trithiane ring **5**, and further loss can give **3**. Precedents are known.[11,17] Compound **12**, $m = n = 2$, A–D = CF_3 apparently gives the analog of **5** by sulfur loss on heating. The latter or another bis(disubstituted methylene)trithiane gives analogs of **3**.[17] A photochemical analogy is also known.[11]

$Ph_2CHCOCl$ and P_2S_5 in pyridine form the two 1,2,4-trithiane derivatives **7** and **8**. Interestingly, diphenyl ketene and P_2S_5 did not give a defined product,[18] but with *p*-thiophosphoric anhydride, the tetraphenyl analog of **3** was obtained[19] probably by dimerization of **6**. An initial formation of **6** and then a reaction analogous to eq 7 can form **7**. It is unclear why only one double bond of **7** is reduced to **8**, but since we were unable to isolate other products from the oil remaining after obtaining **7** and **8**, mechanistic speculations are unwarranted.

Dimesityl Thioketene. The spectral data of the blue solution left little doubt that it contains the thioketene **2**, formed by the thionation or the dissociation of **3** (eqs 4 and 5). Most thioketenes tend to dimerize to 2,4-bis(dialkylmethylene)-1,3-dithietanes.[1b,c] However, $t\text{-}Bu_2C{=}C{=}S$ is obtained by thionation of $t\text{-}Bu_2C{=}C{=}O$ or $t\text{-}Bu_2CHCOCl$ with P_2S_5 in pyridine.[7b] Our thionation resembles this synthesis, but **2** apparently disappears under the thionation conditions by reacting rapidly with P_2S_5 or with **17**, according to eqs 6 and 7.

The ease of cleavage of dimer **3** to **2** is remarkable. [2 + 2] Cycloreversion of 2,4-bis(alkylidene)-1,3-dithietanes usually requires high temperature,[20] and bis(trifluoromethyl) thioketene was prepared by this route.[21] The steric crowding in dimer **3** is probably responsible for its slow cleavage under mild conditions.

Static and Dynamic Behavior of 3. A. Static Conformation. The Cambridge Structural Database lists eight X-ray diffraction structures **12**, $m = n = 1$. Except for one, all are thioketene dimers (A = D, B = C). They are centrosymmetric, with planar dithiacyclobutane rings with C–S bond lengths of 1.74–1.79 Å,

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(16) Scheeren, J. W.; Ooms, P. H. J.; Nivard, R. J. F. *Synthesis* **1973**, 149.

(17) (a) Kirby, A. J. *Tetrahedron* **1966**, *22*, 3001. (b) Raash, M. S. *J. Org. Chem.* **1970**, *35*, 3470.

(18) Staudinger, H. *Justus Liebigs Ann. Chem.* **1907**, *356*, 51.

(19) Dunmur, R. E.; Fluck, E. *Phosphorus* **1974**, *5*, 13.

(20) Seybold, G.; Heibl, C. *Chem. Ber.* **1977**, *110*, 1225.

(21) Raasch, M. S. (a) *Chem. Commun.* **1966**, 577. (b) *J. Org. Chem.* **1970**, *35*, 3470.

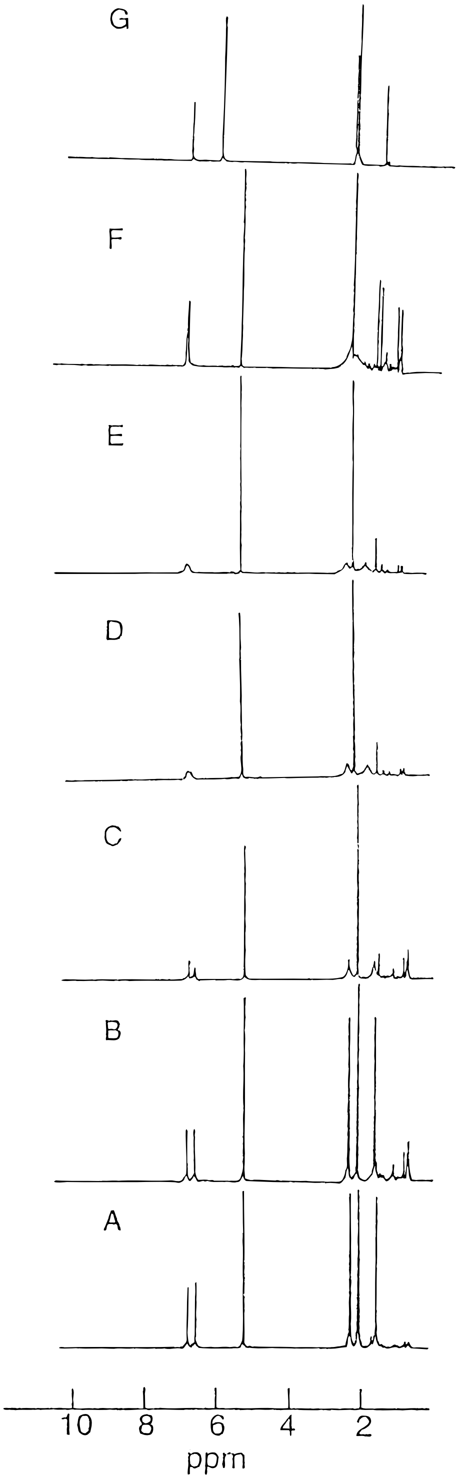

Figure 5. A dynamic NMR experiment for **4** in CD_2Cl_2. A: At 160 K; B: at 220 K; C: at 250 K; D: at 275 K; E: at 278 K; F: at 295 K; G: at 400 K in $Cl_2CDCDCl_2$.

in line with C_{sp^2}-S bond lengths in other systems. The SCS and CSC angles (ca. 98° and 82°, respectively) are in the range as in all known structures. The twist in the same direction around the Mes-C= bonds on each side is consistent with the propeller conformation of diarylvinyl moieties.[9,10] The Mes-C= torsion angles of 59.8° are similar to that for $Mes_2C{=}C(OH)Pr$-*i*.[22]

Structure **3** resembles a tetramesitylethylene with a "spacer" between the two Mes_2C= moieties. However, whereas in tetramesitylethylene the mutual interaction between the two close moieties leads to twist of all rings in the same direction,[23a] in the X-ray diffraction of the isolated crystal of **3** the two moieties have opposite helicities. However, the two diastereomeric conformations were apparently observed in solution.

B. Dynamic Behavior. Two possible dynamic processes in polyarylvinyl propellers[9a] may be relevant to that observed for **3**. (i) Rotation around the C=C bond will exchange the two geminal rings and may lead to coalescence. The high barrier to such rotation in tetramesitylethylene[23b] and the stability of methoxy-substituted trimesitylvinyl acetates and ethers to $E \rightleftharpoons Z$ isomerization[24] exclude this route. (ii) Rotation around the Mes-C= bonds can proceed either by independent rotation of each ring or by correlated rotation. Correlated rotations in vinylic propellers[9a] are discussed in terms of flip mechanisms involving helicity reversal, based on the definitions and analysis of Mislow for rotations around Ar−C bonds.[25] A flip is a passage of a ring during its rotation through a plane perpendicular to the reference plane, while the nonflipping rings rotate in the opposite direction and pass through the reference plane. We define the reference plane in **3** by the $(C_{ipso})_2C{=}C$. According to the number of the flipping rings the routes are called *n*-ring flips with $n = 0, 1, 2$ in our system (Figure 6).

The two important features of the DNMR behavior are the following: (a) four aromatic signals at slow exchange coalesce to one average signal; (b) four *o*- and *p*-Me signals coalesce to one signal, due to accidental isochronicity of the average *para* and *ortho* signals.

The two Mes_2-C= groups are treated as independent. Three- or four-ring flips are regarded as occurring accidentally simultaneously and not as a correlated rotation of all rings. Only zero-, one-, and two-ring flips are therefore analyzed.

Rotation around the double bond cannot be followed by NMR since it will exchange homotopic sites (e.g., a and $\bar{a}$). A ring flip exchanges the magnetic sites b and $\bar{d}$, a and $\bar{e}$, b and $\bar{e}$, a and $\bar{d}$, a and d, and b and e (cf. Figure 3) with a consequent coalescence of the corresponding signals. The 180° rotation with retained helicity will lead to coalescence of sites a and b, and d and e. Table 2 lists the exchanging sites by the various rotation routes. Only inversion of helicity, i.e., by the flip routes, will lead to (stereo) isomerization. Only the one-ring and two-ring flip routes account for exchange of all the groups residing in diastereotopic sites, leading at a fast exchange to one average aromatic signal.

For 2,2-dimesityl-1-*R*-ethenols[9] a 1-ring flip takes place only when R = H since interference by the hydrogen for passage of the mesityl ring via the reference plane is small. When R = bulkier alkyl, the low energy route is the two-ring flip. The average $\Delta G^{\#}_{c}$ value of 12.7 kcal mol^{-1} for **3** resembles the two-ring flip barriers for the 2,2-dimesityl-1-alkylethenols (10.5−12.5 kcal mol^{-1}).[9b,c] A likely mechanism for **3** is therefore a two-ring flip.

Static and Dynamic Behavior of 4. A. Static Conformation. The Cambridge Structural Database lists only the partial structure of 3,6-bis(2-oxobut-3-

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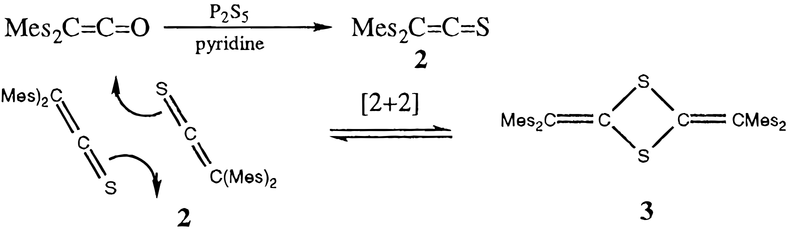
[22] Kaftory, M.; Nugiel, D. A.; Biali, S. E.; Rappoport, Z. *J. Am. Chem. Soc.* **1989**, *111*, 8181.

[23] (a) Blount, J. F.; Mislow, K.; Jacobus, J. *Acta Crystallogr. Sect. A.* **1972**, *28*, S12; Nazran, A. S.; Lee, F. L.; Gabe, E. J.; Lepage, Y.; Northcolt, D. J.; Park, J. M.; Griller, D. *J. Phys. Chem.* **1984**, *88*, 5251. (b) Gur, E.; Kaida, Y.; Okamoto, Y.; Biali, S. E.; Rappoport, Z. *J. Org. Chem.* **1992**, *57*, 3689.

[24] Rochlin, E.; Rappoport, Z. (a) *J. Org. Chem.* **1994**, *59*, 3857. (b) Unpublished results.

[25] For a review see, Mislow, K. *Acc. Chem. Res.* **1976**, *9*, 26.

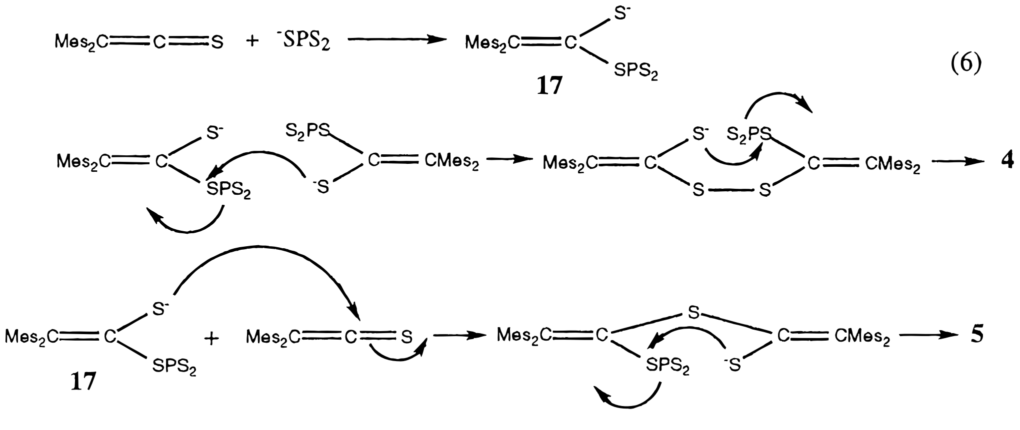
Scheme 4



(4)

(5)

Scheme 5



(6)

(7)

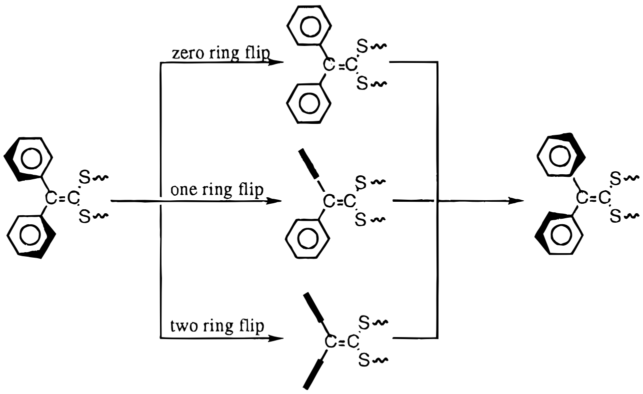


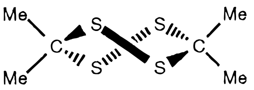
Figure 6. The zero-, one-, and two-ring flips for the diarylvinyl group in one half of 2,4-bis(diarylmethylene)-1,3-dithietane. The solid rectangle indicates a ring perpendicular to the reference plane.

Table 2. Magnetic Sites in 3 and 4 Which Exchange by Flip and Nonflip Routes

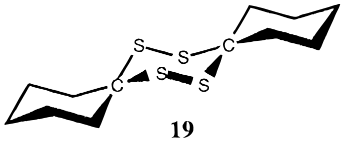
compound	ring flip route	flip	nonflip
3	zero-ring	$(a\bar{d})(b\bar{e})(c\bar{f})(ad)(be)(cf)$ $(\bar{a}d)(\bar{b}e)(\bar{c}f)(\bar{a}\bar{d})(\bar{b}\bar{e})(\bar{c}\bar{f})$	(a)(b)(c)(d)(e)(f)
	one-ring	$(a\bar{e})(b\bar{d})(c\bar{f})(a\bar{d})(b\bar{e})(ad)$ $(bc)(cf)(\bar{b}d)(\bar{a}e)(\bar{c}f)(\bar{b}e)$ $(\bar{a}d)(\bar{a}\bar{d})(\bar{b}\bar{e})(\bar{c}f)$	(ab)(ba)(c)(de)(ed)(f)
	two-ring	$(a\bar{e})(b\bar{d})(c\bar{f})(a\bar{d})(be)(cf)$ $(\bar{a}e)(\bar{b}d)(\bar{c}f)(\bar{a}\bar{d})(\bar{b}\bar{e})(\bar{c}f)$	(ab)(ba)(c)(de)(ed)(f)[a]
4	zero-ring	(ae)(bf)(ac)(bd) (cg)(dh)(eg)(fh)	(a)(b)(c)(d)(e)(f)(g)(h)
	one-ring	(be)(af)(bf)(ae)(ac)(bd) (ch)(dg)(dh)(cg)(ge)(fh)	(ab)(cd)(ef)(gh)
	two-ring	(af)(be)(ac)(bd) (ch)(dg)(ge)(hf)	(ab)(cd)(ef)(gh)[a]

[a] 180° rotation of the two geminal rings.

ylidene)-1,2,4,5-tetrathiane as having structure **12**, $m = n = 2$ (A = D = Me; B = C = Ac).[26] The molecule is centrosymmetric and nearly planar, and there is no additional information for comparison with **4**. Two other 1,2,4,5-tetrathiane-containing structures, but lacking the 3,6-exocyclic bonds, are known. 3,3,6,6-Tetramethyl-*s*-tetrathiane (**18**) exists as a D_2 twist-boat (TB) conformation both in the solid[27] and in solution[28a] and has significantly short S−S bonds of 2.015 Å[27] compared with the average length (2.08 Å). The tetrathiane **19** exists as a chair conformation in the solid, but with only a 0.75 kcal mol^{-1} preponderance over the TB in solution[29] with an S−S bond length of 2.035 Å.[30]



18



19

The tetrathiane ring in **4** has a nonperfect TB conformation (Figure 1) since the two C=C bonds are at a angle of 166.5°, rather than 180°. The S−S bond lengths of 2.039 and 2.044 Å are close to that in orthorbombic S_8 (2.037 Å).[31] The C_{sp^2}−S bonds of 1.764−1.780 Å are shorter than the C_{sp^3}-S bonds in **18** and **19** (1.84 Å) which are typical for a S−C single bond due to the carbon sp^2 hybridization. All the Mes-C= torsion angles of 58.7−62.0° are in the same direction. Again, we envision the structure as having two independent propeller moieties. The double bond torsional angles of 13.5° and 15.1° are higher than for **3** but resemble that for Mes$_2$C=C(OH)-Bu-*t*.[22]

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[26] Alcock, N. W.; Kirby, A. J. *Tetrahedron* **1966**, *22*, 3007.

[27] Korp, J. D.; Bernal, I.; Watkins, S. F.; Fronczek, F. R. *Tetrahedron Lett.* **1981**, *22*, 4767.

[28] (a) Bushweller, C. H. *J. Am. Chem. Soc.* **1967**, *89*, 5978. (b) Bushweller, C. H. *ibid.* **1968**, *90*, 2450. (c) Bushweller, C. H.; Golini, J.; Rao, G. U.; O'Neil, J. W.*ibid.* **1970**, *92*, 3055. (d) Bushweller, C. H. *Ibid.* **1969**, *91*, 6019.

[29] From a correlation between S−S bond lengths and dihedral angles of the S−S valencies (Hordvik, A. *Acta Chem. Scand.* **1966**, *20*, 1885), this bond length corresponds to ca. 90° angle, as was indeed observed.

[30] Bushweller, C. H.; Bhat, G.; Letendre, L. J.; Brunelle, J. A.; Bilofsky, H. S.; Ruben, H.; Templeton, D. H.; Zalkin, A. *J. Am. Chem. Soc.* **1975**, *97*, 65.

[31] Abraham, S. C. *Acta Cryst.* **1955**, *8*, 661.

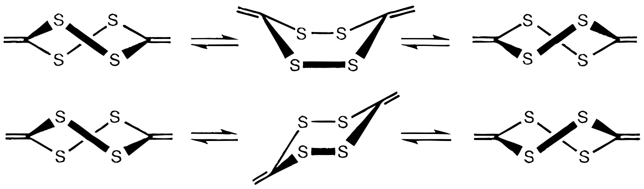

Figure 7. Possible routes for a TB $\rightleftharpoons$ TB equilibration in 3,6-divinylidene-1,2,4,5-tetrathiane.

Whereas six-membered rings containing one, two, three, or five sulfur atoms are generally more stable in the chair conformations,[14,28a] for the 1,2,4,5-tetrathiane rings, investigated by Bushweller's group,[28] the TB conformation is mostly preferred. For the parent 1,2,4,5-tetrathiane, both the chair and a less stable twist conformer were identified in solution.[32] The barrier to the TB $\rightleftharpoons$ chair interconverison is relatively high (15–16 kcal mol^{-1}). Even a cyclohexane ring with exocyclic 1,4-double bonds, e.g., 1,4-cyclohexanedione, also exist in a TB conformation.[33]

B. Dynamic Behavior. The rotational routes described for **3** are also applicable for **4**, but an additional TB $\rightleftharpoons$ TB tetrathiane ring interconversion involving either a boat or a chair conformation as an intermediate or a transition state (Figure 7) should be also considered. Relevant for the analysis is that with the change 160 K→ 400 K the five observed (+ 1 hidden) aromatic signals at slow exchange coalesce to a single average signal. Since the observed ratio **14a,b:15a,b:16a,b** of 1:2:1 differs from the predicted one, we cannot assign the different signals to the different stereoisomers.

We regard **4** as a combination of *independent*, two dimesitylvinyl groups and a TB 1,2,4,5-tetrathiane ring. Hence, we consider only zero-, one-, or two-ring flips for dynamic processes the $Mes_2C=$ moiety undergoes. We use Figure 4 for magnetic sites assignment and analysis using a scheme analogous to Figure 6 which assumes that at slow exchange all processes take place at a TB conformation.

If we assume that the ring undergoes a TB $\rightleftharpoons$ TB interconversion without a detectable intermediate and that the activation energy for the interconversion of each one of the stereoisomeric pairs is similar, the process will exchange the $(d\bar{f})(c\bar{e})(\bar{d}f)(\bar{c}e)(a\bar{g})(\bar{b}h)(\bar{a}g)(b\bar{h})$ sites, giving four aromatic signals at fast exchange. Consequently, the results are inconsistent with a ring inversion process *alone*. It should be coupled to other processes, thus reducing the number of observed signals. Analysis similar to that for the dynamic process of **3** suggests that these are rotations around the Mes-C= bonds. The magnetic sites exchanged in the various rotation routes are summarized in Table 2. The flip routes exchange diastereotopic groups between stereoisomers having identical TB conformations of the central ring, i.e., in **14a, 15a**, or **16a** (or **14b, 15b**, and **16b**). We assume that all the *n*-ring flips having the same *n* have the same energy.

The only route in Table 2 which exchanges all the groups at diastereotopic sites and hence give only one average aromatic signal is a one-ring flip with a barrier of $\Delta G^{\#}_{c} = 13.3$ kcal mol^{-1}. If we assume a TB $\rightleftharpoons$ chair interconversion barrier of 16 kcal mol^{-1} for **4**, as determined by Bushweller for four tetrathiane rings,[28,30] then the one-ring flip for **4** is the threshold process. The ring inversion cannot be studied since all the diastereotopic sites are already exchanged by the flip process. However, as mentioned above the observed threshold mechanism for $Mes_2C{=}CR^1R^2$ was uniformly a two-ring flip when $R^1 = R^2 \neq$ H, Ar. Moreover, the $\Delta G^{\#}_{c}$ value is only 0.6 and 1.6 kcal mol^{-1} lower than that of the two-ring flip for **3** whose Mes-C= torsion angle resemble those of **4**, and for $Mes_2C{=}C(OH)$Pr-i where these angles are slightly higher.[9b,c] These analogies strongly suggest a threshold two-ring flip route which, however, is insufficient to render equivalent all the *o*-Me groups in the three diastereomers (Table 2). Hence, we assume that coalescence of all *o*-Me groups into a single signal involves both Mes rings rotation and ring inversion. This does not necessarily contradict analogy with Bushweller's data since the effect of the $Mes_2C=$ groups on the ring inversion is unknown. We then regard the central ring as being planar on the average, and the analysis is identical to that given for **3**.

Formation of 5. The ^{1}H NMR spectrum of pure **4** obtained by crystallization, differed from that of the crude yellow oil obtained from the **4**-containing fraction from chromatography on silica. The rt spectrum of the latter in CD_2Cl_2 contained the two signals of **4**, and additional two aromatic signals at 6.75 and 6.80 ppm and four aliphatic signals at δ 2.13, 2.14, 2.18, and 2.20 ppm. In $Cl_2CDCDCl_2$ at 400 K these signals were sharpened and appeared at δ 2.22, 2.23, 2.24, 2.27, 6.77, and 6.82 in relative intensities of 6:6:3:3:2:2. This suggested that crude **4** was accompanied by another compound.

The mass spectrum of the same sample showed two signals with (presumably) molecular peaks at m/z 652 and 620. Two different spectra taken at different times gave different relative intensities. At a lower temperature the m/z 620 peak was the highest and was accompanied by signals at 588 (26%), 294 (100%), 262 (47%), 246 (57%), 245 (25%), and 231 (25%), whereas at a higher temperature the highest peak was at m/z 652. This suggested again that the presence of an additional compound, i.e., 3,5-bis(dimesitylmethylene)-1,2,4-trithiane, **5**, with *M* at m/z 620. Crystallization of the mixture from petroleum ether gave pure **4**, and several recrystallizations of the filtrate enriched it to a 3:7 **4:5** mixture, but pure **5** was not obtained so far.

Analysis of the static ^{1}H NMR spectrum of **5** at 400 K assumes that any dynamic process taking place is fast on the NMR time scale and that **5** is an average planar molecule with a C_{2v} symmetry. The lack of a C_2 axis or a plane of symmetry passing through the four C=C carbons means that the mesityl-Me groups of one ring are in a diastereotopic site compared with those in the geminal ring. Hence, each of the signals at 2.22 and 2.23 ppm is ascribed to the two *o*-Me groups of one mesityl ring. Likewise, the signals at 2.24 and 2.27 ppm are ascribed to the two *p*-Me groups on geminal rings, and the signals at 6.77 and 6.82 ppm are ascribed to the two *m*-H of each one of the geminal mesityl rings. Unfortunately, the DNMR study of the 7:3 **5:4** mixture was too complex for obtaining a $\Delta G^{\#}_{c}$ value for **5**.

Experimental Section

Solvents and Materials. Preparation of solvents and the apparatus used were described in a previous publication.[34] P_2S_5 was purchased from BDH. Dimesityl ketene[4,9a] and ditipyl ketene[5] were prepared as previously described.

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[32] For a review see: Susilo, R.; Gmelin, R.; Roth, K.; Bauer, R. Z. *Naturforsch.* **1982**, *37B*, 234. Franck, W. *Sulfur Rep.* **1991**, *10*, 233.

[33] Grothand, P.; Hassel, O. *Proc. Chem. Soc.* **1963**, 218. Mossel, A.; Romers, C.; Havinga, E. *Tetrahedron Lett.* **1963**, 1247.

[34] Selzer, T.; Rappoport, Z. *J. Org. Chem.* **1996**, *61*, 5462.

Dimesityl Thioketene, 2,4-Bis(dimesitylmethylene)-1,3-dithietane (3), 3,5-Bis(dimesitylmethylene)-1,2,4-trithiane (5), and 3,6-Bis(dimesitylmethylene)-1,2,4,5-tetrathiane (4). A suspension of dimesityl ketene (0.5 g, 1.8 mmol) and P_2S_5 (0.45 g, 2 mmol) in pyridine (8 mL) was refluxed for 21 h, after which the ketene peak at 2100 cm^{-1} disappeared completely. A transient blue color appeared and disappeared rapidly at the beginning of the reaction. After reaching rt, the solution was cooled to 0 °C, an aqueous phosphate buffer solution (pH 6.8, 16 mL) was slowly added and the mixture was stirred for 2 h. The organic phase was extracted with ether (5 × 20 mL), washed with dilute HCl (3 × 30 mL), saturated aqueous $NaHCO_3$ solution (2 × 30 mL), and water, and dried ($MgSO_4$). The ether was evaporated, and the remaining brown solid was chromatographed on silica with 95:5 petroleum ether−CH_2Cl_2 eluent.

The yellowish first fraction in the eluent turned blue after standing for a few hours at rt. When kept in the cold for one week yellow crystals, 37 mg (7%) of 2,4-bis(dimesitylmethylene)-1,3-dithietane (**3**), mp 312−314 °C, were separated. IR ν_{max} (Nujol): 1600 cm^{-1} ($C{=}C$); ^1H NMR (CD_2Cl_2) δ: 2.17 (36H, s), 6.77 (8H, s); ^{13}C NMR (CD_2Cl_2) δ: 20.8, 21.1, 121.1 ($Mes_2C{=}$), 128.2, 129.5, 132.3, 136.8, 137.8 ($C{=}CS_2$). Mass spectrum: m/z (relative abundance, assignment): 588 (100%, M^+), 294 (23%, $Mes_2C{=}C{=}S^+$), 262 (20%, $Mes_2C{=}C^+$), 246 (19%), 231 (8%), 175 (3%, $MesC{=}C{=}S^+$), 119 (3%, Mes^+). Microanalysis: C, 81.55; H, 7.49; S, 10.41. Calcd for $C_{40}H_{44}S_2$: C, 81.63; H, 7.47; S, 10.89%. X-ray diffraction: space group C_{mca}, $a = 25.424(4)$ Å, $b = 14.087(2)$ Å, $c = 11.274(2)$ Å, $V = 4037.5(8)$ Å^3, $z = 4$, $\rho_{calc} = 1.03$ g cm^{-3}, μ(Cu K$_\alpha$) = 13.42 cm^{-1}, $R = 0.056$, $R_w = 0.081$.[13]

Recrystallization of the second fraction from petroleum ether gave yellow crystals (0.1 g, 17%) of 3,6-bis(dimesitylmethylene)-1,2,4,5-tetrathiane (**4**), mp 275−7 °C. IR ν_{max} (Nujol): 1614 cm^{-1} ($C{=}C$); ^1H NMR ($Cl_2CDCDCl_2$; 400 K) δ: 2.21 (24H, s), 2.25 (12H, s), 6.79 (8H); ^{13}C NMR ($Cl_2CDCDCl_2$; 330 K) δ: 22.2, 22.5, 130.8, 136.6, 138.4, 138.9, 140.4, 141.1 (4 Mes-C + 2C=C). Mass spectrum: m/z (relative abundance, assignment): 652 (4%, M^+), 620 (16% ($(Mes_2C{=}C)_2S_3^+$), 588 (5% $(Mes_2C{=}C)_2S_2^+$), 358 (3%, $Mes_2C{=}CS_3^+$), 326 (3%, $Mes_2C{=}S_2^+$), 294 (100%, $Mes_2C{=}C{=}S^+$), 262 (7%, $Mes_2C{=}C^+$), 246 (28%), 245 (12%), 231 (12%). Microanalysis: C, 73.97; H, 7.72. Calcd for $C_{40}H_{44}S_4$: C, 73.57; H, 6.79%. X-ray diffraction: Space group $P\bar{1}$, $a = 13.378(2)$ Å, $b = 15.227(3)$ Å, $c = 11.719(2)$ Å, $\alpha = 104.44(1)°$, $\beta = 110.02(1)°$, $\gamma = 95.43(1)°$, $V = 2129.2(8)$ Å^3, $z = 2$, $\rho_{calc} = 1.02$ g cm^{-3}, μ(Mo K$_\alpha$) = 2.35 cm^{-1}, $R = 0.062$, $R_w = 0.086$.[13]

The filtrate obtained after separation of **4** showed (by ^1H NMR) both additional amounts of **4** and 3,5-bis(dimesitylmethylene)-1,2,4-trithiane (**5**). Repeated crystallization from petroleum ether (60−80 °C) gave a 7:3 **5:4** mixture from which the following spectra for **5** were determined, although further enrichment by **5** was not obtained. ^1H NMR ($Cl_2CDCDCl_2$; 400 K) δ: 2.222 (12H, s), 2.228 (12H, s), 2.235 (6H, s), 2.271 (6H, s), 6.765 (4H, s), 6.824 (4H, s). Mass spectrum: m/z (relative abundance, assignment): 620 (17%, M^+), 588 (26%, $(Mes_2C{=}C)_2S_2^+$), 294 (100%, $Mes_2C{=}C{=}S^+$), 279 (15%), 262 (47%, $Mes_2C{=}C^+$), 246 (57%), 245 (25%), 231 (25%).

Dimesityl Thioketene (2). The blue solution was characterized by the following spectra as containing dimesityl thioketene (**2**): UV λ_{max} (CH_2Cl_2): 582 nm. IR ν_{max}(Nujol): 1608 ($C{=}C$), 1742 cm^{-1} ($C{=}C{=}S$). ^1H NMR ($CDCl_3$) δ: 2.16 (12H, s), 2.27 (6H, s), 6.89 (4H, s). ^{13}C NMR ($CDCl_3$) δ: 20.7, 21.0, 86.3 ($C{=}C{=}S$), 126.1, 129.8, 137.2, 137.7, 257.0 ($C{=}C{=}S$). Mass spectrum: m/z (relative abundance, assignment): 294 (100%, M^+), 279 (12%, $M^+ - Me$), 246 (7%, $M^+ - SH - Me$), 233 (10%).

3,5-Bis(diphenylmethylene)-1,2,4-trithiane (7) and 3-(Diphenylmethylene)-5-(diphenylmethyl)-1,2,4-trithiane (8). A suspension containing diphenylacetyl chloride (2 g, 8.7 mmol) and P_2S_5 (2 g, 9 mmol) in pyridine (28 mL) was refluxed for 17 h. All the precursor had disappeared. The solution was cooled to 0 °C, aqueous phosphate buffer (pH 6.8, 50 mL) was added, and the solution was stirred for 2 h. The organic phase was extracted with ether (5 × 20 mL), washed with dilute HCl (3 × 30 mL), then with saturated $NaHCO_3$ solution (2 × 30 mL), and water (30 mL), and dried ($MgSO_4$). Evaporation of the ether left a brown solid which was chromatographed on silica with 8:2 petroleum ether: ether eluent. Two compounds were separated and identified. (i) 3,5-Bis(diphenylmethylene)-1,2,4-trithiane (**7**), (0.27 mg, 14%), mp 195−6 °C (lit. 193−4 °C).[11] IR ν_{max}(Nujol): 1594 cm^{-1} ($C{=}C$). ^1H NMR ($CDCl_3$) δ: 7.24−7.39 (20H, m); ^{13}C NMR ($CDCl_3$) δ: 127.9, 128.0, 128.2, 128.3, 129.4, 129.4, 135.7, 136.5, 141.2, 142.0. Mass spectrum: m/z (relative abundance, assignment): 452 (28%, M^+), 420 (6%, $M - S^+$), 211 (19%, $Ph_2C{=}C{=}SH^+$), 210 (100%, $Ph_2C{=}C{=}S^+$), 178 (9%, $Ph_2C_2^+$), 165 (35%, Ph_2CH^+), 89 (5%, PhC^+), 77 (4%, Ph^+). HRMS: 452.0721. Calcd for $C_{28}H_{20}S_3$: 452.0727. Microanalysis: C, 74.67; H, 4.23. Calcd for $C_{28}H_{20}S_3$: C, 74.30; H, 4.45%.

(ii) 3-(Diphenylmethylene)-5-(diphenylmethyl)-1,2,4-trithiane (**8**) (60 mg, 3%), mp 190−1 °C. IR ν_{max}(Nujol): 1598 cm^{-1} ($C{=}C$); ^1H NMR ($CDCl_3$) δ: 4.56 (1H, d), 5.75 (1H, d), 7.16−7.37 (20H, m). ^{13}C NMR ($CDCl_3$) δ: 55.2, 68.9, 127.3, 127.5, 127.5, 127.7, 127.71, 127.75, 128.2, 128.3, 128.76, 128.81, 129.1, 129.4, 132.5, 140.9, 141.7, 142.09, 142.17, 142.56.

Mass spectrum: m/z (relative abundance, assignment): 454 (18%, M^+), 253 (11%, $C_{15}H_9S_2^+$), 242 (18%, $Ph_2C{=}CS_2^+$), 212 (22%, $Ph_2CHCH{=}S^+$), 211 (33%, $Ph_2C_2SH^+$), 210 (100%, $Ph_2C{=}C{=}S^+$), 208 (10%, $Ph_2C_2S^+ - 2H$), 180 (6%, $Ph_2C{=}CH_2^+$), 178 (18%, $Ph_2C_2^+$), 167 (24%, Ph_2CH^+), 166 (15%, Ph_2C^+), 165 (52%, $Ph_2C^+ - H$), 152 (7%, $Ph_2^+ - 2H$), 89 (7%, PhC^+), 77 (8%, Ph^+); HRMS: 454.0880. Calcd for $C_{28}H_{22}S_3$: 454.0884. Microanalysis: C, 73.92; H, 5.14. Calcd for $C_{28}H_{22}S_3$: C, 73.96; H, 4.87%.

2,4-Bis(ditipylmethylene)-1,3-dithietane (10). A suspension of ditipyl ketene (0.08 g, 0.18 mmol) and P_2S_5 (0.1 g, 0.45 mmol) in pyridine (5 mL) was refluxed for 15 h. All the ketene had disappeared. The solution was cooled to 0 °C, a phosphate buffer (pH 6.8, 10 mL) was added, the mixture was stirred for 2 h, and the organic phase was extracted with ether (3 × 20 mL), washed with dilute HCl solution (20 × 3 mL), saturated aqueous $NaHCO_3$ solution (3 × 20 mL), and water (30 mL), and dried ($MgSO_4$). The ether was evaporated, and the orange oil obtained was separated on a preparative TLC plate using petroleum ether as eluent. Two compounds were separated. (i) A colorless solid (20 mg, 24%), mp 212−3 °C (lit.[5] 212−3 °C), identified as ditipylacetic acid, by its NMR spectrum. (ii) 2,4-Bis(ditipylmethylene)-1,3-dithietane (33 mg, 40%) which was obtained as an orange oil which could not be induced to crystallize. IR ν_{max}(Nujol): 1592 cm^{-1} ($C{=}C$). ^1H NMR ($CDCl_3$) δ: 0.87−1.35 (72H), 2.65−3.20 (12H, m), 6.90, 6.97, 7.06 (8H, 3s). Mass spectrum: DCI$^+$ m/z (relative abundance, assignment): 725 (45%, MH_3-Tip$^+$), 521 (23%, $MH_3 - 2Tip^+$), 464 (100%, $Tip_2C{=}C{=}SH_2^+$).

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Supporting Information Available: ORTEP drawings of **3** and **4** and details of data acquisition (6 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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