Heterocyclic Aromatic Non-Kekulé Molecules. Synthesis and Solution-Phase Chemistry of the Singlet Biradicals 3,4-Dimethylenefuran and 3,4-Dimethylenethiophene

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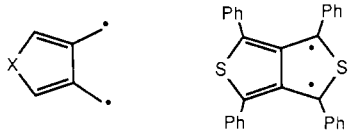
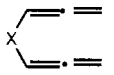
Abstract: The title biradicals **1** and **2** are generated in solution by thermal or photochemical decomposition of the corresponding diazenes, 1,4-dihydrofurano[3,4-*d*]pyridazine (**15**) and 1,4-dihydrothieno[3,4-*d*]pyridazine (**16**), whose syntheses are described. The biradicals both dimerize, but in the presence of trapping agents, both react with electron-deficient alkenes to form furano(thieno)[3,4-*d*]cyclohexanes (fused adducts). The furan biradical **1**, however, gives predominantly a bridged adduct. The cycloadditions are strictly stereospecific and seem to occur by concerted four-center transition states. Competition studies show that the relative reactivities of alkenes toward the thiophene biradical **2** are quantitatively the same whether the biradical is generated from the diazene precursor **16** or from diallenyl sulfide **6**. The latter observation confirms earlier proposals in the literature that biradical **2** could be involved in the chemistry of **6**. The reactivity order of the biradicals parallels that of cyclopentadiene toward the test series of alkenes, the selectivities in both series showing a near-unit slope in a bilogarithmic plot, despite the factor of 10^{10} by which the biradical absolute rates exceed those of the diene.

3,4-Dimethylenefuran (**1**) and 3,4-dimethylenethiophene (**2**) are π-conjugated non-Kekulé molecules[2-6] for which full-valence structures can be written only by expansion of the heteroatom octet. A number of structurally related compounds (e.g. **4**) had been reported earlier by Cava and Potts and their respective co-workers.[7-13] Also, the monocyclic substances **1–3** had been postulated as transient intermediates in reactions of the bis-allenyl compounds **5–7** by Braverman[14] and by Garratt,[15] and **1** was



1: X = O
2: X = S
3: X = NEt

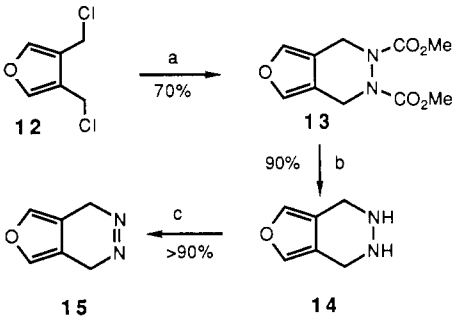
4



5: X = O
6: X = S
7: X = NEt

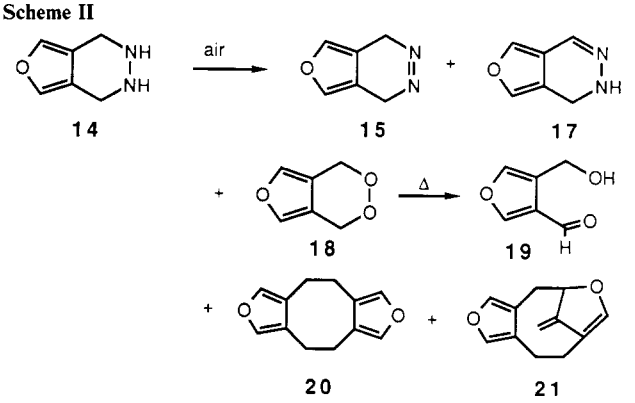
plausibly invoked as a product of the pyrolysis of 2,3-dimethylene-7-oxabicyclo[2.2.1]heptane by Vogel.[16] However, no isolation or characterization of a member of the parent series had been carried out when we began the work described here.[3-6] The heterocycles are formal analogues of the disjoint[17] hydrocarbons tetramethyleneethane (**8**)[18] and its cyclic derivatives **9**[19] and **10**.[20]

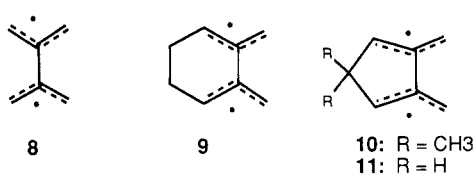
Scheme I



Methods: (a) NaH, DMSO, $(HNCO_2Me)_2$; (b) KOH, H_2O; (c) $MeO_2CN{=}NCO_2Me$

Scheme II





8 **9** **10**: R = CH3 **11**: R = H

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Compounds **1–11** are of particular interest as potential tests of quantum mechanical theories[17,21–27] of the electronic spin of the ground state of non-Kekulé molecules, which predict that violations of Hund's rule should be likely in this series.

In an accompanying paper[28] we describe in more detail the computational design and experimental investigation of molecules designed to address this question. Prominent among the test biradicals are the heterocyclic aromatic species **1** and **2**, which are predicted[24–28] to have singlet ground states. The present work reports their solution-phase behavior, from which insights may be obtained on the spin state of the reactive species and on their electronic structures. The succeeding paper[28] describes their chemical and spectroscopic properties under persistent conditions in rigid media.

Results

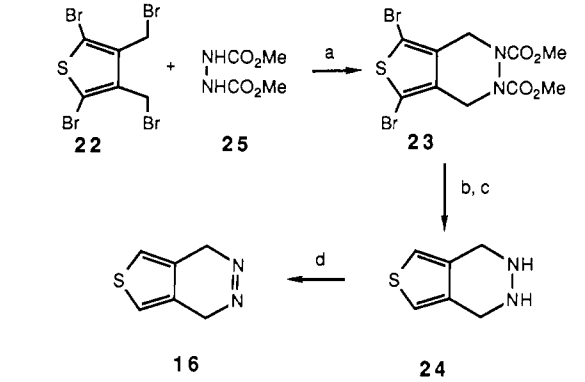
Synthesis of Diazene Precursors of 3,4-Dimethylenefuran (1) and 3,4-Dimethylenethiophene (2). After preliminary, unsuccessful experiments to generate the two biradicals from other precursors, we concentrated our efforts on the synthesis of the two diazenes **15** and **16**. The 3,4-dimethylenefuran precursor **15** was prepared from the known[29a,b] 3,4-bis(chloromethyl)furan by the synthesis shown in Scheme I, which is similar to that used by Carpino[29c] to make a diazene precursor of *o*-quinodimethane. The hydrazine **14** required protection from air, and samples of it often contained 5–10% of diazene **15** and products apparently derived from it, namely, the hydrazone **17**, the (previously known[14,15]) peroxide **18**, and the 3,4-dimethylenefuran dimers **20** and **21** (Scheme II).

The results suggested that O_2 might be an efficient reagent for the deliberate conversion of the hydrazine **14** to the desired diazene **15**, as is the case in several prior syntheses[30,31] of tetrahydropyridazines. However, at the temperature necessary to carry out this reaction, even when catalyzed by Pd/C,[31] the diazene was thermally unstable. Thus, below −10 °C there was essentially no reaction after 48 h, while at 0 °C small amounts of diazene **15** and dimers **20** and **21** could be detected by ^{1}H NMR, but the major component in solution was the peroxide **18**. When the reaction was allowed to go to completion, a 75% yield of **18** was obtained. The peroxide was reasonably stable and could be isolated as white crystals, mp 54–56 °C, after solution chromatography. It could be reduced with $LiAlH_4$ to 3,4-bis(hydroxymethyl)furan. Attempted gas chromatography (GC) of **18** led to the isomer 4-(hydroxymethyl)furan-3-carboxaldehyde (**19**).

These observations were both frustrating and encouraging, since although we were not yet able to isolate diazene **15**, the formation of the products in Scheme II suggested that the generation and capture of the biradical **1** were taking place. After abandoning the use of O_2 as oxidant, we tried several other traditional[32] hydrazine-to-diazene oxidants without success. These included Ag_2O, yellow HgO, MnO_2, $K_3Fe(CN)_6$, *t*-BuOCl, and *N*-phenyltriazolinedione (PTAD). The first five of these oxidants gave hydrazone **17** as the only identified product; of these, MnO_2 gave the cleanest reaction, which was actually useful for the preparation of **17**. On the other hand, PTAD, which was successful in another hydrazine-to-diazene conversion,[33] gave no products we could identify, even when the reaction was run at −78 °C with less than 1 equiv.

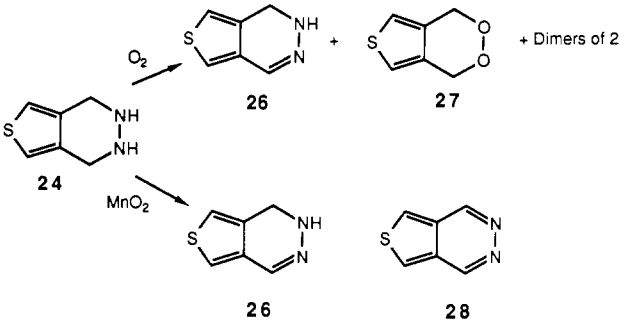
Conversely, the much less reactive dimethyl (or diethyl) azodicarboxylate, DMAD (or DEAD), cleanly effected oxidation of hydrazine **14** to diazene **15** and became the reagent of choice for this key step. The reaction takes place rapidly at −10 °C in a variety of solvents. The main factor limiting the usable range of solvents is the very polar nature of the hydrazine precursor **14**, which is soluble in H_2O, MeOH, EtOH, CH_2Cl_2, $CHCl_3$, tetrahydrofuran, 2-methyltetrahydrofuran, benzene, and toluene but only slightly soluble in Et_2O and insoluble in alkanes. Furthermore, in methanol-d_4 at room temperature the diazene **15** tautomerizes to the hydrazone **17** more rapidly than in aprotic solvents. In fact, the conversion to **17** is competitive with thermal deazetation under these conditions. Therefore, for most of the dimerization or trapping studies described below, the oxidation and deazetation were carried out in the same solvent, usually $CDCl_3$ or CH_2Cl_2. In practice, the hydrazine **14** was titrated with a solution of the bright yellow-orange DMAD in the same solvent until the color persisted. At this point, the solution was back-titrated with a little **14** to remove the excess DMAD. For quantitative work, it was necessary to do this because control experiments showed that DMAD increased the rate of disappearance of diazene **15**, presumably by a bimolecular reaction in competition with thermal deazetation. The solutions obtained by this means were usable for most purposes, since the reduction product, dimethyl hydrazodicarboxylate (DMHD), was unreactive

Scheme III



Methods: (a) DMSO, NaH; (b) H_2, Pd/C, K_2CO_3, EtOAc; (c) KOH, H_2O; (d) DMAD or DEAD

Scheme IV



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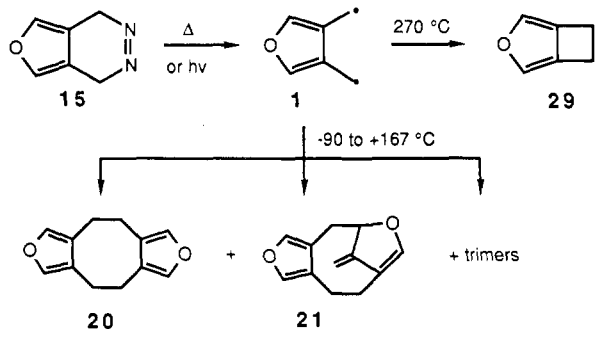
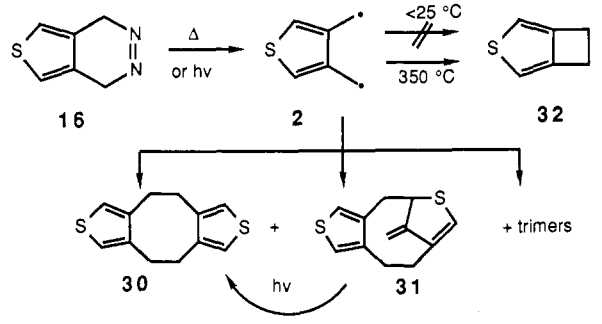
Scheme V



Scheme VI



under the conditions of our further experiments. If necessary, it could be removed from benzene or toluene solutions by precipitation at or below −10 °C.

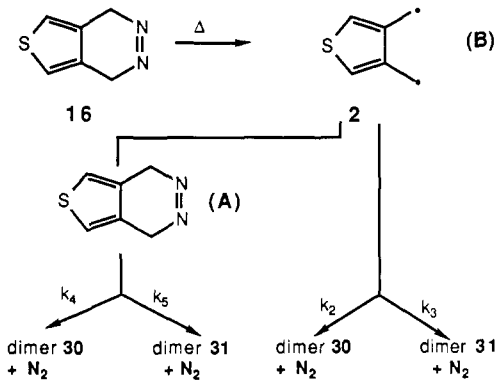
Diazene **16**, the precursor of 3,4-dimethylenethiophene, was prepared in a slightly different sequence (Scheme III), starting with the known[34] tetrabromide **22** (*a potent irritant*!), which in turn was available in four steps from 2,3-butanedione and dimethyl thiodiacetate. Slight modifications (see the Experimental Section) of the literature procedure permitted the preparation of multigram quantities of **22**.

Again, DMAD or DEAD proved to be the best reagents for the hydrazine-to-diazene conversion. With other oxidants, the hydrazine **24** gave mixtures of products (Scheme IV). Thieno-[3,4-*d*]pyridazine (**28**)[35] was a minor product from the MnO_2 oxidation. It is not known whether the hydrazone **26** is formed directly from the hydrazine **25** or from the diazene **16**. That the latter is a conceivable intermediate is suggested by the observation that a trace amount of trifluoroacetic acid quantitatively converted diazene **16** to hydrazone **26** in methanol-d_4 at −20 °C.

Chemistry of 3,4-Dimethylenefuran (1) and 3,4-Dimethylenethiophene (2) Generated from Diazene Precursors 15 and 16. Dimerization and Ring Closure. When a solution of **15** is allowed to warm to temperatures above 0 °C or is photolyzed at 310–380 nm, a complex mixture of dimers and trimers of biradical **1** is formed (Scheme V). The two major products, which account for approximately 40% of the material balance, are the previously reported[15d] dimer **20** and the new anti-Bredit dimer **21**.[36] Small amounts (2–3% each) of four trimeric species also are detectable. Significantly, although the monomeric ring-closure product **29**[15a] is stable under these conditions, none of it is observed in the solution-phase reactions. About 5% yield of **29** can be obtained by flash vacuum pyrolysis (FVP) of **15** (270 °C, 3×10^{-5} Torr). Pending evidence to be provided below, we postulate (Scheme V) that all these reactions involve biradical **1** as an intermediate.

The two dimeric products **20** and **21** are formed in a ratio of about 3 by irradiation of **15** in a rigid 2-methyltetrahydrofuran glass at −196 °C followed by thawing to −90 °C. Similar results were observed (Scheme VI) in the thermal deazetation of the diazene **16** in the thiophene series, where the ratio of dimers **30**:**31** was about 1.3. The absolute isolated yield of these products was 40.5% in a preparative-scale experiment. Small amounts of trimeric products also were observed. Again, no trace of the cyclobutane ring-closure product **32** is observed in the room temperature reactions, although it can be found in the products of the flash vacuum pyrolysis of the diazene **16** at 350 °C (Scheme VI).

Scheme VII



An initially startling result was obtained in the 350-nm photolysis of the diazene **16** in CH_2Cl_2 solution at −28 °C, which led to a 55% yield of dimeric material consisting solely of the symmetrical species **30**. Since the thermal decomposition of diazene **16** in the dark had given a mixture of *both* dimers **30** and **31** (Scheme VI), one superficially attractive interpretation of the photochemical result was that the diazene excited state could lead to a different reactive intermediate than the one generated thermally. However, a control experiment, which showed that the unsymmetrical dimer **31** (λ_{max} = 233 nm, $\epsilon = 5.8 \times 10^3$ M^{-1} cm^{-1} and λ_{max} = 303 nm, $\epsilon = 2.13 \times 10^3$ M^{-1} cm^{-1}) undergoes a smooth, formal [1,3]sigmatropic photochemical rearrangement to the symmetrical dimer **30**, casts serious doubt on this hypothesis. We think it is more likely that any **31** formed in the photochemically initiated dimerization is irreversibly converted to **30** in a secondary reaction. Further evidence that one and the same intermediate is formed photochemically and thermally from **16** is found in the trapping reactions to be described. Note that under the conditions of the present thermal and photochemical experiments, which were done at or below room temperature, the cyclobutane **32** is not among the products (<1%).

Although Schemes V and VI propose direct dimerizations of biradicals **1** and **2**, we have entertained the possibility that dimer formation might occur by a reaction between one molecule of biradical and one of diazene, as is exemplified in Scheme VII for the case of biradical **2**. There is evidence[6] that biradicals **1** and **2** react with their diazene precursors **15** and **16** under the conditions of solid state NMR spectroscopy (in low-temperature matrices of 2-methyltetrahydrofuran or methanol), where the viscosity of the medium would be expected to retard sharply the competing direct biradical dimerization rate. When the biradical **2**, for example, is generated thermally in the solution phase, the kinetics of competing biradical dimerization and biradical-plus-diazene reaction, represented as in eq 1–6, provide the basis for detection of any contribution from the latter process.

$$\text{diazene } \mathbf{16} \text{ or bis-allene } \mathbf{6} \text{ (A)} \xrightarrow{k_1} \text{biradical } \mathbf{2} \text{ (B)} \quad (1)$$

$$2\text{B} \xrightarrow{k_2} \text{dimer } \mathbf{30} \quad (2)$$

$$2\text{B} \xrightarrow{k_3} \text{dimer } \mathbf{31} \quad (3)$$

$$\text{B} + \text{A} \xrightarrow{k_4} \text{dimer } \mathbf{30} \quad (4)$$

$$\text{B} + \text{A} \xrightarrow{k_5} \text{dimer } \mathbf{31} \quad (5)$$

$$-\text{d[A]}/\text{d}t = k_1[\text{A}] + (k_4 + k_5)[\text{B}][\text{A}] \quad (6)$$

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(36) An analogous anti-Bredt dimer has been observed from 2,3-dimethylenecyclohexa-1,3-diene: ref 19a, c.

Table I. Kinetics of Decomposition of Diazene **16** in $CDCl_3$ Solvent

addend	concn, mM	equiv	T, K	$k \times 10^3$ s
none			298	1.92 ± 0.19[a]
dimethyl maleate	3.65	1	298	1.93 ± 0.19[a]
dimethyl maleate	18.2	5	298	2.03 ± 0.20[a]
none			285	2.17 ± 0.22[b]
dimethyl maleate	250	2	285	2.67 ± 0.27[b]
fumaronitrile	75	1	285	2.90 ± 0.29[b]
fumaronitrile	300	4	285	2.55 ± 0.26[b]
fumaronitrile	300	4	285	2.49 ± 0.25[b]

[a] Measured by UV–vis spectroscopy. [b] Measured by ^1H NMR spectroscopy.

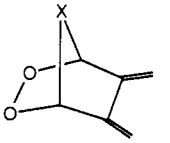
Formally, the rate law (eq 6) for the disappearance of starting diazene A in the competing mechanism hypothesis could fit the observed (see below) first-order behavior, provided that the second term is much smaller than the first. However, the fraction of dimeric product from the biradical-plus-diazene pathway would depend upon the concentration of diazene. The ratio of dimers **30**:**31** from the direct dimerization would be given by k_2/k_3, whereas that from the biradical-plus-diazene pathway would be given by k_4/k_5. Provided that these ratios are not accidentally equal, the total ratio **30**:**31** would change with a change in the initial diazene concentration and also would change during a run, since the diazene concentration would fall as the extent of conversion increases. Neither of these effects is observed in control experiments: the **30**:**31** ratio remains 1.29 ± 0.04 over five initial concentrations (2–20 mM) of diazene **16** in two solvents (CH_2Cl_2 and CH_3CN) and four extents of conversion (28–87%). Moreover, the ratio **30**:**31** from the thermal cyclization of diallenyl sulfide **6** (see below), where the biradical-plus-diazene pathway cannot be involved, is the same, 1.4 ± 0.1. Therefore, the biradical-plus-diazene pathway for dimer formation makes no detectable contribution under these solution-phase conditions.

Although an extensive search has not been carried out, we have been alert to the possibility of chemically induced nuclear polarization (CIDNP) in the NMR spectra of freshly formed dimers of **2**. The observation[37] of such signals in the dimers of the trimethylenemethane derivative 2-isopropylidenecyclopentane-1,3-diyl showed[38] the presence of at least one triplet molecule in the dimer-forming pathway, and a corresponding result in the present case would have important implications for the accessibility of the (presumably) higher energy high-spin state of biradical **2**. However, no CIDNP signals have been observed so far.

Trapping Experiments. Reaction with O_2. When solutions of either of the diazenes **15** or **16** are allowed to warm to room temperature under an atmosphere of O_2, the corresponding peroxides **18** and **27** are formed in high yield. From the hydrazine **14**, for example, the overall yield of **18** for the steps of oxidation to the diazene, decomposition, and trapping is 79%. Peroxide **27** had been found in the cyclization reaction of diallenyl sulfide by Garratt and co-workers,[15] who suggested that it arose from capture of a triplet state of the biradical **2**. We are not aware of any experimental evidence that *requires* this interpretation, and results to be described indicate that the cycloaddition chemistry of both **1** and **2** with alkenes occurs entirely from the singlet state. Conceivably, O_2 may react selectively with the triplet, and it is true that a direct concerted singlet biradical-plus-O_2 reaction in which both C–O bonds are made simultaneously is spin-forbidden. However, such a prohibition does not apply to a singlet-plus-O_2 reaction in which the bonds are formed in successive steps via a triplet adduct biradical which then undergoes intersystem crossing and ring closure. For the present, therefore, we minimize the number of mechanistic hypotheses with the assumption that the singlet is the reactive species in peroxide formation.

Since the concentration of O_2 in these solutions is modest (probably <20 mM[39] in $CDCl_3$), the high yields of peroxide suggest that O_2 must be an extremely efficient trap for the reactive intermediates. This is in accord with the lifetime measured[4] in laser flash photolysis experiments, which show an O_2 trapping rate approaching the diffusion-controlled limit.

It is noteworthy that the reaction with O_2 is highly regiospecific for the fused adducts **18** and **27**, since neither of the bridged peroxides **33** or **34** is observed.



33: X = O
34: X = S

Reactions with Alkenes. The intermediates generated in a nitrogen-purged solution from either diazene failed to react with simple or electron-rich alkenes (2,3-dimethyl-2-butene, vinyl acetate), giving instead the same products obtained in the absence of trapping agents. However, with electron-poor alkenes, 1:1 cycloadducts of biradicals **1** and **2** often could be isolated as pure products in high yields, even when the alkene concentration was only 0.1 M. None of the dimeric products **20**/**21** or **30**/**31** was seen under these conditions, although at still lower concentration, as in the reaction of diazene **15** with 0.002–0.01 M acrylonitrile, the yield of adducts of **1** declined and dimers were formed. In some cases, difficulties in isolation interfered, as in the reactions of **2** with dimethyl maleate and maleonitrile, but the actual formation of 1:1 adducts monitored by NMR spectroscopy was nearly quantitative. Acyclic conjugated dienes (*cis,cis*- and *trans,trans*-2,4-hexadiene), even at high concentration (~4 M), were less efficient, only 50% yields (1,2- rather than 1,4-) of cycloadducts being obtained.

The greater reactivity of conjugated and electron-poor alkenes as diylophiles toward biradicals **1** and **2** is qualitatively reminiscent of the reactivities of alkenes as dienophiles in the Diels–Alder reaction. We expand upon this topic in a later section of this paper, where the patterns are quantitatively correlated and rationalized.

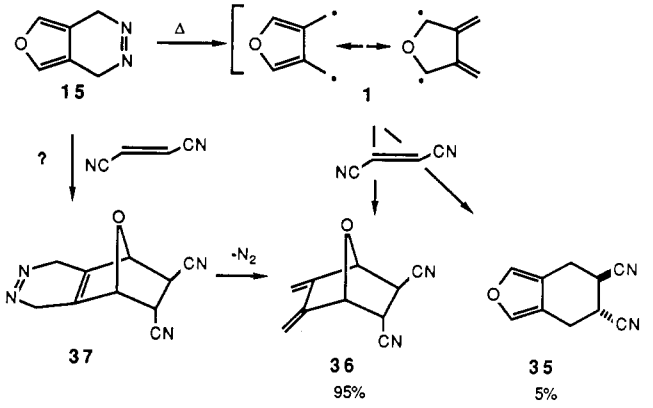
Kinetic Evidence for a Reactive Intermediate in the Thermal Deazetation of Diazenes 15 and 16. Schemes V–VII propose a unimolecular rate-determining deazetation of a diazene precursor and formation of a biradical intermediate which can be intercepted in a subsequent step. This requires that the disappearance of the diazene obey first-order kinetics and that the rate be independent of the concentration of the trapping agent. In studies of the decompositions of diazenes **15** (followed by UV–vis spectroscopy) and **16** (followed by both NMR and UV–vis spectroscopy), we found adherence to this requirement. The rate constants for the reactions of diazene **16** are shown in Table I. The reactions were cleanly first-order through ~3 half-lives, and the rate constants, within the experimental error of about 10%, were independent of the concentration of trapping agent (dimethyl maleate or fumaronitrile) up to 0.3 M (Table I). The apparent anomaly of the rates at 285 K (measured by NMR) being about 10% faster than those at 298 K (measured by UV–vis) probably is attributable to a systematic error in one or both of the sets of data.

Regiospecificity. Furan Series. The intermediates in the furan series generated from diazene **15** give rise to two kinds of 1:1 cycloadducts. With fumaronitrile in N_2-purged $CDCl_3$, for example, bridged product **36** is favored by a 95:5 ratio over fused product **35** (Scheme VIII). Similar preferences for the formation of fused vs bridged cycloadducts were observed with acrylonitrile (88:12), maleonitrile (96:4), and dimethyl fumarate (78:22). The structure of the major adduct (**38**) in the acrylonitrile series was assigned by NMR spectroscopy and confirmed by independent synthesis from the Diels–Alder (ZnI_2-catalyzed) adduct of 3,4-bis(hydroxymethyl)furan and acrylonitrile (Scheme IX).

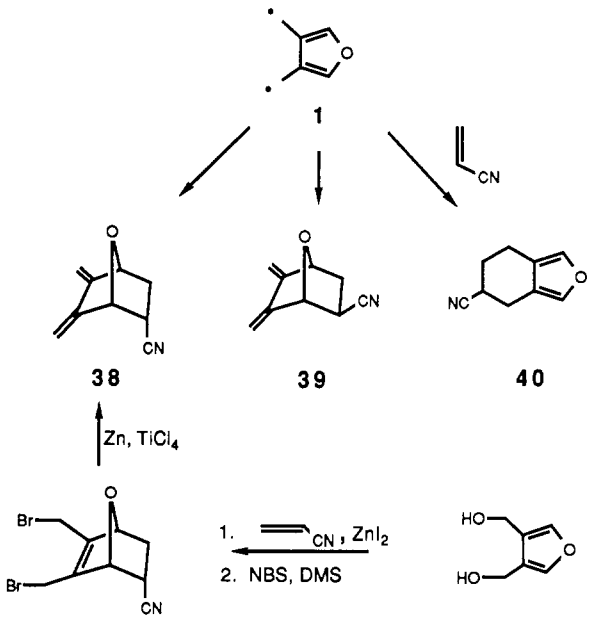
Since furans are reactive in the Diels–Alder cycloaddition, the possibility existed that bridged formal adducts of biradical **1** might arise by a separate pathway involving preliminary Diels–Alder reaction of *diazene* ***15*** with the alkene, for example, fumaronitrile,

(37) Berson, J. A.; Bushby, R. J.; McBride, J. M.; Tremelling, M. *J. Am. Chem. Soc.* **1971**, *93*, 1544.
(38) Closs, G. L. *J. Am. Chem. Soc.* **1971**, *93*, 1546.
(39) Adam, W.; Hannemann, K.; Wilson, R. M. *J. Am. Chem. Soc.* **1986**, *108*, 929.

Scheme VIII



Scheme IX

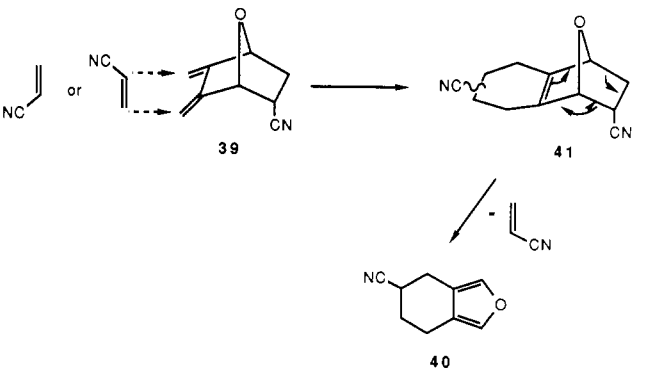


followed by deazetation of the extremely unstable[40] 3,6-dihydropyridazine **37** (Scheme VIII). Because it would require a major second-order component in the rate law, which already has been shown to be absent, this alternative cannot be a significant pathway for the formation of bridged cycloadduct **36**.

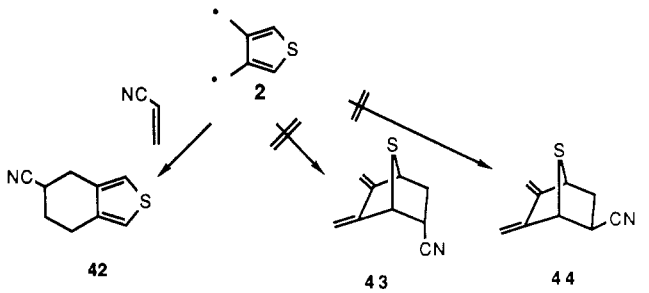
With acrylonitrile, the ratio of endo bridged (**38**) to exo bridged (**39**) to fused (**40**) isomers (Scheme IX) from the furan biradical **1** is 64:24:12. It is essentially independent of whether the reactive intermediate is generated by photolysis of the diazene **15** photochemically (350 nm, −20 °C) or thermally (25–60 °C) and is also invariant to changes in concentration of the trapping agent in the range 0.003–14 M acrylonitrile. Dimerization of the biradicals competes with trapping at millimolar concentration of the trapping agent.

It is possible to shift the product composition toward fused cycloadduct, for example, **40** from acrylonitrile, at a high concentration of the trapping agent by raising the temperature. This effect begins to be noticeable with >0.25 M acrylonitrile at 167 °C: adduct **40** becomes more prominent as the concentration of acrylonitrile is increased until, at 14 M, it is the only product. However, this behavior has nothing to do with the regiospecificity of the biradical-plus-olefin reaction, as was revealed by a control experiment, which showed that both bridged adducts **38** and **39** are 90% transformed into the fused isomer **40** when heated with 14 M acrylonitrile for 4 min at 167 °C. This "rearrangement"

Scheme X



Scheme XI



apparently involves Diels–Alder addition of acrylonitrile to the diene system of each bridged adduct to give the mixture of cyclohexenes **41**, which under the high temperature of the experiment suffers Diels–Alder cycloreversion in the opposite sense to release a *different* molecule of acrylonitrile and generate the furan ring of fused adduct **40** (Scheme X).

Two other points concerning the 167 °C acrylonitrile trapping merit comment. First, the **38**:**39**:**40** ratio of 57:24:17 observed at this temperature when the acrylonitrile concentration is <0.25 M probably is the actual kinetically controlled ratio from the trapping, since it is invariant over the range 0.25–0.002 M. Apparently, 4 min at 167 °C are insufficient conditions to allow any of the secondary "rearrangement" reaction to occur. Second, whereas the yield of cycloadducts does not change in the concentration range 0.25–1 M, it decreases by 4% at [acrylonitrile] = 0.01 M and by 51% at [acrylonitrile] = 0.002 M. In the latter two cases, the remainder of the material appears as dimers. A plausible interpretation of this recognizes that the activation energy for deazetation of the diazene **15**, the precursor of biradical **1**, is higher than those for dimerization or trapping of the biradical. Thus, high-temperature conditions, by increasing the rate of the formation of the biradical relative to its disposal, will increase its steady-state concentration. This will favor the process of dimerization, which is kinetically second-order in biradical, relative to capture, which is first-order in biradical. It is noteworthy that even when dimerization is competitive with trapping, the 167 °C ratio of cycloadducts, 57:24:17, remains the same. Similarly, the 25 °C ratio, 64:24:12, is not changed even when trapping is carried out at [acrylonitrile] = 0.003 M in $CDCl_3$ solution saturated with O_2, conditions under which competitive formation of peroxide lowers the relative yield of acrylonitrile adduct to 40%.

The absence of any effect of dilution or oxygen on the relative distribution of cycloadducts in the reactions of biradical **1** makes a sharp contrast with the behavior of the trimethylenemethane derivative 2-isopropylidenecyclopentane-1,3-diyl. In the latter system, the products are very sensitive to these conditions, and the effects can be analyzed in terms of two sequentially formed reactive species, a singlet and a triplet.[41-43] All of the trapping

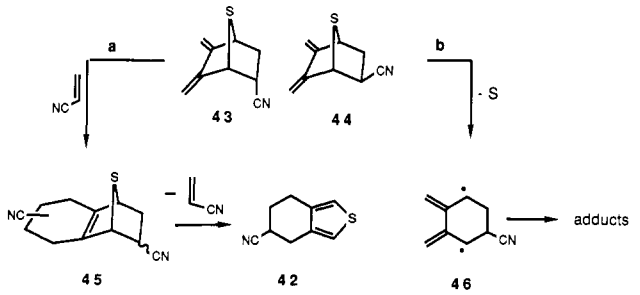
(40) (a) Gillis, B. T.; Beck, P. E. *J. Org. Chem.* **1963**, *28*, 3177. (b) Askani, R. *Chem. Ber.* **1965**, *98*, 2551. (c) Rieber, N.; Alberts, J.; Lipsky, J. A.; Lemal, D. M. *J. Am. Chem. Soc.* **1969**, *91*, 5668. (d) Berson, J. A.; Olin, S. S. *J. Am. Chem. Soc.* **1969**, *91*, 777.

(41) Corwin, L. R.; McDaniel, D. M.; Bushby, R. J.; Berson, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 276.

(42) Berson, J. A. *Acc. Chem. Res.* **1978**, *11*, 446.

(43) Berson, J. A. In *Diradicals*; Borden, W. T., Ed.; Wiley-Interscience: 1982.

Scheme XII



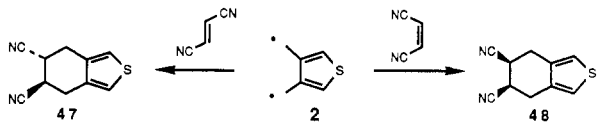
results in the present study to date therefore are most economically interpreted to mean that only one reactive intermediate from the deazetation of diazene **15** has been intercepted. For the present, of course, it is not possible to tell whether more than one species may be *formed* nor is the prediction justified that other conditions may not still be found to permit another one to be detected.

Regiospecificity. Thiophene Series. In the cycloadditions of 3,4-dimethylenethiophene, **2**, generated inter alia from the corresponding diazene **16**, either photochemically at −78 °C or thermally at 25 °C, the only observed products are the fused isomers (Scheme XI). For example, adduct **42** was isolated in 87.5% yield from the thermal decomposition of **16** in a solution containing excess acrylonitrile. Scrutiny of the reaction mixtures by ^{1}H NMR spectroscopy in searches for bridged adducts **43** and **44** (Scheme XI) in this case or for their counterparts in reactions of eight other alkenes gave no evidence for the formation of even small amounts (<1%) of such products, which should have been recognized easily by, among others, their characteristic exocyclic methylene resonances at chemical shifts near 5 ppm. The regioselectivity of 3,4-dimethylenethiophene (**2**) apparently is the reverse of that of 3,4-dimethylenefuran (**1**).

Since the bridged adducts **43** and **44** are not available from the cycloadditions of **2** and since we so far have not succeeded in synthesizing them by an independent route, control experiments on the stability of these compounds under the reaction conditions have not been done. Therefore, we must admit the formal possibility that the exclusive formation of fused adduct **42** may not represent the actual course of the cycloaddition itself but rather could be the consequence of a secondary conversion of any bridged products to fused products by either or both of two hypothetical processes (Scheme XII): (a) a Diels–Alder mediated "rearrangement" analogous to that observed in the high temperature reactions in the furan series (Scheme X) or perhaps (b) decomposition by loss of the bridging sulfur atom, as has been observed[44-46] at high temperatures in 7-thiabicyclo[2.2.1]hepta-2,5-dienes. However, alternative a would require that the 7-thiabicyclo[2.2.1]hept-2-ene intermediate **45** in the hypothetical "rearrangement" (Scheme XII) be thermally unstable at or below room temperature, a property that is difficult to reconcile with the existence of several examples[47,48] of 7-thiabicyclo[2.2.1]-hept-2-enes in the literature. Alternative b would produce a substituted 1,2-dimethylenecyclohexane-1,4-diyl **46**, which would have been expected to react with trapping agents to give stable products,[19,20] but such products were not formed in detectable amounts. We conclude that neither alternative is a likely explanation for the regiospecifically fused cycloadditions observed with the 3,4-dimethylenethiophene biradical and that it is more probable that the result represents a true kinetic preference in the cycloaddition of the intermediate.

We are not sure of the reasons for the regiospecificity for bridged cycloadducts from the furan biradical **1**. Reaction to form fused cycloadduct is more exothermic by about 16 kcal/mol as estimated by group additivity calculations,[49] so the preference for reaction in the bridged mode must overcome whatever part of this extra driving force is in the transition state. Semiempirical (AM-1-CI, INDO/S-CI)[27,28] and ab initio[25,26] quantum mechanical calculations agree that the π-electron coefficients at the furan ring positions of biradical **1** are slightly greater than those at the exocyclic positions in the appropriate frontier orbital, which would be consistent with the observed preference for reaction to give bridged product. However, one may doubt that this is the only factor determining the regiospecificity, since similar semiempirical calculations suggest that the π-electron distribution is only slightly less biased in this direction in the thiophene biradical **2**. The exothermicity, however, favors fused addition in the case of **2** by 29 kcal/mol or 13 kcal/mol more than in the case of **1**. We think this factor plays a significant role in producing the switch in regiospecificity from **1** → mostly bridged adduct to **2** → entirely fused adduct.

Scheme XIII



Stereospecificity of the Cycloadditions. Thermal Reactions. Stereochemistry has been a classical test of mechanism in cycloadditions since the earliest discoveries in the realm of the Diels–Alder reaction, and the strict cis-addition course of such processes still constitutes one of the most compelling evidences of concert. We have now found similar behavior in the cycloadditions of biradicals **1** and **2**. Scheme VIII already has reported the cis addition of **1** to fumaronitrile.

This observation by itself might be compatible with a two-step mechanism, since the addition of the *triplet* state of the TMM biradical 2-isopropylidenecyclopentane-1,3-diyl to fumaronitrile is also highly stereospecific for trans product, even though it occurs by a nonconcerted pathway.[41-43] The decisive experiment, of course, is the addition to the corresponding cis alkene, maleonitrile, which gives largely trans product from the TMM triplet but entirely cis product from the singlet.[41-43]

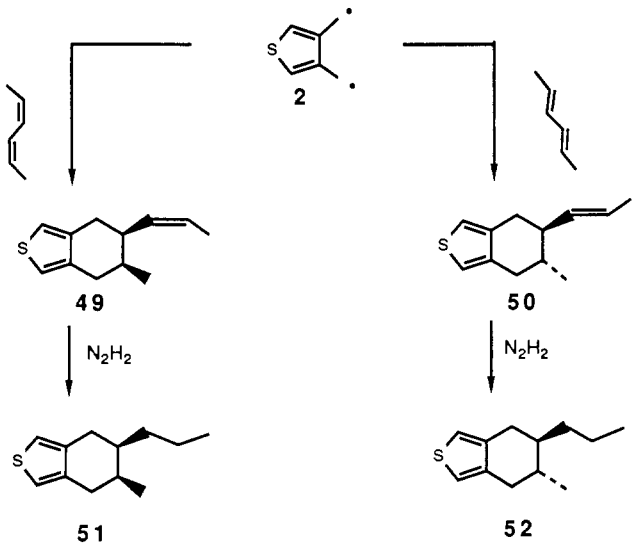
The results in the case of the furan derivative **1** are not as compelling as might be desired, because the regiospecificity of the reaction is so high (96% bridged, 4% fused) that although it is easy to find a small amount of trans product in the bridged series, it is difficult in the fused series. There is also a problem in the analysis of the addition reaction mixtures by GC, which is not readily reproducible, perhaps because of some decomposition of the adducts. Nevertheless, it is clear that the reactions of **1** with both fumaronitrile and maleonitrile are completely stereospecific within the limits of ^{1}H NMR and GC detection (>95%).

The analyses can be made more sensitive in the case of the adducts from the thiophene analogue **2**. Thermal decomposition of the diazene precursor **16** in CH_2Cl_2 or pentane solutions containing carefully purified maleonitrile (0.0058–1.32 M) or fumaronitrile, each >99.5% stereochemically homogeneous, gave the trans and cis cycloadducts, **47** and **48**, respectively, with no cross-contamination. The limit of detection of the "wrong" stereoisomer was 0.4% by capillary GC analysis (Scheme XIII). Similarly, dimethyl maleate gave 99.7% stereospecifically pure cis-fused adduct. The trace of trans adduct observed is probably attributable to the very small amount of residual fumarate ester in the carefully purified maleate sample. Since dimethyl fumarate is about 500 times as reactive as dimethyl maleate toward biradical **2** (see below), even a small amount of stereochemical contamination of the starting alkene would be greatly magnified and therefore detectable in the product.

The reaction of **2** and dimethyl maleate is slow (see below), so at low concentrations (0.0072–0.0029 M) of the trapping agent,

(44) (a) Kuhn, H. J.; Gollnick, K. *Tetrahedron Lett.* **1972**, 1909. (b) Kuhn, H. J.; Gollnick, K. *Chem. Ber.* **1973**, *106*, 674.
(45) Kobayashi, K.; Mutai, K. *Chem. Lett.* **1977**, 1149.
(46) Helder, R.; Wynberg, H. *Tetrahedron Lett.* **1972**, 605.
(47) Katsuki, H.; Nishizawa, H.; Kitagawa, S.; Ochi, M.; Yamasaki, N.; Matsuoka, K.; Tokuroyama, T. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 544.
(48) Cantrell, T. *J. Org. Chem.* **1974**, *39*, 2242.
(49) Benson, S. W.; Cruickshank, F. R.; Golden, D. M.; Haugen, G. R.; O'Neal, H. E.; Rodgers, A. S.; Shaw, R.; Walsh, R. *Chem. Rev.* **1969**, *69*, 279.

Scheme XIV



substantial amounts (30–53%, respectively) of biradical dimer products are observed. Nevertheless, even under these conditions, which favor a relatively long lifetime of the biradical, no loss of stereospecificity in the adduct is observed. Again, this contrasts strikingly with the TMM cycloadditions,[41-43] where such conditions lead to triplet-derived, stereorandomized products because the trapping agent concentration is too low to intercept the singlet in the cascade mechanism (precursor → singlet biradical → triplet biradical).

The significance of the persistence of the stereospecificity with trapping-agent concentration in the reactions of 3,4-dimethylenethiophene (**2**) therefore must be that the ratio of rates of (trapping of singlet)/(intersystem crossing) is much greater for singlet **2** than for singlet TMM. Obviously, one impediment to the operation of the cascade mechanism would be a ground state for **2** that is singlet by a large enough energy gap to slow down the rate of intersystem crossing to the triplet.

Conjugated dienes also intercept the biradical **2** stereospecifically (Scheme XIV). The product **49** of cis addition to *cis,cis*-hexa-2,4-diene can be reduced to the dihydro derivative **51**, which is distinct from and not detectably (<0.5%) contaminated by the dihydro derivative **52** obtained from **50**, the adduct from *trans,trans*-hexa-2,4-diene.

Photochemical Reactions. When the biradical **2** is generated photochemically from diazene **16** at −26 °C, a temperature at which thermal decomposition of **16** does not occur at an appreciable rate, the product from maleonitrile was again stereospecifically cis, but that from dimethyl maleate contained about 17% of the trans isomer. This complication is not mechanistically significant in the present context. It was traced to the competing isomerization of the alkene trapping agent under the photochemical conditions, both the cis nitrile and the cis ester being recovered from the reactions detectably contaminated with their trans isomers. Control experiments showed that the presence of hydrazone **26** promoted this photoinduced cis → trans isomerization. The greater loss of stereospecificity in the maleate photoinduced cycloaddition again is plausibly attributed to the large reactivity ratio of fumarate:maleate (see below). Thus, the simplest interpretation is that the direct photoinduced decomposition of diazene **16** produces the same intermediate as that generated in the thermal reaction. Further support for this conclusion comes from the relative reactivity data to be presented.

L. C. Bush in our laboratory[50a] has made an effort to photosensitize the decomposition of diazene **15** in the hope of generating the triplet state of biradical **1**, which by analogy to TMM chemistry[41-43] should add nonstereospecifically to alkenes. Irradiation (350 nm) of solutions of **1** and xanthone, thioxanthone, or Michler's ketone (E_T = 74.0, 65.5, and 61–65.7 kcal/mol, respectively[50b]) at −15 °C with the sensitizer in sufficient concentration to absorb >95% of the incident light, *followed by low-temperature NMR spectroscopy of the solutions*, showed no decomposition of the diazene. In the absence of sensitizer, under otherwise similar reaction and monitoring conditions, 100% deazetation occurred. We conclude that these addenda are not efficient in sensitizing the photodecomposition of diazene **1**. These results elicit a cautionary note which is self-evident upon reflection: When the precursor of a reactive intermediate is both thermally and photochemically labile, it is important to make sure that the products observed from an attempted photosensitization experiment are not thermally derived. For example, in the present case, inclusion of a trapping agent with the sensitizer, followed by photolysis and conventional room-temperature workup, gave the same mixture of products obtained in the absence of sensitizer. From this observation alone, it would have been unwarranted to draw any mechanistic conclusions on the nature of the reactive intermediate supposedly generated by sensitization, since it is now clear that all of the products must have been formed by a thermal pathway.

Table II. Relative Rates of Reaction of Biradicals **2** and **1** with Alkenes in CH_3CN Solvent

	2			**1**
alkene	from **6**[a] by compet	from **16**[a] by compet	from **16**[b] directly	from **15**[b] directly
maleic anhydride	89	70	57	20
maleonitrile	3.8	3		
fumaronitrile	1.5	1.4	1.1	5.1
dimethyl fumarate	1.0	1.0	1.0	1.0
acrylonitrile	0.0083	0.01	0.0024	0.0067
dimethyl maleate	0.0013	0.0017		

[a] GC analysis of binary product mixtures from a series of pairwise competition experiments at 298 K (see ref 5a). [b] Absolute rate measurements by time-resolved optical spectroscopy at 260 K (see ref 5b). The temperature effect on the relative rates is small, and no attempt is made here to extrapolate the data of the third column to the slightly higher temperatue of the first two.

Relative Rates of Reaction of Alkenes with 3,4-Dimethylenefuran (1) and 3,4-Dimethylenethiophene.[51] Two purposes are served by the establishment of a reactivity order of alkenes toward the biradicals **1** and **2**: to provide insight into the mechanism of the cycloaddition and to help test more precisely the identity of the actual reactive intermediate from different sources. We have done this by competition experiments[5a] and by nanosecond flash photolysis and time-resolved spectroscopy[5b] for the case of the thiophene biradical **2** and by the latter technique for the case of the furan biradical **1**. Details of the competition experiments are reported in the Experimental Section, and the flash photolysis data will be included in a separate paper. The thiophene biradical **2** for study by competition was generated from the diazene **16**, either thermally or photochemically. It also was generated thermally from the bis-allene **6** by a modification of the method of Braverman[14] and of Garratt.[15] We confirm the previous finding[15f] that the dimerization of **6** is a first-order reaction, which is consistent with a rate-determining unimolecular formation of a reactive intermediate. We now find that the cycloaddition with maleic anhydride proceeds at the same rate as the dimerization, which again suggests a unimolecular rate-determining step. The reactivity order for cycloadditions of the furan biradical **1** was determined from absolute rate measurements[5b] in which the intermediate was generated by flash photolysis from diazene **15**.[5b] Table II collects the reactivity data.

It will be noted that the competition results on **2** (Table II, first two columns) serve as a "fingerprint" to identify the characteristic reactivity pattern of the intermediate from the diazene **16** as the same as that from the bis-allene **6** and hence strongly support the

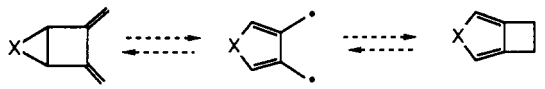
(50) (a) Bush, L. C., unpublished research report, Yale University, 1987. We thank L. C. Bush for this result. (b) Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; Wiley-Interscience: New York, 1972; p 350.

(51) (a) Preliminary communications: ref 5a,b. (b) Reference 15b and references cited therein.

conclusion that both precursors generate the same product-forming entity. Furthermore, the ratio of the two dimers **30** and **31** (Scheme VI) from the diazene **16** (1.35 ± 0.5) is essentially identical with that from the diallenyl sulfide **6** (1.37 ± 0.5), which again is consistent with a common origin.

The directly observed rates (Table II, third column) were obtained by following the intensity of the 572-nm absorption band of the biradical **2** in the solution phase on the nanosecond time scale.[5b] A band with the same absorption maximum is responsible for the visible color of matrix-immobilized specimens of **2** observed at low temperatures.[4,28] The directly observed relative rates match those from the competition experiments (Table II), which strongly implies that the spectroscopically monitored purple species in the flash kinetic experiments is the same one responsible for the actual cycloaddition chemistry in preparative runs. Moreover, as is described elsewhere in detail,[52] the reactivity order as measured by competition is not significantly altered, aside from a small temperature effect, when the intermediate **2** is generated photochemically from diazene **16** at −26 °C.

There remains the question of whether the actual reactive species in the dimerizations and cycloadditions are the biradicals **1** and **2** or some other structure with which the biradicals rapidly interconvert. In such a hypothesis, the carrier of the purple color which is monitored in the flash photolysis experiments[5a,5b] merely acts as the visible identification tag for the true reactant, which might have no optical absorption detectable under these conditions. Abstractly, this subtle issue is chiefly of philosophical interest. Concretely, however, it can be addressed by nominating candidates for the role of the silent reactant and examining their compatibility with the facts. The two most likely candidates are the bicyclic cyclobutane derivatives **53** and **54**, hypothetically obtained by



53: X = O
54: X = S

1: X = O
2: X = S

29: X = O
32: X = S

forming a covalent bond in **1** or **2**. The furan and thiophene derivatives **29** and **32** are both known compounds,[51b] and we have established by independent syntheses and direct control experiments that, under the conditions of the present studies, they are stable and do not dimerize or react with the olefinic trapping agents we have used. Moreover, as we have already mentioned, they are not formed in detectable amounts (<1%) in any of the solution phase reactions ascribed here to biradicals **1** and **2**.

Compounds **53** and **54** are not known, but to attribute to them the role of the active species requires the additional hypothesis that ring closure of the biradical to give the highly strained bicyclic compound (**53** or **54**) be much faster than that to give the far more stable aromatic compound (**29** or **32**). Also, it requires that the absolute rates of reaction of **53** and **54** approach the diffusion-controlled limit and be much faster than the corresponding reactions of the biradical carrier of the purple color.[5b] We believe that these requirements are sufficiently implausible to exclude **53** and **54** from the consideration as the actual reactive intermediates.

Mechanistic Parallel of Singlet Biradical Cycloadditions and Diels–Alder Reactions. The strict stereospecificity of the cycloadditions of alkenes to 3,4-dimethylenethiophene (**2**) (see above) suggests that the actual product-forming biradical intermediate is a singlet species and that the reaction involves concerted formation of both new carbon–carbon bonds. (We do not address here the subtle issue of whether both bonds are formed to the same extent in the transition state.) The analogy that springs to mind for this process is the stereochemistry of the Diels–Alder reaction. If the analogy has a fundamental mechanistic origin, there should be further correspondences in behavior. One obvious point of comparison is in the relative reactivity pattern of the series of dienophilic alkenes whose diylophilic ranking is given in Table II. In fact, the diylophilic order toward **2** is quantitatively correlated ($r > 0.99$) in a bilogarithmic plot by the dienophilic order, obtained from measurements of the rates of Diels–Alder reactions[53] of the same alkenes toward cyclopentadiene (Table III). This correlation contrasts with the much inferior correlation ($r = 0.89$) obtained between the reactivities of **2** and those of the growing polystyrene radical,[54,55] a model reaction for addition to alkenes by a one-bond-at-a-time mechanism.

It seems likely that the underlying basis for the reactivity order of alkenes with the singlet biradicals **1** and **2** is the same as that of the same alkenes in the Diels–Alder reaction, which has been rationalized[56] by frontier orbital theory. In this view, the rates are decisively influenced according to an inverse function of the energy separation between the HOMO of the diene (or biradical) and the LUMO of the electron-poor alkene.

Perhaps the most appropriate analogues of the reactions of alkenes with **1** and **2** are those with the singlet TMM biradical 2-isopropylidenecyclopentane-1,3-diyl, **55**. In fact, the alkene reactivities correlate well for the three systems when the point for the most reactive alkene, maleic anhydride, is omitted (Table II). We suspect[5a,b,57] that the deviation of the latter point is due

Table III. Linear Regression Analysis of Relative Diylophilic Reactivity of Alkenes toward 3,4-Dimethylthiophene **2** Generated from Diazene **16** with Respect to Other Reactants

other reactant	method	slope[d]	*r* value	*y* intercept
2 from **6**	Δ, 298 K, CH_2Cl_2	0.98	0.9984	0.01
2 from **6**	Δ, 298 K, CH_3CN	0.96	0.9993	−0.02
cyclopentadiene[a]	Δ, 298 K, CH_2Cl_2	1.18	0.9945	0.08
cyclopentadiene[a]	Δ, 298 K, CH_3CN	1.11	0.9928	−0.1
cyclopentadiene[a]	*hν*, 247 K, CH_2Cl_2	1.25	0.9913	−0.15
polystyrene radical[b]	Δ, 298 K	2.03	0.8930	0.01
singlet TMM **55**[c]	Δ, 298 K, CH_2Cl_2	1.40	0.9971	−0.21
singlet TMM **55**[c]	Δ, 298 K, CH_3CN	1.32	0.9963	−0.37
singlet TMM **55**[c]	*hν*, 247 K, CH_2Cl_2	1.53	0.9977	−0.28

[a] Solvent dioxane, 283 K, ref 56. [b] Reference 57. [c] Solvent CH_3CN, 333 K, ref 57. [d] Reactivity of **2** and other reactant plotted as ordinate and abscissa, respectively (see, for example, Figure 1).

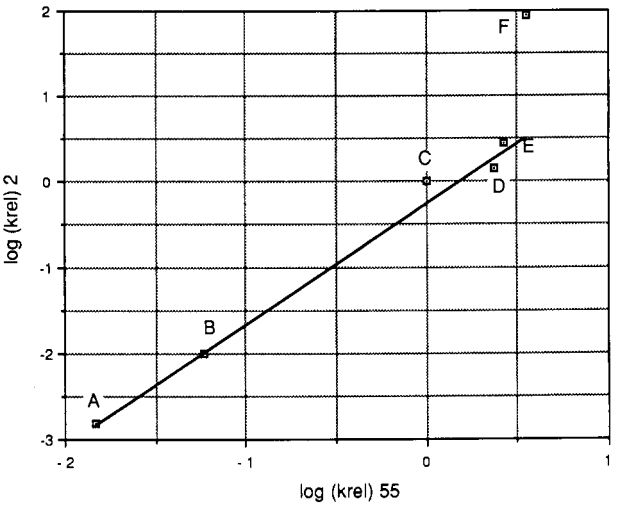


Figure 1. Relationship of relative diylophilic reactivity of alkenes reacting with singlet TMM biradical (**55**) vs that of the same alkenes reacting with 3,4-dimethylenethiophene biradical (**2**) generated thermally from diazene **16** at 298 K: (A) dimethyl maleate, (B) acrylonitrile, (C) dimethyl fumarate, (D) fumaronitrile, (E) maleonitrile, (F) maleic anhydride. The linear regression analysis (see Table III) omitted the defined reference point (C) and the maleic anhydride point (F).

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(53) For reviews, see: (a) Sauer, J.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 779. (b) Sauer, J.; Wiest, H.; Mielert, A. *Chem. Ber.* **1964**, *97*, 3183.

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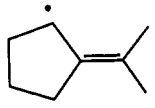
(55) Huyser, E. S. *Free Radical Chain Reactions*; Wiley-Interscience: New York, 1970; p 358.

(56) References 5b, 53, and references cited therein.



55

to the approach of the rate of the **55**–maleic anhydride reaction to the diffusion-controlled limit. This would level out the reactivity of **55** at the upper end of the series by a reactivity-saturation effect, as is apparent in the plot (Figure 1). Experimental support for the idea of very high rates for the reactions of maleic anhydride with singlet biradicals is now available from the absolute rate constants measured[5b] for **1** and **2**. In each of the latter cases, the rates span about 4 orders of magnitude, and the values for the reactions of **1** and **2**, respectively, with maleic anhydride, 1.2×10^9 and 5.7×10^8 M^{-1} s^{-1}, are close to the diffusion-controlled limit.

We have previously commented[5a] on the possibility that in the reaction of electron-rich biradicals like **1** and **2** with a very electron-deficient diylophile like maleic anhydride the cycloaddition mechanism might change over from a conventional four-center process to an electron-transfer-initiated one, in which formation of a radical ion pair is the first step. This might account in an alternative way for the observed sudden jump in relative reactivity at the most reactive end of this series. Our previous reluctance to accept this interpretation was based upon the absence of any appreciable effect of solvent polarity on the *relative* rates. The *absolute* rates now available,[5b] which again show virtually no solvent effect, support our earlier opinion that a changeover in mechanism along the series is unlikely to be lurking in the data.

The kinetic and stereochemical parallelisms between the cycloadditions of singlet biradicals **1** and **2** and the Diels–Alder reactions of conventional dienes, in our view, suggest a close mechanistic relationship of these reactions. Prior experience[41-43,57] with the similar behavior of the singlet state of the TMM biradical **55** had led us to the expectation of such correspondences, but we confess to having been not quite prepared for the insensitivity of the kinetic relationship to the absolute rates of the reactions. According to the so-called "reactivity–selectivity principle", the relative reactivity scale of the olefinic trapping reagents should become compressed as the reaction rate increases. One could hardly imagine a more dramatic violation of this "principle" than the slopes of the regression lines (Table III) of the relative reactivities of cyclopentadiene and biradical **2**, which are near unity even though the absolute rates[5b] of the reactions of **2** exceed those of cyclopentadiene by some 10 orders of magnitude. Thus, the $\Delta G^{\ddagger}$ values for the reactions of the diyls are much smaller than those for the reactions of ordinary dienes, but the *differences* ($\Delta\Delta G^{\ddagger}$) among the members of the two series change very little. Although a detailed interpretation of this parallelism would be premature, we suggest that the persistence of the discriminatory ability of the series of alkenes may be favored by early transition states for *both* their Diels–Alder reactions and their cycloadditions. Frontier orbital interactions (diene or diyl HOMO–alkene LUMO) then would be expected to play a major role in determining the rate,[5b,53] and the variation of these interactions with olefin structure should remain comparable.

Experimental Section

Instruments and Equipment. ^1H NMR spectra were recorded on a JEOL FX 90-Q (90 MHz) or a Bruker WM-250 (250 MHz) spectrometer. ^{13}C NMR spectra were obtained on a Bruker WM-250 (62.5 MHz) spectrometer. Chloroform (δ 7.24), acetone (δ 2.07), methanol (δ 3.30), diethyl ether (δ 3.34), tetrahydrofuran (δ 3.58), or benzene (δ 7.15) were used as internal references for ^1H NMR. Chloroform (δ 77.0) was used as an internal standard for ^{13}C NMR. The spectra are reported as follows: chemical shift, multiplicity, number of protons, coupling constants (when available). Variable-temperature NMR spectra were obtained on the Bruker WM-250 spectrometer using a Bruker-VT 1000 Cu Const. variable-temperature controller. Low-resolution mass spectra were recorded on a Hewlett-Packard 5985 GC/MS spectrometer at 70 or 20 eV EI energies. GC/MS spectra utilized a 3 ft × $^1/_8$ in. 3% OV-101 on Anakrom ABS 110–120-mesh glass column. High-resolution mass spectra were obtained by Daniel Pentek using the Kratos MS80 RFA.

Analytical fused silica capillary GC was performed on either a Varian 3700 or a Hewlett-Packard 5890 gas chromatograph with split/splitless injection and flame-ionization detection. A Perkin-Elmer 900 gas chromatograph equipped with a flame-ionization detector was used for $^1/_8$ in. packed column work. The retention times of molecules of interest are listed in the supplementary material. GC peak areas were measured with Hewlett-Packard 3390A or 3393A electronic integrators. Relative detector-response factors and methods for determining them are described in the supplementary material. Infrared spectra (IR) were recorded on a Nicolet 5-SX FTIR spectrometer. Ultraviolet–visible (UV) spectra were obtained on a Cary 219 spectrophotometer. Melting points were obtained with a Thomas-Hoover capillary melting point apparatus and are uncorrected.

Photolyses were conducted with either a Rayonet photoreactor, RPR-100 equipped with 3500-Å lamps, a 450-W medium-pressure Hanovia lamp, or an Osram 200-W high-pressure Hg arc lamp.

Solvents. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under N_2 before use. Acetonitrile, dichloromethane, pentane, benzene, and dimethyl sulfoxide (DMSO) were distilled from CaH_2 under N_2 before use. Ethanol was dried over sodium and distilled from magnesium before use. 2-Methyltetrahydrofuran (MTHF) was distilled from potassium permanganate under N_2 and stored over $LiAlH_4$, and it was distilled from the $LiAlH_4$ under N_2 before use. Acetonitrile, chloroform, and dichloromethane used in kinetic studies were passed over neutral alumina activity I before use. Anhydrous diethyl ether was used as obtained from either Baker or Mallinckrodt.

General Procedures. Unless otherwise noted, all reactions were performed under a N_2 atmosphere in base-washed glassware that was either flame or oven dried. Quantitative GC studies were carried out on samples which had been degassed (three freeze–pump–thaw cycles) and sealed, unless otherwise noted. Pyrex tubes (6 mm) used for kinetic analyses were oven dried but otherwise untreated.

1,2,3,4-Tetrahydro-*N*,*N*′-dicarbomethoxyfurano[3,4-*d*]pyridazine (13, Scheme I). 3,4-Bis(chloromethyl)furan (**12**)[58] was prepared by addition of a solution of 2.1 mL (20 mmol) of 3,4-bis(hydroxymethyl)furan (Aldrich) in 3.4 mL of $CHCl_3$ via a syringe pump to a cold solution of $SOCl_2$ (4.5 mL, 62 mmol, distilled from $(PhO)_3P$[59]), pyridine (4.2 mL, 52 mmol), and $CHCl_3$ (6.5 mL). When the addition was completed (~2 h), the red solution was stirred for an additional 10 min, poured onto ice, and extracted twice with CH_2Cl_2. The combined organic layers were washed with 5% HCl, 5% NaOH, and brine and then were dried over K_2CO_3. Concentration in vacuo gave a red-orange oil, which upon gradient elution (5% CH_2Cl_2/pentane → 100% CH_2Cl_2) afforded 2.1 g (64%) of dichloride **12** and 0.14 g (4%) of the cyclic sulfite.

Compound **12**: white flakes, mp 27–28 °C; R_f 0.36 (20% CH_2Cl_2/pentane); ^1H NMR (90 MHz) δ 7.45 (s, 2 H), 4.58 (s, 4 H); MS *m/e* 164, 166, 168 (M, 9.1:5.7:1), 129, 131 (M − Cl), 94 (M − 2Cl), 65, 39.

Cyclic sulfite: white flakes, mp 64–65 °C; ^1H NMR (90 MHz) δ 7.37 (br s, 2 H), 5.76 (dd, J = 13.6, 1.0 Hz, 2 H), 4.56 (app d, 2 H, J = 13.8); MS *m/e* 174 (M, 26), 110 (M − SO_2, 26), 109 (M − SO_2H, 100), 81 (20), 53 (31).

The diol could be regenerated from the sulfite by treatment with 50% NaOH in MeOH at 25 °C for 30 min.

Sodium hydride (Alfa, 60% dispersion in oil, 519 mg, 13.0 mmol) was washed with pentane three times and then heated and stirred at 65 °C with dry dimethyl sulfoxide (12 mL) for 12 h. To this hot solution was added dimethyl hydrazodicarboxylate (1.01 g, 6.80 mmol) in DMSO (6 mL). The reaction mixture was stirred at 65 °C for an additional 30 min and then treated with dichloride **12** (1.02 g, 6.18 mmol) added in solid form and followed by a rinse of DMSO (2 mL). After 1 h, the mixture was cooled to room temperature and poured into water (50 mL), and the product was extracted with CH_2Cl_2 (4 × 20 mL). The combined organic layers were washed with water (3 × 20 mL) and brine and dried over $MgSO_4$. Chromatography of the residue (SiO_2, 60 g, 20-mm diameter column, 50% ether/pentane → 100% ether) gave 1.04 g (70%) of the bis-carbamate **13** as a colorless, viscous oil, which crystallized in the freezer or from ether/pentane.

13: R_f 0.20 (50% ether/pentane), mp initially 80–84 °C, after standing 5 months mp 109–111 °C (phase change of crystals?); ^1H

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NMR (90 MHz) δ 7.26 (br s, 2 H), 5.11 (app d, 2 H, J = 15 Hz), 4.24 (app d, J = 15 Hz), 3.77 (s, 6 H). At 250 MHz, the CH_2 signals are less well-defined. In C_6D_6 at 250 MHz, poorly resolved signals of two conformers (A:B ~2:1) can be seen. Conformer A: δ 6.61 (br s), 5.2–5.0 and 4.0–3.8 (AA'BB' pattern), 3.40 (br s). Conformer B: δ 6.61 (br s), 4.8–4.6 and 4.3–4.1 (AA'BB' pattern), 3.32 (br s). ^{13}C NMR (62.5 MHz) δ 155.8 (s), 136.6 (d), 116.5 (s), 53.5 (q), 40.8 (br m); MS m/e 240 (M, 7), 225 (M – CH_3, 2), 208 (M – CH_3OH, 4), 181 (M – CO_2-CH_3, 24), 180 (M – CH_3OH, CO, 15), 165 (M – CH_3O, CO_2, 95), 149 (M – CH_3OH, CO_2CH_3, 74), 121 (14), 106 (63), 94 (M – $(NCO_2CH_3)_2$, 100), 66 (23), 65 (21), 59 (28); IR (film, NaCl) 3500 (br, C=O overtone?), 3030, 2980, 2880, 1740 (br), 1550, 1450, 1370 (br), 1320, 1250 (br), 1170, 1110, 1030, 890, 760 cm^{-1}; HRMS calcd for $C_{10}H_{12}N_2O_5$ 240.0746, found 240.0754.

1,2,3,4-Tetrahydrofurano[3,4-*d*]pyridazine (14, Scheme I). All operations on the hydrazine **14** and the diazene **15** were performed in inert atmospheres. A suspension of the bis-carbamate **13** (112.5 mg, 0.468 mmol) in N_2-purged 1 M KOH (4.7 mL, 4.7 mmol) was stirred at 95 °C for 2 h, during which time the solution became homogeneous. After cooling of the mixture to room temperature, the hydrazine was obtained by direct extraction of the reaction mixture with CH_2Cl_2 (4 × 5 mL), drying over $MgSO_4$, filtering under N_2, and concentration in vacuo as 51.4 mg (88%) of a colorless, viscous oil.

14: R_f 0.18 (10% $MeOH/CH_2Cl_2$); t_R = 16.4 min [100 °C (5 min), 10 °C/min to 280 °C]; ^1H NMR (250 MHz) δ 7.20 (t, 2 H, J = 0.7), 3.97 (d, 4 H, J = 0.7), 3.50–2.50 (br s, 2 H, NH); in toluene-d_8 δ 6.81, 3.49, 2.40; in benzene-d_6 δ 6.82, 3.48, 2.5–2.0; in CD_3OD δ 7.27, 3.90; ^{13}C NMR (toluene-d_8 reference at 20.4 ppm) δ 136.1 (d), 120.0 (s), 43.7 (t).

1,4-Dihydrofurano[3,4-*d*]pyridazine (15, Scheme I). The general procedure for this preparation consisted of the treatment of a solution of the hydrazine **14** (0.5–0.005 M in $CDCl_3$, CH_2Cl_2, CH_3CN, Et_2O, THF, 2-MTHF, MeOH, EtOH, benzene, or toluene) at ~−10 °C with a solution of dimethyl (Aldrich) or diethyl[60] azodicarboxylate at a known concentration in the same solvent added by syringe until a yellow-orange color persisted. The titration became slower near the endpoint, so the solution was stirred rapidly for at least 2 min to ensure complete reaction. The reaction mixture was then back-titrated with more of the hydrazine solution until it was colorless. The amount of diazene present was estimated on the assumption of quantitative oxidation. Solutions prepared in aprotic solvents are stable at −25 °C for up to 2 weeks.

15: ^1H NMR (250 MHz) δ 7.31 (s, 2 H), 5.08 (s, 4 H); benzene-d_6 δ 6.68, 4.45; toluene-d_8 δ 6.66, 4.41; CD_3OD δ 7.41, 5.10; ^{13}C NMR (62.5 MHz, toluene-d_8) δ 135.3 (d), 112.5 (s), 56.0 (t); UV ($CHCl_3$) λ_{max} = 363 nm ($\epsilon \sim 220 \pm 40$ M^{-1} cm^{-1}).

The following ^1H NMR signals (250 MHz, δ) are characteristic of reagents or other products in these reactions: Dimethyl azodicarboxylate, 4.08 (s); dimethyl hydrazodicarboxylate, ~6.7 (br, NH, 2 H), 3.77 (s, 6 H); diethyl azodicarboxylate, 4.50 (q, J = 7 Hz, 4 H), 1.42 (t, J = 7 Hz, 6 H); diethyl hydrazodicarboxylate, ~6.8 (br, NH, 2 H), 4.21 (q, J = 7 Hz, 4 H), 1.28 (t, J = 7 Hz, 6 H).

1,2-Dihydrofurano[3,4-*d*]pyridazine (Hydrazone 17). To a solution of hydrazine **14** (5.1 mg, 0.041 mmol) in THF which contained ~5 mg of Na_2SO_4 was added, at ~−8 °C, 7.1 mg (0.082 mmol) of MnO_2. After 1 h, the cold reaction mixture was filtered through Celite on a medium glass frit. The solids were washed with CH_2Cl_2, and the filtrate was concentrated in vacuo to give 5.0 mg (100%) of a colorless oil, which crystallized upon being cooled to −15 °C. The white material soon became yellow upon exposure to air at room temperature, and an attempt to prepare a mp sample in a capillary tube resulted in a yellow gum.

17: R_f 0.53 (10% $MeOH/CH_2Cl_2$); t_R = 16.4 min [100 °C (5 min), 10 °C/min to 280 °C]; ^1H NMR (250 MHz) δ 7.51 (br s, 1 H), 7.42 (br s, 1 H), 7.19 (br s, 1 H), ~5.8 (br, NH), 4.22 (br s, 2 H); benzene-d_6 δ 7.34 (br s, 1 H), 6.75 (br s, 1 H), 6.58 (br s, 1 H), ~5.2 (br, NH), 3.51 (br s, 2 H).

UV (EtOH) λ_{max} = 222 nm ($\epsilon \approx 5000$ M^{-1} cm^{-1}), 270 nm ($\epsilon \approx 6000$ M^{-1} cm^{-1}); (CH_3CN) λ_{max} = 225, 273 nm; at 320 and 350 nm, $\epsilon \approx 500$ and 50 M^{-1} cm^{-1}, respectively. Unidentified impurities in the hydrazone solutions show ^1H NMR resonances at δ 9.26 (s) and 8.28 (s) in the ratio of 1:1. The hydrazone solutions in $CDCl_3$ turn brown and deposit a brown solid within a few days. Photolysis (unfiltered high-pressure Hg arc or Rayonet 350-nm lamp) of the $CDCl_3$/hydrazone solutions at 77 K or at 0 °C for 2 h causes yellowing which persists upon warming the sample to room temperature, but no new identifiable signals appear in the NMR spectrum.

Oxidation of the Hydrazine 14 by Oxygen. Formation of the Peroxide 18 (Scheme II). An approximately 0.05 M solution of the hydrazine **14** and toluene internal standard in $CDCl_3$ was stirred under an atmosphere of O_2 (balloon) at room temperature for 3 h. Analysis by ^1H NMR spectroscopy showed the presence of 19% of recovered hydrazine **14**, 12% of hydrazone **17**, and 61% of peroxide **18** (75% yield based upon hydrazine reacted). The peroxide, a volatile white solid, can be isolated by chromatography in 5% ether/pentane: mp 54–56 °C; R_f 0.27 (5% ether/pentane); t_R = 12.9 min (peroxide **18**) and 13.9 min (hydroxy aldehyde **19**) [100 °C (5 min), 10 °C/min to 280 °C]; ^1H NMR (250 MHz) δ 7.27 (s, 2 H), 5.17 (d, J = 0.7, 4 H); MS m/e 126 (M, 53), 109 (M – O, 12), 108 (M – OH, 100), 94 (M – O_2, 22), 80 (M – CO_2H, 24), 69 (11), 52 (18), 51 (13); UV (ether) λ_{max} = 214 nm; HRMS calcd for $C_6H_6O_3$ 126.0317, found 126.0316.

4-(Hydroxymethyl)furan-3-carboxaldehyde (19). Preparative GC (0.25 in. × 3 ft 5% OV-101 column, 160 °C, injector and detector at 180 °C) of peroxide **18** afforded one peak, collected as a colorless oil. By ^1H NMR, this material contained 90% hydroxy aldehyde **19** and 10% peroxide: R_f 0.05 (30% ether/pentane); ^1H NMR (250 MHz) δ 9.95 (d, 1 H, J = 0.6 Hz), 8.12 (d, 1 H, J = 1.5 Hz), 7.45 (br s, 1 H), 4.62 (s, 2 H), ~2.0 (br s, OH, 2 H); MS m/e 126 (M, 35), 125 (M – H, 7), 109 (M – OH, 8), 108 (M – H_2O, 100), 94 (0), 80 (M – HCO_2H, 23), 69 (9), 52 (17), 51 (11); IR (film, NaCl) 3450 (br), 1780, 1540, 1140, 1040, 1010, 880 cm^{-1}; HRMS calcd for $C_6H_6O_3$ 126.0317, found 126.0317.

Thermal Decomposition of Diazene 15. Formation of Dimers and "Trimers". When a solution of diazene **15** is allowed to warm above 0 °C, two main dimers can be isolated by chromatography in ether/pentane.

Symmetrical dimer 20: R_f 0.32 (5% ether/pentane); t_R = 15.4 min [160 °C (5 min), 10 °C/min to 260 °C]; mp 164–165 °C; ^1H NMR (250 MHz) δ 7.16 (s, 4 H), 2.69 (s, 8 H); MS m/e 188 (M, 100), 173 (M – CH_3, 10), 159 (12), 145 (12), 131 (21), 119 (11), 117 (12), 115 (12), 91 (15); HRMS calcd for $C_{12}H_{12}O_2$ 188.0838, found 188.0823.

Unsymmetrical dimer 21: R_f 0.32 (5% ether/pentane), t_R = 14.6 min [160 °C (5 min), 10 °C/min to 260 °C]; ^1H NMR (250 MHz) δ 7.14 (t, 1 H, J = 1.5 Hz), 7.09 (br s, 1 H), 6.08 (br s, 1 H), 4.98 (dd, 1 H, J = 5.0, 1.2 Hz), 4.90 (t, 1 H, J = 1.3 Hz), 4.85 (dd, 1 H, J = 1.3, 0.7 Hz), 3.11 (dd, 14.4, 5.0 Hz, 1 H), 2.75–2.55 (m, 3 H), 2.18 (dt, 14.5, 1.3 Hz, 1 H), 1.98 (dt, 1 H, J = 12.5, 7.3 Hz); MS m/e 188 (M, 76), 173 (M – CH_3, 11), 159 (15), 145 (16), 141 (13), 132 (13), 131 (36), 129 (15), 119 (28), 117 (24), 116 (18), 115 (21), 108 (31), 105 (15), 91 (48), 86 (65), 84 (100), 77 (15), 40 (22).

HRMS calcd for $C_{12}H_{12}O_2$ 188.0838, found 188.0838.

"Trimers" also are formed in this decomposition. Four of these substances are found in small, roughly equal amounts (~2–3% each). They can be identified by GC with t_R of 27.1, 28.2, 29.7, and 30.1 min [160 °C (5 min), 10 °C/min to 260 °C]; MS m/e 282 (M, 100), 264 (29), 187 (53), 186 (26), 159 (20), 133 (32), 131 (23), 115 (29), 95 (27), 92 (41), 77 (41), 65 (28).

In addition, a compound of uncertain structure, R_f 0.24 (10% ether/pentane), t_R = 14.4 min [160 °C (5 min), 10 °C/min to 260 °C] is formed. By mass spectroscopy, its composition seems to be that of dimer plus 32 mass units: ^1H NMR (250 MHz) δ 7.10 (d, 2 H, J = 1.3 Hz), 5.36 (d, 2 H, J = 1.7 Hz), 5.00 (br s, 2 H), 4.85 (d, 2 H, J = 1.0 Hz), 3.08 (ddd, 2 H, J = 15.5, 3.2, 1.3 Hz), 2.80 (dd, 2 H, J = 15.5, 2.9 Hz); MS m/e 220 (22), 206 (16), 205 (M – CH_3, 100), 188 (83), 159 (22), 142 (32), 131 (42), 129 (28), 128 (24), 119 (35), 117 (30), 116 (26), 115 (42), 105 (22), 77 (40), 65 (22).

Cyclobuta[1,2-*c*]furan (29) by Flash Vacuum Pyrolysis of Diazene 15. In 100-μL portions, a solution of **15** (~0.034 M) in $CDCl_3$ was injected into a quartz tube heated at 270 °C in a Hoskins electric furnace (Model FD 303A) and connected to a vacuum line kept at 3 × 10^{-3} Torr. The pyrolysate was collected in a trap cooled with liquid N_2. The volatile cyclobutafuran and $CDCl_3$ were transferred under vacuum into an NMR tube. NMR and GC analysis showed the material to be quite pure.

29: t_R = 16.9 min [50 °C (10 min), 10 °C/min to 280 °C]; ^1H NMR (250 MHz) δ 6.99 (s, 2 H), 3.16 (s, 4 H); in benzene-d_6 δ 6.83 (s, 2 H), 2.74 (s, 4 H).

The addition of 0.9 μL (>10 equiv) of acrylonitrile to the NMR solution followed by 5 days of standing at room temperature resulted in no reaction.

2,5-Dibromo-3,4-bis(bromomethyl)thiophene (22, Scheme III). The method of Zwanenburg and Wynberg[34] was employed with a few minor modifications. 3,4-Dimethylthiophene-2,5-dicarboxylic acid monomethyl ester was not purified by crystallization from aqueous acetic acid (1:4 by volume). Instead, it was either sublimed at 175 °C (0.1 Torr) or crystallized from aqueous methanol (1:5 by volume). Also, in our hands, neutralization of a solution containing saponified monomethyl ester led to the precipitation of 3,4-dimethylthiophene-2,5-dicarboxylic acid. The highest yields of 2,5-dibromo-3,4-dimethylthiophene were obtained when the solution was kept basic during the addition of bromine. Generally, crude 2,5-dibromo-3,4-dimethylthiophene was carried on to 2,5-di-

(60) Kauer, J. C. *Organic Syntheses*; Wiley: New York, 1963; Collect. Vol. IV, **1966**, 3016.

bromo-3,4-bis(bromomethyl)thiophene (**22**). Tetrabromide **22** was purified by flash chromatography, using pentane as eluent (R_f 0.35).

1,2,3,4-Tetrahydro-*N*,*N*'-dicarbomethoxy-6,8-dibromothieno[3,4-*d*]pyridazine (23, Scheme III). Sodium hydride (938 mg of a 61.14% oil dispersion, 23.9 mmol) was placed in a 100-mL round-bottom flask. The NaH was washed three times with 10 mL of dry pentane and then dried in vacuo. Thirty milliliters of dimethyl sulfoxide (DMSO) was added to the dry, gray powder. The heterogeneous mixture was heated to 65 °C, while being stirred vigorously. One-half hour after hydrogen evolution ceased, dimethyl hydrazodicarboxylate (DMHD) (1.77 g, 11.95 mmol) was added in 25 mL of DMSO. Generally, the solution became quite gelatinous upon addition of DMHD. After 30 additional minutes, a solution of 2,5-dibromo-3,4-bis(bromomethyl)thiophene (4.65 g, 10.86 mmol) in 20 mL of DMSO was added. The solution immediately turned brown. After stirring for 40 min at 65 °C, the solution was cooled to room temperature and quenched with 50 mL of water. The water layer was extracted three times with 75 mL of dichloromethane, and the combined organic layers were dried over $MgSO_4$. After removal of the solvent in vacuo, the residue was chromatographed on silica gel (gradient elution: 10–20% ethyl acetate/pentane). A white, granular solid (R_f 0.14, 20% ethyl acetate/pentane) was obtained in 45% yield: mp 164–166 °C; ^{1}H NMR (90 MHz, $CDCl_3$) δ 4.95 (d, 1 H, J = 16.3 Hz), 4.04 (d, 1 H, J = 16.3 Hz), 3.76 (s, 3 H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 156.2, 133.9, 107.1, 54.5, 45.5 (br); FTIR ($CDCl_3$) 2957 (w), 1725 (vs), 1450 (s), 1396 (s), 1368 (s), 1216 (s) cm^{-1}; GC/MS ($T_{initial}$ = 80 °C, rate = 20 °C/min, T_{max} = 200 °C, t_R = 8.6 min) m/e 416 (M^+ + 2, 4.5), 414 (M^+, 8), 339 (M^+ – 75, 100), 268 (M^+ – 146, 31); HRMS calcd for $C_{10}H_{10}Br_2N_2O_4S$ 413.8708, found 413.8690.

1,2,3,4-Tetrahydro-*N*,*N*'-dicarbomethoxythieno[3,4-*d*]pyridazine. Hydrogen was bubbled slowly through a gently refluxing solution of **23** (3.1 g, 7.5 mmol) in 100 mL of ethyl acetate in which was suspended 1 g of 10% palladium on charcoal. The hydrogenolysis, which took approximately 14 h to complete, was effected by stirring in a 250-mL three-necked round-bottom flask, equipped with a condenser and oil bubbler. Potassium carbonate (2.92 g, 21.1 mmol) was present in order to neutralize the HBr formed. After completion of the reaction, the hot solution was purged with N_2 and filtered through Celite. The pad of Celite was washed three times with 25 mL of diethyl ether. The solutions were combined and washed three times with 20 mL of water, dried over $MgSO_4$, and concentrated in vacuo. Crystallization from ether yielded 1.68 g (87.6%) of a white solid (R_f 0.06, 20% ethyl acetate/pentane): mp 134–137 °C; ^{1}H NMR (90 MHz, $CDCl_3$) δ 6.91 (s, 1 H), 5.08 (br d, 1 H, J = 15.6 Hz), 4.23 (br d, 1 H, J = 15.6 Hz), 3.66 (s, 3 H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 156, 133, 120, 54.3, 46 (br); FTIR ($CDCl_3$) 2965 (w), 1720 (vs), 1452 (s), 1384 (s), 1220 (s) cm^{-1}; GC/MS ($T_{initial}$ = 80 °C, rate = 20 °C/min, T_{max} = 200 °C; t_R = 5.6 min) m/e 257 (M^+ + 1, 1.5), 256 (M^+, 11.9), 181 (M^+ – 75, 100), 165 (M^+ – 91, 43), 122 (M^+ – 134, 48), 110 (M^+ – 146, 76); HRMS calcd for $C_{10}H_{12}N_2O_4S$ 256.0519, found 256.0540.

1,2,3,4-Tetrahydrothieno[3,4-*d*]pyridazine (24, Scheme III). Hydrazine (**24**) preparations ranged from slightly less than 0.1 to 1.0 mmol. Care was taken to maintain a nitrogen atmosphere above the hydrazine material throughout its preparation and subsequent handling. A typical preparation was carried out in the following way.

The above debrominated bis-carbamate (35 mg, 0.14 mmol) was placed in a 15-mL round-bottom flask containing 7 mL of water and potassium hydroxide (1.1 g, 19.6 mmol). Nitrogen was bubbled through the solution at room temperature for ~10 min. The heterogeneous mixture was then heated to between 90 °C and 95 °C for 3.5 h, while a positive N_2 pressure was maintained above it. After cooling to room temperature, the solution was extracted four times with 20 mL of methylene chloride. The combined extracts were dried over $MgSO_4$, and the solvent was removed in vacuo. When breaking the vacuum on the rotovap, the chamber was filled with N_2. The white residue of **24** (18.6 mg, 95%) usually contained about 5% of hydrazone, as measured by ^{1}H NMR: ^{1}H NMR (250 MHz, MeOH-d_4) δ 7.05 (s, 1 H), 4.02 (s, 2 H); ^{1}H NMR (90 MHz, $CDCl_3$) δ 6.94 (s, 1 H), 4.13 (s, 2 H), 2.63 (br s, 1 H, concentration dependent); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 135.7, 118.9, 49.0; FTIR ($CDCl_3$) 3670, 3154, 1465, 1380 cm^{-1}; UV (CH_2Cl_2) λ_{max} = 241 nm, ϵ = 4.5 × 10^3 M^{-1} cm^{-1}; DIP/MS ($T_{initial}$ = 30 °C, $t_{initial}$ = 1 min, rate = 30 °C/min, T_{max} = 300 °C) m/e 141 (M^+ + 1, 11), 140 (M^+, 100), 110 (M^+ – 30, 84); HRMS calcd for $C_6H_8N_2S$ 140.0409, found 140.0418.

1,4-Dihydrothieno[3,4-*d*]-1,4-dihydropyridazine (16, Scheme III). Although the diazene **16** was at least sparingly soluble in solvents as nonpolar as pentane, hydrazine **24** was not. Therefore, oxidations were routinely carried out in chloroform, methylene chloride, 2-methyltetrahydrofuran, ethanol, methanol, or acetonitrile. Diethyl ether was used, but it was less satisfactory due to the low solubility of the hydrazine in this solvent. Experiments utilizing pentane or diethyl ether were performed by pumping off the solvent (usually methylene chloride) from a previously prepared diazene sample and taking the residue up in the appropriate solvent. Pentane and diethyl ether also served to separate the azo compound from most of the hydrazone (**26**) and dimethyl hydrazodicarboxylate byproducts.

Solutions of diazene **16** were routinely prepared by titrating a hydrazine solution in an acetone/ice bath with a solution of dimethyl azodicarboxylate (DMAD) in the same solvent under an inert atmosphere. The preparation was carried out much as one would a typical titration. The yellow-orange color of DMAD was used as an indicator. Diazene solutions were back-titrated until the yellow color disappeared. ^{1}H NMR experiments at −20 °C indicated that the oxidation was essentially quantitative. The only side product was the tautomeric hydrazone (**26**), which could often be fully accounted for in the hydrazine precursor.

16: ^{1}H NMR (250 MHz, $CDCl_3$, 253 K) δ 7.1 (s, 1 H), 5.13 (s, 2 H); ^{1}H NMR (250 MHz, MeOH-d_4, 243 K) δ 7.24 (s, 1 H), 5.16 (s, 2 H); ^{13}C NMR (62.5 MHz, $CDCl_3$, 253 K) δ 119.1, 128.3, 62.2; UV ($CDCl_3$/2-methyltetrahydrofuran (1:2.6), 213 K) λ_{max} = 368 nm, ϵ = 236 M^{-1} cm^{-1}.

1,2-Dihydrothieno[3,4-*d*]pyridazine (Hydrazone 26). Method A. Manganese dioxide (6 mg, 6.9 × 10^{-2} mmol) was added to 1 mL of a tetrahydrofuran solution containing hydrazine **24** (3.8 mg, 2.7 × 10^{-2} mmol) and 15 mg of anhydrous sodium sulfate. The mixture was stirred in an acetone/ice bath (~−10 °C) for 1 h. The cold solution was filtered through a pad of Celite, which was then copiously washed with dichloromethane. The washings were concentrated in vacuo, leaving behind a white solid (3.5 mg, 92%), which rapidly discolored upon standing in air: ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.29 (s, 1 H), 7.15 (s, 1 H), 6.88 (s, 1 H), 4.3 (s, 2 H), NH (bd s, concentration dependent); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 132.9, 123.2, 122.3, 121.1, 119.0, 53.3; FTIR ($CDCl_3$) 2975, 1454, 1262 cm^{-1}; UV (CH_2Cl_2) λ_{max} = 298 nm, ϵ = 4.5 × 10^3 M^{-1} cm^{-1}, λ_{max} <225 nm, ϵ = 368 M^{-1} cm^{-1}; HRMS calcd for $C_6H_6N_2S$ 138.0261, found 138.0256.

Method B. To a 0.11 M solution of diazene **16** in MeOH-d_4 at 0 °C, was added 2 mL of trifluoroacetic acid. After 2 h, ^{1}H NMR revealed quantitative conversion to the hydrazone: ^{1}H NMR (250 MHz, MeOH-d_4) δ 7.65 (br s, 1 H), 7.31 (s, 1 H), 7.20 (br s, 1 H), 4.36 (s, 2 H).

Dimerization of 3,4-Dimethylenethiophene (2). A deaerated (2 mL) methylene chloride solution of diazene **16** (13.6 mg, 0.1 mmol, based upon DMAD titration) was allowed to stir under N_2 at room temperature for 4 h. Low-resolution GC/MS analysis of the crude solution indicated the presence of two products with molecular ions corresponding to dimers of 3,4-dimethylenethiophene. Partial separation of the two dimers (R_f 0.1, pentane) was achieved via flash chromatography (gradient elution: 0–5% ether/pentane). The less polar dimer stains red with *p*-anisaldehyde. The other dimer stains dark blue with *p*-anisaldehyde. Further purification was accomplished by preparative gas chromatography (5% OV-101 on Chromosorb W, 2.5 ft × 0.25 in., T_{column} = 115 °C). The more volatile of the two dimers, a clear liquid, is assigned the anti-Bredt dimer structure **31** (Scheme VI). The other crystalline dimer is the previously reported[15] symmetrical one **30**. The dimers were isolated in a collective 40.5% yield (2.6 and 2.9 mg, dimers **31** and **30**, respectively). Capillary gas chromatography (50 m methyl silicone) indicated that each fraction was greater than 98.5% pure.

4,5,9,10-Tetrahydrocycloocta[1,2-*c*:5,6-*c*']dithiophene (30): ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.82 (s, 1 H), 2.94 (s, 2 H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 30.8, 122.2, 143.4; UV (CH_2Cl_2) λ_{max} = 236 nm, ϵ = 1.18 × 10^4 M^{-1} cm^{-1}.

10-Methylene-9-thiabicyclo[5.2.1]dec-7-eno[3,4-*c*]thiophene (31): ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.89 (d, 1 H, J = 3.3 Hz), 6.77 (d, 1 H, J = 3.3 Hz), 5.48 (br s, 1 H), 5.14 (br s, 1 H), 5.00 (br s, 1 H), 3.97 (br s, 1 H), 3.07 (dd, 1 H, J = 13, 4.7 Hz), 2.61–2.83 (m, 4 H), 2.05–2.15 (m, 1 H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 29.5, 33.7, 41.6, 58.5, 104.5, 112.0, 122.6, 126.5, 127.7, 139.1, 142.9, 156.6; FTIR ($CDCl_3$) 3154, 2954, 2930, 1635, 1558 cm^{-1}; UV ($CDCl_3$) λ_{max} = 303 nm, ϵ = 2.13 × 10^3 M^{-1} cm^{-1}, λ_{max} = 232 nm, ϵ = 5.8 × 10^3 M^{-1} cm^{-1}; GC/MS ($T_{initial}$ = 80 °C, rate = 20 °C/min, T_{max} = 200 °C, t_R = 5.20 min) m/e 221 (M^+ + 1, 6), 220 (M^+, 100), 205 (M^+ – 15, 45), 187 (M^+ – 33, 31), 110 (M^+ – 110, 35); HRMS calcd for $C_{12}H_{12}S_2$ 220.0382, found 220.0382.

Reactions of the Biradical Intermediates 1 and 2 with Various Trapping Agents. Examples of the procedures are given below in the description of the competition experiments. The details of the preparative reactions and the properties of the adducts obtained are given in the supplementary material.

Kinetics of Decomposition of Diazenes 15 and 16. Method A. Measured via UV Absorption Spectroscopy. Solutions of **15** or **16** (7 mM) in $CDCl_3$ were deaerated by bubbling N_2 through at 0 °C. The samples were then transferred to a reduced-volume quartz UV cuvette (1-cm path length) and capped. The decay of the azo absorption was followed over

a minimum of 2 half-lives at 298 K. Decomposition was measured both by scanning from 500 to 330 nm and by continually monitoring the absorption at 368 nm. The decomposition was measured in the absence and presence of dimethyl maleate.

Method B. Measured via NMR Spectroscopy. A 1-mL stock solution of **15** or **16** (0.15 M) in $CDCl_3$ (passed over neutral alumina, activity I) was used to prepare three samples. One sample contained no added trap. The other two samples contained 1 and 4 theoretical equiv (based upon the assumed concentration of diazene from the DMAD titration) of fumaronitrile (0.6 M stock solution). The composition of each sample tube is listed below. Each tube was subjected to three freeze–pump–thaw degassing cycles before being sealed. During the thawing process, the tubes were immersed in an acetone/ice bath, so as to prevent any adventitious azo decomposition outside of the NMR probe. The tubes were stored in liquid nitrogen while awaiting their analysis in the precooled (285 K) 250-MHz ^1H NMR probe. Immediately prior to placement in the probe, the tubes were thawed at −60 °C so as to eliminate the possibility of the breakage within the probe. The spectrometer was programmed to collect eight scans per spectrum (total acquisition time <22 s) every 4.5 min (270 s). A total of 28–30 spectra were collected for each sample. The rate constants are presented in the text (Table I).

4-Thiahepta-1,2,5,6-tetraene (6). The following procedure differs in detail from those[14,15] previously reported. A sample of 100 μL (0.909 mmol) of dipropargyl sulfide (4-thiahepta-1,6-diyne, **53**)[61] was dissolved in 0.4 mL of CD_3CN (previously filtered through a 1-g plug of neutral stage I alumina and deaerated with a stream of N_2 immediately before use) in a 5-mm NMR tube and cooled to −35 °C. A small amount (2–5 mg) of solid potassium *tert*-butoxide was added to the solution under a stream of N_2. The tube was shaken once and then allowed to stand at −35 to −30 °C for 2–3 days. The product composition was monitored periodically by ^{1}NMR at <−20 °C. The amount of the desired diallene **6** reached a maximum of about 70–75% of the C_6H_6S mixture after ∼60 h. The major byproducts were the dienynes 4-thiahepta-1,2-dien-6-yne (**54**) and 4-thiahepta-1,2-dien-5-yne (**55**), which accounted for 20–25% of the C_6H_6S material. The yield of **6**, determined by ^1H NMR integration of the product resonances and comparison to that of CHD_2CN, was 75%.

The reaction was stopped by addition of 5 μL of H_2O, and the solvent was removed under vacuum (0.1 Torr) at −30 °C. The remaining yellow oil was dissolved in 5 mL of deaerated pentane at −30 °C and then filtered cold under N_2 through a plug of neutral alumina. The pentane was then bulb-to-bulb distilled away at −30 °C and 0.1 Torr, leaving a clear oil, which ^1H NMR spectroscopy (<−20 °C) showed to consist of 70–75% of diallenyl sulfide **6**, 20–25% of the above two dienynes, and 5% of two diynes (4-thiahepta-1,6-diyne (**53**) and 4-thiahepta-2,5-diyne (**56**)). With this method, stock solutions of **6** in $CDCl_3$, CD_2Cl_2, or CD_3CN were prepared. Such solutions were stable for months at −78 °C. Absolute concentrations of **6** were measured by ^1H NMR integration vs an added standard (benzene, toluene, or 2-methoxynaphthalene): ^1H NMR (250 MHz, CD_3CN, −20 °C) δ 5.88 (t, 1 H, J = 6.5 Hz), 5.06 (d, 2 H, J = 6.5 Hz); for **54**, δ 5.91 (t, 1 H, J = 6.6 Hz), 5.06 (d, 2 H, J = 6.6 Hz), 3.35 (d, 2 H), 2.46 (t, 1 H); for **55**, δ 5.79 (t, 1 H, J = 6.3 Hz), 5.13 (d, 2 H, J = 6.3 Hz), 1.96 (s, 3 H); for **56**, δ 1.98 (s, 1 H); ^{13}C NMR (62.5 MHz, $CDCl_3$, −20 °C) for **6**, δ 206.3 (s), 85.3 (d), 80.8 (t).

Thermal decomposition of **6** was complete after 10 h at 25 °C in CH_2Cl_2 solution. The symmetrical and unsymmetrical dimers **30** and **31** (Scheme VI) were formed in 37% and 26% yield, respectively (capillary GC analysis). In a separate run, the decomposition was interrupted by addition of acrylonitrile after 45 min. The ratio of the two dimers was essentially unchanged, but the yields were only 16% and 12%.

Reaction of 6 with Maleic Anhydride. To 0.7 mL of a 0.14 M stock solution of the diallene **6** in CD_2Cl_2 at −30 °C was added 1.5 μL of toluene and 130.4 mg (0.133 mmol) of maleic anhydride (freshly recrystallized three times from ether under N_2) in 0.35 mL of $CDCl_3$ (deaerated and filtered through a 1-g plug of neutral stage I alumina just prior to use) to give a solution 0.0932 M in **6**, 0.126 M in maleic anhydride, and 0.0134 M in toluene. This solution was then placed in the probe of a 250-MHz ^1H NMR spectrometer held at 26 °C. The decay of the diallene **6** was monitored over a period of 3 h by the acquisition of spectra at 20-min intervals. The concentrations of **6** were determined from the integrated intensity of the methine protons relative to that of the methyl group in toluene. Compound **6** diminished in concentration by first-order kinetics with a half-life of 54.8 min, $k = 2.1 \times 10^{-4}$ s^{-1}. Signals of the maleic anhydride adduct grew in simultaneously. After a sufficient time, the yield of adduct estimated by integration was essentially quantitative. The other C_6H_6S isomers remained unchanged over the 3-h course of the reaction. The rate of decomposition of **6** under the same conditions (except for the absence of maleic anhydride) was the same, $k = 2.1 \times 10^{-4}$ s^{-1}.

After 5 h at room temperature, the solvent was removed in vacuo, and pure fused adduct was obtained by crystallization at −78 °C from ether. This substance has been reported in earlier work by Garratt:[15] ^1H NMR (250 MHz, $CDCl_3$) δ 7.60 (s, 1 H), 3.52–3.62 (m, 2 H), 3.25–3.35 (dd, 1 H), 2.80–2.95 (m, 1 H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 173.5, 133.8, 121.4, 40.6, 25.7; MS m/e 208.1 (M^+, 22.9), 180.1 (M^+ − 28, 11.9), 135.1 (M^+ − 73, 100).

Competitive Trapping Experiments with Biradical 2 Generated from Diallene 6. A representative procedure was carried out as follows. To a deaerated Pyrex 5-mm tube equipped with a septum and cooled to −30 °C were added 20 μL of **6**/CD_2Cl_2 stock solution (prepared as described above, 0.14 M in **6** and 0.044 M in 2-methylnaphthalene), 110 μL of 0.219 M maleonitrile in CH_2Cl_2, and 90 μL of 0.598 M fumaronitrile. The maleonitrile had been freshly purified by preparative GC on a 5 ft × 0.25 in. Carbowax 20 M column; the fumaronitrile had been twice recrystallized from ether, and the CH_2Cl_2 had been distilled from CaH_2. This generated a solution (220 μL) containing 0.013 M **6**, 0.004 M 2-methoxynaphthalene, 0.1095 M maleonitrile, and 0.2445 M fumaronitrile. This tube was then placed on a vacuum line, subjected to three freeze–pump–thaw cycles, and sealed. It was then allowed to warm to room temperature and to stand for 10 h in the dark. The tube was then opened, and the contents were subjected to at least duplicate analyses on a 50-m methyl silicone fused silica capillary GC column. Product ratios, identities, and yields were determined by relative peak integrations, retention times, and response factors previously determined on authentic materials and by comparison to peaks of the internal standard 2-methoxynaphthalene. Since the reactions occurred under pseudo-first-order conditions, the relative rate constants given in the text are derived directly from the relative reactivities. In the specific instance described, the ratio of reactivities of maleonitrile and fumaronitrile was found to be 1.23 and 1.17 in duplicate runs. The yield of adducts was approximately 100%. In all cases, the adducts were identified as resulting from fused-syn reaction.

Competitive Trapping Experiments with Biradical 3,4-Dimethylenethiophene (2). Thermally Generated from Diazene 16. Stock solutions of diazene **16** containing *n*-nonane or *n*-decane as an internal standard and stock solutions of the appropriate olefins were used to prepare tubes composed of between 6 and 10 mM diazene and at least 10 equiv of each olefin. The tubes were allowed to decompose in the dark at 298 K. Initial studies were carried out in dichloromethane. Multiple combinations of olefins were studied in order to check for internal consistency. A less expansive study was conducted using acetonitrile as solvent. During early analyses, the sample tubes were subjected to three degassing cycles before being sealed. In later analyses, it was determined that due to the high concentration of olefins, evacuation of the sample tube at 77 K, and immediate sealing was sufficient to exclude any peroxide formation. Product analyses were carried out using capillary GC (Varian, 50 m methyl silicone, 50 m OV-225 B).

Competitive Trapping Experiments with 2 Photochemically Generated from Diazene 16. Samples in methylene chloride were prepared as described above. The tubes were photolyzed in the Rayonet photoreactor (350 nm lamps) for 7 h at −26 °C. Tubes were examined by ^1H NMR (250 MHz) at 253 K prior to photolysis. Photolysis was carried out in the Rayonet photoreactor (λ_{max} = 350 nm). The tubes were placed in an unsilvered dewar which was filled with ethanol. Coils connected to a Neslab coolant system were placed in the bottom of the dewar. With the coils, the ethanol was cooled to −26 °C. The temperature gradient within the dewar was minimized by stirring its contents with a magnetic stirrer. Photolysis was continued for 1.75 h. In a control experiment using a fumaronitrile trap, two samples were prepared. One tube had aluminum foil wrapped around it. Analysis by ^1H NMR (250 MHz) at 253 K of the two tubes after photolysis indicated that no reaction had taken place in the tube which had been wrapped with aluminum foil. Conversion of >95% had been achieved in the unwrapped tube. The only product evident by ^1H NMR was the fused-trans isomer **47**. Upon warming to room temperature, capillary GC confirmed that the contents of the unwrapped tube had reacted in a highly stereospecific fashion (maximum limit of stereorandomization: 0.9%).

Competition between fumaronitrile and dimethyl fumarate was also measured at an intermediate temperature (−10 °C). Product and olefin stability with respect to the photolysis conditions were also confirmed. 2-Methoxynaphthalene was added as an internal standard after photolysis. Analysis was conducted using Capillary GC (Hewlett-Packard, 25 m phenyl methyl silicone, 50 m OV-225B).

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Registry No. 1, 95406-66-9; **2**, 105064-76-4; **6**, 61838-64-0; **6**/maleic anhydride fused adduct, 66642-71-5; **12**, 6372-18-5; **13**, 119694-51-8; **14**, 119694-52-9; **15**, 105064-77-5; **16**, 114563-79-0; **17**, 119694-53-0; **18**, 25337-34-2; **19**, 18800-15-2; **20**, 56147-00-3; **21**, 105064-78-6; **22**, 22025-28-1; **23**, 119694-54-1; **24**, 119694-56-3; **26**, 119694-57-4; **29**, 6681-01-2; **30**, 56146-99-7; **31**, 114688-48-1; **35**, 119694-59-6; **36**, 119694-58-5; **37**, 119720-76-2; **38**, 105064-79-7; **39**, 105064-80-0; **40**, 105064-81-1; **53**, 13702-09-5; 3,4-bis(hydroxymethyl)furan, 14496-24-3; 3,4-bis(hydroxymethyl)furan cyclic sulfite derivative, 119694-50-7; 1,2,3,4-tetrahydro-*N*,*N*'-dicarbomethoxythieno[3,4-*d*]pyridazine, 119694-55-2; maleic anhydride, 108-31-6; maleonitrile, 17656-09-6; fumaronitrile, 764-42-1; dimethyl fumarate, 624-49-7; acrylonitrile, 107-13-1; dimethyl maleate, 624-48-6; 3,4-furandimethanol, 14496-24-3; *endo*-5,6-bis(bromomethyl)-7-oxabicyclo[2.2.1]hept-5-ene-2-carbonitrile, 119694-60-9.

Supplementary Material Available: Experimental details of the preparation and characterization of cycloadducts of diyls **1** and **2** with alkenes (16 pages). Ordering information is given on any current masthead page.

Ground-State Multiplicities of 3,4-Dimethylenefuran and 3,4-Dimethylenethiophene. Experimental Tests of ab Initio and Semiempirical Theories of Heteroatom-Bridged Disjoint Biradicals

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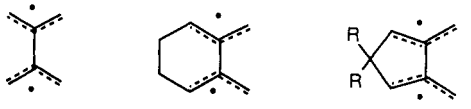
Abstract: The structure and spin state of 3,4-dimethylenefuran, 3,4-dimethylenethiophene, and 3,4-dimethylenepyrrole are explored by AM1-CI and other computational methods. In agreement with previous semiempirical and ab initio calculations, the present results predict that these species should have singlet ground states. The experimental study of low-temperature preparations of the first two members of this series is in accord with the predictions. These molecules both are intensely purple compounds (λ_{max} 560 and 572 nm, $\epsilon = 5.3 \times 10^3$ and 5.2×10^3 M^{-1} cm^{-1}, respectively). A new photobleaching reaction of 3,4-dimethylenefuran gives 2-(1-cyclopropenyl)-2-propen-1-al.

Quantum mechanical theory is confronted by a particularly searching test in the relationship between structure and spin state of π-conjugated non-Kekulé molecules.[1,2] In many such cases, the exchange energy favors the state of higher multiplicity, and hence Hund's rule applies. However, qualitative[1-5] and semiempirical[6,7] theories, supported by ab initio computational results,[7a,8,9] predict that in disjoint or quasi-disjoint molecules, like tetramethyleneethane (TME) **1** and its derivatives **2**–**4**, the exchange energy should be very small. This prediction, which we refer to as the "disjoint conjecture", is a consequence of the connectivity pattern in such molecules. If the biradical can be (mentally) constructed by a union of two π-conjugated monoradicals at "inactive" sites (where the NBMOs have zero Hückel coefficients), the electron distributions in the frontier MOs are confinable to separate locations in space, and hence to first-order, the Coulombic repulsion that normally favors the triplet in nondisjoint molecules vanishes. Moreover, the singlet should be preferentially favored by dynamic spin polarization.[1,3] These considerations open the possibility of a violation of Hund's rule, and in fact, the best available ab initio calculations[8,9] predict singlet ground states by 1–2 kcal/mol for **1** and **3**. However, the current interpretations of the linear electron spin resonance (ESR) Curie plots for **1**, **2**, and **4** (a close relative of **3**) favor a triplet ground state in each case.[10,11,14]



1 **2** **3**: R = H **4**: R = CH_3

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