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Reaction of Electrophiles with Unsaturated Systems: Triazolinedione–Olefin Reactions[1]

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Mechanisms of the reaction of 1,2,4-triazolinediones (4-RTAD, R = phenyl and methyl) with some olefins have been examined. The principal products are those of an ene reaction (eq 1) and diazetidine formation (overall, (2 + 2) addition, eq 2 and 3). The diazetidine from adamantylideneadamantane and MeTAD shows (X-ray analysis) a central carbon–carbon bond length of 1.635 Å. Rates of reaction increase with increasing alkylation (range: k(tetramethylethylene)/k(1-hexene) = 30000). The intramolecular isotope effects k_H/k_D for reaction of PhTAD with *cis*-, *trans*-, and *gem*-tetramethylethylene-d_6 (Stephenson isotope effect test) are 1.1, 3.7, and 5.6, ascribed to rate-determining conversion of olefin and RTAD to an intermediate (considered to be an aziridinium imide, **2**). Solvent effects are small and similar for the ene reaction, diazetidine formation (2 + 2), and a Diels–Alder reaction. The unexpectedly slow rate of reaction of norbornene, the moderate rate of reaction of adamantylideneadamantane, and the relative rates of various cis–trans olefin pairs are consistent with a "perpendicular planes" approach of RTAD and olefin (Figure 4a,c). Some comparisons are made between RTAD and other electrophiles. Product selectivities in the ene reactions of PhTAD and singlet oxygen differ markedly (see Schemes I and III). Some striking similarities are noted in the sensitivity of the rate to substituent for the doubly bonded electrophiles RTAD and singlet oxygen as well as for the singly bonded electrophile Br–Br. Features in common with these electrophiles are low lying LUMO's and relatively small gaps between the HOMO and LUMO levels of each of these electrophiles.

Triazolinedione, RTAD, is a molecule of special interest and versatility. It reacts rapidly with conjugated dienes in a Diels–Alder fashion,[2a] with various olefins in an ene fashion to afford *N*-allylurazoles (eq 1),[2b,c,d] and with some olefins in what is overall a (2 + 2) reaction to afford 1,2-diazetidines[2e] (e.g., eq 2)—a set of three reaction types also shown by singlet oxygen.[2f] RTAD also reacts with certain strained single bonds.[2g] Another notable feature is the reaction of RTAD with some olefins to afford products of ionic rearrangement.[2h–k] In this paper we describe some aspects of products and rates in RTAD–olefin reactions.

RTAD–Olefin Reactions: Evidence for Intermediates. Trapping experiments (external traps[2e,3a,b] and internal traps[3c]) have pointed to the presence of an intermediate, usually formulated as a 1,4-dipole (1). We have examined the ene reaction of RTAD (eq 1) and have applied the Stephenson isotope effect test[4] (use of *cis*- and *trans*-tetramethylethylene-d_6 [TME-d_6]) to this reaction.[5]

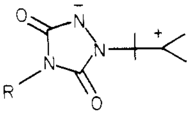

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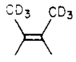
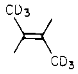
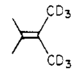
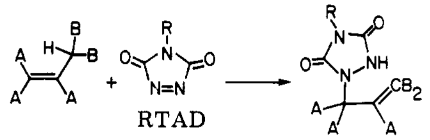
Table I. Isotope Effects in the Ene Reaction (Eq 1) of Triazolinediones (RTAD) with Tetramethylethylenes-d_6 in $CDCl_3$ at 25 °C

compd	RTAD	k_H/k_D
	R = CH_3	1.08 ± 0.1
	R = C_6H_5	1.1
	R = CH_3	3.8 ± 0.2
	R = C_6H_5	3.7
	R = CH_3	5.7
	R = C_6H_5	5.6



(1)

We have also determined the isotope effect with *gem*-TME-d_6.[6] The results are summarized in Table I. The principal conclusion[5] is rate-determining conversion of RTAD and TME to an intermediate in which little or no breaking of "allylic" C–H is involved—an intermediate in which conversion on to product involves a large isotope effect when CH_3 and CD_3 are on the same *side* of the double bond (*trans*- and *gem*-TME-d_6) and a negligible effect when the reactant is *cis*-TME-d_6. The results are accommodated by an aziridinium imide, **2**, for the intermediate, and by a reaction profile as shown in Figure 1.[7]

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(1) (a) This work has been supported by the National Science Foundation. (b) Presented in part at the symposium "Stereochemistry and Reactivity in π Systems" at Texas Christian University, May, 1982. Acknowledgement is made to Verlag Chemie International, Inc. covering reproduction of some of the material from the chapter by F. D. Greene in the symposium volume: "Stereochemistry and Reactivity of Systems Containing π Electrons"; Watson, W. H., Ed.; Verlag Chemie International, Inc.: New York, 1983.

(2) (a) Burrage, M. E.; Cookson, R. C.; Gupte, S. S.; Stevens, I. D. R. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1325. (b) Pirkle, W. H.; Stickler, J. C. *J. Chem. Soc., Chem. Commun.* **1967**, 760. (c) Ohashi, S.; Leong, K.; Matyjaszewski, K.; Butler, G. B. *J. Org. Chem.* **1980**, *45*, 3467. (d) Ohashi, S.; Butler, G. B. *Ibid.* **1980**, *45*, 3472. (e) von Gustorf, E. K.; White, D. V.; Kim, B.; Hess, D. Leitich, J. *Ibid.* **1970**, *35*, 1155. (f) Wasserman, H. H.; Murray, R. W. "Singlet Oxygen"; Academic Press: New York, 1979. (See also: Frimer, A. A. *Chem. Rev.* **1979**, *79*, 359.) (g) Amey, R. L.; Smart, B. E. *J. Org. Chem.* **1981**, *46*, 4090. Cheng, M. H.; Dougherty, D. A. *J. Org. Chem.* **1981**, *46*, 4093. (h) Adam, W.; DeLucchi, O.; Peters, K.; Peters, E.-M.; von Schnering, H. G. *J. Am. Chem. Soc.* **1982**, *104*, 161. (i) Weber, W., Erden, I., deMeijere, A. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 387. (j) Gassman, P. G.; Hoye, R. C. *J. Am. Chem. Soc.* **1981**, *103*, 2496. (k) Toong, Y. C.; Borden, W. T.; Gold, A. *Tetrahedron Lett.* **1975**, 1549.

(3) (a) Hall, J. H.; Jones, M. L. *J. Org. Chem.* **1983**, *48*, 822. (b) Turner, S. R.; Guilbault, L. J.; Butler, G. B. *Ibid.* **1971**, *36*, 2838. (c) Wagener, K. B.; Turner, S. R.; Butler, G. B. *Ibid.* **1972**, *37*, 1454.

(4) (a) Grdina, Sr. B.; Orfanopoulos, M.; Stephenson, L. M. *J. Am. Chem. Soc.* **1979**, *101*, 3111. (b) Stephenson, L. M. *Tetrahedron Lett.* **1980**, *21*, 1005.

(5) Seymour, C. A.; Greene, F. D. *J. Am. Chem. Soc.* **1980**, *102*, 6384.

(6) *gem*-TME-d_6 was prepared in a simple sequence from isobutyric acid via a β-lactone. See the Experimental Section.

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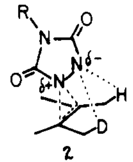

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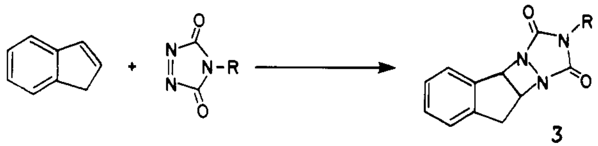
Several questions are of interest: (a) What is the nature of the product-determining step? (b) What is the nature of the rate-determining step? (c) Is an intermediate usually involved, and what can one learn about it?

Products of Reaction of RTAD with Olefins. (a) Olefins with Allylic Hydrogens. This reaction usually results in the ene products[2b,c] (eq 1). We have examined some aspects of selectivity in the ene reaction. The results are summarized in Scheme I.

(b) Aryl Alkyl Olefins. *trans*-1-Phenylpropene reacts with RTAD to afford mixtures of products involving addition to the double bond and an aryl ring; no ene reaction at the allylic hydrogens of the methyl group is observed. Reaction of indene with RTAD affords the diazetidine 3[2e,8] (eq 2).



(2)

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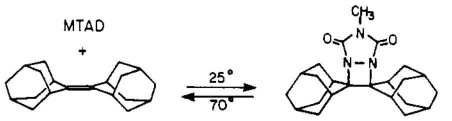
(c) Olefins Lacking Allylic Hydrogen. (i) 4,4-Dimethyldihydropyran (4). In benzene, MeTAD and 6 afford the diazetidine b, an isolable species (Scheme II). In acetone, the first-formed species is again the diazetidine (observed in the NMR). Upon standing, the diazetidine is converted to vinylurazole c and to a tetrahydrooxadiazine[3b] d.

(ii) Adamantylideneadamantane (Ad=Ad). This olefin reacts with RTAD at room temperature to afford a 1:1 adduct (eq 3),[5] shown by X-ray analysis to be the



(3)

diazetidine 5. The diazetidine has a skewed structure (Figure 2), similar in some respects to the dioxetane[9] formed from Ad=Ad and singlet oxygen. Bond distances of interest are summarized in Table II. In particular, the C–C bond (C_{10}–C_{20} connecting the two adamantyl units is unusually long (1.635 Å);[10] the corresponding C–C bond in the dioxetane is 1.549 Å.[9]

Adduct 5 is quite labile, reverting to reactants on heating in solution at 70 °C. Efforts to detect or to trap (by nucleophiles or proton donors) an intermediate in the RTAD–Ad=Ad reaction—in the forward or the reverse direction—have been unsuccessful.

Rates. Rates of reaction of PhTAD with olefins (measured by following the rate of disappearance of PhTAD spectrophotometrically) are summarized in Table III along with some data on PhTAD reactions by Butler.[2d]

Effect of Solvent. Solvent effects on reactions of RTAD with various substrates have been examined by

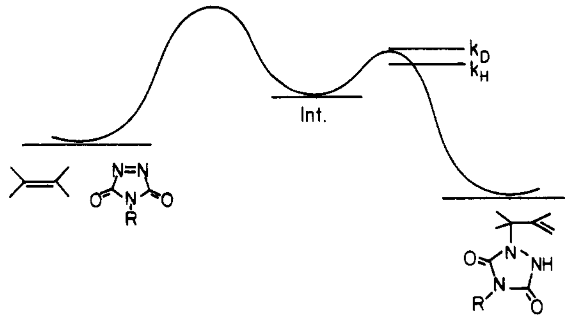


Figure 1. Reaction profile for tetramethylethylene and RTAD.

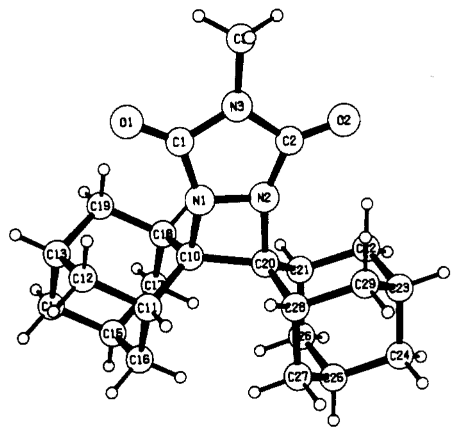
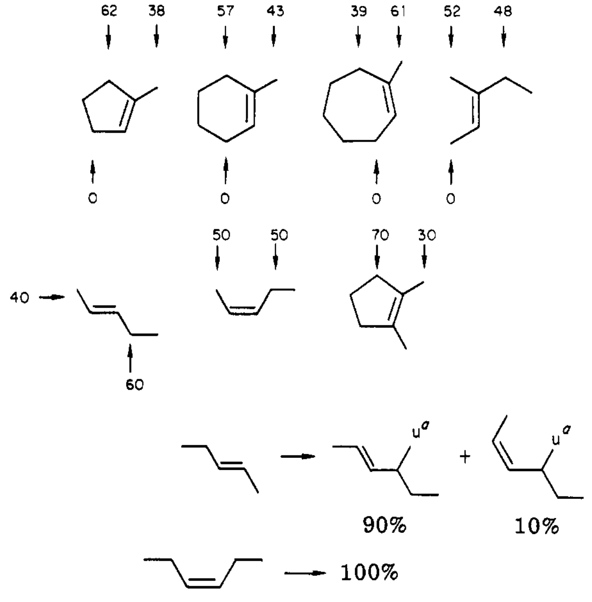


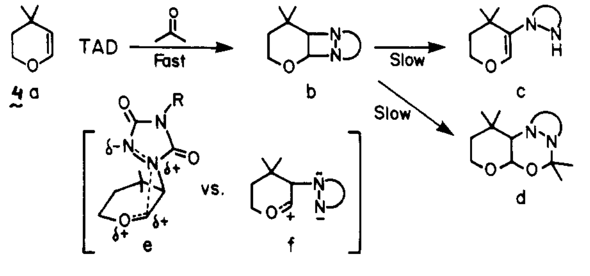
Figure 2. Structure of 5, the 1:1 adduct of adamantylideneadamantane and *N*-methyltriazolinedione.

Scheme I. Selectivities in PhTAD–Olefin Ene Reactions (Eq 1)



[a] U = urazolyl (see eq 1).

Scheme II



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(7) Note that the isotope effects of Table I are strong evidence against a "4 + 2" path for this ene reaction.

(8) Pincock, J. A.; Druet, L. M. *Tetrahedron Lett.* **1980**, *21*, 3251.

(9) Hess, J.; Vos, A. *Acta Crystallogr., Sect. B.* **1977**, *33B*, 3527.

(10) For other examples of long C–C single bonds, see: Osawa, E.; Ivanov, P. M.; Jaime, C. *J. Org. Chem.* **1983**, *48*, 3990 and references cited therein. See also: Cardillo, M. J.; Bauer, S. H. *J. Am. Chem. Soc.* **1970**, *92*, 2399.

Table II. Bond Lengths (Å) in Diazetidine 5

N_1–N_2	1.399	N_1–C_1	1.354
N_2–C_{20}	1.500	C_1–N_3	1.399
C_{20}–C_{10}	1.635	N_3–C_2	1.393
C_{10}–N_1	1.514	C_2–N_2	1.343

Table III. Rates of Reaction of Phenyltriazolinedione with Alkenes in CH_2Cl_2 at 23.5 °C

olefin	$k_2 \times 10^2$, $M^{-1}\ s^{-1}$	olefin	$k_2 \times 10^2$, $M^{-1}\ s^{-1}$
1-hexene	1.0[a]	norbornene	0.0733 ± 0.002
cis-2-butene	38.0 ± 1	1-methylcyclopentene	192 ± 7
trans-2-butene	18.0 ± 0.3	1-methylcyclohexene	52.7 ± 1.6
isobutylene	19.4 ± 0.9	1-methylcycloheptene	513 ± 9
cis-3-hexene	89.1 ± 1.6	2-methyl-2-butene	650[b]
trans-3-hexene	15.0 ± 0.2	2,3-dimethyl-2-butene	30 000[c]
cis-diisopropylethylene	1.2 ± 0.05		
trans-diisopropylethylene	3.85 ± 0.07		
cyclopentene	12.3 ± 0.01		
cyclohexene	5.0[a]		

[a] From ref 2d, converted to 23.5 °C by the factor 0.92. [b] Estimated value from ref 2d with a factor of 4.5 for $k(CH_2Cl_2)/k(C_6H_6)$. [c] Estimated value from Figure 3 with a factor of 5.5 for $k(CH_2Cl_2)/k(CH_3CN)$.

Table IV. Activation Parameters for Reactions of Phenyltriazolinedione in Benzene at 25 °C

olefin	overall rxn	ΔH^*, Kcal/mol	ΔS^*, eu
trans-3-hexene	ene	9.3	-34
Ad=Ad[a]	(2 + 2)	10.6	-33

[a] Ad=Ad is adamantylideneadamantane.

several groups.[2a,d,3a,11] Summarized in Figure 3 are the results of solvent effects for six RTAD–olefin reactions. The reactions with tetramethylethylene[12] and with *trans*-3-hexene[2b,12] afford ene products; the reactions with Ad=Ad,[12] indene,[12] and 2-chloroethyl vinyl ether[3a] afford diazetidines; the reaction with 1,3-cyclooctadiene[11] affords the Diels–Alder adduct. A comparison of activation parameters for two of the cases of Figure 3 is shown in Table IV.

Discussion

The results of this study provide information on the reaction of RTAD with olefins with regard to rate-determining steps and product-determining steps. The principal reactions are ene reaction (eq 1) and diazetidine formation (eq 2 and 3).

As noted by Butler,[2d] increasing alkylation increases the rate of reaction. Also, approximately the same increase in rate is produced by placement of the two alkyl groups on the same end or on opposite ends of the double bond [compare relative k's for 1-hexene (1) vs. *cis*-2-butene (38), *trans*-2-butene (18), and isobutylene (19)], Table III. This pattern is observed with various electrophiles and has usually been ascribed to a three-center (e.g., bromonium ion like) transition state.[13]

In Figure 3 are summarized the effects of solvent on three types of RTAD–olefin reactions: ene reaction, diazetidine formation, and (4 + 2) cycloaddition. The reactions show a rather similar, and modest, response to solvent. The rates do not show a simple relationship to E_T values (e.g., all of the rates in benzene are faster than in THF, and all of the rates in CH_2Cl_2 are faster than in acetonitrile). Within the limited set of THF, acetone, and acetonitrile, three of the reactions (tetramethylethylene, indene, and Ad=Ad) show a stronger response to solvent polarity than do the others, possibly suggestive of increased ionic character to the transition states of the former. Note, however, that 2-chloroethyl vinyl ether[3a] shows a smaller response to solvent. An important part of the problem of all of these solvent effects may lie in specific solvation of reactants,[14] in particular of the RTAD. Overall, the lack of a marked effect of solvent polarity on rate is suggestive that transition states for RTAD–olefin reactions are not closely related to 1,4-dipoles (1).[3a,d,15]

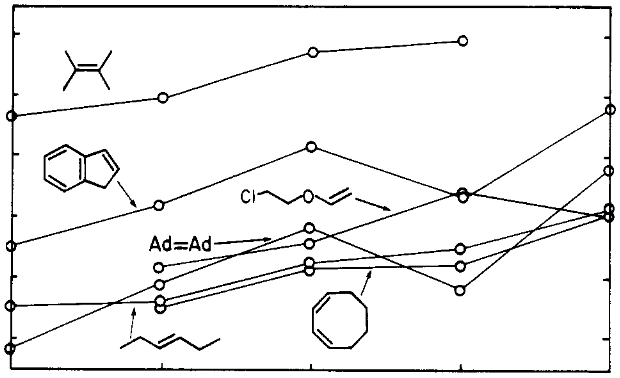


Figure 3. Effect of solvent on rates of reaction of olefins with RTAD: tetramethylethylene,[12] indene,[12] adamantylideneadamantane,[12] 2-chloroethyl vinyl ether,[3a] and *trans*-3-hexene[2b,12] with PhTAD at 25 °C; 1,3-cyclooctadiene[11] with MeTAD at 20 °C.

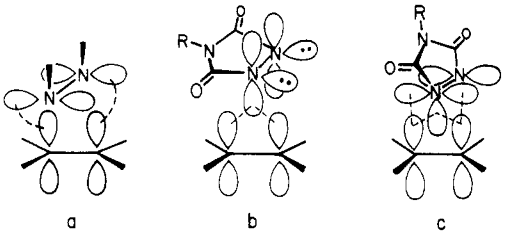
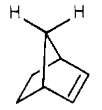


Figure 4.

Comparison of the cis–trans pairs in Table III shows cis more reactive than trans for 1,2-dimethyl and 1,2-diethyl (a common pattern in "three-center" olefin electrophile reactions);[13] for 1,2-diisopropyl, the trans is more reactive. Comparison of *cis*-diethyl vs. *cis*-diisopropyl shows a 70-fold difference in rate, suggestive of the importance of steric effects in these reactions. A further indication is seen in the comparisons of cyclopentene (12), norbornene (0.073), and cyclohexene (5.0) with PhTAD. In a number of cases of electrophilic addition, norbornene is comparable to or faster than cyclohexene,[13] in marked contrast to these PhTAD results.



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[11] Isaksen, H.; Snyder, J. P. *Tetrahedron Lett.* **1977**, 889.

[12] This work.

[13] (a) Freeman, F. *Chem. Rev.* **1975**, *75*, 439. (b) Schmid, G. H.; Garratt, D. G. In "The Chemistry of Double-Bonded Functional Groups"; Patai, S., Ed.; Wiley: New York, 1977; Part 2, Chapter 9.

[14] (a) For a study of the heats of solution of tetracyanoethylene and its relation to cycloaddition rates, see: Haberfield, P.; Ray, A. K. *J. Org. Chem.* **1972**, *37*, 3093. (b) G. B. Butler also has called attention to the possible role of RTAD–solvent complex interaction (reflected in the variation of λ_{max} of RTAD) in the effect of solvent on RTAD–olefin reactions (see ref 2d, p 3473).

[15] For example, compare the small effects in Figure 3 with the large effects in some TCNE–vinyl ether reactions: Huisgen, R. *Acc. Chem. Res.* **1977**, *10*, 117.

Possible geometries of RTAD–olefin interactions are shown in Figure 4.

The array (b) does not appear to account for the cis–trans comparisons and the slowness of norbornene; transition states resembling a (2s + 2a) interaction (Figure 4a) or a three-center interaction (Figure 4c) seem in better accord with the relative *k*'s. The relative slowness of norbornene may be due to interference between the triazolinedione moiety and the 1,4-CH_2 bridging group.

The reaction of RTAD with the hindered olefin adamantylideneadamantane (Ad=Ad) is rather facile and shows an entropy of activation (Table IV), very similar to that for the simple ene reaction of RTAD with *trans*-3-hexene (−33 eu and −34 eu), implying no unusual steric problem in the RTAD–Ad=Ad reaction. These findings also seem to be in better accord with a transition state like Figure 4a or Figure 4c (i.e., a "perpendicular planes" approach of the reactants)[5] rather than Figure 4b.

In summary, the rates of PhTAD–olefin reactions show a sensitivity to alkyl substituent suggestive of net charge transfer from olefin to PhTAD at the transition state but low sensitivity to solvent polarity. This latter may be due to a somewhat diffuse charge distribution in the PhTAD–olefin transition state or to as yet unclarified solvent–solute interactions. The reaction is also subject to steric effects suggestive of (expectedly) close contact between RTAD and olefin at the transition state.

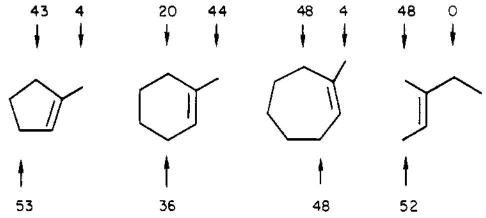
The preceding points pertain primarily to the rate-determining step of RTAD–olefin reactions. What can one say about product-determining steps? As noted earlier in this paper, the isotope effects in the RTAD–tetramethylethylene-d_6 reactions provide strong evidence that the rate-determining step and the product-determining step in that example are not the same, i.e., that an intermediate intervenes between reactants and product (see Figure 1). Other examples of this study are not as definitive on the role of intermediates, but do provide further information on product selectivities. One case of interest is 4,4-dimethyldihydropyran (Scheme II). The finding of the tetrahydrooxadiazine d is suggestive of the trapping of an intermediate. However, the first-formed species is the diazetidine b (isolable when the solvent is benzene, and observed in the NMR when the solvent is acetone) which then is converted in the acetone solution to vinylurazole c and tetrahydrooxadiazine d. These findings indicate the difficulty of obtaining evidence on intermediates involved in the *initial* step—conversion of reactants to diazetidine b—in that the product is labile in polar media, readily undergoing carbon–nitrogen cleavage to afford species (e.g., an aziridinium imide e or a 1,4-dipole f) convertible to the vinyl urazole c by prototropic shift and to tetrahydrooxadiazine d by reaction with acetone. Species e or f also may be involved in the initial reaction sequence by which diazetidine is formed from 4 and PhTAD but the available data do not require it in this case. A recent report indicates that intermediates *are* involved in the conversion of PTAD and 2-chloroethyl vinyl ether to the corresponding diazetidine.[3a]

Table V. Relative Rates of Reaction of Electrophiles (Phenyltriazolinedione, Singlet Oxygen, and Bromine) with Alkenes

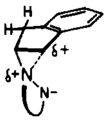
olefin	PhTAD[a]	$^1O_2$[b]	Br_2[c]
CH_2=CH-*n*-Bu	0.067		0.018
trans-EtCH=CHEt	1.00[a]	1.00[b,d]	1.00[c,e]
cis-EtCH=CHEt	5.9	5.1	1.8
$CH_2=C(CH_3)_2$	1.3	0.52	1.5
trans-$CH_3CH=CHCH_3$	1.2	0.94	0.46
cis-$CH_3CH=CHCH_3$	2.5	6.2	0.71
$CH_3CH=C(CH_3)_2$	43	94	36
$(CH_3)_2C=C(CH_3)_2$	2000	2900	500
cyclopentene	0.82	7.5	1.5[f]
cyclohexene	0.33	0.47[g]	0.42[f]
1-CH_3-cyclopentene	13	63[g]	
1-CH_3-cyclohexene	3.5	10[g]	3.1[d]
1-CH_3-cycloheptene	34	95[g]	

[a] In CH_2Cl_2, 23.5 °C (see Table III). [b] In CS_2, 25 °C (ref 19). [c] In CH_3OH, 0.2 M NaBr, 25 °C (ref 20a, relative k_g values). [d] $k = 7.7 \times 10^3\ M^{-1}\ s^{-1}$ (ref 19). [e] $k_g = 1.85 \times 10^3\ M^{-1}\ s^{-1}$ (ref 20a). [f] Reference 13a and 13b (p 777). [g] In CH_3OH (ref 2 f, p 292–294, scaled to *k* for cyclopentene).

Scheme III. Selectivities in $^1O_2$-Olefin Ene Reactions[17a,b]



Other unsymmetrical olefins providing results of interest are the aryl olefins and the alkyl aryl olefins. Reaction of RTAD with styrenes[16a] and stilbenes[16b] affords products involving addition to the double bond and an aryl ring.[16c] With *trans*-1-phenylpropene, reaction with RTAD also affords products of this type and no ene reaction at the hydrogens of the methyl group. Indene provides opportunities for cycloaddition (i.e., overall, Diels–Alder addition to olefin and a π bond of the aromatic ring)[16c] and/or ene reaction with a benzylic allylic hydrogen. Instead, reaction of indene with RTAD affords the diazetidine 3[2e,8] (see eq 2). The lack of ene reaction may be associated with a reaction path involving some charge separation with a larger fraction of the positive charge at the benzyl position than at alkyl (6). The absence of overall cycloaddition into the benzene ring in this case may be due to the added strain associated with a bicyclic array (7).



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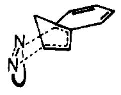

7

Also of interest are some comparisons of reactions of alkyl olefins with RTAD and with singlet oxygen. With both reagents the predominant path is ene reaction. There are *similarities* in relative rates (Table V, discussed below) and *differences* in product selectivities (compare Schemes I and III).

Reaction of RTAD with trisubstituted olefins shows marked preference for abstraction of allylic hydrogen from the more substituted *end* of the double bond, and little preference for the disubstituted *side* of the double bond (Scheme I). In contrast, the ene reactions of singlet oxygen with such olefins (Scheme III)[17a,b] show little preference for reaction at the more substituted *end* but a marked preference for reaction at the more substituted *side* (PSEA—"preference for syn ene addition"). The prefer-

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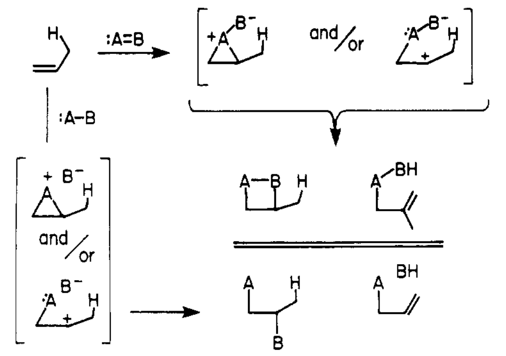
[16] (a) Cookson, R. C.; Giliani, S. S. H.; Stevens, I. D. R. *J. Chem. Soc. C* **1967**, 1905. (b) Greene, F. D., in preparation. (c) Wagner-Jauregg, T. *Synthesis* **1980**, 769.

[17] (a) Orfanopoulos, M.; Grdina, M. B.; Stephenson, L. M. *J. Am. Chem. Soc.* **1979**, *101*, 275. (b) Schulte-Elte, K. H.; Rautenstrauch, V. *Ibid.* **1980**, *102*, 1738. (c) The larger isotope effects for *gem*- than for *trans*-TME-d_6 (Table I) also are in accord with these interpretations, via β-deuterium isotope effects on the developing double bonds in the transition states for H (and D) transfer.

Scheme IV



ential formation of ene products from attack at the more substituted end of the double bond in the RTAD–olefin reaction is consistent with a transition state (for the hydrogen abstraction step) involving some charge separation or involving considerable double bond development (with the attendant greater stabilization of the more substituted double bond).[17c]

The reaction of doubly bonded electrophiles (A=B, e.g., RTAD, R—N=O,[18] and $^1O_2$) with olefins ultimately affords products with four-membered rings or products involving cleavage of an allylic hydrogen or ionic rearrangement.[2h,3c] The overall pattern has many similarities to singly bonded electrophiles (A–B, e.g., Br_2), summarized in Scheme IV. In systems of the type shown in this scheme there may be many arrays in which the energy balance between extremes (closed form, three-center species; open forms, 1,4-dipoles or 1,4-diradicals) may be shifted one way or the other by variations in electrophile, olefin, or solvent.

Comparisons of rates of reaction of PhTAD,[15] singlet oxygen,[19] and bromine[20] are shown in Table V. Some data are available for trifluoronitrosomethane, which undergoes a rapid ene reaction with olefins;[18a] relative rates at −78 °C are 1-butene (1.0), isobutene (14), *trans*-2-butene (21), *cis*-2-butene (170). One notes a remarkable similarity in sensitivity of these reactions to substituent effects in the alkenes.[21] Plots of $\log^{k}{}_{\mathrm{PhTAD}}$ vs. log k for singlet oxygen or bromine are linear showing rather little scatter and *slopes near unity.* The close parallel in sensitivity to substituent effect for singlet oxygen and PhTAD is all the more surprising in the light of the fact that the singlet oxygen rate constants are approximately 10^5 greater than those for PhTAD. The relationships are summarized in Table VI. The singlet oxygen data are quite recent;[19] the paper reports that the variations in rates are largely determined by changes in the entropy of activation, a surprising situation. We are inclined to attribute the marked similarity in relative rates in the reactions of Table V to related degrees of electron donation from olefin to electrophile at the transition states.[22] A detailed comparison of activation data for PhTAD–olefin reactions and their relation to the singlet oxygen data may be of interest.

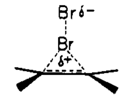
Table VI. Comparison of Rates of Reaction of Some Electrophiles with Olefins

$$\log k^{a}{}_{\mathrm{PhTAD}} = X \log k^{a}{}_{\mathrm{electrophile}} + C$$

electrophile	X	C	correlation coeff, r
$^1O_2$	0.88^b	-4.18^b	0.983^b
$^1O_2$	0.86^c		0.94^c
Br_2	0.99^b	-3.70^b	0.978^b
Br_2	1.06^c		0.96^c
CF_3NO	$(0.7)^d$		$(0.94)^d$

[a] Units, $M^{-1}\ s^{-1}$. [b] Table V, acrylic olefins. [c] Table V, all olefins. [d] Reference 18a, only four olefins (see text).

Features in common for RTAD, RNO, Br_2, and $^1O_2$ are low lying HOMO levels[23a] and relatively small gaps between HOMO and LUMO[23b]—i.e., *low lying LUMO levels.*[23c] This may be adequate to account for similarities in sensitivity to substituents in reactions with olefins (and possibly other substrates). However, it may be of interest to consider the problem in more detail. The Br_2–olefin reaction has long been viewed as proceeding via a three-center cyclic bromonium species.[24] This reaction seems in good accord with a transition state involving net transfer of charge from olefin to Br_2, probably via an "S_N2-like" interaction between the π orbital of olefin (HOMO) with σ^* orbital (LUMO) of Br_2. A lone pair of electrons of Br_2 also may be directly involved in the bromonium ion by way of back bonding—the p orbital of Br_2 (HOMO′) with the π^* orbital of olefin (LUMO′).[24b] What carryover, if any, is there from this model to the RTAD–olefin reaction? As indicated above, the main feature in common is net charge transfer from olefin (π, HOMO) to RTAD (π^*, LUMO). Several geometries are consistent with this (e.g., Figure 4a,b).[25] A further point concerns the role of the lone pair electrons of the electrophile (:A=B). At what point and in what way is this lone pair of electrons involved? In going from reactants to products we start with a lone pair on A (e.g., azo nitrogen of RTAD), and in the product we again have a lone pair on A. An intermediate appears to be needed in at least some of the cases (e.g., the tetramethylethylenes-d_6) and may be involved in many cases. This intermediate appears to have the structural characteristics of an aziridinium imide (2) in which a lone pair of electrons of electrophilic reactant has changed to a σ bond of the aziridinium species. Is that lone pair of any help in the transition state of the rate-determining step



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(18) (a) Barlow, M. G.; Haszeldine, R. N.; Murray, K. W. *J. Chem. Soc., Perkin Trans. 1* **1980**, 1960. (b) See also: Seymour, C. A.; Greene, F. D. *J. Org. Chem.* **1982**, *47*, 5226 and references therein.

(19) Hurst, J. R.; Schuster, G. B. *J. Am. Chem. Soc.* **1982**, *104*, 6854.

(20) (a) Dubois, J.-E.; Mouvier, G. *Bull. Soc. Chim. Fr.* **1968**, 1426. (b) Fukuzumi, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1982**, *104*, 7599.

(21) Solvents are different, and more information on solvent effects in these types of reactions is needed. One does note, however, that substituent effects on bromination of alkenes are rather independent of solvent. (See: Ruasse, M.-F.; Dubois, J.-E. *J. Am. Chem. Soc.* **1975**, *97*, 1977 and ref 8 therein.) See also: Modro, A.; Schmid, G. H.; Yates, K. *J. Org. Chem.* **1977**, *42*, 3673.

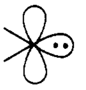
(22) For a detailed analysis of the reactions of bromine with alkenes and arenes in terms of solvation of charge-transfer ion pairs, see ref 20b.

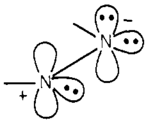
(23) (a) IP's (eV): Br_2 = 10.55, CF_3NO = 11.1, CH_3TAD = 10.2 (private communication from R. Gleiter), $^3O_2$ (1 eV below $^1O_2$) = 12.3 (Kimura, K.; Katsumata, S.; Achiba, Y.; Yamazaki, T.; Iwata, S. "Handbook of HeI Photoelectron Spectra"; Halsted Press: New York, 1981. Rao, C. N. R.; Basu, P. K., Hegde, M. S. *Appl. Spectrosc. Rev.* **1979**, *15*, 1). (b) Reflected in the absorption in the visible region for RTAD, RNO, Br_2; ΔE for $^1O_2$ ($^1\Delta_g$) to the $^1\Sigma_g{}^+$ state is 0.65 eV (ref 2a, p 2). (c) The lower lying the LUMO level of electrophile, the smaller will be the HOMO (olefin)–LUMO (electrophile) gap, and consequently the stronger the interaction and the faster the rate of olefin–electrophile reaction (e.g., see: Fleming, I. "Frontier Orbitals and Organic Chemical Reactions"; Wiley: New York, 1976; Chapter 1). Note also that the relative rates of $^1O_2$, Br_2, CF_3NO, and RTAD with olefins parallel the relative LUMO energy levels predicted from 23a and 23b (e.g., $^1O_2$: fastest rate, lowest LUMO).

(24) Bromination of adamantylideneadamantane affords a "bromonium bromide-like" complex: Strating, J.; Wiering, J. H.; Wynberg, H. *J. Chem. Soc., Chem. Commun.* **1969**, *907.* (b) Olah, G. A.; Schilling, P.; Westerman, P. W.; Lin, H. C. *J. Am. Chem. Soc.* **1974**, *96*, 3581.

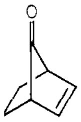
(25) Note that Figure 4c does *not* have stabilizing overlap of olefin (π, HOMO) with RTAD (π^*, LUMO).

of :A=B–olefin reactions, i.e., does the transition state resemble the proposed intermediate aziridinium imide? Orbital symmetry considerations are not in accord with a *symmetrical* three-center array, Figure 4c, for the transition state in the reaction of RTAD and olefin.[25] The transition state might involve some "three-center" character but with unequal degrees of bonding of an azo nitrogen with the two carbons of the double bond, for example, as with the "three-center" addition of a carbene into a double bond.[26] One notes a resemblance between a carbene and a polarized representation of RTAD.





In an effort to ascertain the degree of negative charge at an azo nitrogen at the transition state, PhTAD was subjected to 7-oxo-2-norbornene (8). A transition state resembling an aziridinium imide might be expected to benefit from the proximity of the carbonyl carbon. However, keto olefin 8 does not react with PhTAD, suggestive that the transition state of this (and perhaps other) RTAD–olefin reactions does not resemble an aziridinium imide; the finding is consistent with retardation of this RTAD–olefin reaction by the electron-withdrawing substituent on the carbon–carbon double bond.[27]



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In summary, these studies have shown that the RTAD–olefin ene reaction, formerly considered to proceed by a (4 + 2) route, does not proceed in that way. The simplest interpretation at this point involves rate-determining conversion to a transition state involving net transfer of charge from olefin to RTAD (and resembling a (2s(olefin, HOMO) + 2a(RTAD, LUMO)) interaction (Figure 4a)), collapse to an intermediate with the structural characteristics of an aziridinium imide (2), followed by conversion to products via abstraction of allylic hydrogen if accessible, or via collapse to a diazetidine, or via conversion to rearrangement products through carbocationic species.[2h]

Experimental Section

4-Phenyl-1,2,4-triazoline-3,5-dione (PhTAD) and the 4-methyl derivative (MeTAD) were prepared by *tert*-butyl hypochlorite oxidation of the corresponding triazolidine-3,5-diones.[28a] PhTAD: red needles; mp 165–170 °C (lit.[28] mp 166–172 °C). Sublimation, 93 °C (0.04 torr), afforded red needles, mp 170–175 °C. MeTAD: bright pink needles; mp 102–104 °C (lit.[28a] mp 104 °C). Sublimation 45–50 °C (0.07 torr) afforded needles, mp 103–104 °C.

Ene Reaction of RTAD with Olefins in CH_2Cl_2. A solution of RTAD and excess olefin in CH_2Cl_2 was stirred at room temperature. After complete discharge of the red color of RTAD, the solvent and excess olefin were removed under reduced pressure. The solid obtained was analyzed by ^1H NMR to determine the relative yields of isomers produced. The ene products were purified by recrystallization from benzene–hexanes. Ene products have been reported for PhTAD and *cis*- and *trans*-2-butene, *cis*- and *trans*-2-pentene, *cis*- and *trans*-3-hexene, isobutene, and cyclohexene;[2c] norbornene affords a rearranged product.[29] New ene products[30] include the following (olefin, products (U = 4-phenylurazolyl)): *cis*- and *trans*-1,2-diisopropylethylene, 2,5-dimethyl-4-U-2-hexene (mp 144–145 °C); cyclopentene, 1-U-2-cyclopentene (mp 146 °C); 1-methylcyclohexene, 1-U-2-methyl-2-cyclohexene (mp 144 °C, yield 57%) and 1-U-2-*exo*-methylenecyclohexane (mp 180 °C, yield 43%); 1-methylcycloheptene, 1-U-2-methyl-2-cycloheptene (mp 138 °C, yield 39%) and 1-U-2-*exo*-methylenecycloheptane (mp 155 °C, yield 61%). Additional yield and product data are summarized in Scheme I.[30c] Indene and PhTAD afford the diazetidine (the (2 + 2) adduct) 1,2,2a,7b-tetrahydro-3*H*-indeno[2.1.c]-1,2-diazete-1,2-dicarboxylic acid *N*-phenylimide: mp 173–175 °C (lit.[2e] mp 166–167.5 °C); IR ($CHCl_3$) 1770 (m), 1715 (vs); ^1H NMR ($CDCl_3$) 3.16 (d/d, 1 H), 3.78 (d, 1 H), 5.30 (t, 1 H), 5.84 (d, 1 H), 7.0–7.4 (m, 4 H); ^{13}C NMR ($CDCl_3$) 161.10 (carbonyl), 160.78 (carbonyl), 142.56, 134.52, 131.14, 130.75, 129.16, 128.60, 128.02, 127.22, 125.84, 125.51, 73.56 (C adjacent to N, benzylic), 67.14 (C adjacent to N), 34.55 (benzylic C). 1-Phenylpropene and PhTAD in CH_2Cl_2 afford two 1:2 adducts;[16b,31] examination of the crude mixture by NMR showed no evidence for any attack on the methyl carbon of 1-phenylpropene.

Reaction of 4-Methyl-1,2,4-triazoline-3,5-dione and 4,4-Dimethyl-2,3-dihydro-γ-pyran (See Scheme II). (a) In Benzene. To a solution of 4,4-dimethyl-2,3-dihydro-γ-pyran (58 mg, 0.5 mmol) in 2 mL of dry benzene, protected from light and moisture, was added *N*-methyltriazolinedione 58 mg, 0.5 mmol). A precipitate appeared within 10 min. After 1 day, filtration gave the (2 + 2) adduct (Scheme II, b) of 4-methyl-1,2,4-triazoline-3,5-dione and 4,4-dimethyl-2,3-dihydro-γ-pyran as an off-white solid (230 mg, 45%, mp 168–177 °C) accompanied by a few larger chunky crystals: mp 173–175 °C; IR (KBr) 1765 (m), 1690 (s), 1655 (s), 1475 (s), 1250 (m), 1230 (m); NMR (CD_3COCD_3) 1.02 (s, 3 H), 1.10 (s, 3 H), 1.5–1.9 (m, 2 H), 2.93 (s, 3 H), 4.1–4.3 (m, 3 H), 5.77 (d, 1 H, J = 7); mass spectrum 225 (M^+).

(b) In CH_2Cl_2. The NMR spectrum of the crude product from reaction of the pyran and MeTAD was consistent with the *quantitative formation of the vinyl urazole* (Scheme II, c). Recrystallization from acetone gave the product 1-(3-oxa-6,6-dimethylcyclohexenyl)-4-methyl-1,2,4-triazolidine-3,5-dione (55 mg, 35%) as colorless rhombic crystals: mp 172.5–173.5 °C; IR ($CHCl_3$) 3400–3100 (br), 2960 (s), 1760 (s), 1700 (vs), 1650 (s), 1470 (s), 1395 (m), 1360 (w), 1330 (w), 1200 (s, br), 1165 (w), 1135 (s), 1010 (w), 995 (m), 850 (m), 830 (m); NMR ($CDCl_3$) 1.13 (s, 6 H), 1.75 (t, 2 H), 3.10 (s, 3 H), 4.10 (t, 2 H), 6.68 (s, 1 H), 9.0 (s, br, 1 H); NMR (CD_3COCD_3) 1.15 (s, 6 H), 1.75 (t, 2 H), 3.00 (s, 3 H), 4.10 (t, 2 H), 6.68 (s, 1 H), 9.0 (s, br, 1 H); mass spectrum 225 (M^+).

Anal. Calcd for $C_{10}H_{15}N_3O_3$: C, 53.32; H, 6.71; N, 18.66. Found: C, 53.24; H, 6.75; N, 18.61.

(c) In Chloroform. 4,4-Dimethyl-2,3-dihydro-γ-pyran and *N*-methyltriazolinedione were allowed to react (1:1) at room temperature in deuteriochloroform while following the reaction by NMR. After 10 min, the major product was the diazetidine. After 24 h, the diazetidine had cleanly isomerized to the vinylurazole.

(d) In Acetone-d_6. 4,4-Dimethyl-2,3-dihydro-γ-pyran and *N*-methyltriazolinedione were allowed to react (1:1) at room temperature in acetone-d_6 while following the reaction by NMR.

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(26) Hoffmann, R. *J. Am. Chem. Soc.* **1968**, *90*, 1475. Hoffmann, R.; Hayes, D. M.; Skell, P. S. *J. Phys. Chem.* **1972**, *76*, 664. **Note added in proof**: For other examples of nitrenium ion type reactivity in cycloadditions, see: Fukunaga, T.; Begland, R. W. *J. Org. Chem.* **1984**, *49*, 813.

(27) Note that norbornene is slow reacting toward PhTAD (Table III).

(28) (a) Cookson, R. C.; Gupte, S. S.; Stevens, J. D. R.; Watts, C. T. "Organic Syntheses"; Wiley: New York, 1971; Vol. 51, p 121. (b) Wamhoff, H.; Wald, K. *Org. Prep. Proceed. Int.* **1975**, *7*, 251. This procedure is easy to perform but we had difficulty freeing the RTAD of succinimide.

(29) Adam, W.; De Lucchi, O.; Erden, I. *J. Am. Chem. Soc.* **1980**, *102*, 4806.

(30) (a) ^1H NMR data and IR data are provided for these compounds in the supplementary material (see paragraph at end of paper). (b) Satisfactory combustion analytical data in C, H (±0.4%) were obtained for these products. (c) Possible isomeric urazoles (e.g., 1-methyl-1-U-2-cyclopentene, 1-methyl-1-U-2-cyclohexene, 1-methyl-1-U-2-cycloheptene, and 3-methyl-3-U-1-pentene [U = 4-phenylurazolyl]) were excluded by the absence in the 250-MHz ^1H NMR spectra of bands expected for the vinyl hydrogens in these structures; the observed ^1H NMR are in quantitative agreement with the product compositions shown in Scheme I.

(31) Seymour, C. A., Ph.D. Dissertation, Massachusetts Institute of Technology, Cambridge, MA, 1982.

After 10 min, the main product was diazetidine. After 1.5 h, the NMR was that of a mixture of the tetrahydrooxadiazine (eq 2, d) and vinylurazole (4:2:1). After 3 h, the NMR corresponded to the tetrahydrooxadiazine and the vinylurazole (8:1).

***cis*- and *trans*-2,3-Bis(trideuteriomethyl)-2-butene (*cis*- and *trans*-TME-d_6) Were Prepared by the Method of Stephenson.**[31,32] **1,1,1-Trideuterio-2-(trideuteriomethyl)-3-methyl-2-butene (*gem*-TME-d_6).** 2,2-Dimethyl-3-hydroxy-3-(trideuteriomethyl)-4,4,4-trideuteriobutyric acid was prepared[33a] from isobutyric acid and acetone-d_6, mp 151 °C (lit.[33b] mp 152–153 °C), and converted to the β-lactone[33b] 3,3-dimethyl-4,4-bis(trideuteriomethyl)oxetan-2-one: mp 131 °C; IR ($CHCl_3$) 1815 cm^{-1}; NMR (CCl_4) 1.26 (s). *gem*-TME-d_6 was obtained in quantitative yield by heating a sealed tube containing the β-lactone in the solvent of choice at 140 °C for 2 h.

Kinetic Isotope Effect Studies for Tetramethylethylenes with Triazolinediones by NMR. To a solution of deuterated olefin in $CDCl_3$ (ca. 0.2 M) in an NMR tube at room temperature was added 4-methyl-1,2,4-triazoline-3,5-dione, MeTAD (sublimed) or 4-phenyl-1,2,3-triazoline-3,5-dione, PhTAD (sublimed) until a pale pink color persisted. The solutions were analyzed by 250-MHz NMR, and kinetic isotope effects were calculated from the integrations (see Table I). Ene product from tetramethylethylene and MeTAD: mp 95–96 °C (lit.[2b] mp 95–96 °C); H NMR ($CDCl_3$) 1.58 (s, 6 H), 1.82 (s, 3 H), 3.04 (s, 3 H), 4.99 (s, 2 H), 7.90 (s, br, 1 H). Ene product from TME and PhTAD: mp 127–128 °C (lit.[2c] mp 130–131 °C); ^1H NMR ($CDCl_3$) 1.60 (s, 6 H), 1.85 (s, 3 H), 4.98 (s, 2 H), 7.38 (s, 5 H), 7.90 (s, br, 1 H).

Kinetic Measurements of the Ene Reaction of PhTAD and Olefin. PhTAD and olefin were allowed to react in a UV cell (usually under pseudo-first-order conditions with olefin in greater than 10-fold excess). The decrease of absorbance (e.g., 543 nm for PhTAD in CH_2Cl_2) was recorded vs. time. Rate constants are summarized in Table III.

(2 + 2) Adduct of 4-Methyl-1,2,4-triazoline-3,5-dione and Adamantylideneadamantane (5). 4-Methyl-1,2,4-triazoline-3,5-dione and adamantylideneadamantane[34] (1:1) were allowed to react in a variety of solvents ($CHCl_3$, CH_2Cl_2, CCl_4, benzene, acetone, ether, and CH_3CN), affording a quantitative yield of the (2 + 2) adduct. Recrystallization from ether gave white needles: mp 220–221 °C (to a red melt); IR ($CHCl_3$) 2910 (s), 2860 (s), 1730 (s), 1675 (vs), 1470 (m), 1455 (m), 1435 (s), 1385 (s), 1320 (w), 1095 (m), 1030 (w), 980 (m), 975 (m), 950 (w), 890 (m), 875 (w); NMR ($CDCl_3$) (250 MHz) 1.79 (m, 12 H), 1.98 (s, br, 4 H), 2.12 (d, 4 H), 2.43 (s, 4 H), 2.66 (d, 4 H), 3.06 (s, 3 H); ^{13}C NMR ($CDCl_3$) 154.43 (2 C, carbonyl), 90.64 (2 C, quaternary), 38.21 (2 C, methylene), 35.44 (4 C, methylene), 34.59 (4 C, methylene), 32.47 (4 C, methine), 26.94 (2 C, methine), 26.73 (2 C, methine), 26.17 (N-CH_3); mass spectrum 268 (60.11).

Anal. Calcd. for $C_{23}H_{31}N_3O_2$: C, 72.41; H, 8.19; N, 11.01. Found: C, 72.47; H, 8.60; N, 10.99.

X-ray Analysis of 5. The crystals were triclinic, space group $P\bar{1}$, with a = 9.306 (3) Å, b = 10.563 (4) Å, c = 10.553 (4) Å, α = 84.61 (3)°, β = 66.08 (3)°, γ = 87.74 (3)°, and d_{calcd} = 1.342 g cm^{-2} for Z = 2 ($C_{23}H_{31}N_3O_2$, M = 381.52). The intensity data were measured on a Hilger-Watts diffractometer (Ni filtered Cu K_α radiation, $\Theta - 2\Theta$ scans, pulse height discrimination). A crystal measuring approximately 0.10 × 0.12 × 0.6 mm was used for data collection. A total of 2539 reflections were measured for $\Theta < 57°$, of which 2190 were considered to be observed [$I > 2.5\sigma(I)$]. As a result of problems encountered during data collection, all *hkl* data were discarded. In addition, six reflections which were strongly affected by extinction were excluded from the final refinement and final difference map.

The structure was solved by a multiple solution procedure[35] and was refined by full-matrix least squares. In the final refinement anisotropic thermal parameters were used for the non-hydrogen atoms and isotropic temperature factors were used for the hydrogen atoms. The hydrogen atoms were included in the structure factor calculations but their parameters were not refined. There was evidence from difference maps for a 2-fold disorder of the methyl group at N(3). Six hydrogen atoms, each with half weight, were used to describe the C(3) methyl group. One set is shown in the figures and the other set is rotated 180° about the C–N bond from these hydrogen atoms. The final discrepancy indices are R = 0.045 and w_R = 0.054 for the remaining 2061 observed reflections. The final difference map has no peaks greater than ±0.2 e A^{-3}.

(2 + 2) Adduct of 4-Phenyl-1,2,4-triazoline-3,5-dione and Adamantylideneadamantane. White crystals; mp 229–231 °C; IR ($CHCl_3$) 1740, 1680 cm^{-1}; NMR ($CDCl_3$) 1.90 (br, 18 H), 2.60 (br, 8 H), 2.85 (br, 2 H), 7.40 (br, cplx, 5 H); ^{13}C NMR ($CDCl_3$) 153.19 (2 C, carbonyl), 91.75 (2 C, quaternary), 38.23 (2 C, methylene), 35.56 (4 C, methylene), 34.67 (4 C, methylene), 32.55 (4 C, methine), 26.99 (2 C, methine), 26.78 (2 C, methine); mass spectrum 268 (45.78), 119 (60.84).

Anal. Calcd. for $C_{28}H_{33}N_3O_2$: C, 75.81; H, 7.50; N, 9.47. Found: C, 75.41; H, 7.62; N, 9.52.

Reversal of (2 + 2) Adduct Formation. A solution of the (2 + 2) adduct of N-phenyltriazolinedione and adamantylideneadamantane in deuteriochloroform and an excess of 2,3-dimethyl-2-butene was heated at reflux for 3 days, protected from moisture, and shielded from light. The solvent was evaporated, and the mixture was analyzed by NMR, showing adamantylideneadamantane and the ene adduct of PhTAD and tetramethylethylene. Chromatography on silica (CH_2Cl_2) afforded the ene adduct of PhTAD and tetramethylethylene and adamantylideneadamantane (IR and mass spectra identical with authentic samples). Subjection of the diazetidine from indene and PhTAD to the above conditions also results in reversal, but at a slower rate.

Attempted Reaction of Bicyclo[2.2.1]hept-2-en-7-one and N-Phenyltriazolinedione. Bicyclo[2.2.1]hept-2-en-7-one[36a] and N-phenyltriazolinedione were heated in refluxing benzene or deuteriochloroform (ca. 1 M) under argon. The solution was decolorized after 24 h. Analysis by NMR showed unchanged ketone and products of decomposition of triazolinedione.[36b] A competition experiment between the keto olefin, norbornene, and PhTAD in $CDCl_3$ at room temperature showed unchanged keto olefin and PhTAD–norbornene product.[29]

Registry No. 4a, 64833-72-3; 5, 90461-89-5; b, 90461-87-3; c, 90461-88-4; $(CH_3)_2C{=}C(CH_3)_2$, 563-79-1; D_2, 7782-39-0; RTAD (R = Ph), 4233-33-4; RTAD (R = Me), 13274-43-6; 1-hexene, 592-41-6; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; isobutylene, 115-11-7; *cis*-3-hexene, 7642-09-3; *trans*-3-hexene, 13269-52-8; *cis*-diisopropylethylene, 10557-44-5; *trans*-diisopropylethylene, 692-70-6; cyclopentene, 142-29-0; cyclohexene, 110-83-8; norbornene, 498-66-8; 1-methylcyclopentene, 693-89-0; 1-methylcyclohexene, 591-49-1; 1-methylcycloheptene, 1453-25-4; 2-methyl-2-butene, 513-35-9; adamantylideneadamantane, 30541-56-1; 4-phenyl-1,2,4-triazoline-3,5-dione/adamantylideneadamantane (2 + 2) adduct, 90461-90-8.

Supplementary Material Available: ^1H NMR and IR data for the ene products of Scheme I; X-ray data (atomic coordinates, thermal parameters, bond lengths, and angles) for the methyltriazolinedione–adamantylideneadamantane adduct (9 pages). Ordering information is given on any current masthead page.

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