energy for this combination is required because, in attaining the transition state for reaction, one or both radicals must be distorted from a strongly preferred planar geometry. However, the small magnitude of the energy barrier to combination in a radical in which the spin density at the α carbon is about as low as that in triphenylmethyl[39] serves to confirm our view[3] that radical lifetimes generally depend very much more on steric than on electronic factors.

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Analysis of the Reactivity of Alkenylidenecyclopropanes in Cycloaddition Reactions

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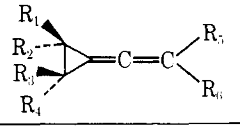
Abstract: The second-order rate constants for the cycloaddition reactions of substituted alkenylidenecyclopropanes with 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) in dichloromethane have been measured and found to fall in the range of ~2 to ~40 M^{-1} sec^{-1}. The reaction of 2-phenylisobutenylidenecyclopropane with PTAD is characterized by $\Delta H^{\ddagger} = 9.6 \pm 1.5$ kcal/mol and $\Delta S^{\ddagger} = -23 \pm 3$ eu. Methyl groups attached to the three-membered ring increase the reactivity of the alkenylidenecyclopropanes, while unsaturated groups, such as phenyl and ethynyl, lead to reductions in reactivity. In the unsymmetrically substituted 2,2-dimethyl- and 2,2,3-trimethylisobutenylidenecyclopropane, the dominant mode of attack by PTAD occurs at the most highly methylated ring carbon atoms. The reactivity and mode of reaction of the substituted alkenylidenecyclopropanes with PTAD is discussed in terms of the ionization potentials of the HOMO's and the results of CNDO calculations and frontier molecular orbital theory. The detailed analysis of the cycloaddition reaction leads to the conclusion that the cycloaddition is concerted and occurs via a very early transition state which is orbitally controlled.

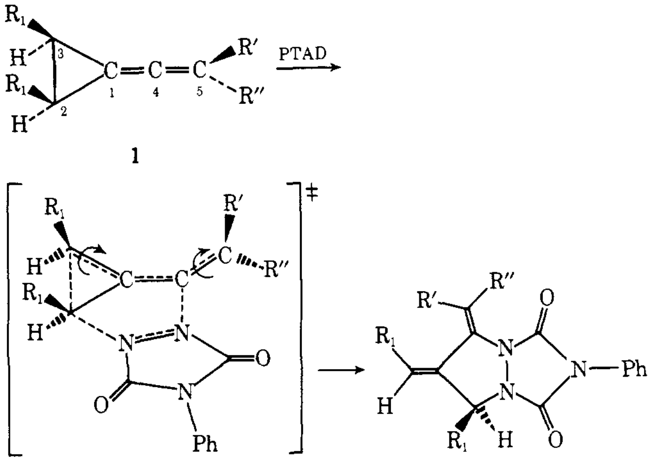
Recent investigations in our laboratories of cycloaddition reactions of cyclopropane-containing compounds have revealed rather dramatic differences in reactivity and mode of reaction. Whereas alkenylidenecyclopropanes (**1**) react rapidly with 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) to produce adducts of general structure **3**,[2] methylenecyclopropanes[3] and vinylcyclopropanes,[4] which represent partial structures within **1**, react slowly to produce [2 + 2] cycloadducts or "ene" products. In order to account for the unusual reactivity of **1** with PTAD, a concerted cycloaddition mechanism involving interaction of the four π and two C_2-C_3 σ electrons of **1** with the two π electrons of PTAD, as illustrated in **2**, was proposed.[2] Subsequent stereochemical studies were fully consistent with the process represented in **2**.[5] We wish now to report the results of a kinetic study of the reaction of substituted alkenylidenecyclopropanes with PTAD, and an analysis of the kinetic and product distribution data in terms of ionization potentials and AO coefficients in the HOMO's as determined by photoelectron (PE) spectroscopic studies and CNDO calcula-

Table I. Second-Order Rate Constants for the Reaction of PTAD in Dichloromethane at 29° with



Compd	R_1	R_2	R_3	R_4	R_5	R_6	k, M^{-1} sec^{-1}
4	C_6H_5	H	H	H	CH_3	CH_3	2.60, 2.64, 2.59[a] 3.12[b] 2.90[c]
5	C_6H_5	H	H	CH_3	CH_3	CH_3	4.53
6	C_6H_5	H	CH_3	H	CH_3	CH_3	5.71
7	CH_3	H	H	CH_3	CH_3	CH_3	5.87, 6.02
8	CH_3	H	CH_3	H	CH_3	CH_3	12.2
9	CH_3	CH_3	H	H	CH_3	CH_3	13.6
10	CH_3	C≡CH	H	H	CH_3	CH_3	1.74
11	CH_3	CH_3	CH_3	H	CH_3	CH_3	15.4
12	CH_3	CH_3	CH_3	CH_3	CH_3	CH_3	37.8
13[d]	C_6H_5	H	H	H	CH_3	CH_2CH_3	1.84
14	C_6H_5	H	H	H	CH_2CH_3	CH_2CH_3	1.03

[a] Duplicate runs at 1.8:1 alkenylidenecyclopropane–PTAD ratio. Unless otherwise noted ~1.5:1 reactant ratios were used. [b] 3.8:1.0 4–PTAD ratio. [c] 6.5:1.0 4–PTAD ratio. [d] As a 1:1 mixture of diastereoisomers.



1

2

3

tions. A detailed analysis of the bonding in alkenylidenecyclopropanes as derived from PE studies and CNDO calculations appears in the following article.[6]

Results

The rates of reactions of substituted alkenylidenecyclopropanes with PTAD in dichloromethane at 29° were followed using a stopped-flow kinetic apparatus. Because initially formed 1:1 adducts can in some cases react more slowly to form 2:1 adducts, rate constants were calculated from data to less than 30% consumption of the PTAD. Excellent linear second-order plots were obtained in all cases. The second-order rate constants for the reactions of variously substituted alkenylidenecyclopropanes are given in Table I. Table II lists second-order rate constants for the reaction of 2-phenylisobutenylidenecyclopropane (**4**) with PTAD in dichloromethane at various temperatures. $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are calculated to be 9.6 ± 1.5 kcal/mol and −23 ± 3 eu. Table III lists rate constants for the reaction of **4** with PTAD in solvents which were shown not to react with PTAD at rates comparable to **4**.

For comparison purposes, attempts were made to measure the rate of reaction of PTAD with a conjugated diene. Attempts to measure the rate of reaction with cyclopentadiene were not successful; the rate of reaction being too fast to measure under our experimental conditions. The rate of reaction of *trans*-1,3-pentadiene could be followed and gave a second-order rate constant of 803 M^{-1} sec^{-1}.

Table II. Second-Order Rate Constants for the Reaction of 4 with PTAD at Various Temperatures

Temp, °C	k, M^{-1} sec^{-1}
29	2.77[a]
15	0.74
7.2	0.59
−17.5	0.133
−20.7	0.108

[a] Average of values given in Table I.

Table III. Rate Constants for the Reaction of 4 with PTAD in Various Solvents at 29°

Solvent	k, M^{-1} sec^{-1}
$CHCl_3$	5.4
CH_2Cl_2	2.6–3.1
CH_3CN	0.33
CH_3COCH_3	0.09

Discussion

Analysis of the data provided in the previous section reveals several very interesting trends. The cycloaddition reactions of alkenylidenecyclopropanes with PTAD are very facile reactions. The very low $\Delta H^\ddagger$ is consistent with a concerted reaction, and is suggestive of a very early transition state.[7] A two-step cycloaddition process via a dipolar intermediate is definitely ruled out by the observed effect of solvent polarity on reaction rate (Table III). The rate of cycloaddition decreases with increasing solvent polarity. In the transition state the polar nature of PTAD has been diminished in its partial conversion to the urazole ring in the product.

The type and number of groups attached to the three-membered ring have a pronounced effect on the rate of reaction. Unsaturated groups (e.g., aryl and ethynyl) attached to the three-membered ring retard the rate of reaction, while alkyl groups accelerate the rate of cycloaddition in spite of apparently large steric effects imposed by the methyl groups on the approach of the PTAD to C_2 (or C_3).

The origin of the rate-accelerating effect produced by methyl groups attached to the three-membered ring may be gained from the results of photoelectron spectroscopic measurements, and the results of CNDO calculations and frontier molecular orbital (FMO) theory.[8] The lowest vertical ionization potentials of the alkenylidenecyclopropanes (corresponding to the HOMO's) decrease with increasing meth-

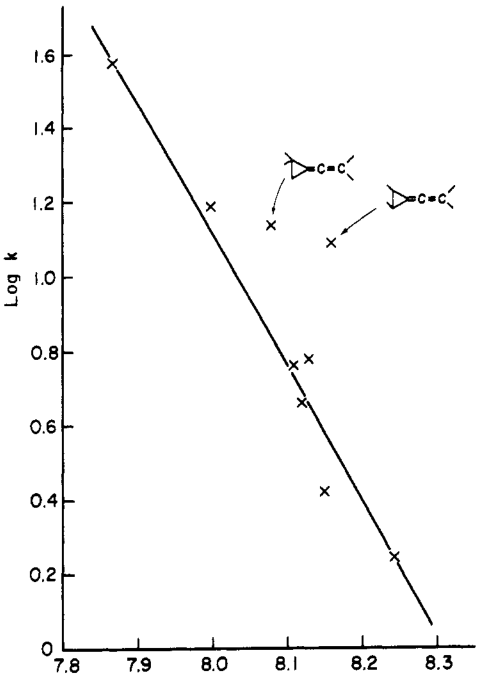


Figure 1. Plot of log k vs. ionization potential of the HOMO's of the alkenylidenecyclopropane.

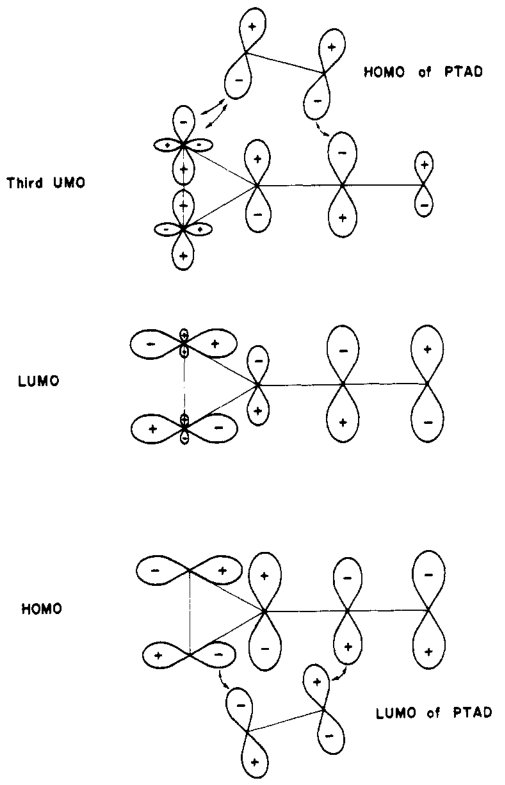


Figure 2. Illustration of the symmetry properties of the HOMO, LUMO, and third UMO of an alkenylidenecyclopropane and FMO orbital interactions with the HOMO and LUMO of PTAD.

Table IV. Photoelectron Ionization Potentials of HOMO's of Alkenylidenecyclopropanes

Substituents on three-membered ring	Vertical IP, eV	k, M^{-1} sec^{-1}
2,2-CH_3, C≡CH (**10**)	8.23	1.74
cis-2,3-$(CH_3)_2$ (**8**)	8.16	12.2
2-C_6H_5 (**4**)	8.15	2.77[a]
trans-2,3-(CH_3) (**7**)	8.13	5.94[a]
trans-2-CH_3-3-C_6H_5 (**5**)	8.12	4.53
cis-2-CH_3-3-C_6H_5 (**6**)	8.11	5.71
2,2-$(CH_3)_2$ (**9**)	8.08	13.6
2,2,3-$(CH_3)_3$ (**11**)	8.00	15.4
2,2,3,3-$(CH_3)_4$ (**12**)	7.87	37.8

[a] Average of values given in Table I.

Table V. CNDO Calculated Energies of HOMO's and the Third UMO's in Alkenylidenecyclopropanes[a]

Compound	HOMO, eV	Third UMO, eV	ΔE, eV	Log k
trans-2,3-$(CH_3)_2$ (**7**)	−10.3850	+7.6867	18.0717	0.774
cis-2,3-$(CH_3)_2$ (**8**)	−10.3441	+7.5915	17.9356	1.086
2,2-$(CH_3)_2$ (**9**)	−10.3196	+7.5398	17.8594	1.134
2,2,3-$(CH_3)_3$ (**11**)	−10.1646	+7.4501	17.6147	1.188
2,2,3,3-$(CH_3)_4$ (**12**)	−10.0259	+7.2624	17.2883	1.577

[a] For details of assumed bond lengths and geometries, see ref 6.

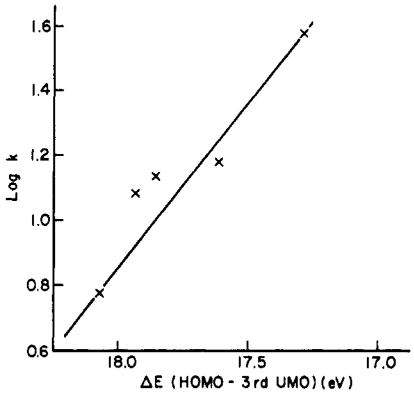
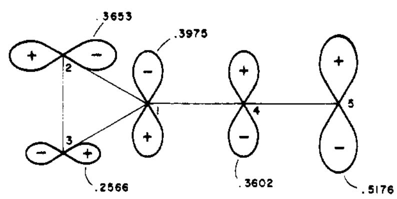


Figure 3. Plot of log k vs. ΔE (HOMO − third UMO) for the methylated alkenylidenecyclopropanes **7**, **8**, **9**, **11**, and **12**.

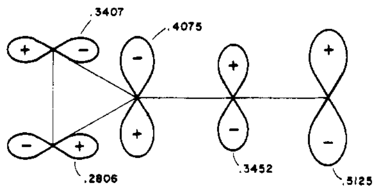
yl substitution on the three-membered ring (see Table IV), and a plot of log k vs. these ionization potentials is reasonably linear (Figure 1). The *cis*-2,3-dimethyl compound **8** deviates appreciably from the plot, the larger rate constant undoubtedly arising from release of steric strain on going to the transition state.

All of the methylated alkenylidenecyclopropanes have been examined by photoelectron spectroscopy and CNDO-SCF-MO calculations.[6] In all cases the HOMO's are derived by interaction of the C_4-C_5 π system with the Walsh orbitals of the three-membered ring, as illustrated in Figure 2. The LUMO's of the alkenylidenecyclopropanes are formed by interaction of the C_4-C_5 π system with a Walsh orbital, but they do not have the correct symmetry for interaction of C_2 (or C_3) and the in-plane p orbital at C_4 with the HOMO of PTAD according to the FMO approach to concerted reactions[8] (see Figure 2). The unoccupied MO of appropriate symmetry for interaction is the third lowest unoccupied MO (see Figure 2) (the π^* MO of the C_1-C_4 bond lies between the LUMO and this MO). According to the CNDO calculations, the energy difference between the HOMO and the third UMO decreases as the number of methyl groups attached to the three-membered ring increases (see Table V). From the FMO approach,[8] this is consistent with the observed increase in rate of reaction with increased methyl substitution (see Figure 3).

The rate retarding effect produced by the phenyl and ethynyl groups (compare the rates of reaction of **5** and **6** with **7** and **8**, and **10** with **9** in Table I) is due to the inductive electron withdrawing properties and not to a conjugative or resonance interaction of the unsaturated groups with the three-membered ring. These results are consistent with



HOMO of 2,2 - Dimethylisobutenylidenecyclopropane



HOMO of 2,2,3 - Trimethylisobutenylidenecyclopropane

Figure 4. Coefficients of the AO's comprising the HOMO's of **11** and **12**.

a recent theoretical analysis by Wilcox and coworkers of the ineffectiveness of the cyclopropyl group in transmitting substituent effects.[9] The PE spectra of **7** and **8** similarly indicate very little interaction between the phenyl group with the three-membered ring.[6]

Analysis of the product distributions derived from the unsymmetrically substituted dimethyl and trimethyl compounds **9** and **11** reveals that the major product in each case is formed by attack of PTAD at the most highly substituted ring carbon (>95% with **9** and 65% with **11**). This behavior is understood by analysis of the orbital coefficients of the HOMO's of **9** and **11** (see Figure 4). In both cases the coefficients of the AO's forming the Walsh-type orbital are higher at the most highly substituted carbon atom. From the FMO analysis of concerted reactions, the larger the coefficients of the interacting orbitals, the stronger the interaction and the more favorable the reaction.[8] The greater preference for attack at the most highly substituted ring carbon of **9** relative to that in **11** must arise from the greater difference between the coefficients at C_2 and C_3 in **9** (0.1087) relative to that in **11** (0.0601). These cycloaddition reactions, therefore, are highly orbitally controlled, occurring via very early transition states in which steric inhibition to attack by the dienophile is not particularly important.

Substitution of methyl by ethyl on the allene chromophore produces a slight rate decrease (compare rates of reaction of **4**, **13** and **14** in Table I). This modest decrease in rate may be due either to steric inhibition to attack on the in-plane p orbital at C_4, or to increased steric strain in the transition state due to the rotations of the groups attached to C_2 (or C_3) and C_5 into a common plane in the product. Because all the other data point to a very early transition state, we feel that the former explanation is probably correct.

The rate data presented herein indicate that alkenylidenecyclopropanes are quite reactive toward concerted cycloaddition; however; a quantitative reactivity comparison with conjugated dienes has not been made previously. We have measured the rate constant for the reaction of *trans*-1,3-pentadiene with PTAD ($k = 803\ M^{-1}\ \text{sec}^{-1}$) and find a difference in reactivity of ~20–300. One cannot help but be surprised by the high reactivity of alkenylidenecyclopropanes in these cycloaddition reactions. However, because of the tendency of alkenylidenecyclopropanes to undergo thermal rearrangement to bisalkylidenecyclopropanes[10,11] and the lower reactivity of other dienophiles relative to PTAD, we have not been able to effect cycloaddition of **4** with less reactive dienophiles.

Experimental Section

Preparation of Alkenylidenecyclopropanes. Alkenylidenecyclopropanes **13** and **14** were prepared according to the procedure of Hartzler[12] involving generation of the appropriate allenecarbene from the corresponding propargyl chloride (all other alkenylidenecyclopropanes have been reported previously) with potassium *tert*-butoxide in the presence of styrene.

13: bp 38–41° (0.55 mm); ir (cap. film) 2010 cm^{-1}; NMR (1:1 mixture of *E* and *Z* isomers) δ 0.89 (2 t's, $\Delta\delta = 0.011$ ppm, $J = 7.1$ Hz), 1.37 (2 X portions of AMX systems, $\Delta\delta = 0.053$ ppm, $J = 5.3, 6.9$ Hz), 1.65 (2 s's, $\Delta\delta = 0.01$ ppm), 1.84 (2 M portions of AMX systems, $\Delta\delta \approx 0.01$ ppm), 2.71 (2 A portions of AMX systems, $\Delta\delta = 0.012$ ppm, $J = 8.7, 5.3$ Hz), 7.25 (s, Ar H).

14: bp 92–94° (3.5 mm); ir (cap. film) 2010 cm^{-1}; NMR ($CDCl_3$) δ 1.02 (t, $J = 7.3$ Hz), 1.55 (dd, X portion of an AMX system, $J = 5.3, 7.0$ Hz), 2.07 (q, $J = 7.3$ Hz, overlaps M portion of AMX system), 2.87 (dd, A portion of an AMX system, $J = 5.3, 8.6$ Hz), 7.22 (s, Ar H).

Preparation of 2-Ethynyl-2-methylisobutenylidenecyclopropane (10).[13] To 16.8 g of potassium *tert*-butoxide in 100 ml of benzene and 25 ml of 2-methyl-2-propanol was added 15.3 g of 3-chloro-3-methyl-1-butyne. Normal work-up[12] followed by fractional distillation of the product gives **10** (12% as a pale yellow liquid): bp 55–56.5° (18 mm); ir (cap. film) $\nu_{\equiv C-H}$ 3292 cm^{-1}, $\nu_{C\equiv C}$ 2116 cm^{-1}, $\nu_{C=C=C}$ 2037 cm^{-1}; NMR ($CDCl_3$) δ 1.42 (s, 3*H*), 1.53 (d, $J = 7.3$ Hz, 1 H), 1.77 (s, 3 H), 1.80 (s, 3 H), 1.84 (d, $J = 7.3$ Hz, 1 H), 1.99 (s, 1 H).

Measurement of Rates of Reaction of Alkenylidenecyclopropanes with PTAD. Solutions of the alkenylidenecyclopropanes (~10^{-2} *M*) and PTAD (~7×10^{-3} *M*) in the appropriate solvent were prepared. The rates of reactions were measured using a Durram stopped-flow kinetic apparatus monitoring the disappearance of PTAD at 542 nm ($\epsilon_{CH_2Cl_2}$ 232).[14] Second-order rate constants were calculated in the normal manner from data out to ~30% reaction, conditions under which the subsequent reaction of PTAD with the diene-containing adducts does not contribute significantly to the disappearance of PTAD.[2]

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(13) Compound **10** is apparently formed to some extent in all alkenylidenecyclopropane preparations via elimination of 3-chloro-3-methyl-1-butyne to 3-methylbut-3-en-1-yne followed by competitive reaction with the dimethylallenecarbene.

(14) The λ_{max} of PTAD in the other solvents differed substantially from that in dichloromethane. The rates of the reactions in the other solvents were monitored at 542 nm using appropriate ϵ's for PTAD at that wavelength.