



Arylalkylcarbenes from Triplet Arylalkyldiazoalkanes

Krista R. Motschieder,¹ John P. Toscano,² and Miguel A. Garcia-Garibay^{1*}

¹Department of Chemistry and Biochemistry

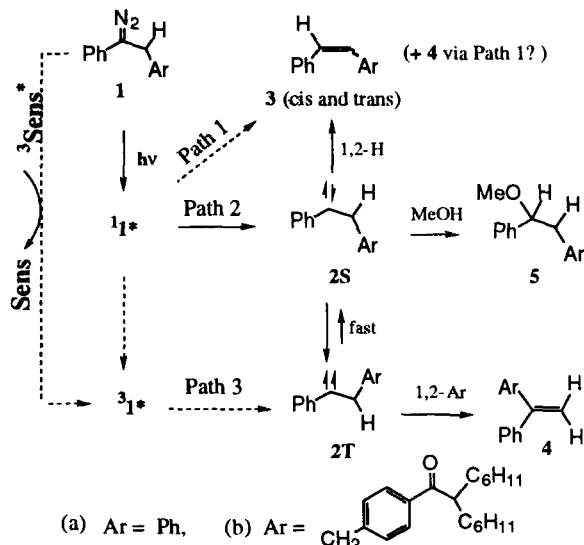
University of California, Los Angeles, California 90024

²Department of Chemistry

Johns Hopkins University, Baltimore, MD 21218

Abstract. Inter- and intramolecular triplet sensitization of two 1,2-diaryldiazoethanes in methanol gives rise to stilbenes **3** and ether **5** by intramolecular 1,2-H shifts and intermolecular reaction with methanol, respectively. The sensitized results were compared with those obtained from direct photolysis to determine the relative importance of excited state reactivity of the diazo precursors. © 1997, Elsevier Science Ltd. All rights reserved.

Scheme 1



Recent studies in our laboratories have addressed the photochemical reactivity of 1,2-diphenyldiazoalkanes such as **1** (Scheme 1) in several solvents,^{1,2} and in the crystalline solid state.³ Following a mechanism proposed by Tomioka,^{4,5} we formulated the formation of products **3**, **4** and **5** in terms of spin-state specific reactions from a rapidly equilibrating carbene (Path 2). We proposed that stilbenes **3** form by 1,2-H shifts from a thermally populated singlet state (**2S**), 1,1-diaryllkenes **4** by 1,2-Ph migrations from the lower-lying triplet (**2T**), while ethers **5** form by insertion of **2S** into the RO-H bond when reactions are carried out in alcohols (Scheme 1).

Considering only Path 2, we recently rationalized the relatively large solvent effects on the reaction.² We suggested that polar solvents favor **3** relative to **4** by increasing the equilibrium population of the (zwitterionic) singlets relative to that of the less polar (biradical) triplets. Since our studies included several alcohol solvents, our interpretation implied that *spin-equilibrated* carbenes may undergo competitive 1,2-R group migrations and alcohol insertion. However, studies with 1-phenylethylidene⁶ and high level ab-initio calculations with 1-vinylethylidene⁷ would suggest that 1,2-H shifts in arylalkyl carbenes may be too slow to compete with alcohol insertion.⁸ It

has also been shown that carbene-like products may arise from excited state^{6,9} and thermal¹⁰ reactions that bypass the intermediate (e.g., Path 1) and one should be concerned that formation of products **3** and **4** in neat alcohols may not come from a carbene intermediate.

In this letter, we report experiments that help establish that products **3** and **4** may indeed compete with alcohol trapping (**5**) from a spin-equilibrated carbene. To bypass the singlet excited diazo (**11***) we accessed the carbene via the triplet surface (Path 3). We expect no reactions from the triplet diazo (**31***) other than the loss of N₂ in a spin-conserving dissociation and, to facilitate the interpretation of the photochemical results, we selected two substrates which yield essentially no 1,2-Ph migration.

Table 1. Product Yields Following Photolysis of **1a** and **1b**.

	$\lambda > 290$		$\lambda > 470$		³ Sens	
	3	5	3	5	3	5
1a	44	56	36	64	25	75
1b	—	—	28	72	29	71

*Values are the average of several experiments. Yield variations fall within ca. 10%. Only traces of **4** were detected by gc.

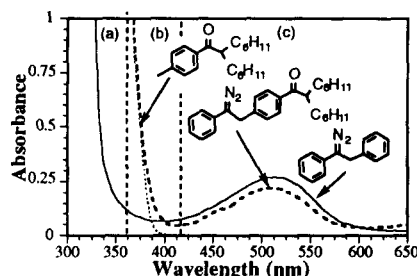


Figure 1. Ultraviolet spectra of compound **1a** (solid line), **1b** (dashed line) and acetophenone (dotted line) in MeOH.

1,2-Diaryldiazoalkanes **1a** and **1b** (Scheme 1) were selected as ideal substrates for controlled energy transfer experiments. Compounds **1a** and **1b** have similar structures but **1b** possesses an arylketone chromophore for intramolecular triplet sensitization. Compounds **1a** and **1b** were prepared from the corresponding hydrazones as reported in the literature.¹¹ The two bulky cyclohexyl groups in **1b** were introduced to facilitate the regioselective synthesis of the desired diazo group in the presence of the sensitizing ketone.¹² Inter-molecular triplet energy transfer to **1a** was accomplished with benzophenone. That the *para*-carbonyl of **1b** does not perturb the diazo chromophore is suggested by its UV-Vis spectrum, which is nearly identical to the added spectra of *para*-methyl- α,α -dicyclohexyl-acetophenone and diazo **1a** (Figure 1). Compounds **1a** and **1b** undergo efficient 1,2-H shifts and MeO-H insertion reactions but give only traces of 1,2-Ph migrations (Table 1). Like other aryldiazo compounds, irradiation of **1a** at 77K gives rise to a triplet ESR spectra that is assigned to a triplet ground state carbene.¹³

The wavelengths and concentrations required for selective excitation of the sensitizer were determined from the UV-Vis spectra, which may be divided in three regions depending on which chromophores absorb. As shown in Figure 1, both arylketone and aryldiazo chromophores overlap in the region of their π,π^* transition (region a), up to about 350 nm. Selective excitation of the n,π^* state of the arylketone may be accomplished in region (b) with $360 \text{ nm} < \lambda < 400 \text{ nm}$, and excitation of the n,π^* state of the aryldiazo by irradiation with $\lambda > 420 \text{ nm}$ in region (c). Direct irradiation of 5 mM **1a** in MeOH was carried out with $\lambda > 290$ (π,π^*) and with $\lambda > 470 \text{ nm}$ (n,π^*). Sensitized irradiations of **1a** were carried out in the presence of 50 mM benzophenone with $360 \text{ nm} < \lambda < 400 \text{ nm}$. All photolyses were carried out in a thermostated bath at 0 °C and analyses were carried out by capillary glc.

The results of irradiation in methanol under three different conditions are summarized in Table 1. Due to wavelength and sensitizer-dependent isomerization, yields of *cis*- and *trans*-stilbenes varied and only

their sum is reported in the table. Excitation of aryldiazo or arylketone chromophores in **1b** gives nearly identical results with 28-29% 1,2-H and 72-71% methanol insertion. Compound **1b** showed no traces of Norrish Type-I¹⁴ and Type-II¹⁵ ketone photochemistry. That population of the triplet diazo occurs efficiently upon excitation of the arylketone chromophore is also shown by the lack of phosphorescence of **1b** at 77K in MCH under conditions where *para*-methyl- α,α -dicyclohexyl-acetophenone was used as a control (Figure 2). As shown in Table 1, product yields obtained upon intermolecular sensitization of **1a** are very similar to those obtained from **1b**. However, direct irradiation of **1a** displays wavelength-dependence

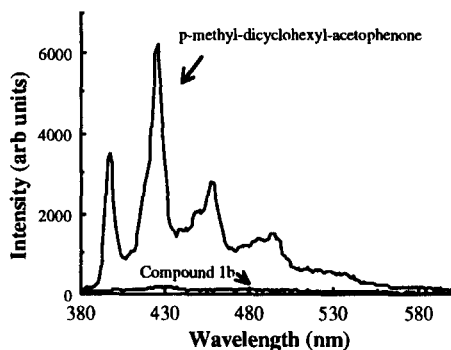


Figure 2. Comparison of the phosphorescence spectra of compound **1b** and *para*-methyl- α,α -dicyclohexyl-acetophenone.

giving increasing amounts of **3** as the excitation wavelength becomes shorter. Excitation with $\lambda > 290$ nm results in higher yield of 1,2-H shift; 44% as compared to 36% observed upon excitation at $\lambda > 470$, or 25% upon triplet sensitization.

The lack of 1,2-Ph migration in **1a** and **1b** in MeOH greatly simplifies interpretation of the results in terms of Scheme 1. Only the competition between 1,2-H and MeO-H insertion needs to be considered. Since it is unlikely that any of these reactions occur in the triplet state of the diazo compound, we postulate that sensitized irradiation results in quantitative yields of carbene formation. Formation of **2T** via Path 3 is followed by intersystem crossing to **2S** before a 1,2-H shift or an insertion reaction become possible. Carbenes from **1a** and **1b** formed in this manner have essentially the same reactivity and give essentially the same product yields. The identity of the intramolecular and intermolecular sensitization demonstrates that there is no interference by the sensitizer in the intermolecular case. Since both stilbenes and ethers originate from **2S**, the same product ratio in direct and sensitized irradiations of **1b** is consistent with a spin-state equilibrated carbene. Given their similarities, it is likely that singlet and triplet carbenes from **1a** can also equilibrate. The wavelength-dependence of **1a** upon direct irradiation is consistent with an excited state reaction (Path 1) that is more important in the upper excited state (π,π^*). Differences in reactivity between n,π^* and π,π^* states can be associated with a slow internal conversion due to the relatively large energy gap between the two excited states, as it is evident in the absorption spectrum.

If our assumption concerning the lack of reactivity from the diazo triplet state is valid, our results suggest that 1,2-H shifts do indeed compete with methanol insertion in 1,2-diarylalkylidenes. Although these results do not distinguish between solvent effects on the spin-state equilibrium^{1,2} or a polar-solvent acceleration of the 1,2-H reaction,¹⁶ they do suggest that the rate of the 1,2-H shift in carbenes **2a** and **2b** in methanol should be about 5 times as fast as that reported for 1-phenylethylidene in acetonitrile¹⁶ (i.e., $k_{1,2-H} \geq 10^9 \text{ s}^{-1}$). Rate differences between 1-phenyl [$\text{Ph}(\text{CH}_3)\text{C}:$] and 1,2-diphenylethylidenes [$\text{Ph}(\text{PhCH}_2)\text{C}:$] are consistent with ab-initio theory⁷ and experimental measurements¹⁷ which suggest that the 2-aryl group should lower the energy of the transition state relative to that of a simple methyl aryl carbene. Finally, by assuming that Paths 2 and 3 give identical yields from a spin-state equilibrated carbene one can calculate the fraction of products formed via Path 1 relative to the fraction of products arising via Path 2.¹⁸

Contributions from Path 1 in **1a** would be *ca.* 15% at $\lambda > 470$ nm and 25% at $\lambda > 290$. If this analysis is correct, our experiments suggest that π, π^* character or high energy content may be important for excited state 1,2-H shifts. The lack of excited diazo reactivity in **1b** would suggest that the n, π^* excited state intersystem crosses to the triplet and denitrogenates to the carbene faster than it can undergo a hydrogen shift and denitrogenation reaction. Analysis of other arylalkyl compounds with and without 1,2-H shifts and/or 1,2-Ph migrations gives results that are consistent with those reported here and will be discussed in the near future.

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- (18) Let x be the fraction of products formed via Path 1 and $1-x$ the fraction of products via Path 2. The yields of 1,2-H shifts and MeO-H insertion from the "true carbene" (sensitized experiments) labeled "a" and "b", respectively, can be used to describes the ratio (y) of 1,2-H and insertion products obtained upon direct irradiation: $y = 1,2\text{-H} / \text{Insertion} = [x + (1-x) a] / [(1-x) b]$.

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