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(23) The boat-chair to twist-boat process is of course reversible in actuality. The computer-driven process follows the lowest energy path for any given constraint, and this does not necessarily lead to the lowest transition state (energy saddle point). It is possible to go from the twist-boat to the boat-chair conformation by "driving" *two* torsional angles, and this process *is* reversible.
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Kinetics of Dye Formation by Oxidative Coupling with a Micelle-Forming Coupler

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Abstract: Rates of dye formation by coupling between quinonediimines (QDI) and a micelle-forming α-naphthol derivative have been measured. The results were found to fit a model which postulates that the QDIs rapidly distribute between the micelles and the aqueous region of the solution. Solubilization of QDIs favors dye formation and reduces side reactions which occur exclusively in the aqueous region. Partition coefficients and specific rates were obtained which showed that charges and hydrophobic characters of QDIs have large effects on the partition coefficient.

The image dyes of many color photographic systems are formed by the reaction of oxidized N,N-disubstituted *p*-phenylenediamines (QDI) and compounds with active methylene or methine groups known as couplers. The mechanism of this reaction has been studied in dilute aqueous solutions using substituted α-naphthols and phenols of low molecular weight.[1] We have recently extended the study to include couplers which are simultaneously ballasted with hydrophobic groups and solubilized with ionizable groups. They are useful in photographic technology as incorporated couplers because their low mobility during development prevents diffusion causing interlayer contamination.[2] Such modifications, however, confer detergent-like properties to these molecules which profoundly alter their reaction kinetics. The latter is the subject of the present report.

We have compared the rate of dye formation between QDIs with various charges and an anionic micelle-forming coupler, 4-chloro-3′,5′-dicarboxy-*N*-octadecyl-1-hydroxy-2-naphthanilide (called coupler II in this report) with the rates of the same QDIs and a lower molecular weight analogous coupler (called coupler I). The structures of the compounds are shown in Chart I.

Differences in rate behavior of couplers I and II are apparent on examination of Figures 1 and 2. The results are interpreted by a model which postulates that (1) the QDI was rapidly distributed between the micellar and the aqueous region, and (2) the observed rate was the sum of two rates, one in each region. Similar models have been used by others to evaluate binding constants and micellar rate constants in systems where the surfactant was added to provide a micellar medium but did not take part directly in the reaction as in our system.[3,4] The use of a nonionic surfactant as a medium for the coupling reaction was published earlier by us.[5]

Kinetic Model. The kinetic data with micelle-forming coupler II (Figure 2) were obtained at concentrations above the critical micelle concentration (cmc). Interpretation of these kinetics should therefore take into account the possibility of reactions in the micellar region as well as in the continuous aqueous region. The proposed kinetic model assumes the distribution of QDI between these regions, with rates in each region determined by the respective reactant concentrations. Since the average micellar size is assumed constant, the ratio of micellar volume to surface is constant and the form of the kinetic expression will be the same whether the micellar reaction takes place at the surface or in the micellar interior. Further speculation as to the more detailed location of the reaction comes from the consideration of the kinetic parameters.

At concentrations above the cmc it is further assumed that, for a given pair of QDI and coupler, the concentration of monomeric coupler remains constant. Although aggregations are expected to depend somewhat on the structure of the QDI, the cmcs are probably of the same order of magnitude as the cmc measured using the cationic dye (see Table I).

Above the cmc we assume that the overall concentration of the coupler is

$$\overline{C} = C_1 + nC_n$$

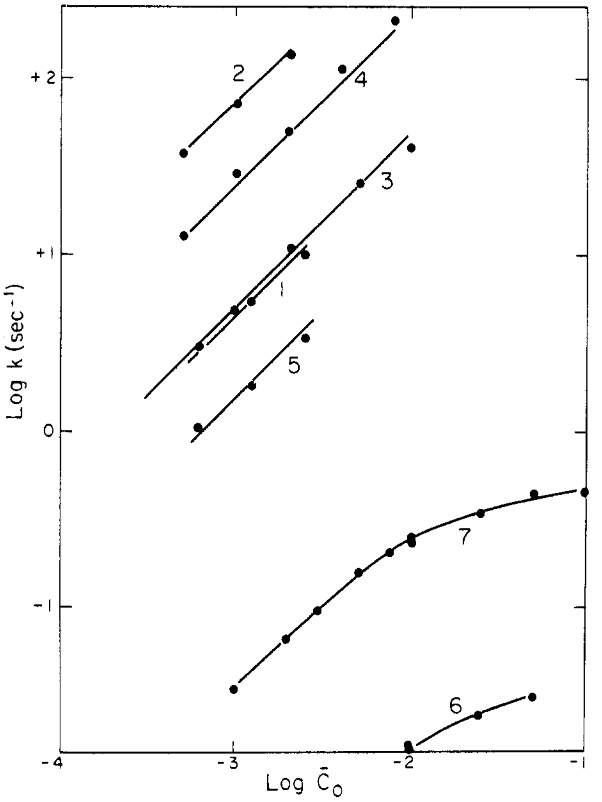


Figure 1. Rate constants for dye formation of coupler I with various quinonediimines as a function of the coupler concentration. Curves are numbered as the QDIs of Table III.

Table I. Critical Micelle Concentration (cmc) of Coupler II

pH	μ	cmc, M	Method	Dye,[a] M
11	0.075	1.3×10^{-5}	Surface tension	
11	0.188	0.8×10^{-5}	Dye adsorption[b]	10^{-7}
9.8	0.01	3.5×10^{-5}	Dye adsorption	10^{-7}
9.8	0.1	0.8×10^{-5}	Dye adsorption	10^{-7}

[a] Pinacyanol was used in dye adsorption experiments. [b] Reference 6.

and the overall concentration of the QDI is

$$\bar{T} = T + T'$$

where C_1 = concentration of monomer, C_n = concentration of micelle units with an average of n monomers, T = concentration of free QDI, and T' = concentration of QDI either complexed with or solubilized by the micelle, all in units of moles/liter of solution.

The total volume of micelles per liter of solution is V_mC_n, where V_m and C_n are the partial molar volume and molar concentration of micelles, respectively. The partition of QDI between the micellar and aqueous region is assumed to be

$$P = (T'/V_mC_n)(1/T) \qquad (1)$$

Therefore,

$$T' = \bar{T}PV_mC_n/(1 + PV_mC_n) \qquad (2)$$

and

$$T = \bar{T}/(1 + PV_mC_n) \qquad (3)$$

The rate of removal of QDI by coupling is expressed as the sum of the rates in the aqueous and micellar regions.

$$-\mathrm{d}\bar{T}/\mathrm{d}t = k_1TC_1 + k_2T' \qquad (4)$$

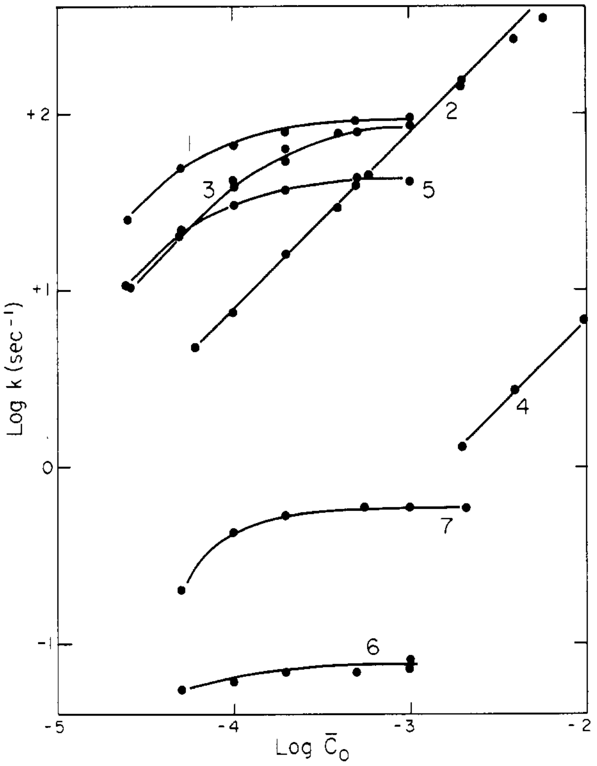


Figure 2. Rate constants for dye formation of coupler II with various quinonediimines as a function of the coupler concentration. Curves are numbered as the QDIs of Table III.

where k_1 = second-order rate constant for coupling in aqueous region and k_2 = first-order rate constant for dye formation of QDI associated with the coupler micelle. It is assumed that solubilized QDI reacts only with its nearest neighbors.

Substituting eq 2 and 3 into eq 4, we obtain a pseudo-first-order rate expression for $\bar{T}$.

$$\frac{-\mathrm{d}\bar{T}}{\bar{T}\mathrm{d}t} = \frac{k_1C_1[1 + (k_2PV_m/k_1nC_1)(\bar{C} - C_1)]}{1 + (PV_m/n)(\bar{C} - C_1)} \qquad (5)$$

If the dye is also distributed rapidly to give a single mean extinction coefficient, then the optical density due to the dye also changes according to the first-order rate law with the same constant as the right-hand side of eq 5.

The parameters k_2 and P can in some cases be obtained experimentally using eq 5. This equation implies that the observed rate constant approaches k_2 with increasing $\bar{C}$. Neglecting the C_1 terms in eq 5, we let $\bar{C}(1/2)$ be the value of $\bar{C}$ when the rate constant is $k_2/2$ to obtain eq 6. The values measured are given in Table III.

$$P = n/V_m\bar{C}(1/2) \qquad (6)$$

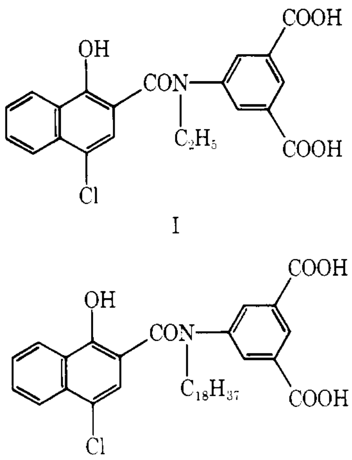
The right-hand side of eq 6 represents the volume ratio of aqueous phase to micellar phase when half the QDI is distributed into the micelles. The distribution coefficient, P, is estimated by evaluating this ratio assuming a density of 1.0 for the coupler. It is not necessary to evaluate n or V_m separately.

The model was further tested by the addition of SO_3^{-2}, a nucleophile which was not solubilized by the micelle, to compete for QDI in the dye-forming mixture. This reaction produced a side product (SP) with the rate expressed by eq 7, with N representing the concentration of sulfite.

$$\frac{\mathrm{d(SP)}}{\mathrm{d}t} = k_3NT \qquad (7)$$

Chart I

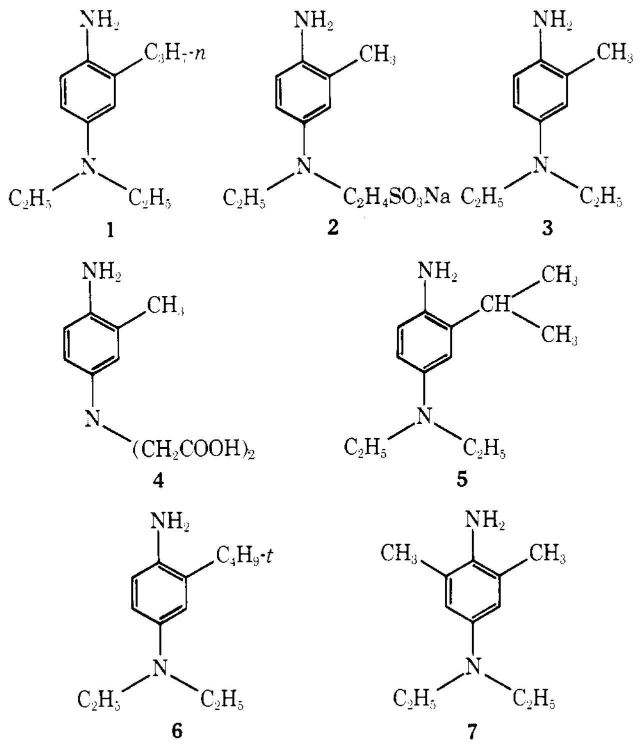
A. Couplers



I

II

B. *p*-Phenylenediamines



Under competition, the ratio of dye to side product is

$$\text{dye/SP} = (k_1C_1 + k_2PV_mC_n)/k_3N \qquad (8)$$

At large $\bar{C}$, when most of the QDI has been extracted into the micelles, the dye formation rate would level off but the SP formation rate would continue to decrease with increasing $\bar{C}$. The dye/SP ratio would continue to increase according to eq 8.

Methods and Results

Critical Micelle Concentrations (cmc). The cmc of coupler II was determined by both surface tension and light absorption of added pinacyanol indicator at 620 nm. When these measurements were plotted vs. the coupler concentration, definite breaks were found at those values recorded in the cmc column of Table I. The results indicate that cmc is $\sim 10^{-5}$ M for coupler II. In the presence of QDI, usually a cation, the couplers probably form mixed micelles and have a lower critical micelle concentration than in the absence of QDI. The cmc measured using pinacyanol as indicator is also likely to be low. Lowering of the cmc by formation of mixed micelles has been shown.[6]

Table II

Reagent	Range of initial concns
p-Phenylenediamines	10^{-6} M → 2×10^{-4} M
$K_3Fe(CN)_6$	2.5×10^{-4} M → 10^{-3} M
Coupler	5×10^{-5} M → 0.1 M
Potassium phosphate buffers	$\mu = 0.375$ or 0.188
In solutions of coupler I → pH 10-11, $\mu = 0.375$	
In solutions of coupler II → pH 11 or above, $\mu = 0.188$	

With coupler I, however, a sharp break observed at $\bar{C} \sim 4 \times 10^{-2}$ M was probably due to complexation between cationic indicator and the anionic coupler. If so, a similar effect between the cationic QDI and coupler ion is expected and may be responsible for the observed kinetics shown later.

Rates of Dye Formation. The QDIs used in these studies were generated in situ by mixing at least 2 equiv of ferricyanide/mol of the corresponding *p*-phenylenediamine.

Rates of dye formation were measured spectrophotometrically in the Durrum-Gibson Model D110 stopped-flow apparatus or the Eastman Kodak Co. Model VI jet mixer.[7] In the jet mixer, solutions of *p*-phenylenediamine, potassium ferricyanide, and coupler in phosphate buffer were mixed sequentially in the order given. In the Durrum stopped-flow apparatus two solutions were mixed; either a premixture of *p*-phenylenediamine (slightly acidic) and $K_3Fe(CN)_6$ was mixed with coupler in buffer, or a premix of coupler and *p*-phenylenediamine in buffer was mixed with $K_3Fe(CN)_6$.

The coupler was always in large (at least tenfold) excess of the initial concentration of QDI. For the experiments with the micelle-forming coupler, the phenylenediamine was preoxidized with a large excess of $Fe(CN)_6^{-3}$ before mixing with the coupler.

Concentrations of reactants varied over a wide range as shown in Table II.

In a few cases where dye formation was slow, corrections were made for deamination of the QDI.[8] Since the observed first-order rate constant (k_{obsd}) is the sum of dye formation constant (k_c) and deamination constant (k_d), then $k_c = k_{\text{obsd}}y$, where y is the fraction of total QDI going to the dye. The values of y were obtained photometrically at the end of the reaction using known extinction coefficients for the dyes. Correction was greatest for dye formation of coupler II and QDI **6**, the diimine with a *tert*-butyl ortho to the coupling site imine. With $\bar{C}_0 = 5 \times 10^{-5}$ M, the fraction going to dye is 0.117.

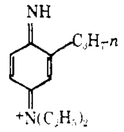
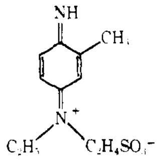
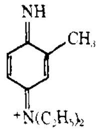
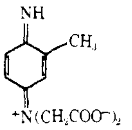
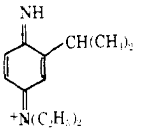
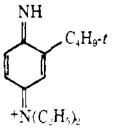
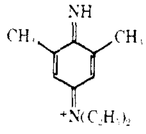
The ionization constants of the naphtholic OH of couplers I and II were measured photometrically; the pK_as are 7.7 and 10, respectively, and reflect the difference in the states of aggregation of the two couplers. Both couplers were almost completely ionized during the rate measurements.

The following results were obtained. The dye-formation rates (pseudo first order) of couplers I and II with various QDIs are summarized in Figures 1 and 2, respectively. The first-order rate constants are plotted vs. the concentration of coupler, both in log scale. The structures of the *p*-phenylenediamines producing the QDIs are given in Chart IB.

A cursory examination of Figures 1 and 2 reveals that, in general, with coupler I the rates follow simple second-order kinetics; i.e., they are proportional to the coupler concentration as well as that of the QDI. In contrast, the pseudo-first-order rate constants of coupler II tend to reach saturation values as the coupler concentration increases.

Equation 5 serves as a basis for interpretation of the rates for coupler II measured above the cmc. In concentration regions above 10^{-4} M where $(\bar{C} - C_1) \sim \bar{C}$, the positive slope on the curve indicates that $k_2 \gg k_1C_1$; this suggests that a given

Table III. Distribution of QDI between Micelle and Aqueous Region and First-Order Rate Constant (k_2) in Micelles[a]

Symbols	Structure of diimine	Coupler II		Coupler I, $\log k_1$
		Log P	Log k_2	
1		4.6	+1.95	3.68
2		<2.6	>3.00	4.87
3		4.1	1.9	3.70
4		<2.2	>1.1	4.40
5		4.5	+1.6	3.20
6		4.9	−1.1	0.40
7		4.3	−0.2	1.56

[a] Rate constant k_1 for coupler I in the aqueous region.

QDI reacts faster with couplers in the micelle than with the monomer at C_1, M. As stated earlier, it is possible in some cases to estimate the distribution coefficient of QDI in the micelles from the graphs using eq 6.

Table III is a list of distribution coefficients, P, and limiting first-order rate constants for the micelle reaction, k_2, for various QDIs. Comparison of the P values indicates that the greater part of the driving force is the attraction of the negatively charged micelle for the positively charged QDI. This is supported by the relatively small values for QDIs with *net* zero or negative charge, QDIs **2** and **4**. In the case of QDI **4**, although the rate constant involving the micellar coupler is expected to be substantially reduced by electrostatic repulsion, this pathway is still predominant since the concentration of micellar coupler is high.

Superimposed on the charge effects are the hydrophobic properties of the QDI. For those with a net +1 charge, the ones with the more bulky alkyl groups which are expected to be more hydrophobic are more favorably distributed into the micelles, cf. **6** and **3** (Table III). The importance of both hydrophobic bonding and charge on micelle solubilization and catalysis has been demonstrated by many other workers.[9]

In comparing k_2 values of QDIs with +1 charge the steric effect of substituents ortho to the coupling amine function are apparent, cf. **6** and **3** (Table III). Also, the k_2 values of coupler II parallel the bimolecular rate constants k_1 of coupler I (Table III). This suggests that the environment for the micelle reaction is waterlike and that the reaction site is at the micelle–H_2O interface rather than in the more hydrophobic interior of the micelle. Most micellar reactions, particularly ionic ones, are believed to occur at the micelle surface.[10]

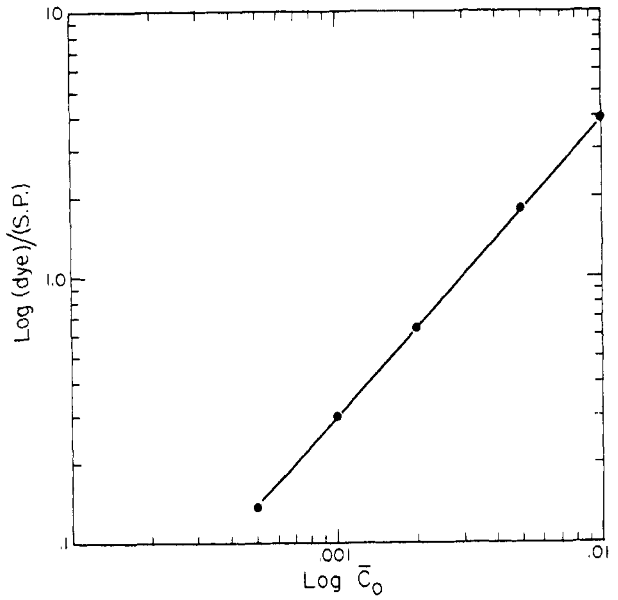


Figure 3. Competition of coupler II and sulfite for QDI 3, pH 11.

Competition for QDI. Sulfite was added to solutions of coupler II to compete for a limited amount of QDI **3** in a series of experiments where sulfite concentration was held constant and the coupler concentration was varied. The following initial concentrations were used: $\bar{T}_0 = 10^{-4}$ M, $(SO_3^{2-})_0 = 0.2$ M, $\bar{C}_0 = 0.5 \times 10^{-3}$ to 10^{-2} M, pH 11, $\mu = 0.375$ (with phosphate). Experimentally, the following three solutions were mixed in the continuous flow machine[7] in the following order: (1) *p*-phenylenediamine, (2) ferricyanide, and (3) coupler with sulfite and buffer. The reaction mixtures were collected and the products analyzed photometrically at λ 700 nm.

The results show that the ratio of dye to sulfonation product, obtained by difference, increases proportionally to the concentration of coupler II in the range 5×10^{-4} to 10^{-2} M. The log (dye)/(SP) vs. log coupler II graph has a slope of 1.1 (Figure 3). Since in this range the rate of dye formation is nearly constant, the increase in (dye)/(SP) must be interpreted as a decrease in sulfonation rate due to protection of the QDI by the micelles.

Materials. The *p*-phenylenediamines used in this report were the same or similar to samples used in earlier reports.[1d,11] Coupler I was the same sample used in an earlier report.[1d] Coupler II was prepared by a procedure similar to that used for coupler I,[1d] replacing the ethyl amino derivative with octadecylamino derivative. Anal. Calcd: C, 69.5; H, 7.6; Cl, 5.6; N, 2.2. Found: C, 69.4; H, 7.3; Cl, 5.4; N, 2.2. TLC analysis showed a single spot.

Conclusions

The experimental results substantiate the model described in an earlier section. Quinonediimines are distributed rapidly between the coupler micelles and the aqueous region. This distribution is largely controlled by the relative charges between the coupler micelles and QDIs. Solubilization of QDI favors dye formation and reduces those side reactions which can take place only in the aqueous region.

Acknowledgment. The authors wish to thank T. O. Parshall of these laboratories for measuring the surface tension of so-

lutions of coupler II, R. Cameron of these laboratories for the preparation of coupler II, and R. Bent for the preparation of the *p*-phenylenediamines.

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Gas-Phase Pyrolysis of Phenyltrimethylsilyldiazomethane. Intramolecular Chemistry of Phenyltrimethylsilylcarbene[1,2a]

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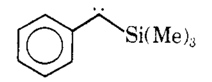
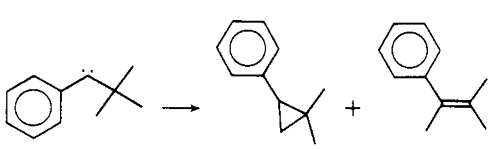
Abstract: The gas-phase generation of phenyltrimethylsilylcarbene through the pyrolysis of phenyltrimethylsilyldiazomethane yields ditrimethylsilylstilbene (13%), 1,1-dimethyl-1-silabenzocyclopentene (15–20%), benzyltrimethylsilane (2%), and styrene (2–5%). The major product arises through a carbene-to-carbene rearrangement. The styrene is probably formed by decomposition of the product of carbon–hydrogen insertion, 1,1-dimethyl-2-phenylsilirane. The product of carbon–silicon insertion, 1,2,2-trimethyl-1-phenylsilene, can be trapped with methanol, carbonyl compounds, and dienes.

Interest has quickened over the last few years in the synthesis of silenes[3-5] and siliranes.[6,7] It is now clear that such compounds are accessible, if reactive, species. One attractive route for the generation of both such intermediates is the intramolecular reaction of α-silylcarbenes. We report here the details of our investigations of the chemistry of one such potential precursor, phenyltrimethylsilylcarbene (**1**). If the all-carbon analogue, phenyl-*tert*-butylcarbene (**2**), is taken as a model, **1** seems a likely source indeed. Gas-phase generation of carbene **2** gives 1-phenyl-2,2-dimethylcyclopropane and 2-methyl-3-phenylbutene in the ratio 85/15. Of course carbene **2** need not be a perfect model for **1**, as it is reasonable to expect formation of species containing sp^2-hybridized silicons to be more difficult than in the corresponding carbon case. Thus it seemed important to minimize the intermolecular reactions of **1** by generating the carbene in the gas phase where difficult intramolecular reactions might prevail.



1

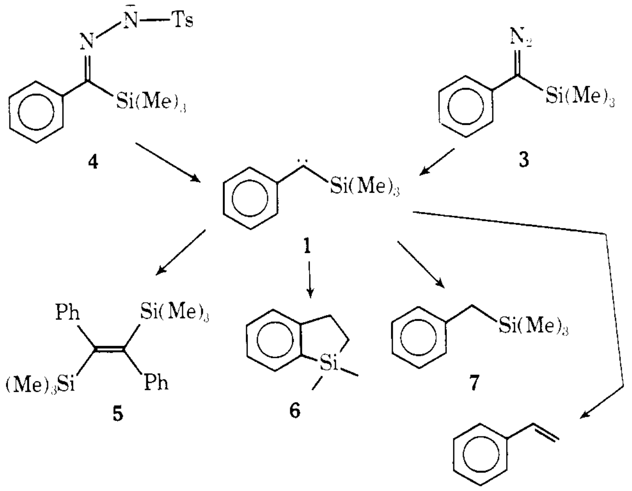


2

85%

15%

Carbene **1** was generated in three ways. The diazo compound **3** was carried with a stream of nitrogen in a vertical flowing system through a 28 × 1 cm Pyrex tube packed with Pyrex chips at a rate of 30 mL/min (method A). The products were condensed in a trap and analyzed. Alternatively, the diazo compound could be decomposed in the inlet of a gas chromatograph held at 300 °C (method B). A third method involved the flash pyrolysis of the lithium salt of the tosylhydrazone of phenyl trimethylsilyl ketone **4** (method C).



Method A gave four products, ditrimethylsilylstilbene (**5**, 13%), 1,1-dimethyl-1-silabenzocyclopentene (**6**, 15%), benzyltrimethylsilane (**7**, 2%), and styrene (2%). Method B gave similar results and method C gave **6** (20%) and styrene (5%). Compound **5** is easily rationalized as the product of either dimerization of **1** or reaction of **1** with **3**. Compound **7** involves abstraction of hydrogen by **1** and is a typical minor product of carbene reactions.

Ando, Jones, Barton, et al. / Gas-Phase Pyrolysis of Phenyltrimethylsilyldiazomethane