



**Table I.** Kinetic Parameters for Thermal Decomposition of Diphenyldiazomethane (3) in Water (2.18 M)/1,2-Dimethoxyethane at 75.0 °C

$[\text{Ph}_2\text{CN}_2]_0 \times 10^2, \text{M}$	$k_{\text{obsd}} \times 10^3, \text{min}^{-1}$	$k_1^a \times 10^3, \text{min}^{-1}$	$(k_2/k_3)^b$	$[\text{azine}]_\infty \times 10^4, \text{M}$
1.65	1.59	1.59	6.05	3.54
1.65	1.60	1.60	6.05	3.59
1.57	1.54	1.52	4.05	2.14
1.57	1.60	1.51	4.05	2.10
1.57	1.56	1.58	4.05	2.38
1.46	1.54			
1.46	1.48			
1.46	1.55			
0.942	1.61			
0.942	1.59			
0.942	1.65			
0.850	1.45			
0.850	1.44			

<sup>a</sup> Calculated employing eq 4. <sup>b</sup> Computed employing eq 5.

lecular decay. The observed rate coefficient for disappearance of 3 in anhydrous 1,2-dimethoxyethane at 75.0 °C ( $k_{\text{obsd}} = 2.71 \times 10^{-3} \text{ min}^{-1}$ ) is increased relative to that in aqueous 1,2-dimethoxyethane, thus excluding the participation of water in the rate-limiting step.<sup>3</sup>

The investigation was systematically extended to a series of para-, mono-, and disubstituted diphenyldiazomethanes prepared in greater than 99% purity by silver(I) oxide oxidation of the corresponding benzophenone hydrazones. All diphenyldiazomethanes studied exhibit strict first-order behavior in both aqueous and anhydrous 1,2-dimethoxyethane over the range of concentrations ( $0.1\text{--}1.5 \times 10^{-2} \text{ M}$ ) employed, with one exception. Decomposition of 4-(methylsulfonyl)diphenyldiazomethane in anhydrous 1,2-dimethoxyethane displays minor deviations toward faster reaction after approximately 1 half-life. The consequences of this acceleration are not believed to be important with respect to the objectives of the present research.

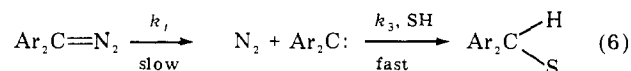
Diphenyldiazomethanes containing resonance electron-donating para substituents (Cl, CH<sub>3</sub>, OCH<sub>3</sub>, CH<sub>3</sub>/CH<sub>3</sub>) yield the corresponding benzhydrols, benzophenone azines (ca. 5%), and benzophenones (ca. 1%) as the sole products of decomposition in water (2.18 M)/1,2-dimethoxyethane. Examination of the kinetic parameters reveals that electron-donating substituents facilitate decomposition, and that for the experimental conditions employed, the observed and unimolecular rate coefficients are identical. The observed kinetic substituent effects in the monosubstituted series are in qualitative agreement with those previously reported for decompositions in *tert*-butyl alcohol/acetonitrile.<sup>7</sup> The rate coefficient for decomposition of 4-methoxydiphenyldiazomethane in anhydrous 1,2-dimethoxyethane ( $k_{\text{obsd}} = 15.4 \times 10^{-3} \text{ min}^{-1}$ ) is enhanced by a factor of 1.9 relative to that in aqueous media. This fact is again consistent with the interpretation<sup>3</sup> that the diarylcarbene is generated and subsequently captured by water as in eq 3.

Decompositions of diphenyldiazomethanes containing resonance electron-withdrawing para substituents (CF<sub>3</sub>, SO<sub>2</sub>CH<sub>3</sub>, CN, NO<sub>2</sub>, CH<sub>3</sub>/NO<sub>2</sub>, NO<sub>2</sub>/NO<sub>2</sub>) provide a dramatic contrast to the prior systems in that azines are not formed. The reaction products are the corresponding benzhydrols along with traces (ca. 1%) of the ketones.<sup>8</sup> Diphenyldiazomethanes containing the cyano or nitro group also yield minor amounts (ca. 10%) of products resulting from insertion into 1,2-dimethoxyethane. This alteration of the product-determining steps has a profound effect upon the kinetic derivations in that the diazo compound is no longer partitioned off by reaction with the generated carbene. The mechanism for decomposition is simplified as follows (eq 6), where SH represents the solvent, both water and

**Table II.** Diphenyldiazomethanes (1). Rate Coefficients for Unimolecular Decomposition,<sup>a</sup> and <sup>13</sup>C NMR Shieldings of Diazomethyl Carbons (Ar<sub>2</sub>C=N<sub>2</sub>)<sup>b</sup>

substituent	$k_1 \times 10^3, \text{min}^{-1}$	$\delta_c^{\text{CN}_2}, \text{ppm}$
H	$1.55 \pm 0.06^c$	62.4
4-Cl	$2.15 \pm 0.07$	62.3
4-CH <sub>3</sub>	$2.56 \pm 0.16$	62.2
4-OCH <sub>3</sub>	$8.14 \pm 0.23$	61.6
4-CF <sub>3</sub>	$2.68 \pm 0.10$	63.1
4-SO <sub>2</sub> CH <sub>3</sub>	$3.58 \pm 0.08$	63.6
4-CN	$3.90 \pm 0.12$	63.9
4-NO <sub>2</sub>	$6.68 \pm 0.28$	64.5
4-CH <sub>3</sub> /4'-CH <sub>3</sub>	$2.05 \pm 0.11$	61.8
4-CH <sub>3</sub> /4'-NO <sub>2</sub>	$11.10 \pm 0.33$	64.2
4-NO <sub>2</sub> /4'-NO <sub>2</sub>	$1.38 \pm 0.12$	64.2

<sup>a</sup> Water (2.18 M)/1,2-dimethoxyethane at  $75.0 \pm 0.05$  °C. Reported values are the average result of a minimum of nine kinetic measurements at three initial diazo concentrations over the range of  $0.1\text{--}1.5 \times 10^{-2} \text{ M}$ . <sup>b</sup> <sup>13</sup>C chemical shift in CDCl<sub>3</sub> solution at  $0 \pm 1$  °C, relative to internal Me<sub>4</sub>Si. The error is estimated to be 0.1 ppm. Broad-band decoupled Fourier transform spectra: Bruker HX-90; 22.625 MHz. <sup>c</sup> Standard deviation.



1,2-dimethoxyethane. Decompositions of these diazo compounds obey a simplified rate expression (eq 7), and the observed rate of reaction is that of unimolecular decay!

$$\frac{-d[\text{Ar}_2\text{CN}_2]}{dt} = k_1[\text{Ar}_2\text{CN}_2] \quad (7)$$

This mechanistic interpretation (eq 6) affords the prediction that the observed rates of decomposition of such diazo compounds should be highly insensitive to solvent composition. Indeed, the respective rate coefficients for thermolysis of 4-cyanodiphenyldiazomethane, 4-nitrodiphenyldiazomethane, and 4,4'-dinitrodiphenyldiazomethane are experimentally indistinguishable in anhydrous and aqueous 1,2-dimethoxyethane. These results also preclude any bimolecular reaction of consequence involving the diazo compound and water.

Average unimolecular rate coefficients for all diphenyldiazomethanes investigated are summarized in Table II. It is immediately evident that all substituents accelerate unimolecular thermal decomposition of para-monosubstituted diphenyldiazomethanes relative to diphenyldiazomethane. A correlation of these rate parameters with Hammett enhanced resonance constants ( $\sigma^+$  and  $\sigma^-$ ) is illustrated in Figure 1. Similar parabolic deviations from linearity are well documented for reactions in which a change in substituent induces a concomitant change in reaction mechanism. Such deviations are also observed for systems in which the measured rate coefficient is a complex function of several rate and equilibrium constants; a substituent change alters the rate-limiting step within the same overall mechanism.<sup>9</sup> Neither of these complications is pertinent to the present system. This conclusion is reinforced by the observation that all para substituents facilitate the first-order thermal decompositions of phenyl azides and 2-azidobiphenyls (7, eq 8) in aprotic hydrocarbon media.<sup>10</sup> The diazo and azido functions are isoelectronic, as are the carbene and nitrene intermediates they generate by unimolecular extrusion of nitrogen. It is expected that such closely related processes will exhibit similar electronic requirements.

Scrutiny of the rate data demonstrates that substituent effects within the disubstituted diphenyldiazomethanes are not directly additive, in the usual sense, as tacitly assumed by

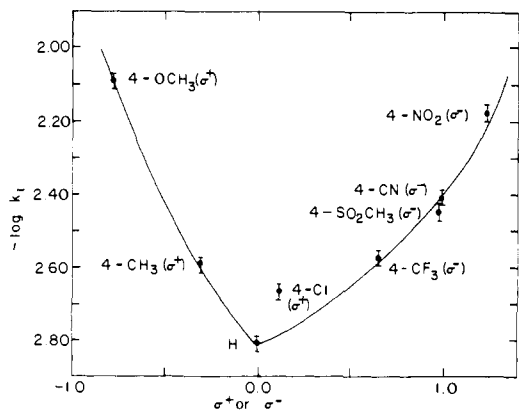
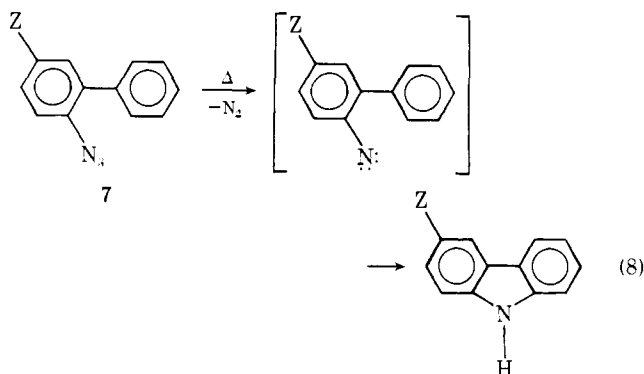


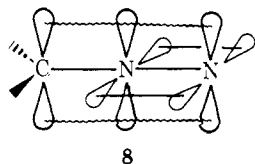
Figure 1. Correlation of the rate coefficients ( $-\log k_1$ ) for unimolecular thermal decomposition of para-monosubstituted diphenyldiazomethanes with Hammett enhanced resonance constants ( $\sigma^+$  or  $\sigma^-$ ).



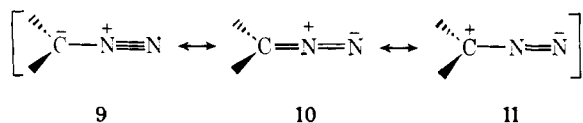
Bethell et al.<sup>7</sup> In fact, incorporation of a second identical para substituent retards unimolecular decomposition relative to the monosubstituted species. Furthermore, 4-methyl-4'-nitrodiphenyldiazomethane decomposes more rapidly than either of the corresponding monosubstituted compounds.

A systematic investigation of ground-state substituent effects in diphenyldiazomethanes by <sup>13</sup>C NMR methods was then initiated. The broad-band decoupled Fourier transform <sup>13</sup>C NMR spectrum of each diazo compound was measured in chloroform-*d* solution at 0°C, relative to internal tetramethylsilane.<sup>11</sup> This experimental probe was chosen because of previous correlations between local  $\pi$ -electron densities and <sup>13</sup>C shieldings in aromatic systems, and the great sensitivity of the technique.<sup>12</sup> The observed shieldings of the carbon atoms of the diazomethyl center ( $\text{Ar}_2\text{C}=\text{N}_2$ ) are summarized in Table II.

Molecular orbital theory describes the diazo moiety as being comprised of two orthogonal  $\pi$  frameworks (8): one encom-



passing the C-N-N structure and containing four electrons, and the other including only the N-N bond with two electrons.<sup>13</sup> These structural features may also be visualized in terms of valence bond canonical forms 9-11. Hückel MO



treatment of diphenyldiazomethane indicates the relative

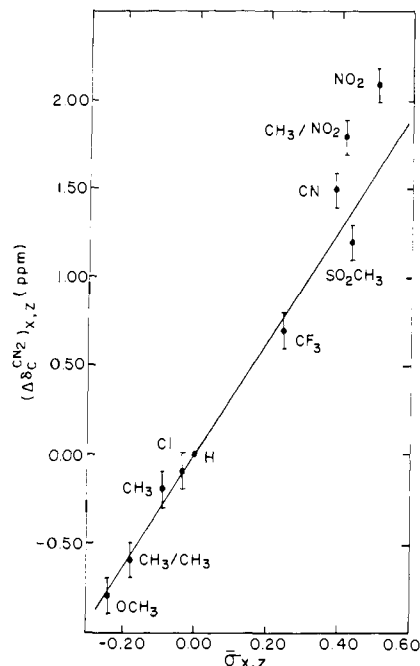


Figure 2. Relative shieldings of the diazo carbons in diphenyldiazomethanes [ $(\Delta\delta_c^{\text{CN}_2})_{x,z}$ ] as a function of synthetic substituent parameters ( $\bar{\sigma}_{x,z}$ ) from the  $\sigma_{\text{R}^-}$  scale.

importance of 9 as shown by the following calculated  $\pi$ -electron densities:<sup>14</sup>

$$\begin{aligned} &+0.8492 \\ (\text{Ph})_2\text{C}-\text{N}-\text{N} \\ &-0.3633-0.2270 \end{aligned}$$

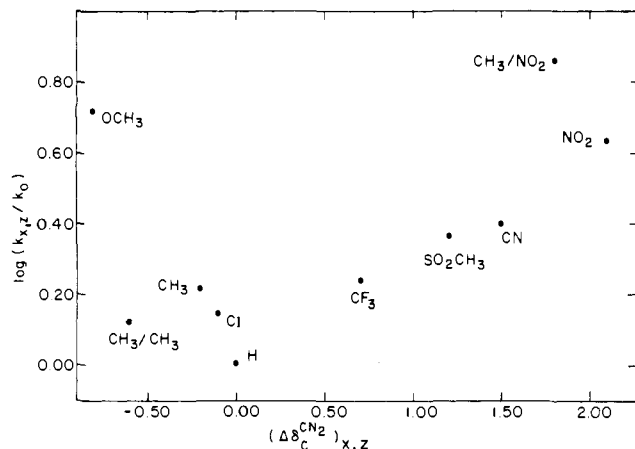
The high-field resonance position for diphenyldiazomethane, 62.4 ppm,<sup>15</sup> is consistent with the high electron density calculated by HMO methods. The carbon shieldings are correlated by the dual substituent parameter treatment employing  $\sigma_{\text{R}^-}$  constants:<sup>16</sup>

$$\begin{aligned} (\Delta\delta_c^{\text{CN}_2})_{x,z} &= 0.87\sigma_1 + 2.17\sigma_{\text{R}^-} \\ \lambda &= 2.49, f = 0.216 \end{aligned} \quad (9)$$

where  $(\Delta\delta_c^{\text{CN}_2})_{x,z}$  represents the chemical shift of the *x* plus *z*th substituted molecule relative to diphenyldiazomethane, that is,  $(\delta_c^{\text{CN}_2})_{x,z} - 62.4$ . Direct additivity of substituent effects was assumed for all disubstituted diphenyldiazomethanes. Figure 2 illustrates the free-energy relationship as a function of synthetic substituent constants,  $\bar{\sigma}_{x,z}$ .<sup>17</sup>

This type of quantitative treatment attributes an observed substituent effect to a combination of polar (I) and  $\pi$ -delocalization (R) effects, where  $\lambda$  ( $\equiv \rho_{\text{R}}/\rho_1$ ) represents the relative importance of R and I contributions. The observed correlation thus provides evidence that valence bond representation 9 predominantly reflects the ground states of diphenyldiazomethanes, regardless of substituents.<sup>18</sup> It is likely that the apparently poor statistical precision of the correlation ( $f = 0.216$ ) is an artifact of the small magnitudes of the relative chemical shifts.<sup>19</sup>

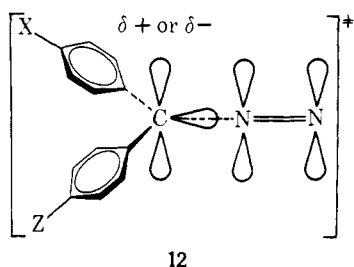
A plot of the logarithms of the relative unimolecular rate coefficients as a function of the relative carbon shieldings, Figure 3, compares the kinetic and ground-state substituent effects. The fact that those effects are not similar in both instances is evident from the random scatter. Since the kinetic effect arises from differences between the ground and transition states, the change in the role of the substituent must be occurring during the activation process. The high enthalpy of activation ( $\Delta H^\ddagger = 27.2 \pm 0.2$  kcal/mol) for thermal decom-



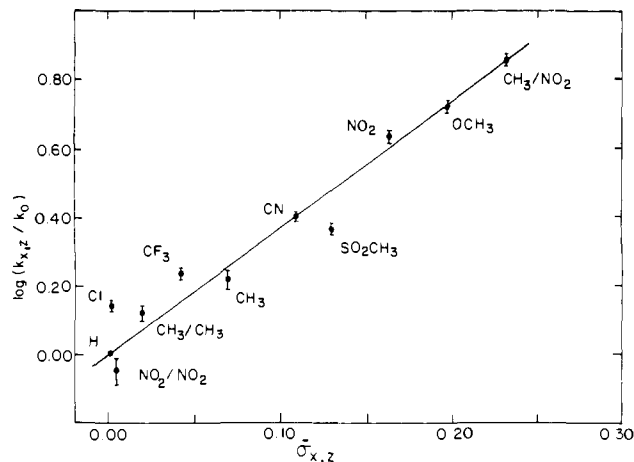
**Figure 3.** Correlation of the relative unimolecular rate coefficients [ $\log(k_{x,z}/k_0)$ ] and relative carbon shieldings [ $(\Delta\delta_c^{CN2})_{x,z}$ ] of diphenyldiazomethanes.

position of diphenyldiazomethane<sup>3</sup> is consistent with this interpretation. It is concluded that substituent effects within the transition states for decomposition are virtually entirely responsible for the observed kinetic behavior!

Any rigorous mechanistic interpretation of the effects of structural alterations upon the rates of unimolecular thermal decomposition of diphenyldiazomethanes to the corresponding carbenes must simultaneously rationalize the observed behavior of both mono- and disubstituted systems. The kinetic substituent effects within the monosubstituted series might, for example, evoke the following hypothesis. A transition state (12) could be envisaged arising from stretching of the car-



bon-nitrogen  $\sigma$  and  $\pi$  bonds with concomitant development of one "p-like" and one "sp<sup>2</sup>-like" orbitals upon carbon. If both aryl groups were effectively coplanar with the developing p orbital, the electronic distribution within that orbital might be subtly controlled by the resonance capability of the para substituent. Electron-donating substituents would facilitate formation of an electron-deficient p orbital while electron-withdrawing groups would induce development of an electron-rich p orbital. While such an argument is generally consistent with the behavior of the monosubstituted diphenyldiazomethanes, it clearly fails to explain the observed effects within disubstituted diphenyldiazomethanes. This failure is most obvious for 4-methyl-4'-nitrodiphenyldiazomethane. Such a model would in fact require incorporation of a 4'-methyl substituent into 4-nitrodiphenyldiazomethane to cause a rate decrease because of its destabilizing influence upon the developing electron-rich orbital. This does not coincide with the facts (see Table II) and is sufficient reason to reject such a mechanism. Furthermore, the above mechanism also fails to correctly represent the behavior of the symmetrically disubstituted diphenyldiazomethanes. Kinetic effects approaching direct additivity would be predicted by such an interpretation, especially since direct additivity is observed within the ground states. Once again, this is contradictory with experiment, thus reinforcing the demise of such an hypothesis.



**Figure 4.** Relative rate coefficients [ $\log(k_{x,z}/k_0)$ ] for the unimolecular thermal decomposition of diphenyldiazomethanes as a function of synthetic substituent parameters ( $\bar{\sigma}_{x,z}$ ) from the  $\sigma_{R^+}$  and  $\sigma_{R^-}$  scales.

Any postulated mechanism must therefore allow for substituent interaction with both orbitals developing within the transition state. Freedom of rotation permitting effective coplanarity of both aryl functions, and thus resonance interaction of both substituents with the same developing orbital, must be ruled out.

These requirements afford a qualitative rationalization of all of the kinetic observations. In the monosubstituted diphenyldiazomethanes, each substituted phenyl group, by whatever be the mechanism, becomes aligned so that the substituent interacts with that developing carbenic orbital which it is capable of stabilizing by direct resonance. A rate enhancement relative to diphenyldiazomethane results. The second phenyl ring must therefore align with the other, remaining developing orbital. A second, added para substituent is thus constrained to interact with this remaining orbital. If this substituent is identical with the first (or of the same type, either electron donating or electron withdrawing), rate retardation, relative to the monosubstituted system, will be observed because of the required destabilization of this remaining orbital. If this second substituent is of an opposite nature, a rate enhancement will be found because of the simultaneous stabilization of both developing orbitals.

The legitimacy of such an explication is established by its ability to quantitatively reflect the behavior of all diphenyldiazomethanes investigated. The kinetic substituent effects may be treated as a summation of independent, yet simultaneous effects upon both the electron-deficient and electron-rich developing orbitals:

$$\begin{aligned} \log(k_{x,z}/k_0) &= -0.70\sigma_{1x} - 0.89\sigma_{R_x^+} \\ &\quad - 0.32\sigma_{1z} + 1.76\sigma_{R_z^-} \quad (10) \\ \lambda^+ &= 1.28, \lambda^- = -5.48, f = 0.091 \end{aligned}$$

in which  $x$  and  $z$  denote electron-donating and electron-withdrawing substituents, respectively. The  $\lambda$  superscripts are those of the resonance substituent constants defining them, and thus refer to the relative electron densities of the respective orbitals. The free-energy relation is illustrated in Figure 4 as a function of synthetic substituent constants,  $\bar{\sigma}_{x,z}$ .<sup>20</sup>

Two features of eq 10 merit specific attention: the negative values of  $\lambda^-$  and  $\rho_{1z}$ . The first merely indicates that inductive and resonance effects of electron-withdrawing substituents are opposed. Other kinetic systems have been observed to manifest similar substituent behavior and there is no reason that it should be considered extraordinary.<sup>21</sup> Indeed, it is not unreasonable that while an electron-withdrawing substituent stabilizes the developing electron-rich orbital via direct resonance,

it also inductively destabilizes the positive charge developing upon the identical carbon atom. Furthermore, it is expected, and observed, that electron-donating substituents would not exhibit such opposing behavior. This becomes obvious as it is realized that conversion of the ground state to the transition state requires greater relative development of positive charge at the carbene center.

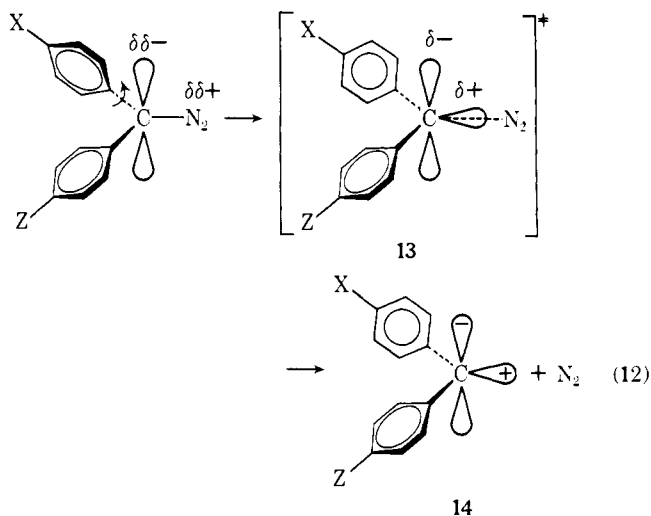
A corollary is the potential simplification of eq 10 by assuming an overall inductive effect arising from a direct combination of individual substituent inductive effects, that is  $\sigma_{1_{X,Z}} = \sigma_{1_X} + \sigma_{1_Z}$ . The inherent failure of such a treatment (eq 11)

$$\log(k_{X,Z}/k_0) = -1.25\sigma_{1_{X,Z}} - 1.97\sigma_{R_X} + 4.85\sigma_{R_Z} \quad (11)$$

is amply described by its poor statistical precision ( $f = 0.355$ ). The superiority of eq 10 thus appears to provide a most interesting demonstration of the opposing operation of classical and  $\pi$ -inductive effects!<sup>22</sup> The classical inductive effect, operating through space and/or the  $\sigma$ -bond framework, reacts to the gross charge development occurring during the activation process. The  $\pi$ -inductive effect, arising from polarization of the  $\pi$  framework within the aromatic moiety, is, however, geometry dependent in the same sense as the direct resonance effect, and therefore manifests itself upon that developing orbital with which it is properly aligned.

Two mechanistic rationalizations of the present results will be discussed in turn. In each instance, the ground state of the diazo compound is one in which there is some twisting of the ring systems from a coplanar conformation. Such a structure allows for reduction of the steric interactions between the ortho-ortho' ring hydrogens while retaining the observed additivity of the ground-state substituent effects (vide supra). Both mechanisms involve polar, singlet-like transition states leading to expulsion of molecular nitrogen in its singlet ground state. Furthermore, both require extensive bond breaking in the transition state, and thus imply two highly developing orbitals upon carbon, one containing a large degree of negative charge and the other strongly positive in character. These considerations are consistent with the large resonance interactions described by eq 10.

The first mechanism to be considered features removal of nitrogen along the line of the C-N-N framework with resultant p and  $sp^2$  orbitals developing upon carbon. The constraints previously described further require concomitant rotation of the aromatic rings to a mutually perpendicular conformation, thus allowing resonance interaction with each orbital developing within the transition state (13, eq 12).<sup>23</sup> The motivating

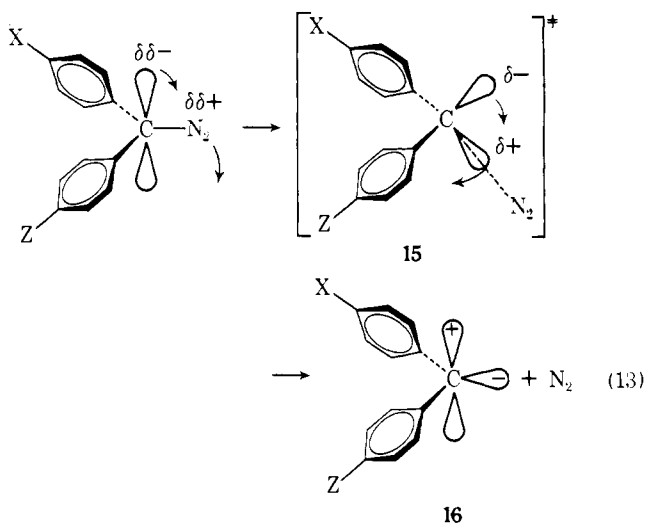


force for rotation within the monosubstituted series would clearly be of electronic origins. Within the symmetrically di-

substituted systems (which decompose more slowly than the monosubstituted derivatives), the driving force would necessarily appear to be steric in nature. It is disturbing that the need for alleviation of such steric congestion in the transition state would predominate over the resultant electronic destabilization, especially since there is no evidence for analogous twisting in the ground state.

The logical question of the electronic distribution within the transition state orbitals bears scrutiny. The developing p orbital might be predicted to be electron rich, thus minimizing electronic reorganization in conversion of the ground state to the transition state. The magnitudes of the resonance parameters of eq 10 are supportive since a developing p orbital should be more efficiently delocalized than a developing  $sp^2$  orbital. Such a process, however, requires generation of the carbene in an excited singlet configuration (14).

The final mechanism to be postulated features pyramidal stereochemistry (the orbital geometry is therefore markedly tetrahedral) upon development of the transition state (15, eq 13). Stretching of the carbon-nitrogen bond is accompanied



by nitrogen bending out of the plane defined by the central carbon and the C-1 and C-1' ring atoms. Both orbitals developing upon carbon are therefore an admixture of p and  $\sigma$  contributions and are capable of effective interaction with the  $\pi$  frameworks of the aromatic ring systems. Most notably, this mechanism suffers from neither of the objections raised against the prior one. A smooth rehybridization occurs in which the electron-rich p and the electron-deficient  $\sigma$  orbitals of the ground state diazo compound are transformed into the respective  $\sigma$  and p orbitals of the carbene. Decomposition thus yields the carbene in its lowest energy singlet configuration (16, eq 13).

Furthermore, no major geometrical reorientation of the aryl functions is required. Molecular models immediately demonstrate that the conformation of each ring system within the ground state is such that simultaneous resonance interaction with each orbital developing within the transition state is necessitated. Nitrogen is extruded either "up" or "down" from the original molecular plane so that the substituted phenyl group interacts with that developing orbital which it can stabilize by direct resonance. Similarly, the remaining aryl group must interact with the remaining orbital with resultant stabilization or destabilization depending upon the nature of the added ring substituent.

## Experimental Section

**Kinetic Procedures and Product Analyses.** 1,2-Dimethoxyethane was fractionally distilled from sodium through a vacuum-jacketed column packed with glass helices. The fraction utilized had a constant boiling point of 84.5°C (uncorrected) at ambient pressure. Water was

Table III. Substituted Diphenyldiazomethanes. Synthetic Conditions and Physical Properties

4 substituent	solvent (reaction time, h)	purification method	mp, °C		visible spectrum <sup>a</sup>		ref
			exptl	lit.	$\lambda_{\max}$ , nm	molar extinction coefficient, M <sup>-1</sup> cm <sup>-1</sup>	
H	Et <sub>2</sub> O (1)	I	29–29.5	29–30	525	90	35
Cl	Et <sub>2</sub> O (1)	I	26–27	26–27	525	97	36
CH <sub>3</sub>	Et <sub>2</sub> O (1)	I	54–55	53–55 dec	530	92	37
OCH <sub>3</sub>	Et <sub>2</sub> O (1)	I	49–50.5		535	96	38
NO <sub>2</sub>	Et <sub>2</sub> O (5)	II, hexane	83–84 dec	82–84	395 (520) <sup>b</sup>	15 100 (168) <sup>b</sup>	39
CN	CHCl <sub>3</sub> (1)	II, hexane	75–76 dec		505	119	40
CF <sub>3</sub>	Et <sub>2</sub> O (1)	II, hexane, –78 °C	43–43.5		510	109	
SO <sub>2</sub> CH <sub>3</sub>	Et <sub>2</sub> O (1)	II, ether	107–107.5 dec		505	125	
CH <sub>3</sub> /NO <sub>2</sub>	Et <sub>2</sub> O (5)	II, hexane	91–92 (d)		398 (520) <sup>b</sup>	18 600 (223) <sup>b</sup>	
CH <sub>3</sub> /CH <sub>3</sub>	Et <sub>2</sub> O (1)	I	100.5–101.5	100–101	535	94	6
NO <sub>2</sub> /NO <sub>2</sub>	CHCl <sub>3</sub> (2)	II, benzene	144–145 dec	143–144 dec	397 (500) <sup>b</sup>	21 500(425) <sup>b</sup>	36a

<sup>a</sup> Water (2.18 M)/1,2-dimethoxyethane at ambient temperature. <sup>b</sup> Parenthetical values refer to the shoulder at which kinetic data were measured.

demineralized and double distilled. Both solvents were scrupulously deoxygenated by conventional freeze-thaw techniques followed by lengthy saturation with purified argon.<sup>24</sup> The degas-saturation cycle was repeated three times. To ensure against contamination, the solvents were mixed, and all subsequent dilutions were made in a glovebox under an inert argon atmosphere.

Kinetic data were procured with an antediluvian Beckman DU spectrometer by following the change in transmittance of a solution of diazo compound of known initial concentration at the wavelength of maximum absorption<sup>25</sup> in the visible spectral region. Calibrated quartz spectrophotometric cells with ground glass stoppers were employed as reaction vessels within the thermostated spectrometer. Kinetic results are identical upon use of new or seasoned cells. Observed rate coefficients,  $-k_{\text{obsd}}$ , were calculated by least-squares fit of the data to an integrated form of the first-order rate expression:<sup>26</sup>

$$A_t = A_0 \exp(-k_{\text{obsd}}t) + A_\infty \quad (14)$$

where  $A_0$ ,  $A_t$ , and  $A_\infty$  are absorbances at times zero,  $t$ , and infinity, respectively. In all cases, graphical treatment gives results analogous to those computed. Values of  $k_2/k_3$  were determined by nonlinear least-squares analysis of eq 5.<sup>27</sup>

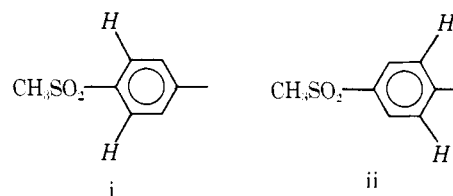
Azine concentrations were calculated from the absorbances at 400 nm of the reaction mixtures at time infinity. Molar extinction coefficients were based upon three separate determinations over a range of concentrations; no deviations from the Beer-Lambert law were observed. The concentration of benzophenone azine (**5**) increases smoothly as a function of time with none of the random variation reported for Pyrex reaction vessels.<sup>3</sup>

The samples from a given series of runs were then combined and concentrated in vacuo, and the residue was dissolved in minimal benzene. Thin layer chromatographic analyses were obtained upon Eastman Chromagram silica gel sheets impregnated with a fluorescent indicator, relative to authentic samples. Gas-liquid chromatographic analyses utilized a Varian Aerograph 920 gas chromatograph with a thermal conductivity detector. Two columns proved advantageous: column A (5% FFAP on Chromosorb W, AW-DMSC, 60/80 mesh, 5 ft × 1/4 in.) and column B (4% SE-30 on Chromosorb G, NAW, 100/120 mesh, 10 ft × 1/8 in.). Quantitative analyses, by comparison to standard mixtures of authentic samples, were based upon peak areas determined by planimetry. Gas chromatography-mass spectrum analyses of the 1,2-dimethoxyethane insertion products were obtained employing a Perkin-Elmer 990 gas chromatograph, with a flame ionization detector, and a Du Pont Instruments 21-490 mass spectrometer. Separations were effected upon column B.

**4-Cyanobenzophenone.** 4-Bromobenzophenone (65.3 g, 0.25 mol) was dissolved in *N,N*-dimethylformamide (100 mL) and cuprous cyanide (26.9 g, 0.30 mol, 1.2 equiv) was added in one portion with stirring.<sup>28</sup> The mixture was refluxed for 3 h during which time it became black and a finely divided precipitate formed. After cooling, the reaction product was added to hydrated ferric chloride (100 g) and concentrated hydrochloric acid (25 mL) in water (150 mL), and this mixture was stirred at 60–70°C for 20 min. A solid was collected by suction filtration and thoroughly washed with water. This crude product was dissolved in dichloromethane (500 mL) and washed with

dilute hydrochloric acid (1:1, 250 mL), water (250 mL), and 10% aqueous potassium hydroxide (250 mL). The organic phase was dried (MgSO<sub>4</sub>) and filtered, and the solvent was removed in vacuo to yield a pale yellow solid (41.1 g, 79%). Recrystallization from ethanol afforded 4-cyanobenzophenone as flocculent, white needles, mp 109–110 °C (lit.<sup>29</sup> mp 107–108 °C).

**4-(Methylsulfonyl)benzophenone Hydrazone.** 4-(Methylsulfonyl)benzophenone (26.0 g, 0.10 mol) was dissolved in absolute ethanol (500 mL); hydrazine (19.2 g, 0.60 mol, 6 equiv, 97% anhydrous) was added in one portion, and the mixture was refluxed (24 h) employing a Soxhlet extractor charged with molecular sieves (20 g, 3A).<sup>30</sup> The reaction mixture was allowed to cool and filtered, and the solvent was removed in vacuo. The resultant material was dissolved in dichloromethane (250 mL) and washed with saturated aqueous sodium chloride (2 × 200 mL). The washes were extracted with dichloromethane (100 mL) and the combined organic phase was washed with water, dried (MgSO<sub>4</sub>), and filtered. Removal of the solvent in vacuo gave the crude hydrazone as a viscous oil. Trituration with methanol afforded a solid (21.0 g, 77%). Recrystallization from ethanol yielded 4-(methylsulfonyl)benzophenone hydrazone as white plates: mp 157–158.5 °C; IR (KBr) 3430 and 3390 (N–H asymmetric stretch), 3310 and 3290 (N–H symmetric stretch), 1300 (complex, –SO<sub>2</sub>– asymmetric stretch), 1145 cm<sup>-1</sup> (–SO<sub>2</sub>– symmetric stretch); NMR (CDCl<sub>3</sub>)  $\delta$  8.11 (d, 2,  $J = 8$  Hz, i), 7.51 (d, 2,  $J = 8$  Hz, ii), 7.33 (s,



5, C<sub>6</sub>H<sub>5</sub>C–), 5.46 (s, 2, –NH<sub>2</sub>), and 3.12 (s, 3, –SO<sub>2</sub>CH<sub>3</sub>); mass spectrum (70 eV)  $m/e$  (rel intensity) 274 (M<sup>+</sup>, 100). Anal. (C<sub>14</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>S) C, H, N.

The other hydrazones were prepared analogously and those previously unreported have the following physical and spectral properties.

**4-(Trifluoromethyl)benzophenone Hydrazone.** White needles from ethanol: mp 120–120.5 °C; IR (KBr) 3395 (N–H asymmetric stretch), 3295 (N–H symmetric stretch), 1325 cm<sup>-1</sup> (C–F stretch); NMR (CDCl<sub>3</sub>)  $\delta$  7.13–7.90 (m, 9, aromatic), 5.38 (s, 2, –NH<sub>2</sub>); mass spectrum (70 eV)  $m/e$  (rel intensity) 264 (M<sup>+</sup>, 100). Anal. (C<sub>14</sub>H<sub>11</sub>F<sub>3</sub>N<sub>2</sub>) C, H, N.

**4-Methyl-4'-nitrobenzophenone Hydrazone.** Yellow prisms from ethanol: mp 97.5–98.5 °C; IR (KBr) 3410 (N–H asymmetric stretch), 3290 (N–H symmetric stretch), 1505 (–NO<sub>2</sub> asymmetric stretch), 1335 cm<sup>-1</sup> (–NO<sub>2</sub> symmetric stretch); NMR (CDCl<sub>3</sub>)  $\delta$  7.02–8.19 (m, 8, aromatic), 5.86 (s, 2, –NH<sub>2</sub>), 2.40 (s, 3, –CH<sub>3</sub>); mass spectrum (70 eV)  $m/e$  (rel intensity) 255 (M<sup>+</sup>, 100). Anal. (C<sub>14</sub>H<sub>13</sub>N<sub>3</sub>O<sub>2</sub>) C, H, N.

**Diphenyldiazomethanes.** The corresponding benzophenone hydrazone (5 mmol) was dissolved in ethyl ether or chloroform (100 mL) and placed in a pressure bottle with anhydrous magnesium sulfate

(0.60 g) and silver(I) oxide<sup>31</sup> (1.27 g, 5.5 mmol, 1.1 equiv). The bottle was sealed, wrapped in a cold, wet towel, and shaken mechanically. The reaction mixture was filtered and the solvent removed in vacuo giving an essentially quantitative yield of the crude diazo compound as a viscous oil or solid.

Purification of the diazo compounds was effected by one of the following techniques. Method I: the crude material was dissolved in a small portion of pentane (5–20 mL), filtered, and cooled at –78 °C. The resultant solid was collected by suction filtration employing a low-temperature crystallizing assembly (Ace Glass) chilled to –20 °C (50% aqueous 2-propanol/dry ice). Method II: the crude product was recrystallized three times from minimal warm hexane, benzene, or ethyl ether by standard techniques and collected. Each sample was desiccated in the dark and used immediately. Table III summarizes the specific reaction conditions and physical properties.

The purity of each diazo compound was determined to be greater than 99% by reacting an aliquot of a weighed sample with a known, excess quantity of benzoic acid in dry benzene.<sup>32</sup> The remaining benzoic acid was titrated to a phenolphthalein end point using standard aqueous sodium hydroxide. Appropriate blank titrations were run with each analysis.

Those substituted diphenyldiazomethanes hitherto unreported, or previously obtained only as oils, were further characterized by their mass spectra. In each case a low-intensity molecular ion peak was discernible. The observed fragmentation patterns are in agreement with those reported for closely related molecules,<sup>33</sup> i.e., loss of molecular nitrogen followed by structural rearrangement.

Diphenyldiazomethane was alternately prepared by heating benzophenone 2,4,6-trimethylbenzenesulfonylhydrazone<sup>34</sup> (1.0 g, 2.6 mmol) and 1,1,3,3-tetramethylguanidine (20 mL, distilled from barium oxide) upon a steam bath for 10 min. The resultant deep red solution was added to a slurry of ice and water (100 mL) and extracted with cold pentane. The organic layer was treated with several small pieces of dry ice to precipitate any remaining tetramethylguanidine as its insoluble carbonate. The solution was then dried (Drierite) and filtered, and the pentane was removed in vacuo to yield a deep red, viscous oil (0.42 g, 82%). Purification was effected by method I (vide supra). Samples prepared in this manner exhibited physical and kinetic properties in agreement with those obtained from the silver(I) oxide reactions.

**4-Cyanobenzhydrol.** 4-Cyanobenzophenone (2.07 g, 0.01 mol) was dissolved in absolute ethanol (75 mL) and sodium borohydride (0.38 g, 0.01 mol, 4 equiv) was added in one portion. After stirring for 3 h, the reaction mixture was hydrolyzed (H<sub>2</sub>O, 75 mL), and the resultant homogeneous solution was extracted with ether. The organic phase was washed with water, dried (MgSO<sub>4</sub>), and filtered, and the solvent was removed in vacuo. Trituration of the viscous oil with pentane afforded a solid (1.71 g, 82%). Recrystallization from hexane yielded 4-cyanobenzhydrol as fine, white needles: mp 67–68 °C; IR (KBr) 3460 (O–H stretch), 2235 (C≡N stretch), 1024 cm<sup>-1</sup> (C–O stretch); NMR (CDCl<sub>3</sub>) δ 7.38 (s, 4, NCC<sub>6</sub>H<sub>4</sub>CH), 7.21 (s, 5, C<sub>6</sub>H<sub>5</sub>CH), 5.67 (s, 1, C<sub>6</sub>H<sub>5</sub>CH), 3.32 (s, 1, CHOH); mass spectrum (70 eV) *m/e* (rel intensity) 209 (M<sup>+</sup>, 84). Anal. (C<sub>14</sub>H<sub>11</sub>NO) C, H, N.

**4-Methylbenzophenone Azine.** 4-Methylbenzophenone hydrazone (1.05 g, 5 mmol) was dissolved in absolute ethanol (50 mL) and concentrated sulfuric acid was added (pH ≈ 3).<sup>30</sup> The reaction mixture was refluxed (12 h) and diluted with hot ethanol (150 mL). Filtration to remove insoluble inorganics, concentration, and cooling yielded the desired product (0.47 g, 49%). Recrystallization from ethanol afforded 4-methylbenzophenone azine as yellow needles: mp 133–136 °C; mass spectrum (70 eV) *m/e* (rel intensity) 388 (M<sup>+</sup>, 100). Anal. (C<sub>28</sub>H<sub>24</sub>N<sub>2</sub>) C, H.

The other azines were prepared analogously.

**4-Cyanobenzophenone Azine.** Yellow needles from ethanol: mp 216.5–217 °C; mass spectrum (70 eV) *m/e* (rel intensity) 410 (M<sup>+</sup>, 100). Anal. (C<sub>28</sub>H<sub>18</sub>N<sub>4</sub>) C, H.

**4-(Trifluoromethyl)benzophenone Azine.** Deep yellow needles from ethanol: mp 145–145.5 °C; mass spectrum (70 eV) *m/e* (rel intensity) 496 (M<sup>+</sup>, 96). Anal. (C<sub>28</sub>H<sub>18</sub>F<sub>6</sub>N<sub>2</sub>) C, H, N.

**4-(Methylsulfonyl)benzophenone Azine.** Yellow needles from ethanol: mp 237–238 °C; mass spectrum (70 eV) *m/e* (rel intensity) 516 (M<sup>+</sup>, 95). Anal. (C<sub>28</sub>H<sub>24</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub>) C, H, N.

**4-Methyl-4'-nitrobenzophenone Azine.** Yellow-orange needles from ethanol: mp 233.5–234 °C; mass spectrum (70 eV) *m/e* (rel intensity) 478 (M<sup>+</sup>, 48). Anal. (C<sub>28</sub>H<sub>22</sub>N<sub>4</sub>O<sub>4</sub>) C, H.

**4,4'-Dinitrobenzophenone Azine.** Orange needles from acetone: mp

>375 °C; mass spectrum (70 eV) *m/e* (rel intensity) 540 (M<sup>+</sup>, 20). Anal. Calcd for C<sub>26</sub>H<sub>16</sub>N<sub>6</sub>O<sub>8</sub>: C, 57.78; H, 2.98. Found: C, 57.26; H, 3.36 (insufficient material).

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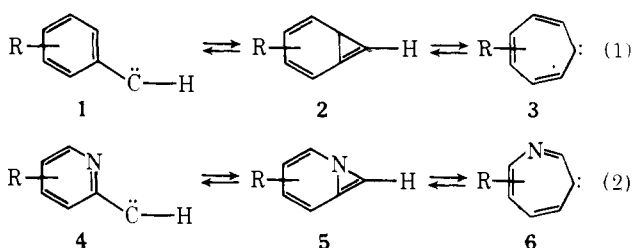
## Chemistry of (2- and 3-Furyl)methylenes and (2- and 3-Thienyl)methylenes<sup>1a</sup>

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**Abstract:** Pyrolysis of diazo(2-furyl)methane (**16a**) and its substituted analogues (**16b-f**), as generated from the corresponding tosylhydrazone sodium salts (**15a-f**), yields  $\gamma,\delta$ -acetylenic  $\alpha,\beta$ -olefinic carbonyl products (**18a-f**, **19a-e**) resulting from furan ring opening. Generation of 2-furylmethylene (**17a**) in decomposition of **16a** is indicated by its trapping with cyclooctane and styrene. There is no evidence for isomerization of **17a** to  $\alpha$ -pyranylidene (**9a**, Z = O; R = H). Diazo(3-furyl)methane (**35**) thermolyzes to *cis*- (**37**) and *trans*- (**38**) 1,2-di(3-furyl)ethylenes; neither ring opening nor ring expansion of 3-furylmethylene (**36**) was detected. Diazo(2-thienyl)methane (**26a**) and its substituted analogues (**26b,c**) decompose thermally with ring opening to  $\alpha,\beta$ -unsaturated,  $\gamma,\delta$ -acetylenic thiocarbonyls (**28a-c**) and their subsequent derivatives (**29a-c**); conversions to the corresponding 1,2-di(2-thienyl)ethylenes (**30a-c** and **31a-c**) are the principal processes, however. The greater resistance of 2-thienylmethylenes (**27**) than 2-furylmethylenes (**17**) to ring opening is rationalized on the basis of the greater resonance energy of the thiophene ring and the lower stability of its ring-opened products. Diazo(3-thienyl)methane (**40**) converts to *cis*- (**42**) and *trans*- (**43**) 1,2-di(3-thienyl)ethylenes at 300 °C. Ring expansions of 2- (**27a-c**) and 3- (**41**) thienylmethylenes to their corresponding  $\alpha$ - and  $\gamma$ -thiopyranylidines (such as **9** and **14**, Z = S) were not observed.

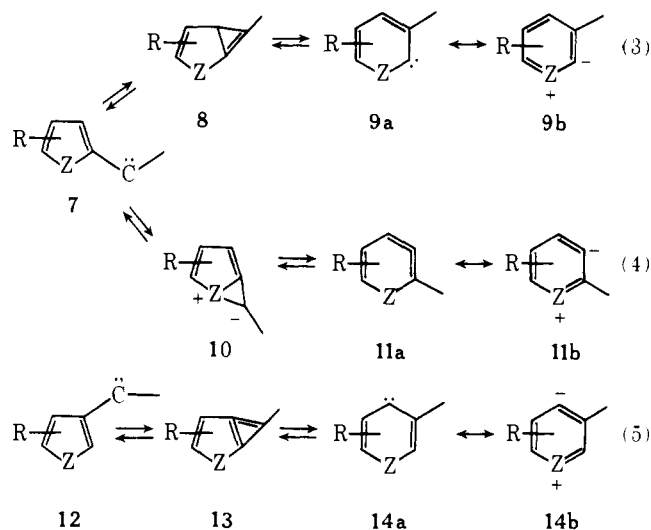
One of the most intriguing carbenic rearrangements is the interconversion (eq 1) of arylmethylenes (**1**) and cycloheptatrienylenes (**3**).<sup>2</sup> These isomerizations are frequently



reversible and apparently involve cyclopropene (**2**) intermediates.<sup>2</sup> Analogous interrelationships (eq 2) are observed for (2-pyridyl)methylenes (**4**) and azacycloheptatrienylenes (**6**) in which an important feature is participation of heterocyclic nitrogen (**5**).<sup>2k,l,3</sup>

The mechanistic features of the above rearrangements (eq 1 and 2) are in principle extendable to five-membered ring, 6  $\pi$ -electron heterylmethylenes. Thus (2-heteryl)methylenes such as **7** (Z = O and S) might (1) isomerize (eq 3) by carbon bridging to six-membered ring 6 $\pi$ -electron  $\alpha$ -heterylidenes (**9a,b**) which are theorized to be highly stabilized<sup>4</sup> or (2) rearrange (eq 4) involving participation of the heteroatom to give species such as **10** and **11a,b** and products derived therefrom. Analogously, (3-heteryl)methylenes (**12**, Z = O and S) would give (1) stabilized six-membered ring, 6 $\pi$ -electron  $\gamma$ -heterylidenes (eq 5, **14a,b**) or (2) cyclic allenes analogous to **11a,b** as derived by cyclization at C-3 or products thereof.

A study is presently reported of the behavior of 1-(2- and 3-furyl)-1-alkylenes (**7** and **12**, Z = O) and 1-(2- and 3-thienyl)-1-alkylenes (**7** and **12**, Z = S). These systems have been found to be of interest in that the (2-heteryl)methylenes (**7**) undergo ring opening, whereas the (3-heteryl)methylenes (**12**) do not isomerize; ring expansion of **7** to **9a,b** or **11a,b** and



of **12** to **14a,b** or allenic intermediates has not been detectable.

### Results

Vacuum pyrolysis of diazo(2-furyl)methane (**16a**), as generated in situ from the sodium salt of furfural tosylhydrazone (**15a**) at ~300 °C,<sup>5</sup> gives the ring-opened products, 2-penten-4-ynals (eq 6), as *cis* (**18a**, 81%) and *trans* (**19a**, 19%) isomers<sup>6</sup> along with 2-furonitrile (1-4%). Similarly, the substituted diazo(2-furyl)methanes **16b,c** as derived from tosylhydrazone salts **15b,c**, decompose to their corresponding carbonyl products, *cis*- (**18b**) and *trans*- (**19b**) hexen-5-yn-2-ones and *cis*- (**18c**) and *trans*- (**19c**) 5-phenyl-2-penten-4-ynals, respectively, in which the *cis* isomers are predominant (Table I). Since isomerizations of (*cis*) **18a-c** to (*trans*) **19a-c**, respectively, occur at the temperatures for decomposition of