J. Am. Chem. Soc. 1989, 111, 3671-3679

the Dox Foundation for fellowships (to K.J.S. and M.M.G., respectively). Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We thank Professor P. J. Garratt for helpful discussions.

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.

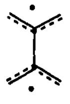
Ground-State Multiplicities of 3,4-Dimethylenefuran and 3,4-Dimethylenethiophene. Experimental Tests of ab Initio and Semiempirical Theories of Heteroatom-Bridged Disjoint Biradicals

Marc M. Greenberg, Silas C. Blackstock, Keith J. Stone, and Jerome A. Berson*

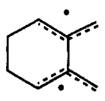
Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut 06511. *Received September 21, 1988*

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.

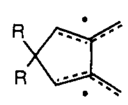
Quantum mechanical theory is confronted by a particularly searching test in the relationship between structure and spin state of π-conjugated non-Kekulé molecules.[1,2] In many such cases, the exchange energy favors the state of higher multiplicity, and hence Hund's rule applies. However, qualitative[1-5] 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$_3$

---

(1) Borden, W. T. *Diradicals*; Wiley: New York, 1982; Chapter 1.
(2) Berson, J. A. In *The Chemistry of the Quinonoid Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1988; Vol. 2, Part 1, Chapter 10.
(3) Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1977**, *99*, 4587.
(4) Ovchinnikov, A. A. *Theoret. Chim. Acta* **1978**, *47*, 297.
(5) Hückel, E. *Z. Phys. Chem., Abt. B* **1936**, *34*, 339.
(6) Lahti, P. M.; Rossi, A.; Berson, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 2273.
(7) (a) Lahti, P. M. Ph.D. Thesis, Yale University, New Haven, CT, 1985. (b) Lahti, P. M.; Ichimura, A. S.; Berson, J. A. *J. Org. Chem.* **1989**, *54*, 958.
(8) Du, P.; Borden, W. T. *J. Am. Chem. Soc.* **1987**, *109*, 930.
(9) Du, P.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1986**, *108*, 8086.
(10) (a) Dowd, P. *J. Am. Chem. Soc.* **1970**, *92*, 1066. (b) Dowd, P.; Chang, W.; Paik, Y. H. *J. Am. Chem. Soc.* **1986**, *108*, 7416.
(11) (a) Roth, W. R.; Erker, G. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 503. (b) Roth, W. R.; Hieber, M.; Erker, G. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 504. (c) Roth, W. R.; Biermann, M.; Erker, G.; Jelich, K. *Chem. Ber.* **1980**, *113*, 586. (d) Roth, W. R.; Scholz, B. P. *Chem. Ber.* **1982**, *115*, 1197. (e) Grimme, W.; Rother, H. J. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 505. (f) Chang, C.-S.; Bauld, N. L. *J. Am. Chem. Soc.* **1972**, *94*, 7593. (g) Bauld, N. L.; Chang, C.-S. *J. Am. Chem. Soc.* **1972**, *94*, 7594. (h) Dowd, P.; Chang, W.; Paik, Y. H. *J. Am. Chem. Soc.* **1987**, *109*, 5284.
(12) Lahti, P.; Rossi, A. R.; Berson, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 4362.
(13) Du, P.; Hrovat, D. A.; Borden, W. T.; Lahti, P. M.; Rossi, A. R.; Berson, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 5072.

0002-7863/89/1511-3671$01.50/0

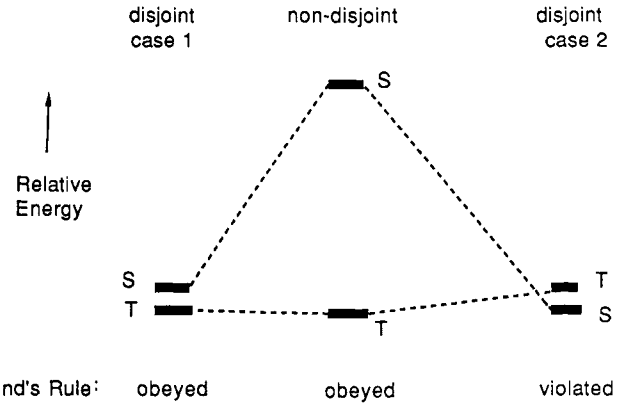
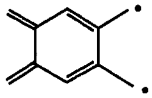
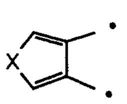


Figure 1. Energy relationships when a nondisjoint system is converted (in a "gedanken experiment") to disjoint ones. In case 1, Hund's rule is obeyed, but in case 2, it is violated. In both cases, the large diminution of the singlet–triplet gap predicted by the disjoint conjecture occurs, but it is difficult to discern in case 1, which usually is indistinguishable from the nondisjoint case by ESR Curie law behavior.

At present, these remain as unresolved conflicts between theory and experiment. Without attempting to adjudicate the problem, we offer the comment that it is not clear whether the apparent disagreement in these cases is trifling or grave. Conceivably, there may be a small flaw in the present level of theory that makes it unable to distinguish a gap $E_S - E_T$ of +1 kcal/mol from one of nearly 0 or −1 kcal/mol. If this is the case, one might expect confidently that the deficiency would be corrected at a slightly higher level of theory. Alternatively, if the singlet–triplet gap in the disjoint-hydrocarbon cases (**1**–**4**) is actually large, for example, 15–20 kcal/mol, as is often calculated for nondisjoint systems,[1,2] then the error of theory is massive, and some fundamental reconsiderations of the disjoint conjecture are in order. Unfortunately, the presently available experiments in the hydrocarbon systems are not capable of addressing this issue, since linear Curie plots can be compatible with either a small gap or a large one.[2] The problem is diagramed in Figure 1. It is a historical accident that, at the moment, the limitations of experiment essentially force one to find a clear violation of Hund's rule in order to establish the occurrence of the major diminution of the triplet preference predicted by the disjoint conjecture. Computationally, the most favorable such case of a disjoint hydrocarbon so far brought to light would seem to be 1,2,4,5-tetramethylenebenzene, **5**, for which a series of semiempirical[6] and ab initio[12,13] calculations predict singlet ground states by some 5–9 kcal/mol. The experimental data[14] on this system have been interpreted in terms of a *triplet* ground state, so again an apparent conflict with theory remains to be resolved. We hope to contribute to the question of the ground state of **5** in future publications, but in the present work, our efforts are directed toward the development of heterocyclic derivatives (**6**–**8**) of TME (**1**), a series of molecules we believe might be used ultimately to adjust the magnitude of the singlet–triplet gap almost at will. Our strategy is to introduce a perturbation sufficient to produce a Hund's rule violation and then to modify the structure gradually through a series of derivatives so as to restore high-spin hegemony. This will map out the domain of Hund's rule and provide needed calibration of the computational method.



5



3: X = CH_2
6: X = O
7: X = S
8: X = NH

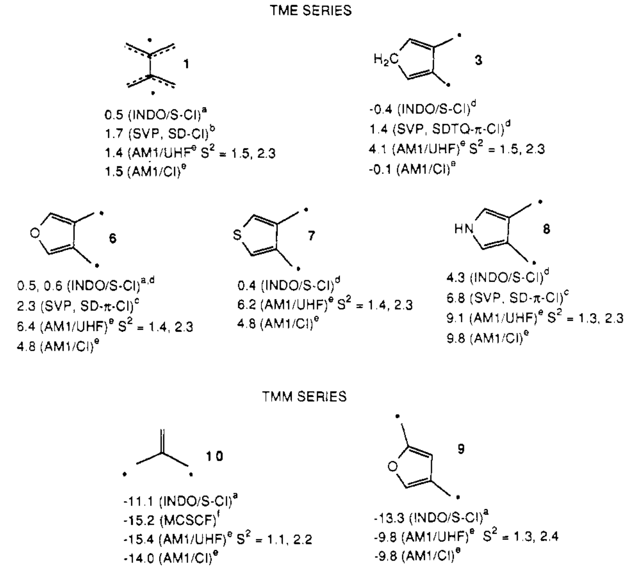


Figure 2. Calculated energy separations ($E_T - E_S$, kcal/mol) of lowest singlet and triplet states of biradicals. [a]Reference 6. [b]Reference 8. [c]Reference 9. [d]Reference 7. [e]This work. [f]Reference 15.

Computational Design of Singlet Biradicals. To evaluate the perturbative effect of heteroatoms on the singlet–triplet separation in the prototypical disjoint (e.g., **1**, TME) and nondisjoint (e.g., **10**, trimethylenemethane, TMM) biradicals, we have carried out a computational study of the five-membered heterocyclic substances of the 3,4- and 2,4-dimethylene series (**6**–**8** and **9**, respectively). These systems embody the further special feature that although they are formally derived from alternant biradicals by linkage of two termini through a heteroatom, their π-orbital arrays include an odd-numbered ring and hence are nonalternant. Therefore, Ovchinnikov's equal-parity criterion for ground-state spin[4] does not apply, and the qualitative prediction that the 3,4-dimethylene series should have singlet ground states whereas the 2,4-dimethylene series should have triplet ground states rests only upon an assumed analogy to the parent hydrocarbons **1** and **10**, respectively. It becomes important to buttress this reasoning with some actual computational results.

Figure 2 shows the data derived from three different kinds of calculations for the two series of compounds. For compounds **1**, **3**, **6**, and **8**, the Borden group[8,9] has furnished several ab initio treatments, selections from which are presented here. Compound **10** (TMM) has been examined many times, and the results of one of the most recent ab initio calculations[15] are listed in Figure 2. Also shown are the data from three semiempirical studies carried out in our laboratory using the INDO/S-CI method of Zerner[16] applied to idealized biradical geometries[6,17] and the AM1/UHF and AM1/CI methods of Dewar[18] with individual optimization of biradical geometries.

All four of the calculations agree that the singlets in the TME series, built upon disjoint-hydrocarbon frameworks, should be far more stable relative to the corresponding triplets than those in

---

(14) Roth, W. R.; Kowalczik, U.; Maier, G.; Reisenauer, H. P.; Sustmann, R.; Müller, W. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1285.

(15) Dixon, D. A.; Dunning, T. H., Jr.; Eades, R. A.; Kleier, D. A. *J. Am. Chem. Soc.* **1981**, *103*, 2878.

(16) (a) Ridley, J. E.; Zerner, M. C. *Theor. Chem. Acta* **1973**, *32*, 11. (b) *Ibid.* **1976**, *42*, 233. (c) Zerner, M. C.; Ridley, J. E.; Bacon, A. D.; Kirchner, R. F.; Cameron, A. Program ZINDO, Florida Quantum Theory Project, Tallahassee, FL.

(17) We report elsewhere (ref 7b) results for some of these compounds using INDO/S-CI methods applied to MNDO-UHF triplet optimized geometries.

(18) With the program of Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902 as modified with the advice of Stephen Blackstock.

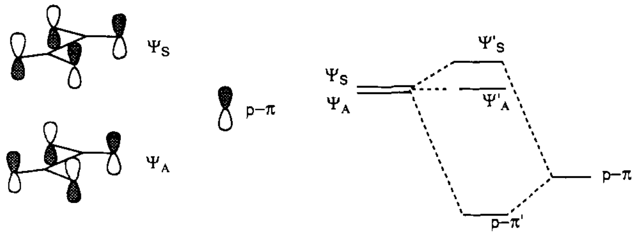
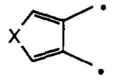


Figure 3. Perburbative interaction of filled heteroatomic p-π-orbital with the NBMOs of tetramethyleneethane.[9]

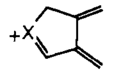
the TMM series. Of the methods, INDO/S-CI consistently stabilizes the singlet the least in the TME series. In fact, in the case of the hydrocarbon dimethylenecyclopentadiene, **3**, it predicts a *triplet* ground state by a fraction of a kilocalorie/mode. Aside from this small excursion into Hund's rule territory, all of the predictions are for singlet ground states in the TME group. How literally one should take the actual numerical results is not obvious, but for the present, a more fruitful line of thinking is stimulated by an examination of qualitative trends.

The interaction[9] of a heteroatom lone-pair orbital with the frontier orbitals of the disjoint hydrocarbon tetramethyleneethane (TME) **1** is shown in Figure 3. Note that it is the symmetric component of the TME frontier orbitals that is of the proper symmetry to mix with the p–π orbital of the heteroatom X. Thus, in the 3,4-dimethyleneheterocycles, e.g., **6–8**, the original TME NBMOs will be split by an amount that, to first order, will be an inverse function of the separation between the unperturbed energies. The energy level of the heteroatom p–π lone-pair orbital will sink with increasing electronegativity. For the first-row elements, where overlap effects might be small, we would expect the splittings of the uncorrelated NBMOs to be in the order X = NH > X = O > X = CH_2. In the second-row case, X = S, the diminished overlap of the sulfur 3p orbital with the carbon π system introduces another factor that makes it difficult to predict qualitatively the overall order of perturbation. The frontier MO splittings should selectively stabilize the singlet in configurational interaction and therefore should produce an order of relative preference for the singlet strongly influenced by the balance of these orbital energy separation and overlap factors. The ab initio calculations (see Figure 2), which do not include the X = S case, show trends which appear to be in the order predicted by the energy-separation effect. These trends persist in the semiempirical CI calculations, which in addition show the singlet–triplet gap for the X = O and X = S cases to be comparable in magnitude.

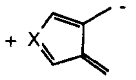
Increasing the HOMO–LUMO separation by the lone-pair perturbation should have the effect of increasing the closed-shell zwitterionic character at the expense of the biradical character of the species. The Borden group[9] has used the square of the ratio of the coefficients (C_i) of the two predominant configurations, $(a_2)^2$ and $(b_1)^2$, in the CI wave function of the singlet as a guide to the biradical character. For a "pure" biradical, this function should have the value 1.00, and deviations from this value measure the amount of zwitterionic character in the biradical. In terms of valence pictures, a larger deviation would correspond to a larger contribution of resonance structures **11b** and **11c** to the resonance hybrid.



11a



11b



11c

The relevant correlated a_2 and b_1 MO's, their energies, and their AO coefficients at the π-electron sites are exemplified in Figure 4, as calculated by the AM1-CI semiempirical method.

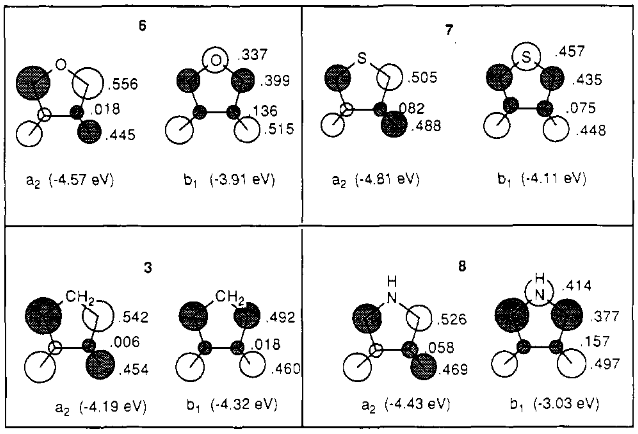


Figure 4. NBMO coefficients and energies by AM1/CI for the lowest singlet states of the species shown.

Table I. Square of the Ratio of the Coefficients of the Two Principal Configurations (a_2 and b_1) in the CI Wave Function of TME Derivatives Bridged by X Derived by Various Computational Methods

		$(C_{a_2}/C_{b_1})^2$		
compd	X	ab initio[a]	INDO/S-CI[b]	AM1/CI[c]
3	CH_2	0.87	1.1	1.2
6	O	1.8	1.8	3.0
7	S		1.4	2.9
8	NH	2.7	3.3	5.2

[a] Reference 9. [b] Reference 7. [c] This work.

In Table I are collected the values of $(C_{a_2}/C_{b_1})^2$ for the TME derivatives. The INDO/S-CI calculations agree with the conclusion[9] from ab initio results that the biradical character of the hydrocarbon **3** is only slightly perturbed in the furan species **6**. Although corresponding ab initio results for the thiophene system **7** are not available, INDO/S-CI predicts that the zwitterionic character of this species should be similar to that of the furan. Both calculations suggest an increased zwitterionic character in the pyrrole **8**. AM1/CI consistently predicts the zwitterionic character in the heteroatomic systems **6–8** to be higher than does either of the other two CI methods.

Although there is no obvious way to associate the absolute value of $(C_{a_2}/C_{b_1})^2$ with an experimental observable, Borden and coworkers[9] have suggested that a reasonable model of a highly zwitterionic species would be carbonyl ylide, $CH_2{=}O^+{-}CH_2^-$, for which the ab initio $(C_{a_2}/C_{b_1})^2$ value is 6.13, clearly much higher than those obtained by ab initio calculations on the 3,4-dimethylene heterocycles of Table I. On this basis, compounds **6–8** would be weakly perturbed TME derivatives. This conclusion, however, is not independent of the calculational method. For example, AM1[CI = 2 OPEN(2,2)] gives 4.6 for the ratio in carbonyl ylide, which is actually *lower* than the value for the pyrrole derivative **8** (Table I) and the $\Delta E_{RHF,UHF}$ criterion of Kahn, Hehre, and Pople,[19] 34 kcal/mol for carbonyl ylide at the 6-31G*/UHF level, corresponds to a species with substantial *biradical* character.

The chemistry of the known members of the series, **6** and **7**, is consistent with their formulation as biradicals. In particular, neither their rates of formation[20] from neutral precursors nor their relative[21a] or absolute[21b] rates of reaction to neutral products is affected appreciably by solvent polarity. Of course, one must admit that these are permissive rather than decisive results, because early transition states conceivably might produce polarity-insensitive rates, even if the first-formed intermediate were zwitterionic.

One might ask whether there is merit in the extreme view that these species, e.g., **6**, should be considered to be Kekulé[22] rather

---

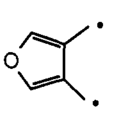
(19) Kahn, S. D.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 1871.

(20) (a) Stone, K. J.; Greenberg, M. M.; Blackstock, S. C.; Berson, J. A. *J. Am. Chem. Soc.*, accompanying paper in this issue. (b) Stone, K. J.; Greenberg, M. M.; Goodman, J. L.; Peters, K. S.; Berson, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 8088.

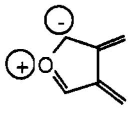
(21) (a) Greenberg, M. M.; Blackstock, S. C.; Berson, J. A. *Tetrahedron Lett.* **1987**, *28*, 4263. (b) Scaiano, J. C.; Wintgens, V.; Bedell, A.; Berson, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 4050.

(22) To call "Kekulé" the structure **6b**, a compound with trivalent oxygen and trivalent carbon, could be considered a contradiction in terms. We tolerate this in order to avoid the term "non-non-Kekulé" or an alternative locution meaning "the opposite of non-Kekulé".

than non-Kekulé compounds because their zwitterionic structures (e.g., **6b**) formally contain one bond more than the biradical



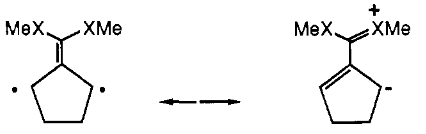
6a



6b

structure **6a**. It then might be argued that the existence of the extra bond requires the frontier electrons to be paired, so no special explanation of a singlet ground state for **6** would be required.

This type of argument cannot be generally valid, since it would lead quite analogously to the prediction of such an extra bond, and hence a singlet ground state, for the trimethylenemethane species **12** and **13**, each of which has heteroatomically derived zwitterionic "full-valence" contributing structures (e.g., **12b** and **13b**). Experimentally, however, both **12**[23a–c] and **13**[23b,c] have

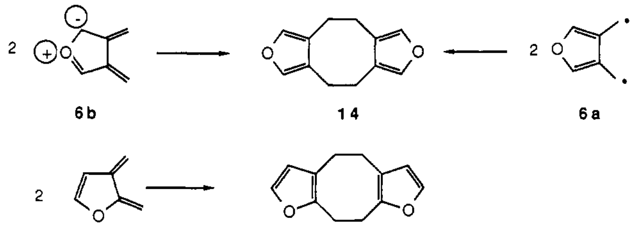


12a: X = O
13a: X = S

12b: X = O
13b: X = S

triplet ground states, which shows that the mere possibility of writing such structures does not guarantee a full extra bond.

Moreover, if the extra bond is to be thought of as real, there must be an energy associated with it, and an appropriate model for the heats of reaction of **6b** would be those of the Kekulé isomer 2,3-dimethylenefuran (**15**), a known compound,[24] which formally has the same number of bonds. For example, it would seem to follow that the dimerizations **6** → **14** and **15** → **16** would be



6b **14** **6a**

15 **16**

approximately equally exothermic except for twice the resonance energy of a furan ring, which actually would favor the dimerization of the Kekulé isomer **15**. Why then is the rate of dimerization of **6** so much faster (a factor of 10^{13})[21b] than that of **15**? In our view, the reason is that the Kekulé compound **15** is a poor model for the non-Kekulé compound **6**. It is precisely because **6** *lacks one bond* that its dimerization releases much more energy ($\Delta H \approx -110$ kcal/mol based on the biradical structure **6a** and calculated with group equivalents[25]) than the dimerization of **15** ($\Delta H \approx -52$ kcal/mol). Part of this extra exothermicity appears as stabilization of the transition state for dimerization of the non-Kekulé compound. Regardless of how one chooses to deal with the semantic problem of the word "non-Kekulé", there is something about the bonding in 3,4-dimethylenefuran (**6**) that sharply differentiates its nature from that of its unambiguously "Kekulé" isomer 2,3-dimethylenefuran (**15**).

Properties of 3,4-Dimethylenefuran (6) and 3,4-Dimethylenethiophene (7) at Low Temperatures in Rigid Media. Photolysis

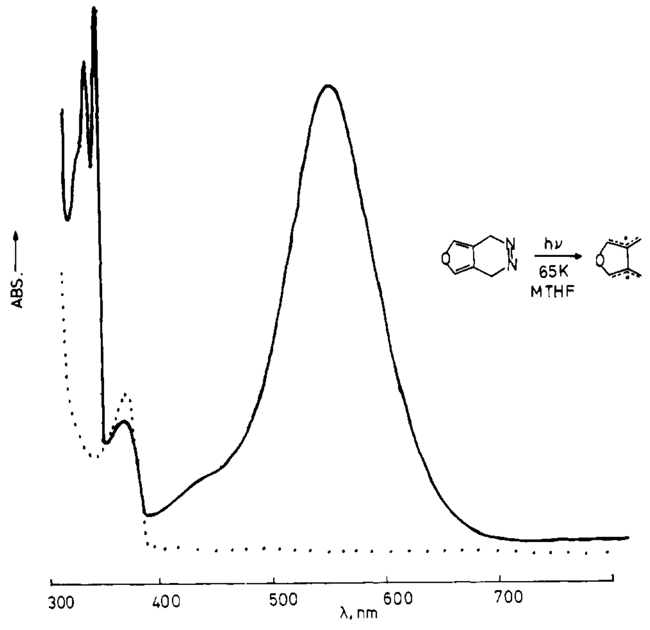
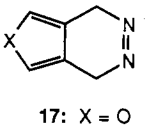
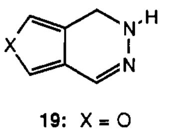


Figure 5. Spectra of diazene precursor **17** before irradiation (dotted curve) and of 3,4-dimethylenefuran (**6**) obtained by irradiation at 65 K in 2-methyltetrahydrofuran glass (full curve).

(~300–400 nm, Oriel 51810 filter, 200-W high-pressure mercury arc) of frozen solutions of the diazene precursors (**17** and **18**) at



17: X = O
18: X = S



19: X = O
20: X = S

<80 K causes the rapid appearance of an intense purple color (blue under some conditions), which we assign to the biradicals themselves. As we describe elsewhere,[20a] it is usually difficult to remove traces of hydrazone (**19** or **20**) from solutions of **17** and **18**, but neither hydrazone is a source of the carrier of the purple color under these conditions.

3,4-Dimethylenefuran (**6**) shows a broad absorption with λ_{max} 560 nm, accompanied by two sharp, strong bands at 338 and 348 nm (Figure 5). The band positions in EtOH are unchanged from those in 2-methyltetrahydrofuran (MTHF). All three bands grow in during irradiation and disappear during thawing or photobleaching (see below) at the same rate.

Similarly, 3,4-dimethylenethiophene (**7**) in MTHF prepared in the same way has an intense, broad band with λ_{max} 568–572 nm. However, in this sample, no absorptions were visible in the valley between the short-wavelength cutoff and the position of the diazene n,π* absorption (λ_{max} 366 nm), a region where the sharp bands of **6** appear. Even had such bands of **7** been blue-shifted as much as 20 nm from those of their counterparts in the spectrum of **6**, they should have been observable had they been of comparable strength. We did find absorptions in this region under somewhat different conditions when a MTHF glass was photolyzed to completion at 77 K. These two bands were barely discernible (Figure 6A) at 354 and 359 nm along with the (slightly red-shifted) main band at 580 nm. Apparently, the two new bands became visible in this experiment because the concentration of residual diazene **16** and hydrazone at the end of photolysis was low enough to open up the near-UV region to scrutiny. That the weak near-UV bands are actually associated with the same transient seen before and not with a nitrogenous impurity or side product became clear in the following experiment.

We developed an independent synthesis of the carrier of the colored transient in rigid media by adapting some chemistry recently reported by Haider, Platz, and co-workers.[26] Irradiation

---

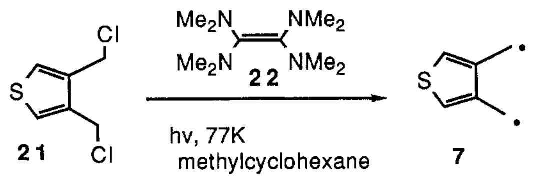
[23] (a) Platz, M. S.; McBride, J. M.; Little, R. D.; Harrison, J. J.; Shaw, A.; Potter, S. E.; Berson, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 5725. (b) Shen, L.; Berson, J. A., unpublished work. (c) Shen, L. Ph.D. Thesis, Yale University, New Haven, CT, 1984.

[24] Trahanovsky, W. S.; Cassady, T. J.; Woods, T. L. *J. Am. Chem. Soc.* **1981**, *103*, 6691.

[25] Cf.: 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.

[26] Haider, K.; Platz, M. S.; Despres, A.; Lejeune, V.; Migirdicyan, E.; Bally, T.; Haselbach, E. *J. Am. Chem. Soc.* **1988**, *110*, 2318.

of a solution of 3,4-bis(chloromethyl)thiophene (**21**) and



1,1,2,2-tetrakis(dimethylamino)ethene (**22**) in methylcyclohexane glass at 77 K for 5 min generated a blue matrix whose UV–vis absorption spectrum is recorded in Figure 6B. It is essentially identical with that of **7** obtained from the diazene precursor (Figure 6A), including the weak UV bands between 350 and 360 nm. From the extinction coefficient (see below), the conversion of dichloride **21** to biradical **7** is estimated to be ~25% in this experiment.

Neither the intensities nor the band shapes of the spectra are sensitive to the nature of the solvent used to make the glass.

To determine the extinction coefficients (ϵ) of biradicals **6** and **7**, the concentrations of the biradicals were measured by assuming that the only photoreaction of either diazene precursor was the formation of its biradical. The decrease in concentration of the diazene precursor was thus equated to the concentration of biradical present. This assumption cannot be seriously in error, since the material balance of products from these preparations is high.[20] Any error introduced by a departure from quantitative photochemical yield of biradical will make the measured extinction coefficients lower than the true values. From partially converted samples of **6** and **7**, ϵ values of $(5.3 \pm 1.1) \times 10^3$ and $(5.18 \pm 1.2) \times 10^3$ M^{-1} cm^{-1}, respectively, were obtained for the long-wavelength bands. The oscillator strengths derived from the integrated intensities were 0.12 and 0.08 for **6** and **7**, respectively.

It was not possible to check this result for **6** by complete conversion because of a secondary photoreaction which consumes the biradical (see below). However, **7** is not subject to this limitation, and exhaustive photolysis of the diazene precursor **18**, combined with the assumption that the resulting concentration of biradical was the same as that of the starting diazene **16**, gave an ϵ value of $(5.0 \pm 1.0) \times 10^3$ M^{-1} cm^{-1} (oscillator strength 0.07), in good agreement with the value obtained by partial conversion.

UV–Vis Spectroscopy of 3,4-Dimethylenefuran (6) and 3,4-Dimethylenethiophene (7) under High-Temperature Matrix-Isolation Conditions. The triplet states of **6** and **7** each are predicted by the theoretical calculations to lie only slightly above the corresponding singlet. If the higher energy state could be significantly populated thermally, it might be possible to detect the process by UV–vis spectroscopy as a temperature-dependent reversible change in position or shape of the absorption spectrum. Accordingly, we have studied the properties of **6** and **7** in media which should remain rigid at temperatures higher than those of the conventional frozen solvent specimens we had used earlier.

Our attempts to incorporate the diazene precursor **18** into adamantane by the methods[34] of cosublimation or cocrystallization have been hindered by technical problems associated with the thermal lability of **18**. In only one of many experiments aimed at incorporating a small amount of **18** in adamantane by rapid coprecipitation was a purple preparation possibly attributable to **7** obtained (see the Experimental Section for details). More reproducible results were obtained when the diazenes **17** or **18** were incorporated into films of polystyrene or poly(methyl methacrylate).[35] Specimens prepared by the methods described in the Experimental Section rapidly turned purple when irradiated in Pyrex tubes at 350 nm in the Rayonet reactor at 77 K. These preparations were stable overnight at 196 K and faded over 2–3 h at 218–223 K. Poly(methyl methacrylate) films <1 mm thick impregnated with either diazene were irradiated in a special low-temperature Pyrex cell (see the Experimental Section) which permitted us to record the long-wavelength band of both biradicals. The spectrum of **7** remained unchanged over the temperature range 77–223 K. Although a second species might escape detection if its spectrum were confined to the far-UV region inaccesible to us or fortuitously happened to overlap that of the ground state of **7**, the present results are more simply understood if only one carrier is responsible for the spectrum over the entire temperature range.

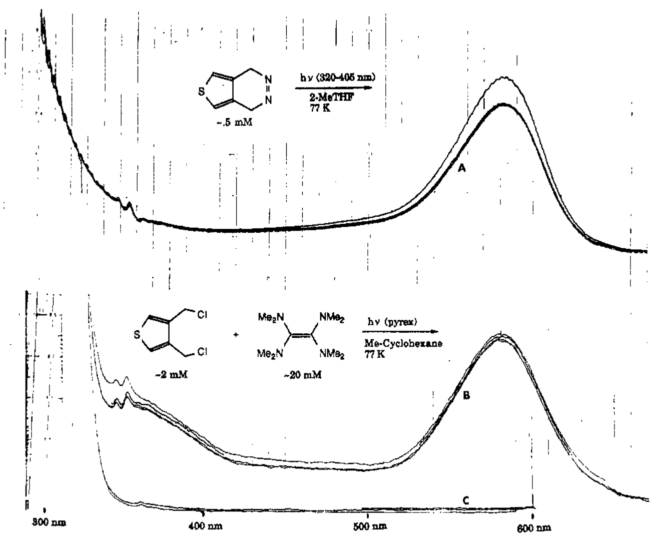


Figure 6. Spectra of 3,4-dimethylenethiophene (**7**) (A) derived from diazene **18**, (B) derived from coirradiation of 3,4-bis(chloromethyl)thiophene (**21**) and 1,1,2,2-tetrakis(dimethylamino)ethane (**22**), and (C) sample in B before irradiation.

Low-Temperature Photochemistry of 3,4-Dimethylenefuran (6). Although glassy preparations of 3,4-dimethylenethiophene (**7**) show no change of visible color or absorption spectrum upon prolonged irradiation at 77 K under a variety of conditions, similar samples of 3,4-dimethylenefuran (**6**) undergo a smooth photoreaction. This process does not occur at an appreciable rate using light of wavelength >420 nm (450-W medium pressure Hg arc, Oriel #51484 filter), which is absorbed primarily by the long-wavelength band (λ_{max} 560 nm) of **6**. However, Pyrex-filtered light (>280 nm), which is absorbed by the near-UV bands of **6**, quickly bleaches the purple color and causes the disappearance of all three absorption bands associated with **6**. The photobleached samples show no new bands above 300 nm.

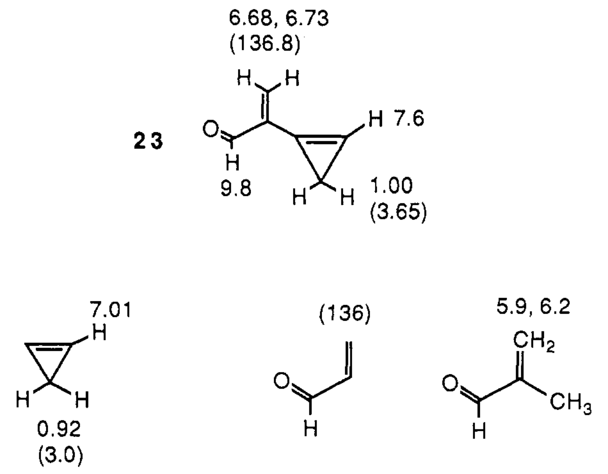
The first hints of the structure of the photoproduct came from the observation[27] of the cross-polarization magic angle spinning (CP MAS) solid-state ^{13}C NMR spectrum of a photobleached sample of **6**-di-$^{13}CH_2$ in MTHF, in which two new absorptions of roughly equal intensity appeared at about 141 and 3 ppm. These features suggested that one of the methylene carbons of **6** remained as an olefinic site in the product and the other one was incorporated into a high-field aliphatic or alicyclic position. The signals diminished or disappeared when the preparation was warmed to room temperature, which suggested that the photoproduct has only limited stability.

Accordingly, the photobleaching experiment was carried out on labeled diazene **17**-di-$^{13}CH_2$ as before except that for spectroscopy the product was immediately transferred to the probe of a ^{13}C NMR spectrometer kept at 183 K. Other than solvent peaks, signals appeared only at 3.65 and 138.6 ppm, approximately the same positions as those observed[27] in the solid-state ^{13}C spectrum. Another photobleaching experiment in a diethyl-d_{10} ether glass allowed the determination of the ^1H NMR spectrum of the product. Thawing of the sample and examination in a 183 K probe showed the complete consumption of the diazene **17** and the essentially quantitative formation of a new species with resonances at δ 9.8 (s, 1 H), 7.6 (s, 1 H), 6.73 (s, 1 H), 6.68 (s, 1 H), and 1.00 (s, 2 H). This spectrum was stable up to about 250 K, at which temperature the photoproduct resonances gradually disappeared and were replaced by several new peaks.

---

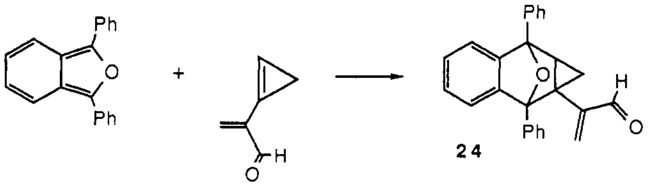
[27] (a) Zilm, K. W.; Merrill, R. A.; Greenberg, M. M.; Berson, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 1567. (b) Zilm, K. W.; Merrill, R. A.; Greenberg, M. M.; Blackstock, S. C.; Berson, J. A., paper in preparation. (c) Zilm, K. W.; Merrill, R. A.; Webb, G. G.; Greenberg, M. M. *J. Am. Chem. Soc.* **1989**, *111*, 1533.

Scheme I. ^{1}H (and ^{13}C) NMR Assignments

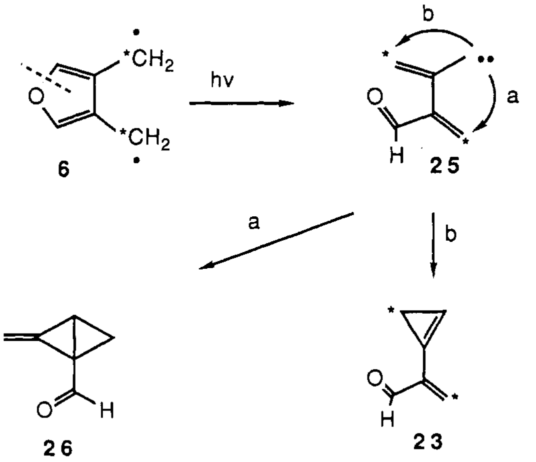


We assign the structure **23** to the photoproduct on the basis of the ^{1}H and ^{13}C NMR resonances, which are reasonably close to those expected by comparison to the model compounds shown (Scheme I).

The photoproduct **23** reacted with 1,3-diphenylisobenzofuran to give a 30% yield (based upon diazene **17**) of the Diels–Alder adduct **24**, whose structure and composition were confirmed by elemental composition and ^{1}H NMR spectroscopy. The stereochemistry of **24** has not been established, although arguments in favor of the isomer with an exo cyclopropane ring have been summarized elsewhere.[28]



The mechanism of the photochemical conversion of the biradical **6** to the cyclopropene **23** seems to be similar to the one postulated for the phototranspositions of dialkylfurans.[29-32] A sufficient hypothesis for the presently known facts is embodied in a reaction through the carbene **25**. Note that the location of the ^{13}C labels in **23**, the product of reaction by path b of this mechanism, would be in the cyclopropene and terminal methylene groups, in accord with the experimental findings.



In principle, the carbene **25** also could have cyclized according to pathway a, which would have led to a different product, the methylenebicyclobutane **26**. Whether some of this competing closure actually occurs cannot now be asserted with confidence, since it may be doubted[33] that the species **26** would have been isolable under the conditions used for workup here.

In Search of the ESR Spectra of 3,4-Dimethylenefuran and 3,4-Dimethylenethiophene. We can summarize a good deal of experimentation aimed at observing the ESR spectrum of a paramagnetic state of biradical **6** or **7** with the statement that no such spectra have yet been seen. Frozen MTHF solutions of diazene **17** or **18** gave rise to intensely purple preparations containing **6** or **7** when irradiated in the microwave cavity of an ESR spectrometer at a frequency of 9.1 GHz, but no trace of a spectrum attributable to a triplet could be discerned over the temperature range between 12 K and the softening point of the matrix near 80 K. Under these conditions, we estimate that $>10^{16}$ biradical molecules were present in the cavity, about 10^5 times the putative limit of sensitivity of the spectrometer. With the previously reported[36] approximation, it may be calculated[37] that the zero field splitting parameter $|D|/hc$ for triplet **6** should be 0.0279 cm^{-1}, which would correspond to a total separation between the outermost lines of about 550 G. This should have been readily apparent.

In an attempt to populate thermally the triplet state of **7** in amounts sufficient to permit detection of an ESR signal, we generated **6** and **7** in poly(methyl methacrylate) films, in which environments the colors of the diyls persist at temperatures >200 K (see above). We irradiated films containing **17** and **18** outside of the cavity at 77 K and determined directly the concentrations (and hence the total number of potential paramagnetic centers) attributable to **6** and **7** by UV–vis spectrometry at 77 K. The number of diyl molecules present in the two preparations were 5.6×10^{15} and 1.6×10^{16}, respectively, each number corresponding to half the number of uncompensated spins that would be present in the sample if all the **6** or **7** were in the triplet state. Films of **18** from the same batch also were irradiated to produce **7** and then examined in the ESR cavity over the temperature range 77–223 K. The purple color persisted throughout, but no evidence of triplet signals was observed.

With the conservative value 5×10^{14} diyl molecules (about 1 order of magnitude lower than we actually measured), we calculate that for a hypothetical energy gap $E_T - E_S$ of 4.5 kcal/mol, the fraction of triplet molecules (with allowance for the statistical factor of 3 favoring the triplet) that would be present in Boltzmann equilibrium with the singlet at 77, 223, and 298 K would be 5×10^{-13}, 1.17×10^{-4}, and 1.5×10^{-3}, respectively, and the actual number of spins present in the high temperature experiment (223 K) would have been about 10^{11}, the probable limit of sensitivity of the spectrometer. Over the experimental range of temperature, the fraction of triplet species would have increased with temperature by a factor of 10^9, whereas the Curie effect would have only negligibly decreased (by a factor of 3) the paramagnetism per spin and hence the inherent spectrometric sensitivity. Therefore, *if* thermal equilibrium is established under our experimental conditions and *if* the failure to observe an ESR signal is caused by insufficient population of the triplet state rather than by rotationally induced uncertainty broadening or other spectroscopic complications, the temperature and spectrometer sen-

---

(28) Greenberg, M. M. Ph.D. Thesis, Yale University, New Haven, CT, 1988.

(29) vanTamelen, E. E.; Whitesides, T. H. *J. Am. Chem. Soc.* **1971**, *93*, 6129.

(30) Padwa, A. In *Rearrangements in Ground and Excited States*; deMayo, P. A., Ed.; Academic Press: New York, 1980; Vol. 3.

(31) Kobayashi, Y.; Kumadaki, I. In *Advances in Heterocyclic Chemistry*; Katritzky, A. R., Ed.; Academic Press: New York, 1982; Vol. 31.

(32) For related results in thiophenes, see: Rendall, W. A.; Clement, A.; Torres, M.; Strausz, O. P. *J. Am. Chem. Soc.* **1986**, *108*, 1691.

(33) Lahti, P. M.; Berson, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 7011.

(34) Walter, H. F.; Beaudry, W. T.; Camaioni, D. M.; Pratt, D. W. *J. Am. Chem. Soc.* **1985**, *107*, 793.

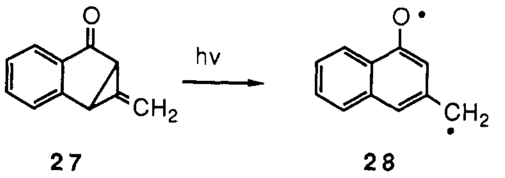
(35) (a) Radziszewski, J. G.; Burkhalter, F. A.; Michl, J. *J. Am. Chem. Soc.* **1987**, *109*, 61. (b) Birney, D. M.; Berson, J. A., unpublished work. (c) Birney, D. M. Ph.D. Thesis, Yale University, 1987.

(36) Rule, M.; Matlin, A. R.; Seeger, D. E.; Hilinski, E. F.; Dougherty, D. A.; Berson, J. A. *Tetrahedron* **1982**, *38*, 787.

(37) With STO-3G ROHF MOs and a geometry optimized at the 3-21G UHF level. We thank Dr. P. M. Lahti for this calculation.

sitivity can be used to deduce a minimum value of about 4.5 kcal/mol for the energy gap separating the ground-state singlet from the triplet.

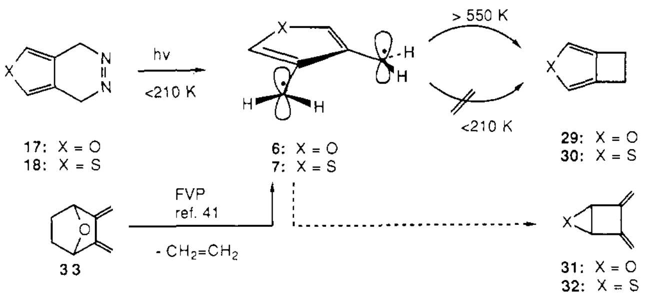
We are of course conscious of the fact that this is in essence a negative result. For example, it could be argued that the attempt to preserve rigid matrix conditions at high temperatures succeeds in maintaining a viscosity high enough to prevent *bimolecular* diffusive mutual annihilation of the biradicals, which in turn preserves the UV–vis spectrum. However, rotational (*unimolecular*) diffusion is required to be slow on the ESR time scale in order to preserve the anisotropic interactions that produce the characteristic features of a triplet ESR spectrum.[38] In other words, the persistence of the UV–vis spectrum guarantees the chemical integrity of the biradicals, but it does not guarantee the existence of necessary conditions for ESR spectroscopy. To this argument, we can offer at present only the following suggestive observation. When a sample of *m*-naphthoquinomethane **27**[36,39] incorporated into poly(methyl methacrylate) in the same way used in the above studies of **6** and **7** was irradiated at 77 K, an ESR spectrum identical with that previously reported[36,39] for the biradical **28** quickly appeared. The signal persisted, with the expected decrease of intensity but with no distortion of line shape, as the temperature was raised to 209 K, where it decayed irreversibly. To the extent that the behavior of **28** in these polymeric films serves as a model for the behavior expected for triplet **6** and **7**, the result casts doubt on the hypothesis that the failure to observe ESR spectra for the latter two diyls is merely due to rotational averaging of the anisotropic interactions.



Although the ESR experiments provide permissive rather than decisive evidence of singlet ground states for **6** and **7**, the CP MAS ^{13}C NMR observations on the two diyls[27] make this assignment of spin multiplicity difficult to escape.

The Barrier to Cyclization. The persistence of the diyls **6** and **7** at temperatures above 200 K means that there is an activation energy of at least 20–25 kcal/mol opposing the internal cyclization to the cyclobutanes **29**/**30** or **31**/**32**. The exact height of the barrier is not known, although the threshold temperature for cyclization probably lies somewhere above the 210 K lower limit necessitated by the present matrix-isolation experiments and below the >550 K flash vacuum pyrolysis (FVP) temperature used[20,41] to obtain cyclobutane derivatives **29**/**30**, presumably through the same diyls **6** and **7**.

Since radical–radical dimerizations occur at nearly every encounter,[40] it seems at first glance incredible that two spin-paired radical sites in close proximity should resist immediate combination to form **29**/**30**, for example. The retardation in rate probably is caused by the necessity to twist the exocyclic methylene groups out of the plane of the furan (**6**) or thiophene (**7**) ring en route to the transition state for ring closure, thereby sacrificing some of the 20 kcal/mol of stabilization associated with the two allylic systems of **6**/**7**. Moreover, a substantial strain energy must be built into forming the cyclobutane ring of either **29**/**30** or **31**/**32**, and the latter two can only be formed at the additional expense of the resonance stabilization energy of an aromatic system.



Conclusions

Both UV/vis and ESR spectroscopy of matrix-immobilized specimens of 3,4-dimethylenefuran (**6**) or 3,4-dimethylenethiophene (**7**) indicate that no other nearby state can be populated thermally over the temperature range 12–220 K. The absence of detectable paramagnetic species provides permissive evidence of singlet ground states, in accord with the predictions of a variety of theoretical calculations on these non-Kekulé molecules.

Experimental Section

Low-Temperature Matrix-Isolation UV-Absorption Spectroscopy. A. With Air Products Displex and Low-Temperature Solution Cell. The solution cell has been described elsewhere.[42] A freshly prepared, deaerated (achieved by bubbling N_2 through the sample at −5 °C for 10 min) 2-methyltetrahydrofuran solution (8 mM) of diazene **18** was mounted on the cold end of the Displex and cooled to 14 K as previously described.[42b] The biradical was generated with broad band filtered irradiation (λ_{max} 355 nm, Oriel #51810) from a 200-W high-pressure Hg arc lamp. Selective irradiation of the 3,4-dimethylenethiophene absorption band (λ_{max} 572 nm) was accomplished with the aid of a long-pass filter (50% transmission at 475 nm, Oriel #51484). Attempts to bleach the purple species were also undertaken with aqueous potassium dichromate (50% transmission at 570 nm) as a filter.

The biradical absorption was irreversibly dissipated when the matrix was warmed to 90 K. Photolysis at 14 K regenerated 3,4-dimethylenethiophene.

B. With the Stationary Pyrex Gas-Cooled Absorption Spectroscopy Apparatus. A freshly prepared 2-methyltetrahydrofuran (MTHF) solution of diazene **18** (0.031 M) was placed in a Pyrex cell (3-mm path length) equipped with 6-mm diameter glass tubing at its outlet. The sample was degassed using three freeze–pump–thaw cycles and sealed as previously described.[20a] Great care must be taken when thawing the sample so as to not crack the brittle cell at extremely cold temperatures. The stationary apparatus was designed by A. Friedli and V. Osterman and built by Ralph Stevens. A board was constructed to serve simultaneously as a mount for the apparatus and as the front wall for the Cary 219 spectrophotometer. The temperature was measured via an iron vs constantan thermocouple. The thermocouple was positioned just below the sample cell by passing it through the gas outlet. In order to keep frost off of the outer surface of the dewar, a defroster fashioned out of glass tubing was used to blow warm nitrogen gas over the outer surface of the dewar. After precooling the Pyrex apparatus to around 150 K, the sample was placed in the apparatus and quickly cooled to 77 K by increasing the nitrogen flow rate. The sample cell was held stationary by plunging its tip into the Styrofoam plug at the top of the apparatus. The Styrofoam plug also served as a good insulator.

Photolysis was carried out without moving the sample with the aid of a fiber optics light pipe, using the previously described lamp and filters. Filtering of infrared irradiation by the use of either water or Oriel #52060 was essential.

C. With a Modified Gas-Cooled Pyrex Cell. Determination of the Extinction Coefficient of Diazene 18. The concentration of a freshly prepared $CDCl_3$ (passed over neutral alumina) stock solution of **18** was determined from ^1H NMR (250 MHz) at 253 K. Acetonitrile (2 μL, 3.83×10^{-2} mmol), passed over neutral alumina before use, was added to the NMR tube for use as an internal standard. Use of a 10-s relaxation delay yielded internally consistent results for the two chemically nonequivalent protons in **18**. The concentration of hydrazone **20** was determined by integration of its methylene group resonance versus that of acetonitrile.

---

(38) For a discussion, see: Platz, M. S.; Berson, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 2358 and references cited therein.

(39) Seeger, D. E.; Hilinski, E. F.; Berson, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 720.

(40) Reviewed by Ingold, K. U. In *Free Radicals*; Kochi, J., Ed.; Wiley: New York, 1973; Vol. 1, p 40.

(41) For the FVP of **33** leading to **30**, see: Vogel, P.; Hardy, M. *Helv. Chim. Acta* **1974**, *57*, 196.

(42) (a) Seeger, D. E.; Lahti, P. M.; Rossi, A. R.; Berson, J. A. *J. Am. Chem. Soc.* **1986**, *104*, 1251. (b) Reference 7a. (c) Modified from a design of Hinsberg, W. D., III, Ph.D. Thesis (with Dervan, P. D.), California Institute of Technology, Pasadena, CA, 1978. We thank these authors for providing us with this information.

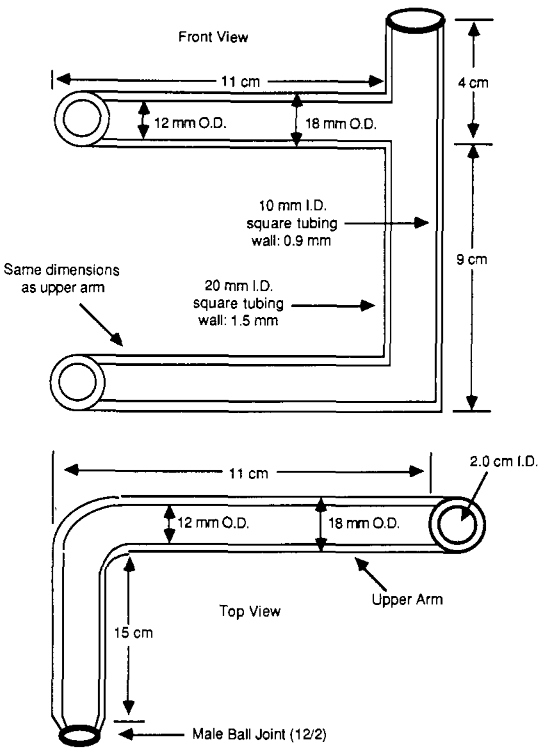


Figure 7. Pyrex dewar for low-temperature UV spectroscopy.

The UV spectrum of a degassed (three cycles) and sealed sample containing 250 μL of diazene **18** stock solution, diluted with 600 μL of 2-methyltetrahydrofuran, was recorded at 213 K with the modified low-temperature absorption cell shown in Figure 7. The principle advantages offered by the modified cell were the ability to photolyze directly and the elimination of the frost problem on the dewar surface. The absorption attributed to the diazene was determined after subtracting that due to the hydrazone **20**. The diazene extinction coefficient was calculated after precise measurement of the cell path length at room temperature, using potassium chromate as a standard.

Determination of Extinction Coefficients of 3,4-Dimethylenefuran and -thiophene. Method 1. In a 4 × 6 mm Pyrex cell, whose path length was also checked using a solution of potassium chromate, was placed 15 μL of the above thiophene diazene (**18**) solution which was used to measure its extinction coefficient. This aliquot was diluted with 800 μL of 2-methyltetrahydrofuran and 50 μL of acrylonitrile. The final diazene (**18**) concentration was therefore calculated to be 0.47 mM. After having been degassed and sealed in the usual manner, the sample was placed in the low temperature apparatus illustrated in Figure 7. The UV absorption spectrum of the sample was recorded at 77 K before photolysis. The sample was irradiated directly through a resealable hole in the wall/mount. The infrared output of the 200-W high-pressure Hg arc lamp was filtered with the use of a 5 cm long solution cell filled with H_2O. Spectra were recorded after 15, 30, 45, and 75 min of photolysis. The point of maximum absorbance was assumed to correspond to 100% diazene consumption. Upon thawing, the sample cell was warmed to −78 °C, whereupon its seal was broken, and dimethyl fumarate (84.5 mg, 0.59 mmol) in 250 mL of THF was added. The cell was then allowed to stand at room temperature for 4 h. After concentration of the solution in vacuo, products were assayed by capillary GC (Varian, 25 m, phenyl methyl silicone).

Method 2. Degassed MTHF solutions (0.028 M and 0.031 M in **18** and **17**, respectively) were positioned in the original stationary apparatus as described above. UV absorption spectra were recorded twice over the complete spectral range (700–320 nm). In addition, the absorbance at the λ_{max} of the respective diazenes was measured over a period of 5–10 min in order to demonstrate the precision of the absorption measurement. Spectra were recorded in a similar manner after photolysis with a fiber optics light pipe assembly. The concentration of either diradical was ascertained from the change in concentration of its diazene precursor.

Wavelength-Dependent Photochemistry of 3,4-Dimethylenethiophene. Pyrex-Filtered, 450-W Medium-Pressure Hanovia Photolysis. Diazene **18** (0.107 M) in MeOH-d_4 was placed in a 5-mm Pyrex NMR tube. The tube was degassed and sealed in the usual manner. A 250-MHz ^{1}H NMR spectrum was recorded at 243 K. Photolysis at 77 K was accomplished by placing the NMR tube in the quartz-tipped dewar filled with liquid nitrogen. The dewar stood adjacent to the Pyrex immersion well containing the medium-pressure 450-W Hanovia lamp. After 6 h of photolysis, the purple tube was transferred to the cold NMR probe again, and its spectrum was recorded. The extent of diazene decomposition was determined after comparing the integration of its signals versus residual protiomethanol before and after photolysis.

Band-pass-Filtered, High-Pressure Hg Arc Photolysis. A 4.06 mM 2-methyltetrahydrofuran solution of **18** was degassed and sealed in a 4-mm i.d. quartz-tipped tube. 3,4-Dimethylenethiophene was generated by photolysis through the above liquid nitrogen filled quartz-tipped dewar, employing band-pass filtering (Oriel #51810). Filtering was then switched to a combination of long-pass (50% transmission at 455 nm) and infrared-blocking filters (Oriel #51484 and #52060 respectively). No visible dissipation of color was observed after 6.5 h of photolysis.

Quartz-Filtered, High-Pressure Hg Arc Photolysis. In a 4-mm i.d. quartz-tipped tube, 200 μL of a 0.05 M 2-methyltetrahydrofuran solution of **18** was degassed and sealed under vacuum in the usual manner. After 1 h of photolysis at 77 K, Pyrex filtering was removed, leaving only the water cell to absorb the infrared irradiation. The infrared-filtered photolysis was continued at 77 K for 6.5 h. After this period of photolysis, no observable bleaching of the sample had occurred. Capillary GC analysis (50 m, methyl silicone) after thawing did not indicate the presence of any 3-thiabicyclo[3.2.0]hepta-1,4-diene (**30**).

Extent of Photoconversion of 18 to 3,4-Dimethylenethiophene at 77 K. A 30 mM (MeOH-d_4) solution of **18** in a 5-mm NMR tube was degassed and sealed in the usual fashion. ^{1}H NMR (250-MHz) spectra were recorded at 263 K before and after photolysis at 77 K. The sample was irradiated for 40 min with a 200-W high-pressure Hg arc lamp, with a band-pass filter (Oriel #51810) and a water cell to absorb IR radiation. Similarly, a MeOH-d_4 solution of **18** (0.11 M) was irradiated at 77 K for 6 h with a 450-W medium-pressure Hanovia lamp, with only Pyrex and water filtering.

Generation of 3,4-Dimethylenethiophene 7 from 3,4-Bis(chloromethyl)thiophene (21). About 1 mL of a solution 0.002 M in the dichloride **21**[43] and 0.02 M in the tetramine **22** (Aldrich) in methylcyclohexane (Fisher), which had been purified by passage through a plug of activated alumina and deaerated by a stream of N_2, was placed under N_2 in a 0.3-cm quartz optical cell equipped with a graded seal to Pyrex tubing. After three freeze–pump–thaw cycles, the cell was sealed under vacuum. The sample was then immersed in an unsilvered Pyrex dewar flask containing liquid N_2, and the UV–vis spectrum of the resulting glass was recorded (Figure 6C). The dewar unit was then removed from the spectrometer housing, and the sample was irradiated at 77 K for 5 min with IR-blocked light from a 200-W high-pressure Hg arc lamp. This produced a blue matrix whose spectrum is shown as Figure 6B. The optical density at 572 nm at this point was ~0.8. With $\epsilon = 5400$ M^{-1} cm^{-1} and $l = 0.3$, we calculate an approximate concentration of 0.5 mM **7**, which corresponds to ~25% conversion of the starting dichloride **21**.

Photobleaching of 3,4-Dimethylenefuran. A degassed and sealed 0.05 M solution of **17** in diethyl-d_{10} ether was photolyzed at 77 K for 2 h and 40 min. The photolysis was conducted at 77 K using the previously described Hanovia set up (see Pyrex Filtered 450-W Medium-Pressure Hanovia Photolysis). A comparison of the 250-MHz ^{1}H NMR spectra at 183 K before and after photolysis revealed new signals at δ 9.8 (s, 1 H), 7.6 (s, 1 H), 6.73 (s, 1 H), 6.68 (s, 1 H), 1.00 (s, 2 H) and complete consumption of the diazene. Similar treatment of a solution of bis-^{13}C-**18**[27] (0.135 M) in 2-methyltetrahydrofuran gave rise to two new ^{13}C signals (62.5 MHz) at 3.65 and 138.6 ppm.

Trapping of 3,4-Dimethylenefuran Photobleaching Product 23 (2-(1′-Cyclopropenyl)-2-propenal) with 1,3-Diphenylisobenzofuran. A degassed and sealed solution (5 mL) of **17** (29 mM) in 2-methyltetrahydrofuran was photolyzed at 77 K with Pyrex and water to filter the polychromatic output of the 200-W high-pressure Hg arc lamp. After the glass had become colorless (~3 h), the sample was thawed and warmed to −78 °C. The seal was broken, and the tube was placed under a nitrogen atmosphere. Ten equivalents (39.5 mg, 0.146 mmol) of 1,3-diphenylisobenzofuran was added in 500 mL of THF. After warming to room temperature over the course of 6 h, the solvent was removed in vacuo. Column chromatography (gradient elution, 0–5% pentane/ether) yielded 16.1 mg (30%) of a 1:1 adduct ($R_f = 0.18$, 10% ether/pentane): ^{1}H NMR (250 MHz, $CDCl_3$) δ 9.24 (s, 1 H), 7.60–7.76 (m, 4 H), 7.43–7.49 (m, 6 H), 7.10–7.27 (m, 4 H), 5.96 (s, 1 H), 5.95 (s, 1 H), 2.50–2.54 (dd, 1 H, $J = 6.9, 4.1$ Hz), 2.38–2.41 (dd, 1 H, $J = 4.9, 4.1$ Hz), 2.03–2.08 (dd, 1 H, $J = 4.9, 6.9$ Hz); FTIR ($CDCl_3$) 1696 cm^{-1}; DIP/MS ($T_{initial} = 30$ °C, rate = 30 °C/min, $T_{max} = 300$ °C, $t_R = 2.1$ min) m/e 365 ($M^+ + 1$, 6.8), 364 (M^+, 25), 346 ($M^+ - 18$, 57), 270 (M^+

---

[43] Zwanenberg, D. J.; Wynberg, H. *J. Org. Chem.* **1969**, *34*, 333. The sample was purified by preparative GC on a 5 ft × $^1/_4$ in. 20% OV-101 column.

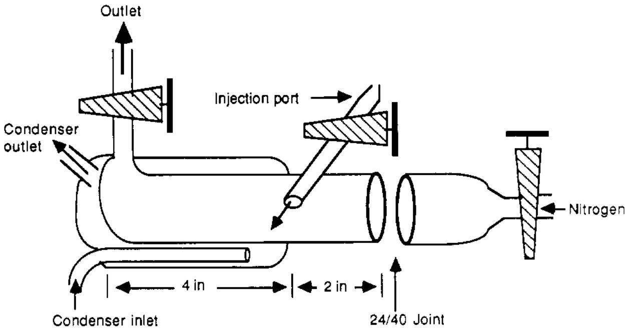


Figure 8. Polymer film deposition apparatus.

- 94, 57%), 259 (M^+ - 105, 69), 105 (M^+ - 261, 83), 77 (M^+ - 287, 100); exact mass calcd for $C_{26}H_{20}O_2$ 364.1464, found 364.1447.

High-Temperature Matrix Isolation of 3,4-Dimethylenethiophene and -furan. A. Deposition of Polymeric Film. Nitrogen was bubbled through a dichloromethane solution (10 mL) containing 250 mg of polymer (either polystyrene or poly(methyl methacrylate)) and **18** or any other substrate (~2 mg) for 3.5 h. During this time, the stirred solution was kept between -15 °C and -50 °C. After purging, the solution was kept under N_2 as 1-mL aliquots were injected into the deposition apparatus depicted in Figure 8. Coolant (-20 °C) was passed through the condenser of the apparatus, which was wrapped with glass wool and aluminum foil. Nitrogen gas, which was passed through coils immersed in a dry ice/acetone bath, was rapidly blown over the deposited solution. When all of the dichloromethane solution was added (~4–6 h), N_2 flow was continued for an additional 4 h before the film was kept under mechanical pump vacuum at -20 °C overnight.

The following morning, the apparatus was vented with N_2 and quickly opened, whereupon the polymer sheet was removed. The sheet either was immediately placed in a tube or mounted using silicone grease to hold it in place on a flat piece of Pyrex with an extension, so as to allow its examination in the portable UV dewar. Samples placed in a tube for photolysis were degassed ($<10^{-6}$ Torr) at -78 °C for 3 h and then sealed.

B. Impregnation of Adamantane. Adamantane (150 mg), in a 15-mL pear-shaped flask with side arm, was taken up in 0.5 mL of dichloromethane and 0.5 mL of pentane. The adamantane was not completely soluble in this mixture, and 0.25 mL of diethyl ether and 1.0 mL of benzene were added. The flask was immersed in an acetone/ice bath (~-8 °C), whereupon some of the adamantane precipitated. A 0.5-mL portion of a methylene chloride solution of **18** (0.05 M) was added to the heterogeneous mixture. After having been stirred for several minutes, the sample was placed under vacuum. A good deal of splattering and bumping accompanied the removal of the solvent. After the solvent was removed entirely, the vessel was vented to N_2 and allowed to warm to room temperature. The lower part of the flask's inner walls, which were partially covered with adamantane, remained colorless. After several hours, this surface acquired a brownish tinge, but a Teflon-coated stir bar, which was partially encrusted with adamantane, appeared to exhibit the purple color characteristic of 3,4-dimethylenethiophene. This color seemed to appear within a few minutes of warming and persisted at room temperature under N_2. It disappeared irreversibly upon warming the flask with a heat gun. Subsequent GC/MS analysis did not reveal the presence of any 3-thiabicyclo[3.2.0]hepta-1,4-diene (**30**).

Electron Spin Resonance (ESR) Studies of 3,4-Dimethylenethiophene. ESR studies were performed on freshly prepared samples of **18** (0.015–0.05 M). Freshly distilled MTHF or ethanol were used as solvents. The samples in 4-mm i.d. Pyrex tubes with quartz tips were subjected to three freeze–pump–thaw cycles and then sealed under vacuum. The tubes were placed in the cavity of the ESR spectrometer and cooled to either 77 K or 9 K, with liquid nitrogen or liquid helium, respectively. Photolysis was carried out inside the ESR cavity using the output from the 200-W high-pressure Hg arc lamp, with a focusing lens and the previously described band-pass and IR filters. That photolysis actually occurred was confirmed by visual examination for the characteristic purple color, which was readily seen.

Studies performed on impregnated poly(methyl methacrylate) samples (prepared as described above) were accomplished by placing the films inside standard ESR tubes, degassing at -78 °C, and sealing under vacuum. The tubes were photolyzed outside of the cavity, so the quantity of the diradicals could be more easily estimated. Photolysis was continued until no further increase in the purple color was apparent. After ESR spectroscopic scrutiny, the samples were removed from the cavity at the maximum temperature to verify the presence of the purple transient.

ESR Instrument settings: receiver gain, 5×10^3–2.5×10^4; modulation amplitude, 2.0×10^{-1}–2.0×10^1; time constant 0.1–0.3 s; scan rate, 2–8 min.

Calculations. All of the AM1 calculations were performed on a Digital VAX 11/750 computer with AMPAC Version I[44] equipped with a modified CI capability. A slight modification of the CI Fortran code proved to be necessary to achieve the desired versatility in choosing the amount of CI used in the calculation. Our modified package allows (a) calculation of CI wave functions with up to 400 microstates, (b) truncation of orbital designated CI space to any number of lowest energy microstates, and (c) control of CI matrix output size.

A. UHF Calculations. The AM1/UHF calculations are geometry optimized at each state within molecular symmetry constraints (C_{2v} for **3**, **6–8**, and **10**, D_{2h} for planar **1**, D_{2d} for bisected **1**, and C_s for **9**). Singlet states emerge significantly spin contaminated, with $\langle S^2 \rangle = 1.1$–$1.5$, and triplet states are mildly so, with $\langle S^2 \rangle = 2.2$–$2.4$. Despite the contamination, $\Delta E_{S,T}$ values and trends determined by AM1/UHF compare favorably with those determined by the spin-exact CI methods, and the UHF calculations permit time-efficient geometry optimizations.

B. CI Calculations. Most of the AM1/CI calculations used π-orbital CI only. An exception was the calculation for the pyrrole derivative **8**, which used the CI space involving the three highest filled orbitals (all π) and the three lowest unfilled orbitals (two π, one σ). For **10**, complete π-CI (four π-electrons, four π-orbitals: 36 singlet microstates) with quintet reference orbitals were used, and state geometries were independently optimized at this level. The other compounds of Figure 2 were calculated by six orbital π-CI (six π-electrons, six π-orbitals: 400 microstates) using the 100 lowest energy microstates. Again, quintet reference orbitals were used, except for **8** and **9**, where triplet reference orbitals were used to avoid a partially filled σ-orbital in the reference configuration. For **6** and **7**, triplet and singlet states were independently geometry optimized at this level. For **1**, **3**, **8**, and **9**, single-point CI calculations at AM1/UHF triplet geometries[45] were used. Vertical $\Delta E_{S,T}$ values for **6** and **7** calculated at AM1/UHF geometries were within 0.7 kcal/mol of those obtained with CI-optimized geometries at each state. Single-point calculations using all 400 microstates for **6** and **7** give $\Delta E_{S,T}$ values within 0.2 kcal/mol of those reported in Figure 2. We therefore feel that truncation of the complete set of p excited states to 100 microstates is justified for the purpose of time efficiency, although in other work on the estimation of electronic excitation energies, we have used full π-CI (400 microstates).

Acknowledgment. We thank the National Science Foundation for support of this work, and the Dox Foundation and the American Cancer Society for graduate and postdoctoral fellowships (to M.M.G. and K.J.S., respectively). Professor M. S. Platz kindly sent us a preprint of ref 25 in advance of publication. We also thank Stephen Blackstock for technical assistance in the modification of the AMPAC program.

Registry No. **1**, 16893-57-5; **3**, 117185-09-8; **6**, 95406-66-9; **7**, 105064-76-4; **8**, 105183-40-2; **9**, 95406-67-0; **10**, 13001-05-3; **17**, 105064-77-5; **18**, 114563-79-0; **21**, 18448-62-9; **22**, 996-70-3; **23**, 119656-70-1; **24**, 119656-71-2; 1,3-diphenylisobenzofuran, 5471-63-6.

---

(44) (a) Reference 18. (b) We thank Dr. T. Clark for providing us with a copy of AMPAC capable of assigning molecular and orbital symmetries and equipped with a speed enhanced diagonalization routine.

(45) Precedent for this procedure is found in the work of Borden, W. T.; Davidson, E. R.; Feller, D. *Tetrahedron* **1982**, *38*, 737.