Tuning the Singlet−Triplet Energy Gap in a Non-Kekulé Series by Designed Structural Variation. The Singlet States of *N*-Substituted-3,4-dimethylenepyrrole Biradicals

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Abstract: Semiempirical quantum chemical calculations (AM1/CI and PM3/CI) confirm the qualitative perturbational prediction that electron-withdrawing groups on the ring nitrogen of a 3,4-dimethylenepyrrole should diminish the energy separation of the singlet and triplet states to near zero. Syntheses of a series of precursors of such biradicals have been developed. Study of the chemistry and spectroscopy of the biradicals has revealed persistent singlet states for the cases where the substituent is methyl, isobutyryl, and pivaloyl. In the cases of *N*-arenesulfonyl-3,4-dimethylenepyrroles, both a singlet and a triplet form can be observed as persistent species. In this paper, the properties of the singlets in this series are described. Although energy transfer from the excited triplet state of the sensitizer xanthone to the diazene precursor of *N*-*p*-toluenesulfonyl-3,4-dimethylenepyrrole is observed by nanosecond time-resolved spectroscopy, the chemical behavior of the biradical intermediate is the same as that observed in the direct photolysis or thermolysis of the diazene. The reactive form of the biradical under these conditions appears to be the singlet.

Experimental Design. Tuning the Multiplet Gap in *N*-Substituted-3,4-dimethylenepyrrole Biradicals. Prediction of the spacings of the lowest energy multiplets of π-conjugated non-Kekulé molecules is a stringent test of theory. Although in most cases these separations are difficult to measure, the effect of structure on the qualitative trends of their direction and magnitude should be estimable by theoretical calculation. We are particularly attracted to the use of computationally designed systematic structural variations as means of tuning the spacings and hence providing experimental tests of such estimates. The necessary elements of this approach are a parent system with near-degenerate multiplet states, a variable structural feature that can be used to perturb their separation, and a theoretical means for selecting potentially fruitful structural alterations. Since the singlet−triplet gap in such species can be made quite small, the tuning process ultimately might offer the power of choice over the multiplicity of the ground state.

The disjoint hydrocarbon biradical tetramethyleneethane (TME, **1**) provides a useful starting structure for such a process. Although the size of the energy separation between the lowest triplet and singlet states of TME is not yet known from experiment, theory[2] predicts a very small gap ($E_T − E_S \sim −1$ to $+2$ kcal/mol). A heteroatom bridge connecting two termini of the TME molecule, as in previous work[3] from this laboratory on 3,4-dimethylenefuran and 3,4-dimethylenethiophene, introduces a variable source of electronic perturbation.
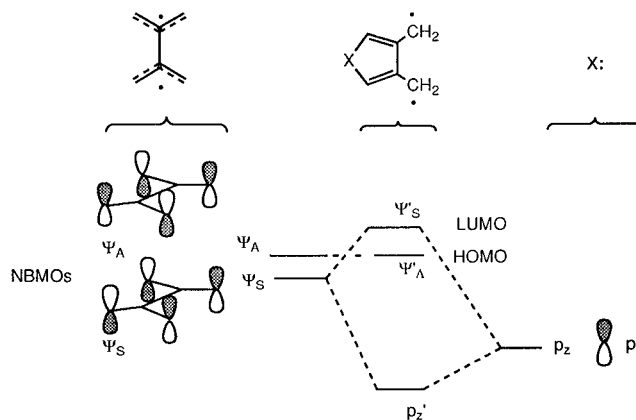

Figure 1. Perturbative interaction of filled heteroatomic p-π orbital with the NBMOs of TME.[4]

The present paper describes the preparation and characterization of the singlet states of several such biradicals, and an accompanying paper[11b] reports results of the search for the corresponding triplet states.

Our present computational approach was implicit in theoretical considerations by Du, Hrovat, and Borden,[4] which were further developed in later corollaries.[3,5,6] Figure 1, a diagram-

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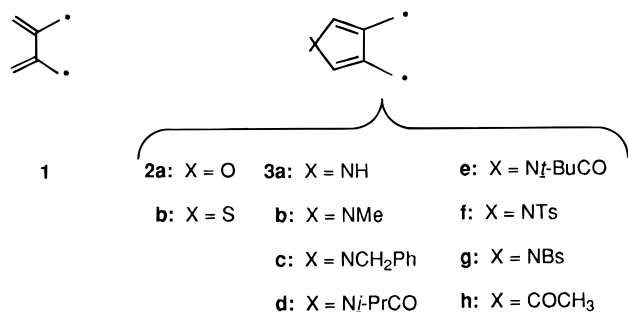
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matic display of the concept, shows the effect of a heteroatom on the frontier orbitals of the disjoint hydrocarbon tetramethyleneethane (TME, **1**). Note that the symmetric component of the TME frontier orbitals is of the proper symmetry to mix with the p_z orbital of the heteroatom X. Thus, in the 3,4-dimethyleneheterocycle, e.g., **2a,b** and **3a−h**, the relative energies of

1

2a: X = O	**3a:** X = NH	**e:** X = N*t*-BuCO
b: X = S	**b:** X = NMe	**f:** X = NTs
	c: X = NCH₂Ph	**g:** X = NBs
	d: X = N*i*-PrCO	**h:** X = COCH₃

the original TME NBMOs (ψ_A, ψ_S) are perturbed by an amount that, to first order, will be inversely proportional to the energy separation between one of them and the lone-pair p_z orbital.

An oversimplified but graphic way to think about the perturbation and its consequences starts with the recognition[4] that the orbital (ψ_S) that is of the proper symmetry to interact with the p_z orbital is initially lower than ψ_A, which is not perturbed by p_z. Therefore, the perturbation of ψ_S by p_z, if *weak*, could bring ψ_S and ψ_A closer together than they are in TME itself, thereby tending to favor a triplet ground state, but if *strong*, could drive Ψ_S enough higher than ψ_A to favor a singlet. Both of the previous examples (**2a,b**) of heterocyclic TME derivatives have singlet ground states whose chemistry is consistent with an S-above-A ordering of the frontier orbitals,[3] which suggests that the perturbations by O and S in the furan and thiophene cases is of the *strong* type.

In the case of the pyrrole TME derivative **3a**, one would expect (and calculations[4−6] confirm) that the perturbation would be even stronger than in the furan and thiophene systems. However, the functional nature of the NH group in the pyrrole offers a special opportunity to manipulate the electronegativity of the heteroatom by replacing H with electron-releasing or electron-withdrawing groups (ERG or EWG) and hence to tune the singlet−triplet gap by variations of the molecular structure. EWGs, for example, would lower the energy of the lone pair p_z orbital in Figure 1 and thereby decrease the perturbation of the symmetric component of the TME NBMOs. A sufficiently EW substituent should result in a triplet−singlet gap similar to those in hydrocarbon TMEs. Three examples of such hydrocarbons exist: TME (**1**) itself,[7] as well as two derivatives, 2,3-dimethylenecyclohexa-1,3-diene (**4**)[8] and 5,5-dimethyl-2,3-dimethylenecyclopenta-1,3-diene (**5**).[9] Experimentally, all three

4   **5**
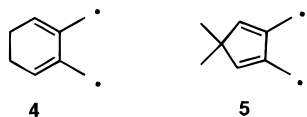
of these compounds have been shown to have thermally accessible and persistent triplet states. Since in the parent NH case **3a**,[3−6] the singlet is predicted to lie only slightly below the triplet, strong EWGs should be able to narrow the multiplet
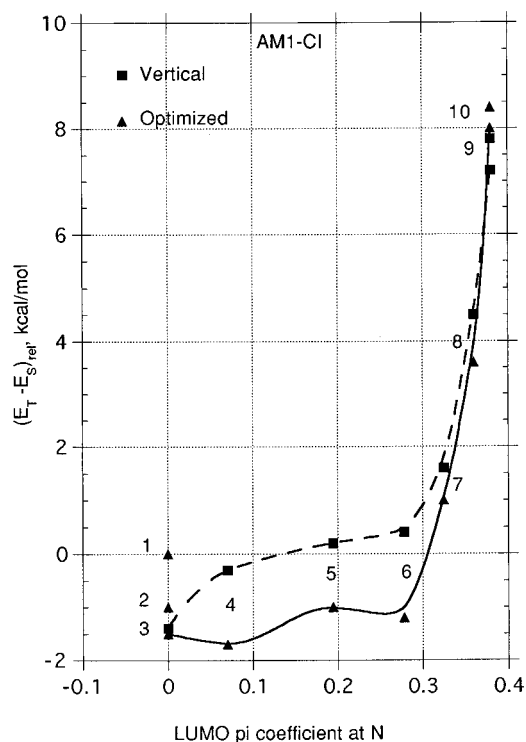
Figure 2. Calculated vertical and optimized triplet−singlet energy separation (relative to that of TME set as zero) as a function of the LUMO π-electron coefficient at N for a series of *N*-substituted-3,4-dimethylenepyrroles and other biradicals. The values were obtained with AM1, OPEN (4,4)CI. The points 1−3 represent compounds as follows: (1) TME, **1**; (2) DCP, **6**; (3) 3,4-dimethylenepyrrolium ion, **7**. Points 4−10 represent *N*-substituted-3,4-dimethylenepyrroles with substituents as follows: (4) *p*-nitrobenzoyl; (5) *p*-benzoylbenzoyl; (6) benzoyl; (7) acetyl; (8) cyano; (9) methyl; (10) hydrogen. The curve is merely a smooth connection of the points.

gap or even reverse the preference and make the triplet the ground state. A goal of the present work is to find examples of this inversion of spin multiplet energies and thereby demonstrate the predicted perturbative effect.

AM1/CI Calculations. Semiempirical calculations with configuration interaction (CI)[3c,5,10] can provide quantitative estimates for the perturbative effect of the N-substituents on the separation of the multiplet energies. We now[11] have applied the AM1/CI method[12] to this problem in the cases of the pyrrole series shown in Figure 2. In order to avoid the interaction of configurations containing σ-MOs, which usually led to spin contamination of the states and impeded standardization of the CI level across the series, we chose as CI space all configurations in which four valence electrons freely occupied four orbitals around the nonbonding level (two above and two below). This reference state, OPEN(4,4), provided a reasonable level of CI while keeping the interaction restricted to π-MOs.

The effect of geometry was studied by performing two sets of calculations of the multiplet separation ($E_T - E_S$), one for the "vertical" separation of the states when both the singlet and triplet are assumed to have the geometry optimized for the spin

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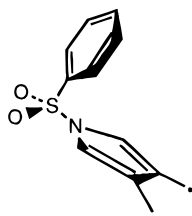
Figure 3. Structure of *N*-benzenesulfonyl-3,4-dimethylenepyrrole biradical as calculated by PM3/CI. Values of bond lengths and angles are given in the text.

state of lower energy, and one for the states with geometries individually optimized. In all of the pyrroles, the nitrogen and its ligand bonds were found to be planar within a few degrees. Whether the actual nitrogen configuration is slightly pyramidalized cannot be answered with confidence from the AM1/CI calculations, since the results seemed to depend upon the level of CI used. In all the calculations, the CH_2 groups were assumed to be coplanar with the heterocyclic ring. Justification of this assumption is given elsewhere.[11c]

Figure 2 provides gratifying computational confirmation of the qualitative perturbational ideas. The LUMO coefficient on nitrogen is taken as a measure of the mixing of the nitrogen lone pair orbital with the TME NBMOs (see Figure 1). The shapes of the curves of Figure 2 are in accord with the expectation that this mixing should decrease as the N-substituent becomes more electron-withdrawing and that, ultimately, the multiplet separation should approach those of the parent hydrocarbons TME (**1**) and 2,3-dimethylenecyclopenta-1,3-diene (DCP, **6**). As a model for a 3,4-dimethylenepyrrole with the TME NBMO-N: interaction fully switched off, we used the hypothetical N-protonated pyrrolium ion species **7**.
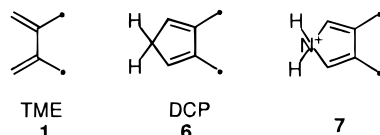
The absolute value of the multiplet gap $(E_T - E_S)$ calculated for TME by the AM1/CI procedure is 7 kcal/mol, which is substantially larger than that obtained by ab initio methods. As we have noted above, triplets have been observed for TME and two derivatives, so that it is likely that the actual gap is small. For the purpose of scaling, we assume that the predictions of the gap by ab initio methods are more accurate than the semiempirical ones, and we arbitrarily assign the gap for TME as 0.0 kcal/mol (see Figure 2) by reference to the small calculated[2] ab initio value. The absolute values of $(E_T - E_S)$ calculated by AM1/CI for the other molecules then are diminished by 7 kcal/mol to give $(E_T - E_S)_{rel}$, thus scaling them to the TME ~ 0 standard. This step cannot be defended rigorously, since there is no guarantee that the departure of the AM1/CI calculated value from the true value is the same in all cases. However, some confidence in the validity of the procedure is provided by the reasonably close match of the scaled AM1/CI value of $(E_T - E_S)_{rel}$ for the NH case **3a**, 8.4 kcal/mol, with the MRSD CI ab initio absolute $(E_T - E_S)$ value, 6.8 kcal/mol.[4] Nevertheless, although the resulting curves of Figure 2 are anchored by reference to ab initio values at both ends, they should be interpreted as indicative of trends rather than as quantitative predictions of the multiplet gaps.

Figure 2 (point 3) shows that in the pyrrolium ion **7**, the N-protonation indeed effectively has turned off the TME NBMO-N lone-pair interaction, as would be expected intuitively. $(E_T - E_S)_{rel}$ is about −1.5 kcal/mol for this biradical, a value

very close to that calculated (point 2, −1.0 kcal/mol) for the hydrocarbon DCP **6**. The effect of geometry optimization for the most EWG-substituted cases (points 4−6, Figure 2) is mainly to lower the $(E_T - E_S)_{rel}$ values.

Both of the curves of Figure 2 decline to nearly flat plateaus in the region of $(E_T - E_S)_{rel} \sim 0$ to −1 kcal/mol. Thus, in the context of the current work, the main message to be read from Figure 2 is that an *N*-alkyl group (*cf.* methyl, point 9) should result in a singlet 3,4-dimethylenepyrrole, and an acetyl substituent (point 7) may be too weakly electron-withdrawing to overcome the preference for a singlet, but 3,4-dimethylenepyrroles with EWG N-substituents as strong as *p*-nitrobenzoyl (point 4) or stronger should produce an accessible triplet state. As tests of these predictions, we have synthesized and studied, with varying degrees of scrutiny, a number of *N*-substituted-3,4-dimethylenepyrroles, including the methyl and benzyl derivatives **3b,c** as examples of cases in which a singlet state is clearly predicted, the isobutyryl and pivaloyl derivatives **3d,e** as examples of moderately EWG cases, and the *p*-toluenesulfonyl and *p*-bromobenzenesulfonyl derivatives **3f,g** as examples bearing strong EWGs. We chose the arenesulfonyl derivatives instead of the *p*-nitrobenzoyl derivative because of anticipated experimental problems in handling the latter hydrolytically active amide. Because the AM1/CI program was not parameterized for sulfonyl functionality, we could not confirm computationally the expected location of the arenesulfonyl points in the plateau region of Figure 2. Our working hypothesis that arenesulfonyl substituents would be sufficiently strong EWGs was based on the assumption that the EW power of the substituent might be estimated roughly by comparison of the acidities of the corresponding acids, which show arenesulfonic acids (pK_a −7) to be much stronger even than *p*-nitrobenzoic acid (pK_a 3.4).

Molecular Geometries by PM3/CI Calculations. We were able to calculate molecular geometries for the benzenesulfonyl derivative by means of another semiempirical algorithm, PM3/CI,[12] which is parameterized for this group. As calculated by PM3/CI, both the singlet and triplet states of the *N*-benzenesulfonylpyrrole biradical prefer the conformation shown in Figure 3. The phenyl and pyrrole rings lie in planes related by the *N-S*-phenyl ipso C angle of ∼100°. This conformation is close to that determined[13 a] by single crystal X-ray analysis for *N*-benzenesulfonylpyrrole, which also shows the rings in nearly perpendicular planes, with the *N-S*-phenyl ipso C angle of ∼105°. In the biradical, the plane defined by these three atoms bisects the O−S−O angle, placing the oxygens on one side of the plane defined by the nitrogen and its attached carbons. The latter structural feature matches that calculated[13b] by ab initio methods for *N*-methylmethanesulfonamide, in which the oxygens lie on one side of the H−N−methyl C plane. It should be noted that although the PM3/CI calculations on *N*-benzenesulfonyl-3,4-dimethylenepyrrole again show little or no pyramidalization at nitrogen, the ab initio calculation[13b] of *N*-methylmethanesulfonamide predicts that a pyramidalized configuration for nitrogen is preferred in that case.[14]

The experimental studies now have demonstrated the existence of persistent singlet states for the *N*-methyl-, *N*-isobutyryl-, and *N*-pivaloyl-3,4-dimethylenepyrroles and of persistent triplet states for the *N*-tosyl and *N*-brosyl compounds. The latter two findings bring welcome confirmation of the validity of the experimental design, but an unexpected complication has

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Scheme 1[a]
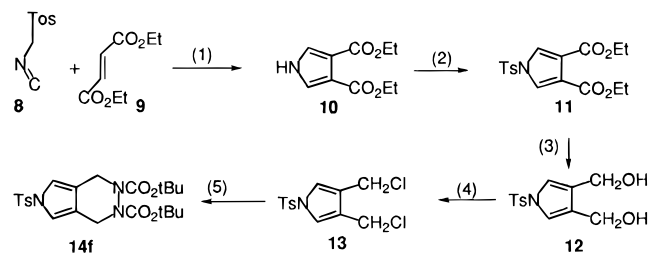
[a] **Methods:** (1) KO*t*-Bu, 18-Crown-6, THF, 63%; (2) TsCl, Bu$_4$NHSO$_4$, KOH, CH$_2$Cl$_2$, 91%; (3) DIBAL, CH$_2$Cl$_2$, 77−91%; (4) Ph$_3$PCl$_2$, CH$_2$Cl$_2$, 78%; (5) N$_2$H$_2$(CO$_2$*t*-Bu)$_2$, NaH, DMSO, 87%; alternatively, **14f** can be obtained in lower yield (67%) but more conveniently by using KO*t*-Bu in THF as the base.

emerged in that we also have found strong evidence of the existence of persistent *singlet* states of the two arenesulfonyl derivatives.

The present paper describes the properties of these singlet biradicals. Experimental documentation is given in three sections: synthesis of the biradical precursors and generation of the biradicals; preparative reaction chemistry of the biradicals and its implications for assignments of the spin multiplicity of the reactive transients; and spectroscopic characterization of the biradicals. An accompanying paper[11b] deals with the triplet states.

Synthesis of N-Substituted-3,4-dimethylenepyrroles. Our first samples of the desired diazene precursors **17a** of *N*-substituted-3,4-dimethylenepyrroles were obtained by rather impractical routes described elsewhere.[11a,17b] Currently we prefer the synthetic approach shown in Scheme 1. It is based upon the ready availability of 3,4-dicarboethoxypyrrole **10** from the *p*-tosylmethyl isocyanide−fumaric ester addition[15−17] and incorporates as a crucial modification the use of the N-tosyl group in the intermediate **13** to suppress the heterolytic reactivity of the chloromethyl groups. Specific methods (Schemes 1 and 2) for the conversion of **10** via **13** to the key intermediate *N*-tosylpyrrolodihydropyridazine biscarbamate **14f** and for the replacement of the tosyl group of **14f** by other N-substituents permit its application to a variety of derivatives.
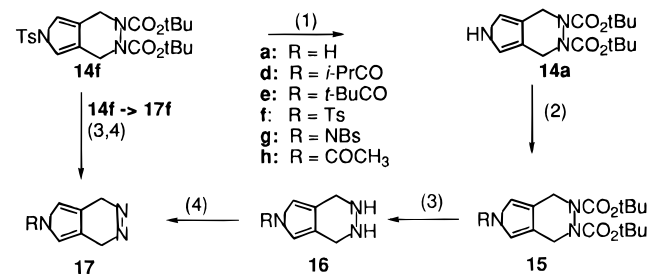
Detosylation of **14f** is effected smoothly by direct saponification with KOH in methanol−THF. The key to the latter process is the resistance of the *tert*-butyl ester functions of the biscarbamate **14f** to alkaline hydrolysis, which permits the selective removal of the tosyl group.[18] Introduction of other substituents on the nitrogen then can be achieved by acylation with an *N*-acylimidazole in the presence of cesium carbonate.

Scheme 2[a]

[a] **Methods:** (1) KOH, MeOH−THF, 70−80%; (2) *N*-acyl- or *N*-arenesulfonylimidazole, Cs$_2$CO$_3$, 90%; (3) HCl (g), Et$_2$O, 85−100%; (4) DMAD.

The *tert*-butyl ester groups of **14f** or of the other N-substituted analogues can be removed with hydrogen chloride in diethyl ether (Scheme 2) to give the hydrazines **16d−f**, which can be converted to the *N*-isobutyryl (**17d**), *N*-pivaloyl (**17e**), *N*-tosyl (**17f**), *N*-brosyl (**17g**), or potentially other diazenes by the usual[3b,c] dimethyl azodicarboxylate (DMAD) dehydrogenation procedure.

Chemistry of the N-Substituted-3,4-dimethylenepyrrole Biradicals from Diazenes 17. **Thermal and Direct Photochemical Generation and Capture**. The chemical interception experiments now to be described were intended to answer two questions: (1) Does the deazetation of a diazene **17** lead to a capturable transient 3,4-dimethylenepyrrole biradical intermediate of structure **3**? (2) If so, is this same intermediate the carrier of the visible color and UV−vis spectrum observed spectroscopically by the methods described below? For question 1, we applied preparative and kinetic procedures used[3] earlier in the cases of the analogous biradicals 3,4-dimethylenefuran **2a** and 3,4-dimethylenethiophene **2b**. Question 2 also can be addressed through an established method.[3,17,19,20] Relative reactivities of a series of trapping olefins, as determined by preparative competition experiments, constitute a characteristic fingerprint for the reactive intermediate. An independent fingerprint is based upon the reactivities determined by direct time-resolved spectroscopic observation of the quenching of a transient chromophore. If the two fingerprints match, the evidence becomes persuasive that the carrier of the spectroscopic signal truly has the structure of the preparatively significant intermediate.

Although much of our detailed knowledge of these biradicals comes from photochemical studies (see below), we also have generated what probably are the same species by thermal deazetation of the corresponding diazenes. The thermal stability (and hence the ease of manipulation) of these precursors is a sensitive function of the nature of the N-substituent. For example, the *N*-methyl diazene **17b** is unstable above −60 °C, but the *N*-tosyl diazene **17f** is reasonably stable at 0 °C. As monitored by ^{1}H NMR spectroscopy, tosyl diazene **17f** decom-

(14) The PM3/CI calculations of $(E_T − E_S)_{rel}$ gave a plot very similar in shape to that obtained with AM1-CI. Again, EW substituents caused a steep diminution of the multiplet energy gap, and the curve reached a plateau of small-to-zero gap. However, the restriction to π-orbitals in the CI space was difficult to achieve in this set of calculations, and the real significance of the $(E_T − E_S)_{rel}$ results is dubious. For example, a closer inspection reveals that although the shape of the PM3/CI and AM1-CI curves are similar, the actual *order* of the points is disturbingly different. Thus, although we had expected arenesulfonyl to be more effective than acetyl in diminishing the preference for the singlet, the PM3-CI calculations reversed this order, predicting that acetyl would be more effective than benzenesulfonyl. Fortunately, our experimental results eventually showed that arenesulfonyl was better for our purpose than aliphatic acyl, although the reasons for this turned out to be more intricate than the simple EWG considerations that had guided our earlier thinking.

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(18) (a) The replacement of *N*-arenesulfonyl groups with hydrogen by photolysis of sulfonamides in the presence of NaBH$_4$ has been reported.[18b−f] We also have applied this reaction to the cases of the tosyl derivative **14f** and the corresponding benzenesulfonyl derivative. (b) Abad, A.; Mellier, D.; Pète, J. P.; Portella, C. *Tetrahedron Lett.* **1971**, 4555. (c) Mellier, D.; Pète, J. P.; Portella, C. *Tetrahedron Lett.* **1971**, 4559. (d) Umezawa, B.; Hoshino, C.; Sawaki, S. *Chem. Pharm. Bull.* **1969**, *17*, 1115; 1120; **1970**, *18*, 182. (e) Art, J. F.; Kestemont, J. P.; Soumillion, J. Ph. *Tetrahedron Lett.* **1991**, *32*, 1425. (f) Horspool, W. M. In *The Chemistry of Sulphonic Acids, Esters and their Derivatives*; Patai, S, Rappoport, Z., Eds.; John Wiley: New York, 1991; Chapter 13. (g) Pillai, V. N. R. *Org. Photochem.* **1987**, *9*, 225.

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Scheme 3

R = *t*-BuCO (**e**)
or Tosyl (**f**)
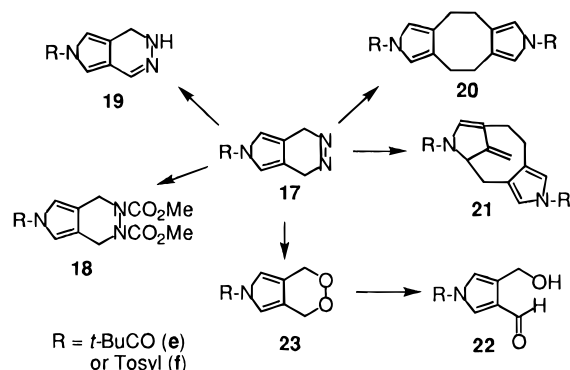
poses in a first-order reaction in CDCl₃ with a half-life of 14.5 min at 5 °C. The *N*-pivaloyl compound **17e** decomposes at 5 °C with a half-life of about 50 min.

In the absence of trapping agents, the biradicals formed in the decompositions of the diazenes dimerize (see Scheme 3). In the case of the *N*-pivaloyl (**17e**) and *N*-tosyl (**17f**) derivatives, for example, we have identified[21] the symmetrical (**20**) and unsymmetrical (**21**) dimers by ^{1}H NMR spectroscopic comparison with the corresponding dimers[3] in the furan and thiophene series. Careful examination of the NMR spectra of solutions of the diazenes during thermal decomposition shows the growth of not only these dimers but also of small amounts of other products: the cyclic peroxide **23** and/or its rearrangement product hydroxyaldehyde **22**; hydrazone **19** formed by tautomerization; and the adduct **18** of the biradical with any inadvertent slight excess of dimethyl azodicarboxylate used in the oxidation step generating the diazene from the hydrazine **17** (see Scheme 2). These reactions closely parallel those observed previously[3] in the furan and thiophene series.

When any of these diazenes is allowed to decompose thermally in the presence of an olefinic trapping agent or dioxygen, 1:1 adducts with the corresponding biradical are formed in high yield. Previous work[3] has shown that the thermal decompositions of the furan and thiophene diazenes give similar adducts. The mechanism of the cycloaddition in the latter cases has been established by kinetic means. The reaction involves two successive steps, namely deazetation to give the biradical reactive intermediates **2a** or **2b**, followed by capture of the biradical. This pathway requires that the overall rate of disappearance of the diazene precursor be kinetically first-order in diazene and zero-order in trapping agent, in agreement with the experimental facts.[3] By analogy, one would expect the same mechanism to prevail in the pyrrole cases studied here. We now have demonstrated this for the cases of the *N*-pivaloyl and *N*-tosyl diazenes **17e**,**f**, for which we observe pseudo-first-order thermal decomposition rate constants, monitored at 10 °C by low-temperature NMR spectrometry, that are essentially independent of the concentration of acrylonitrile, maleonitrile, or dioxygen in the reaction mixture.

Structures of the Adducts. The adducts obtained from alkene cycloadditions to the *thermally generated N*-pivaloyl and *N*-tosyl biradicals are shown in Table 1, which shows also the corresponding results for the trapping reactions (described below) of maleonitrile (MN) with the biradical **3f** generated by direct *photolysis* of the diazene **17f**. The structures and configurations were established by ^{1}H and ^{13}C NMR spectroscopy and high-resolution mass spectroscopy. Details are given in the Supporting Information.

Capture of the *N*-Tosyl Biradical 3f Thermally and Photochemically Generated from the Diazene 17f. When

(21) See the Supporting Information.

solutions of the *N*-tosyl diazene **17f** containing appropriately substituted alkenes, such as dimethyl maleate, dimethyl fumarate, maleonitrile, fumaronitrile, acrylonitrile, and the three stereoisomeric 2,4-hexadienes, were warmed to the diazene's decomposition temperature (<25 °C), the *N*-tosyl biradical **3f** could be captured to give fused (**24f**) and bridged (**25f**) 1:1 adducts (Table 1). In these cases, the reaction was *stereospecific* for syn addition (*cis*-alkenes gave only cis adducts, and *trans*-alkenes gave only trans adducts). The regiochemistry of the addition varied with the trapping agent. With fumaronitrile (FN), the fused trans adduct predominated over the bridged trans one by a ratio of 92:8, whereas with maleonitrile, the cis endo bridged product was favored over the cis fused one by a ratio of 57:43. Note that the regiospecificity (fused/bridged product ratio) of capture by FN is higher with the *N*-tosyl biradical **3f** (92:8) than with the *N*-pivaloyl biradical **3e** (see below: 64:36 in MTHF, 45:55 in CH₂Cl₂).

The thermal reactions with the nitrile trapping agents proceeded in good yield and gave little or no dimeric material **20f** or **21f**. With the sluggishly reactive (see below) *cis,trans*-2,4-hexadiene as trapping agent, the presence of these dimers of the biradical was evident, but even so, it was possible to isolate a 47% yield of adduct. Again, the reaction appeared to be highly stereospecific. The formation of only one adduct from *cis,trans*-2,4-hexadiene (Table 1) suggests that there also may be a regiospecific preference for addition of the biradical at a trans rather than a cis double bond of the diene.

When the decomposition of the diazene **17f** in the presence of maleonitrile, acrylonitrile, or *cis,cis*-2,4-hexadiene was effected by photolysis (λ = 355−360 or 370 nm) of solutions at temperatures below the threshhold for thermal decomposition, the products were nearly the same as those observed in the thermal decomposition (Table 1). Control experiments showed that the products were stable under the conditions of photolysis.
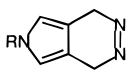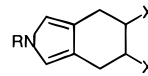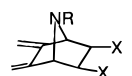
The structure of the adducts, the strict stereospecificity of the cycloadditions, and other evidence to be described, point to the singlet *N*-tosyl biradical **3f** as the reactive entity in the thermal and direct photochemical deazetations of the diazene **17f**.

Capture of the *N*-Pivaloyl Biradical 3e Thermally and Photochemically Generated from the Diazene 17e. The cycloadditions of the thermally generated biradical **3e** also are completely stereospecifically syn, but both fused and bridged regioisomers are formed in each case (Table 1). Direct photolysis (370 nm) of the *N*-pivaloyl diazene **17e** gave the same stereospecific products as the thermal reactions (shown in Table 1) but in different proportions of regioisomers. The apparent anomaly was resolved when it was found that the adducts undergo secondary photochemistry at unequal rates upon continued irradiation. This photoreaction, whose nature we do not yet know, precludes the use of the fused:bridged product ratio as a fingerprint for a particular reactive intermediate in the photodeazetation of *N*-pivaloyl diazene **17e**. Nevertheless, we are confident that the singlet biradical **3e** is the common reactive species in the thermal and direct photochemical deazetation of this diazene.

Relative Reactivities of Alkenes Toward Singlet Biradicals 3e,f by Competition Experiments. Comparison with Reactivities by Absolute Rate Measurements. Using methods similar to those previously described,[3b] we have measured the relative rates of reaction of the thermally or photochemically generated singlet biradicals *N*-pivaloyl- (**3e**) and *N*-tosyl-3,4-dimethylenepyrrole (**3f**) in solvent MTHF (or CH₂Cl₂) at 25 °C with a series of alkenes: dimethyl maleate (ME), acrylonitrile (AN), dimethyl fumarate (FE), fumaronitrile (FN), maleonitrile

Table 1. Distribution of Products (%)[a,h] Obtained from Alkenes and Biradicals **3e,f** Generated Thermally or Photochemically (*hν*) from Diazenes **17e,f**

17	alkene[b]	24	25
f: R = Ts	FN	*trans* (92[c])	*trans* (8[c])
	MN	*cis* (43 ± 3[c,f])	*cis endo* (57 ± 3[c,f])
			cis exo (∼0[c])
	MN(*hν*)	*cis* (49[c])	*cis endo* (51[c])
			cis exo (∼0[c])
	AN	(80[c])	*endo* or *exo* (20[c])
	AN (*hν*)	(82[c])	*endo* or *exo* (18[c])
	cis,cis-2,4-hexadiene[d]	*cis* (92[c]), *trans* (8[c])	∼0[c,e,g]
	cis,cis-2,4-hexadiene (*hν*)	*cis* (92[c]), *trans* (8[c])	∼0[c,e,g]
	cis,trans-2,4-hexadiene	*cis* (∼100[c])	∼0[c]
	cis,trans-2,4-hexadiene (*hν*)	*cis* (∼100[c])	∼0[c]
	trans,trans-2,4-hexadiene	*trans* (∼100[c])	∼0[c]
	trans,trans-2,4-hexadiene (*hν*)	*trans* (∼100[c])	∼0[c]
e: R = *t*-BuCO	FE	*trans* (70)	*trans* (30)
	ME	*cis* (82)	*cis endo* or *exo* (9)
			cis exo or *endo* (9)
	FN	*trans* (64,[a] 45[c])	*trans* (36,[a] 55[c])
	MN	*cis* (52,[a] 44[c])	*cis endo* or *exo*(56[c])
			cis exo or *endo* (∼0[e])
	AN	(61,[a] 41[c])	*endo* or *exo* (24[a])
			exo or *endo* (15[a])
			endo + *exo* (59[c,g])

[a] Solvent is 2-methyltetrafuran (MTHF) unless otherwise indicated. [b] FE = dimethyl fumarate, X = X′ = CO$_2$Me. ME = dimethyl maleate, X = X′ = CO$_2$Me. FN = fumaronitrile, X = X′ = CN. MN = maleonitrile, X= X′ = CN. AN = acrylonitrile, X = CN, X′ = H. From *cis,cis*- and *cis,trans*-2,4-hexadiene, X = *cis*-propenyl, X′ = Me; from *trans,trans*-2,4-hexadiene, X = *trans*-propenyl, X′ = Me. [c] Solvent CH$_2$Cl$_2$. [d] Initial composition 97% *cis,cis*-, 3% *cis,trans*-. [e] A trace peak of a third product of retention time close to that of the bridged product is observed. [f] Average of two separate runs. [g] Analysis by NMR. [h] Analysis by HPLC unless otherwise indicated.
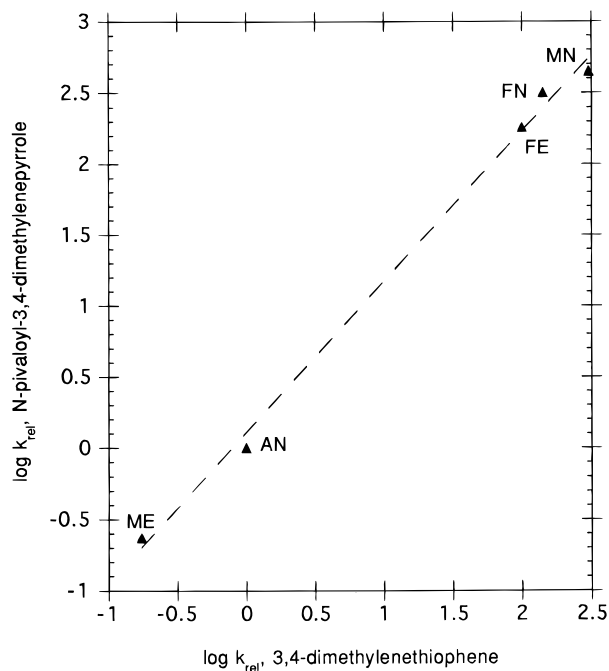
Figure 4. Linear regression analysis of log relative rate of capture of the *N*-pivaloyl-3,4-dimethylenepyrrole and 3,4-dimethylenethiophene[3b,d] biradicals by alkenes. The alkene points are dimethyl maleate (ME), acrylonitrile (AN), dimethyl fumarate (FE), fumaronitrile (FN), and maleonitrile (MN).

(MN), and *N*-methylmaleimide (MM). The results are given in Table 2 (columns 1−4). Table 2 also lists relative reactivities[3] for the singlet 3,4-dimethylenefuran (**2a**) and 3,4-dimethylenethiophene (**2b**) biradicals and for a singlet state of the TMM biradical 2-isopropylidenecyclopentane-1,3-diyl, **26**[22] (columns 5−7) . We estimate that the experimental error in each of the relative reactivities in the present work is about 15%.
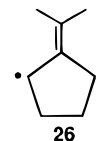

26

Table 2, column 1, shows the reactivity sequence for the *N*-pivaloyl-3,4-dimethylene biradical **3e** in MTHF solvent. A comparison value, not shown in Table 2, is the FN/AN ratio of 400 in CH$_2$Cl$_2$ for the capture of the **3e** intermediate generated by 370 nm photolysis of **17e**. As was previously reported,[17] the relative rates for the *N*-tosyl (**3f**) biradical correlate linearly with those of the 3,4-dimethylenethiophene biradical **2b**[3b] in a log−log relationship, with a slope of 1.24 (*r* = 0.990). A similar relationship is now seen in the case of the relative reactivities of the *N*-pivaloyl system **3e** and **2b** (Figure 4), where the slope is 1.07 (*r* = 0.998).

Laser flash photolysis[17a] (355 nm) of the *N*-tosyl diazene **17f** in CH$_2$Cl$_2$ solution generates a species of λ_{max} 593 nm, which also can be observed in the blue matrix-immobilized ESR-silent preparations described below. As has been reported elsewhere,[17a] monitoring the 593 nm absorption of samples containing alkene trapping agents in fluid media allows one to obtain absolute and hence relative rate constants (Table 2, column 3) for the capture of the transient, which we believe to be the singlet *N*-tosyl-3,4-dimethylenepyrrole biradical **3f**. The absolute rate constants can be derived from the relative values in Table 2 and the FN value[17a] of 3.2 × 10^7 M^{-1} s^{-1}. The relative rate constants are to be compared with the values from competition experiments on CH$_2$Cl$_2$ solutions of **17f** and pairs of alkenes photolyzed at 370 nm and monitored by high-performance liquid chromatography (HPLC) of the products. In the case of the pairwise competition FN:FE, any unreacted diazene **3f** after photolysis was quenched with maleic anhydride. The latter results are given in Table 2, column 2.

Table 2.   Relative Rates of Reaction of Singlet Biradicals with Alkenes[a]

alkene[f]	biradical						
	3e[b,h]	**3f**[d,i]	**3f**[d,e,g]	**3f**[d,h,j]	**2a**[c,g]	**2b**[c,g]	**26**[c,h]
MA		>27400	51300[g]		2930	7000	235
MM				14100			
MN	487			4230		300	180
FN	343[k]	1593	2240[g]	2240	761	140	160
FE	183	513	507[e,g]	746	149	100	67
AN	1.0		1.0[g]	1.0	1.0	1.0	3.8
ME	0.233					0.17	1.0
cis,cis-HD				~0.002			

[a] Compounds **3e**,**f**: present work; compounds **2a−b** and **26**: text refs 3 and 22, respectively. [b] Solvent 2-methyltetrahydrofuran. [c] Solvent acetonitrile. [d] Solvent CH_2Cl_2. [e] Diethyl fumarate used as trapping alkene instead of dimethyl fumarate. [f] MA = maleic anhydride; MM = *N*-methylmaleimide; MN = maleonitrile; FN = fumaronitrile; FE = dimethyl fumarate; AN = acrylonitrile; ME = dimethyl maleate; *cis,cis*-HD = *cis,cis*-2,4-hexadiene. [g] Transient generated by laser flash photolysis at 355 nm and rate determined by nanosecond time-resolved spectroscopy. [h] Thermally initiated preparative competition experiment. [i] Photochemically initiated (370 nm) preparative competition experiment. [j] Competition ratios in column 4 determined by direct comparison of MM vs FN, FN vs MN, FN vs FE, and AN vs *cis,cis*-HD. FN vs AN is assumed to be the same as in column 3. [k] Not shown in the table is the value 400 for the FN/AN reactivity ratio toward **3e** generated by 370 nm photolysis in CH_2Cl_2.

The relative rate value for **3f** reaction with FN vs. FE was independently confirmed by a competition for the *thermally* generated reactive intermediate. In this case, the unreacted diazene **17f** was quenched with *N*-methylmaleimide. The observed rate ratio FN:FE of 3.0 (Table 2, column 4) was in good agreement with the value 3.3 obtained in the previous series of experiments (Table 2, column 2) in which the transient was generated by solution-phase direct photolysis of the diazene **17f**.

Placing the data points of columns 2 and 3 of Table 2 on a common basis shows that the relative values of the second-order rate constants directly determined (column 2) for three members of the series were MA 101 ± 20, FN 4.4 ± 1, and FE 1.0, a series to be compared with the competitively determined values for the same alkenes of > 54 ± 8, 3.3 ± 1, and 1.0 (Table 2, column 3). The competition factor for maleic anhydride (Table 2, column 2) is a minimum value, since the adduct is unstable upon storage in the reaction mixture and quickly declines in concentration. Within the limitations imposed by this circumstance, no significant differences appear between the relative reactivities determined by the two methods. The agreement supports the proposal that the reactive entity responsible for the preparative formation of the cycloadducts of Table 1 from the thermolysis and 370 nm photolysis of *N*-tosyl diazene **17f** is the same singlet species as the spectroscopically observed carrier of the 593 nm absorption in the laser flash photolysis[17a] and matrix photolysis (see below) experiments.

Although the reactivity of *cis,cis*-2,4-hexadiene is too low for accurate measurement by the competition method, an approximate determination (Table 2, column 4) shows it to be ~0.2% as reactive as acrylonitrile. Thus, the diylophilic reactivities of alkenes toward the *N*-tosyl biradical **3f** cover a range of at least 2.5×10^6.

Origin of the Reactivity Sequence. We favor a frontier MO (FMO) rationalization of the reactivity sequence observed here and in other cycloaddition reactions of singlet 3,4-dimethyleneheterocycles,[3,17a,19,20] in which diyl HOMO−diylophile LUMO interaction dominates. One might imagine a subtly different interpretation in which the diazene rapidly forms a charge-transfer complex with the alkene, which then slowly decomposes by deazetation of the diazene moiety. Capture of the newly formed biradical by its solvent-caged olefin partner then completes the reaction. In this mechanism, FMO control would be exerted over the equilibrium constant for diazene−alkene complex formation, rather than in the diyl addition transition state.

Several lines of evidence argue against this interpretation:

(1) in the flash photolysis studies[17a] of the series in which the *diyl* (rather than the alkene) structure is varied, the rates correlate with the diyl HOMO energy, not with the diazene HOMO energy; (2) we find no UV−vis or NMR evidence of charge-transfer complex formation in cooled solutions of diazene−alkene mixtures; (3) in the thermal cycloadditions, the hypothetical preassociation mechanism would predict second-order kinetics, whereas the observed kinetics always are first-order in diazene and zero-order in alkene. We conclude that FMO influence is being exerted in the diyl−alkene cycloadditon transition state itself.

As we have previously shown, the variations in the rates of these reactions are controlled largely by changes in the entropy of activation, not in the enthalpy of activation. How the variations in diyl HOMO−alkene LUMO *energy* differences are translated into variations in activation *entropies* has been explained by a surface-crossing model.[20]

Attempts to Effect Chemical Interception of a Triplet State of the *N*-Tosyl-3,4-dimethylenepyrrole Biradical 3f. In the thermolysis or direct photolysis of diazenes **17e**,**f**, the species trapped in the reactions described so far appear to be well-defined singlets. There remains the question whether the corresponding triplet species can be trapped under other conditions. Based upon precedent in previous work from this laboratory,[22a−e] which demonstrated the generation and capture of both the singlet and triplet states of a trimethylenemethane (TMM) derivative, 2-isopropylidenecyclopentane-1,3-diyl **26**, we applied three tests: the first was the dilution effect on the product composition in cycloadditive capture of the biradical when the transient is formed in its singlet state by pyrolysis or direct photolysis;[22c] the second was the effect on the distribution of products when the transient was generated by triplet photosensitization;[22d] the third was the CIDNP effect in the ^{1}H NMR spectrum of freshly generated dimers of biradical **3f**.[22e,f] A fourth test generated the triplet biradical **3f** in matrix-immobilized admixture with a trapping agent and then liberated the partners for reaction by thawing the matrix.

Dilution Effects. In the TMM system (**26**), the energy of the triplet lies below that of the singlet. Hence, initial generation of the singlet can be followed by competition between intermolecular capture of the singlet by alkenes and essentially

(22) Summarized: (a) Berson, J. A. *Acc. Chem. Res.* **1978**, *11*, 446 and references cited therein. (b) Berson, J. A. In *Diradicals*; Borden, W. T., Ed.; Wiley: New York, 1982; Chapter 4. (c) Duncan, C. D.; Corwin, L. C.; Davis, J. H.; Berson, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 2350. (d) Berson, J. A.; Duncan, C. D.; O'Connell, G. C.; Platz, M. S. *J. Am. Chem. Soc.* **1976**, *98*, 2358. (e) Bushby, R. J.; McBride, J. M.; Tremelling, M.; Berson, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 1544. (f) Closs, G. L. *J. Am. Chem. Soc.* **1971**, *93*, 1545

irreversible intersystem crossing to the triplet, which in turn can be captured. The singlet and triplet forms of that TMM display differing chemistry: the singlet reacts both regiospecifically and stereospecifically, giving largely fused product by syn addition, whereas the triplet reacts with little specificity, giving both bridged and fused products by both syn and anti addition. Increasing dilution of the reaction mixture decreases the rate of capture of the initially formed singlet, thereby relatively favoring intersystem crossing and shifting the product composition in favor of triplet-derived adducts.

In the present work, we examined the effect of changing the concentration of maleonitrile on the products of its capture of *N*-tosyl biradical **3f** generated by direct photolysis of diazene **17f** at −40 °C, a temperature at which the diazene is thermally stable. Any unreacted **17f** was scavenged with maleic anhydride or *N*-methylmaleimide, and the products were analyzed by HPLC. For maleonitrile concentrations of 3.17, 6.24, 28.5, and 80 mM the only products observed by HPLC analysis were the cis adducts, fused cis, and bridged cis-endo. The trans fused adduct could not be detected in these reaction mixtures. With 1.6 M maleonitrile, the fused adduct mixture consisted of 97.2% cis and 2.8% trans. The small amount of trans adduct at high concentration presumably came from the ∼0.5% of fumaronitrile in our maleonitrile samples. We conclude that no dilution effect occurs in the reactions of the tosyl biradical **3f**. Several hypotheses to explain this result may readily be imagined, but the main conclusion in the context of the objectives here is that the triplet state of **3f** has not been trapped under these conditions. Moreover, in this case, the dilution test fails to answer whether the triplet even has been formed.[23]

Photosensitization Experiments. Triplet sensitizers with triplet energies in the range 62−74 kcal/mol[24a] should be appropriate for the sensitization of a diazene, whose triplet energy is likely to be in the range 55−65 kcal/mol.[24b] Preliminary tests showed that several such sensitizers indeed facilitated the photodeazetation of the *N*-tosyl diazene **17f** and that xanthone was the most efficient of the sensitizers tried. A more direct demonstration of triplet energy transfer was provided by a nanosecond time-resolved study of the quenching of the xanthone triplet absorption, λ_{max} 630 nm, by the *N*-tosyl diazene **17f**. As Figure 5 shows, the pseudo-first-order rate constant for decay of the xanthone triplet depends linearly ($r = 0.987$) on the concentration of diazene **17f**. The seond-order quenching rate constant derived from the slope of the linear correlation of Figure 5 is 1.5×10^9 M^{-1} s^{-1}. This rate is near the diffusion-controlled limit and is in accord with the Dexter mechanism[25] of energy transfer. Although new UV−vis maxima that might be associated with a transient triplet state of biradical **3f** could not be observed under the laser flash conditions, the quenching experiments suffice to demonstrate the occurrence of energy transfer to diazene **17f**. To our knowledge, this is the first such observation with a precursor of a tetramethyleneethane derivative.

Capture of the Transient Produced by Photosensitization. Transfer of triplet energy to the diazene **17f** presumably creates the (localized) lowest triplet of the azo chromophore. If this state deazetates to the triplet state of biradical **3f**, one might hope to capture the latter as characteristic cycloadducts with appropriate trapping agents. However, we anticipated that the

Figure 5. Quenching of the xanthone triplet absorption by *N*-tosyl diazene **10f** in CH$_2$Cl$_2$ solution at −50 °C.

competing photosensitized stereomutation of the alkenic trapping agents would impede our attempts to demonstrate this by stereochemical means.

A similar problem arose in the studies of the TMM **26**,[22d] where the stereochemical criterion for triplet formation in the photosensitization experiments also had to be abandoned because of competing stereomutation of the alkene trapping agents. However, it was possible there to demonstrate the interception of triplet **26** from the *regiochemistry* of xanthone-photosensitized cycloadditions. These gave ratios of fused and bridged products close to those observed in the "infinitely" dilute thermal reactions, which had been identified as indicative of triplet chemistry. Attempts to apply this strategy to the case of the *N*-tosyl-3,4-dimethylenepyrrole biradical **3f** failed, however, because the regiochemistry of the cycloadditon to alkenes was independent of whether the reactive intermediates were generated from diazene **17f** by thermolysis, direct photolysis, or xanthone-sensitized photolysis (see below).

In an attempt to minimize the alkene stereomutation problem, we used alkenes that are relatively inefficient triplet quenchers as trapping agents: the *cis,cis*-, *cis,trans*-, and *trans,trans*-2,4-hexadienes (see Table 1). Indeed, we found that these substances interconvert only slowly under the conditions of the xanthone photosensitization experiments. However, the yields of cycloadducts formed were too low to permit accurate determinations of products.

Better yields of adducts were obtained with maleonitrile as the trapping agent, but this alkene was known[24a] to be an efficient triplet quencher, and in fact we found that stereomutation was so severe that no conclusions on the trapping stereochemistry could be reached.

However, photolyses of diazene **17f** *to very low conversion* in the presence of very pure MN under xanthone-photosensitized conditions gave recovered alkene with a ratio MN/FN of 99:1, thus preserving the alkene stereochemistry to a degree sufficient to detect even a small amount of non-stereospecific cycloadditon. Any remaining diazene was quenched thermally with maleic anhydride. Aside from the maleic anhydride adduct, the only products were the MN adducts, cis-endo bridged and cis fused in the ratio of 56:44. These values agree with those obtained (Table 1) in the thermal and direct photolytic experiments (57:43 and 51:49, respectively). Significantly, none of the corresponding trans adducts could be detected.

The results strongly suggest that even when produced by photosensitization, biradical **3f** ultimately reacts by *stereospecific* syn addition with pure MN to give the same regioisomeric

(23) It is not clear from this, however, whether the exclusively singlet-derived products are formed because the **3f** biradical spin states reach an equilibrium strongly favoring the singlet ^{1}**3f** before capture, or because the singlet reacts much faster than the triplet. For this reason, this experiment cannot be used to assign the spin of the ground state.

(24) (a) Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973; p 3. (b) Engel, P. S.; Steel, C. *Acc. Chem. Res.* **1973**, *6*, 275.
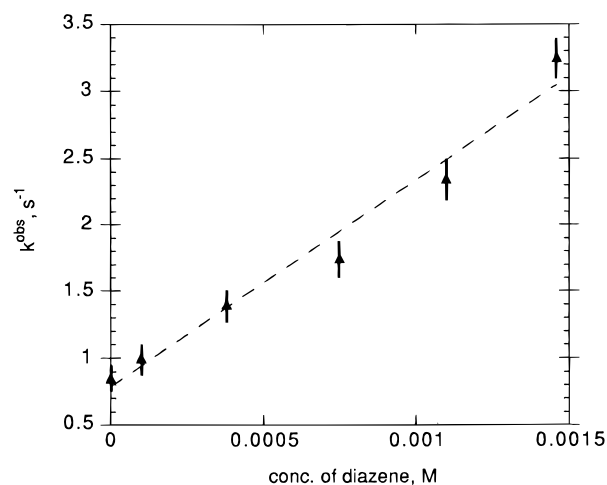
(25) Dexter, D. L. *J. Chem. Phys.* **1953**, *21*, 836.

mixture obtained in the reactions of singlet **3f** (Table 1). Thus, if triplet **3f** is formed under these conditions, either its chemistry is exactly the same as that of the singlet, or more probably, *its rate of trapping by MN is too slow to compete with intersystem crossing to the singlet, which then is essentially the exclusive biradical reaction partner in the alkene cycloadditon.*[23]
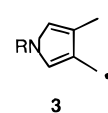
CIDNP Effects. Fast thermolytic generation of the triplet TMM [3]**26** in fluid solution from the diazene precursor led to the formation of dimers of **26** with numerous strongly emissive ^{1}H NMR resonances.[22e] This observation was interpreted[22f] as direct evidence of the involvement of at least one triplet of **26** in the dimerization. In the thermal decomposition of **17f**, the precursor of the biradical **3f**, similar attempts did not produce discernible emissions or enhanced absorptions in the dimers' ^{1}H NMR spectrum. This result is not surprising, since the ordering of the multiplet energies in **26** is clearly T-below-S (by about 13−15 kcal/mol).[22a−e] Formation of [3]**26** thus follows hard on the heels of thermal generation of [1]**26** and leads readily to magnetically polarized dimer, whereas [3]**3f** may lie uphill from thermally generated [1]**3f** in solution, and dimers are formed from the singlet without polarization.

Generation of Triplet Biradical 3f in the Presence of Trapping Agent in Matrix-Immobilzed Form Followed by Annealing. A frozen solution of diazene **17f** and excess fumaronitrile in CD_2Cl_2 was irradiated at 77 K with monochromatic 265 nm light, conditions that produce the characteristic ESR spectrum assigned[11b] to the triplet biradical [3]**3f**. The temperature was raised to 196 K, warm enough to melt the glass but well below the thermal decomposition point of the diazene. The sample was re-glassed at 77 K, re-irradiated, and re-thawed for a total of 75 1-min irradiations. After the sample had thawed to 230 K, the NMR spectrum (taken at −40 °C) showed that little or none of the diazene had been consumed (<2%), and none of the trapping products could be discerned. Apparently, under these conditions, only a very small amount of the diazene is converted to [3]**3f**, which is in accord with the results of a spin-count experiment.[11b] Similar low conversions are observed in fluid solutions with monochromatic 265 nm light.

A maleonitrile trapping experiment was carried out in MTHF at −40 °C with $NiSO_4$-filtered light (230−325 nm). Note that at 5 K, these irradiation conditions produce a much stronger ESR spectrum than is obtained with monochromator-filtered 265 nm light.[11b] Treatment with *N*-methylmaleimide to quench residual diazene and conventional work-up still showed no detectable trace of maleonitrile or fumaronitrile trapping product (HPLC analysis). A separate control experiment showed that authentic trapping products **24** and **25 (X = CN)**, were readily decomposed by 265 nm irradiation, each adduct's concentration being diminished by 41% (NMR analysis relative to dimethyl hydrazodicarboxylate internal standard) after 12 min photolysis in solution at −30 °C. (As we already have noted, under our conditions, monochromatic 370 nm light is without effect on the products **24** and **25 X = X′ = CN**). We believe that the major reasons for the failure to observe the trapping products of the triplet [3]**3f** in the matrix experiments with MN at 265 nm are the low photoconversions **17f** → [3]**3f** and the photochemical instability of the trapping products under the irradiation conditions. We ultimately found[11b] that the cycloadducts of the **3f** manifold with dimethyl azodicarboxylate (DMAD) are relatively photostable and can be isolated. This has important implications in another context,[11b] but the DMAD diylophile of course cannot be used as a stereochemical probe.

Thus, four unsuccessful attempts have been made here to demonstrate the independent capture chemistry of the triplet [3]**3f**. Of the four methods, the photosensitization and matrix-thawing

Table 3. Optical Absorption Maxima of Singlet *N*-Substituted-3,4-dimethylenepyrrole Biradicals (**3**)[a,b]


3

formula	R	λ_{max}, nm	ϵ, M^{-1} cm^{-1}
3b	CH_3	600	*a*
3h	$COCH_3$	650	*a*
		536	*a*
3d	CO*i*-Pr	656	*a*
3e	CO*t*-Bu	665	~4900
		(580?)	~3500
		544	~3900
3f	Ts	590	~5000
		343	*a*
		300(?)	*a*
3g	Bs	595	*a*

a Not measured. *b* In MTHF glass at 77 K.

approaches might have had the best chance for success, since at least they generate the elusive triplet *first*. The other two methods, thermally initiated CIDNP and dilution, both generate the singlet first. It will be self-evident that interception of the triplet under the latter conditions is inherently difficult.

Generation and Characterization of the Kinetically Stable Singlet States of 3,4-Dimethylenepyrrole Biradicals in Low-Temperature Matrices. In either fluid media or solvent glasses, each of the diazene precursors **17b,d,e,f,g,h** showed absorbances near 370 nm as expected for the azo n,π* chromophore. Irradiation of glassy 2-methyltetrahydrofuran (MTHF) samples of any of these at 370 nm at 77 K generated a blue color and a UV−vis absorption spectrum dominated by a broad band centered in the region 590−665 nm (see Table 3), which we assign to the corresponding biradicals **3**. As already has been described,[17a] a 590 nm absorption can be detected by nanosecond time-resolved spectroscopy of flash-photolyzed fluid solutions of the precursor diazene **17f**. We propose that the singlet species **3f** is the common carrier of the spectra in the solution and matrix phases, and we think it is likely that the corresponding singlets **3b,d,e,g,h** are responsible for the blue color and long-wavelength absorption in the other instances.

The extinction coefficients (ϵ) of the matrix-immobilized transients **3f,g** were difficult to determine accurately because of secondary photobleaching of the new chromophore, which precluded attempts to achieve complete photoconversion of the precursor **17f** (or **17g**) to the biradical **3f** (or **3g**) (see below). A rough value of $\epsilon \sim 5000$ M^{-1}cm^{-1} for **3f** was obtained from low-conversion experiments in which the concentration of the biradical was estimated from the decrease in intensity of the 370 nm azo absorption of the precursor **17f**, combined with the assumption that the photoproduct from **17f** was entirely the biradical **3f**. The estimate probably is close to the true extinction coefficient, since it gives the value $2k_t = 2.8 \times 10^{10}$ M^{-1} s^{-1} when used in conjunction with the nanosecond laser flash photolysis measurements[17a] to calculate the rate constant for dimerization of **3f** in fluid CH_2Cl_2 solution at 220−230 K. This value is close to the diffusion-controlled rate 1.5×10^{10} M^{-1} s^{-1} calculated from theory. Also, it matches the rates determined experimentally[17a,19,20] for other singlet biradical dimerizations, including the 3,4-dimethylenethiophene singlet, for which the extinction coefficient could be measured[3c] directly on matrix-immobilized samples. A similar value of ϵ, 4900 M^{-1} cm^{-1}, is observed for the N-pivaloyl derivative **3e**.
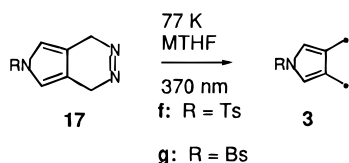
In addition to the 590 nm band, the tosyl biradical **3f** showed an absorption maximum at 343 nm and possibly at 300 nm. Although diazene absorbances in the same general regions made these short-wavelength bands difficult to detect in most samples, the presence of absorptions there authentic to **3f** was suggested by the fact that the 340 and 300 nm regions were active in its photobleaching.

With the 1000 W Hg−Xe monochromator system, secondary photobleaching seems to have its maximum near 400 nm, although the absorption spectrum of the blue samples does not show a maximum there. Samples obtained by fully photobleaching **3f** showed no UV−vis absorption beyond 350 nm.

The complex NMR spectrum of the product(s) of photobleaching can be recorded at 183 K in solution but rapidly disappears at 243 K. A firm assignment of structure is not yet available.[17b]

We also have observed that *thermal* decomposition (270−300 K) of diazene **17f** in a co-solid with adamantane, followed by cooling of the sample to 77 K, gave a visibly blue preparation. A similar blue color often was seen during the preparation of solid samples of the hydrazine **16f** (Scheme 2). Presumably, the solid acts as a support for a small amount of biradical **3f** formed by adventitious oxidation of the hydrazine and deazetation of the resulting diazene. The identity of the oxidant is not clearly established. Ordinary molecular dioxygen would seem to be a likely candidate, but the blue color appeared even in samples that we had made extra efforts to protect from air. The blue preparations remained so at *room temperature* in the dark under vacuum for about 1h, and for weeks in a dark freezer at 190 K. Such observations recall those previously reported[3c] for the thiophene biradical **2b**. They indicate that despite its extraordinarily fast dimerization in fluid media, the singlet biradical **3f**, when isolated and immobilized, is a kinetically stable species, even at room temperature. We postpone to the accompanying paper[11b] a discussion of the question whether the singlet is actually the ground state of *N*-tosyl-3,4-dimethylenepyrrole **3f**, but we note here that blue matrix-immobilized preparations of singlet **3f** showed no ESR signals of a triplet species even after storage for as long as a month at 77 K.

Conclusions. The chemistry of the transients formed upon thermal, direct photochemical, or photosensitized deazetation of the precursors of a series of *N*-substituted-3,4-dimethylenepyrroles strongly suggests that the reactive entities captured in cycloadditions to alkenes are singlet biradicals. These ESR-silent, deeply colored singlet species can be detected directly in the matrix immobilized state by their persistent UV−vis absorption. These absorptions also appear in the solution phase during nanosecond laser flash photolysis, and their kinetic behavior can be monitored by nanosecond time-resolved spectroscopy. The relative reactivities of UV−vis-active transients, as measured in this way, match those measured by in preparative competition experiments. This concordance, combined with the structures of the adducts with alkenes, demonstrates that the transient blue species are indeed singlet 3,4-dimethylenepyrroles.[26,27]

Experimental Section. General synthetic and spectroscopic procedures are described in the Supporting Information.

Syntheses of Schemes 1 and 2. See Supporting Information.

Preparation and Characterization of the Products Listed in Table 1. See Supporting Information.

Kinetics of Thermal Deazetation of *N*-Toluenesulfonyl Diazene 17f and *N*-Pivaloyl Diazene 17e Monitored by NMR. (Details are given in the Supporting Information). The kinetics were carried out by procedures similar to those described elsewhere.[3b] At 283 K, the rates for **17f** in $CDCl_3$ were strictly first-order ($r^2 = 0.996−0.999$). The rate constants ($\times 10^4$ s) k_d were independent of the concentration [MN] of maleonitrile: [MN] = 0.0 M, k_d = 8.6 (8.0 measured by a second investigator); [MN] = 0.026 M, k_d = 9.2; [MN] = .059 M, k_d = 7.2 (measured on a different day); [MN] = 0.1 M, k_d = 9.5.

Similarly, for **17e** in $CDCl_3$ at 277.9 K, for [MN] = 0.0 M, $[O_2]$ = 0.0 M. k_d = 2.4; for $[O_2]$ = saturated in $CDCl_3$, 2.0, 2.3; for [MN] = 0.354 M, k_d = 2.5. See Supporting Information.

Quantum Chemical Calculations. The AM1/CI results are given in the Supporting Information to our preliminary communication[11a] and ref 17b. These results are given again together with the PM3/CI results in the Supporting Information to the present paper.

Supporting Information Available: Synthetic details of Schemes 1 and 2, preparations and characterizations of trapping products listed in Table 1 and Scheme 3, descriptions of trapping studies and analyses of product ratios, results of AM1/CI and PM3/CI calculations, and kinetics of thermal deazetation of diazenes **17e,f** (72 pages). See any current masthead page for ordering and Internet access instructions.

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(26) (a) Our so far unsuccessful attempts to observe a solid state ^{13}C NMR signal for singlet **3f** by methods used in other systems[27] are described elsewhere: (b) Reference 17b, pp 99−106.

(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.; Webb, G. G.; Greenberg, M. M.; Berson, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 1523. (c) Greenberg, M. M.; Blackstock, S. C.; Berson, J. A.; Merrill, R. A.; Duchamp, J. C.; Zilm, K. W. *J. Am. Chem. Soc.* **1991**, *113*, 2318. (d) Reynolds, J. H.; Berson, J. A.; Kumashiro, K. K.; Duchamp, J. C.; Zilm, K. W.; Rubello, A.; Vogel, P. *J. Am. Chem. Soc.* **1992**, *114*, 763. (e) Reynolds, J. H.; Berson, J. A.; Kumashiro, K. K.; Duchamp, J. C.; Zilm, K. W.; Scaiano, J. C.; Berinstain, A. B.; Rubello, A.; Vogel, P. *J. Am. Chem. Soc.* **1993**, *115*, 8073.