$k_4 \gg k_5K[OH^-]$ as discussed earlier in other reactions.[7]

There appears to be different opinions about assigning the factors which control the rate enhancement of intramolecular reactions.[26] The observed values of activation parameters at 0.02 M NaOH (Table II), where contribution of the k_3 step is nearly 100%, are comparable with those of various intramolecular nucleophilic reactions.[25,27] The comparison of these values with those obtained recently in neutral hydrolysis of phenyl benzoate[24] indicates that the entire rate acceleration in the pH-independent hydrolytic cleavage of **2** comes from a favorable ΔS^* value while the ΔH^* value is actually unfavorable compared with that of phenyl benzoate. The activation parameters obtained at 0.4 M NaOH, where the contributions due to the k_3 and k_4 steps constitute ~40% and ~60% of the rate, respectively, indicates that an increase in the contribution of the k_4 step to the total rate decreases the values of both ΔH^* and ΔS^*. Significantly low values of ΔH^* ΔS^* were obtained for the k_4 step (Table II) which are comparable with those obtained in alkaline hydrolysis of monomethyl phthalate[28] and di-*n*-butyl phthalate.[29] The similarity of activation parameters obtained for hydrolytic cleavages of phenyl salicylate[30] and methyl salicylate under comparable conditions indicates the involvement of an almost similar reaction mechanism. In the hydrolysis of phenyl salicylate, the nucleophilic attack could be considered as the rate-determining step because of the considerably high acidity of the leaving group compared with the nucleophile. However, in the hydrolysis of **2**, both the leaving group and nucleophile have almost similar acidities[20] in **5** and **6**. But the probable intramolecular hydrogen bonding in **10** will make the expulsion of the leaving group more facile than that of nucleophile. Under such circumstances, we propose that nucleophilic attack is more likely to be the rate-determining step in the hydrolytic cleavage of **2**.

A kinetically indistinguishable additional step in Scheme II as shown in eq 11 may be ruled out on the basis of the

$$5 \xrightleftharpoons{K^{11},\ OH^-} 6 + H_2O \qquad (11)$$

observed values of ΔS^* obtained for both the k_3 and k_4 steps. A significant role for eq 11 should result in approximately similar values of ΔS^* for both the k_3 and k_4 steps provided nucleophilic attack is the rate-determining step.

Acknowledgment. We are very grateful to the Research and Higher Degrees Committee of Bayero University for a research grant to purchase a UV–visible spectrophotometer.

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Thermolysis of Vinyldiazomethanes as a Method for the Generation of Vinylcarbenes and a Comparison with Cyclopropene Photochemistry

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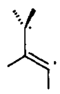
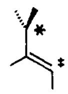
The pyrolysis of the vinyldiazomethanes **6** (X = H), **8**, **9**, and **10** gives mixtures of 3*H*-pyrazoles and cyclopropenes. The kinetics and product distribution for each case lead to a determination of the rate of vinylcarbene formation and, therefore, a direct determination of the relative carbene stabilities. The conclusion is that carbene **14** is more stable than **15**. These results are then used as a basis for a discussion of the carbenes generated from the singlet photochemistry of unsymmetrical cyclopropenes, **11**.

Introduction

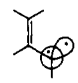
Vinvylcarbenes have attracted considerable interest recently as probable intermediates in a variety of related reactions. Examples include the pyrolysis of cyclopropenes,[1] the singlet photochemistry of cyclopropenes,[2] and the pyrolysis[3] and photolysis[4-6] of vinyldiazomethanes. As is well recognized, there are a variety of electronic states possible for vinylcarbenes: a nonplanar singlet and triplet corresponding to **1a** (the singlet could, depending on the substituents present, have ionic character **1b** or **1c**), planar singlets of the type **2b** (2π or σ^2)[7,8] and **2c** (4π or p^2), and both singlet and triplet corresponding to **2a** (3π or σp). Both molecular orbital calculations[7-9] and ESR results[6,10] indicate that triplet **2a** is the most stable of the states, but



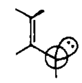
1a



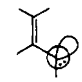
1b, ‡,* = −,+
c, ‡,* = +,−



2a



2b



2c

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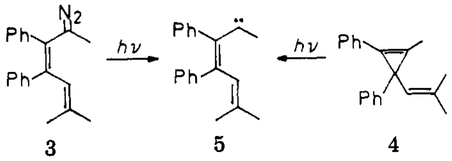
it is unlikely to be the first formed intermediate in most of the reactions for which vinylcarbenes are proposed.

For example, in the pyrolysis of cyclopropenes, a combination of experimental results[1] and ab initio calculations[7] suggests that the transition state for σ-bond cleavage resembles **1a**, and the intermediate first formed is a singlet like **2a**. In contrast, for the photochemistry of cyclopropenes, the excited singlet correlates with **2b**.[2] Both of these conclusions are reached on the basis of orbital correlations. More detailed ab initio calculations[9] using extensive configuration interaction indicate that an avoided crossing allows adiabatic conversion of the ground state of cyclopropene to the most stable singlet, **2b**, and the excited singlet of cyclopropene to the less stable singlet, **2a**. The cyclopropene triplet excited state apparently does not react to form products resulting from σ-bond cleavage but instead tends to dimerize.[11,12] Recently, Zimmerman and co-workers[5,13] have observed products of σ-bond cleavage in the sensitized irradiations of 3-vinyl substituted cyclopropenes, but detailed evidence suggests that vinylcarbenes are not involved. For the pyrolysis of vinyldiazomethanes, concerted loss of nitrogen in the linear mode is thermally forbidden[14] in that the singlet vinylcarbene formed initially would not be the ground-state singlet, **2b**, but rather the doubly excited state, **2c**.[3] If the loss of nitrogen were nonlinear,[14] **2b** could be formed directly. Finally, the photolysis of vinyldiazomethanes is the usual method of generating triplets like **2a**,[6,10] but the multiplicity of the reacting excited state is unknown in most cases. Possibly, the ground-state triplet is formed by intersystem crossing from one of the singlets. Very recently, in fact, the direct irradiation (excited singlet) and the thermolysis of 4,4-dimethyldiazocyclohex-2-ene have been shown to give stereochemically different products in the trapping of the carbene by 2-butene.[15] Moreover sensitized irradiation (excited triplet) gave the same product distribution as the thermolysis. These results were interpreted by invoking the equilibration of the singlet (**2b**) and triplet (**2a**) for the pyrolysis and sensitized irradiation and possibly a different singlet (**2c**) for the direct irradiation.

From this summary, it is obvious that, since vinylcarbenes are not an intermediate but several intermediates, quite different chemistry and product distribution may result, depending on the method of generation. For instance, Zimmerman[5] has recently used the photolysis of the butadienyldiazomethane, **3**, as a "fingerprint" for the carbene expected from the photochemistry of cyclopropene, **4**. The different product distribution obtained for the two cases led to the conclusion that the mechanism for formation of ring-opened products in the direct irradiation of **4** must involve other pathways than only the formation of **5**. However, the possibility of different electronic states of **5** from the two routes was not considered.[16] Similarly, from our results on the pyrolysis of the series of vinyldiazomethanes, **6**,[3] the stability of the vinylcarbenes formed does not correlate with the regioselectivity of the ring opening observed in the direct photolysis of the related cyclopropenes, **7**.[17] Clearly, more extensive studies in this area are required.



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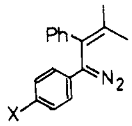

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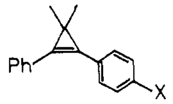

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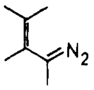
The objective of this work was to assess the effect of phenyl substitution on the stability of vinylcarbenes as an approach to understanding the surprising regiochemistry observed for the ring opening of a number of 1-methyl-2-phenyl-substituted-cyclopropenes, **11**, in their excited singlet state. In all cases, product distribution reflects favored cleavage of the methyl-substituted rather than the phenyl-substituted σ bond.[2,5,10,13,18] An example is shown in eq 1.[18] Although the determination of the product composition is complicated by photochemical conversion of the 2-methyl-1-phenyl isomer (**13**) to the 1-methyl-2-phenyl one (**12**), at low conversions the ratio of **12**/**13** is 4:1. If vinylcarbenes are intermediates in these conversions,[19] then **15** is formed in preference to **14**. On pyrolysis of the same cyclopropene, the second product is the exclusive one, which implies that carbene **14** is more stable than **15**. However, this conclusion ignores the possibility that, in the thermolysis, the regiochemistry of ring opening is related to a vinylcarbene that is electronically different from that formed by photolysis. We now report results for the pyrolysis of the vinyldiazomethanes **8**–**10** and the information these results reveal about the corresponding vinylcarbenes.



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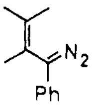

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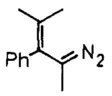

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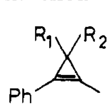

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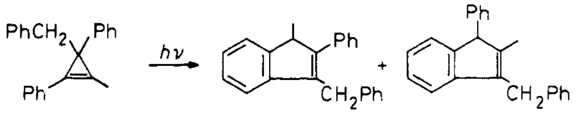
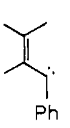


12 13



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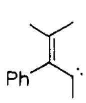

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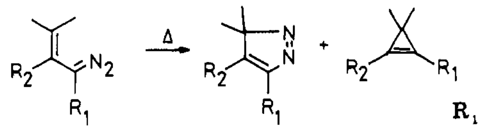
Table I. Rate Constants and Product Ratios for the Thermolysis of Vinyldiazomethanes 8-10 as a Function of Temperature in 5% Pyridine-Benzene

no.	t, °C	$k_{obsd} \times 10^4$,[a] s^{-1}	% cyclopropene[b]	% pyrazole[b]	$k_c \times 10^4$,[c] s^{-1}	$k_p \times 10^4$,[c] s^{-1}
8	36.3	3.71 ± 0.08	<2	>98	<0.074	>3.63
	49.5	15.4 ± 0.5	<2	>98	<0.31	>15.1
9	70.8	1.01 ± 0.01	75	25	0.76	0.25
	80.8	3.05 ± 0.01	80	20	2.4	0.61
	89.1	7.9 ± 0.2	81	19	6.4	1.5
	99.3	27.0 ± 0.5	84	16	23	4.4
10	32.3	0.21 ± 0.01	8	92	0.016	0.19
	42.1	0.66 ± 0.07	14	86	0.090	0.57
	51.5	1.9 ± 0.2	14	86	0.27	1.7
	60.5	5.2 ± 0.4	18	82	0.92	4.3

[a] Errors quoted are the mean deviations of two to four runs. [b] Estimated error ±5%. [c] Estimated error between 5 and 10% based on *a* and *b*.

Results

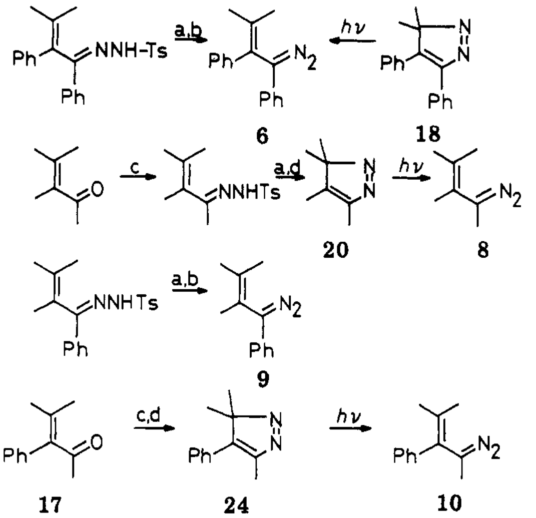
Synthesis of Vinyldiazomethanes 6 (X = H) and 8–10. Vinyldiazomethanes have been prepared previously by photolysis of the corresponding 3*H*-pyrazoles with filtered light to avoid photochemical decomposition of the diazo compound.[3,4] This procedure was used for 6 (X = H), 8, and 10. For 8 and 10, the pyrazoles were prepared by pyrolysis of tosylhydrazone salts of the corresponding ketones 16[20] and 17.[21] The diazo compounds 6 (X = H) and 9 were prepared at room temperature by stirring the tosylhydrazone salts in pentane. This procedure was only satisfactory for the cases that had phenyl substitution at the diazo carbon. The other two tosylhydrazone salts required higher temperatures, and therefore the intermediate diazo compound reacted further to form the pyrazole. These preparations are summarized in Scheme I.



			R_1	R_2
6	18	19	Ph	Ph
8	20	21	CH_3	CH_3
9	22	23	Ph	CH_3
10	24	23	CH_3	Ph

Thermolysis of Vinyldiazomethanes: Product Distribution. The thermolysis of vinyldiazomethanes is well known to give 3*H*-pyrazoles[3,22] and cyclopropenes[3] as products. The ratio of these two products is very dependent on the substitution pattern, and in many simple alkyl-substituted cases only the pyrazoles are observed.[22] Possible products are outlined in eq 2. Cyclopropenes 19[4], 21,[23] and 23[24] and pyrazoles 18[4] and 20[25] are known compounds. The pyrazoles 22 and 24 were isolated from the reaction mixtures and characterized by spectral and elemental analysis (see Experimental Section). Product ratios from the thermolysis of the vinyldiazomethanes were obtained by multiple integration of the methyl region of the ^{1}H NMR spectrum and are reported in Table I. The spectra of these reaction mixtures indicated no products other than the cyclopropene and the pyrazole; therefore, the combined yield must be greater than 95%. The average deviation of the multiple integrations was always less than ±2%; therefore, the error in product composition is estimated as less than ±5%. The tetramethyl compound, 8, gave no observable cyclopropene, 21. Since 8 is generated by photolysis of pyrazole 20 (Scheme I), a given sample could be cycled several times. After three such cycles, no cyclopropene from pyrolysis of 8 could be detected. This determination is complicated by the fact that generation of the diazo compound 8 by photolysis of 20 always gives some cyclopropene because of secondary photolysis of 8[3,4] itself. However, the amount of cyclopropene was always the same before and after pyrolysis of 8. Therefore, the yield of cyclopropene from the pyrolysis is estimated in Table I as less than 2%.

Scheme I. Synthesis of Vinyldiazomethanes[a]



[a] a = *t*-BuOK; b = RT, pentane; c = TsNHNH$_2$; d = reflux, hexane.

Thermolysis of Vinyldiazomethanes: Kinetics. The rates of decomposition of the diazomethanes were monitored by two different methods. For compounds 6 (X = H) and 9, the disappearance of the characteristic diazo band was measured spectrophotometrically. For compounds 8 and 10, colored impurities led to curved rate plots. Since, by ^{1}H NMR spectra, these impurities were not observable and, therefore, were present in very small amounts, the rates were measured by determining relative concentrations by integration of the methyl region of the spectrum. Details of these methods are given under Experimental Section. All rates were measured in 5% pyridine in benzene in order to avoid acid-catalyzed decomposition.[3] The results are listed in Table I as k_{obsd} (s^{-1}). The k_{obsd} values can be divided into k_c for cyclopropene formation and k_p for pyrazole formation using the product ratios. In Table II, activation parameters obtained from ln (k/T) vs. $1/T$ plots for both paths of decomposition of the diazomethanes 6 (X = H), 9, and 10 are listed; those

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Table II. Activation Parameters for the Thermolysis of Vinyldiazomethanes 6 (X = H), 8, 9, and 10 and Rate Constants Extrapolated to 49.5 °C

no.	$\Delta H_c^{\ddagger}$, kcal/mol	$\Delta S_c^{\ddagger}$, eu	$\Delta H_p^{\ddagger}$, kcal/mol	$\Delta S_p^{\ddagger}$, eu	$k_c \times 10^6$, s^{-1}, 49.5 °C	$k_p \times 10^6$, s^{-1}, 49.5 °C
6 (X = H)[a]	27	+2	25	−7	4.0	1.7
8			20	−7	<30	1500
9	29	+8	25	−7	4.0	1.9
10	28	+7	22	−9	21	130

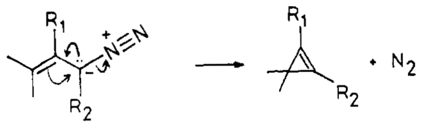
[a] Data from ref 3.

for 8 are unavailable for cyclopropene formation, since none was detected. As discussed previously,[3] the estimated error in $\Delta H^{\ddagger}$ is approximately 1 kcal/mol, and in $\Delta S^{\ddagger}$, 3 eu. As well, in Table II, the rates obtained either directly at, or by extrapolation of the activation plots to, 49.5° are given for all four compounds.

Discussion

The main objective of this work is to compare the kinetics for the thermal decomposition of the vinyldiazomethanes **9** and **10**. These results will lead to a better understanding of the singlet photochemistry of 1-phenyl-2-methylcyclopropene derivatives (i.e., **11**), where product distributions demonstrate that the vinylcarbene **15** is formed in preference to **14**. The data necessary for this comparison are in Table II. The separation of the observed rate into the two pathways k_c (cyclopropene formation) and k_p (3*H*-pyrazole formation) assumes that, at the temperatures necessary for the decomposition of the vinyldiazomethanes, the 3*H*-pyrazoles are thermally stable, i.e., the product distribution is determined by the kinetics of the initial process. Control experiments established this fact; moreover, a recent detailed kinetic study of the pyrolysis of 3,3-dimethyl-3*H*-pyrazoles demonstrated that carbon–nitrogen bond cleavage leading to vinyldiazomethanes or to cyclopropenes would require an activation energy of approximately 40 kcal/mol.[26]

The entropies of activation from Table II are quite consistent with the two processes occurring. For pyrazole formation, conversion from the acyclic to the cyclic system gives the expected negative $\Delta S^{\ddagger}$ value. For cyclopropene formation, the rate-determining step is a unimolecular dissociation to molecular nitrogen and a vinylcarbene derivative; the expected positive $\Delta S^{\ddagger}$ values are obtained. In fact, the pyrolysis of diphenyldiazomethane has a reported $\Delta S^{\ddagger} \simeq 0$ eu,[27,28] which is somewhat lower than would be expected. The higher values obtained here are perhaps more reasonable. Note that these values exclude the possibility that cyclopropene formation results from a concerted intramolecular displacement of nitrogen as represented by a transition state like **25**. Here $\Delta S^{\ddagger}$ would be expected to be more negative than that observed. The other important aspect for comparison between **9** and **10** is that the entropies of activation are, within experimental error, identical for the two compounds. Thus, comparisons between the two can be made by examining either rate constants or enthalpies of activation, since entropy differences will not complicate any of the arguments. This is an important point because the differences in $\Delta H^{\ddagger}$ are small and the error is estimated at ±1 kcal/mol (see above). However, these small differences lead to obvious rate differences. The discussion that follows is therefore to explain these rate differences but, obviously, in only a semiquantitative way.



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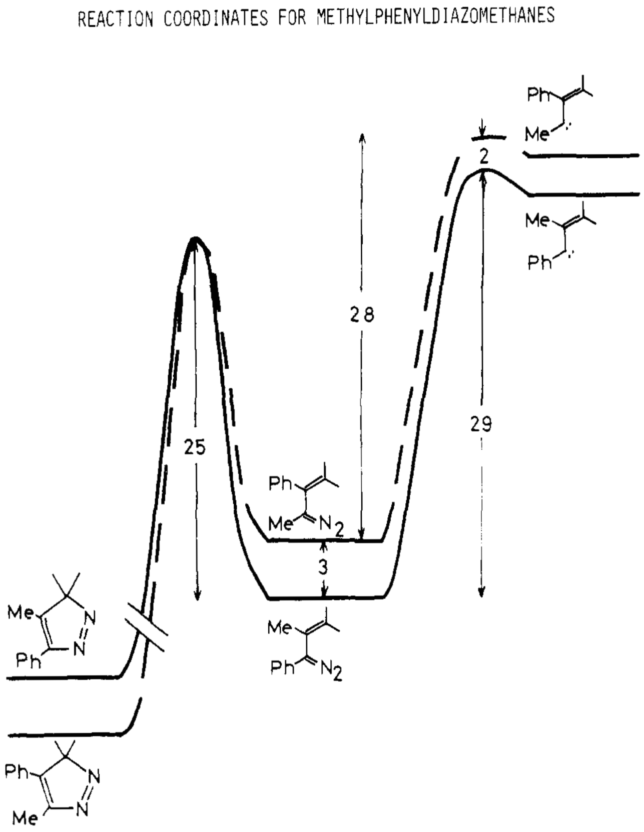

Figure 1. Reaction coordinate scheme for the thermal decomposition of methylphenyldiazomethanes. Numerical values are in units of kilocalories per mole.

The first fact that struck our attention about these rates was the observation that the 1-phenyldiazo compound **9** actually reacted some five times slower than the 2-phenyl isomer **10** for cyclopropene formation (i.e., k_c in Table II). This, of course, implies that the 1-phenylcarbene **14** is formed more slowly than the corresponding 2-phenylcarbene **15**. At first sight then it seemed that the surprising regiochemistry observed in photochemical cyclopropene cleavages where **15** is preferred to **14** might simply be a result of some unusual substituent effect in vinylcarbenes. This kinetic effect, however, arises from differences between the ground and transition state energies. Fortunately, the diazo compounds also undergo ring closure to 3*H*-pyrazoles. This process is also much faster for the 2-phenyl isomer but now by a factor of 68 (i.e., k_p in Table II). This rate difference can be used to assess the critical factor in the thermal chemistry of these vinyldiazomethanes: ground state energy differences between **9** and **10**.

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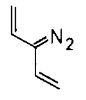
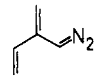
The arguments which follow are outlined in the potential energy surfaces in Figure 1. In this figure, the diazo compounds **9** and **10** are shown in the center with the right-hand pathway proceeding to the two corresponding carbenes and the left-hand pathway to the pyrazoles. The surface for the 1-phenyl case is shown as a solid line and that for the 2-phenyl isomer as a dashed line.

In this drawing, **9** is shown as 3 kcal/mol more stable than **10**. Several arguments support this conclusion. The first is a result of our MNDO calculations[29] for the heats of formation at the geometry of minimized energy for the model compounds **26** and **27**. By this method, **26** is more stable than **27** by 3.4 kcal/mol. This should give a good estimate for the differences between **9** and **10**, assuming a conjugative vinyl group is a reasonable model for a phenyl group. The reason for this difference in stability can be easily seen. The diazo carbon in **9** is linearly conjugated through the double bond and the phenyl ring, whereas in **10** the diazo carbon is cross conjugated to the styrene-type system. Even simple Hückel calculations give a π-delocalization energy of 0.24 β favoring pentadienyl over 2-methylenebutadienyl. This ~3 kcal/mol difference can then be used to explain the potential energy surfaces for 3*H*-pyrazole formation.



26



27

Ring closures to the 3*H*-pyrazole isomers have enthalpies of activation of 25 kcal/mol for the conversion **9** to **22** and 22 kcal/mol for **10** to **24**. (Table II). We also know that the reverse reactions, which are not observable, have activation energies greater than 35 kcal/mol (see above). Therefore, the transition state for the cyclization process should be neither early nor late (Hammond postulate). However, for the two isomeric pyrazoles, conjugative arguments again predict that the 4-phenyl-3*H*-pyrazole **24** (linear conjugation) should be more stable than the 5-phenyl-3*H*-pyrazole (**22**) (cross conjugation). A referee has suggested that steric inhibition of conjugation might be particularly large for **24** so that **24** would be less stable than **22**. This is certainly a reasonable point but it is not supported by UV absorption spectra that show **24** with longer wavelength bands of higher extinction coefficient than **22**. The potential energy surfaces must therefore cross as shown in Figure 1. The reasonable place for them to cross is near the maxima as phenyl conjugation switches from stabilizing diazo compound **9** relative to **10** to stabilizing 3*H*-pyrazole **24** relative to **22**. This, of course, implies that substituent effects for this process should be very small in agreement with the low ρ values (ca. −0.4) observed for phenyl groups at C-1 or C-3 of vinyldiazomethanes.[3,22] As was discussed previously,[3] this low negative ρ value reflects the decrease in polarity as a negative charge at C-1, and C-3 of the vinyldiazomethane is donated toward the diazo nitrogen. The transition state is therefore less polar than the starting material. This is quite different from the transition state for 1,3-polar additions to aromatic olefins. For instance, the reaction of diazomethane with styrenes has $\rho = +0.9$, indicating a transition state more polar than starting material as the negative charge increases at the α carbon of styrene.[30] We thus attribute the rate difference of 68 in favor of **10** over **9** for pyrazole formation mainly to this 3 kcal/mol difference in ground state energy.

If this estimate of the difference in ground state energy is correct, then the pathway for carbene formation to the right in Figure 1 is reasonable. The activation enthalpy for this process is high; therefore, the transition state should be late and resemble the carbene in energy and geometry (Hammond postulate). Consequently, the difference in activation enthalpy of 1 kcal/mol (28 kcal/mol for **10** and 29 kcal/mol for **9**, Table II) combined with the difference in ground state energy of 3 kcal/mol leads to the result that the 1-phenylcarbene **14** is 2 kcal/mol more stable than the 2-phenylcarbene **15**. We conclude then that the order of stability of these two carbenes is as expected, and no special effects are required in order to explain this order. Again, this order is as calculated by MINDO/3 methods for vinyl rather than phenyl substituted model compounds, although the calculated difference of approximately 16 kcal/mol is far greater than the experimentally determined one.[31]

The data reported in Table II for the other vinyldiazomethanes **6** and **8** support this conclusion that ground state energy differences are important in determining relative reactivities. Of course, in these two cases comparisons are more difficult because the compounds are no longer isomeric. However, the qualitative trends are reasonable. The tetramethyl compound, **8**, reacts faster than any of the others, but the carbene to cyclopropene process is not detectable. In effect, the carbene process remains slow (probably similar in rate to **10**), but the cyclization to pyrazole becomes very fast because the double bond is unsubstituted by a phenyl group and, therefore, more reactive to cyclization. Finally, the 1,2-diphenylvinyldiazomethane, **6**, reacts at virtually an identical rate to the 1-phenyl compound, **9**.

Some comment must be made about the difference in interpretation given here as compared to that used by Miller and Shechter to explain the previously reported kinetics of ring-substituted diphenyldiazomethane decompositions.[32] In that case, both electron-donating and electron-withdrawing substituents increased the rate and, in fact, the fastest rate was obtained for the 4-CH_3, 4′-NO_2 case. We have observed similar behavior in a less extensive series of ring-substituted 1-phenylvinyldiazomethanes.[3] By an analysis of ^{13}C chemical shifts for the diazo carbon, Miller and Shechter concluded that ground state substituent effects were unimportant, and the observed kinetic behavior was explained entirely by transition state substituent effects. We have no explanation for the dominance of ground-state effects in our current work as compared to these other systems. Unfortunately, we cannot isolate sufficient quantities of our diazo compounds to obtain ^{13}C NMR spectra or to do the more definitive experiment of measuring heats of formation.

The conclusion that the 1-phenylcarbene **14** is more stable than the 2-phenylcarbene **15** must now be related to the results obtained for cyclopropene singlet photochemistry of systems like **11**, where the same two carbenes are generated. First, however, a discussion of the electronic state of the carbenes generated in the two types of reactions is required.

As has been discussed before,[3,14] thermal loss of nitrogen from a diazo compound can occur along two different pathways: linear and nonlinear. The linear mode is thermally forbidden in the sense that the carbene generated will not be the ground singlet but rather a doubly excited state corresponding to **2c** (p^2). The nonlinear mode

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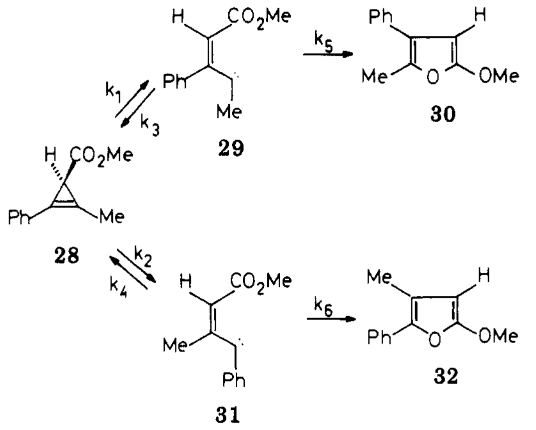
[29] M. J. S. Dewar and W. Thiele, *J. Am. Chem. Soc.*, **99**, 4899 (1977).

[30] P. K. Kadaba and T. F. Colturi, *J. Heterocycl. Chem.*, **6**, 829 (1969).

[31] J. A. Pincock and R. J. Boyd, *Can. J. Chem.*, **55**, 2482 (1977).

[32] R. J. Miller and H. Shechter, *J. Am. Chem. Soc.*, **100**, 7920 (1978).

Scheme II



will lead directly to the ground-state singlet **2b** (σ^2). These qualitative arguments have been confirmed by MO calculations of the potential energy surfaces for diazomethane decomposition,[33] which imply that the activation barrier present in the linear mode disappears in nonlinear pathways. It seems reasonable to expect that, even if the transition state has an electronic distribution that reflects bond reorganization toward the p^2 carbene, this carbene will decay in an unactivated pathway to σ^2.[3] Therefore, although it is impossible to determine which of the two paths is occurring, it seems reasonable to expect that the nonlinear mode might be preferred and that σ^2 will be the carbene formed in the decomposition of diazomethanes.

Turning to the singlet photochemistry of cyclopropenes, the decision as to which carbene is formed as the initial intermediate is also difficult. Padwa[2] has stated that, according to calculations, the excited singlet state of cyclopropene correlates with σ^2. This assumes that the cyclopropene σ bond breaks heterolytically in the excited state via a switterion like **1b**. Rotation into planarity then gives **2b** (σ^2). However, the heterolytic cleavage to **1c** and then to **2c** (p^2) seems to be an equally good correlation for a singlet. The choice between the two zwitterions and, hence, the two carbenes may then be substituent dependent. In fact, in the most detailed study of substituent effects on photochemical cyclopropene ring openings, compounds **7** cleave preferentially on the side of the more electron-donating aromatic ring.[17] Thus, the carbene carbon may be initially electron deficient as the σ bond breaks (i.e., like **1c**).

Very recent ab initio MO calculations[9] for both thermal and photochemical ring cleavages of cyclopropenes show that, although there is an intended correlation between s_1 of the cyclopropene and the σ^2 carbene, an avoided crossing puts the σp carbene on the same surface as excited cyclopropene. However, this avoided crossing occurs far along the reaction coordinate. By this stage of the reaction, substituent effects would already have determined the selectivity for bond cleavage by their influence on the intended correlation rather than the actual correlation that results because of the avoided crossing.

There is, however, a difficulty in interpreting results on regioselectivity of ring opening for these photochemical reactions. Cyclopropene to vinylcarbene conversions are known to be reversible both thermally[1] and photochemically.[11] This means that product distribution may reflect different rates of return to cyclopropene for the two possible carbenes rather than selectivity of ring opening. This can be shown by examining the rate scheme for the one case where photochemical racemization of an optically active cyclopropene, **28** (absolute configuration unknown), has been determined. Experimentally, the only product observed is **30** (no **32**), and racemization occurs about 2.5 times as fast as product formation.[11] The possible paths are outlined in Scheme II with the rate constants shown; note that the photochemical steps are shown as k_1 or k_2, since the light intensity is obviously constant for both. Two extreme cases are possible. In the first, photochemical selectivity is such that $k_1 >> k_2$, and only the less stable carbene **29** is formed. Product **30** is the only one possible, and racemization reflects $k_3 \simeq 2.5k_5$. In the second, $k_5 >> k_3$ and $k_4 >> k_6$. This implies racemization is only via carbene **31** and product formation by carbene **29**. Simple steady-state kinetics applied to **29** and **31** then lead to the expression:

$$\frac{\text{racemization}}{\text{product formation}} = \frac{k_2}{k_1} + \frac{k_3}{k_5} \simeq 2.5$$

Since $k_5 >> k_3$, k_3/k_5 is small and $k_2/k_1 \simeq 2.5$. Now photochemical selectivity favors the more stable carbene **31** but the only product obtained is from **29**. As discussed by Zimmerman,[5] there is no obvious reason why carbene return should be preferred for **31** over **29**, but is is a possibility nevertheless. Clearly, cases between these two extremes are also likely.

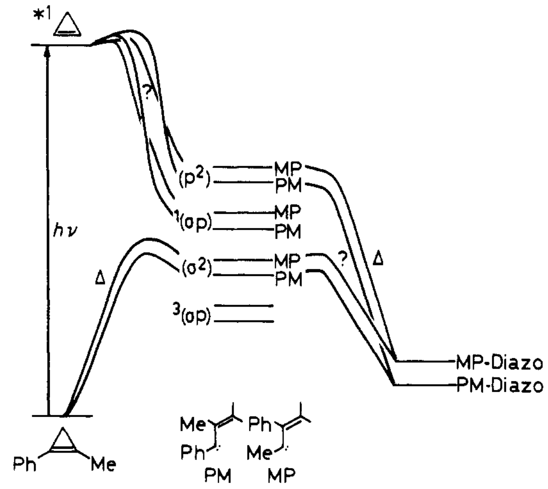


Figure 2. Correlation diagram relating cyclopropenes, vinyldiazomethanes, and vinylcarbenes.

To summarize the results reported here, it seems probable that both the pyrolysis of vinyldiazomethanes and the singlet photochemistry of cyclopropenes proceed by paths that are intended to correlate with vinylcarbene singlets, probably of electronic configuration σ^2. In this configuration, of the two possible carbenes, **14** is more stable than **15** as expected. The singlet photochemistry is simply explained as outlined above if **14** is formed in preference to **15**, but product distribution reflects return to cyclopropene. If, however, **15** is formed in preference to **14**, then some special effect must be involved to explain the photochemical reactions. Padwa[18] has suggested that Michl's "funnel theory" of excited-state to ground-state conversions[34] can be applied here. The assumption is that there is close approach of the excited singlet surface of cyclopropene with the ground-state surfaces of the two possible vinylcarbenes. This enhances internal conversion but preferentially to the less stable of two carbenes. As pointed out above, this explanation ignores the fact that the funnel occurs far along the reaction coordinate after the selectivity

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(33) J. Lievin and G. Verhaegen, *Theor. Chim.* Acta, **45**, 269 (1977).

(34) J. Michl, *Mol. Photochem.*, **4**, 243, 257 (1972).

for bond cleavage has already been determined. Therefore, the only way to form **15** in preference to **14** is by a lower activation barrier and surface crossing as shown in Figure 2. As yet, there seems to be no satisfactory explanation for why phenyl substitution might lead to a higher activation barrier for σ bond cleavage. Moreover, MO calculations by the MINDO/3 method[31] suggest that the process is unactivated.

Thus, it is clear that the results for the thermal chemistry of vinyldiazomethanes give valuable information for interpreting the chemistry of vinylcarbenes but that more detailed photochemical studies are required to answer the question of regioselectivity in ring opening.

Experimental Section

Unless otherwise specified, ^{1}H NMR spectra were obtained with a Varian T-60 spectrometer using tetramethylsilane as an internal standard. Chemical shifts are reported as δ values. Infrared spectra were recorded on Perkin-Elmer 237B Grating spectrophotometer using sodium chloride plates. Mass spectra were recorded on a Dupont-CEC Model 21-104 mass spectrometer. Melting points were taken on a Fisher-Johns apparatus and are uncorrected.

Photolysis Equipment. (A) Irradiations were carried out in Pyrex NMR tubes using a 200-W Hanovia, medium-pressure mercury-arc lamp with a quartz cooling jacket. The filter system consisted of a 2 × 15 cm test tube filled with a 0.4 M solution of $SnCl_2 \cdot 2H_2O$ in 10% HCl and immersed in a 150-mL beaker containing a solution of 1.0 M $CoSO_4 \cdot 7H_2O$ and 0.1 M $NiSO_4 \cdot 6H_2O$ in 5% H_2SO_4 (path length ≥ 2 cm). This system transmits light between 325 and 410 nm.

(B) Irradiations were carried out in Pyrex NMR tubes using GE 1-kW, medium-pressure mercury-arc lamp with a quartz cooling jacket, which was immersed in a constant temperature bath at 10 °C. The filter system consisted of a Corning 7-37 glass filter. All of the filter system and the NMR tube, except the window part, were covered with aluminum foil to prevent any reflected light reaching the solution. This system transmits light between 320 and 380 nm.

Preparation of 1,2-Diphenyl-3-methyl-2-buten-1-one Tosylhydrazone. To 5.02 g (0.021 mol) of 1,2-diphenyl-3-methyl-2-buten-1-one[35] were added 3.82 g (0.021 mol) of hydrazine, 20 mL of ethanol, and 0.05 mL of concentrated HCl. The mixture was refluxed for 16 h. While the mixture cooled, a white solid precipitated, which was filtered and recrystallized from ethanol: yield 2.86 g (33%); mp 156–157°C; NMR ($CDCl_3$) δ 1.6 (3 H, s), 2.03 (3 H, s), 2.43 (3 H, s), 7.0–8.4 (15 H, br m); IR ($CHCl_3$) 3690, 3620, 3245, 3040, 2400, 1600, 1490, 1375, 1335 cm^{-1}; mass spectrum, *m/e* 250 (20), 249 (100), 205 (28). Anal. Calcd for $C_{24}H_{24}N_2SO_2$: C, 71.25; H, 5.98; N, 6.92; S, 7.92. Found: C, 71.12; H, 5.89; N, 6.77; S, 7.83.

Preparation of 1,2-Diphenyl-3-methyl-1-diazo-2-butene (6, X = H). In a 25-mL round-bottom flask equipped with a magnetic stirring bar and drying tube, 263 mg (0.6 mmol) of the tosylydrazone was dissolved in 5 mL of anhydrous tetrahydrofuran. The solution was stirred slowly, and 0.12 g (1.07 mmol) of potassium *tert*-butoxide was added quickly. The solution turned yellow immediately. After the solution was stirred for 10 min, the solvent was removed under vacuum at room temperature. The flask was then covered with aluminum foil, and 20 mL of *n*-pentane was added. The solution was stirred overnight. Filtration and evaporation of the solvent yielded a pink residue: NMR (CCl_4) δ 1.90 (3 H, s), 1.95 (3 H, s), 6.78–7.28 (10 H, m); IR (CCl_4) 2040 cm^{-1}.

Preparation of 2,3-Dimethyl-1-phenyl-2-buten-1-one Tosylhydrazone. The ketone[36] (1.25 g, 7.2 mmol) was dissolved in 8 mL of ethanol, and to the solution was added 1.35 g (7.2 mmol) of tosylhydrazine and 0.01 mL of concentrated HCl. The mixture was refluxed for 17 h, diluted with 4 mL of ethanol, and cooled. A white solid appeared, which was filterd and recrystallized from ethanol: yield 1.28 g (52%); mp 159.5–161 °C; NMR ($CDCl_3$) δ 1.32 (3 H, br s), 1.65 (3 H, br s), 1.85 (3 H, s), 2.40 (3 H, s), 7.26–8.0 (10 H, m); IR ($CHCl_3$) 3690, 3640, 3250, 3040, 2400, 1600, 1490, 1445, 1380, 1345 cm^{-1}; mass spectrum, *m/e* 188 (13), 187 (100), 143 (12). Anal. Calcd for $C_{19}H_{22}N_2SO_2$: C, 66.63; H, 6.48; N, 8.17; S, 9.36. Found: C, 66.53; H, 6.42; N, 8.22; S, 9.22.

The two other tosylhydrazones were prepared in a similar way.

3,4-Dimethyl-3-penten-2-one Tosylhydrazone: yield 75%. Recrystallization in excess of methanol gave an analytical sample: mp 179–181 °C; NMR ($CDCl_3$) δ 1.33 (3 H, br s), 1.57 (3 H, br s), 1.68 (3 H, s), 1.90 (3 H, s), 2.25 (3 H, s), 7.31 (2 H, d, J = 8 Hz), 7.55 (1 H, br s), 7.83 (2 H, d, J = 8 Hz); IR ($CHCl_3$) 3005, 2915, 1605, 1380, 1335 cm^{-1}; mass spectrum, *m/e* 126 (71), 125 (100), 110 (39), 109 (53), 95 (22), 91 (51), 81 (53). Anal. Calcd for $C_{14}H_{20}N_2SO_2$: C, 59.97; H, 7.19; N, 9.99; S, 11.43. Found: C, 59.83; H, 6.98; N, 10.12; S, 11.51.

4-Methyl-3-phenyl-3-penten-2-one Tosylhydrazone: yield 60%. Recrystallization from methanol gave an analytical sample: mp 162–164 °C; NMR ($CDCl_3$) δ 1.60 (3 H, s), 1.80 (3 H, s), 1.85 (3 H, s), 2.48 (3 H, s), 6.7–7.0 (2 H, m), 7.07–7.50 (5 H, m), 7.78–8.0 (3 H, m); IR ($CHCl_3$) 3024, 2910, 1600, 1380, 1335 cm^{-1}; mass spectrum, *m/e* 158 (23), 144 (28), 143 (50), 139 (26), 130 (37), 104 (100), 103 (43), 91 (58). Anal. Calcd for $C_{19}H_{22}N_2SO_2$: C, 66.63; H, 6.48; N, 8.17; S, 9.36. Found: C, 66.49; H, 6.48; N, 8.11; S, 9.52.

Preparation of 2,3-Dimethyl-1-phenyl-1-diazo-2-butene (9). The tosylhydrazone (0.258 g, 0.75 mmol) was dissolved in 5 mL of anhydrous tetrahydrofuran, and potassium *tert*-butoxide (0.12 g, 1.07 mmol) was added quickly. The solution turned pink on stirring for 10 min. The solvent was then removed under vacuum at room temperature. The flask was covered with aluminum foil, and 25 mL of *n*-pentane was added. After stirring overnight, the solution was filtered. Evaporation of the solvent under vacuum at room temperature gave a pink residue: NMR (CCl_4) δ 1.72 (3 H, br s), 1.90 (6 H, s), 6.72–7.40 (5 H, m); IR (CCl_4) 2035 cm^{-1}.

Kinetics of the Thermolysis of Diazoalkane 9. Solutions of $\sim 10^{-4}$ M diazo compound **9** in 5% pyridine in benzene were sealed in 5-mL ampules (10 per kinetic run). Since diazo compounds decompose in visible light, these ampules were wrapped in aluminum foil. The ampules were then placed in a constant-temperature bath for the kinetic run and taken out at appropriate times and immediately quenched in ice-cold water. The absorbance of the solutions was then measured at 325 nm to monitor the disappearance of the diazo compound. Measurements were taken with a Unicam SP-500 spectrophotometer. First-order rate constants were then obtained by the usual ln $(A_\infty - A)$ method with points for 2 half-lives; correlation coefficients were always greater than 0.99. A typical run at 80.8 °C gave [time, min (absorbance)]: 0 (0.432), 15 (0.357), 30 (0.313), 45 (0.264), 61 (0.230), 75 (0.203), 90 (0.183), 120 (0.151), ∞ (0.120); $k = 3.05 \times 10^{-4}$ s^{-1} (r = 0.999). The average values of two to four runs at each temperature are listed in Table I.

Preparation of 5-Phenyl-3,3,4-trimethyl-3*H*-pyrazole (22). To 2.8 g (8.2 mmol) of the tosylhydrazone dissolved in 100 mL of anhydrous tetrahydrofuran was added 1.5 g (13.4 mmol) of potassium *tert*-butoxide. The mixture was stirred for 1 h, followed by evaporation of the solvent under vacuum. To the pink solid was added 125 mL of *n*-hexane, and the mixture was stirred for 24 h at room temperature, followed by reflux for 24 h, cooled, and filtered, and the solvent was evaporated under vacuum. A dark-orange heavy oil was obtained (1.1 g). Analysis of this oil by ^{1}H NMR showed that it contained the desired pyrazole and 1-phenyl-2,3,3-trimethylcyclopropene[24] in the ratio of 1:4. The cyclopropene was removed under vacuum (2–3 mm, 20 °C) using a dry ice–acetone trap. To the residual heavy oil was added 1 mL of *n*-hexane, and the solution was cooled to dry ice temperature for 1 h. The solution was then kept at -15 °C for 24 h when a yellow solid precipitated. The supernatant liquid was separated from the solid with a syringe, and the solid was recrystallized in *n*-hexane. A few more crystals were obtained from the mother liquor and supernatant liquid. An analytical sample of the pyrazole was obtained by sublimation (0.03 mm, 40–42 °C): mp 66–68 °C; 80-MHz NMR ($CDCl_3$) δ 1.41 (6 H, s), 2.13 (3 H, s), 7.4–7.8 (5 H, m); Perkin-Elmer 180 IR (CCl_4) 2990, 2930, 1495, 1460, 1385, 1360, 1330 cm^{-1}; UV (MeOH) λ_{max} 332 nm (ϵ 250), 280 (2200); mass spectrum, *m/e* 186 (21), 144 (21), 143 (87), 128 (33),

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(35) W. H. Williams and W. R. Dolbier, *J. Am. Chem. Soc.*, **94**, 3955 (1972).

(36) J. Colonge and J. Chambian, *Bull. Soc. Chim. Fr.*, 999 (1947).

107 (47), 106 (100), 104 (26), 103 (25), 77 (42). Anal. Calcd for $C_{12}H_{14}N_2$: C, 77.38; H, 7.58; N, 15.04. Found: C, 77.51; H, 7.03; N, 15.20.

Product Composition for the Thermolysis of Diazoalkane 6. The diazo compound **6** was dissolved in 0.5 mL of 5% pyridine in benzene-d_6 and sealed in a Pyrex NMR tube after three freeze–pump–thaw cycles. The tube was placed in a constant-temperature bath until the red color of the diazo compound had disappeared. The relative compositions of cyclopropene and pyrazole were determined by the intensities of their methyl signals in ^{1}H NMR spectra. The percent composition at various temperatures are listed in Table I.

Preparation of 4-Methyl-3-phenyl-3-penten-2-one (17). This enone was prepared according to the procedure for the preparation of 1-(4-methoxyphenyl)-3-methyl-2-phenyl-1-butanone by Arnold et al.[6b] Pure enone distilled at 40–44 °C (0.1 mm) as a faint yellow liquid. The NMR spectrum agreed with that reported by Friedrich and Fiato:[21] NMR (CCl_4) δ 1.62 (3 H, s), 1.88 (3 H, s), 2.00 (3 H, s), 7.20 (5 H, m).

Generation of 4-Methyl-3-phenyl-2-diazo-3-pentene (10). To a solution of 0.31 g (0.91 mmol) of the tosylhydrazone in 12 mL of anhydrous tetrahydrofuran was added 0.14 g (1.25 mmol) of potassium *tert*-butoxide. The solution turned greenish-yellow immediately. The solution was stirred magnetically overnight. The solvent was evaporated on the rotary evaporator and the flask was then covered with aluminum foil, 40 mL of n-hexane was added, and the solution was refluxed for 10 h. Filtration and evaporation of the solvent gave a pink residue: yield 0.036 g. The NMR spectrum indicated the presence of 20% cyclopropene **23**[24] and 80% of 3*H*-pyrazole **24**. The residue was dissolved in 0.5 mL of 5% pyridine in benzene and photolyzed using photolysis equipment "A". The photolysis was stopped when the deep-red solution showed maximum diazo concentration by NMR: δ 1.42 (s), 1.57 (s), 1.72 (s). A sample of this intense red-colored solution was examined by infrared spectroscopy, and it showed a characteristic band at 2035 cm^{-1} in CCl_4.

Kinetics and Product Composition Analysis for Thermolysis of Diazoalkane 10. Diazoalkane **10** as generated above was dissolved in 0.5 mL of 5% pyridine in benzene-d_6 and sealed in a Pyrex NMR tube. The tube was placed in a constant-temperature bath shielded from light. The tube was taken out at appropriate intervals of time and immediately quenched in ice-cold water for a few minutes. Three quick NMR spectra (T-60) were taken of the solution, scanning between δ 0.0 and 3. Relative compositions of the diazo compound, pyrazole, and cyclopropene were calculated by separately averaging the signal intensities for each of them. A typical run at 60.5 °C gave the following measurements: time, s (% diazo): 0 (28.5), 100 (26.1), 250 (24.2), 400 (22.2), 550 (20.5), 700 (18.8), 900 (16.7), 1100 (15.2). First-order rate constants were then obtained by a plot of ln (% diazo) vs. time. Correlation coefficients were always greater than 0.99. The average values of two to four runs at each temperature are listed in Table I. To obtain the product composition, the thermolysis was continued at the constant temperature until all the diazo compound disappeared. The percent compositions are also listed in Table I.

Preparation of 4-Phenyl-3,3,5-trimethyl-3*H*-pyrazole (24). The tosylhydrazone (2.0 g, 5.8 mmol) was dissolved in 100 mL of anhydrous tetrahydrofuran, and potassium *tert*-butoxide (1.0 g, 8.9 mmol) was added quickly. The solution was stirred overnight, the solvent was removed under vacuum, and the residue was refluxed with 100 mL of *n*-heptane for 12 h. Filtration and evaporation of the solvent gave a pink residue (ca. 0.9 g). To this residue was added 0.5 mL of *n*-hexane, and the solution was cooled in dry ice for 1 h. Then the flask was kept at −15 °C for 24 h, and a solid crystallized. The "supernatant liquid" was taken out with a syringe and saved, and the solid was quantitatively transferred to a sublimation apparatus. The temperature of the water passing through the condenser was kept at 0–5 °C. Sublimation at 34–35 °C (0.05 mm) gave faint pink crystals, which lose color on standing. The supernatant liquid was once again cooled to dry ice temperature, and the whole process was repeated. Total yield of the pyrazole obtained was 0.45 g (41%): mp 46.5–47.5 °C; NMR (CCl_4) δ 1.40 (6 H, s), 2.37 (3 H, s), 7.07–7.50 (5 H, m); IR (CCl_4) 2994, 2940, 1602, 1498, 1450, 1385, 1358 cm^{-1}; UV (MeOH) λ_{max} 342 (ϵ 900), 287 (5, 800); mass spectrum, 186 (100), 185 (25), 144 (25), 143 (94), 128 (46), 115 (26). Anal. Calcd for $C_{12}H_{14}N_2$: C, 77.38; H, 7.58; N, 15.04. Found: C, 77.12; H, 7.33; N, 14.76.

Preparation of 3,4,5,5-Tetramethylpyrazole (20). To 0.9 g (3.2 mmol) of the tosylhydrazone were added 40 mL of anhydrous tetrahydrofuran and sodium methoxide (0.35 g, 6.4 mmol). The solution was refluxed for 3 h. Cooling and evaporation of the solvent gave a white solid. To this white solid was added 60 mL of *n*-heptane, and the mixture was refluxed for 5 h. Cooling, followed by filtration and evaporation of the solvent under vacuum (15 mm, 50 °C), gave a faint yellow liquid (0.12 g, 30%), whose NMR agreed with that reported in literature.[25]

Generation of 3,4-Dimethyl-2-diazo-3-pentene (8). 3,4,5,5-Tetramethylpyrazole (0.03 g) dissolved in 0.5 mL of 5% pyridine in benzene-d_6 was photolyzed in a sealed Pyrex NMR tube using photolysis equipment "B". Photolysis was discontinued when the diazo concentration was found to be maximum as monitored by ^{1}H NMR: δ 0.93 (s), 1.17 (s), 1.28 (s), 1.50 (s).

Kinetics of the Thermolysis of Diazoalkane 8. A sample of diazoalkane **8** as generated above was placed in a constant-temperature bath, removed at suitable times, and quenched in an ice bath. Relative compositions of the diazoalkane and pyrazole were obtained by the intensities of their high-field ^{1}H NMR signals. ^{1}H NMR spectra were recorded with a CFT-20 spectrometer operating at 80 MHz. The probe temperature was kept at 5–10 °C. The spectra were electronically integrated. Rate constants obtained are listed in Table I.

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Registry No. **6** (X = H), 50555-62-9; **8**, 82323-71-5; **9**, 82323-72-6; **10**, 82323-73-7; **14**, 82323-74-8; **15**, 82323-75-9; **17**, 53546-26-2; **18**, 36697-16-2; **19**, 50555-61-8; **20**, 5363-08-6; **21**, 26385-95-5; **22**, 82323-76-0; **23**, 50902-98-2; **24**, 82323-77-1; 1,2-diphenyl-3-methyl-2-buten-1-one tosylhydrazone, 82323-78-2; 1,2-diphenyl-3-methyl-2-buten-1-one, 29689-80-3; 2,3-dimethyl-1-phenyl-2-buten-1-one tosylhydrazone, 82323-79-3; 3,4-dimethyl-3-penten-2-one tosylhydrazone, 82323-80-6; 4-methyl-3-phenyl-3-penten-2-one tosylhydrazone, 82323-81-7; 2,3-dimethyl-1-phenyl-2-buten-1-one, 52776-41-7; tosylhydrazine, 1576-35-8.