

## Excited Precursor Reactivity, Fast 1,2-H Shifts, and Diffusion-Controlled Methanol Insertion in 1,2-Diphenylalkylidenes

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The photochemistry of several arylalkyldiazo compounds has been investigated by steady-state direct and triplet sensitized irradiations and by nanosecond laser flash photolysis. Steady-state photolyses in methanol yielded methyl ethers and alkenes as the only significant products. Ethers were formed by denitrogenation of the diazo compound followed by carbene insertion into the MeO–H bond, and alkenes were obtained by 1,2-R (R = H, Ph) migrations both in the free carbene and in the singlet excited state of the diazo precursor. Evidence for the excited-state precursor reaction came from differences in product yields as a function of excitation wavelength and excited-state multiplicity. The yields of methyl ethers increased with increasing excitation wavelengths and were greatest upon triplet-state sensitization but were never the sole products formed despite expected diffusion-controlled insertion rates. Accordingly, the formation of pyridine ylides analyzed by laser flash photolysis in the presence of high concentrations of the base yielded relatively modest transient absorptions. The kinetics of the 1,2-H reaction, analyzed by time-resolved detection of stilbene in the case of 1,2-diphenylethylidenes, displayed fast and slow components. The fast component was attributed to stilbene that formed from the excited-state precursor and from the originally formed singlet carbene within the 20 ns pulse. The long-lived component was attributed to a spin-state equilibrated carbene with a lifetime of 70–80 ns in fluorocarbon solvents. Analysis of the long-lived component by a Stern–Volmer treatment upon addition of MeOH gave a lower limit for the reaction rate constant with a value of  $k_{1,2-H} > 5 \times 10^9 \text{ s}^{-1}$  in a mixed Freon–methanol solvent. It is concluded that the combined effect of phenyl substituents at the carbon bearing the migrating group and high solvent polarity can lead to intramolecular 1,2-H shifts and 1,2-Ph migrations that are fast enough to compete with diffusion-controlled intermolecular MeO–H insertion in concentrated MeOH solutions.

### I. Introduction

Several interesting aspects of arylalkylcarbene reactivity have been recently unveiled with the application of fast kinetic methods and increasingly powerful computational resources. Improved calculations of carbene structures,<sup>1,2</sup> singlet–triplet gaps,<sup>3–9</sup> and transition states<sup>10–14</sup> have led to a better understanding of sub-

stituent effects and environmental factors.<sup>15,16</sup> At the same time, laser flash photolysis experiments have confirmed unusual dynamics and kinetic complexities<sup>17–19</sup> suspected from classical product analysis studies.<sup>20,21</sup> Among these complexities, the formation of carbene-like products from nitrogenated precursors (Scheme 1, path

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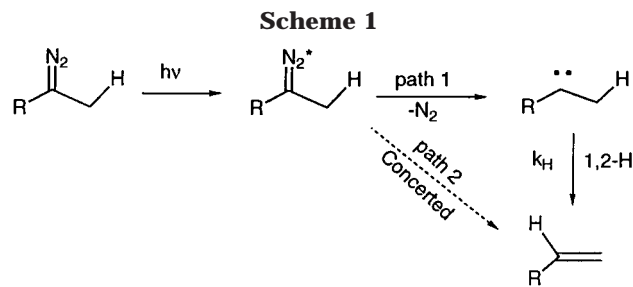
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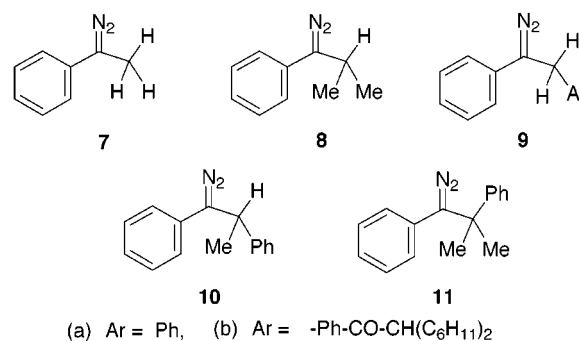


2), which was originally suspected in gas-phase studies over 30 years ago,<sup>22</sup> has been established in several cases.<sup>17,23–25</sup> This information suggests the revision and refinement of some kinetic schemes involving reactions that have previously been exclusively assigned to the carbene (Scheme 1, path 1).

In particular, work at UCLA has recently addressed the photochemistry of 1,2-diphenyldiazoalkanes such as **1** (Scheme 2) in several solvents,<sup>26,27</sup> and in the crystalline state.<sup>28</sup> Arylalkylcarbenes **2** produced from **1** in glassy matrices and in crystals give EPR signals characteristic of carbenes with a triplet ground state.<sup>29–31</sup> It is known that product selectivities from diazo compounds such as **1** are highly susceptible to subtle changes in experimental conditions, which has been interpreted in terms of carbene processes, i.e., following path 1 in Scheme 2. Whereas product selectivities in the liquid phase depend strongly on solvent and temperature, reactions in the highly rigid and organized environment of a crystalline diazo precursor can be highly selective.<sup>15,28,31</sup> Using Scheme 2 as analyzed in detail below, we drew some interesting conclusions regarding the effects of solvent polarity on the singlet–triplet energy gap of arylalkylcarbenes such as **2**.<sup>26,27,32</sup> Our studies spanned solvents from pentane to methanol and assumed that a free spin-equilibrated carbene **2** may undergo intramolecular 1,2-H shifts and 1,2-Ph migrations to give products **3** and **4** in competition with bimolecular reactions with alcohols to give ethers such as **5**. Although it had been known for some time that singlet halocarbenes<sup>33</sup> and thermally populated singlet diarylcarbenes<sup>34,35</sup> react with MeOH at diffusion-controlled rates (i.e.,  $k_{\text{MeOH}} \approx 0.5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ), it was assumed that 1,2-H shifts giving rise to **3** were

fast enough to compete with the bimolecular process. However, results from the Ohio State University with 1-phenyldiazoethane and other arylalkyl diazoalkanes<sup>24,36</sup> question the validity of those assumptions. In particular, it was shown that 1-phenyldiazoethane undergoes an excited-state 1,2-H shift that bypasses the carbene (path 2) and that the carbene itself undergoes 1,2-H shift reactions that are much slower than previously assumed (i.e.,  $k_{1,2\text{-H}} \leq 6 \times 10^6 \text{ s}^{-1}$ ).<sup>36</sup> If this were also the case for carbenes such as **2**, the conversion of **2S** to **3** could not compete with the reaction from **2S** to **5** in neat alcohols. Carbene-like products **3** (and **4**) might then be formed only from an excited diazo reaction as indicated by Path 2.

In this paper, we report triplet sensitized steady-state and laser flash photolysis experiments with the five arylalkyl compounds below, addressing the feasibility of concurrent 1,2-R shifts and diffusion-controlled bimolecular reactions. Because methyl group migration is comparatively slow, compound **8** only undergoes 1,2-H shifts, as does compound **7**. Compound **11** can only undergo 1,2-Ph migrations for the same reason. Compounds **9a**, **9b**, and **10** can, in principle, undergo both reactions. It is suggested that 1,2-H(Ph) shifts in excited-state 1,2-diphenyldiazoalkanes account for approximately 0–30% of the products observed and that 1,2-H(Ph) migrations from the carbenes compete with diffusion-controlled trapping when the rate of the 1,2-rearrangement is increased by polar solvents<sup>24</sup> and “bystander” substituents at the carbon bearing the migrating group.<sup>11,37</sup>



## Results

**Preparation of Diazo Compounds and Product Characterization.** All the diazo compounds used in this study were obtained in high purity from the analogous aryl ketone hydrazones by oxidation with yellow HgO and base.<sup>38</sup> Compounds **7**, **8**, and **9a** were prepared from commercially available acetophenone, isobutyrophenone, and deoxybenzoin, respectively. Aryl ketones used to prepare compounds **10** and **11** were obtained by mono- and dialkylation of deoxybenzoin with MeI by conventional methods.<sup>39</sup> The  $\alpha,\alpha$ -dicyclohexylacetophenone derivative **9b** was synthesized as shown in Scheme 3, starting from  $\alpha,\alpha$ -dicyclohexylacetic acid (**12**). The acetophenone chromophore was selected as an intramolecular sensitizer for triplet excitation experiments, and the two

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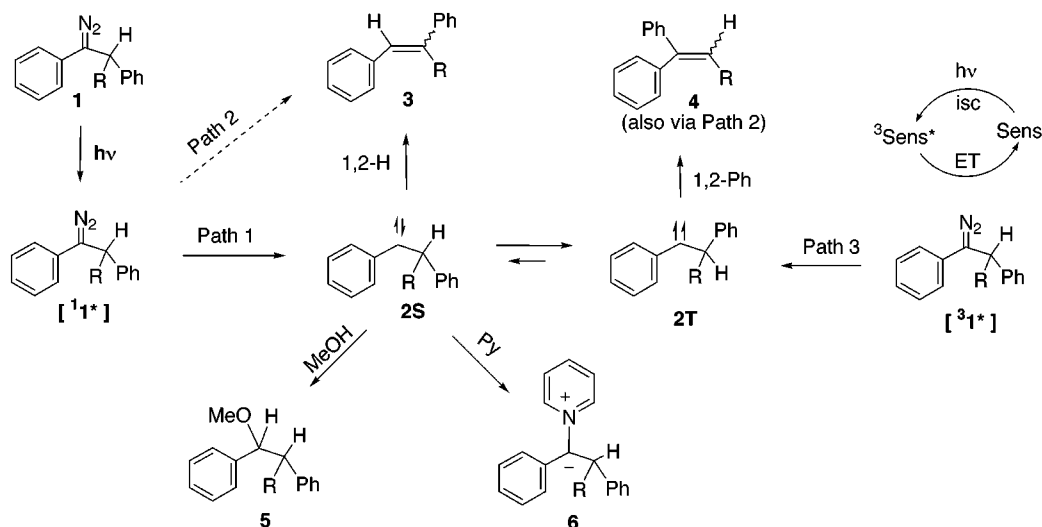
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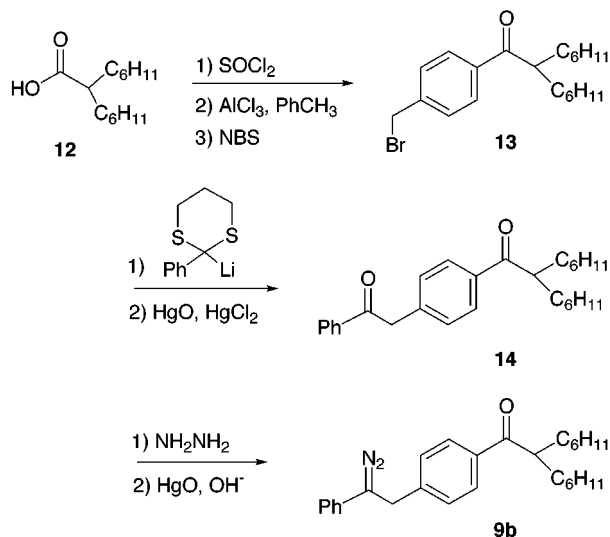
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Scheme 2



Scheme 3



bulky cyclohexyl groups were added to protect it from the reaction conditions used to prepare the aryldiazo chromophore.

Denitrogenation products were obtained by steady-state irradiation of compounds **7–11** in dilute (2–5 mM) deoxygenated benzene solutions with  $\lambda > 290$  nm. Irradiation under these conditions results in almost exclusive excitation of the very intense  $\pi, \pi^*$  transition of the diazo chromophore. Products obtained in benzene are consistent with those reported in the literature, which may be construed in terms of carbene 1,2-H shifts and 1,2-Ph migrations. Azines formed by reaction of the carbene and diazo compound were not detected in significant amounts. Product yields were quantified by gas chromatography, and their retention times were established by co-injection with authentic samples. As indicated in Table 1, compounds **7** and **8** lead to styrene and 2,2-dimethylstyrene, respectively, from formal 1,2-H shifts.<sup>24</sup> Irradiation of compounds **9a** and **9b** led to the corresponding stilbenes from formal 1,2-H shifts. Despite having one  $\alpha$ -aryl group, only traces (<1–2%) of 1,1-diarylethanes from 1,2-Ar migrations were observed. As reported by Tomioka,<sup>30</sup> compound **10** undergoes concurrent 1,2-H shifts and 1,2-Ph migrations in 74% and 26% yields, respectively. In the case of **9** and **10**, we made no

attempts at analyzing the selectivity of the *cis*- and *trans*-stilbene products because photoisomerization occurs under the reactions conditions. Compound **11** has no  $\alpha$ -hydrogen and, as expected, gives 1,1-diphenyl-2-methylpropene from a 1,2-Ph migration as the main observable product (>98%).

#### Direct and Sensitized Irradiations in Methanol.

Although little is known about diazo compound photochemistry, it is thought that the triplet excited diazo compound will form the triplet carbene without concerted 1,2-R reactions such as those observed in the singlet excited-state reactions. It is also expected that neither the triplet excited-state diazo nor the triplet carbene will react with singlet carbene traps such as methanol or pyridine.<sup>26,40</sup> As indicated on the right side of Scheme 2, the triplet carbene may be reached by excitation and intersystem crossing of a suitable sensitizer such as benzophenone, which then transfers triplet energy to the diazo compound,<sup>20,41–43</sup> Most compounds studied were sensitized with benzophenone in the spectral window between 360 and 400 nm where there is little absorption by the aryldiazo chromophore.<sup>32</sup> To investigate the possibility of interference by the intermolecular sensitizer, we analyzed compound **9b** with an acetophenone unit built into the molecule (Scheme 3). Direct irradiation of all compounds was carried out in the UV region at  $\lambda > 290$  and at the weak diazo  $n, \pi^*$  transition at  $\lambda > 450$  nm where the aryl ketone chromophore in **9b** cannot absorb. The results in Table 1 give the yields of products from 1,2-H shifts, 1,2-Ph migrations, and methyl ether formation under the three different excitation conditions.

As shown in Table 1, direct irradiation of compounds **7–11** in MeOH yields the methyl ethers from RO–H insertion reactions as the main products in competition with the alkene products observed in benzene. Alkenes were observed from diazo compounds possessing either or both 1,2-H and 1,2-Ar migration pathways. That triplet sensitization occurs cleanly under the conditions

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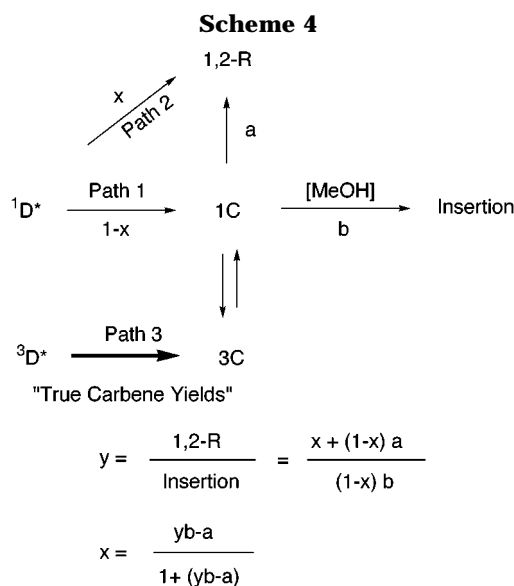
**Table 1.** Percent Yields from Steady-State Photolysis of Aryldiazo Compounds 7–11 in Benzene and upon Direct and Sensitized Irradiations in Methanol<sup>a,b</sup>

Compound	Benzene $\lambda > 290$ nm		Methanol $\lambda > 290$ nm			Methanol $\lambda > 460$ nm			Methanol Sensitized			% Path 1 at $\lambda$ (nm) <sup>d</sup>		
	1,2-H	1,2-Ph	1,2-H	1,2-Ph	Ins <sup>c</sup>	1,2-H	1,2-Ph	Ins <sup>c</sup>	1,2-H	1,2-Ph	Ins <sup>c</sup>	290	460	
7		100	n.a.	23	n.a.	77	13	n.a.	87	6	n.a.	94	82	91.5
8		100	n.a.	55	n.a.	45	45	n.a.	55	20	n.a.	80	66	69
9a		99	<1	44	<1	56	36	<1	64	25	<1	75	74	86
9b		99	<1	-	-	-	28	<1	72	29	<1	71	-	100
10		74	26	28	6	63	41	5	54	6	1	82	71	61
11		n.a.	>98	n.a.	54	46	n.a.	58	42	n.a.	32	68	68	62

<sup>a</sup>Product yields are normalized to 100%; <sup>b</sup>Typical errors in the values quoted are *ca.* 10%; <sup>c</sup>Yield of methanol insertion (methyl ether) product; <sup>d</sup>Percentage of 1,2-H(Ph) migration from the free carbene. See text for details.

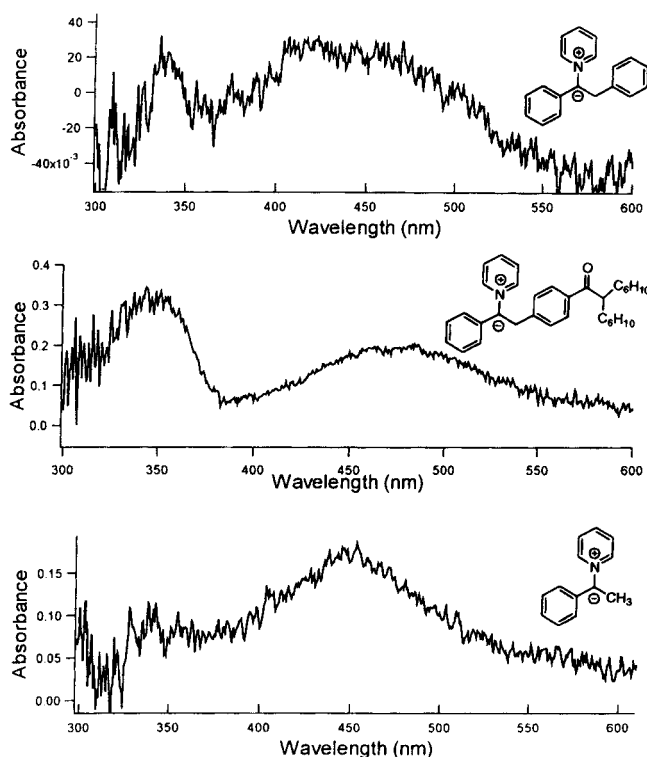
used is suggested by the very similar (within experimental error) results with compounds **9a** and **9b**, and we conclude that there are no complications when the reaction is sensitized in the presence of 50 mM benzophenone. Quantitative phosphorescence quenching of the triplet aryl ketone in **9b** by the diazo chromophore in rigid glasses at 77 K indicates that intramolecular energy transfer occurs efficiently. Significant differences in product yields for a given diazo precursor were observed not only as a function of the multiplicity of the excited state of the diazo compound, but also as a function of irradiation wavelength. An increase of about 10% in the yield of ethers is observed for compounds **7–9a** when the excitation wavelength changes from that of the  $\pi,\pi^*$  transition in the UV ( $\lambda > 290$  nm) to that of the  $n,\pi^*$  transition in the visible ( $\lambda > 460$  nm). A further increase in the yield of ethers when the reaction is carried out with triplet sensitization is strong evidence for 1,2-H reaction from the singlet state of the diazo compound. In the case of 1-phenylethyldene, for example, the yield of 1-phenyl-1-methoxyethane increases from 77% at  $\lambda > 290$  to 87% at  $\lambda > 450$  to as much as 94% when the experiment is conducted with benzophenone sensitization. Changes in product ratios as a function of wavelength are smaller for compounds **10** and **11**. In the case of compound **10**, the ratio of products from 1,2-H and 1,2-Ph increases from 2.84 in benzene to 4.67 in MeOH at  $\lambda > 290$  to 6.0 in MeOH upon triplet sensitization. Compound **11** undergoes a 1,2-Ph migration in competition with the MeO–H insertion. The yield of ether increases from ~45% upon direct photolysis to 68% when the reaction is triplet sensitized.

The relative contributions to product formation from excited-state and carbene reactions may be estimated with the assumption that triplet sensitization experiments represent the true reactivity of the free carbene intermediate. For this analysis, it is assumed that the singlet carbene can achieve a steady-state concentration, and the total yield is set equal to the sum of all the products, which are expressed as fractions. The simplest case is that of compounds possessing only singlet-state



reactions as shown in Scheme 4. The fraction of 1,2-H shift products via Path 2,  $x$ , can be calculated relative to the fraction of products via Path 1, or  $1-x$ , by assuming that Paths 1 and 3 give identical yields from a spin-state equilibrated carbene. The yields of 1,2-H shifts and MeO–H insertion from the "true carbene" in neat methanol are known from the sensitized experiments and may be labeled  $a$  and  $b$ , respectively. These can be used to describe the ratio  $y$  of 1,2-H and insertion products obtained upon direct irradiation.

With  $y$ ,  $a$ , and  $b$  known from direct and sensitized experiments, respectively, solution for  $x$  gives the fraction of product from the excited diazo. As indicated in Table 1 in the column labeled Path 1, the percentage of carbene calculated in this manner for compounds **7–11** ranges between 100% ( $x = 1.0$ ) for **9b** to 60–70% ( $x = 0.6–0.7$ ) for compound **10**. Although the extent of the excited-state reaction is greater at the shorter wavelengths for compounds **7–9**, the wavelength dependence of compounds **10** and **11** is comparatively smaller.



**Figure 1.** Transient absorption spectra of compounds **7**, **9a**, and **9b** by LFP in Freon-113 in the presence of pyridine.

**Laser Flash Photolysis in the Presence of Pyridine.** Although arylalkylcarbenes have no useful spectroscopic transitions for direct detection by laser flash photolysis, they form strongly absorbing ylides (**6**, Scheme 2) upon reaction with pyridine.<sup>19,44</sup> Ylides formed from sterically unencumbered arylalkyl carbenes such as 1-phenylethylidene have a broad absorption band with a  $\lambda_{\max}$  at 450 nm (Figure 1).<sup>17,36</sup> It is known that pyridine does not react with the excited state of the diazo precursor or with the triplet carbene, but it reacts with many singlet carbenes at near diffusion controlled rates. One of the most useful experimental parameters in the analysis of carbenes by the pyridine ylide method is the maximum yield of ylide obtained at high concentrations of pyridine. The yields of ylide determined for a series of analogous compounds is proportional to the efficiency of carbene formation, provided that the extinction coefficient for ylide absorption does not vary within the series. Ylide yields may be used to determine the extent of excited-state reactions competing with carbene formation when the corresponding carbenes are sufficiently long-lived and the extinction coefficients of their ylides are very similar. This strategy was attempted with compounds **9–11** in parallel experiments with compounds **7** and **8**, which had been measured previously.<sup>24</sup>

Nanosecond laser flash photolysis experiments were carried out with samples having an OD between 0.5 and 0.9 at an excitation wavelength of 308 nm from a XeCl excimer laser (150 mJ, 18 ns) in Freon-113 solvent. As reported in ref 31, addition of pyridine to 1-phenyldiazoethane **7** gave a strong ylide signal with  $\lambda_{\max}$  at 450 nm that reached saturation at about 2 M pyridine in Freon-113. Also as reported, a much weaker signal was detected

**Table 2.** Relative Intensities and  $\lambda_{\max}$  of Pyridine Ylides Observed by LFP<sup>a</sup>

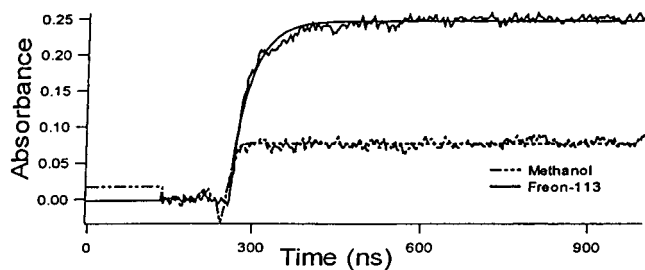
Compound	Pyridine Ylide	
	$\lambda_{\max}$ (nm)	% Carbene from $A_Y^\infty$
<b>7</b>	450	70
<b>8</b>	440	13
<b>9a</b>	430	27
<b>9b</b>	350, 430	14
<b>10</b>	430	9
<b>11</b>	360	4

<sup>a</sup>Assuming no variation in the extinction coefficient of the ylide.

from experiments carried out with 2-methyl-1-phenyldiazoethane **8**, even after addition of 2–5 M pyridine. Measurements with compounds **9a**, **9b**, **10**, and **11** under identical conditions also gave weak ylide signals with their  $\lambda_{\max}$  displaced to shorter wavelengths (Table 2). Whereas ylides derived from compounds **9a** and **10** have a unique  $\lambda_{\max}$  at 430 nm, the transient from compound **9b** has a second maximum at 350 nm, which may be attributed to triplet–triplet transitions involving the aryl ketone chromophore (see Figure 1). Compound **11** showed no absorption in the 450 nm range upon laser flash photolysis and has a single band with a  $\lambda_{\max}$  of 355 nm that is very similar to that previously observed in the ylide formed by trapping phenyl-*tert*-butyl carbene.<sup>24</sup> It has been pointed out that this unusually short wavelength of absorption may be the result of a strong perturbation of the ylide chromophore by the severe steric hindrance of the neighboring tetrasubstituted carbon.

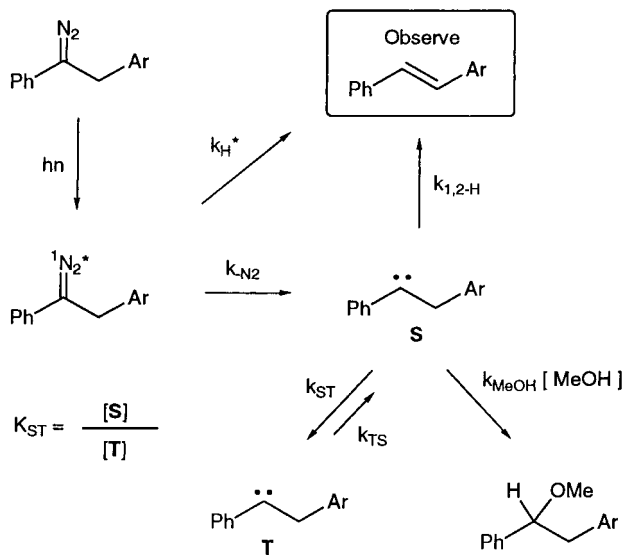
The maximum intensities of the transient absorption at high concentration of pyridine,  $A_Y^\infty$ , obtained from compounds **8–11** in the 430–450 nm range were used to estimate the yields of ylide at high concentrations of pyridine. The yields of ylide measured for compounds **7** and **8** were consistent with those reported in the literature.<sup>24</sup> By comparing the  $A_Y^\infty$  values from compounds **9–11** to those of **7** and **8** obtained under identical conditions, we were able to compute their corresponding trappable carbene yields (Table 2). If these values were taken as the absolute yields of carbene, one would conclude that 1,2-diphenyldiazoalkanes give yields of 1,2-diphenylethylidenes that are systematically lower than the yields of carbenes obtained with phenyldiazoalkanes by about 30%. For this conclusion to be correct, it is necessary that 1,2-H shifts in **9–11** are slow compared with bimolecular trapping by pyridine. However, it is shown below that 1,2-H shifts do seem to compete with bimolecular trapping in the presence of MeOH, a polar solvent which is expected to accelerate 1,2-H shifts.

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**Figure 2.** LFP of **9b** detected at 300 nm upon 266 nm excitation in pure Freon-113 (top trace) and with 6 M MeOH (bottom trace).

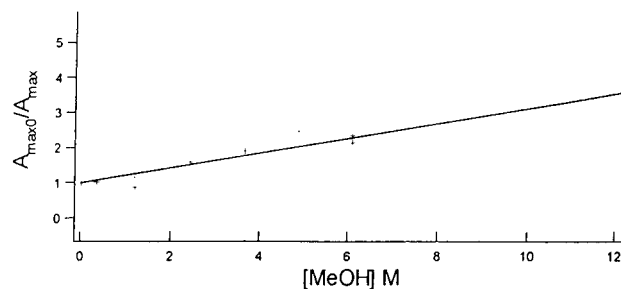
**Scheme 5**



Therefore, we were prompted to question the validity of the assumption that the 1,2-H shifts did not compete with pyridine trapping in Freon-113 as well.

**Flash Photolysis Measurements of Stilbene Growth in Compounds **9a** and **9b**.** Using a XeCl excimer laser as the excitation source,<sup>45</sup> we were able to detect the real-time growth of stilbene from compounds **9a** and **9b** in the 290–300 nm range (Figure 2). With absorbances as high as 0.25 OD units, time constants for stilbene growth in Freon-113 were calculated to be ca. 70 and 80 ns from **9a** and **9b**, respectively. These values reflect the lifetimes of the diazo precursor, the free carbene, and/or the excited diazo, as limited by their intramolecular 1,2-H reactions. Experiments run with **9b** upon addition of up to 6 M MeOH and in the pure alcohol solvent quenched only 60% of the total signal, uncovering a nontrappable reaction path that forms stilbene within the time resolution of the instrument, as limited by the 20 ns laser pulse (Figure 2).

Laser flash photolysis experiments at 308 nm with **9b** promote transitions of the aryl ketone and aryldiazo groups so that concurrent singlet and triplet excited-state chemistry may be expected. The fast component may be attributed a priori to the singlet excited-state reaction, labeled  $k_H^*$  in Scheme 5, and the slow component may be attributed to the reaction from the spin-equilibrated carbene. However, an observed time constant for stilbene growth of 80–90 ns in Freon-113 for the slow component



**Figure 3.** Stern–Volmer plot of the maximum absorbance of stilbene from compound **9b** with MeOH as a quencher.

in the absence of MeOH suggests that the elementary rate constant for the 1,2-H shift may be large enough to contribute to the fast component.

The slow component ( $\tau = 1/k_{\text{slow}} = 70\text{--}80$  ns) may be attributed to stilbene formation from a spin-state equilibrated free carbene which, in the presence of MeOH, will have a rate constant given by

$$k_{\text{slow}} = K_{ST} k_{1,2-H} + K_{ST} k_{\text{MeOH}} [\text{MeOH}] \quad (1)$$

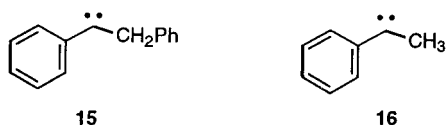
As indicated in Scheme 5,  $K_{ST}$  is the singlet–triplet equilibrium constant defined as  $K_{ST} = [S]/[T]$ ,  $k_{1,2-H}$  is the elementary rate of 1,2-H shifts from the singlet carbene, and  $k_{\text{MeOH}}$  is the bimolecular rate constant for MeOH trapping. Both  $K_{ST}$  and  $k_{1,2-H}$  will likely vary with methanol concentration.<sup>26,27,36</sup> The first term in eq 1 is responsible for the 70–80 ns lifetime ( $1/k_{\text{slow}}$ ) of the long-lived component, and the second term is responsible for its quenching by added MeOH. Although precise rate constants upon addition of MeOH were difficult to fit, a Stern–Volmer analysis with the absorbance values of the slow component from **9b** gave linear plots with  $k_q\tau$  values of  $0.21 \text{ M}^{-1} \text{ s}^{-1}$  (Figure 3). If one assumes diffusion-controlled values for singlet carbene MeOH insertion (i.e.,  $k_q = k_{\text{MeOH}} \approx 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ), one may calculate the lifetime of the singlet carbene to be  $\tau_S \approx 0.21$  ns in Freon-113 at ambient temperature, assuming that  $K_{ST}$  and  $k_{1,2-H}$  do not vary with methanol concentration. This lifetime reflects the time “spent” periodically by the spin-equilibrated carbene in the singlet state, which is the time during which it is available for reaction with MeOH in Freon as a solvent. This lifetime is determined by the rates of intramolecular reaction and singlet-to-triplet intersystem crossing as given by eq 2:

$$\tau_S = 1/(k_{1,2-H} + k_{ST}) = 0.21 \text{ ns} \quad (2)$$

The value of 0.21 ns for the lifetime of the singlet carbene constitutes an upper limit for the time constant of the singlet-state 1,2-H shift, which gives a lower limit of  $k_{1,2-H} > 5 \times 10^9 \text{ s}^{-1}$  in Freon-113 at ambient temperature. However, it is important to note that methanol, being polar, may reduce the singlet–triplet separation<sup>26,27</sup> and increase the absolute rate constant  $k_{1,2-H}$  relative to Freon-113.<sup>36</sup> Thus, the magnitude of  $k_{1,2-H} > 5 \times 10^9 \text{ s}^{-1}$  for carbene **15** deduced in Freon-113 containing methanol may be substantially larger than the value of this rate constant in a nonpolar solvent such as pure Freon-113. Previously,<sup>36</sup> we reported a  $k_{1,2-H} < 6 \times 10^6 \text{ s}^{-1}$  for carbene **16** derived from **7** in heptane. We attribute the large difference in  $k_{1,2-H}$  values for carbenes **15** and **16** to the polar solvent and to the presence of the second

(45) Soundararajan, N.; Jackson, J. E.; Platz, M. S.; Liu, M. T. H. *Tetrahedron Lett.* **1988**, *29*, 3419–3422.

phenyl group which weakens the migrating C–H bond and stabilizes a developing positive charge at the alpha carbon.



Unimolecular reaction rates of  $5 \times 10^9 \text{ s}^{-1}$  in methanol can compete efficiently with diffusion-controlled and pseudo-unimolecular reactions. Thus, we conclude that the fast component of stilbene formation in methanol, and perhaps in Freon-113, will contain contributions not only from an excited-state reaction but also from the singlet carbene before it undergoes intersystem crossing. This result indicates that kinetic resolution of excited diazo and carbene dynamics will require analysis in the picosecond time scales.

### Discussion

Differences in direct and sensitized photochemical experiments are not consistent with a common precursor for product formation under all experimental conditions. Because we expect that the triplet-state surface of the diazo compound should be dissociative and have little access to stable closed-shell molecules, we postulate that triplet sensitization is devoid of excited-state reactions other than denitrogenation to give a free carbene intermediate. We propose that results from sensitization experiments in Table 1 represent the true reactivity from a free carbene intermediate.

Turning our attention to direct irradiations, it is interesting to note that differences in product ratios as a function of irradiation wavelength are rare for polyatomic molecules in condensed media, as they constitute a violation to the Kasha–Vavilov rule.<sup>46</sup> The rule states that all photochemical processes are independent of excitation wavelength, as they should all take place from the lowest excited state. Exceptions to the rule occur when the rates of internal conversion are slow by virtue of a large energy gap between the electronic-states involved. Accordingly, in the case of arylalkyldiazo compounds, there is an energy gap of about 30 kcal/mol between the  $n, \pi^*$  transition in the visible and the  $\pi, \pi^*$  transition in the UV.

As shown in Table 1, product yields at  $\lambda > 450 \text{ nm}$  are closer to those obtained upon sensitization than product yields obtained with  $\lambda > 290 \text{ nm}$ . The differences in product yields as a function of irradiation wavelength may occur from differences in the efficiency of the excited-state reaction from S1 and S2, from differences in intersystem crossing yields and differences in carbene yields from singlet and triplet excited states, or from generation of carbenes in different electronic states. Because it is unlikely that singlet diazo compounds will undergo intersystem crossing to the triplet state, differences in product ratios probably do not reflect differences in carbene yields from singlet and triplet excited states. The generation of different electronic states of the carbene from different electronic configurations in the

excited states of the precursor is possible and cannot be strictly eliminated. However, the most likely candidate for the noncarbene precursor is the excited state of the precursor.

With respect to the generality of the wavelength and multiplicity dependence of the product yields, although excited-state 1,2-H and 1,2-alkyl migrations have been postulated before, our results with compounds **10** and **11** are the first experimental evidence suggesting the occurrence of excited-state 1,2-Ph migrations. Compound **9b** was the only example for which no differences in product yields were observed upon direct and sensitized irradiations. *By accessing the carbene surface from the singlet and the triplet state, this compound strongly suggests that a 1,2-H shift and a MeOH insertion in pure methanol may occur concurrently from a spin-state equilibrated (or nearly spin-equilibrated) carbene.* The lack of multiplicity dependence for **9b** probably comes from perturbations brought about by the ketone chromophore. Although the UV spectrum of **9b** is almost a perfect match with the summed spectra of  $\alpha, \alpha$ -dicyclohexyl acetophenone (**12**) and 1,2-diphenyldiazoethane (**9a**), there may be enough mixing to modify the excited-state reactivity of the diazo chromophore. Interestingly, the similarity of the chemical results from sensitized irradiations in compounds **9a** and **9b** indicates that perturbations to the singlet carbene by the aryl substituent are not very important.

The extent of excited-state reaction estimated with the pyridine ylide method (28%) and by methanol trapping and triplet sensitization (20%) for compound **7** are in excellent agreement with each other. However, the extent of excited-state reaction estimated by MeOH trapping in the case of compound **8** is much smaller (44%) than that suggested by the maximum yield of pyridine ylide in Freon-113 (~95%). Disagreement may occur if sensitization is incomplete, if there are reaction pathways from the triplet excited state that bypass the carbene (reducing the carbene yield), or if the carbene reaction with MeOH were much slower than the reaction with pyridine. We believe that these factors are unlikely. It is more likely that the extinction coefficients of the pyridine ylides vary over the series of compounds studied, as do their absorption maxima, and overestimate the extent of pathway 2.

It is expected that methyl and phenyl groups at the migrating origin and polar solvents will accelerate the carbene 1,2-H shifts<sup>37</sup> to the extent that they may become competitive with intermolecular trapping. In the case of compounds **9–11**, there is no correlation between the extent of the excited-state reaction estimated by triplet sensitization in methanol and by the pyridine ylide method in Freon-113 solvent. While carbene yields estimated in methanol are high and range between 60% for **11** to 100% for **9b** (Table 1), the corresponding values with pyridine in Freon-113 are as low as 4% for **11** and 14% for **9b** (Table 2). Differences observed with neat MeOH and pyridine-containing Freon may arise from differences in solvent polarity, which are known to affect both the singlet–triplet interconversion rates and equilibria, as well as the rate of the singlet state 1,2-R reactions. It is also possible that ylides from **9–11** may have somewhat different spectral properties as compared to those of **7**, so that a calculation of their ylide yields may require a correction by differences in their extinction coefficients at the wavelength of measurement.

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## Conclusions

Although some of the assumptions involved in the triplet sensitization experiments and the methanol trapping rates will have to be confirmed, interpretation of the data in terms of an excited-state reaction (~30%) and competition between carbene 1,2-H(Ph) shifts and diffusion-controlled trapping reactions seems to be very robust. This interpretation is supported by the well documented role of substituents at the migrating origin, which have a very strong accelerating effect on the rates of 1,2-H shifts and 1,2-Ph migrations. For instance, whereas methylchlorocarbene has a 1,2-H-limited lifetime of 330 ns<sup>47</sup> (or ~700 ns<sup>48</sup>), the lifetimes of propylchlorocarbene,<sup>48</sup> benzylchlorocarbene<sup>49</sup> and  $\alpha$ -methylbenzylchlorocarbene<sup>47</sup> are reduced to 17, 18, and 2 ns, respectively. The combined effect of a phenyl and a methyl group at the migrating origin accelerate the 1,2-H shift by a factor of ca. 150. Transition-state energies with zero point energy corrections calculated at the B3LYP/6-311\*\*G//B3LYP/631G\* level recently published<sup>11</sup> account well for these rate differences and confirm the importance of stabilizing a developing positive charge at the migrating origin. The same conclusion was reached experimentally from the effect of solvents on the rate of the reaction.<sup>36</sup> The rate of 1,2-H shift in phenylethylidene is increased by more than a factor of 30, from  $k_{1,2-H} < 6 \times 10^6 \text{ s}^{-1}$  in hydrocarbons to  $2 \times 10^8 \text{ s}^{-1}$  in acetonitrile. To conclude, although 1,2-H shifts in 1-phenylethylidene are fairly slow, it is reasonable that rates of 1,2-H shifts in 1,2-diphenylethylidenes in methanol should have rate constants in the subnanosecond regime when the effect of the phenyl group at position 2 (~150-fold) and the effect of solvent polarity (~30-fold) are taken into account.

## Experimental Section

**General.** UV spectra were obtained on a Varian Cary 2300 spectrophotometer and a Beckman DU 650 spectrophotometer. GC data was obtained on a Hewlett-Packard 5890 Series II gas chromatograph, with an HP 3396 Series II integrator. An HP-1 cross-linked methyl silicone gum column and an HP-20M Carbowax 20M column were used. Both are 25 m  $\times$  0.20 mm, with a 0.20  $\mu\text{m}$  film thickness. A Spex Fluorolog spectrofluorimeter with double grating monochromator was used to obtain fluorescence and phosphorescence spectra. Front surface illumination and detection was used. Phosphorescence measurements used a pulsed lamp with a 10  $\mu\text{s}$  pulse width. A custom sample holder held a Dewar with a Pyrex cold finger to keep the samples at 77 K during the analysis. The nanosecond laser flash photolysis apparatus at The Ohio State University has been described in detail in ref 18.

**Materials.** Dicyclohexylacetic acid (99%), deoxybenzoin (97%), and isobutyrophenone (97%) were purchased from Aldrich. Acetophenone, benzaldehyde, and toluene (Certified A.C.S.) were purchased from Fisher. All commercial reagents were of the highest grade available. Solvents were dried according to accepted literature methods and were kept over 4 Å molecular sieves.

**General Procedure for Analytical Photolysis.** Solutions for photolysis were prepared by dissolving the diazo compound in MeOH to make a 5 mM solution. For sensitized experiments, benzophenone was added to make the solutions 25 mM in sensitizer. Samples were deoxygenated by 5–10 freeze–

pump–thaw cycles or by bubbling Ar through the sample for at least 20 min prior to irradiation with a 400 W medium-pressure Ace-Hanovia Hg arc lamp. A 150 W PTI medium-pressure Hg arc lamp with a monochromator was also used for some experiments. Samples were immersed in a controlled temperature bath. Direct irradiations at  $\lambda > 290 \text{ nm}$  were carried out with Pyrex filters, and for  $\lambda > 470 \text{ nm}$  a cutoff filter was used. A combination of a 360 nm cutoff and a 300–400 nm band-pass from Melles Griot was used for sensitized irradiation when not using the PTI lamp. Samples were irradiated until the characteristic pink color of the diazo compound had completely disappeared, or when necessary, they were quenched with a small amount of dimethylacetylene dicarboxylate (DMAD) to remove unreacted diazo. The samples were analyzed in duplicate by GLC, and the average values are reported.

**General Procedure for Synthesis of Hydrazones.** All hydrazones were prepared from the corresponding ketone, which was either purchased or synthesized by methods described below. In a typical reaction, the ketone is heated to reflux in EtOH. A slight excess of hydrazine is added slowly, and the reaction is allowed to reflux for 1–12 h. Reaction progress is monitored by IR, TLC, and/or GC, and more hydrazine may be added as needed until the reaction is complete. The solution volume is reduced and then cooled to induce crystallization of the hydrazone. The white crystals are filtered and washed several times with cold EtOH, followed by recrystallization from  $\text{CHCl}_3/\text{EtOH}$  if needed.

**General Procedure for Synthesis of Diazo Compounds.** Diazo compounds were prepared from the appropriate hydrazone by HgO oxidation. In a typical reaction, 10–25 mg of the hydrazone is suspended in 25 mL of pentane, along with 5 equiv of  $\text{MgSO}_4$  and a large excess of HgO. Several drops of anhydrous concentrated KOH/EtOH are added, and the reaction is allowed to stir in the dark at room temperature for several hours. Reaction progress is monitored by IR and/or GC. When the reaction is complete, the pale pink pentane solution is filtered several times to remove all traces of mercury, and solvent is removed to give dark pink fluid or crystals. A quantitative yield is assumed. Samples are stored in the dark at 0 °C.

**Synthesis of Compounds 7, 8, 9a, and 10.** The preparation of these compounds has been previously reported.<sup>25,32</sup>

**Synthesis of Compound 9b.** Compound 9b was prepared as shown in Scheme 3. The preparation and characterization of all compounds is described below.

**2,2-Dicyclohexyl-1-(4'-methyl)-phenylethanone.** A mixture of dicyclohexylacetic acid (2.5 g, 11.1 mmol), and 3.3 g (2.0 mL, 27.8 mmol) of thionyl chloride was refluxed in 25 mL methylene chloride for 1.5 h. The solvent and unreacted  $\text{SOCl}_2$  were removed by rotary evaporation. The resulting acid chloride was dissolved in 20 mL of toluene. A 2.5 g (18.7 mmol) portion of  $\text{AlCl}_3$  was added slowly, and the reaction was stirred for 1 h. The reaction was quenched by pouring into several volumes of water, and the aqueous layer was extracted twice with ether. The combined organic layers were washed twice with water and dried over  $\text{MgSO}_4$ . Removal of the solvent gave a yellow oil. Crystallization from pentane gave 2.4 g (72%) in two crops of white crystals, mp 55–60 °C. <sup>1</sup>H NMR ( $\text{CDCl}_3$ , 200 MHz)  $\delta$ : 0.76–1.32 (m, 12H), 1.62–1.94 (m, 10H), 2.40 (s, 3H), 3.28 (t,  $J = 7.3 \text{ Hz}$ , 1H), 7.24 (d,  $J = 8.2 \text{ Hz}$ , 2H), 7.87 (d,  $J = 8.2 \text{ Hz}$ , 2H). <sup>13</sup>C NMR ( $\text{CDCl}_3$ , 90 MHz)  $\delta$ : 21.53, 26.44, 26.51, 26.76, 29.81, 31.85, 37.83, 55.73, 128.26, 129.16, 137.73, 143.31, 205.08. FTIR (KBr pellet)  $\text{cm}^{-1}$ : 1663. EI HRMS: calculated for  $\text{C}_{21}\text{H}_{30}\text{O}$  298.2297, found 298.2288.

**2,2-Dicyclohexyl-1-(4'-bromomethyl)-phenylethanone (13).**<sup>33</sup> The Friedel–Crafts adduct (1.50 g, 5.03 mmol), 1.34 g (7.55 mmol) of *N*-bromosuccinimide (NBS), and 0.12 g (0.50 mmol) of benzoyl peroxide were dissolved in 15–25 mL of  $\text{CCl}_4$ . The solution was heated to vigorous reflux for up to 24 h, until the reaction showed no further progress by TLC and GC. The reaction mixture was cooled and filtered to remove solids, and then solvent was removed to give an oil which was 80% pure by GC analysis. Flash chromatography was used to purify the mixture, but some ketone starting

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(48) LaVilla, J. A.; Goodman, J. L. *J. Am. Chem. Soc.* **1989**, *111*, 6877–6878.

(49) Liu, M. T. H.; Bonneau, R. *J. Am. Chem. Soc.* **1990**, *112*, 3915–3919.



material remained.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz)  $\delta$ : 0.80–1.23 (m, 12H), 1.53–1.83 (m, 10H), 3.26 (t,  $J = 7.3$  Hz, 1H), 4.48 (s, 2H), 7.44 (d,  $J = 8.2$  Hz, 2H), 7.91 (d,  $J = 8.2$  Hz, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 90 MHz)  $\delta$ : 26.39, 26.47, 26.73, 29.82, 31.85, 32.23, 37.88, 56.09, 128.60, 129.15, 139.86, 142.13, 204.88. FTIR (thin film)  $\text{cm}^{-1}$ : 1674. EI LRMS: calculated for  $\text{C}_{21}\text{H}_{29}\text{OBr}$  376.1, found 294.0 ( $\text{M}^+ - \text{C}_5\text{H}_{11}$ ).

**1-(2-Phenyl-2-oxoethylthioacetal)-4-(2,2-dicyclohexyl-1-oxoethyl)-benzene.** A solution of 2-phenyl-1,3-dithiane (0.74 g, 3.79 mmol) in 10 mL of dry THF under nitrogen was cooled to  $-40$  °C. A solution of *n*-butyllithium in hexane (1.60 mL, 4.17 mmol) was added slowly. After 1 h of stirring at this temperature, a solution of crude (65% by GC) bromoketone **21** (0.65 g, 1.72 mmol) in dry THF was added, and the reaction continued stirring at  $-40$  °C for 2 h. Butyllithium was quenched by slowly pouring into several volumes of water. The organic layer was extracted three times with ether and dried over  $\text{MgSO}_4$ . Solvent was removed to give 1.3 g of yellow oil, which by GC was 60% pure (0.78 g, 92%). Flash chromatography was used to purify the mixture, but 2-phenyl-1,3-dithiane remained as an impurity. (This accounts for the additional signals in the NMR spectra).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz)  $\delta$ : 0.76–1.24 (m, 12H), 1.58–1.91 (m, 10H), 2.65 (m, 5H), 3.18 (t,  $J = 7.3$  Hz, 1H), 3.27 (s, 2H), 6.78 (d,  $J = 8.2$  Hz, 2H), 7.30 (m, 4H), 7.67 (m, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 90 MHz)  $\delta$ : 24.92, 26.42, 26.49, 26.77, 27.52, 29.80, 331.78, 32.09, 37.76, 51.29, 55.95, 59.44, 127.14, 127.18, 127.73, 128.33, 128.72, 129.34, 130.95, 138.79, 139.42, 140.13, 205.30. EI HRMS: calculated for  $\text{C}_{31}\text{H}_{40}\text{OS}_2$  492.2521, found 492.2520.

**1-(2-Phenyl-2-oxoethyl)-4-(2,2-dicyclohexyl-1-oxoethyl)-benzene (14).** The crude thioacetal (0.60 g, 1.05 mmol, 14% 2-phenyl-1,3-dithiane by GC) was suspended in 15 mL of a 9:1 (v/v) solution of methanol/water and heated slightly to improve solubility. A solution of 0.50 g (2.1 mmol) of  $\text{HgCl}_2$  in 5 mL of the same solvent mixture and 0.20 g (0.94 mmol) of  $\text{HgO}$  were added, and the mixture was refluxed under nitrogen for 4–6 h. The solution was filtered through a glass microfiber filter to remove solids, which were then washed with acetone to remove residual organic products. The methanol/water solution was condensed, left to stand for several hours, cooled with ice, and filtered. The diketone (0.26 g, 63%) was obtained in two crops, mp 154–157 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz)  $\delta$ : 0.80–1.24 (m, 12H, H), 1.56–1.86 (m, 10H), 3.26 (t,  $J = 7.3$  Hz, 1H), 4.32 (s, 2H), 7.33 (d,  $J = 8.3$  Hz, 2H), 7.54, (m, 3H), 7.91 (d,  $J = 8.3$  Hz, 2H), 8.00 (m, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 90

MHz)  $\delta$ : 26.42, 26.49, 26.74, 29.85, 31.85, 37.88, 45.19, 55.93, 128.49, 128.56, 128.75, 129.05, 129.72, 133.44, 136.41, 139.38, 196.87, 205.24. FTIR (thin film)  $\text{cm}^{-1}$ : 1728, 1669. EI HRMS: calculated for  $\text{C}_{28}\text{H}_{34}\text{O}_2$  402.2559, found 402.2561.

**1-(2-Phenyl-2-oxoethylhydrazone)-4-(2,2-dicyclohexyl-1-oxoethyl)-benzene.** Diketone **14** (0.05 g, 0.12 mmol) was suspended in 5 mL of dry ethanol under nitrogen. The reaction mixture was heated slightly until the diketone dissolved, 0.04 mL (1.27 mmol) of hydrazine was added, and the solution was refluxed for 4–8 h. The reaction mixture was cooled to 0 °C with ice for several hours, and the product crystallized out of solution. Filtration and washing with cold ethanol of two crops followed by drying under vacuum yielded 0.047 g (90%) of off-white crystals, mp 147–150 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz)  $\delta$ : 0.67–1.18 (m, 12H), 1.54–1.78 (m, 10H), 3.15 (t,  $J = 7.3$  Hz, 1H), 3.99 (s, 2H), 5.30 (broad s, 2H), 7.30 (m, 5H), 7.61 (m, 2H), 7.81 (d,  $J = 8.3$  Hz, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 90 MHz)  $\delta$ : 26.40, 26.47, 26.73, 29.83, 31.85, 32.16, 37.86, 55.95, 125.55, 128.09, 128.33, 128.50, 128.94, 138.74, 138.95, 140.41, 147.76, 204.95. FTIR (thin film)  $\text{cm}^{-1}$ : 3393, 1669. EI HRMS: calculated for  $\text{C}_{28}\text{H}_{36}\text{ON}_2$  416.2828, found 416.2840.

**1-(2-Phenyl-2-diazoethyl)-4-(2,2-dicyclohexyl-1-oxoethyl)-benzene (9b).** Hydrazone (0.04 g, 0.096 mmol) was suspended in 25 mL of pentane, along with 0.06 g (0.5 mmol) of  $\text{MgSO}_4$  and 1.0 g (4.62 mmol) of  $\text{HgO}$ . Several drops of concentrated  $\text{KOH}/\text{EtOH}$  were added, and the reaction was allowed to stir for 2 h. Then, 2  $\mu\text{L}$  of hydrazine was added to catalyze the reaction. The reaction was monitored by IR and GC, and when no hydrazone remained the pale pink pentane solution was filtered through a glass microfiber NMR filter to remove all traces of mercury. Solvent was removed to give dark pink crystals. A quantitative yield is assumed.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 360 MHz)  $\delta$ : 0.67–1.15 (m, 12H), 1.45–1.80 (m, 10H), 3.13 (t,  $J = 7.3$  Hz, 1H), 3.78 (s, 1H), 6.81 (m, 2H), 7.20 (m, 5H), 7.78 (d,  $J = 8.3$  Hz, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 90 MHz)  $\delta$ : 26.41, 26.48, 26.74, 29.83, 30.99, 31.84, 37.86, 56.01, 121.38, 123.65, 128.32, 128.34, 128.66, 130.98, 139.06, 139.40, 142.44, 205.06. IR (thin film)  $\text{cm}^{-1}$ : 2041, 1673, 1605.0, 1446.8, 1234.6, 993.5.

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