Thiocarbonyl Ylides. Generation, Properties, and Reactions[1]

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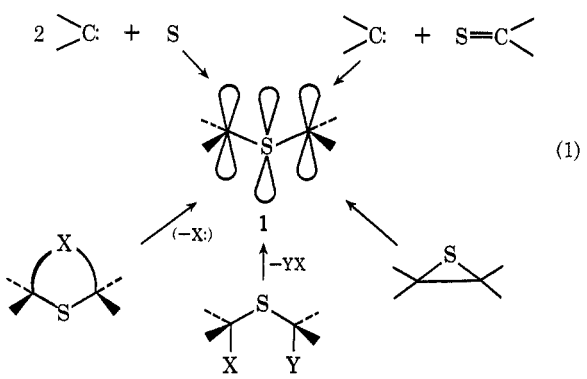
Several 2,5-dialkylsubstituted Δ^3-1,3,4-thiadiazolines have been prepared. On heating these afford unstable thiocarbonyl ylides, R_2CSCR_2, which are characterized by their tendency to yield episulfides on ring closure or cycloadducts on reaction with dipolarophiles such as dimethyl acetylenedicarboxylate or diethyl azodicarboxylate. The stereochemistry of these processes is in accord with predictions based on orbital symmetry considerations: conrotatory ring closure and retention of configuration during cycloaddition. The stereochemical behavior was established with *cis*- and *trans*-2,5-diethyl-Δ^3-1,3,4-thiadiazolines and *cis*- and *trans*-2,5-di-*tert*-butyl-Δ^3-1,3,4-thiadiazolines. Syntheses of the thiadiazolines are accomplished by (a) condensation of a carbonyl compound, hydrazine, and hydrogen sulfide to afford a 1,3,4-thiadiazolidine that is subsequently dehydrogenated; (b) addition of hydrogen sulfide to an azine followed by dehydrogenation of the 1,3,4-thiadiazolidine; (c) reaction of hydrogen sulfide with the addition products of chlorine with azines. The activation parameters for decomposition of the thiadiazolines were determined. On the basis of steric considerations, thiocarbonyl ylides are concluded to be nonplanar. Factors affecting reactivity are discussed.

The term "thiocarbonyl ylide"[3] denotes the electrically neutral entity consisting of two trivalent carbon atoms bonded to a central sulfur atom. The simplest geometrical formulation is planar **1**, which, from a pedagogical point of view, could be derived by the routes illustrated in eq 1. The components of **1**, albeit greatly



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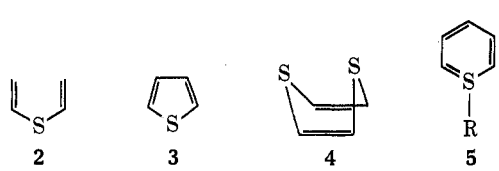
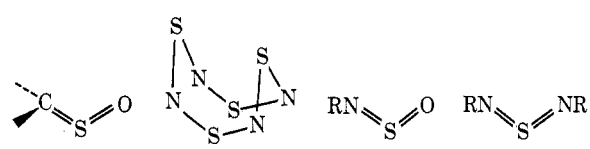
perturbed electronically and/or geometrically, are recognized in a diversity of compounds, including, for example, divinyl sulfide (**2**), thiophene (**3**), and 1,4-dithiadiene (**4**).



2 **3** **4** **5**

Our interest in generating simple examples of thiocarbonyl ylides was grounded in a variety of motives.

First, fundamental information pertinent to the long-standing question of the nature of sulfur bonding might be forthcoming. Especially the suggestion of Schomaker and Pauling[4] that in thiophene the sulfur atom may offer extra resonance possibilities by expanding its valence shell to accommodate two extra electrons has provided the impetus for numerous theoretical and experimental investigations. This question is still surrounded in controversy.[5] One notes that for thiocarbonyl ylides, like thiophene, electronic arrangements involving d-orbital participation are not mandatory; in this wise an essential difference exists with, say, thiabenzenes (**5**) wherein the illustrated resonance structure requires the accommodation of two electrons in a sulfur 3d shell.[6] Hopefully, comparison of the chemical properties of thiocarbonyl ylides with those of structurally and electronically related systems including, for example, sulfines (**6**),[7] tetrasulfur tetranitride (**7**) (the nature of the bonding here being a subject of discussion),[8] *N*-sulfinyl compounds (**8**),[9] sulfur diimides (**9**),[9] sulfur dihalides,[10] and sulfur dioxide[11,12] would shed light on the means by which bonding occurs.



6 **7** **8** **9**

Second, important stereochemical questions are associated with thiocarbonyl ylides. Presuming for the sake of argument the applicability of the planar formulation (**1**), it is readily demonstrated that the molecular orbital description of the system will qualitatively resemble that of the allyl anion. As such, highly prob-

(1) Preliminary communications: (a) R. M. Kellogg and S. Wassenaar, *Tetrahedron Lett.*, 1987 (1970); (b) R. M. Kellogg, S. Wassenaar, and J. Buter, *ibid.*, 4689 (1970).

(2) NATO Postdoctoral Fellow at the University of Groningen, 1969–1970.

(3) This name is based on the nomenclature suggested by R. Huisgen, *Angew. Chem.*, **75**, 604 (1963).

(4) V. Schomaker and L. Pauling, *J. Amer. Chem. Soc.*, **61**, 1769 (1939).

(5) See, for a theoretical discussion of the situation in thiophene, M. J. Bielefeld and D. D. Fitts, *ibid.*, **88**, 4804 (1966).

(6) C. C. Price, J. Follweiler, N. Pirelahi, and M. Siskin, *J. Org. Chem.*, **36**, 791 (1971); (b) C. C. Price, M. Siskin, and C. K. Miao, *ibid.*, **36**, 794 (1971); (c) A. G. Hortmann and R. L. Harris, *J. Amer. Chem. Soc.*, **92**, 1803 (1970).

(7) See, for example, (a) J. Strating, L. Thijs, and B. Zwanenburg, *Tetrahedron Lett.*, 65 (1966); (b) B. Zwanenburg, L. Thijs, and J. Strating, *Recl. Trav. Chim. Pays-Bas*, **86**, 577 (1967); (c) B. Zwanenburg, L. Thijs and J. Strating, *ibid.*, **90**, 614 (1971); (d) B. Zwanenburg and J. Strating, *Quart. Rep. Sulfur Chem.*, **5**, 79 (1970); (e) G. Optiz, *Angew. Chem.*, **79**, 161 (1967).

(8) (a) O. Glemser, *ibid.*, **75**, 697 (1963). (b) H. G. Heal, "Inorganic Sulfur Chemistry," G. Nickless, Ed., Elsevier, New York, N. Y., 1968, p 459. (c) For a 1,3-dipolar addition of **7**, see M. R. Brinkman and C. W. Allen, *J. Amer. Chem. Soc.*, **94**, 1550 (1972).

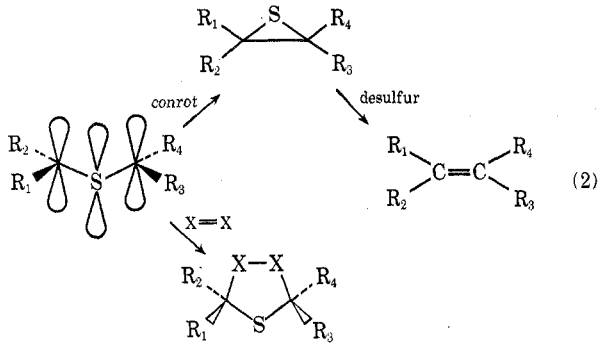
(9) W. Wucherpfennig and G. Kresze, *Tetrahedron Lett.*, 1671 (1966); (b) G. Kresze and H. Grill, *ibid.*, 4117 (1969); (c) H. Grill and G. Kresze, *ibid.*, 1427 (1970); (d) G. Kresze and W. Wucherpfennig, *Angew. Chem.*, **79**, 109 (1967), and references contained therein.

(10) For a description, see F. A. Cotton and E. Wilkinson, "Advanced Inorganic Chemistry," Interscience, New York, N. Y., 1966, pp 534–540.

(11) For early studies on the addition of sulfur dioxide to dienes, see H. J. Backer, J. Strating, and C. M. H. Kool, *Recl. Trav. Chim. Pays-Bas*, **58**, 778 (1939).

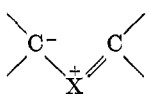
(12) For an early MO description, see (a) H. P. Koch and W. E. Moffit, *Trans. Faraday Soc.*, **47**, 7 (1951); (b) also L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, 3rd ed, Ithaca, N. Y., 1960.

able closure to isomeric episulfide (thiirane) structures is anticipated to occur with *conrotation* of the substituents (eq 2). On the other hand, thiocarbonyl



(2)

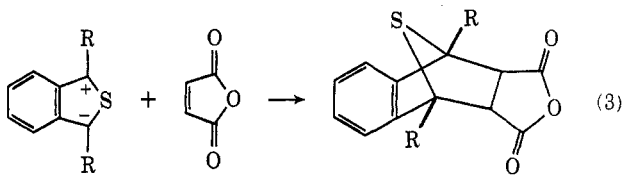
ylides obviously have 1,3-dipolar characteristics;[13] the expected cycloadditions should occur with *retention of configuration* (eq 2). These predictions, derived from conservation of orbital symmetry requirements,[14] have been amply confirmed for azomethine ylides (**10a**)[15] and carbonyl ylides (**10b**),[16] and more indirectly for the allyl anion itself.[17] We wished to test experimentally the validity of these considerations for thiocarbonyl ylides.



10a, X = NR
b, X = O

Synthetic utility proved a third motive. Successful realization of ring closure to episulfides would open a route to the possibly stereospecific syntheses of olefins (eq 2).[18] Moreover, the anticipated cycloadditions would provide routes to the synthesis of a variety of otherwise difficultly accessible heterocyclic compounds.

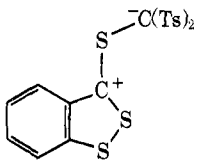
At the outset of this work, little was known about thiocarbonyl ylides. Questions of the importance of conjugation through sulfur had led to the occasional consideration of such structures.[19] The participation of this component in the cycloadditions of benzo[*c*]thiophenes (eq 3) was recognized by Pedersen.[20,21] Several



(3)

R = H[20a]
R = aryl[21]

thiophene analogs with expanded valence shells for sulfur are known[22] as well as a fascinating mesoionic structure containing the thiocarbonyl ylide system.[23] Thiocarbonyl ylide intermediates were implicated in the deprotonations of some alicyclic sulfonium salts[24] and a colored intermediate formed during low temperature irradiation of tetraphenylepisulfide might be a thiocarbonyl ylide.[25] Recently **11** was isolated as a stable substance.[26]



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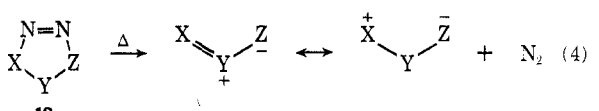
We report here our attempts to obtain a variety of thiocarbonyl ylides.

Results and Discussion

Synthesis of Precursors.—An ultimately successful approach to the generation of examples of **1** hinged on the assumption that elimination of nitrogen from the appropriate heterocyclic system (**12**) would lead to the thiocarbonyl ylide. Clear analogy for this assumption exists in the successful preparation of a variety of 1,3-dipolar intermediates[8] by the scheme depicted in eq 4. This generalized route also succeeds for the synthesis of carbonyl ylides.[16] Obtainment of the requisite Δ^3-1,3,4-thiadiazolines (**12**, X = Z = CR_2; Y = S) seemed a synthetically reasonable goal although only concurrently with our own efforts were the first examples (**13** and **14**) of this ring system reported.[27] The 1,3-4-thiadiazoline structure was established un-



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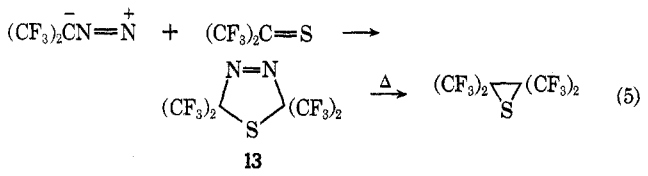
(13) R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968).
(14) R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81**, 797 (1969).
(15) (a) R. Huisgen, W. Scheer, and H. Huber, *J. Amer. Chem. Soc.*, **89**, 1753 (1967); (b) R. Huisgen, W. Scheer, and H. Mäder, *Angew. Chem. Int. Ed. Engl.*, **8**, 602 (1969); (c) R. Huisgen, W. Scheer, H. Mäder, and E. Brunn, *ibid.*, **8**, 604 (1969); (d) R. Huisgen and H. Mäder, *ibid.*, **8**, 604 (1969); (e) P. B. Woller and N. H. Cromwell, *J. Org. Chem.*, **35**, 888 (1970); (f) J. H. Hall and R. Huisgen, *Chem. Commun.*, 1187 (1971); (g) J. H. Hall, R. Huisgen, C. H. Ross, and W. Scheer, *ibid.*, 1188 (1971).
(16) (a) R. W. Hoffmann and H. J. Luthardt, *Chem. Ber.*, **101**, 3851, 3861 (1968); (b) P. Rajagopalan and B. G. Advani, *Tetrahedron Lett.*, 2689 (1967); (c) W. J. Linn and R. T. Benson, *J. Amer. Chem. Soc.*, **87**, 3657 (1965); (d) E. F. Ullmann and W. A. Henderson, Jr., *ibid.*, **88**, 4942 (1966); (e) P. Brown and R. C. Cookson, *Tetrahedron*, **24**, 2551 (1968); (f) T. Do-Minh, A. M. Trozzolo, and G. W. Griffin, *J. Amer. Chem. Soc.*, **92**, 1402 (1970); (g) D. R. Arnold and L. A. Karnischky, *ibid.*, **92**, 1404 (1970); (h) D. Seyferth and W. Tronich, *J. Organometal. Chem.*, **18**, P8 (1969); (i) C. W. Martin, J. A. Landgrebe, and E. Rapp, *Chem. Commun.*, 1438 (1971); (j) A. Dahmen, H. Hamberger, R. Huisgen, and V. Markowsky, *ibid.*, 1192 (1971).
(17) (a) P. Eberhard and R. Huisgen, *J. Amer. Chem. Soc.*, **94**, 1345 (1972); (b) R. Huisgen and P. Eberhard, *ibid.*, **94**, 1346 (1972).
(18) The principle of olefin synthesis by a "twofold extrusion process" has been elegantly enunciated by D. H. R. Barton and B. J. Willis, *J. Chem. Soc., Perkin Trans. I*, 305 (1972); *Chem. Commun.*, 1225 (1970). Among the compounds investigated was a thiadiazolidine (see further) that was concurrently prepared by our group.[1] We are grateful to Professor Barton for correspondence on this matter.
(19) See, for an early example, E. B. Knott, *J. Chem. Soc.*, 916 (1955).
(20) (a) C. T. Pedersen, *Acta Chem. Scand.*, **20**, 2314 (1966); (b) G. Wittig, E. Knaus, and K. Niethammer, *Justus Liebigs Ann. Chem.*, **630**, 10 (1960).
(21) R. Mayer, H. Kleinert, S. Richter, and K. Gewald, *Angew. Chem.*, **74**, 118 (1962).
(22) See, for example, (a) M. P. Cava and G. E. M. Husbands, *J. Amer. Chem. Soc.*, **91**, 3952 (1969); (b) J. D. Bower and R. H. Schlessinger, *ibid.*, **91**, 6891 (1969).
(23) H. Gotthardt and B. Christl, *Tetrahedron Lett.*, 4743, 4747, 4751 (1968).
(24) M. Takaku, S. Mitamura, and H. Nozaki, *ibid.*, 3651 (1969).
(25) R. S. Becker, R. O. Bost, J. Kolc, N. R. Bertonière, R. L. Smith, and G. W. Griffin, *J. Amer. Chem. Soc.*, **92**, 1302 (1970).
(26) S. Tamagaki and S. Oae, *Tetrahedron Lett.*, 1159 (1972).
(27) W. J. Middelton, *J. Org. Chem.*, **34**, 3201 (1969).

ambiguously by nmr spectroscopy and the expected episulfides were secured on thermolysis (eq 5 and 6).[28]



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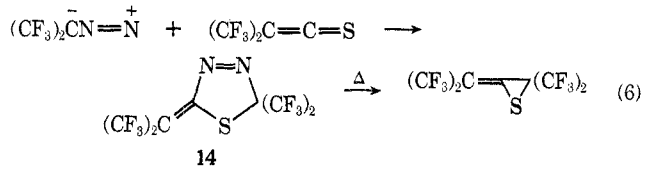

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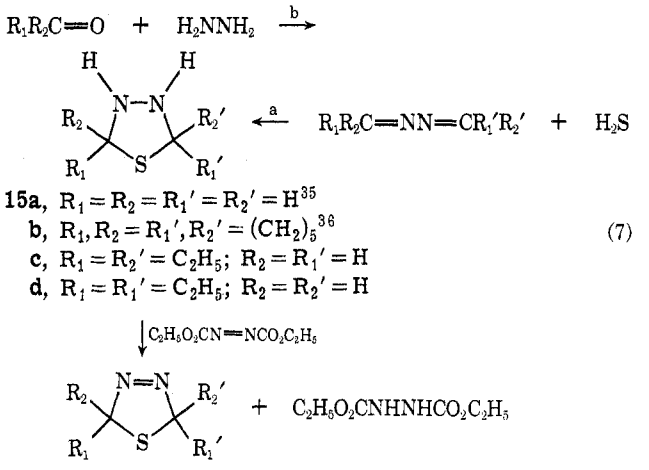
We investigated the addition of diazoalkanes to aliphatic thiocarbonyl compounds as a potential route to the desired precursors (being unaware at the time of the work of Middelton).[27,30] Although these efforts appeared to lead to partial success, we were discouraged from extensive investigation of this route owing to the difficulties, dangers, and unpleasantness associated with aliphatic diazo[32] and thiocarbonyl[33] compounds.[34] (The decision to work with aliphatically substituted derivatives was dictated by the knowledge that with the more stable aryl substituted systems only episulfide is obtained.[28,29]) A more pleasing route was the dehydrogenation of 1,3,4-thiadiazolidines (**15**), two syntheses of which had appeared in the literature (eq 7).[35,36] Neureiter[35a] had reported **15a** as the product of diazine with H_2S (route a). Earlier, Rühlmann[36] had reported some examples of a simple condensation reaction (route b), which seemed potentially amenable to considerable variation in substrate. The dehydrogenation step necessary for conversion of **15b**, chosen as a test case, to the thiadiazoline **16b** failed with heavy metal oxides, which gave only the metal sulfide. The dehydrogenation was successfully accomplished with diethyl azodicarboxylate which dehydrogenates hydrazines and other substrates presumably *via* a con-



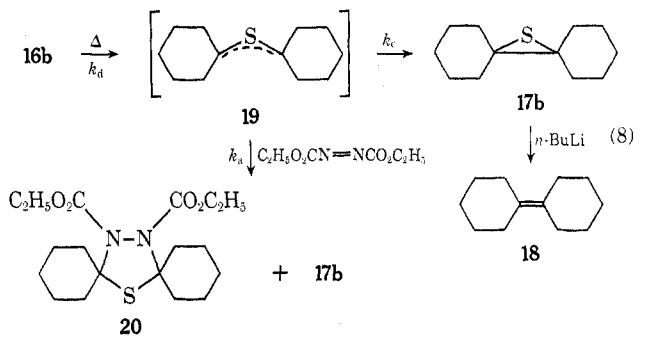
(7)

15a, $R_1=R_2=R_1'=R_2'=H$[35]
b, $R_1,R_2=R_1',R_2'=(CH_2)_5$[36]
c, $R_1=R_2'=C_2H_5$; $R_2=R_1'=H$
d, $R_1=R_1'=C_2H_5$; $R_2=R_2'=H$

16b-d

certed, six-membered transition state.[37] In ether solution **15b** reacted exothermically with this reagent affording **16b** as a stable, crystalline solid. The ir (KBr) showed a strong, characteristic absorption for -N=N- at 1570 cm^{-1} and the uv in ethanol exhibited two low intensity absorptions at 289 nm (ϵ 340) and 322 (240). This type of uv absorption was found to be characteristic of most thiadiazolines.

Chemical and Kinetic Evidence.—Pyrolysis of **16b** occurred smoothly either in the melt or in hydrocarbon solution beginning at about 80°. There was obtained in quantitative yield the episulfide **17b**, which, in addition to correct analytical data, afforded cyclohexylidenecyclohexane (**18**) in 77% yield on treatment with *n*-butyllithium (eq 8). Tentative evidence that



(8)

19 20

16b, on decomposition, affords an intermediate (**19**) was obtained from the observation (eq 8) that cycloadduct **20**, identified by analysis and spectroscopy, was obtained along with **17b** when **16b** was allowed to decompose in the presence of diethyl azodicarboxylate. Episulfide **17b** failed to react with this reagent eliminating this potential route to **20**.

If the scheme given in eq 8 is correct, namely that **16b** affords **19** with rate constant k_d and that **19** is partitioned between ring closure to **17b**, rate constant k_c, and that cycloaddition affords **20**, rate constant k_a, then, assuming a steady-state concentration of **19**, eq 9 may be

$$\frac{\ln\{[ADC]_0/([ADC]_0 - [20])\}}{[17b]} = \frac{k_a}{k_c} \quad (9)$$

derived where $[ADC]_{t=0}$ is the concentration of diethyl azodicarboxylate at the start of the reaction. By glpc using appropriate internal standards it was shown that

(28) Staudinger[29] had suggested that addition of a diazo compound to a thiocarbonyl compound should yield a Δ^2-1,2,3-thiadiazoline (i). Since

i

with, for example, diphenyl diazomethane and thiobenzophenone, only tetraphenyl episulfide could be isolated, the question was somewhat academic at the time. With a variety of aryl-substituted diazo compounds and thiocarbonyl compounds we observed spontaneous nitrogen elimination and episulfide formation even at −70°.

(29) H. Staudinger and J. Siegwart, *Helv. Chim. Acta*, **3**, 833 (1920).

(30) The Δ^3-1,3,4-thiadiazoline 1,1-dioxide structure is obtainable by the addition of diazo compounds to sulfur dioxide.[31] Pyrolysis of these compounds affords modest yields of the respective olefins (see also ref 18).

(31) (a) G. Hesse and E. Reichold, *Chem. Ber.*, **90**, 2106 (1957); (b) H. H. Inhoffen, R. Jonas, H. Kroesche, and U. Eder, *Justus Liebigs Ann. Chem.*, **694**, 19 (1966).

(32) G. M. Kaufman, J. A. Smith, G. G. Vander Stouw, and H. Shechter, *J. Amer. Chem. Soc.*, **87**, 935 (1965).

(33) R. Mayer, "Organosulfur Chemistry," M. J. Janssen, Ed., Interscience, New York, N. Y., 1967, pp 219–240.

(34) A. P. Krapcho, D. R. Raa, M. P. Silvon, and B. Abegaz, *J. Org. Chem.*, **36**, 3885 (1971), reported the successful isolation of 1,3,4-thiadiazolines from the reactions of diazomethane with some spiro thioketones.

(35) (a) N. Neureiter, *J. Amer. Chem. Soc.*, **81**, 2910 (1959). (b) We have repeated this work and have also identified **15a**, formed in low yield. Dehydrogenation to the desired thiadiazoline has thus far failed (T. Beetz, unpublished results).

(36) K. Rühlmann, *J. Prakt. Chem.*, [4] **8**, 285 (1959).

(37) F. Yoneda, K. Suzuki, and Y. Nitta, *J. Amer. Chem. Soc.*, **88**, 2328 (1966).

the yield of **20** plus **17b** was equal to the amount of **16b** consumed; hence $[ADC]_{t=t} = [ADC]_{t=0} - [20]$, which relationship is used to integrate the rate expression leading to eq 9. Calculated values for k_a/k_c as function of diethyl azodicarboxylate concentration are given in Table I. As can be seen the values of k_a/k_c are

TABLE I
VALUE OF k_a/k_c AS A FUNCTION OF DIETHYL AZODICARBOXYLATE CONCENTRATION

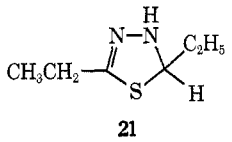
[ADC], mol/l.[a,b]	[20]/[17b]	k_a/k_c
0.103	2.32	37.7
0.129	3.06	35.9
0.161	4.10	35.2
0.204	5.13	32.4
0.249	7.33	36.2
	Av	35.5 ± 1.3

[a] Concentration of **16b** was 9.95×10^{-2} *M* for all experiments. [b] All experiments were run at 97° until **16b** was completely decomposed. Solvent was cyclohexane.

virtually invariant. A second prediction of eq 8 is that the rate constant, k_d, for decomposition of **16b** will not vary with diethyl azodicarboxylate concentration. At 97° in the absence of azodicarboxylate, $k_d = 5.36 \times 10^{-4}$ sec^{-1} for a 10^{-1} *M* solution of **16b**, whereas, with 0.204 *M* azodicarboxylate, $k_d = 5.07 \times 10^{-4}$ sec^{-1}. We submit that these product and kinetic data demonstrate the existence of an intermediate in the decomposition of **16b**, namely the thiocarbonyl ylide **19**.

Stereochemical Aspects.—With strong evidence for the existence of a thiocarbonyl ylide in hand, attention was turned to the stereochemistry of ring closure and cycloaddition. After extensive modification (Experimental Section) of the described procedure,[36] a moderate yield of **15c,d** was obtained. The isomer ratio was established by observing the resonances in the nmr spectrum for the 2,5 protons. On repeated recrystallization the major isomer, mp 70–72°, was obtained uncontaminated with the minor isomer. Unfortunately, despite the utmost care the minor isomer decomposed into azine and H_2S as soon as it was concentrated in the mother liquors.

The pure isomer, mp 72°, was dehydrogenated at −10° with diethyl azodicarboxylate. Work-up was carried out at 5–10° affording material that was clearly the desired thiadiazoline **16**. The symmetry of nmr spectrum precluded structure **21**. Spontaneous evolu-



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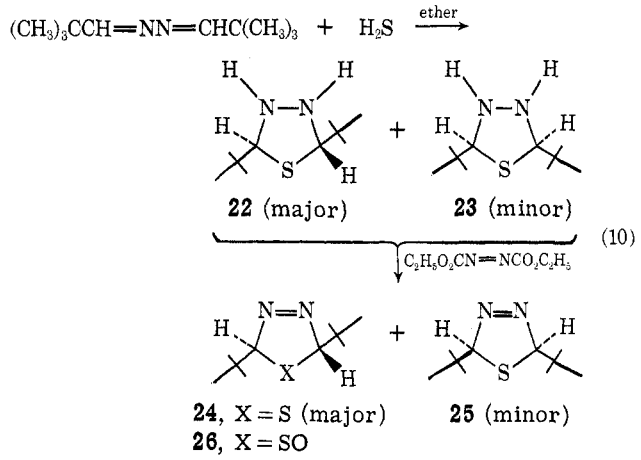
tion of nitrogen began at 30–35°. Dehydrogenation of a 75:25 mixture of **15c,d** afforded in a 75:25 ratio the previously obtained thiadiazoline plus a new thermally unstable isomer. Stereochemical assignments could be made at this point from the observation that the major isomer in CCl_4 solution showed in the nmr spectrum a complex multiplet at δ 5.90–6.25 for the 2,5 protons, whereas the minor isomer displayed at δ 4.0 a broadened quartet (J = 6.2 Hz) for the 2,5 protons (broad hump in benzene). The difference in chemical shift for these isomers is in complete accord with the idea that the major isomer is *trans*-**16c** (derived from **15c**) and the minor isomer is *cis*-**16d** (derived from **15d**).[38] Analyses of **16c,d** could not be obtained owing to their instability.

A second approach to obtaining disubstituted thiadiazolines suitable for resolution of stereochemical problems was investigated simultaneously. Condensation at room temperature of the azine of pivaldehyde and excess hydrogen sulfide in ether solution in a sealed tube (eq 10) led to precipitation of an unstable white



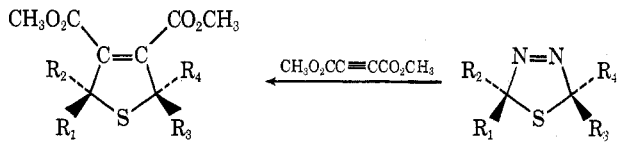
22 (major) **23** (minor) (10)

24, X = S (major) **25** (minor)
26, X = SO

solid that at −20° in $CDCl_3$ solution displayed nmr absorptions for *tert*-butyl (δ 1.01), NH (3.41), and tertiary protons (4.43) consistent with a thiadiazolidine structure (**22**). Several minor peaks remained unassigned. This material was immediately dehydrogenated with diethyl azodicarboxylate. After work-up and careful recrystallization from methanol, **24** was obtained in good yield. The structure of **24** was established by correct elemental analysis and by the nmr spectrum, which showed singlets for *tert*-butyl (δ 0.92) and the 2,5 protons (5.62). Unambiguous assignment of trans stereochemistry was obtained on oxidizing **24** to sulfoxide **26**, which showed nonequivalent *tert*-butyl (δ 1.07 and 1.40) and nonequivalent, coupled 2,5 protons (doublets, J = 1.4 Hz, at 4.05 and 5.68) consistent only with trans stereochemistry. (Despite repeated attempts a sulfoxide from **16c**, for which similar stereochemical proof would be desirable, could not be obtained.) Reexamination of the nmr spectra of freshly prepared thiadiazoline mixtures revealed, in addition to **24**, extra nmr singlets at δ 1.15 (*tert*-butyl) and 5.52 (2,5 H). These were attributed to cis isomer **25**, present in ~0.6:1 ratio with **24**. By avoiding warming, the concentration of **25** could be raised to about equal to that of **24** by crystallizing out **24**. In addition, some episulfide (see further) was present. By careful preparative layer chromatography, a pure mixture of **24** and **25** was obtained. The latter decomposes spontaneously unless kept cold. Although **25** could not be isolated free from **24**, the proposed structure was amply verified by subsequent reactions (below).

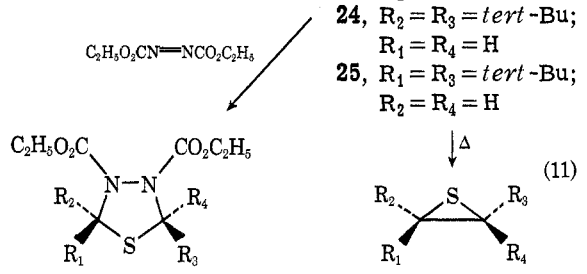
The results of the stereochemical investigations with **16c–16d** and **24–25** are summarized in eq 11. Trans isomer **16c** contaminated with <3% **16d** (nmr analysis) on pyrolysis afforded in quantitative yield a mixture consisting of 93 ± 2% **27** and 7 ± 2% **28** (glpc anal-

(38) (a) N. S. Crossley and C. Djerassi, *J. Chem. Soc.*, 1459 (1962); (b) R. U. Lemieux and J. D. Stevens, *Can. J. Chem.*, **44**, 249 (1966); (c) E. L. Eliel, M. H. Gianni, T. H. Williams, and J. D. Stothers, *Tetrahedron Lett.*, 741 (1962).



31, $R_2 = R_3 = C_2H_5$; $R_1 = R_4 = H$
32, $R_1 = R_3 = C_2H_5$; $R_2 = R_4 = H$
33, $R_2 = R_3 = tert$-Bu; $R_1 = R_4 = H$

16c, $R_2 = R_3 = C_2H_5$; $R_1 = R_4 = H$
d, $R_1 = R_3 = C_2H_5$; $R_2 = R_4 = H$
24, $R_2 = R_3 = tert$-Bu; $R_1 = R_4 = H$
25, $R_1 = R_3 = tert$-Bu; $R_2 = R_4 = H$



(11)

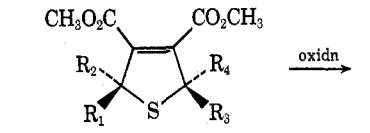
34, $R_2 = R_3 = C_2H_5$; $R_1 = R_4 = H$
35, $R_1 = R_3 = C_2H_5$; $R_2 = R_4 = H$
36, $R_2 = R_3 = tert$-Bu; $R_1 = R_4 = H$

27, $R_2 = R_3 = C_2H_5$; $R_1 = R_4 = H$
28, $R_1 = R_3 = C_2H_5$; $R_2 = R_4 = H$
29, $R_2 = R_3 = tert$-Bu; $R_1 = R_4 = H$
30, $R_1 = R_3 = tert$-Bu; $R_2 = R_4 = H$

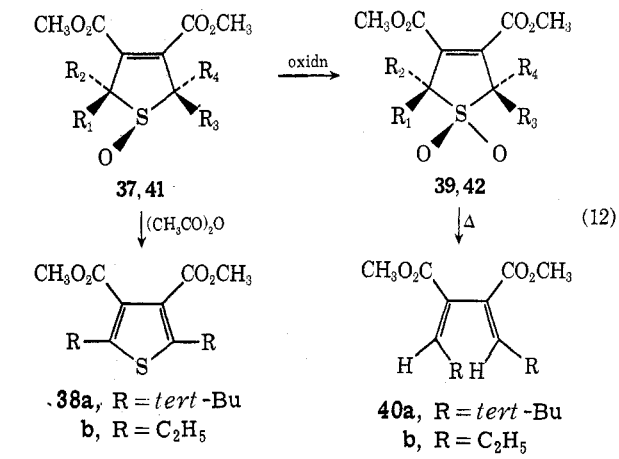
ysis). The episulfides were identified by comparison with independently synthesized samples.[39] The major product **27** is obviously that derived from predicted conrotatory ring closure (eq 2). Pyrolysis of a mixture of 80 ± 3% **16c** and 20 ± 3% **16d** afforded in quantitative yield a mixture of 69 ± 2% **27**and 31 ± 2% **28**. Using the data for pure **16c**, the ring closure of **16d** is calculated to proceed essentially 100% conrotatorily. (This obviously suggests "leakage" of the thiocarbonyl ylide derived from **16c** to disrotatory product **28**. However, the necessity of using imprecise nmr analyses to determine **16c**:**16d** ratios suggests caution in drawing conclusions.)

Far more dramatic evidence for conrotatory ring closure was obtained with **24** and **25**. Pyrolysis of repeatedly recrystallized **24** afforded in quantitative yield *exclusively* **29**,[40] the stereochemistry of which was established by desulfurization with *n*-butyllithium affording *cis*-di-*tert*-butylethylene.[41] Isomer **25**, present as a mixture with **24**, could be selectively pyrolyzed at 40° at which temperature **24** fails to decompose. There was obtained *exclusively* **30**, identified by desulfurization to *trans*-di-*tert*-butylethylene.

The cycloaddition reactions illustrated in eq 11 are within experimental error completely stereospecific. Nearly quantitative yields can usually be obtained by using 2–3-fold excesses of dipolarophile. The general principle used for stereochemical assignment of the trans cycloaddition products with dimethyl acetylenedicarboxylate is given in eq 12. Sodium metaperiodate or *m*-chloroperbenzoic acid oxidation of **33** led to sulfoxide **37** with nonequivalent *tert*-butyl groups in the



33, $R_2 = R_3 = tert$-Bu; $R_1 = R_4 = H$
31, $R_2 = R_3 = C_2H_5$; $R_1 = R_4 = H$



(12)

38a, $R = tert$-Bu
b, $R = C_2H_5$

40a, $R = tert$-Bu
b, $R = C_2H_5$

nmr spectrum. Further oxidation led to sulfone **39** in which C_2 symmetry was reestablished. Pyrolysis afforded exclusively the known[42] diene **40** by the expected disrotatory course of the retro reaction.[43,44] An analogous cycle was carried out with *trans*-**31** yielding ultimately the known[42] *Z,E*-diene **40b**. The sulfone **42** appears to epimerize readily. Both sulfoxides **37** and **41** could be dehydrated to the respective thiophenes **38a,b**.[45] Similar stereochemical proofs were carried out for **34**–**36**; these are described in the Experimental Section.

Unfortunately, **25** stubbornly refused to react with dipolarophiles. Only trans episulfide **30** was obtained on attempted reaction with dimethyl acetylenedicarboxylate or dicyanoacetylene. With diethyl azodicarboxylate some dehydrogenation to 2,5-di-*tert*-butyl-1,3,4-thiadiazole took place. Stereospecific addition could be established with **16d**, however. A 20:80 mixture of **16d** and **16c** (determined by nmr) afforded 22:78 mixture (glpc analysis) of **32** and **31**, respectively. The cis isomer **32** was isolated by preparative glpc and it was identified by its nmr spectrum, which, in addition to the expected ethyl and methoxy absorptions, showed the 2,5 tertiary protons at 0.36-ppm higher field than those of **31** as is expected for the cis configuration.[38] No further transformations were carried out with **32** owing to the extreme difficulty in obtaining pure material, caused by the ready dehydrogenation to thiophene **38b**.

The results of eq 11 demonstrate that thiocarbonyl ylides react in accord with Woodward–Hoffmann predictions, namely retention of configuration during cycloaddition ($[4_s + 2_s]$ reaction) and conrotatory ring closure, and this even in the face of serious steric interactions as illustrated with **24** where ring closure results in the energetically unfavorable cis positioning of two *tert*-butyl groups. Although the observation is qualitative, the difference in proclivity for cycloaddition of

(39) N. P. Neureiter and F. G. Bordwell, *J. Amer. Chem. Soc.*, **81**, 578 (1959).

(40) If **24** has not been recrystallized several times, small amounts of *trans*-**30** are obtained. This was apparently the cause of the formation of small amounts of this isomer reported previously.[1b]

(41) W. H. Puterbaugh and M. S. Newman, *J. Amer. Chem. Soc.*, **81**, 1611 (1959).

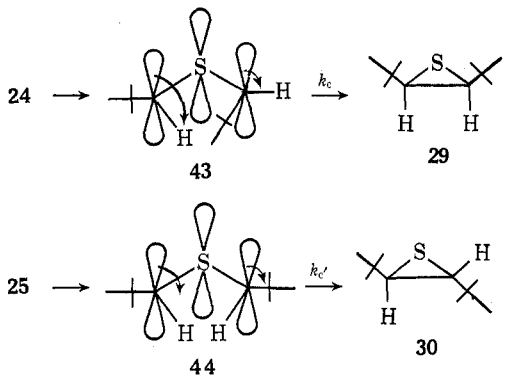
(42) R. M. Kellogg, *ibid.*, **93**, 2344 (1971).

(43) W. L. Mock, *ibid.*, **88**, 2857 (1966).

(44) S. D. McGregor and D. M. Lemal, *ibid.*, **88**, 2858 (1966).

(45) M. P. Cava and N. M. Pollack, *ibid.*, **88**, 4112 (1966).

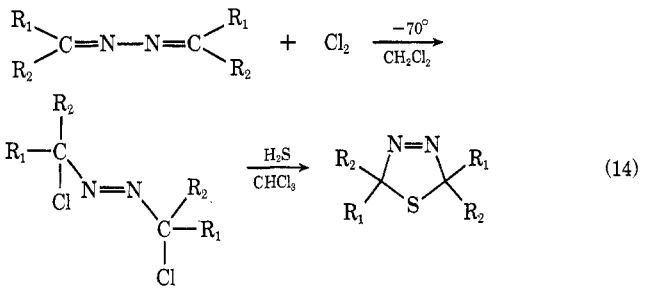
the thiocarbonyl ylides **43** and **44**, derived from **24** and **25** (eq 13), respectively, can likely be attributed to



(13)

steric effects. In **43** developing steric interactions will diminish the rate constant for ring closure, k_c, relative to k_c' for **44** (drawn in the sterically more probable "W" conformation). This will result in a longer lifetime for **43** relative to **44** allowing the former to have a greater chance of undergoing bimolecular cycloaddition, as is indeed observed.

General Synthesis of Thiadiazolines.—We next initiated a search for general syntheses of a variety of thiadiazolines. The routes proceeding through thiadiazolidines, formed either by condensation of a carbonyl component, hydrazine, and hydrogen sulfide or by addition of hydrogen sulfide to azines (eq 7) were applicable only to special cases likely owing to the instability of thiadiazolidine relative to azine and hydrogen sulfide. The most successful general method that we developed is shown in eq 14. This synthesis



(14)

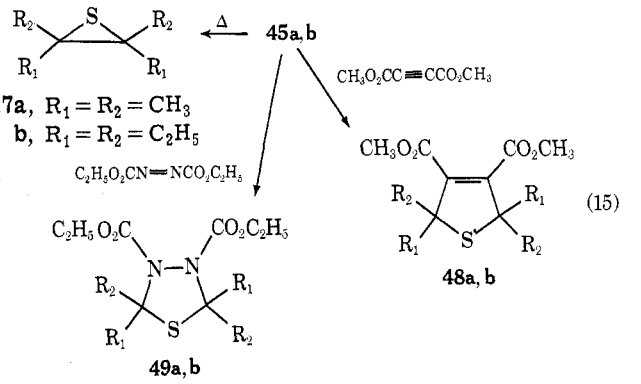
45a, $R_1 = R_2 = CH_3$
b, $R_1 = R_2 = C_2H_5$
c, $R_1 = R_2 = (CH_2)_2CH(tert\text{-}Bu)(CH_2)_2$
d, $R_1, R_2 = (CH_2)_6$
e, $R_1 = tert\text{-}Bu$; $R_2 = CH_3$

is deliberately designed to avoid the unstable thiadiazolidine stage by "oxidizing" the azine prior to ring closure. The 1,4 addition of chlorine to (chiefly aliphatic) azines is a smooth reaction[46-48] and the dichloroazoalkanes formed are extremely subject to reaction with nucleophilic species. These reactions are presumed to involve a carbonium ion intermediate (**46**).

$$R_1R_2\overset{+}{C}\text{—}N\text{=}N\text{—}C(Cl)R_1R_2$$
46

This knowledge hinted that reaction with a bidentate nucleophile might succeed since the steric constraint engendered by the trans geometry of the azo compound could be released in the intermediate carbonium ion allowing ring closure. After considerable experimentation it was found that ring closure occurred on allowing the dichloroazoalkane to react with hydrogen sulfide gas in chloroform solution. The thiadiazolines **45** were obtained in 60–100% yield. The conditions are admittedly rather bizarre for a carbonium ion reaction, and indeed another mechanism could be operative. However, success does recommend this technique. The compound **45c** was also prepared by the thiadiazolidine method similar to that in eq 7. In most cases the thiadiazolines were also oxidized to their respective sulfoxides and sulfones (Experimental Section).

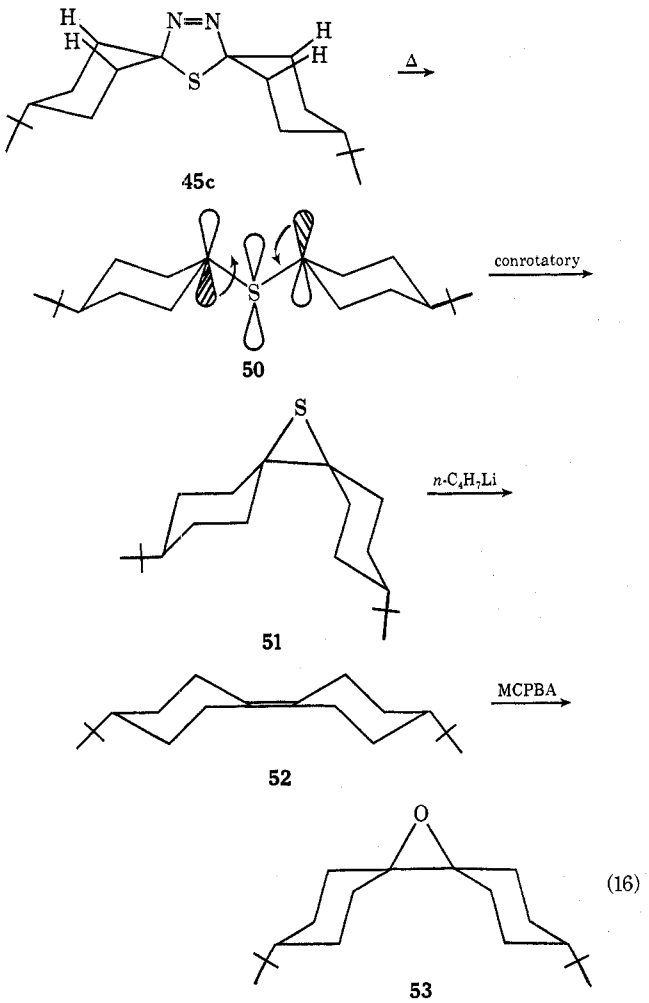
Comments on Thiadiazoline Reactions.—Several points observed in the reactions of **45a–e** deserve mention. Both **45a** and **45b** reacted as expected affording the episulfides **47a,b** on pyrolysis either neat or in methylcyclohexane. In the presence of either dimethyl acetylenedicarboxylate or diethyl azodicarboxylate the corresponding cycloadducts **48** and **49** are isolated (eq 15). The episulfides **47** can be converted to the respective olefins.[49]



(15)

Rather interesting stereochemical aspects are associated with **45c**. Its nmr spectrum displays a single absorption for the *tert*-butyl groups and in the presence of tris(dipivalomethanato)europium a broad, poorly resolved triplet corresponding to four protons is shifted downfield. This points to a symmetrical structure, and likely that with the azo bridge located equatorially, since the broad triplet probably arises from axial protons[50] and in the indicated structure (eq 16) the axial protons are indeed brought into the vicinity of where complex forming is expected. Pyrolysis of **45c** gave a single episulfide, mp 205–207°, that had nonequivalent *tert*-butyl groups (δ 0.85 and 0.90). We believe this to be **51** formed from *conrotatory* ring closure of thiocarbonyl ylide **50**. On treatment with *n*-butyllithium **51** afforded olefin **52** (equivalent *tert*-butyl groups). Epoxidation of **52** gave **53** with equivalent *tert*-butyl groups. The indicated configuration (eq 16) is based on the rather tenuous assumption that less 1,3-diaxial interaction will be involved in the indicated direction of

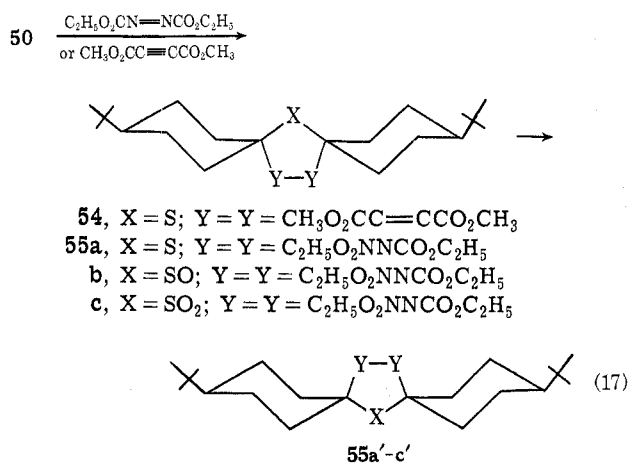
(46) S. Goldschmidt and B. Acksteiner, *Justus Liebigs Ann. Chem.*, **618**, 173 (1958).
(47) E. Benzing, *ibid.*, **631**, 1 (1960).
(48) D. S. Malament and J. M. McBride, *J. Amer. Chem. Soc.*, **92**, 4586, 4593 (1970).
(49) F. G. Bordwell, N. M. Andersen, and B. M. Pitt, *ibid.*, **76**, 1082 (1959).
(50) (a) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance," Vol. 2, Pergamon Press, Oxford, 1966, p 703; (b) P. D. Readio and P. S. Skell, *J. Org. Chem.*, **31**, 759 (1966).



(16)

attack. As expected **53** could not be converted to an episulfide on treatment with thiocyanate.

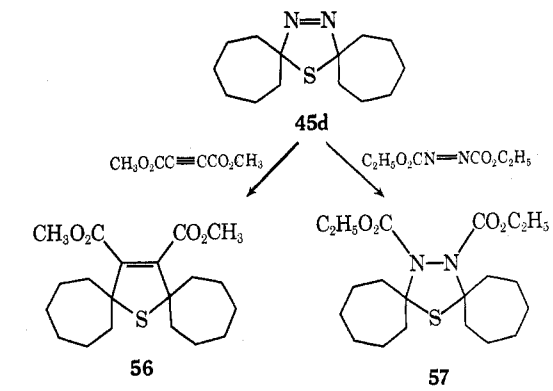
Cycloaddition of **51** to dimethyl acetylenedicarboxylate proceeded sluggishly giving in 13% yield (after extensive purification) a cycloadduct **54** (eq 17).



(17)

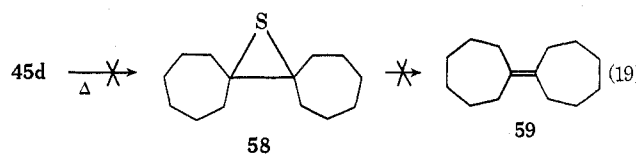
This appeared to be a single isomer as judged by the sharp melting point (133–135°) and the appearance of a single sharp absorption for the *tert*-butyl protons in the nmr spectrum (however, the methoxy absorption was suspiciously broadened). Inspection of models leads to the anticipation that the direction of approach leading to **54** involves the least steric interaction. However, reaction with diethyl azodicarboxylate led in 95% yield to an ~60:40 mixture of cycloadducts for which structures **55a** and **55a′** are suggested. That a mixture is present is indicated by overlapping quartets and triplets for the methylene and methyl resonances, respectively, in the nmr spectrum. This nonequivalence is maintained in the sulfoxides **55b** and **55b′** and the sulfones **55c** and **55c′**. Although the nmr spectra of **54** and **55a** and **55a′** were affected by europium complexes, no conclusions could be drawn.

The cycloheptyl compound **45d** underwent cycloaddition with dimethyl acetylenedicarboxylate and diethyl azodicarboxylate giving **56** and **57**, respectively (eq 18).[51] Despite repeated attempts under a wide



(18)

variety of conditions neither episulfide **58** nor cycloheptylidenecycloheptane **59** could be secured on pyrolysis of **45d** (eq 19). Only intractable materials

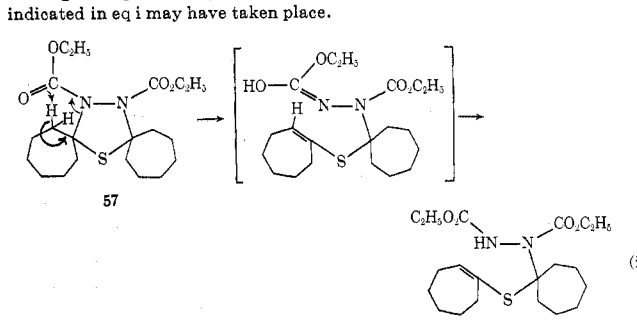


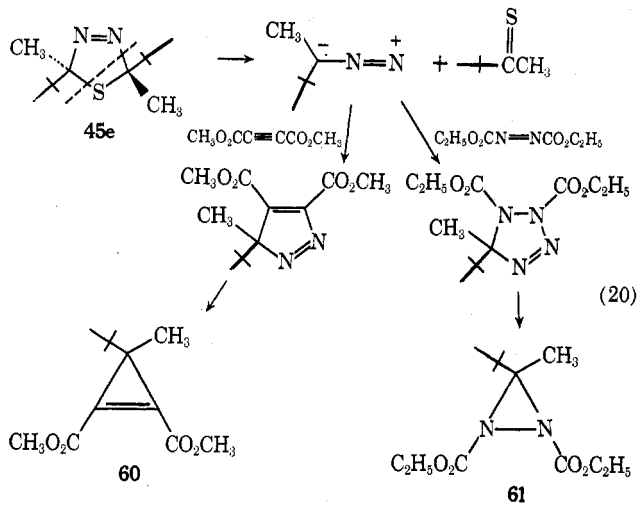
(19)

were isolated. The causes for the failure of this reaction are mysterious.

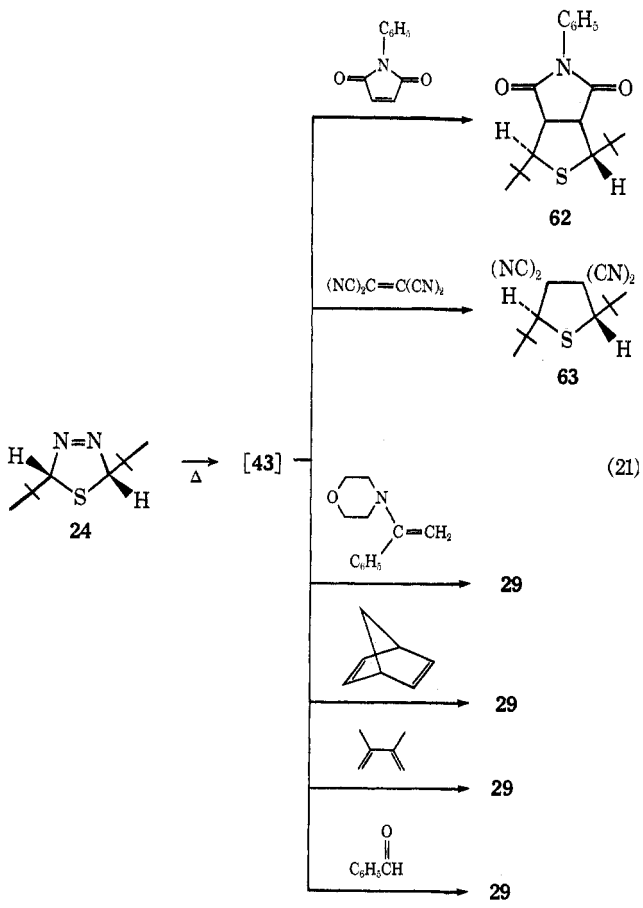
Thiadiazoline **45e** on pyrolysis under a variety of conditions gave extremely complex mixtures that may contain small amounts of olefin. Decomposition in the presence of dipolarophiles also failed to give the expected cycloadducts. Although the reactions are difficultly reproducible, low yields of compounds with nmr and mass spectra consistent with **60** and **61** were obtained from attempted cycloadditions. This might be accounted for by the route suggested in eq 20 wherein cleavage to a diazo compound and a thiocarbonyl compound occurs.

(51) On attempted distillation **57** rearranged to a isomer containing a vinylic proton, an NH group, and nonequivalent carbomethoxy groups. At the high temperature (130°) required for distillation, the rearrangement indicated in eq i may have taken place.





Cycloaddition reactions were attempted with a variety of dipolarophiles using the thiocarbonyl ylide **43** derived from **24** (eq 21). This intermediate is one of



the most reactive towards cycloaddition. The cycloadducts **62** and **63** were obtained in good yield, but attempted cycloaddition with enamines, 2,3-dimethylbutadiene, norbornadiene, or benzaldehyde, led to *cis*-**29** as the exclusive product.

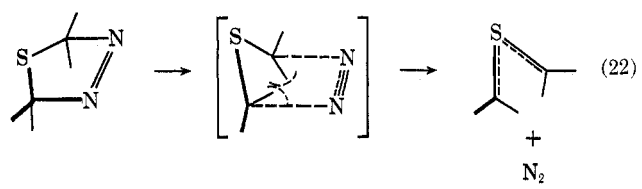
Kinetic Parameters for Thiadiazoline Decomposition.—In Table II the activation parameters are compiled for the decomposition of a variety of thiadiazolines. All compounds decomposed smoothly following first-order kinetics through at least two half-lives and the rate constants (checked with **16b**) were independent of concentration in the range 10^{-1}–10^{-2} M. For the compounds measured the relative rates corrected to 25° span a range of nearly 10^5 or $\sim 10^4$ if one rejects **45e** as a reference because products from its decomposition are anomalous. Obviously a variety of factors reflected in modest changes in $\Delta H^{\ddagger}$ and appreciable fluctuations in the size of $\Delta S^{\ddagger}$ cause these rather large rate variations. Comparing **45a** with 3,3,-5,5-tetramethylpyrazoline ($\Delta H^{\ddagger}_{298°}$ = 37.1 kcal/mol, $\Delta S^{\ddagger}_{250°}$ = 4.6 eu in the gas phase)[52] a lowering of $\Delta H^{\ddagger}$ by 11 kcal/mol is noted. Although hydrocarbon analogs are not known for the other isomers tabulated in Table II, roughly similar lowering of activation energies for decomposition would be expected. Two major factors are presumed operative in increasing so drastically the rate of nitrogen elimination from thiadiazolines relative to pyrazolines. First, the presence of a sulfur atom will relieve some steric interaction relative to the pyrazoline. One expects puckered conformations[53] for thiadiazolines as illustrated as in eq 22.

TABLE II

KINETIC PARAMETERS FOR THE DECOMPOSITION OF THIADIAZOLINES

Compd	$\Delta H^{\ddagger}_{298°}$, kcal/mol[a]	$\Delta S^{\ddagger}_{298°}$, eu[b]	k_{25}, sec^{-1}	Rel reactivity
45c	31.4	11.6	$8.50.10^{-9}$	73.8
45d	26.8	7.9	$3.09.10^{-6}$	26,800
45e	30.8	1.1	$1.15.10^{-10}$	1.0
45b	28.1	4.7	$5.62.10^{-8}$	489
45a	26.0	3.3	$9.3.10^{-7}$	8,080
16b	29.2	7.0	$2.82.10^{-8}$	245
15c[c]	26.9	11.1	$1.02.10^{-5}$	87,900
24	30.1	9.7	$2.82.10^{-8}$	245

[a] Maximum errors ±1.0 kcal/mol. [b] Maximum errors ±3.0 eu. [c] Determined by nmr spectroscopy.



This is well illustrated by the upfield shifts of the tertiary protons of *cis*-**25**, relative to those of *trans*-**24**, and *cis*-**16**, relative to those of *trans*-**16**, arising from the tendency of the alkyl substituents to remain equatorial forcing the axially located hydrogen atoms into the shielding region of the azo group (eq 22).[54] An increase in puckering in the transition state may involve less nonbonding interactions between the departing nitrogen and sulfur than in the pyrazolines. This may account for the troubles with **45e** where a *tert*-butyl and a methyl substituent are forced together. Second, and likely more important, sulfur substituents α to an azo functionality are known to exert a presumed resonance effect which lowers the activation energies for decomposition.[55] The thiocarbonyl ylide formed can be viewed as a stabilized 1,3 biradical[13,56] and the transition state will likely benefit from this potential stabilization. However, since stabilization is

(52) R. J. Crawford, A. Mishra, and R. J. Dummel, *J. Amer. Chem. Soc.*, **88**, 3959 (1966).

(53) E. L. Eliel, "The Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N. Y., 1962, pp 248–252.

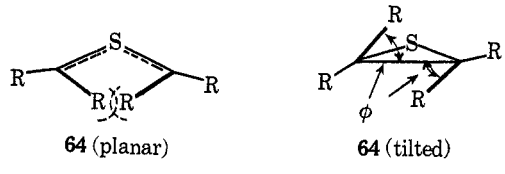
(54) J. J. Uebel and J. C. Martin, *J. Amer. Chem. Soc.*, **86**, 4618 (1964).

(55) See, for example, A. Ohne and Y. Ohnishi, *Tetrahedron Lett.*, 4405 (1969).

(56) (a) L. Salem, *Chem. Commun.*, 981 (1970); (b) E. F. Hayes and A. K. Q. Sin, *J. Amer. Chem. Soc.*, **93**, 2091 (1971).

gained, at least to the first approximation, by overlap of the developing carbon p orbital with the sulfur 3p orbital, the transition state will likely be a complicated conformational compromise allowing the developing p orbitals on carbon in so far possible to overlap with the sulfur 3p orbital. Although the relative rate differences among the various thiadiazolines are large, it is difficult to distinguish unambiguously a trend of steric effects that rationalizes the rates of decomposition. Similar problems attend interpretations of activation parameters for pyrazoline decomposition.[57]

The Geometry of Thiocarbonyl Ylides.—The intermediate generated on decomposition of thiadiazolines obediently behaves according to the Woodward–Hoffmann predictions for the formulation **1**. But does planar **1** represent the correct geometry for the thiocarbonyl ylide? The somewhat embarrassing answer must be *no*, at least for certain examples. Consider for example the thiocarbonyl ylide **64** (R = CH_3) derived from **45a**. The C–S–C bond angle[58,59] should not exceed 120° (measured for SO_2)[60] and will be likely closer to that in di-*p*-tolyl sulfide, 109°.[59,61] Using this bond angle and also the carbon–sulfur bond lengths for this molecule, 1.75 Å, and normal carbon–carbon and carbon–hydrogen bond lengths for **64** (R = CH_3), in a planar arrangement the closest approach of nuclear centers of hydrogens on the inner methyl groups is 0.3 Å. Presuming that this obviously untenable situation is relieved by tilting of one p orbital upward by an angle φ and the other downward also by angle φ, then, when the distance of closest approach of the two hydrogen atoms is the sum of the Van der Waals radii, $2\varphi = 92°$. This is readily determined from straightforward geometrical considerations.



64 (planar) **64** (tilted)

The tilted model is crude but the conclusion is inescapable, namely, that at least in **64** (the situation is even worse in the tetraethyl derivative) a fully planar geometry is impossible. Spreading of the C–S–C angle to even 120° helps relieve, but does not remove, steric interactions. The same problem is present even in less highly substituted intermediates such as **43** where severe *tert*-butyl–hydrogen interaction is expected in a planar conformation. If the tilted formulation of **64** is correct, the bonding likely involves some form of p–d hybridization.

(57) (a) A "recoil" effect resulting in inversion of configuration at the carbon atom is suggested to be operative at least in bicyclic compounds: E. L. Allred and R. L. Smith, *ibid.*, **91**, 6766 (1969). (b) Strong conformational preferences in the transition states for decomposition of diazabicyclo[2.1.0]pentane derivatives has been demonstrated by J. A. Berson and S. S. Olin, *ibid.*, **91**, 777 (1969).

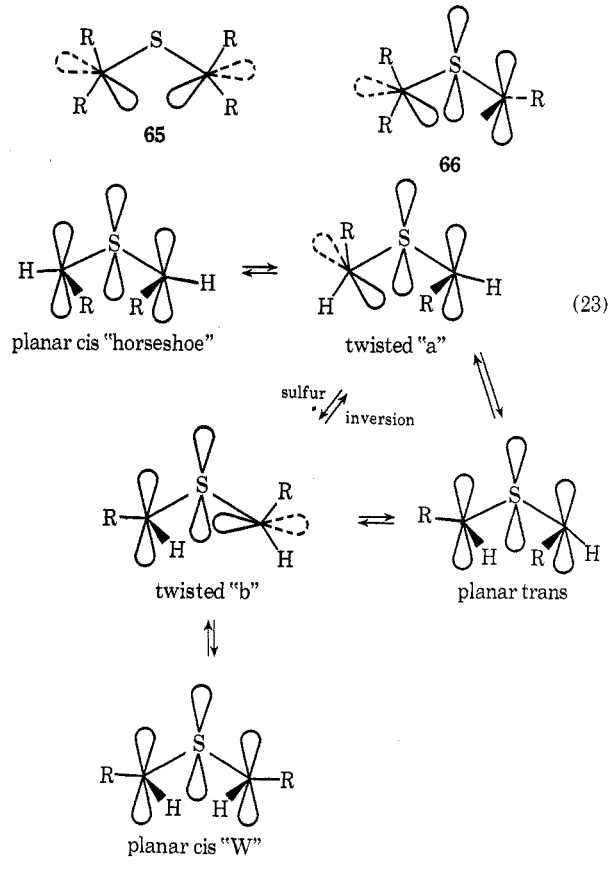
(58) That thiocarbonyl ylides should be nonlinear follows directly from application of Walsh's rules: (a) A. D. Walsh, *J. Chem. Soc.*, 2260, 2266, 2288, 2296, 2301 (1953); (b) Y. Takahata, G. W. Schnuelle, and R. G. Parr, *J. Amer. Chem. Soc.*, **93**, 784 (1971); (c) H. B. Thompson, *ibid.*, **93**, 4609 (1971).

(59) For a general review of the geometry of sulfur compounds, see S. C. Abrahams, *Quart. Rev.*, **X**, 407 (1956).

(60) M. H. Sirvetz, *J. Chem. Phys.*, **19**, 938 (1951).

(61) W. R. Blackmore and S. C. Abrahams, *Acta Crystallogr.*, **8**, 329 (1959).

Are there geometrical alternatives to a tilted model? Two conceivable possibilities are **65** and **66**. The geometry of **65** is that of an episulfide save that the C–S–C interior angle is widened. Collapse to an episulfide seems the most obvious fate of **66**.[62] The half-twisted geometry of **66** is more intriguing. But can **66** pass the crucial test of predicting conrotatory ring closure? Owing to the expectations that the C–S–C bond angle is not 180°,[58] disubstituted **66** has two forms (which is not the case in a linear allene). The *completely hypothetical* isomerization sequence of eq 23 illustrates some geometrical relationships. The twisted "a" and "b" forms are derivable from *either* cis or trans geometrical forms; as such they bear no geometrical "memory" of their origin with respect to cis or trans (but there is memory for the type of cis). Likewise any electronic "memory" is difficult to see; formulation of ring closure as a [$2_a + 2_s$] reaction leads to no unique stereochemical predictions. Stereospecific cycloaddition is also difficult to rationalize. Unequivocal rejection of an intermediate at this stage of knowledge is unwise, but the evidence now in hand does suggest that the tilted model **64** is a better approximation than twisted **66** (or **65**) for the thiocarbonyl ylide structure. One also notes that the di-*p*-tolyl sulfide is tilted 32–35° in the crystal structure.[59]



If thiocarbonyl ylides do not have a planar structure, is the simple Woodward–Hoffman argumentation used in the discussion invalid? Most likely not, if the tilted structure **64** provides a fair estimate of the true geometry. No obvious reason is present why a tilted

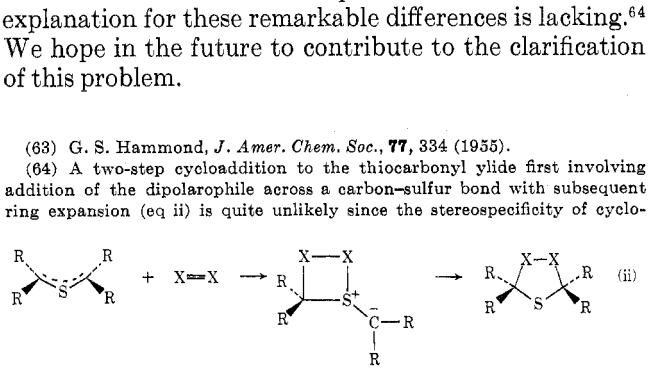
(62) See ref 13 for calculations on the trimethylene with equivalent geometry.

structure should not have roughly the same ordering of molecular orbitals as in a planar arrangement, although this conclusion has not yet been supported by calculation. But note, however, that the most dramatic tests of conrotatory ring closure are provided with the di-*tert*-butyl derivatives **43** and **44**. *Conrotatory* ring closure of **43**, for example, if in tilted conformation **64**, could involve a synchronous movement of one (inner) substituent downwards through an angle of $\sim 120° - \varphi$ and the other upward through essentially the same angle (presuming that in the episulfide the substituents make a 120° angle with the carbon–carbon bond). Steric interference will develop late in the transition state. A disrotatory motion could involve either (a) passing through a hindered planar conformation with *tert*-butyl–hydrogen interactions or (b) a movement wherein one (inner) substituent moves through an angle of $\sim 120° - \varphi$ while the other (inner) substituent moves through an angle $120° + \varphi$. The latter motion, besides being completely nonsynchronous, also involves interaction of the inner substituents. Thus, if the transition state is reached early,[63] the conrotatory motion in **43** may well be energetically more favorable *on steric grounds*, at least in the early stages of the reaction. Trans episulfide **30** is expected from **44** purely on steric arguments. With the thiocarbonyl ylides bearing ethyl groups, which are sterically less demanding than *tert*-butyl, there may well be some "leakage" of *trans*-thiocarbonyl ylide to trans episulfide **28**. The suggestion is, therefore, that there may be a built-in stereochemical bias favoring conrotatory ring closure and that this could significantly augment (or mask) any electronic effect. The high retention of configuration during cycloaddition is logical since any "leakage" would involve less likely complete cis–trans isomerization of the thiocarbonyl ylide.

A final point deals with the problems raised on comparing the chemistry of thiocarbonyl ylides with that of sulfur dioxide, sulfur diimides (**9**), *N*-sulfinyl compounds (**8**), and sulfines (**6**). Of this series only thiocarbonyl ylides isomerize to the three-membered rings (episulfides). Thiocarbonyl ylides react with good dipolarophiles yielding products derived from addition at the two carbon atoms; tetrasulfur tetranitride (**7**) behaves similarly,[8c] but sulfur dioxide adds dienes across the sulfur atom,[11,43,44] and sulfines,[7] *N*-sulfinyl compounds,[9] and sulfur diimides[9] add dienes across a carbon–sulfur or a nitrogen–sulfur bond whereas thiocarbonyl ylides (at least those prepared so far) do not react with dienes. At the present time a consistent explanation for these remarkable differences is lacking.[64] We hope in the future to contribute to the clarification of this problem.

(63) G. S. Hammond, *J. Amer. Chem. Soc.*, **77**, 334 (1955).

(64) A two-step cycloaddition to the thiocarbonyl ylide first involving addition of the dipolarophile across a carbon–sulfur bond with subsequent ring expansion (eq ii) is quite unlikely since the stereospecificity of cyclo-



addition is hard to rationalize. The type of reaction has been observed for *N*-sulfinyl compounds[9c] but only with ketenes, which are known to participate readily in [2 + 2] dimerizations.[14]

Experimental Section

All melting points were determined with calibrated thermometers on a melting point block; boiling points are uncorrected. Uv, ir, and nmr spectra were obtained on common laboratory instruments; mass spectra (also coupled with glpc) were taken on an AEI MS 9 instrument.

All chemicals cited without reference were either in stock or were prepared by well-known laboratory methods. Elemental analyses were carried out at this university. In some cases difficulty was experienced with sulfur or nitrogen determinations; in that case mass spectral determination of the molecular weight was done.

Preparation of 2,2,5,5-bis(pentamethylene)-1,3,4-Δ³-thiadiazoline (16b) was accomplished from the analogous[1,3,4] thiadiazolidine (**15b**) prepared as described.[36] The crude thiadiazolidine was dissolved in ether and treated with an equimolar amount of diethyl azodicarboxylate, whereupon a vigorous reaction ensued. After standing overnight the reaction mixture was evaporated to dryness and the residue taken up in petroleum ether (bp 40–60°). The diethyl hydrazodicarboxylate, mp 133° (lit.[65] mp 129–131°), dissolves only slightly in hydrocarbon solvents and may be filtered off readily. The filtrate, after removal of solvent, was chromatographed over Al_2O_3 using benzene as eluent. The crude product was recrystallized from methanol giving **16b** in 54% yield (based on cyclohexanone using impure **15b**): mp 81–82° (without decomposition); ir (KBr) 1579 cm^{-1} (N=N); uv max (96% EtOH) 2890 Å (ε 342) and 3220 (238). Reactions using purified **15b** (involving extra loss of material) gave **16b** quantitatively.

Anal. Calcd for $C_{12}H_{20}N_2S$: C, 64.23; H, 9.00; S, 14.29; N, 12.48. Found: C, 64.15; H, 8.95; S, 14.22; N, 12.44.

Pyrolysis of 16b was carried out by refluxing a sample (500 mg, 2.23 mmol) in 100 ml of petroleum ether (bp 80–100°) for 5 hr. Removal of the solvent left virtually pure **17b** (449 mg, 2.29 mmol, 103% yield). This was recrystallized from methanol to give an analytical sample, mp 75–77°, uv max (96% EtOH) 2590 Å (ε 50).

Anal. Calcd for $C_{12}H_{20}S$: C, 73.39; H, 10.29; S, 16.33; mol wt, 196. Found: C, 73.24; H, 10.19; S, 16.33; mol wt (osmometry in C_6H_6), 199.9.

Desulfurization of 2,2,3,3-bis(pentamethylene)episulfide (17b) was done with a sample of **17b** (250 mg, 2.3 mmol) dissolved in 10 ml of dry ether. This was treated at room temperature with *n*-butyllithium (10 ml, 0.8 *M* in ether solution). A yellow precipitate formed during addition. After 3 hr at room temperature, water was added, and the organic layer was extracted with ether. The ether layer was washed with dilute NaOH and with water. After the mixture was dried over M_5SO_4, there was obtained cyclohexylidenecyclohexane (**18**) (290 mg, 1.76 mmol, 77%), mp 55° (lit.[66] mp 55, 54.5–55.5°).

Cycloaddition of 16b (486 mg, 2.17 mmol) was carried out with diethyl azodicarboxylate (271 mg, 1.56 mmol) in 15 ml of petroleum ether (bp 80–100°). The solution was refluxed for 5 hr and the solvent was removed. The semisolid residue was chromatographed over 100 g of Al_2O_3 (neutral); elution with 150 ml of 10% ether–90% benzene gave **17b** (100 mg, 0.51 mmol, 23%) (a portion of the episulfide was lost during manipulation). The rest of the organic material was eluted with 100% ether giving 2,2,5,5-bis(pentamethylene)-3,4-dicarboethoxy-1,3,4-thiadiazolidine (**20**) as a clear oil (230 mg, 0.62 mmol, 40%) that solidified on standing. Three recrystallizations from methanol gave an analytical sample: mp 65–67.5°; ir (KBr) 1720 cm^{-1} (C=O); nmr (CCl_4) δ 1.23 (t, J = 7.0 Hz, 6 H, CH_3), 1.40–2.20 (complex m, 20 H, ring (CH_2), 4.10 (q, J = 7.0 Hz, 4, OCH_2CH_3).

Anal. Calcd for $C_{18}H_{30}N_2O_4S$: C, 58.34; H, 8.10; N, 7.56; S, 8.65. Found: C, 58.02; H, 8.23; N, 7.57; S, 8.62.

Various attempts were made to obtain a cycloaddition product from **16b** and dimethyl acetylenedicarboxylate. Although nmr spectra were consistent with the formation of small amounts of adduct, the chief product was **17b** and only this product could be obtained on working up the reaction mixture.

Stability of 17b in the presence of diethyl azodicarboxylate was checked by refluxing **17b** (420 mg, 2.14 mmol) with the

(65) N. Rabjohn, *Org. Syn.*, **28**, 58 (1948).

(66) (a) R. Criegee, E. Vogel, and H. Höger, *Chem. Ber.*, **85**, 144 (1952). (b) S. D. Koch, R. M. Kliss, D. V. Lopiekes, and R. J. Wineman, *J. Org. Chem.*, **26**, 3122 (1961).

ester (270 mg, 1.55 mol) in 20 ml of petroleum ether (bp 80–100°) for 4.5 hr. The ir spectra of the sample after evaporation of the solvent showed only peaks for **17b** and azo ester. *No* absorptions for **20** were detectable.

Oxidation of 16b was carried out with 1.00 g (4.46 mmol) dissolved in 30 ml of absolute MeOH. $NaIO_4$ (1.65 g, 7.7 mmol) dissolved in H_2O was added and the reaction mixture was warmed for about 1 hr. The reaction mixture was poured into H_2O, extracted three times with $CHCl_3$, and dried over $MgSO_4$. Removal of the solvent left crude 2,2,5,5-bis(pentamethylene)-1,3,4-Δ^3-thiadiazoline *S*-oxide, mp 146–144° (980 mg, 4.08 mmol, 91%). Recrystallization from MeOH gave an analytical sample: mp 148–149.5° dec; ir (KBr) 1550 and 1535 (N=N), 1045 and 1055 cm^{-1} (S—O).

Anal. Calcd for $C_{12}H_{20}N_2OS$: C, 60.00; H, 8.33; N, 11.66; S, 13.35. Found: C, 59.62; H, 8.50; N, 11.53; S, 13.19.

The analogous sulfone has been prepared.[18]

Kinetics of 16b Decomposition.—Solutions (1.0×10^{-1} M in methyl cyclohexane) were made 0.0 to 0.25 *M* in diethyl azodicarboxylate. After mixing, a portion of the solution was sealed in heavy-walled Pyrex tubes that were then sealed in the cold. *In one case an extremely violent explosion occurred on warming to room temperature. The cause is unknown. Considerable caution in handling these compounds is strongly advised.* The samples were held at 98.0° for 7 hr, 40 min, after which time no **16b** remained. Analysis by glpc (3-ft glass SE-30, 98° for 12 min, 15°/min to 142°) established that for all samples [**17b**] + [**20**] = $[\mathbf{16b}]_0$; known standards were used for calibration. Careful injection technique was required to prevent desulfurization of the episulfide even in a glass-lined injection port. The value of k_a/k_c was calculated from these data.

The rate of decomposition of **16b** at 97.0° was determined by monitoring the decrease in the uv absorption band at 327 mμ.

Synthesis of *cis,trans*-2,5-diethyl-1,3,4-thiadiazolidines (15c,d) was accomplished by a modified version of the described procedure.[36] In our hands no detectable amount of desired product was obtained by following the directions given. The following modification proved successful. Propionaldehyde (136 g, 2.36 moles), which had been distilled *immediately* before use, was placed in a glass Friedel–Crafts vessel with the stirring rod attached to a vibrator. This solution was cooled in a solid CO_2–acetone bath and to the *vigorously stirred* solution was added H_2S (39.7 g, 1.17 mmol) as rapidly as possible. Uptake is initially slow but, once it has begun, proceeds rapidly; care must be taken to avoid adding too much H_2S. To the cold solution was added immediately thereafter a solution of 98% hydrazine hydrate (58.5 g, 1.17 mmol) over a period of about 30 min. (Essentially the same results are obtained by condensing the desired amount of hydrogen sulfide at −70° and pressing this over into a propionaldehyde solution at −70°; hydrazine is then added.) The reaction mixture, which often became partially solid, was allowed to come to room temperature, whereupon a mixture of 200 ml of water and 200 ml of diethyl ether was added. The layers were separated and the ether layer was washed with water and dried over $MgSO_4$. Removal of the solvent left 141 g (0.965 mol, 83%) of crude white crystals. The ratio of trans to cis isomers was determined by monitoring the nmr absorptions for the tertiary protons in benzene solution: for *trans*-**15c** a triplet (J = 6.4 Hz) at δ 4.32 is seen and for the *cis*-**15d** a triplet (J = ~6.7 Hz) at 4.25 is observed.

The crude material could be purified by recrystallization from petroleum ether (bp 60–80°). The solid was dissolved in the solvent at room temperature and then chilled to about −20° to reprecipitate it. After three–four cycles, with considerable loss of material, pure **15c** was obtained: mp 70–72°;[67] nmr (C_6H_6) δ 0.90 (t, 6, J = 6.0 Hz, CH_3), 1.20–1.70 (complex m, 4, CH_2), 3.20 (br s, 2, NH), 4.32 (t, 2, J = 6.4 Hz, tertiary H). The nmr of the mother liquors was monitored after each stage in the crystallization with the thought that **15d** should be concentrated here. However, only a small amount of trans isomer and, for the rest, propionaldehyde azine, were observed. The cis isomer obviously decomposes spontaneously on attempted concentration. Moreover, mixtures of **15c,d**, after standing for ~1 week in the refrigerator, consisted only of pure **15c** and propionaldehyde azine.

Preparation of isomerically pure *trans*-2,5-diethyl-1,3,4-Δ^3-thiadiazoline (16c) was carried out by dehydrogenation of **15c** (900 mg, 6.15 mmol, 99% trans by nmr) in 20 ml of ether solution at −15°. A cold solution of diethyl azodicarboxylate (1.07 g, 6.15 mmol) in 10 ml of ether was added to the solution. The reaction mixture was kept in the freezer overnight after which time all color had disappeared. The reaction mixture was concentrated on the solvent stripper taking care that the temperature did not rise above ~10°. The semisolid material was taken up in 20 ml of ice-cold pentane and the diethyl hydrazodicarboxylate (995 mg, 5.66 mmol, 92% yield) was filtered off and washed with cold pentane. The pentane solution was washed with chilled $NaHSO_3$ solution to remove the last traces of azo ester and thereafter was washed with ice–water and dried over $MgSO_4$ in the cold. Removal of the solvent at low temperature left **16c** as an oil (885 mg, 6.15 mmol, 100% yield) which solidified in the freezer but became liquid at room temperature and began to evolve gas spontaneously beginning at ~30–35°. This material had nmr (C_6H_6) δ 0.83 (t, 6, J = 7.5 Hz, CH_3), 1.50–2.11 (complex m, 4, CH_2), 5.67–6.04 (complex m, 2, tertiary H). The spectrum was virtually identical in CCl_4.

The above experiment was repeated using a 75:25 mixture of **15c** and **15d**. The nmr of the dehydrogenated product showed a broad, unresolved hump for the tertiary H of the **16d** (along with the absorptions for **16c**). In CCl_4 solution, however, the tertiary protons for **16d** appeared at δ 4.00 as a slightly broadened q (J = 6.2 Hz). The absorptions from both the **16c** and **16d** disappeared completely at 50–60° in the nmr and were replaced by absorptions for the diethyl episulfides **27** and **28**, respectively.

Reaction of 16c,d with Dimethyl Acetylenedicarboxylate.—A sample of isomerically pure (99%) **15c** (3.65 g, 25 mmol) was dehydrogenated in quantitative yield to **16c**. This was dissolved in ~30 ml of ether and diethyl azodicarboxylate (8.2 g, 57.7 mmol) was added. A distillation head was fitted to the flask and, as the ether was distilled off, petroleum ether (bp 60–80°) was added from a dropping funnel. (The low solubility of dimethyl acetylenedicarboxylate in petroleum ether necessitates this procedure.) The final temperature was ~80° and this temperature was maintained for ~1 hr, after which time gas evolution, as evidenced by frothing, had ceased. The solution was concentrated and the excess ester was separated. The petroleum ether layers were combined; the solution was washed with H_2O and dried over $MgSO_4$. Removal of the solvent and distillation gave, after a forerun of residual acetylenic ester, 5.25 g (20.4 mmol, 81%) of *trans*-2,5-diethyl-3,4-dicarbomethoxy-2,5-dihydrothiophene (**31**): 100-MHz nmr (C_6D_6) δ 0.92 (t, 6, J = 7.0 Hz, CH_3), 1.52–1.90 (complex m, 4, CH_2), 3.42 (s, 6, OCH_3), 4.42–4.62 (complex m, 2, tertiary H). Rather surprisingly the tertiary proton appeared as a broad triplet when decoupled from the methylene protons; no temperature dependence of the spectrum was noted.[68]

Anal. Calcd for $C_{12}H_{18}O_4S$: C, 55.80; H, 7.02; S, 12.41. Found: C, 55.28; H, 7.11; S, 12.53.

The above experiment was repeated starting from a mixture of 20% **16d** and 80% **16c** (determined by nmr analysis directly after preparation by dehydrogenation of the respective thiadiazolidines). Reaction with dimethyl acetylenedicarboxylate gave a mixture of 22% **32** and 78% **31** [as determined by glpc (4-ft DEGS, 200°)]. The cis isomer **32** was separated by preparative glpc using a glass 4-ft DEGS column at 200° equipped with glass injection port liner and a stainless steel splitter; the gas flow was sufficient to give retention times of <4 min. If these precautions were not followed, partial to complete dehydrogenation to 2,5-diethyl-3,4-dicarbomethoxythiophene (**38b**) took place. A few milligrams of pure **32** had nmr (CAT in CCl_4) δ 0.94 (t, 6, J = 7.0 Hz, CH_3), 1.77 (center, complex m, 4, CH_2), 3.67 (s, 6, OCH_3), 4.00–4.32 (complex m, 2, tertiary H). In the unseparated mixture the tertiary protons were clearly seen in $CDCl_3$ solution as a triplet (J = 7.4 Hz further split into doublets (J = 1.8 Hz) by coupling with diastereomeric methylene protons.

Oxidation of 31 with 2 equiv of *m*-chloroperbenzoic acid afforded crude *trans*-2,5-diethyl-3,4-dicarbomethoxy-2,5-dihydrothiophene *S*-oxide (**41**): nmr (CCl_4) δ 1.11 (t, J = 7 Hz, 3, CH_3CH_2), 1.13 (t, J = 7 Hz, 3, CH_3CH_2), 1.45–2.25 (complex m, 4, CH_2CH_3), 3.70 (s, 6, OCH_3), 3.84–4.10 (complex m, 2, tertiary H). A sample of this material (1 g, 3.65 mmol) was refluxed for 1 hr in acetic anhydride. The material was poured into water and extracted with chloroform, and the chloroform extract was washed with sodium bicarbonate solution and there-

(67) The reported[36] mp of 72° was likely determined on a repeatedly recrystallized sample that was essentially pure **15c**.

(68) These spectra were run by Dr. R. A. Raphael at the University of East Anglia, England.

after with water. After drying over magnesium sulfate and removal of the chloroform there was obtained 3,4-dicarbomethoxy-2,5-diethylthiophene (**38b**, 930 mg, 100%): nmr (CCl_4) δ 1.27 (t, J = 7.0 Hz, 6, CH_3CH_2), 2.92 (q, J = 7.0 Hz, 4, CH_2CH_3), 3.75 (s, 6, OCH_3).

Anal. Calcd for $C_{12}H_{16}O_4S$: C, 56.23; H, 6.29; S, 12.51. Found: C, 55.58; H, 6.45; S, 12.31.

Oxidation of **31** with 2 equiv. of MCPBA gave *trans*-2,5-diethyl-3,4-dicarbomethoxy-2,5-dihydrothiophene *S*-dioxide (**42**): nmr (CCl_4) δ 1.11 (t, J = 7 Hz, 6, CH_3CH_2), 1.95 (br quintet, J = ~7 Hz, CH_2CH_3), 3.84 (s, 6, OCH_3); the tertiary H's are buried under the absorption at δ 3.84. The material could not be obtained crystalline. Pyrolysis at ~250° for a few minutes afforded chiefly the known[42] diene **40b**.

Oxidation of a mixture of **31** and **32** afforded a mixture of sulfones. The cis sulfone showed a separate triplet at δ 1.08 in the nmr spectrum. Pyrolysis of this mixture afforded **40b** and chiefly *E*,*E*-diene[42] from the cis sulfone.

Cycloaddition of 16c with Diethyl Azodicarboxylate.—Isomerically pure **16c** (400 mg, 2.78 mmol) was dissolved in petroleum ether (bp 40–60°) to which azo ester (1.43 g, 8.22 mmol) was added. The solution was refluxed for 3 hr after which time nmr indicated a 100 ± 4% yield of cycloadduct. The solution was washed with $NaHSO_3$ until the color disappeared, was washed once with water and dried over $MgSO_4$. After removal of the solvent the residue was distilled to afford 720 mg (2.48 mmol, 89%) of *trans*-2,5-diethyl-3,4-dicarboethoxy-1,3,4-thiadiazolidine (**34**): bp 96–98° (0.05 mm); nmr (CCl_4) δ 1.33–1.80 (complex m, 4, CH_3CH_2), 1.20 (t, J = 7.5 Hz, 6, OCH_2CH_3), 5.49 (t, J = 6.5 Hz, 2, tertiary H).

Anal. Calcd for $C_{12}H_{22}N_2O_4S$: C, 49.63; H, 7.65; N, 9.65; S, 11.04. Found: C, 49.72; H, 7.75; N, 9.58; S, 11.07.

A sample of **34** (250 mg, 0.863 mmol) was dissolved in ~10 ml of MeOH. A solution of $NaIO_4$ (280 mg, 1.13 mmol) in a minimal amount of water was added; the resulting solution was refluxed briefly and allowed to stand overnight. Filtration afforded 167 mg (0.845 mmol, 98%) of $NaIO_3$. Water was added to the filtrate, the resulting solution was extracted with benzene, and the organic layer was dried over $MgSO_4$. Removal of the solvent left 250 mg (0.818 mmol, 97%) of the crude *trans*-2,5-diethyl-3,4-dicarboethoxy-1,3,4-thiadiazolidine *S*-oxide which was not purified further. It had ir (neat) 1720 (C=O), 1060–1075 cm^{-1} (S—O); nmr (CCl_4) δ 1.08 [t (poorly resolved), 6, J = ~7 Hz, CH_3], 1.25 (t, 3, J = 7 Hz, OCH_2CH_3), 1.28 (t, 3, J = 7 Hz, OCH_2CH_3), 1.45–2.00 (complex m, 4, CH_2), 4.17 (q, 2, J = 7 Hz, OCH_2), 4.20 (q, 2, J = 7 Hz, OCH_2), 4.82 (t, 1, J = 7.5 Hz, tertiary H), 5.21 (very br s,[69] 1, tertiary H); nmr (C_6H_6) δ 0.87–1.28 (complex set of absorptions, 14, 12 CH_3 + CH_2CH_3), 2.06 (q, 2, J = 7.5 Hz, CH_2CH_3), 4.00 (q, 2, J = 7 Hz, OCH_2), 4.05 (q, 2, J = 7 Hz, OCH_2), 4.83 (t, 1, J = 7.5 Hz, tertiary H), 5.24 (very br s, 1, tertiary H).

The above sulfoxide (100 mg, 0.327 mmol) was dissolved in $CHCl_3$ and a solution of 85% *m*-chloroperbenzoic acid (70 mg, 0.35 mmol) was added. The solution was allowed to stand overnight. Work-up afforded 100 mg (0.310 mmol, 95%) of *trans*-2,5-diethyl-3,4-dicarboethoxy-1,3,4-thiadiazolidine *S*-dioxide as an oil, which slowly crystallized. Recrystallization from a large volume of pentane gave 49.3 mg (0.531 mmol, 47%) of analytically pure sulfone: mp 75–76°; ir (KBr) 1720 (C=O), 1340 (S—O), 1110 cm^{-1} (S—O); nmr (CCl_4) δ 1.12 (t, 6, J = 7.5 Hz, CH_3), 1.34 (t, 6, J = 7.5 Hz, CH_3), 4.62 (q, 4, J = 7.0 Hz, OCH_2), 4.49 (d, 1, J = 5.5 Hz, tertiary H), 4.64 (d, 1, J = 5.5 Hz, tertiary H). The OCH_2CH_3 quartet has a half-width of 1 Hz in both CCl_4 and benzene precluding the idea of two overlapping absorption patterns; the tertiary protons apparently show up as the X portion of an ABX system.

Anal. Calcd for $C_{12}H_{22}N_2O_6S$: C, 44.70; H, 6.89; N, 8.69; S, 9.94. Found: C, 44.69; H, 6.92; N, 8.65; S, 9.94.

Pyrolysis of 16c and 16d.—A sample of **16c** of at least 97% isomeric purity (allowing for nmr error or ±3%) was allowed to decompose in refluxing petroleum ether (bp 40–60°). Analysis by nmr indicated a quantitative conversion to episulfide; this was shown to consist of 7 ± 2% *trans*-2,3-diethyl episulfide (**28**) and 93 ± 2% *cis*-2,3-diethyl episulfide (**27**) by glpc (glass 3-ft SE-30, 80°). A similar experiment with a mixture of 80 ± 3% **16c** and 20 ± 3% **16d** gave again in quantitative yield a mixture of 69 ± 2% **27** and 31 ± 2% **28**.

(69) Broadening seems to arise from conformational effects. This problem is being investigated further.

Synthesis of *trans*- and *cis*-2,3-Diethyl Episulfides.—A sample of *trans*-2,3-diethyl epoxide was prepared by treatment of *trans*-3-hexene with *m*-chloroperbenzoic acid following the normal procedure.[70] The material had bp 104–106° (atm); nmr (CCl_4) δ 0.98 (t, 6, J = 6.5 Hz, CH_3), 1.24–1.70 (complex m, 4, CH_2), 2.50 (t, 2, J = 5 Hz, 2,3 H).

Anal. Calcd for $C_6H_{12}O$: C, 71.93; H, 12.10. Found: C, 71.75; H, 12.09.

After some initial experimentation, it was found that the above epoxide could be converted to **28** only by drastically increasing the severity of the normal reaction conditions.[71] The epoxide (1.5 g, 15 mmol) was mixed with KSCN (2.0 g, 20.6 mmol) in 2 ml of H_2O and 2 ml of ethanol. Sufficient ethanol was added to give a homogenous solution. This was refluxed with stirring for 3 days and thereafter stirred at room temperature for 5 days. Work-up and distillation gave **28** (0.50 g, 4.46 mmol, 30%): bp 120–122° (atm); nmr (CCl_4) δ 1.03 (t, 6, J = 7.0 Hz, CH_3), 1.23–2.05 complex m, 4, CH_2), 2.48 (broadened t, 2, J = ~4.5 Hz, 2,3 H). The low yield was caused chiefly by difficulties in distilling **28** which foams badly.

Anal. Calcd for $C_6H_{12}S$: C, 61.99; H, 10.43; S, 27.58. Found: C, 61.65; H, 10.30; S, 26.59.

Preparation of *cis*-**27** was accomplished in a similar manner. Reaction of the disodium salt of acetylene with ethyl bromide gave diethylacetylene, which was hydrogenated over palladium on barium sulfate in pyridine solution. There was obtained *cis*-3-hexene: ir (pure) 830 cm^{-1} (cis C=C), no absorption at 970 cm^{-1}; nmr (CCl_4) δ 0.97 (t, J = 7 Hz, 6 H, CH_3), 2.0 (quintet, J = ~7 Hz, 4 H, CH_2), 5.23 (br t, J = ~7 Hz, 2 H, vinyl H). Oxidation with *m*-chloroperbenzoic acid gave *cis*-2,3-diethyl epoxide, bp 106–109° (atm), in 53% yield: ir (neat) 900 cm^{-1} (epoxide); nmr (CCl_4) δ 1.0 (t, J = 7.0 Hz, 6 H, CH_3), 1.46 (br q, J = ~7 Hz, 4 H, CH_2), 2.70 (complex m, 2 H, tertiary H).

Treatment of this epoxide in 50:50 water–methanol with excess KSCN for 3 days at 40° gave **27**, bp 138–140° (atm), in 49% yield: ir (neat) 900, 1070 cm^{-1}; nmr (CCl_4) δ 1.10 (t, J = 7 Hz, 6 H, CH_3), 1.33–1.99 (complex m, 4 H, CH_2), 2.65–2.90 (complex m, 2 H, tertiary H). This spectrum was identical with that of **27** obtained from pyrolysis of **16c**.

Anal. Calcd for $C_6H_{12}S$: C, 62.00; H, 10.41. Found: C, 62.38; H, 10.45.

The products **27** and **28** were coinjected with samples obtained from pyrolysis of **16c** and **16d**. The expected peak enhancement was seen confirming the stereochemical assignments.

Preparation of 2,5-Di-*tert*-butyl-1,3,4-Δ^3-thiadiazolines (24) and (25).—An ~5% by weight solution of pivaldehyde azine in ether was prepared. This was put in a heavy-walled tube, which was then cooled to −70°; hydrogen sulfide (excess) was condensed in the tube, which was then sealed. The tube was shaken for 32 hr at room temperature, cooled to −70° and broken. After evaporation of the hydrogen sulfide at −30°, a slight excess of diethyl azodicarboxylate was added (at −30°). The contents were well stirred and allowed to stand overnight at −30° and then for several hours at −5°. The reaction mixture was taken up in pentane and washed with aqueous sodium bisulfate until colorless. The pentane solution was then dried over $MgSO_4$. Nmr analysis of this crude product revealed it to consist of 41.5% trans isomer **24** and 25% cis isomer **25** with 21% *cis*-2,3-di-*tert*-butyl episulfide (**29**) and 12.5% *trans*-2,3-di-*tert*-butyl episulfide (**30**) (see further for assignment of nmr resonances). Trace quantities of pivaldehyde azine and 2,5-di-*tert*-butyl-1,3,4-thiadiazole were also seen. The episulfides appear to arise from routes other than through the thiadiazolines since these were stable under the careful work-up conditions. Recrystallization out of methanol gave pure **24** in ~40% yield. (In some runs the yield was as high as 70% apparently owing to the formation of less episulfide during ring closure.) This isomer has mp 62–63° dec; ir (KBr) 1585 cm^{-1} (N=N); nmr (CCl_4) δ 1.07 (s, 18, *t*-Bu), δ 5.95 (s, 2, 2,5 H).[72]

Anal. Calcd for $C_{10}H_{20}N_2S$: C, 59.95; H, 10.07; N, 13.98; S, 16.00. Found: C, 59.81; H, 10.27; S, 16.09.

(70) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., p 136.

(71) H. R. Snyder, J. M. Stewart, and J. B. Ziegler, *J. Amer. Chem. Soc.*, **69**, 2672 (1947).

(72) The position of this absorption appears to be both solvent and concentration dependent.

An acceptable nitrogen analysis could not be obtained.

The concentration of **25** [nmr (CCl_4) δ 1.15 (s, 18, *t*-Bu), 5.52 (s, 2, 2,5 H)] was equal to that of **24** in the mother liquors. Careful chromatography in the cold over silica gel allowed the isolation of a 50:50 mixture of **24** and **25**. The isomer **25** could be stored indefinitely in the cold but began to decompose at room temperature.

Oxidation of 24 to *trans*-2,5-di-*tert*-butyl-1,3,4-Δ^3-thiadiazoline *S*-oxide (26) with (*m*-chloroperbenzoic acid) afforded, after recrystallization from petroleum ether (bp 40–60°), in 46% yield (quantitatively nmr but much lost in recrystallization) the solid sulfoxide **26**: mp 99–105° dec; ir (KBr) 1060 cm^{-1} (S→O); nmr (CCl_4) δ 1.07 [s, 9 H, $(CH_3)_3C$], 1.40 [s, 9 H, $(CH_3)_3C$], 4.05 [d, J = 1.4 Hz, 2(5) H], 5.68 [d, J = 1.4 Hz, 5(2) H].

Anal. Calcd for $C_{10}H_{20}N_2OS$: C, 55.50; H, 9.34; N, 12.95; S, 14.82. Found: C, 55.42; H, 9.27; N, 12.78; S, 14.73.

Attempted oxidation to the sulfone failed to afford a pure product.

Pyrolysis of 24 was carried out in refluxing methylcyclohexane for 5 hr. Removal of the solid left a liquid (100% yield determined by nmr): uv (EtOH) 2650 Å (ϵ 105); nmr (CCl_4) δ 1.15 [s, 18 H, $(CH_3)_3C$], 2.78 (s, 2 H, 2,3 H); mass spectrum *m/e* 172 (parent, calcd for $C_{10}H_{20}S$ 172), 140 (S), 125 (CH_3S), 115 (*t*-Bu). Distillation of the episulfide was difficult owing to severe foaming.

In a flame-dried three-necked flask swept with dry nitrogen, a solution of phenyllithium was prepared from the reaction of iodobenzene (3.2 g, 15.7 mmol) with lithium wire (203 mg, 29 mg-atoms) in ether solution. The above crude episulfide **29** (400 mg, 2.32 mmol) dissolved in ether was added to the phenyllithium solution. Turbidity developed immediately. After refluxing for ~1 hr, the solution was poured into water; the stench of phenylthiol was noted. The ether solution was washed repeatedly with $NaHCO_3$ solution and dried over $MgSO_4$. Distillation at 12 mm (very difficult owing to foaming, boiling point not measured) gave 210 mg (1.5 mmol, 65%) of a clear liquid olefin: $n^{28}D$ 1.4582 (lit.[73] $n^{20}D$ 1.4269); ir (pure) 3040 and 3060 (vinyl H), 740 cm^{-1} (cis C=C), no absorption at 970 cm^{-1} (trans C=C);[72] mass spectrum *m/e* 140 (parent, calcd for $C_{10}H_{20}$ 140, rel intensity 8), 97 (C_3H_7, 18), 83 (*t*-Bu, 72), 70 [$(CH_3)_3CCH_2$, 100];[74] nmr (CCl_4) δ 1.14 [s, 18 H, $(CH_3)_3C$], 5.13 (s, 2 H, vinyl H). These data identify the olefin as *cis*-di-*tert*-butylethylene and its precursor as *cis*-2,3-di-*tert*-butyl episulfide (**29**).

Pyrolysis of 25 was accomplished using a 50:50 mixture of **24** and **25**. At 40° **25** decomposes selectively affording a single episulfide **30** [nmr (CCl_4) δ 0.93 (s, 18, *t*-Bu), 2.52 (s, 2, 2,3 H)]. This was isolated by preparative plate chromatography over silica gel (benzene eluent). Desulfurization with phenylithium proceeded sluggishly. Exclusively *trans*-2,3-di-*tert*-butylethylene was formed: nmr (CCl_4) δ 0.98 (s, 18, *t*-Bu), 5.40 (s, 2, vinyl H); mass spectrum *m/e* 140 (parent, rel intensity 40), 69 (100).[73,74]

Cycloadditons of 25 were attempted with two–threefold molar excesses of dicyanoacetylene and dimethyl acetylenedicarboxylate. Reactions were carried out at 40° with 50:50 mixture of **24** and **25**; **24** does not react at this temperature. Only **30** was formed. With diethyl azodicarboxylate about an equal mixture of **30** and 2,5-di-*tert*-butyl-1,3,4-thiadiazoline was obtained.

Cycloadditions of 24 were carried out with various dipolarophiles. With diethyl azodicarboxylate in methyl cyclohexane using a three-fold excess of dipolarophile there was obtained after distillation, bp 122° (0.4–0.5 mm), in 90% yield *trans*-2,5-di-*tert*-butyl-3,4-dicarboethoxy-1,3,4-thiadiazolidine (**36**): ir (pure) 1720 cm^{-1} (C=O); nmr (CCl_4) δ 0.95 [s, 18 H, $(CH_3)_3C$], 1.30 [t, J = 7.5 Hz, 6 H, CH_3CH_2O], 4.23 (q, J = 7.5 Hz, 4 H, CH_3CH_2O), 5.39 (s, 2 H, 2,5 H).

Anal. Calcd $C_{16}H_{30}N_2O_4S$: C, 55.46; H, 8.73; N, 8.08; S, 9.25. Found: C, 55.78; H, 8.72; N, 7.92; S, 9.01.

Oxidation with *m*-chloroperbenzoic acid to the sulfoxide afforded in 67% yield a white solid: mp 57–59°; ir (pure) 1740 (C=O), 1050 and 1090 cm^{-1} (S→O); nmr (CCl_4) δ 1.07 [s, 9 H, $(CH_3)_3C$], 1.20 [s, 9 H, $(CH_3)_3C$], 1.29 (t, J = 7.0 Hz, 3 H, CH_3CH_2O), 1.33 (t, J = 7.0 Hz, 3 H, CH_3CH_2O), 4.19 (q, J = 7.0 Hz, 2 H, CH_3CH_2O), 4.27 (q, J = 7.0 Hz, 2 H, CH_3CH_2O), and δ 4.78 (br s, 2 H, 2,5 H).

Anal. Calcd for $C_{16}H_{30}N_2O_5S$: C, 53.02; H, 8.34; N, 7.72; S, 8.85. Found: C, 52.67; H, 8.24; N, 7.78; S, 8.82.

Oxidation with *m*-chloroperbenzoic acid to the sulfone afforded in 96% yield a white solid: mp 64–66°; ir 1730 (C=O), 1330 cm^{-1} (S→O); nmr (CCl_4) δ 1.17 [s, 18 H, $(CH_3)_3C$], 1.34 (t, J = 7.0 Hz, 6 H, CH_3CH_2O), 4.27 (q, J = 7.0 Hz, 4 H, OCH_2CH_3), 4.50 (br s, 2 H, 2,5 H). Expansion and attenuation of the area between δ 4.0 and 4.6 by means of the CAT showed only the sharp methylene quartet (half-width 2 Hz) and the broadened singlet for the 2,5 protons.

Anal. Calcd for $C_{16}H_{30}N_2O_6S$: C, 50.77; H, 7.99; N, 7.40; S, 8.47. Found: C, 50.68; H, 7.94; N, 7.37; S, 8.33.

Reaction of **24** with dimethyl acetylenedicarboxylate yielded after purification in 67% yield *trans*-2,5-di-*tert*-butyl-3,4-dicarbomethoxy-2,5-dihydrothiophene (**33**): mp 119.5–120°; nmr (CCl_4) δ 0.95 [s, 18 H, $(CH_3)_3C$], 3.70 (s, 6 H, OCH_3), 4.30 (s, 2 H, 2,5 H).

Anal. Calcd for $C_{16}H_{26}O_4S$: C, 61.11; H, 8.34; S, 10.20. Found: C, 61.14; H, 8.21; S, 10.29.

Oxidation to *trans*-2,5-di-*tert*-butyl-3,4-dicarbomethoxy-2,5-dihydrothiophene *S*-oxide (**37**) with *m*-chloroperbenzoic acid gave in 92% yield a white solid: mp 168–169°; nmr (CCl_4) δ 1.05 [s, 9 H, $(CH_3)_3C$], 1.20 [s, 9 H, $(CH_3)_3C$], 3.63 [d, J = 1.5–2.0 Hz, 1 H, 2(5) H], 3.76 (s, 6 H, OCH_3), 3.84 [d, J = 1.5–2.0 Hz, 1 H, 5(2) H].

Anal. Calcd for $C_{16}H_{26}O_5S$: C, 58.16; H, 7.93; S, 9.70. Found: C, 57.72; H, 7.75; S, 9.54.

Treatment of **37** (1 g, 3 mmol) in refluxing acetic anhydride afforded after work-up 930 mg (100%) of 3,4-dicarbomethoxy-2,5-di-*tert* butylthiophene (**38a**): nmr (CCl_4) δ 1.42 (s, 18 H, *t*-Bu), 3.73 (s, 6 H, OCH_3)

Oxidation to the sulfone with *m*-chloroperbenzoic acid afforded in 96% yield *trans*-2,5-di-*tert*-butyl-3,4-dicarbomethoxy-2,5-dihydrothiophene *S*-dioxide (**39**): mp 185–187°; nmr (CCl_4) δ 1.09 [s, 18 H, $(CH_3)_3C$], 3.70 (s, 2 H, 2,5 H), 3.75 (s, 6 H, OCH_3).

Anal. Calcd for $C_{16}H_{26}O_6S$: C, 55.47; H, 7.57; S, 9.25. Found: C, 55.49; C, 7.69; S, 9.05.

Cycloaddition was carried out with **24** (350 mg, 1.75 mmol) with tetracyanoethylene (224 mg, 1.73 mmol). A methylcyclohexane solution was refluxed overnight. After removal of solvent the crude product was chromatographed over Al_2O_3 eluting with benzene. Recrystallization from petroleum ether (bp 40–60°) containing a trace of benzene gave 530 mg (1.73 mmol, 100%) of *trans*-2,5-di-*tert*-butyl-3,3,4,4-tetracyanosulfolane (**63**): mp 144.5–145.5°; ir (KBr) 2280 cm^{-1} (C≡N); nmr (CCl_4) δ 1.34 [s, 18 H, $(CH_3)_3C$], 3.90 (s, 2,5 H).

Anal. Calcd for $C_{16}H_{20}N_4S$: C, 63.97; H, 6.71; N, 18.64; S, 10.67. Found: C, 64.02; H, 6.81; N, 18.68; S, 10.77.

Trans stereochemistry is presumed by analogy.

Cycloadditon of **24** (350 mg, 1.75 mmol) with *N*-phenylmaleimide (303 mg, 1.75 mmol) gave, after refluxing overnight in methylcyclohexane solution, a crude, white solid (630 mg). This was recrystallized from methanol–water to afford 407 mg (1.18 mmol, 67% yield) of cycloadduct **62**: mp 151–152°; ir (KBr) 1710 cm^{-1} (1770 cm^{-1}, w) (C=O); nmr (CCl_4) δ 1.07 [s, 9 H, $(CH_3)_3C$], δ 1.18 [s, 9 H, $(CH_3)_3C$], 3.29–3.75 (m, 4 H, 2,5 H, 3,4 H), 7.16–7.50 (m, 5 H, C_6H_5).

Anal. Calcd for $C_{20}H_{27}NO_2S$: C, 69.53; H, 7.88; N, 4.05; S, 9.28. Found: C, 69.48; H, 7.92; N, 4.02; S, 9.51.

Oxidation to the sulfoxide with *m*-chloroperbenzoic acid was carried out in 95% yield affording a solid, mp 235–236°. Nmr (CCl_4) consisted of two sets of *tert*-butyl peaks, δ 1.03 and 1.40 and δ 1.23 and 1.40, in the ratio of ~2:1, likely corresponding to the ratios of isomeric sulfoxides. Complex absorptions at δ 2.63–3.93 (4 H) and 7.20–7.50 completed the spectrum.

Oxidation to the sulfone with MCPBA afforded in 55% yield a solid, mp 278–280°.

Anal. Calcd for $C_{20}H_{27}NO_4S$: C, 63.63; H, 7.21; N, 3.71; S, 8.49. Found: C, 63.59; H, 7.17; N, 3.69; S, 8.55.

When **24** was decomposed in refluxing methylcyclohexane with equivalent amounts of 3-morpholinostyrene, 2-morpholinobutene-2, bicyclo[2.2.1]hepta-2,5-diene, or 2,3-dimethylbutadiene, only **29** obtained from ring closure of the thiocarbonyl ylide could be detected. With benzaldehyde chiefly **29** was formed, although a small amount of another product may have been present.

Experiments with 29 were carried out. With diethyl azodicarboxylate in refluxing methylcyclohexane no cycloaddition

(73) A. R. Bader, R. P. Buckley, F. Leavitt, and M. Szwarc, *J. Amer. Chem. Soc.*, **79**, 5621 (1957).

(74) See, for example, P. Natalis and J. F. Franklin, *Bull. Soc. Chim. Belg.*, **75**, 328 (1966).

took place; the episulfide was quite stable. Similar results were obtained with dimethyl acetylenedicarboxylate. On irradiation in ether solution (medium pressure, Hg lamp) **30** slowly accumulated as determined by glpc. Simultaneously, considerable destruction of starting material took place.

Pyrolysis of 39 was accomplished either in the injection port of the glpc (250°) or in a Pyrex tube at ~250°. Nmr and glpc analyses established that quantitative conversion to a mixture consisting of 90% *Z,E*, 6% *E,E*-, and 4% *Z,Z*-dienes[42] had taken place.

General Procedures.—A number of the procedure are repetitious and hence are described briefly here.

A. Synthesis of Thiadiazolines from Dichloroazo Compounds.—The azine was prepared from reaction of the carbonyl component with hydrazine; it was distilled or recrystallized before use. About a 10% by weight solution of azine in methylene chloride was made and this solution was cooled to −70°. In a dimly lighted hood chlorine was passed through the solution until a yellow color persisted. The solution was warmed to 10–15° and the methylene chloride was removed on a rotatory evaporator. The crude dichloroazo compound, formed nearly quantitatively, was dissolved in chloroform or ether and put in a heavy-walled Pyrex tube; excess hydrogen sulfide was added; and the tube was sealed shut. The tube was rocked at room temperature for 1–2 days and then opened. After evaporation of the hydrogen sulfide, the crude thiadiazoline was purified by either crystallization or distillation.

B. Cycloaddition of the Thiadiazolines with Diethyl Azodicarboxylate.—The thiadiazoline (2.5 mmol) in methylcyclohexane was dropped slowly in a refluxing solution of azo ester (7.5–12.5 mmol) in methylcyclohexane, after which the reaction mixture was refluxed for another 12–24 hr. After evaporation of the solvent, cooling in ice, and dilution with diethyl ether, the resulting solution was washed with 10% Na_2SO_3 solution and water, respectively; if necessary the washings were repeated. The solution was then dried over $MgSO_4$, filtered, and evaporated, and the product was isolated by means of distillation *in vacuo* or recrystallization. In some cases column chromatography was used. The problem was to get rid of the hydrazo ester formed after extractions (washings) with Na_2SO_3 solution.

C. Cycloaddition with Dimethyl Acetylenedicarboxylate.—To a refluxing solution of acetylenic ester (10 mmol) in methylcyclohexane–benzene (10:1) was dropped slowly a solution of the thiadiazoline (5 mmol) dissolved in the same solvent mixture. Refluxing was continued for 12–24 hr. After the solvents had been removed by evaporation, *n*-heptane or *n*-pentane, in which dimethyl acetylenedicarboxylate is very insoluble, was added allowing separation of much excess ester. Sometimes it was necessary to repeat the evaporation and addition of heptane to remove the still present ester. The cycloadduct could then be isolated by distillation or recrystallization from petroleum ether (bp 40–60°). In some cases a fivefold excess of acetylenic ester was used. The chromatography was done with aid of silica gel and elution with a mixture of petroleum ether (bp 40–60°) and ether (10%); the cycloadduct was then eluted.

D. Synthesis of the Sulfoxides and the Sulfones.—The substrate (thiadiazoline, thiadiazolidine, or dihydrothiophene, 5 mmol) and *m*-chloroperbenzoic acid (5 mmol) in chloroform was stirred overnight and 0.5 hr at 40–50° thereafter. After evaporation in the cold, ether was added. The resulting ether solution was washed with 10% Na_2SO_3 solution, $NaHCO_3$ solution, and distilled water, respectively. After drying and evaporation, often recrystallization from a mixture of petroleum ether (bp 40–60°) and a little ether was sufficient to give pure sulfoxide. We also used chromatography in some cases, with a silica gel column and elution with benzene and ether respectively.

The procedure for the synthesis of the sulfones can be followed as above using 2 equiv of *m*-chloroperbenzoic acid.

Preparation of 2,2,5,5-tetramethyl-1,3,4-Δ³-thiadiazoline (45a) was carried out in 81% yield. The compound, mp 95.5–97° dec, had ir (KBr) 1580 cm^{-1} (N=N), nmr (CCl_4) δ 1.70 (s, 12 H).

Anal. Calcd for $C_6H_{12}N_2S$: C, 49.96; H, 8.39; N, 19.42; S, 22.23. Found: C, 49.84; H, 8.67; N, 19.42; S, 21.86.

Oxidation to 2,2,5,5-tetramethyl-1,3,4-Δ³-thiadiazoline *S*-dioxide gave in 53% yield white crystals: mp 72–73° dec; ir (Nujol) 1590 (N=N), 1060 cm^{-1} (S→O); nmr (CCl_4) δ 1.47 (s, 6 H), 1.70 (s, 6 H).

Anal. Calcd for $C_6H_{12}N_2OS$: C, 44.97; H, 7.55; N, 17.48; S, 20.01. Found: C, 44.90; H, 7.93; N, 17.32; S, 20.01.

Oxidation to 2,2,5,5-tetramethyl-1,3,4-Δ³-thiadiazoline *S*-dioxide gave in 51% yield a white solid: mp 112.5–114.5° dec; ir (Nujol) 1310 cm^{-1} (SO_2); nmr (CCl_4) δ 1.65 (s, 12 H).

Anal. Calcd for $C_6H_{12}N_2O_2S$: C, 40.89; H, 6.86; N, 15.90; S, 18.20. Found: C, 41.20; H, 6.91; N, 16.06; S, 18.18.

Cycloadditions of 45a were carried out with diethyl azodicarboxylate using a 1.7 excess. There was obtained in 81% crude yield 2,2,5,5-tetramethyl-3,4-dicarboethoxy-1,3,4-thiadiazolidine (**49a**) as a heavy oil: bp 85° (0.1 mm); ir (neat) 1730 cm^{-1} (C=O); nmr (CCl_4) δ 1.25 (t, J = 7.0 Hz, 6 H, OCH_2CH_3), 1.60–2.10 (br, poorly resolved d, 12 H, CH_3), 4.12 (q, J = 7.0 Hz, 4 H, OCH_2CH_3); mass spectrum m/e 290 ($C_{12}H_{22}N_2O_4S$), 217 ($CO_2C_2H_5$), 216 [$(CH_3)_2C{=}S$].

Anal. Calcd for $C_{12}H_{22}N_2O_4S$: C, 49.64; H, 7.64; N, 9.65; S, 11.03. Found: C, 49.37; H, 7.65; N, 9.26.

An acceptable sulfur analysis could not be obtained.

Oxidation to 2,2,5,5-tetramethyl-3,4-dicarboethoxy-1,3,4-thiadiazolidine *S*-dioxide was carried out (the sulfoxide could not be obtained crystalline and was not investigated further). There was obtained in 73% yield a solid: mp 41–43°; ir (Nujol) 1740 (C=O), 1350 cm^{-1} (SO_2); nmr (CCl_4) δ 1.25 (br t, J = 7.0 Hz, 6, OCH_2CH_3), 1.42–δ 1.93 (v br s, 12 H, CH_3), 4.15 (slightly br q, J = 7.0 Hz, 4 H, OCH_2CH_3).

Anal. Calcd for $C_{12}H_{22}N_2O_6S$: C, 44.71; H, 6.88; N, 8.68; S, 9.95. Found: C, 44.80; H, 6.91; N, 8.65; S, 10.22.

Cycloaddition of 45a with dimethyl acetylenedicarboxylate with 3.3-fold excess of acetylenic ester gave in 45% yield after distillation and recrystallization from pentane 2,2,5,5-tetramethyl-3,4-dicarbomethoxy-2,5-dihydrothiophene (**48a**) as a white solid: mp 80–82.5°; ir (KBr) 1740 cm^{-1} (C=O); nmr (CCl_4) δ 1.61 (s, 12 H, CH_3), 3.75 (s, 6 H, OCH_3).

Anal. Calcd for $C_{12}H_{18}O_4S$: C, 55.79; H, 7.04; S, 12.41. Found: C, 55.88; H, 7.09; S, 12.39.

Oxidation to 2,2,5,5-tetramethyl-3,4-dicarbomethoxy-2,5-dihydrothiophene *S*-oxide was accomplished by treating **48a** (3.0 g, 11.6 mmol) dissolved in methanol with sodium metaperiodate (2.8 g, 13 mmol) dissolved in water. The temperature was held at 25–40° for 4 hr. The precipitate of sodium iodate was filtered off, the methanol was evaporated down, and the resulting solution was extracted three times with 100 ml of ether. After drying there was obtained 3.05 g (11.1 mmol, 96%) of sulfoxide as a white solid: mp 73–74°; ir (Nujol) 1710 (C=O), 1030 cm^{-1} (S→O); nmr (CCl_4) δ 1.37 (s, 6 H, CH_3), 1.55 (s, 6 H, CH_3), 3.75 (s, 6 H, OCH_3).

Anal. Calcd for $C_{12}H_{18}O_5S$: C, 52.54; H, 6.62; S, 11.69. Found: C, 52.63; H, 6.67; S, 12.02.

Oxidation to the sulfone afforded in 99% yield 2,2,5,5-tetramethyl-3,4-dicarbomethoxy-2,5-dihydrothiophene *S*-dioxide: mp 104–105.5°; ir (Nujol) 1720 (C=O), 1320 cm^{-1} (SO_2); nmr (CCl_4) δ 1.51 (s, 12 H, CH_3), 3.75 (s, 6 H, OCH_3).

Anal. Calcd for $C_{12}H_{18}O_6S$: C, 49.64; C, 6.25; S, 11.05. Found: C, 49.89; H, 6.25; S, 11.06.

Pyrolysis of 45a was accomplished by carefully heating 300 mg (2.08 mmol) in a microdistillation apparatus. After nitrogen evolution had ceased the product was distilled; it became solid on standing. After one recrystallization from methanol there was obtained 207 mg (85%) of tetramethyl episulfide, mp 54–56° (lit.[75] mp 76°), nmr (CCl_4) δ 1.60.

Anal. Calcd for $C_6H_{12}S$: C, 62.00; H, 10.41; S, 27.59. Found: C, 62.05; H, 10.53; S, 27.67.

The synthesis of 2,2,5,5-tetraethyl-1,3,4-Δ³-thiadiazoline (45b) was accomplished in 86% yield: bp 60° (0.8 mm); ir (pure) 1585 cm^{-1} (N=N); nmr (CCl_4) δ 0.97 (t, J = 7.0 Hz, 12 H, CH_3), 1.67–2.34 (m, 8 H, CH_2CH_3).

Anal. Calcd for $C_{10}H_{20}N_2S$: C, 59.95; H, 10.06; S, 16.00; N, 14.00. Found: C, 59.63; H, 9.97; S, 16.12; N, 13.39.

Oxidation gave 2,2,5,5-tetraethyl-1,3,4-Δ³-thiadiazoline *S*-oxide, mp 46–48°, in 76% yield: ir (Nujol) 1585 (N=N), 1045 and 1065 cm^{-1} (S→O),

Anal. Calcd for $C_{10}H_{20}N_2OS$: C, 55.52; H, 9.32; S, 14.82; N, 12.95. Found: C, 55.53; H, 9.21; N, 12.94; S, 14.77.

Further oxidation afforded 2,2,5,5-tetraethyl-1,3,4-Δ³-thiadiazoline *S*-dioxide, mp 108–109.5°, in poor yield (not determined accurately): mass spectrum m/e 232 ($C_{10}H_{20}N_2O_2S$), 168 (SO_2), 140 ($SO_2 + N_2$).

Cycloaddition with 45b were carried out first with 1.7 mole equiv of diethyl azodicarboxylate. There was obtained 92%

(75) M. A. Youtz and P. P. Perkins, *J. Amer. Chem. Soc.*, **51**, 3508 (1929); the reason for the discrepancy in melting point is unknown.

of 2,2,5,5-tetraethyl-3,4-dicarboethoxy-1,3,4-thiadiazolidine (**49b**) as a heavy oil: bp 112° (0.125 mm); ir (neat) 1730 cm^{-1} (C=O); nmr (CCl_4) δ 1.02 (t, J = 7.0 Hz, 6 H, CH_2CH_3), 1.25 (t, J = 7.0 Hz, 6 H, OCH_2CH_3), 1.59–2.40 (m, 4, CH_2CH_3), 4.10 (q, J = 7.0 Hz, 4 H, OCH_2CH_3); mass spectrum m/e 346 ($C_{16}H_{30}N_2O_4S$), 317 (C_2H_5), 273 ($CO_2C_2H_5$).

Anal. Calcd for $C_{16}H_{30}O_4N_2S$: C, 55.46; H, 8.73; N, 8.09; S, 9.26. Found: C, 55.88; H, 8.76.

Repeated attempts to determine nitrogen and sulfur led to divergent results.

Oxidation to 2,2,5,5-tetraethyl-3,4-dicarboethoxy-1,3,4-thiadiazolidine *S*-oxide gave in 72% yield a white solid: mp 57–59°; ir (Nujol) 1740 (C=O), 1060 cm^{-1} (S→O).

Anal. Calcd for $C_{16}H_{30}O_5N_2S$: C, 53.02; H, 8.34; N, 7.73; S, 8.84. Found: C, 52.85; H, 8.23; N, 7.52; S, 9.34.

Oxidation to 2,2,5,5-tetraethyl-3,4-dicarboethoxy-1,3,4-thiadiazolidine *S*-dioxide gave in 78% yield a white solid: mp 108–109.5°; ir (Nujol) 1740 (C=O), 1390 cm^{-1} (SO_2).

Anal. Calcd for $C_{16}H_{30}O_6N_2S$: C, 50.76; H, 7.99; N, 7.40; S, 8.47. Found: C, 51.14; H, 8.04; N, 7.40; S, 8.53.

Cycloaddition of 45b with dimethyl acetylenedicarboxylate (fourfold excess) gave on distillation in 30% yield 2,2,5,5-tetramethyl-3,4-dicarbomethoxy-2,5-dihydrothiophene (**48b**), bp 110–114°, (0.25 mm), which after recrystallization from methanol had mp 40–42.5°; ir 1740 cm^{-1} (C=O); nmr (CCl_4) δ 1.00 (t, J = 6.8 Hz, 6 H, CH_2CH_3), 1.80 (q, J = 6.8 Hz, 4 H, CH_2CH_3), 3.69 (s, 6, OCH_3).

Anal. Calcd for $C_{16}H_{26}O_4S$: C, 61.10; H, 8.34; S, 10.21. Found: C, 61.07; H, 8.26; S, 10.48.

Pyrolysis of 45b was accomplished by refluxing 0.5 g (2.5 mmol) in methylcyclohexane. On removal of solvent tetraethyl episulfide remained in quantitative yield as determined by nmr. Distillation [bp ~75° (12 mm)] went with difficulty owing to foaming. The product had nmr (CCl_4) δ 1.0 (t, J = 7 Hz, 12 H, CH_3), 1.83 (q, J = 7 Hz, 8 H, CH_2).

Anal. Calcd for $C_{10}H_{20}S$: C, 69.70; H, 11.70; S, 18.60. Found: C, 69.49; H, 11.63; S, 18.69.

Synthesis of 2,2,5,5-bis[(3-*tert*-butyl)pentamethylene]-1,3,4-Δ^3-thiadiazoline (45c) was accomplished in 21% yield by addition of hydrogen sulfide to the azine followed by dehydrogenation. Treatment with hydrogen sulfide of the product of addition of chlorine to the azine afforded **45c** in 80% yield. The compound had mp 126–128° dec; ir (KBr) 1590 cm^{-1} (N=N); nmr (CCl_4) δ 0.90 [s, 18 H, $(CH_3)_3C$], 1.11–2.50 (complex m, 16 H, ring CH_2). The spectrum with europium complex is described in the text.

Anal. Calcd for $C_{20}H_{36}N_2S$: C, 71.37; H, 10.79; N, 8.31; S, 9.53. Found: C, 71.42; H, 10.83; N, 8.30; S, 9.50.

The sulfoxide of **45c** was prepared in 68% yield as a solid: mp 164–166° dec; ir (Nujol) 1580 (N=N), 1040 cm^{-1} (S—O); nmr (CCl_4) δ 0.92 [s, 18 H, $(CH_3)_3C$], 1.10–2.52 (complex m, 18 H, ring CH_2).

Anal. Calcd for $C_{20}H_{36}N_2OS$: C, 68.15; H, 10.29; N, 7.95; S, 9.09. Found: C, 68.09; H, 10.29; N, 7.77; S, 9.40.

An acceptable sample of the corresponding sulfone could not be obtained.

Cycloadditions of 45c with diethyl azodicarboxylate in fourfold excess gave after work-up in 95% yield (calculated for cycloadduct) a thick syrup: ir (pure) 1720 cm^{-1} (C=O); nmr (CCl_4) δ 0.88 [s, 18 H, $(CH_3)_3C$], 1.23 (br t, J = 7.0 Hz, 6 H, OCH_2CH_3), 1.40–2.20 (complex m, 18 H, ring CH_2), 4.10 (q, J = 7.0 Hz, 2 H, OCH_2CH_3), 4.12 (q, J = 7.0 Hz, 2, OCH_2CH_3). The ratio of the δ 4.10 to 4.12 quartets is 2:1.

The basic structure 2,2,5,5-bis[(3-*tert*-butyl)pentamethylene]-3,4-dicarboethoxy-1,3,4-thiadiazolidine (**55**, **55′**) is assigned to this material. Experiments with europium shift reagent failed to produce more clearly defined spectra. Attempted distillation failed; some rearrangement of the undistilled material appeared to take place (see experiment with **57**). The mass spectrum showed the parent peak at m/e 482 (calcd for $C_{26}H_{46}N_2O_4S$ 482).

Cycloaddition of 45c with dimethyl acetylenedicarboxylate using a fourfold excess of dipolarophile afforded, after repeated recrystallizations from methanol and chromatography over Al_2O_3 to remove (**51**), in 13% yield 2,2,5,5-bis[(3-*tert*-butyl)pentamethylene]-3,4-dicarbomethoxy-2,5-dihydrothiophene (**54**): mp 131–133°; ir (KBr) 1730 cm^{-1} (C=O); nmr (CCl_4) δ 0.88 [s, 18 H, $(CH_3)_3C$], 1.10–2.10 (complex m, 18 H, ring CH_2), 3.67 (br s, 6 H, OCH_3) (experiments with europium shift reagent failed to improve the spectrum); mass spectrum m/e 450 (parent, calcd for $C_{26}H_{42}O_4S$ 450), 428 (S), 393 [$(CH_3)_3C$]. A satisfactory elemental analysis could not be obtained; the C:H ratio was correct but the S value varied badly.

Pyrolysis of 45c was carried out by heating (320 mg (0.455) mmol) in methylcyclohexane for 5 hr. Removal of the solvent and recrystallization from methanol gave 290 mg (0.94 mmol, 99%) of 2,2,3,3-bis[(3-*tert*-butyl)pentamethylene] episulfide (**51**): mp 205–207°; ir (KBr) 2950, 1440, 1360 cm^{-1}; nmr ($CDCl_3$) δ 0.85 [s, 9 H, $(CH_3)_3C$], 0.90 [s, 9 H, $(CH_3)_3C$], 1.70–2.20 (complex m, 18 H, ring CH_2).

Anal. Calcd for $C_{20}H_{36}S$: C, 77.85; H, 11.76; S, 10.39. Found: C, 77.48; H, 11.72; S, 10.28.

Desulfurization of **51** (230 mg, 0.75 mmol) with phenyllithium (procedure used for *tert*-butyl episulfides) afforded 194 mg (0.70 mmol, 93%) of 4,4′-di-*tert*-butylcyclohexylidenecyclohexane (**52**) which was sublimed (164 mg obtained) and recrystallized from methanol to afford a sample of mp 121–124°; ir (KBr) 3000, 2900, 1450, 1370 cm^{-1}; nmr (CCl_4) δ 0.85 [s, 18 H, $(CH_3)_3C$], 1.05–2.0 (complex m, 10 H, ring CH_2), 2.50–2.90 (br m, 8 H, ring CH_2).

Anal. Calcd for $C_{20}H_{36}$: C, 86.87; H, 13.13. Found: C, 86.63; H, 13.07.

A sample of **52** (84 mg, 0.302 mmol) was treated with excess (60 mg) *m*-chloroperbenzoic acid in $CHCl_3$ solution. After standing overnight the solution was worked up to afford 2,2,3,3-bis[(3-*tert*-butyl)pentamethylene] epoxide (**53**), 88 mg, 0.3 mmol, 100%), which was recrystallized from methanol: mp 158–160°; ir (Nujol) 3000, 2900, 1460, 1360, 900 cm^{-1}; nmr (CCl_4) δ 0.87 [s (very slightly broadened), 18 H, $(CH_3)_3C$], 1.17–1.70 (complex m, 18 H, ring CH_2).

Anal. Calcd for $C_{20}H_{36}O$: C, 82.12; H, 12.40. Found: C, 81.83; H, 12.44.

Attempts to convert **53** into an episulfide by treatment with KSCN in methanol–water led only to eventual decomposition of the epoxide. No trace of an episulfide could be isolated.

Synthesis of 2,2,5,5-bis(hexamethylene)-1,3,4-Δ^3-thiadiazoline (45d) proceeded in 50% yield: mp 73–75° dec; ir (Nujol) 1590 cm^{-1} (N=N); nmr (CCl_4) δ 1.70 and 2.02–2.50 (br m).

Anal. Calcd for $C_{14}H_{24}N_2S$: C, 66.62; H, 9.58; N, 11.10; S, 12.70. Found: C, 66.43; H, 9.51; N, 10.94; S, 13.10.

Cycloaddition of 45d with diethyl azodicarboxylate was carried out with a threefold excess of dipolarophile. After work-up there was obtained 490 mg (1.23 mmol, 31% yield) of 2,2,5,5-bis(hexamethylene)-3,4-dicarboethoxy-1,3,4-thiadiazolidine (**57**) as a thick syrup: ir (pure) 1720 cm (C=O); nmr (CCl_4) δ 1.26 (t, J = 7.0 Hz, 6 H, OCH_2CH_3), 1.43–1.97 and 1.97–2.41 (br s, 24 H, ring CH_2), 4.11 (q, J = 7.0 Hz, 4 H, OCH_2CH_3); mass spectrum m/e 398 (parent, calcd for $C_{20}H_{34}N_2O_4S$ 398), 365 (HS), 325 ($CO_2C_2H_5$), 270 ($C_7H_{12}S$). On distillation, bp 130° (0.2–0.3 mm), a heavy liquid was obtained the nmr of which was virtually unchanged in the region of δ 0.9–2.5 except for a broadening of the methyl triplet. However, *two* quartets at δ 4.11 and 4.13 were present as well as a single vinylic proton at δ 5.74 (br t, J = 6.0 Hz). A number of changes occurred in the 650–1200-cm^{-1} region of the ir; however most significant was the appearance of an N–H absorption at 3400 cm^{-1}. The mass spectrum still showed the parent peak at m/e 398. A satisfactory elemental analysis could not be obtained.

Cycloaddition of 45d with dimethyl acetylenediacarboxylate using a 5.7-fold excess of dipolarophile gave, after distillation of unreacted ester and some unidentified material, an undistillable residue (~30–40% assuming pure cycloadduct) that slowly become crystalline on standing. After several recrystallizations from methanol sufficient material was obtained for analysis and spectral determinations. The material assigned the structure of 2,2,5,5-bis(hexamethylene)-3,4-dicarbomethoxy-2,5-dihydrothiophene (**56**) had mp 76.5–78°; ir (pure) 1710, 1740 cm^{-1} (C=O); nmr (CCl_4) δ 1.53 (br s) 1.80–2.30 (complex m, total 24 H), 3.70 (s, 6 H, OCH_3).

Anal. Calcd for $C_{20}H_{30}O_4S$: C, 65.55; H, 8.25; S, 8.75. Found: C, 65.54; H, 8.21; S, 8.70.

Pyrolysis of 45d was attempted a number of times but no well-defined product was ever isolated. Pyrolysis in methylcyclohexane gave one major and two minor products as obtained by glpc. Isolation by preparative glpc gave products with analytical data corresponding to mixture of sulfur-containing products. A small amount of cycloheptylidenecycloheptane could have been present. One product had physical properties and an analysis close to that expected for cycloheptyl thioketone. Treatment of the crude pyrolysis mixture with *n*-butyllithium gave a product (isolated by preparative glpc) which was probably *n*-butyl-

cycloheptyl sulfide. Pyrolysis of **45d** in the presence of triethyl phosphite of tris(dimethylamino)phosphine failed to give any characterizable product.

The synthesis of *trans*-2,5-di-*tert*-butyl-2,5-dimethyl-1,3,4-Δ^3-thiadiazoline (45e) was accomplished in 98% yield. The product had mp 103–105°; ir KBr) 1580 cm^{-1} (N=N); nmr (CCl_4) δ 1.07 (s, 18 H, *t*-Bu), 1.67 (s, 6 H, CH_3).

Anal. Calcd for $C_{12}H_{24}N_2S$: C, 63.10; H, 10.59; N, 12.27; S, 14.04. Found: C, 62.76; H, 10.61; N, 12.22; S, 13.95.

Oxidation with 1 equiv of *m*-chloroperbenzoic acid afforded *trans*-2,5-di-*tert*-butyl-2,5-dimethyl-1,3,4-Δ^3-thiadiazoline *S*-oxide in 73% yield: mp 102–103°; ir (KBr) 1580 (N=N, 1050 and 1080 cm^{-1} (SO); nmr (CCl_4) δ 1.01 (s, 9 H, *t*-Bu), 1.24 (s, 9 H, *t*-Bu), 1.41 (s, 3 H, CH_3), 1.47 (s, 3 H, CH_3). This spectrum is consistent only for a trans configuration of the *tert*-butyl and methyl groups, respectively.

Anal. Calcd for $C_{12}H_{24}N_2OS$: C, 58.97; H, 9.89; N, 11.46; S, 13.12. Found: C, 58.72; H, 10.06; N, 11.30; S, 13.19.

Further oxidation afforded *trans*-2,5-di-*tert*-butyl-2,5-dimethyl-1,3,4-Δ^3-thiadiazoline *S*-dioxide in 90% crude yield. After repeated recrystallization and chromatography an analytical sample was obtained: mp 78–80°; ir (KBr) 1540 (N=N?), 1380 cm^{-1} (SO_2?); nmr (CCl_4) δ 1.27 (s, 18 H, *t*-Bu), 1.58 (s, 6 H, CH_3).

Anal. Calcd for $C_{12}H_{24}N_2O_2S$: C, 55.36; H, 9.29; N, 10.75; S, 12.31. Found: C, 55.23; H, 9.18; N, 10.56. Analyses for sulfur consistently gave incorrect results.

Pyrolysis of 45e led to complex reaction mixtures that were often red colored. Usually peaks at δ 1.17 and 1.70 appeared in the nmr spectrum; these were in the ratio expected for *tert*-butyl and methyl groups, respectively. In addition extra complex absorptions in the aliphatic region were present. Attempts at desulfurization of the crude product with triethyl phosphite or *n*-butyllithium led to no conclusive result. Pyrolysis of **45e** in the presence of triethyl phosphite or tris(dimethylamino)phosphine failed to give characterizable products.

Cycloadditions with 45e—The crude products obtained from attempted cyclization had always very complex nmr spectra. The reaction with diethyl azodicarboxylate, (threefold excess) was performed by pyrolyzing the reaction mixture in methylcyclohexane in a sealed tube at 130°. Distillation afforded a modest (30%) yield of a fraction, bp 100–110° (0.25 mm), that had ir (neat) 1720 cm^{-1} (C=O); nmr (CCl_4) δ 1.18 (s, 9 H, *t*-Bu), 1.28 (t, J = 7.0 Hz, 6 H, CH_2CH_3), 1.75 (s, 3 H, CH_3), 4.18 (q, J = 7.0 Hz, 4 H, OCH_2CH_3). The parent in the mass spectrum was at m/e 258 ($C_{12}H_{22}N_2O_4$) with strong fragmentations at m/e 243, 216, 172, 171, 144, 129, 101, 69, and 57. This was thought to be **61**.

With dimethyl acetylenedicarboxylate (fourfold excess) pyrolysis in methylcyclohexane gave a complex reaction mixture that was subjected to distillation. One fraction (~20%) on redistillation afforded a single product: bp 105–110° (0.05 mm); ir (neat) 1740 cm^{-1} (C=O); nmr (CCl_4) δ 1.07 (s, 9 H, *t*-Bu), 1.68 (s, 3 H, CH_3), 3.82 (s, 6 H, OCH_3). Structure **60** was tentatively assigned to this material. Too little material remained for further investigation.

Kinetics of Decomposition of Thiadiazolines and Activation Parameters.—The thiadiazolines were made up as 10^{-2} M solutions in methylcyclohexane and individual samples were sealed in heavy-walled Pyrex tubes. Pyrolysis was carried out in a thermostated oil bath with ±0.1° temperature control. The rate of reaction was followed by monitoring the decrease in uv absorption at 320 mμ. Small infinity absorptions remained, apparently due to a slight amount of absorption by episulfide.

The relative instability of **16c** prevented use of the uv technique. A 0.73 M solution in cyclohexane was allowed to decompose in the nmr spectrometer. Disappearance of the δ 5.67–6.02 multiplet (*t*-H) was used to monitor the reactions; the high concentration was necessary to obtain reproducible results. Benzene was used as an internal standard. The temperature was determined by the ethylene glycol technique; a check was carried out every 20–30 min during the run, but no variation in temperature could be observed. An attempt to determine the activation parameters for the cis isomer **16d** failed. A cis–trans mixture was used and separate monitoring of the cis and trans tertiary protons was attempted. The cis compound appeared to decompose more slowly than the trans, but no reliable activation data could be obtained.

Registry No.—**15c,** 30465-38-4; **15d,** 30465-39-5; **16b,** 28037-21-0; **16c,** 30465-41-9; **17b,** 19566-11-1; **20,** 28037-23-2; **24,** 30465-43-1; **25,** 36614-90-1; **26,** 30465-44-2; **27,** 30465-45-3; **28,** 30465-46-4; *cis*-**32,** 30646-53-8; **33,** 30465-51-1; **34,** 28163-94-2; **36,** 36635-87-7; **36** sulfoxide, 36614-97-8; **36** sulfone, 36611-65-1; **37,** 36611-66-2; **38b,** 36614-44-5; **39,** 36611-67-3; **41,** 36635-88-8; **42,** 30465-50-0; **45a,** 36635-89-9; **45a** sulfoxide, 36614-45-6; **45a** sulfone, 36614-46-7; **45b,** 36614-47-8; **45b** sulfoxide, 36614-48-9; **45b** sulfone, 36614-49-0; **45c,** 36614-50-3; **45c** sulfoxide, 36614-51-4; **45d,** 36614-52-5; **45e,** 36635-90-2; **45e** sulfoxide, 36611-69-5; **45e** sulfone, 36611-70-8; **48a,** 36614-53-6; **48a** sulfoxide, 36614-54-7; **48a** sulfone, 36614-55-8; **48b,** 36614-56-9; **49a,** 36614-57-0; **49a** sulfone, 36614-58-1; **49b,** 36614-59-2; **49b** sulfoxide, 36614-60-5; **49b** sulfone, 36614-61-6; **51,** 36614-62-7; **52,** 36635-91-3; **53,** 36614-63-8; **54,** 36614-64-9; **55a,** 36614-77-4; **56,** 36614-78-5; **57,** 36614-79-6; **60,** 36614-80-9; **61,** 36614-81-0; **62,** 36614-82-1; **62** sulfoxide, 36614-83-2; **62** sulfone, 36614-84-3; **63,** 36611-89-9; 2,2,5,5-bis(pentamethylene)-1,3,4-Δ^3-thiadiazoline *S*-oxide, 30167-48-7; *trans*-2,5-diethyl-3,4-dicarbomethoxy-2,5-dihydrothiophene, 30465-50-0; *trans*-2,5-diethyl-3,4-dicarboethoxy-1,3,4-thiadiazoline *S*-oxide, 30504-12-2; *trans*-2,5-diethyl-3,4-dicarboethoxy-1,3,4-thiadiazolidine *S*-dioxide, 30504-13-3; *trans*-2,3-diethyl epoxide, 36611-93-5; *cis*-2,3-diethyl epoxide, 36611-94-6; tetramethyl episulfide, 36614-86-5; tetraethyl episulfide, 36614-87-6.

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