

## Solvent Effects on the Singlet - Triplet Equilibrium and Reactivity of a Ground Triplet State Arylalkyl Carbene

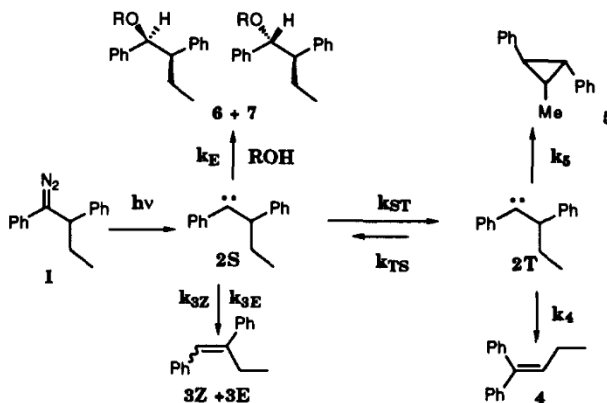
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**Abstract.** Results from intramolecular singlet and triplet specific reactivity in solvents of different polarity suggest that the spin state equilibrium of 1,2-diphenyl-1-butylidene, a triplet ground state carbene, is largely susceptible to solvent polarity. The results are consistent with stabilization of the zwitterionic singlet state in solvents of high polarity.

Unimolecular carbene reactivity is often characterized by low activation energies, large and negative activation entropies and by divergent reactivity from energetically close singlet and triplet states.<sup>1</sup> It has been shown<sup>2</sup> that ground triplet states 1,2-diphenylalkylidenes (**2**) react via singlet state (**2S**) 1,2-shifts to give (*Z*)- and (*E*)-1,2-diphenyl-1-alkenes (**3Z** and **3E**) while the triplet state (**2T**) undergoes 1,2-Ph migrations to give 1,1,-diphenyl-1-alkenes (**4**). The formation of 1,2-diphenyl-cyclopropanes (**5**) from the triplet state, has also been recently reported (Scheme 1).<sup>3</sup>

Scheme 1



It has been observed that the selectivity of 1,2-diphenylalkyl carbenes is low and that their reactivity has a pronounced susceptibility to environmental effects.<sup>2,4</sup> Satisfactory explanations have been offered for

temperature effects and rigidity<sup>2a,4</sup> but there has been no explanation offered for large variations in product yields occurring in different solvents. We have recently reported<sup>3</sup> competition experiments between intra- and intermolecular reactivity with methanol in benzene solvent to test for rapid spin state equilibration and spin state specificity as required by the Bethel mechanism (which is illustrated in Scheme 1).<sup>5</sup> By using the yields of intramolecular reaction products as spin-specific internal clocks, strong deviations from the Bethel mechanism were observed. With additional experiments carried out with 3-pentanol in acetonitrile, two solvents with identical polarity values,<sup>6,7</sup> we suggested that those deviations come from a large sensitivity of the S-T equilibrium constants (and S-T energy gaps) to the polarity of the solvent.<sup>3</sup>

In order to confront the above hypothesis, we have carried out a systematic study with solvents covering a wide polarity range and with relatively different properties. These included aliphatic and aromatic hydrocarbons such as pentane and benzene, ylid-forming acetonitrile and benzonitrile as well as a set of reactive alcohols with different steric requirements, acidity and (presumably) aggregation properties. The only obvious ordering parameter in this set is the polarity given by their  $E_T(30)$  values.<sup>6</sup> Photolyses were carried out with the filtered output ( $\lambda > 350$  nm) of a medium pressure mercury lamp in thoroughly deoxygenated 5 mM solutions of **1**. Product yields were determined by capillary gas chromatographic analysis and the results from duplicate experiments are included in Table 1.<sup>8</sup>

**Table 1.** Product Distribution<sup>a</sup> from **1** in Solvents of Different Polarities

Solvent	$E_T(30)$	3Z	4	3E	5	6 : 7 <sup>b</sup>
pentane	30.9	23.4	40.9	8.8	26.9	-
benzene	34.5	24.1	44.6	9.6	21.7	-
Cl-Benzene	37.5	29.0	40.3	8.7	22.0	-
CN-Benzene	42.0	32.9	35.7	10.4	21.0	-
MeCN	46.0	37.1	33.3	16.9	12.6	-
3-Pent-OH	46.0	21.6	17.4	7.6	8.5	28.7 : 10.6
2-PrOH	48.6	21.9	13.2	6.9	6.7	43.6 : 22.0
EtOH	51.9	23.2	9.7	8.3	5.7	37.5 : 10.9
MeOH	55.5	25.0	5.5	7.0	3.5	44.3 : 14.1

a) Average from at least two irradiations and two chromatographic runs each (ca. error  $\pm 10\%$ ). b) Relative stereochemistry not determined

The ratio of intramolecular triplet and singlet products [ $P_T / P_S = (4 + 5) / (3Z + 3E)$ ] contains information on the lifetime and equilibrium populations of each of the two spin states as determined by their rates of intramolecular reaction and intersystem crossing and is the parameter chosen for analysis in Figure 1. Given the variety of solvents included in the analysis, and the fact that simultaneous bimolecular reactivity and aggregation may occur in alcohol solvents,<sup>9</sup> the correlation is remarkable. Since the ratios  $3E / 3Z$  and  $4 / 5$  remain relatively constant, rate constants for unimolecular reactions from each manifold in different solvents are relatively unaffected. We define  $k_S = (k_{3Z} + k_{3E})$  and  $k_T = (k_4 + k_5)$  to obtain a simple expression for  $P_T / P_S$ :

$$\frac{P_T}{P_S} = \frac{\Phi(4 + 5)}{\Phi(3Z + 3E)} = \frac{k_T k_{ST}}{k_S (k_T + k_{TS})} \quad (1)$$

The derivation of Eq. 1 also assumes that the singlet and triplet states equilibrate with rates of intersystem crossing ( $k_{ST}$  and  $k_{TS}$ ) that are much larger than the rate constants leading to individual products.<sup>5</sup> In agreement with Eq. 1,  $P_T / P_S$  remains linear in the presence of competing *bimolecular* spin state specific reactions such as the controversial reaction with methanol,<sup>10</sup> the possible formation of ylids<sup>11</sup> or reaction with hydrocarbon solvents<sup>12</sup> (products from the latter two were not observed). The linear dependence of the product ratio with solvent polarity agrees with direct picosecond laser-induced-fluorescence measurements by Eisenthal *et al.* who first found the dependence of  $k_{ST}$  on the polarity of the medium as given by its  $E_T(30)$  values.<sup>7,13</sup> This effect results in a decrease of the equilibrium constant, defined as  $K_{ST} = k_{ST} / k_{TS}$ , and is presumed to come from a relative stabilization of the zwitterionic singlet state.

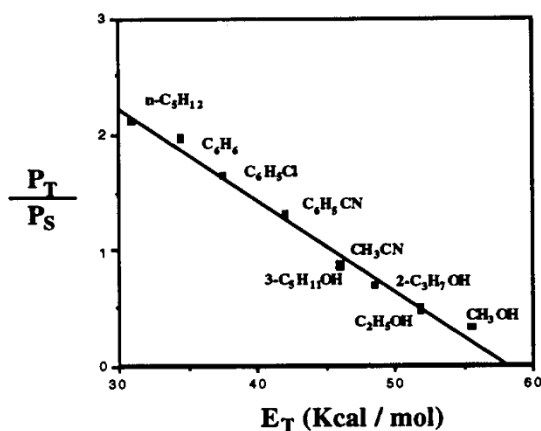


Figure 1. Effect of solvent polarity as given by  $E_T(30)$  on the ratio of triplet to singlet products from 1,2-diphenyl-1-butylidene.

The results in Figure 1 indicate that spin state equilibration is fast relative to reaction even in pure alcohol solvents, suggesting either very fast intersystem crossing rates, or reaction rates that are lower than diffusion control.<sup>5</sup> Although the yields of insertion products **6** and **7** in alcohol solvents increase in the order observed with diarylcarbenes<sup>10c</sup> and strongly support a spin state specific reaction, our results do not distinguish the detailed mechanism of reaction via protonation or ylide formation.<sup>14</sup> Our results, however, agree with observations in MeOD indicating that formation of olefins following carbene protonation and elimination represents a relatively minor pathway (~10%).<sup>14a</sup> It is interesting to point out that the conditions of the Bethel mechanism seem to be fully satisfied in solvent systems where no changes in polarity occur as a function of composition (e.g., MeCN and 3-PentOH). The excellent correlation with Eq. 1 suggests that reactions involving the excited state diazo compound, which have been postulated with several related compounds, are unlikely, unless rather special kinetic circumstances may be satisfied.<sup>11c,15</sup>

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