With dichloro-**16** compounds in acetonitrile, ϕ_F is reduced further ($3-4 \times 10^{-5}$), with computed singlet lifetimes below 10 ps. Here ϕ_R's in the range of 0.1–0.2 in acetic acid or acetonitrile are observed. In cyclohexane, the value for ϕ_F is 1×10^{-3}, and the compounds are photoactive for Wagner–Meerwein rearrangement in cyclohexane, although with moderately low quantum efficiences. Thus, both fluorescence and reactivity quantum yields show large solvent effects.

The veratrolo–benzo compounds **17** follow a similar pattern. Monosubstitution with a nonleaving group (OH, OAc) leads to reduction of ϕ_F and $^1\tau$ by a factor of 15–20. In **17**, unlike **16**, methanesulfonate is a nucleofuge, and this substitution reduces ϕ_F and $^1\tau$ to values similar to those produced by chlorine substitution. Like dichloro-**16**, dichloro-**17** isomers have ϕ_F and $^1\tau$ values lower than monochlorinated species.

In addition to the effect of substitution on fluorescence intensity, we note an effect on the wavelengths of the fluorescence maxima (the fluorescence spectra are broad and structureless). In the dibenzo (**16**) system, both mono- and disubstitution lead to a 4-nm increase. The increase is considerably greater in the veratrolo–benzo systems (**17**), where monosubstitution leads to a 14- to 15-nm red shift and disubstitution to an 18- to 20-nm shift. These results may be rationalized by the assumption that the S_1 states of the substituted compounds have some degree of charge transfer, greater in the veratrolo–benzo compounds, which have lower excited-state oxidation potentials,[3] than in the benzo compounds, without a similar degree of charge transfer in the ground state.

As mentioned above, compounds **16** with monohydroxy, -acetoxy, and -(methanesulfonyl)oxy groups and **17** with monohydroxy and -acetoxy groups have moderately (ca. 10-fold) reduced ϕ_F and $^1\tau$ values, compared with the hydrocarbons, although they are not photoactive, within the limits of our measurements. These data and those on emission wavelengths suggest that charge transfer promotes decay modes of S_1 to S_0, although the manner in which this is accomplished remains to be elucidated. In this regard, corresponding data[15] on toluene, benzyl alcohol, and benzyl acetate in cyclohexane may be of interest. The latter two compounds have ϕ_F's of 0.08 and 0.07, values somewhat less than 50% of that of toluene, 0.17, and the (measured) singlet lifetimes are 29 and 17 ns, as compared with that of toluene of 34 ns. It has also been shown[16] that the decrease in quantum yields (measured in cyclohexane) for benzyl alcohol ($\phi_F = 0.074$) compared with toluene ($\phi_F = 0.23$) was greater than that for β-phenylethyl alcohol ($\phi_F = 0.094$) and that γ-phenylpropyl alcohol ($\phi_F = 0.16$) had a still greater fluorescence yield. All of these are photoinert.[17] While these reductions are not as dramatic as those we report, they are qualitatively similar. They show that the radiationless decay modes are markedly dependent upon the distance between the aromatic ring and the carbon–X bond. The fixation of bond distances and bond angles in the rigid bicyclooctane system compared with these acyclic systems appears to be reflected in the enhanced effects we observe.

We conclude that ideas regarding electron transfer[1-5] as the key step in photosolvolysis and Wagner–Meerwein photorearrangements in these bridged systems are consistent with and confirmed by results described in this paper.

Experimental Section

All of the compounds used, except the veratrolo–benzo "hydrocarbon" **17** (X = Y = H), have been previously reported.[1-5] **17** (X = Y = H) was prepared from *trans*-**17** (X = Y = Cl) by Dr. M. Z. Ali by azobis(isobutyronitrile)-promoted reduction with tri-*n*-butyltin hydride.

Samples were purified by repeated recrystallization (filtered through and collected on sintered-glass funnels). Solutions were generally prepared at about 10^{-3}–10^{-4} M in spectrograde solvents, placed in fluorescence cells, covered with septa and deoxygenated in a stream of nitrogen.

Fluorescence spectra were measured on a Perkin-Elmer Model MPF-2A fluorimeter using an excitation bandwidth of 10 nm. Fluorescence quantum yields were determined relative to that of anisole in cyclohexane, whose yield was taken as 0.29.[15] Relative integrated fluorescence intensities of deoxygenated solutions were corrected for differences in light absorption by the samples and the standard over the excitation bandwidth and for the refractive index of the solvent. It was assumed that all fluorescences were similar enough that corrections for wavelength-dependent instrumental response were not necessary.

Acknowledgment. The authors are indebted to the National Science Foundation (Grant CHE 85-03422 and predecessor grants) for partial support of this work.

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Reactions of Triazolinediones with Alkoxy-Substituted 1,3-Butadienes. Rearrangements of 2 + 2 to 4 + 2 Cycloadducts

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Abstract: The reactions of *N*-methyl- and *N*-phenyltriazolinedione with electron-rich 1,3-butadienes are reported. Reaction with (*Z*,*Z*)-1,4-di-*tert*-butoxy-1,3-butadiene in acetone produced two acetone insertion products and two 4 + 2 adducts. The major 4 + 2 adduct was the unanticipated *cis*-2,5-di-*tert*-butoxy compound. At low temperatures two intermediates were observed by NMR that rearranged and reacted with acetone at temperatures higher than −50 °C to give the four products. These intermediates were identified spectroscopically as 2 + 2 adducts. Potential mechanisms for these reactions are discussed.

Triazolinediones **1** are singlet oxygen mimics,[1] undergoing 2 + 2, 4 + 2, and ene reactions. They also undergo reactions with azines[2] and sulfides[3] that mirror singlet oxygen reactivity. The recent focus of interest in triazolinedione chemistry, stimulated by this similarity to singlet oxygen,[1a] has revolved around the

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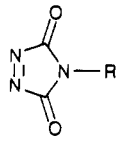
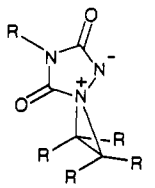


1a, R = Ph
b, R = CH_3

question of the intermediacy of aziridinium imides (AZI) in the



AZI

ene and cycloaddition reactions. Greene[4] used the Stephenson isotope effect test[5] to provide compelling evidence for AZI's in the ene reaction, and Nelsen[6] directly observed what appears to be an AZI intermediate in the 2 + 2 cycloaddition of a triazolinedione to adamantylideneadamantane.

We recently examined the reactions of a series of electron-rich dienes[7] with singlet oxygen, which provide evidence for perepoxide intermediates and their reactions (Scheme I) to form zwitterions and biradicals. The structural similarity between perepoxides and AZI's and the possibility that one can use the apparently more easily observable AZI's to learn something about perepoxide chemistry provided the impetus for the present study. We report here the reactions of **1a** and **1b** with a series of alkoxy-substituted butadienes **2–6** (Scheme II), which reveal the following: (1) 2 + 2 cycloadditions to these dienes are not as prevalent with triazolinediones as with singlet oxygen;[7] (2) (*Z*,*Z*)-diene **6** reacts to give products with unexpected stereochemistry; and (3) two intermediates, which precede formation of the products in the reaction of (*Z*,*Z*)-diene **6**, can be observed by low-temperature NMR.

Results

The reactions of dienes **2–6** were conducted by adding solids **1a** and **1b**[8] to acetone-d_6 mixtures of the dienes at −78 °C. Dienes **2–5** gave exclusively 4 + 2 adducts **7–9** (Scheme II). In contrast, with singlet oxygen, **2** gave 35%, **3** 13%, **4** 100%, and **5** 75% of the respective 1,2-dioxetane.[7a,e]

The (*Z*,*Z*)-diene **6**, however, gave two 4 + 2 adducts and two tetrahydro-1,3,4-oxadiazines **10** and **11**. The major product of the reaction was the unexpected *trans*-di-*tert*-butoxy 4 + 2 adduct **9**. The *cis*-di-*tert*-butoxy 4 + 2 adduct was formed *in half or less than half* the yield of its trans isomer. The formation of ketone-trapped adducts, the tetrahydro-1,3,4-oxadiazines, has previously been observed in the reactions of **1a** with enol ethers[9] and has been used to implicate zwitterionic intermediates.

The ^1H NMR and ^{13}C NMR data for products from the reactions of dienes **2–6** with **1b** are given in Tables I and II, respectively. Spectral data for the reactions of triazolinedione **1a** are very similar and are found in the Experimental Section. Coupling constants were assigned by exhaustive single-frequency

Scheme I

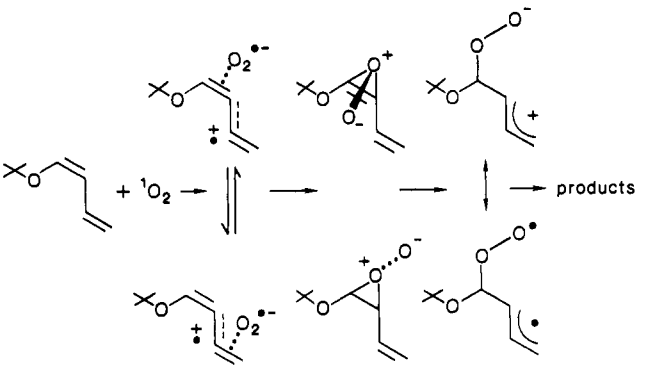


Table I. ^1H NMR Data for the Reactions of **1b** with Dienes **2–6**[a]

	7b	8b	9b	10b	11b
$\delta(H_1)$	5.66	5.81	5.63	5.01	5.37
$\delta(H_2)$	5.97	6.07	5.99	4.73	4.86
$\delta(H_3)$	6.06			4.55	4.59
$\delta(H_4)$	4.24			6.52	6.49
$\delta(H_5)$	3.84				
$\delta(N-CH_3)$	2.97	2.97	2.99	2.94	2.91
$\delta(t\text{-Bu})$	1.27	1.32	1.25	1.28	1.26
				1.30	1.27
J_{12}[b]	4.21	2.93	2.56	1.46	2.93
$J_{12'}$		1.65	1.10		
J_{13}					
J_{14}					
J_{15}	1.46				
J_{23}	10.07			7.42	8.42
J_{24}	1.83			1.10	1.10
J_{25}	2.30				
J_{34}	4.21			6.41	6.41
J_{35}	1.83				
J_{45}	17.0				

[a] All chemical shifts reported relative to TMS in acetone-d_6 at room temperature. [b] All J values are reported in hertz.

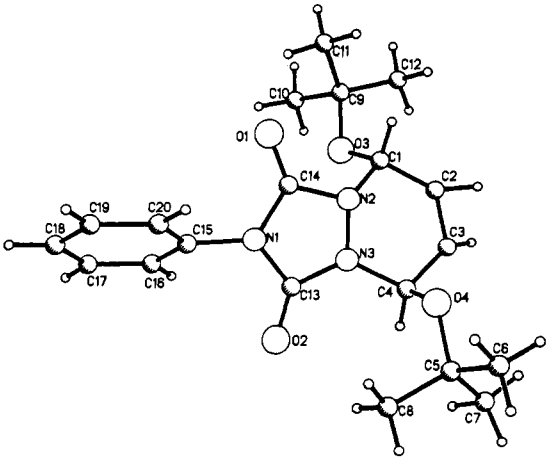


Figure 1. ORTEP drawing of the structure of **9a**.

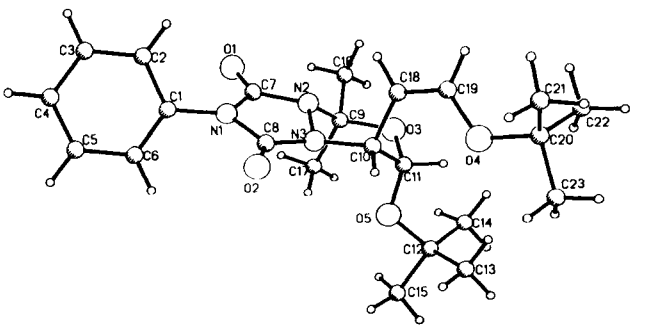


Figure 2. ORTEP drawing of the structure of **10a**.

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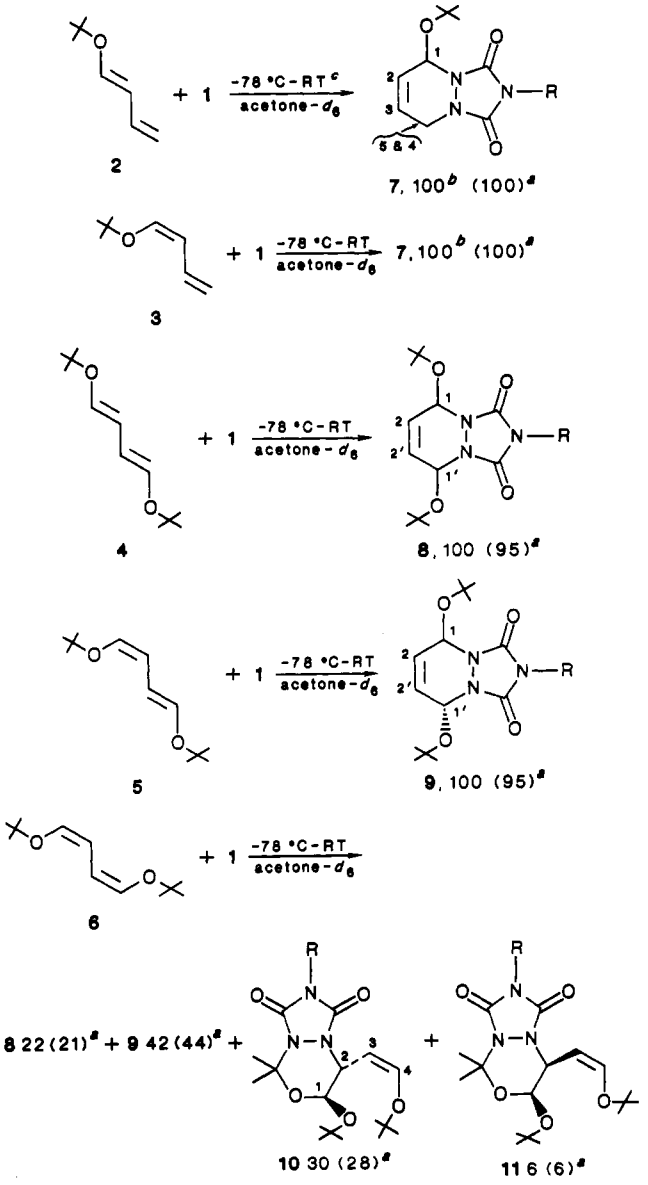
Table II. ^{13}C NMR Data for the Reaction of **1a** and **1b** with Dienes **2–6**[a,b]

	7b	8b	9b	10a	11a
$\delta(C_1)$	73.0 (157)	73.0 (159)	73.0 (159)	94.0[c,d] (167)	90.8[c,d] (162)
$\delta(C_2)$	126.4 (166)	127.5 (170)	127.0 (168)	55.3 (148)	53.0 (142)
$\delta(C_3)$	123.9 (162)			101.0 (164)	98.0 (162)
$\delta(C_4)$	44.6 (143)			143.6 (179)	144.5 (177)
$\delta(N\text{-}CH_3)$	24.9 (141)	25.0 (142)	24.9 (142)		
$\delta(CO)$	152.8	152.0	153.6	152.2	151.1
	155.6			152.6	151.9
$\delta(t\text{-}BuOCH_3)$	29.0 (125)	28.7 (125)	28.9 (127)	28.2, 28.7 (127, 128)	28.1, 28.7
$\delta(t\text{-}BuO)$ q	75.1	76.0	75.1	76.3, 77.7	76.4, 76.9

[a] All chemical shifts reported relative to TMS in acetone-d_6 at room temperature. [b] Values in parentheses are the 1-bond carbon–hydrogen coupling constants. [c] Trideuteriomethyls and associated quaternary carbon not observed. [d] Phenyl carbons reported in the Experimental Section.

Scheme II



[a] NMR yields (%) in parentheses are for R = Me, and outside parentheses for R = Ph. [b] Reactions done in CH_2Cl_2. [c] "–78 °C–RT" indicates **1** was added to an acetone solution of the diene at –78 °C and the resulting mixture was allowed to slowly warm to room temperature.

decoupling experiments. In addition, the structures of **9a** and **10a** were confirmed by X-ray crystallography (Figures 1 and 2).

When the reactions of **6** were monitored by low-temperature NMR at –65 °C, two intermediates were detected in a ratio of approximately 3:1 for **1a** and 4:1 for **1b**. These intermediates are indefinitely stable below –50 °C but decompose slowly at higher temperatures to give the four products **8–11**. Viable candidates

Table III. ^1H NMR Data for **12b**, **13b**, **15**, and **16**[a]

	12b[b]	13b[b]	15	16
$\delta(H_1)$	6.00	6.07	6.38	6.35
$\delta(H_2)$	5.72	5.03	5.99	6.41
$\delta(H_3)$	4.91	4.69	4.82	4.97
$\delta(H_4)$	6.76	6.93	6.85	6.80
$\delta(N\text{-}CH_3)$	2.92	2.95		
$\delta(t\text{-}Bu\text{-}CH_3)$	1.31	1.33	1.24	1.22
	1.29	1.31	1.12	1.12
J_{12}[c]	6.96	5.30	6.2	5.1
J_{23}	10.25	9.60	10.6	10.6
J_{34}	6.23	6.41	6.2	6.2

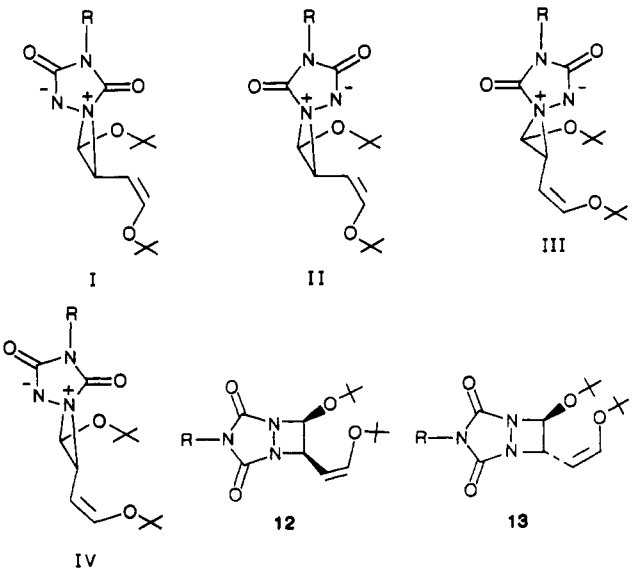
[a] In acetone-d_6 relative to TMS. [b] At –65 °C. [c] All J values are reported in hertz.

Table IV. ^{13}C NMR Data for **12b**, **13b**, **15**, and **16**[a,b]

	12b[c]	13b[c]	15	16
$\delta(C_1)$	87.7 (172)	90.3 (172)	100.94	99.14[d]
$\delta(C_2)$	63.2 (148)	66.6 (153)	80.41	*e*
$\delta(C_3)$	99.7 (166)	94.6 (166)	97.59	96.40[d]
$\delta(C_4)$	145.5 (177)	148.9 (181)	147.04	146.25
$\delta(NCH_3)$	26.0 (141)	26.0 (141)		
$\delta(t\text{-}BuCH_3)$	27.8, 28.0 (127, 127)	27.8, 28.0 (127, 127)	26.57, 26.05	26.78, *e*
$\delta(t\text{-}Bu)$ q	77.5, 77.7	77.9, 78.8	77.01	76.63
			75.33	74.76

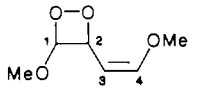
[a] In acetone-d_6 relative to TMS. [b] Values in parentheses $^1J_{CH}$. [c] At –65°C. [d] Assignments may be switched. [e] Not observed; buried under another peak.

for these intermediates include the four isomeric AZI's I–IV and the two 2 + 2 adducts **12** and **13**. The major intermediate appears



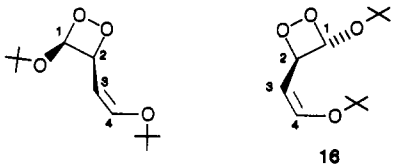
to be cis-disubstituted I, II, or **12** and the minor intermediate trans-disubstituted III, IV, or **13**. These stereochemical assignments are based upon the observation that J_{cis} is larger than J_{trans} in both four-membered[10] and three-membered rings.[11] Hall,[12]

for example, has reported that J_{cis} is 1–2 Hz larger than J_{trans} in alkoxy-substituted 1,2-diazetidines. The ^1H and ^{13}C NMR spectra of the intermediates are very similar to those of the recently studied dioxetanes[7] and are also similar to those anticipated for an AZI.[11] The $^1J(^{13}C-H)$ coupling constants in the intermediates, 172 Hz at carbon 1 and 148 and 153 Hz at carbon 2, however, are too small for the hybridization of the aziridine ring carbons in I–IV. The one-bond carbon–hydrogen coupling constant at carbon 2 in I–IV should be larger than the coupling observed in ethylenimine (168.1 Hz)[11] as predicted by the well-documented effect of electron-withdrawing substituents.[13] The one-bond carbon–hydrogen coupling constant, however, in dioxetane **14** (177 Hz at



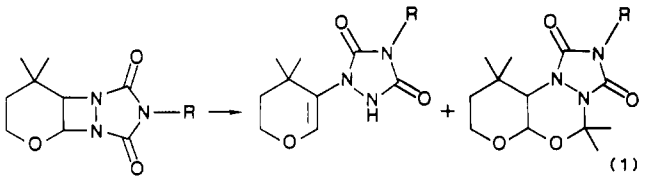
14

carbon 1 and 153 Hz at carbon 2) is consistent with that observed in the intermediates. Consequently, we assign **12** and **13** as the structures of the major and minor intermediates, respectively. The ^1H and ^{13}C NMR data for **12b** and **13b** are reported in Tables III and IV along with the spectral data for the stereochemically similar dioxetanes **15** and **16** for comparison.



15 **16**

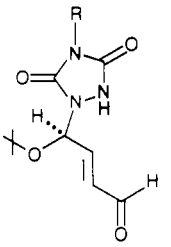
It is surprising that the carbon 1–nitrogen bond in **12** and **13** can cleave so readily to insert acetone. Several alkoxy-substituted 1,2-diazetidines[9] have been synthesized and are stable in acetone for extended periods of time. Greene[1a] reported that the diazetidine formed in the reaction of 4,4-dimethyldihydropyran is stable in nonpolar solvents but is converted slowly in acetone to a vinylurazole and a tetrahydrooxadiazine (eq 1). In CD_3Cl **12** and **13** decompose readily above −40 °C.



(1)

In the reactions of **1a** and **1b**, preference for formation of cis-substituted intermediates can be rationalized by invoking an attractive interaction between the alkoxy group and allylic moiety in a zwitterionic intermediate. A similar preference for cis-substituted dioxetanes has been observed in the reactions of singlet oxygen with these same dienes.[7] A thermodynamic study of alkyl 1-propenyl ethers[15] has demonstrated that this electronic preference actually increases with the bulk of the alkoxy group. Similar counter steric effects have been observed in halopropenes[16] and trifluoromethyl-substituted enol ethers.[17]

When acetone and acetone-d_6, which had not been rigorously dried, were used as solvents in the reactions of **6**, only hydrolysis products **17a** and **17b** were observed. These products are identical



17a,b

with those formed when water is added to performed intermediates **12** and **13** and the reaction mixture is allowed to warm to room temperature.

Addition of 10 mol % of **1b** to **6** at −78 °C in acetone-d_6 resulted in formation of the two intermediates in their usual isomeric ratios with no concomitant isomerization of the unreacted diene. Addition of 2.2 equiv of **4** to the preformed intermediates in the reaction of **6** with **1b** in acetone-d_6 at −78 °C resulted in formation of the usual ratio of products upon warming to room temperature with no apparent incorporation of the (*E*,*E*)-diene. These experiments rule out the possibility that isomerized diene is produced by cycloreversion of the 1,2-diazetidines or by cleavage of a 1,4-zwitterion. Cycloreversion of a 1,2-diazetidine[4] and cleavage of a 1,4-zwitterion[18] have been reported in other systems.

All attempts to observe intermediates in the reactions of dienes **2–5** failed. The 4 + 2 adducts were observed by low-temperature NMR at −65 °C immediately after mixing the dienes with **1a** or **1b**.

Discussion

Nonstereospecific 4 + 2 reactions between dieneophiles **1** and diene **6** are exceptions to the normal axiom of stereochemical integrity in Diels–Alder reactions. Scheme III depicts several mechanistic pathways for these novel reactions and provides a convenient framework for making the following mechanistic suggestions.

(1) We suggest that the reactions of **1a** and **1b** with **6** are initiated by interactions of the triazolinediones with the s-trans conformation of the diene (Scheme III). Calculations,[19] cryogenic deposition experiments,[20] and UV studies of 1,3-butadienes[21] suggest that the planar s-trans conformation is energetically preferred to the s-cis conformation. Many unsaturated reagents, however, choose to react with the s-cis conformation to give Diels–Alder products because no reaction surface for interaction with the s-trans conformation is accessible. Such is not the case for triazolinediones, which can undergo both 4 + 2 and 2 + 2 cycloadditions. If the initial interactions of the triazolinediones were with the s-cis conformation, 4 + 2 adducts would almost certainly have been observed since, in all cases of which we are aware, s-cis-tied dienes give exclusively 4 + 2 adducts.[22]

(2) Formation of AZI's I or II (Scheme III) prior to zwitterion formation provides an explanation for the insensitivity of the rate of reactions of triazolinediones with enol ethers[12] as a function

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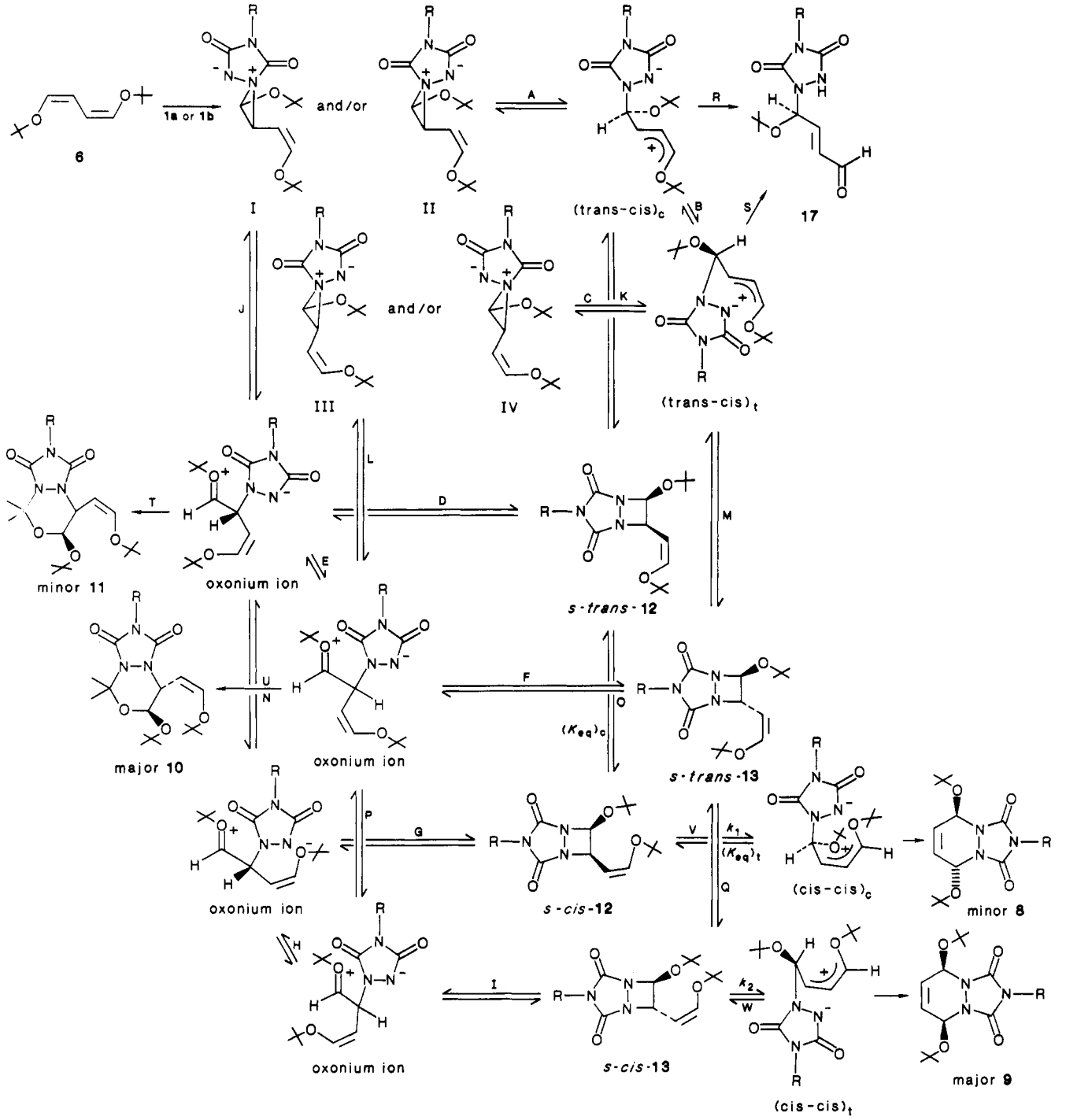
Scheme III. Mechanism for the Reaction of (*Z*,*Z*)-Diene **6** with Triazolinedione[a]



[a] Processes E and H appear to interconvert enantiomers but represent bridges to an enantiomeric diagram, which has been omitted for simplicity.

of solvent. Structurally similar perepoxides have received considerable support[23] as intermediates in solvent-insensitive singlet-oxygen ene reactions. Hall[12] has invoked charge-transfer complexes to rationalize the lack of a solvent effect in the reactions of enol ethers with triazolinediones but was unsuccessful in detecting these intermediates spectroscopically.

(3) The metastable AZI's I or II can open to form either the s-cis oxonium ion or the $(trans–cis)_c$ zwitterion, paths J and A in Scheme III, respectively. The formation of tetrahydro-1,3,4-oxadiazines **10** and **11** (paths T and U) provides evidence for oxonium ion intermediates and the isolation of hydrolysis product **17** (paths R and S) for zwitterionic intermediates. The zwitterion can either close to form the major 2 + 2 adduct **12** (path K) or rotate to the $(trans–cis)_t$ zwitterion (path B), which closes to form the minor trans-substituted 1,2-diazetidine **13**. Diazetidines **12** and **13** are depicted in both their s-cis and s-trans conformations. The observed stereochemical integrity of the double bond not involved in these 2 + 2 cycloadditions, despite the involvement of zwitterionic intermediates, is consistent with the reported high barriers for allylic cation isomerization.[24]

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(4) The conversions of diazetidines **12** and **13** to products **8–11** and **17** are also suggested to proceed through oxonium ions and zwitterions (bottom half of the diagram in Scheme III). The s-cis conformers of **12** and **13** form (cis–cis) zwitterions (paths V and W), and the s-trans conformers open to (trans–cis) zwitterions (paths K and M). It is the (cis–cis) zwitterions that are structurally capable of collapsing to form the 4 + 2 adducts **8** and **9**.

(5) The most abundant intermediate **12** is sterically prohibited from collapsing directly either by a concerted[25] or by a stepwise pathway to form the major 4 + 2 adduct **9**. Berson and co-workers[26] in extensive investigations of 1,3-sigmatropic shifts[27] have demonstrated that antarafacial migrations are high-energy processes. Stepwise crossover by rotational interconversion of the $(cis–cis)_c$ and $(cis–cis)_t$ zwitterion would require rotation of the sterically demanding *tert*-butoxy or triazolinedione ring through their inner cavities.

(6) Indirect pathways (e.g. DEFQW or GHIW) for the collapse of **12** to the major 4 + 2 adduct **9** exist and involve interconversion of cis- and trans-1,2-diazetidienes **12** and **13**. If these interconversions are rapid relative to 4 + 2 adduct formation, as they appear to be, the [**8**]/[**9**] ratio is just a function of their rates of formation, k_1 and k_2, and the equilibrium constants, $(K_{eq})_c$ and $(K_{eq})_t$, for the s-cis/s-trans equilibria (Scheme III).

(7) Formation of **9** is favored because $(K_{eq})_t$ is larger than $(K_{eq})_c$. This suggestion can be verified by using eq 2 and assuming that

$$[\mathbf{8}]/[\mathbf{9}] = k_1(K_{eq})_c[\mathbf{12}]/k_2(K_{eq})_t[\mathbf{13}] \qquad (2)$$

$k_1/k_2 = 1$ and that the ratio [**12**]/[**13**] at low temperature reflects their equilibrium populations. Although these are crude approximations, the calculated equilibrium constant ratio of approximately 0.05 appears to be reasonable. This reflects a 1.2 kcal/mol larger $\Delta G°$ for the *cis*-1,2-diazetidine than for the *trans*-1,2-diazetidine conformational interconversion. Similar or slightly larger changes for conformational interconversions for several polyenes[28] have been calculated by MMP2.

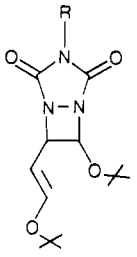
(8) Foote and Jensen[29] have reported the stereospecific conversion of what appears to be a cis-disubstituted 1,2-diazetidine to a cis 4 + 2 adduct without concomitant isomerization to the *trans*-diazetidine. The absence of this diastereomeric interconversion in their alkyl-substituted 1,2-diazetidine, despite the availability of pathway KBM (Scheme III), suggests that **12** and **13** may be interconverting exclusively via oxonium pathways DEF or GHI.

(9) The syn- and/or anti-trans-substituted aziridinium imides III and IV could be intermediates in the conversion of *s-trans*-**13** to an oxonium ion (path MCL) or could be involved in the interconversion of zwitterions (path B) or oxonium ions (paths E and H), but our studies do not demand it. Formations of three-membered rings are entropically favored over the formations of four-membered rings. Foote,[30] on the basis of isotope effect studies, has also suggested that a pathway exists for interconversion of AZI's.

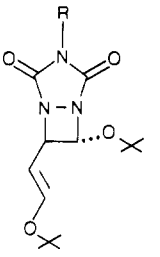
(10) Our studies do not allow us to determine whether a syn and/or anti (I or II, respectively, in Scheme III) aziridinium imide is the initially formed intermediate. The cis effect[31] in the singlet-oxygen ene reaction has been interpreted in terms of an electronic stabilization[32] of the most hindered (syn) perepoxide, but, on the other hand, no cis effects are observed in triazolinedione ene reactions.[1a]

(11) Vinylcyclobutane–cyclohexane rearrangements occur at high temperatures through diradical intermediates.[33] The reactions of **6** at low temperature, however, are more consistent with a concerted reaction or a reaction proceeding through dipolar intermediates. Cyanoalkenes also undergo 2 + 2 cycloaddition to aryl-[34] and cyclopropyl-substituted[35] dienes, in which the s-cis conformation is sterically inaccessible. Solvent effects and substituent effects in the rearrangements of these 2 + 2 adducts to cyclohexenes also support an ionic pathway for rearrangement.

A similar mechanism to that depicted in Scheme III is probably not operative in the reactions of the (*E*,*E*)- and (*E*,*Z*)-dienes because only the expected 4 + 2 Diels–Alder products are formed, 2 + 2 adducts were not observed at low temperatures, and there is no reason to believe that 2 + 2 adducts **18** and **19**, if formed,



18



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would be unstable. Concerted pathways for the reactions of these dienes are likely; however, detailed experimental studies to delineate the mechanisms of these reactions have not been completed.

Conclusion

Unexpected rapid conversions of vinyl-substituted 1,2-diazetidines to tetrahydropyridazines were observed. The ability of these 1,2-diazetidines to undergo rapid diastereomeric interconversions and rearrangements to 4 + 2 adducts may be related to the presence of the electron-donating *tert*-butoxy group. Putnam and co-workers[36] reported that a tetrafluorovinyl-substituted 1,2-diazetidine did not undergo rearrangement even at 90 °C.

No direct experimental evidence for the formation of aziridinium imides was obtained. The initial formation of aziridinium imides, however, was suggested in order to rationalize the previously reported insensitivity of the rates of additions of triazolinediones to enol ethers to changes in solvent polarity.

The effect of substituents on these novel reactions is currently under investigation and will be reported in the near future.

Experimental Section

Preparative gas chromatographic separations were carried out on a GOW-MAC Series 550 thermal conductivity detector gas chromatograph utilizing a 0.25 in. by 20 ft column packed with 20% Carbowax 20M on NAW Chromosorb W 80/100.

Proton and carbon NMR spectra were obtained on a JEOL FX270 at 270 and 67.83 MHz, respectively, and the chemical shifts, referenced to Me_4Si. Mass spectra were obtained on a VG-ZAB-1F by electron impact ionization.

Acetone-d_6 (Wilmad) was stored over 4A molecular sieves. Bulk acetone was distilled from $KMnO_4$, dried over $CaSO_4$, and stored over 4A molecular sieves. Methylene-d_2 chloride (Aldrich) and chloroform-d_1 (Aldrich) were filtered through activity 1 basic alumina prior to use.

4-Phenyl-1,2,4-triazoline-3,5-dione (**1a**) and 4-methyl-1,2,4-triazoline-3,5-dione (**1b**) were synthesized from 4-phenylurazole and 4-methylurazole, respectively, by the method of Cookson et al.[8]

trans-1-*tert*-Butoxy-1,3-butadiene (**2**) and *cis*-1-*tert*-butoxy-1,3-butadiene (**3**) were synthesized by the method of Everhardus et al.[37]

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(1*E*,4*E*)-1,4-Di-*tert*-butoxy-1,3-butadiene (**4**), (1*E*,4*Z*)-1,4-*tert*-butoxy-1,3-butadiene (**5**), and (1*Z*,4*Z*)-1,4-di-*tert*-butoxy-1,3-butadiene (**6**) were synthesized by the method of Hiranuma and Miller[38] and purified by preparative gas chromatography.[7a]

The usual NMR-scale reactions of dienes **2–6** were performed by adding 1 equiv of solid **1a** or **1b** to approximately 0.75 mL of an acetone-d_6 solution of the diene at −78 °C in an NMR tube. The red color of the resulting mixtures vanished within 60 s. Proton and carbon spectra were immediately obtained at −65 °C. Proton spectra of the solutions, resulting from the reactions of the triazolinediones with dienes **2–5** at −78 °C, indicated immediate formation of the 4 + 2 adducts **7–9**. When the analogous reactions were performed at room temperature, the same products were formed. In contrast, proton spectra of the solutions, which resulted upon reaction of the triazolinediones with diene **6** at −78 °C, were consistent with formation of intermediates **12a**, **12b**, **13a**, and **13b**. When the solutions of these intermediates were allowed to slowly warm to room temperature, compounds **8–11** were formed. Separation of compounds **8–11** was accomplished via column chromatography over 60–200-mesh silica gel with ethyl acetate/hexane as eluant. All products were recrystallized from acetone/hexane.

2-*tert*-Butoxy-8-phenyl-1,6,8-triazabicyclo[4.3.0]nonane-7,9-dione (7a): ^{1}H NMR (acetone-d_6) δ 1.30 (s, 9 H), 4.01 (dddd, *J* = 17.0, 2.2, 1.7, 1.5 Hz, 1 H), 4.36 (ddd, *J* = 17.0, 4.2, 1.7 Hz, 1 H), 5.78 (dd, *J* = 4.4, 1.5 Hz, 1 H), 6.04 (dddd, *J* = 10.3, 4.4, 2.2, 1.7 Hz, 1 H), 6.12 (ddd, *J* = 10.3, 4.2, 1.7 Hz, 1 H), 7.39–7.59 (m, 5 H); ^{13}C NMR (acetone-d_6) δ 29.0 (q, *J* = 125 Hz), 44.7 (d, *J* = 146 Hz), 73.4 (d, *J* = 159 Hz), 75.3 (s), 123.9 (t, *J* = 164 Hz), 126.2 (d, *J* = 166 Hz), 126.5 (d, *J* = 166 Hz), 128.5 (d, *J* = 162 Hz), 129.6 (d, *J* = 162 Hz), 132.9 (s), 151.6 (s), 154.0 (s); mp 132.5–133.5 °C; MS for $C_{16}H_{19}N_3O_3$ calcd 301.1428, found 301.1247; IR ($CHCl_3$, cm^{-1}) 1721.

2-*tert*-Butoxy-8-methyl-1,6,8-triazabicyclo[4.3.0]nonane-7,9-dione (7b): Mp 95 °C; MS for $C_{11}H_{17}N_3O_3$ calcd 239.1271, found 239.1266.

***cis*-2,5-Di-*tert*-butoxy-8-phenyl-1,6,8-triazabicyclo[4.3.0]nonane-7,9-dione (8a)**: ^{1}H NMR (acetone-d_6) δ 1.36 (s, 18 H), 5.93 (dd, *J* = 2.9, 1.5 Hz, 2 H), 6.14 (dd, *J* = 2.9, 1.5 Hz, 2 H), 7.36–7.53 (m, 5 H); ^{13}C NMR (acetone-d_6) δ 28.8 (q, *J* = 125 Hz), 73.2 (d, *J* = 159 Hz), 76.1 (s), 126.7 (d, *J* = 170 Hz), 127.6 (d, *J* = 170 Hz), 128.5 (d, *J* = 170 Hz), 129.5 (d, *J* = 160 Hz), 132.9 (s), 150.5 (s); mp 151–152 °C; MS for $C_{20}H_{27}N_3O_4$ calcd 373.2003, found 373.1984; IR ($CHCl_3$, cm^{-1}) 1712.

***cis*-2,5-Di-*tert*-butoxy-8-phenyl-1,6,8-triazabicyclo[4.3.0]nonane-7,9-dione (8a)**: IR ($CHCl_3$, cm^{-1}) 1707.

***cis*-2,5-Di-*tert*-butoxy-8-methyl-1,6,8-triazabicyclo[4.3.0]nonane-7,9-dione (8b)**: mp 124–125 °C; MS for $C_{15}H_{25}N_3O_4$ calcd 311.1847, found 311.1881; IR ($CHCl_3$, cm^{-1}) 1696.

***trans*-2,5-Di-*tert*-butoxy-8-phenyl-1,6,8-triazabicyclo[4.3.0]nonane-7,9-dione (9a)**: ^{1}H NMR (acetone-d_6) δ 1.29 (s, 18 H), 5.75 (dd, *J* = 2.6, 1.1 Hz, 2 H), 6.06 (dd, *J* = 2.6, 1.1 Hz, 2 H), 7.39–7.53 (m, 5 H); ^{13}C NMR (acetone-d_6) δ 29.0 (q, *J* = 125 Hz), 73.5 (d, *J* = 155 Hz), 75.5 (s), 126.5 (d, *J* = 155 Hz), 127.2 (d, *J* = 177 Hz), 128.8 (d, *J* = 155 Hz), 129.8 (d, *J* = 162 Hz), 132.7 (s), 152.4 (s); mp 173–174 °C; MS for $C_{20}H_{27}N_3O_4$ calcd 373.2003, found 373.1995; IR ($CHCl_3$, cm^{-1}) 1727.

***trans*-2,5-Di-*tert*-butoxy-8-methyl-1,6,8-triazabicyclo[4.3.0]nonane-7,9-dione (9b)**: mp 102–103 °C; MS for $C_{15}H_{25}N_3O_4$ calcd 311.1847, found 311.1849; IR ($CHCl_3$, cm^{-1}) 1716.

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***trans*-2-(*cis*-2-*tert*-Butoxyethenyl)-3-*tert*-butoxy-5,5-bis(trideuteriomethyl)-8-phenyl-1,6,8-triaza-4-oxabicyclo[4.3.0]nonane-7,9-dione (10a)**: ^{1}H NMR (acetone-d_6) δ 1.31 (s, 9 H), 1.31 (s, 9 H), 4.68 (dd, *J* = 7.7, 6.2 Hz, 1 H), 4.84 (ddd, *J* = 7.7, 1.5, 1.1 Hz, 1 H), 5.09 (d, *J* = 1.5 Hz, 1 H), 6.57 (dd, *J* = 6.2, 1.1 Hz, 1 H), 7.39–7.51 (m, 5 H); mp 113–114 °C; IR ($CHCl_3$, cm^{-1}) 1710.

***cis*-2-(*cis*-2-*tert*-Butoxyethenyl)-3-*tert*-butoxy-5,5-bis(trideuteriomethyl)-8-phenyl-1,6,8-triaza-4-oxabicyclo[4.3.0]nonane-7,9-dione (11a)**: ^{1}H NMR (acetone-d_6) δ 1.26 (s, 9 H), 1.30 (s, 9 H), 4.69 (dd, *J* = 8.4, 6.2 Hz, 1 H), 4.99 (ddd, *J* = 8.4, 2.9, 1.1 Hz, 1 H), 5.48 (d, *J* = 2.9 Hz, 1 H), 6.55 (dd, *J* = 6.2, 1.1 Hz, 1 H), 7.39–7.51 (m, 5 H).

***cis*-6-(*cis*-2-*tert*-Butoxyethenyl)-7-*tert*-butoxy-3-phenyl-1,3,5-triazabicyclo[3.2.0]nonane-2,4-dione (12a)**: ^{1}H NMR (acetone-d_6) δ 1.30 (s, 9 H), 1.34 (s, 9 H), 4.98 (dd, *J* = 10.3, 6.2 Hz, 1 H), 5.93 (dd, *J* = 10.3, 7.0 Hz, 1 H), 6.20 (d, *J* = 7.0 Hz, 1 H), 6.81 (d, *J* = 6.2 Hz, 1 H), 7.45–7.63 (m, 5 H); ^{13}C NMR (acetone-d_6) δ 26.6 (q, *J* = 125 Hz), 26.8 (q, *J* = 125 Hz), 62.4 (d, *J* = 149 Hz), 76.5 (s), 76.5 (s), 87.1 (d, *J* = 172 Hz), 98.3 (d, *J* = 170 Hz), 125.7 (d, *J* = 165 Hz), 127.7 (d, *J* = 157 Hz), 128.4 (d, *J* = 162 Hz), 131.7 (s), 144.5 (d, *J* = 177 Hz), 160.2 (s), 161.6 (s).

***trans*-6-(*cis*-2-*tert*-Butoxyethenyl)-7-*tert*-butoxy-3-phenyl-1,3,5-triazabicyclo[3.2.0]nonane-2,4-dione (13a)**: ^{1}H NMR (acetone-d_6) δ 1.30 (s, 9 H), 1.37 (s, 9 H), 4.84 (dd, *J* = 9.2, 6.6 Hz, 1 H), 5.13 (dd, *J* = 9.2, 5.1 Hz, 1 H), 6.29 (d, *J* = 5.1 Hz, 1 H), 7.01 (d, *J* = 6.6 Hz, 1 H), 7.45–7.63 (m, 5 H); ^{13}C NMR (acetone-d_6) δ 26.7 (q, *J* = 125 Hz), 26.8 (q, *J* = 125 Hz), 66.0 (d, *J* = 147 Hz), 76.8 (s), 77.9 (s), 89.5 (d, *J* = 172 Hz), 96.5 (d, *J* = 158 Hz), 125.0 (d, *J* = 165 Hz), 127.5 (d, *J* = 157 Hz), 128.4 (d, *J* = 162 Hz), 131.1 (s), 148.2 (d, *J* = 179 Hz), 158.7 (s), 160.4 (s).

Allylic urazole 17a: ^{1}H NMR (acetone-d_6) δ 1.35 (s, 9 H), 6.28 (dd, *J* = 4.0, 1.5 Hz, 1 H), 6.42 (ddd, *J* = 15.6, 8.1, 1.5 Hz, 1 H), 7.02 (dd, *J* = 15.6, 4.0 Hz, 1 H), 7.37–7.75 (m, 5 H), 9.57 (br s, 1 H), 9.68 (d, *J* = 8.1 Hz, 1 H).

Allylic urazole 17b: ^{1}H NMR (acetone-d_6) δ 1.31 (s, 9 H), 2.97 (s, 3 H), 6.16 (dd, *J* = 4.0, 1.5 Hz, 1 H), 6.35 (ddd, *J* = 15.6, 7.7, 1.5 Hz, 1 H), 6.90 (dd, *J* = 15.6, 4.0 Hz, 1 H), 9.19 (br s, 1 H), 9.63 (d, *J* = 7.7 Hz, 1 H); ^{13}C NMR (acetone-d_6) δ 25.0 (q, *J* = 142 Hz), 28.1 (q, *J* = 127 Hz), 76.9 (s), 78.9 (d, *J* = 153 Hz), 134.3 (d, *J* = 162 Hz), 151.6 (d, *J* = 160 Hz), 154.2 (s), 155.5 (s), 193.7 (d, *J* = 175 Hz); mp 133–133.5 °C.

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Registry No. 1a, 4233-33-4; **1b**, 13274-43-6; **2**, 52752-58-6; **3**, 52752-57-5; **4**, 86528-14-5; **5**, 86528-15-6; **6**, 79989-51-8; **7** (R = Ph), 110529-29-8; **7** (R = Me), 110529-30-1; **8** (R = Ph), 110529-31-2; *cis*-**8** (R = Me), 110529-32-3; *trans*-**8** (R = Me), 110567-62-9; **9** (R = Ph), 110529-33-4; **10** (R = Ph), 110529-34-5; **10** (R = Me), 110529-35-6; **11** (R = Me), 110611-23-9; **11** (R = Ph), 110611-24-0; **12** (R = Ph), 110529-36-7; **12** (R = Me), 110529-37-8; **13** (R = Ph), 110611-25-1; **13** (R = Me), 110611-26-2; **17** (R = Ph), 110529-38-9; **17** (R = Me), 110529-39-0.