The sequence (R5) + 2(R6) leads to autocatalytic production of $HBrO_2$, but the second-order destruction by (R4) creates a steady state given by eq 2.

$$[HBrO_2]_B = \frac{k_5}{2k_4}[BrO_3^-][H^+] = 1 \times 10^{-4}[BrO_3^-][H^+] \quad (2)$$

Hence the concentration of bromous acid is over 10^5 times as great when process B is taking place as when process A is.

The rate of process B is proportional to $[HBrO_2]$, and the rate is related to $[Br^-]$ much as the current in a thyratron tube is related to the grid potential. Thus if the concentration of bromide ion is sufficiently great the residual rate of (B) is very small and is independent of bromide concentration, while at very low concentrations of bromide ion the rate of (B) is very much greater but is again independent of bromide concentration. When the concentration of Br^- drops below a certain critical value, the concentration of $HBrO_2$ increases autocatalytically from the value of eq 1 to that of eq 2. The transition involves the competition between (R2) and (R5), and our analysis predicts the critical concentration is given by eq 3.

$$[Br^-]_{crit} = \frac{k_5}{k_2}[BrO_3^-] = 3 \times 10^{-6}[BrO_3^-] \quad (3)$$

In terms of the numerical data reported above, the critical concentration (points B and F in Figure 1) should be 2×10^{-7} *M* for the concentrations in that run and should vary proportionately with bromate concentration; we observe a critical concentration of 1×10^{-6} *M* in Figure 1 and find the value increases linearly but less than proportionately with increasing bromate concentration.

Several factors mitigate any possible concern over the apparent discrepancies. The less than proportional variation of critical bromide concentration with bromate concentration arises because a finite time is necessary to convert $[HBrO_2]$ from the value of eq 1 to that of eq 2, and the rate of change of $[Br^-]$ during that time is a function of $[BrO_3^-]$. The silver bromide impregnated electrode does not behave ideally below 10^{-6} *M* in static systems, and we have no assurance that the apparently ideal behavior is indeed so at the still lower concentrations in the dynamic system of Figure 1. The quantitative analysis of the various rate constants has made no attempt to correct for unknown activity coefficient effects in 1 *M* sulfuric acid. Finally, Lee and Lister[8] estimated the free energy of formation of bromide ion at 25° on the basis of a 50° extrapolation of a ratio of rate constants measured over a 20° range; if the correct value is 1.0 kcal/mol less positive than they report, k_5/k_2 would predict a critical bromide concentration in exact agreement with our observations and the thermodynamics of (R6) would be in better agreement with the requirements of our mechanism.

The above argument demonstrates that irreversible processes A and B will take place under different conditions in the same system and that a solution reacting by (A) will of necessity convert itself to one reacting by (B). If we are to explain oscillation, we must get back from (B) reaction to (A) reaction. The cerium(IV) produced in (B) reacts with the organic species by overall processes (R9) and (R10) whose kinetics have been elucidated by Kasperek and Bruice.[4]

$$6Ce^{4+} + CH_2(COOH)_2 + 2H_2O \longrightarrow 6Ce^{3+} + HCOOH + 2CO_2 + 6H^+ \quad (R9)$$

$$4Ce^{4+} + BrCH(COOH)_2 + 2H_2O \longrightarrow Br^- + 4Ce^{3+} + HCOOH + 2CO_2 + 5H^+ \quad (R10)$$

If most organic matter is unsubstituted malonic acid (as at point C of Figure 1), the system is unable to restore the high bromide concentration needed for reaction A and an extensive induction period at low bromide concentration ensues. As the concentration of bromomalonic acid increases, (R10) become increasingly more important. The bromide ion produced by (R10) is destroyed by (R2) as long as the process (R5) + 2(R6) is able to maintain the bromous acid concentration at the value of eq 2. When the rate of (R10) becomes sufficiently great, $[HBrO_2]$ drops rapidly to the value of eq 1, process B is "turned off," and $[Br^-]$ rises rapidly until the rate of production by (R10) is balanced by the rate of destruction by process A initiated by (R3). The oscillatory cycle can then begin again.

The critical bromide concentration at points D and H when cerium(IV) is present is less than the concentration at points B and F when it is not. The difference arises because (R6) is reversible and because cerium(IV) can also oxidize $BrO_2\cdot$, but these complications cannot be discussed in this brief communication.

Because cerium species are present in small concentration compared to bromate and malonic acid, they do not contribute to the stoichiometry of the overall reaction, which is given by process C.

$$3BrO_3^- + 5CH_2(COOH)_2 + 3H^+ \longrightarrow 3BrCH(COOH)_2 + 2HCOOH + 4CO_2 + 5H_2O \quad (C)$$

This process is the result of the sequence x(A) + $(3 - x)$(B) + $(2 - 2x)\cdot$(R9) + $2x$(R10), where x may have any value between zero and unity. It is the free energy change of process C that drives the overall reaction, and it is the failure of bromate ion and malonic acid to react directly with each other at a significant rate that permits the very complicated way by which the overall process is achieved. Indubitably the free energy of the system as a whole is decreasing monotonically throughout the entire process represented by Figure 1!

A longer manuscript will be presented describing our experimental observations and the detailed thermodynamics and kinetics of this fascinating system.

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Photodimerization of Arylazirenes. Some Aspects of the Mechanism[1]

Sir:

Recently[2] we recorded the results of a study dealing

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(1) Photochemical Transformations of Small-Ring Heterocyclic Compounds. XXXIII. For part XXXII, see: A. Padwa and A. Battisti, *J. Amer. Chem. Soc.*, **94**, 521 (1972).

(2) A. Padwa and J. Smolanoff, *ibid.*, **93**, 548 (1971).

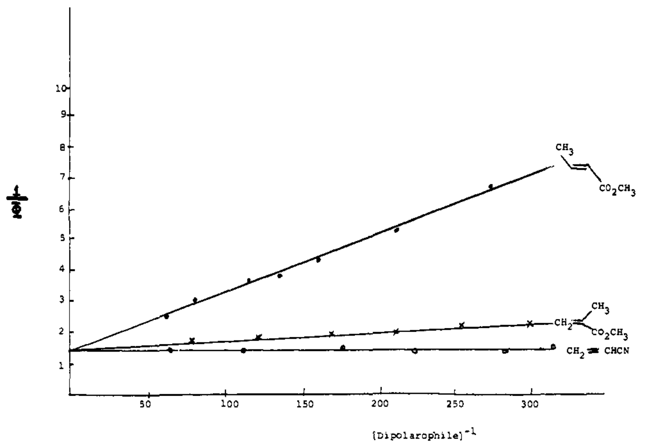


Figure 1. Plot of [quantum yield of cycloaddition]$^{-1}$ against [dipolarophile]$^{-1}$.

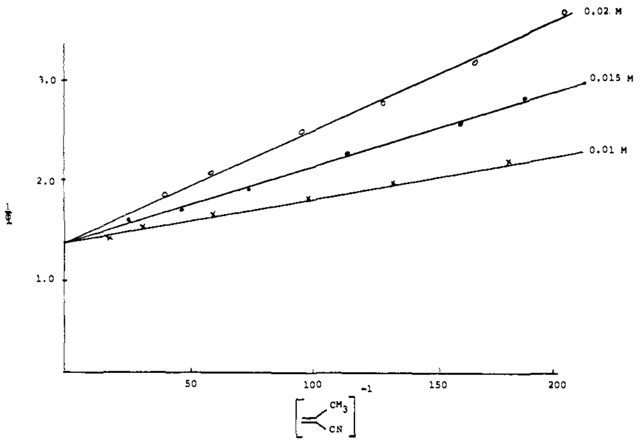
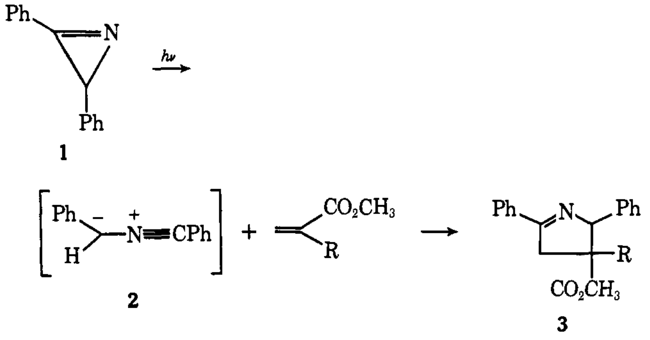
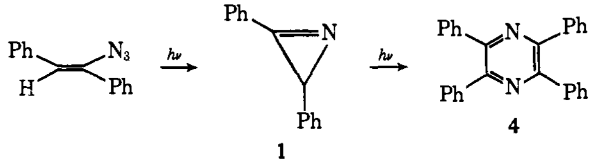


Figure 2. Plot of [quantum yield of cycloaddition]$^{-1}$ against [α-methylacrylonitrile]$^{-1}$ as a function of diphenylazirene concentration.

with the photocycloaddition of arylazirenes with electron-deficient olefins to give Δ^1-pyrrolines. The formation of the adduct was interpreted as proceeding by way of irreversible opening of the azirene ring to form a nitrile ylide intermediate **2**, which is then trapped by a suitable dipolarophile.[3] Irradiation of **1** in cyclohexane or with olefins of low dipolarophilic activity[4] (such as methyl β-methylcrotonate) produced no photoadduct but instead gave tetraphenylpyrazine (**4**, 40%) on extended photolysis. Hassner and Levy[5] have also reported the formation of tetraphenylpyrazine (40%) from the irradiation of α-azido-*trans*-stilbene.[5] We now wish to report the details of an extensive investigation on the mechanism of the photodimerization of diphenylazirene. On the basis of the data obtained in our studies, we wish to suggest that the dimerization proceeds by addition of the nitrile ylide **2** to ground-state azirene with the formation of a 1,3-diazabicyclo[3.1.0]hex-3-ene intermediate. On further irradiation this species is converted to tetraphenylpyrazine.





These conclusions are confirmed by a study of the variation of the quantum yield of adduct formation as a function of the concentration of added dipolarophile at 3130 Å. The results of the quantum yield measurements in degassed pentane solution are given in Figures 1 and 2. Although a good linear relationship is found between the inverse of the quantum yield of cycloaddition and the inverse of concentration of dipolarophile, the slope of the line varies both with the structure of the dipolarophile and the concentration of diphenylazirene used. At infinite dipolarophile concentration the quantum yield for cycloaddition is 0.8, showing that the major pathway from the excited singlet state[2] of azirene involves bond rupture and formation of nitrile ylide **2**. The plots shown in Figures 1 and 2 are consistent with the mechanism shown in Scheme I, where Ao = diphenylazirene, NY = nitrile ylide, and O = dipolarophile. By making the usual steady-state assumption, we can write

Scheme I

$$\text{Ao} \xrightarrow{h\nu} \text{A}^{*1}$$

$$\text{A}^{*1} \xrightarrow{k_1} \text{Ao}$$

$$\text{A}^{*1} \xrightarrow{k_2} \text{NY}$$

$$\text{NY} + \text{O} \xrightarrow{k_3} \text{adduct}$$

$$\text{NY} + \text{Ao} \xrightarrow{k_4} \text{dimer}$$

$$\frac{1}{\Phi_{\text{adduct}}} = \frac{1}{\tau k_2}\left[1 + \frac{k_4[\text{Ao}]}{k_3[\text{O}]}\right]$$

where τ is the excited singlet state lifetime. According to this mechanistic scheme, the slope of the plot should be dependent on both the initial concentration of diphenylazirene as well as the magnitude of k_3. Quantitatively, if $k_3 \gg k_4[\text{Ao}]$, then little variation in slope is to be expected as the concentration of **1** is increased. This is the case with acrylonitrile, an olefin of high dipolarophilic activity. In cases where k_3 and $k_4[\text{Ao}]$ have similar values (such as with methyl acrylonitrile) the slope of the plot *will* depend on the concentration of diphenylazirene.

The present results make it clear that these effects can only be explained by the reaction of nitrile ylide **2** with diphenylazirene. Further support for this contention was obtained by irradiating diphenylazirene for shorter periods of time. Photolysis in cyclohexane

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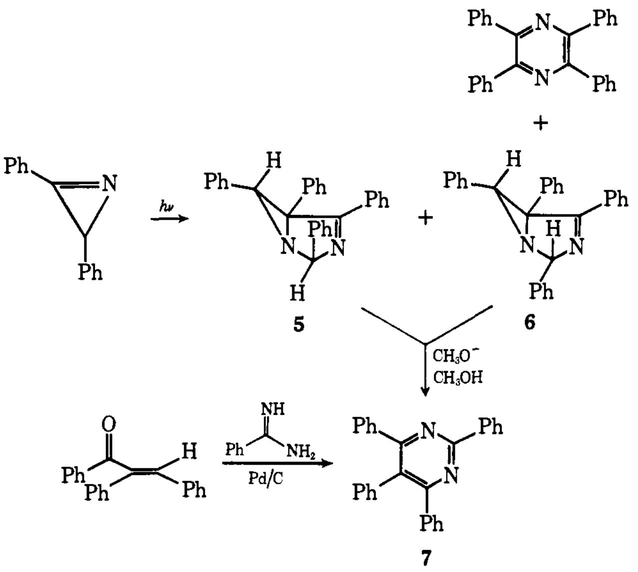
(3) R. Huisgen, H. Stangl, H. J. Sturm, and H. Wagenhofer, *Angew. Chem., Int. Ed. Engl.*, 1, 50 (1962).

(4) R. Huisgen, *ibid.*, 2, 633 (1963).

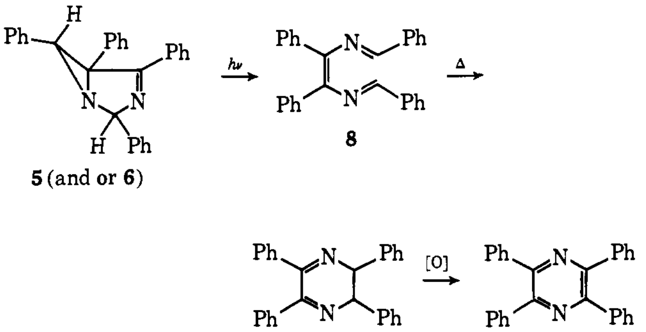
(5) A. Hassner and L. A. Levy, *J. Amer. Chem. Soc.*, 87, 4203 (1965).

afforded three products which were separated by liquid–liquid partition chromatography. The fastest moving component in the llpc separation proved to be tetraphenylpyrazine (25%). The products with longer retention times were shown by their elemental analyses and by their mass spectra to be dimeric.[6] The nmr spectra (CDCl$_3$) of **5** (τ 3.84 (s, 1 H), 6.86 (s, 1 H), and 2.90 (m, 20 H)) and **6** (τ 4.78 (s, 1 H), 7.04 (s, 1 H), and 2.85 (m, 20 H)) led to their assignment as *endo*- and *exo*-2,4,5,6-tetraphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene. Chemical confirmation of these structures was obtained by treating **5** and/or **6** with sodium methoxide in methanol to give tetraphenylpyrimidine (**7**), mp 183–184°.

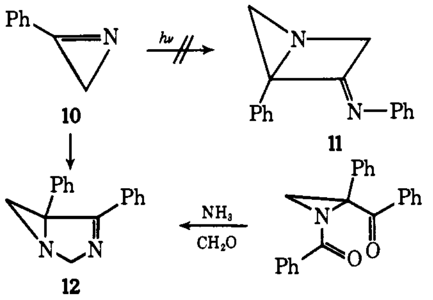


Compound **7** was independently synthesized by treating 1,2-diphenylacrylophenone with benzamidine followed by oxidation over palladium on charcoal.

The formation of products **5** and **6** can be interpreted in terms of 1,3-dipolar addition of **2** onto diphenylazirene. On irradiation, dimers **5** and **6** are converted to tetraphenylpyrazine. This latter transformation presumably proceeds by ring opening to enediimine **8** which thermally cyclizes to a dihydropyrazine (**9**) as was previously observed with related 1,3-diazabicyclohexenes.[7–9] Oxidation of **9** during work-up nicely rationalizes the formation of tetraphenylpyrazine.



Woerner, Reimlinger, and Arnold[10,11] have recently reported that irradiation of 2-phenylazirene (**10**) results in the formation of 4-phenyl-3-phenylimino-1-azabicyclo[2.1.0]pentane (**11**). We have also isolated, from the photolysis of **10**, a dimer consistent with that described by these workers to which we assign an alternate structure, 4,5-diphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene (**12**), based on the data and an independent synthesis.[6] Again, the formation of this dimer can be interpreted in terms of 1,3-dipolar addition of the initially generated nitrile ylide onto phenylazirene.



We hope to report on the generality of related 1,3-dipolar additions to azirenes at a future date.

Acknowledgment. We wish to thank the National Science Foundation (Grant No. GP-24449) for financial support.

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[6] All compounds analyzed satisfactorily. Complete spectroscopic and degradative details will be given in our full manuscript.

[7] A. Padwa, S. Clough, and E. Glazer, *J. Amer. Chem. Soc.*, **92**, 1778 (1970).

[8] A. Padwa and E. Glazer, *Chem. Commun.*, 838 (1971).

[9] T. DoMinh and A. M. Trozzolo, *J. Amer. Chem. Soc.*, **92**, 6997 (1970).

[10] F. P. Woerner, H. Reimlinger, and D. R. Arnold, *Angew. Chem., Int. Ed. Engl.*, 7, 130 (1968).

[11] F. P. Woerner and H. Reimlinger, *Chem. Ber.*, **103**, 1908 (1970).

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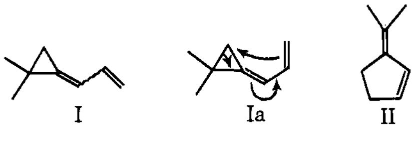
The Allylidenecyclopropane–Methylenecyclopentene Energy Surface. Evidence for a "Conducted Tour" Mechanism

Sir:

Thermal isomerization[1] of allylidenecyclopropane (I) to isopropylidenecyclopentene (II) represents a class of pericyclic rearrangements formally corresponding to ${}_{\sigma}2 + {}_{\pi}4$ addition of a cyclopropane σ bond to a diene system (*cf.* Ia).



While direct and symmetry allowed, this concerted mechanism fails to explain the reported regiospecificity of the rearrangement. From its mode of synthesis[1] the diene I must be a mixture of isomers It and Ic, and whereas concerted formation of II from It is sterically feasible, the reported absence of cyclopentene III (the expected product from Ic) is difficult to explain.

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[1] T. C. Shields, W. E. Billups, and A. R. Lepley, *J. Amer. Chem. Soc.*, **90**, 4749 (1968); T. C. Shields and W. E. Billups, *Chem. Ind. (London)*, 619 (1969).