# Reaction of Arylcarbenes with Methanol: Triplet-State Reactivity or Spin-State Equilibrium as a Moving Target?

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The spin-state-dependent reactivity of arylcarbenes with ground triplet states and thermally accessible singlets continues to attract much interest and some controversy.[1-7] With assumptions of spin-state-specific reactivity and unperturbed equilibration proposed by Bethel,[2] the singlet–triplet equilibrium constants ($K_{eq} = k_{ST}/k_{TS}$) and singlet-triplet energy gaps ($\Delta G_{ST} = -RT \ln K_{eq}$) of some arylcarbenes have been proposed.[3,4] In the best studied example, isoprene and methanol have been employed as the spin-state-specific traps for the triplet and singlet states of diphenylcarbene.[3,4,5] However, while the specificity of the triplet-state reaction has not been contested, the specificity of the singlet reaction with methanol has been questioned on the basis of inconsistencies between activation barriers predicted by the Bethel model (5–8 kcal/mol) and those obtained experimentally (1–4 kcal/mol).[6] Alternatives to the Bethel mechanism that account for those differences have been proposed. The first one is based on a surface crossing reaction between the triplet-state carbene and methanol, and the second considers solvent effects capable of modifying $\Delta G_{ST}$.[6,7] Interestingly, in the absence of convincing experimental evidence, the more profane spin-forbidden reaction has attracted more attention than the alternatively mundane solvent perturbation. A promising approach for a qualitative but definitive evaluation of the Bethel mechanism involves a competition reaction in arylalkylcarbenes displaying simultaneous singlet and triplet *unimolecular* reactivity. Under these conditions, the rates of bimolecular reactions are "timed" relative to spin-state-specific unimolecular clocks in the absence of absolute rate measurements.

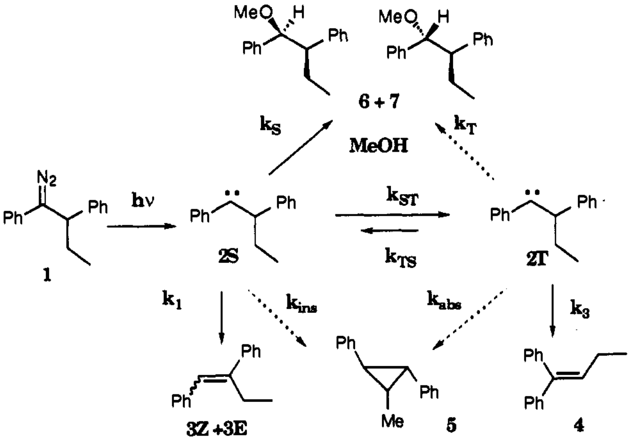
Triplet ground-state carbenes derived from 1,2-diphenyl-1-diazoalkanes[8,9] display spin-state-specific reactivity[10] and constitute a promising model for this study. In agreement with reports on the chemistry of 1,2-diphenyl-1-diazopropane, irradiation of 1,2-diphenyl-1-diazobutane (**1**, Scheme I) in pentane or benzene gives rise to isomeric stilbenes **3(*Z*)** and **3(*E*)** via singlet-state 1,2-H shifts and to 1,1-diphenyl-1-butene (**4**) via triplet 1,2-Ph migration (Table I).[11] We also observed the formation of *trans*-1,2-diphenyl-3-methylcyclopropane (**5**), whose analog was not reported in previous studies on 1,2-diphenyl-1-diazopropane.[9,10] A careful reinvestigation of the latter compound showed that the corresponding cyclopropane forms in yields lower than 5% under several irradiation conditions.[12] Cyclopropane **5** could form via insertion into the C–H bond, $k_{ins}$, by **2S** or via triplet hydrogen abstraction ($k_{abs}$) by **2T** followed by closure of the intermediate 1,3-biradical (evidence for the latter is shown below).[13] Photolysis of **1** in neat methanol gave rise to the same products along with 63% of the diastereoisomeric methyl ethers **6** and **7** (Table I).[14]

**Table I.** Product Distribution from Photolysis of 1,2-Diphenyldiazobutane[a]

| solvent | 3(*Z*) | 4 | 3(*E*) | 5 | 6 + 7[b] | Φ (P₁)/ Φ (P₃) |
|---|---|---|---|---|---|---|
| pentane | 23.4 | 40.9 | 8.8 | 26.9 | | 0.48 |
| benzene | 24.1 | 44.6 | 9.6 | 21.7 | | 0.51 |
| MeOH | 21.6 | 5.2 | 6.4 | 2.3 | 63 (74:26) | 3.73 |
| MeCN | 37.1 | 33.3 | 16.9 | 12.6 | | 1.18 |
| 3-$C_5H_{12}OH$ | 21.6 | 17.4 | 7.6 | 8.5 | 37.2 (75:25) | 1.17 |

[a] Product ratios measured in 5 mM solutions are the average of two independent runs (ca. ±10% error). Irradiations were performed with a Hanovia 450-W medium-pressure lamp (cutoff $\lambda \geq 350$ nm) with thoroughly deoxygenated samples. [b] The relative stereochemistry of **6** and **7** was not determined. In the case of 3-pentanol, the values refer to the diastereomeric 3-pentyl ethers.

**Scheme I**



While comparison of the results in hydrocarbon solvents and in methanol are suggestive, a systematic increase of the amount of methanol in benzene should increase the yields of **6** and **7** and redistribute the yields of intramolecular products according to the kinetics of the system. The consequences of various reaction alternatives with methanol can be analyzed in terms of eq 1, which is a general steady-state expression deduced from Scheme II for the ratio of intramolecular singlet and triplet products which, for simplicity, we group together as $\Phi(P_1)$ and $\Phi(P_3)$.[15,16]

$$\frac{\Phi(P_1)}{\Phi(P_3)} = \frac{k_1(k_3 + k_{TS})}{k_3 k_{ST}} + \frac{k_1}{k_3}\frac{k_T[\text{MeOH}]}{k_{ST}} \qquad (1)$$

Within the limits of the Bethel mechanism, one expects $\Phi(P_1)/\Phi(P_3)$ to be independent of methanol concentration as $k_T$ is

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(11) Analyses were carried by GLC and GLC-MS. Peak assignments were confirmed by coinjection with authentic samples and/or by correlation with integrated 500-MHz $^1H$ NMR data.

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(14) Compounds **6** and **7** were prepared by $LiAlH_4$ reduction of 1,2-diphenylbutanone followed by treatment with MeI.

(15) The following yield expressions were utilized: $\Phi(P_1) = k_1/(k_1 + k_{ST} + k_S[\text{MeOH}])$ and $\Phi(P_3) = \{k3/k3 + k\text{TS} + k\text{T}[\text{MeOH}])\}\{k_{ST}/(k_1 + k_{ST} + k_S[\text{MeOH}])\}$.

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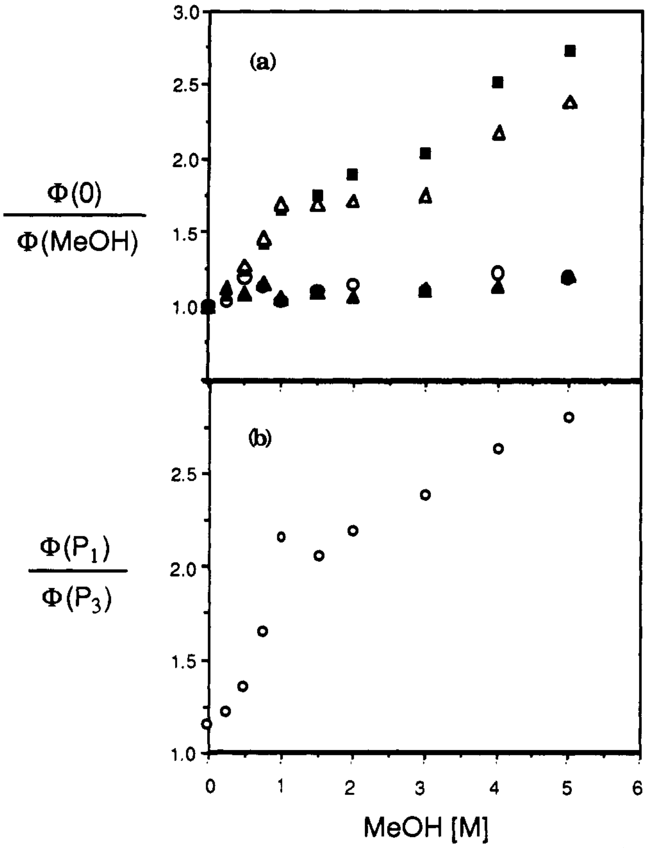
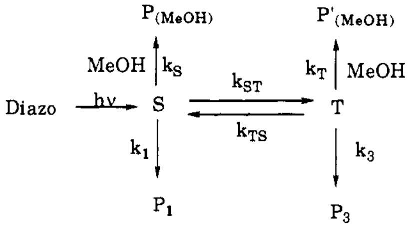


**Figure 1.** (a) Effect of added methanol to benzene solutions of **1** presented as Stern–Volmer plots. Compound **3(*Z*)**, ▲; **3(*E*)**, ○; **4**, △; and **5**, ■. (b) Changes in $\Phi(P_1)/\Phi(P_3)$ as a function of the methanol concentration.

**Scheme II**



assumed to be zero. The product ratio should become linearly dependent on methanol when $k_T$ is nonzero and both $k_{TS}$ and $k_{ST}$ remain constant. Any methanol dependence of $k_{ST}$ and/or $k_{TS}$ in eq 1 also removes the system from the Bethel mechanism, causing complex changes in $\Phi(P_1)/\Phi(P_3)$.

With experiments carried out with $10^{-3}$ to 5 M methanol, a Stern–Volmer analysis from product yield data in Figure 1a helps justify the assignment of the precursor of **3(*E*)** and **3(*Z*)** as the singlet carbene and of products **4** and **5** as the triplet. Different slopes for the two groups of products are indicative of different precursors which,[16] in agreement with previous assignments,[9,10] we assume are the two spin states of the carbene.[17] With **3(*Z*)** and **3(*E*)** coming from **2S** [$\Phi(P_1) = \Phi 3(Z) + \Phi 3(E)$] and **4** and **5** coming from **2T** [$\Phi(P_3) = \Phi 4 + \Phi 5$,] our results show that $\Phi(P_1)/\Phi(P_3)$ has a strong concentration dependence between $10^{-3}$ and 5 M methanol (Figure 1b). Changes in stereoselectivity of ether formation with values of $\Phi 6/\Phi 7$ from 2.5 to 3.6 were observed as the concentration of methanol was changed from ca. $10^{-3}$ to 1.0 M. While these changes may be interpreted in terms of methanol reaction with the two spin states of the carbene,[18] the possibility of carbene reaction with methanol monomers and oligomers[19] or of a different mechanism as a function of solvent polarity should also be considered.[20]

Turning our attention to Figure 1b and our expectations from eq 1, no support is found for a spin-state-specific reaction under rapid and unperturbed preequilibrium. This would require the formation of **6** and **7** *at the expense of all intramolecular products regardless of their spin-state precursor.* The nonlinearity of the $\Phi(P_1)/\Phi(P_3)$ plot in Figure 1b is also inconsistent with unperturbed preequilibrium and simultaneous singlet and triplet reactivity, as this would lead to $\Phi(P_1)/\Phi(P_3)$ values that are *linearly proportional* to methanol concentration. Figures 1a–c are not conclusive as to whether ethers **6** and **7** originate from **2S** only or from both **2S** and **2T** but unambiguously demonstrate the limitation of the Bethel mechanism. In order to distinguish between simultaneous singlet and triplet reactivity or a singlet-state-specific reaction coupled to solvent-induced reorganization of the equilibrium values, one needs a solvent system where polarity is maintained while the concentration of alcohol is changed.[7] It has been shown that acetonitrile and 3-pentanol satisfy this requirement with $E_T(30)$ polarity values of 46.0 and 45.7 kcal/mol, respectively.[7] *Changes in $\Phi(P_1)/\Phi(P_3)$ in this solvent system should result only from direct triplet-state reactivity if $k_{ST}$ and $k_{TS}$ are not altered.* Analysis of the data in Table I shows that, within experimental error, there are no changes in $\Phi(P_1)/\Phi(P_3)$ in these solvents in spite of the formation of substantial amounts of insertion products (37%) in 3-pentanol. This suggests that equilibrium between the two spin states of arylcarbenes behave as a moving target when the polarity of the medium changes and supports previous suggestions[6] of a revision of the singlet-triplet energy gaps determined form the simple Bethel mechanism.

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