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INTRAMOLECULAR REACTIVITY OF FUNCTIONALIZED ARYLCARBENES: 2-ALLYLOXYPHENYLCARBENES

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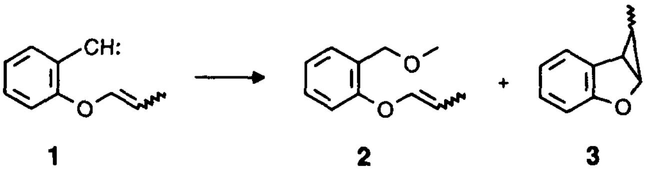
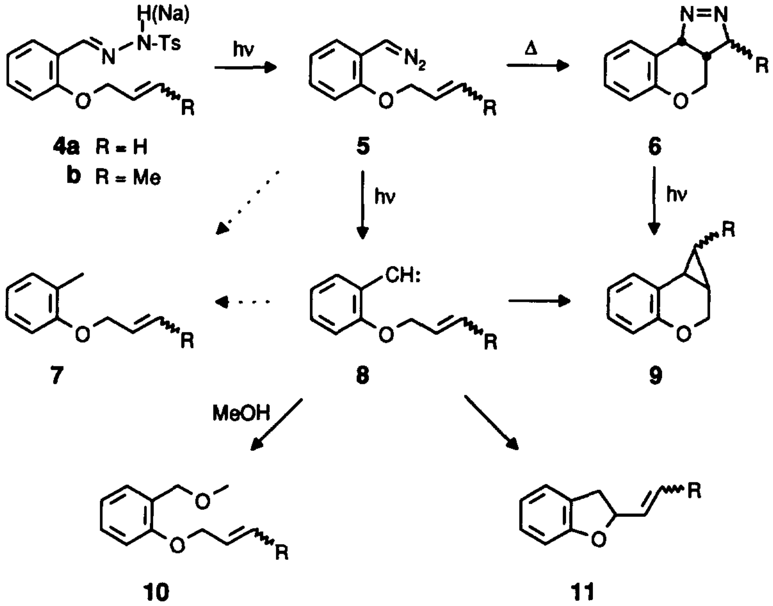
Abstract: 2-Allyloxyphenylcarbenes (**8**) undergo intramolecular addition (→ **9**) and (formal) C-H insertion (→ **11**) competitively. Stereochemical labels indicate that **11** and major amounts of **9** arise from triplet **8**. The intermolecular O-H insertion of singlet **8** with methanol (neat) is ca. 50 times faster than intramolecular addition. Under these conditions, intramolecular reactions and intersystem crossing of triplet **8** proceed at similar rates ($k_T \sim k_{TS}$). © 1997 Elsevier Science Ltd. All rights reserved.

It is widely believed that spin-state-specific mechanisms can be assigned to the reactions of carbenes.[1] If spin inversion is relatively slow, $k_{ST}<k_S$ and $k_{TS}<k_T$, the mechanism depends on how the carbene is generated. Methylene is an eminent example of such behavior. In the case of rapid intersystem crossing, $k_{ST}>k_S$ and $k_{TS}>k_T$, the reaction is channelled through the most favorable transition state, regardless of the spin state in which the carbene is formed. It appears that arylcarbenes belong to the second category. Although the triplet is the ground state of phenylcarbene,[2] the reaction of phenylcarbene with alkenes gives cyclopropanes with greater than 95% retention of configuration.[3,4] The stereospecificity of the addition of phenylcarbene to 2-butene was not affected by dilution with perfluorocyclobutane,[5] nor by sensitization with benzophenone.[6] These results clearly indicate that $k_{TS}>k_T$. Entirely different behavior was encountered with 1-propenyloxy groups attached to the *ortho* position of phenylcarbene.[7] The generation of **1** by direct photolysis afforded predominantly **2** whereas sensitization led to preferential formation of **3**; *E*-**1** and *Z*-**1** gave virtually the same mixture of *cis*-**3** and *trans*-**3**. In contrast to phenylcarbene, triplet rather than singlet **1** undergoes efficient intramolecular addition; $k_T>k_{TS}$.



In order to elucidate the effect(s) of intramolecularity, we have lengthened the "tether" which connects the double bond to the arene ring. In earlier work we observed that 2-(2-propenyloxy)-phenyldiazomethane (**5a**) undergoes cycloaddition (→ **6a**) competitively with photolysis (→ **8a**).[8] As

9a is formed by two routes (**5a** → **6a** → **9a** and **5a** → **8a** → **9a**), the ratio of **11a** : **9a** decreases with time. Extrapolation to $t = 0$ gives the ratio at which **9a** and **11a** originate from the carbene **6a**. More conveniently, the same ratio is obtained by irradiation of the tosylhydrazone sodium salt **4a** in which **5a** is generated and immediately photolyzed. In the presence of methanol, the ether **10a** and small amounts (<5%) of **7a** are also formed. Reduction products such as **7** do not necessarily arise from carbenes.[9] Therefore, **7** is not included in the product distributions (Table 1).



On benzophenone sensitization, both **9a** and **11a** were found to increase at the expense of **10a**.[10] The ratio of **11a** : **9a** also increased with the concentration of sensitizer and was smaller in cyclohexane than in methanol (Fig. 1). These observations indicate that ^{3}**8a** contributes more to the formation of **11a** than to that of **9a**.

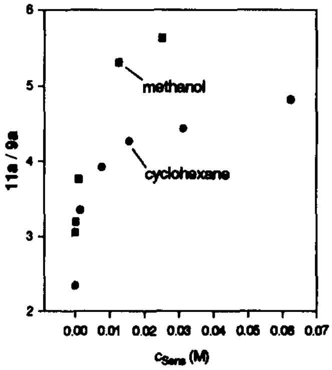
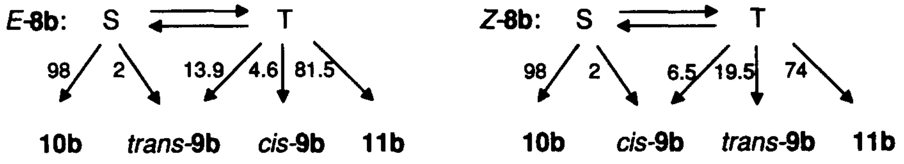


Figure 1. Product Ratios from Photolyses of 4a-Na

For further insight, 2-(2-butenyloxy)phenylcarbenes (**8b**) were generated from appropriate tosylhydrazone precursors **4b**.[11] The carbenes **8b** provide products that arise exclusively from the triplet state (*cis*-**9b** from *E*-**4b**, *trans*-**9b** from *Z*-**4b**) and from the singlet state (**10b**), respectively. The contributions of ^{1}**8b** and ^{3}**8b** to product formation can then be dissected[7b] as shown in Eq. (1). The formal C-H insertion leading to **11** proceeds by a triplet abstraction-recombination process for which ample precedent with 2-alkoxyphenylcarbenes exists.[12] The products of intramolecular addition, *cis*-**9b** and *trans*-**9b**, originate in the same ratio from *E*-^{3}**8b** and from *Z*-^{3}**8b**, as well as from sensitized photolyses of the pyrazolines *cis*-**6b** and *trans*-**6b**, i.e., conformational equilibration of the intervening 1,5-biradicals is rapid relative to ring closure. The ratio of hydrogen abstraction (leading eventually to **11b**) to intramolecular addition differs slightly for *E*-^{3}**8b** and *Z*-^{3}**8b**. Singlet **8b** is efficiently trapped by methanol but contributes little to the formation of **9b** (Table 1).



(1)

Table 1. Product Distributions (%) Obtained from Photolyses of **4**-Na

substrate	solvent	Ph_2CO (M)	9		10	11	% S[a]
			cis	*trans*			
4a-Na	methanol	-	2.0		92.0	6.0	
		0.010	4.1		74.0	21.9	
		0.025	5.4		64.2	30.4	
	cyclohexane	-	30.0		-	70.0	
		0.016	19.0		-	81.0	
		0.125	12.7		-	86.3	
E-**4b**-Na	methanol	-	0.4	2.9	91.0	5.7	93
		0.016	1.1	5.0	73.5	20.7	75
		0.125	1.5	7.1	54.7	36.7	56
	cyclohexane[b]	-	3.6	25.4	-	71.0	14
		0.250	3.7	14.6	-	81.7	3
Z-**4b**-Na	methanol	-	2.3	0.7	94.4	2.6	96
		0.016	3.2	6.0	70.3	20.5	72
		0.125	4.0	8.5	52.9	34.6	54
	cyclohexane	-	22.8	17.2	-	60.0	17
		0.250	12.8	19.8	-	67.4	6

[a] Fraction of products originating from the singlet state.

[b] The product of C-H insertion with the solvent (14.5%) was also observed. Our data do not allow to assign the formation of this product to a specific spin state.

In many respects the reactivity of **8** is similar to that of **1**. Relative to O-H insertion with MeOH, the intramolecular addition of ^{1}**8** is as inefficient as that of ^{1}**1**. However, the stereoselectivities of *E*-**8b** and *Z*-**8b** does not fully converge on sensitization, in contrast to that of **1**. For photolyses of **4b** in methanol, plots of the fraction of singlet products vs. concentration of sensitizer (Fig. 2) clearly indicate that **8** ($k_T \sim k_{TS}$) ranges between **1** ($k_T > k_{TS}$) and phenylcarbene ($k_T < k_{TS}$).

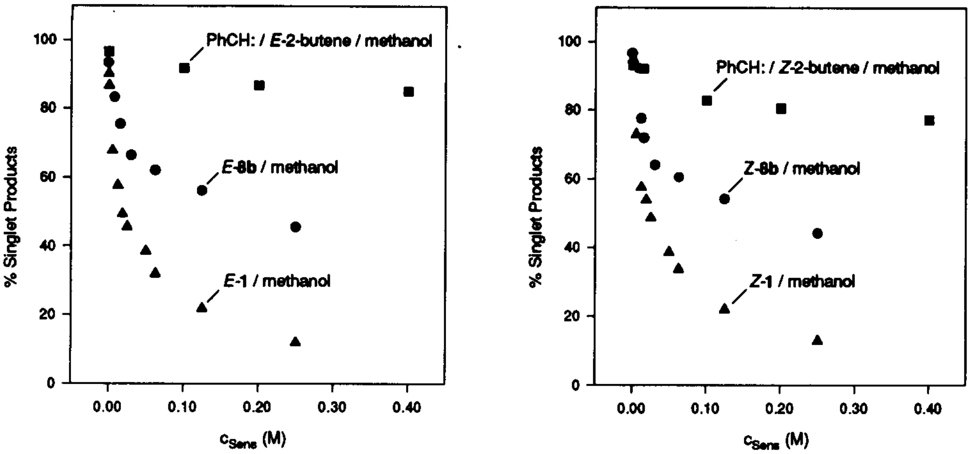


Figure 2. Effect of benzophenone-sensitization on the product distribution of various carbenes

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10. The ratio of **11**: **9** also decreases on continued irradiation in the presence of benzophenone. Therefore, product distributions were extrapolated to *t* = 0 for all photolyses recorded in Table 1.

11. Solutions of the appropriate aldehydes [(a) Oppolzer, W.; Weber, H. P. *Tetrahedron Lett.* **1970**, 1121. (b) Shimuzu, T.; Hayashi, Y.; Kitora, Y.; Teramura, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2450] in MeOH were treated with tosylhydrazine to give *E*-**4b**, 72%, m.p. 131 °C, and *Z*-**4b**, 81%, m.p. 116 °C.

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