

## Dimesitylcarbene: The Distinct Chemistries of its Singlet and Triplet States

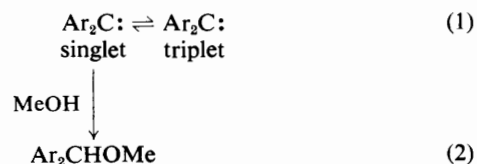
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Dimesitylcarbene is unique amongst the diarylcarbenes thus far investigated since its triplet state cannot readily convert into the singlet state.

The singlet states of diarylcarbenes are thought to insert into the O-H bonds of alcohols and to add stereospecifically to olefins. By contrast, their triplet ground states are thought to be efficient hydrogen abstracting agents and are believed to add non-stereospecifically to olefins.<sup>1-12</sup>

The experimental data supporting these hypotheses are equivocal. For example, optical absorption spectra due to the triplet states of diphenylcarbene,<sup>5,8,13</sup> fluorenylidene,<sup>11,12</sup> and 1-naphthylcarbene<sup>14</sup> are all quenched by methanol. To explain these results, investigators have suggested that the triplet and singlet states are in thermal equilibrium, reactions (1) and (2). This description of the mechanism rests on the assumption that it is the spin-state of the carbene which controls its mode of reaction. However, the experimental observations can simply be interpreted in terms of a direct reaction between the triplet state and alcohol.<sup>4</sup> Clearly, this paradox would be resolved to some extent if diarylcarbenes could be discovered



where the triplet state carried out a chemistry which was completely distinct from that of the singlet, and hence, which reacted without conversion into the singlet state. In this work we have developed the observation<sup>15</sup> that dimesitylcarbene, in sharp contrast to other diarylcarbenes, did not react with its parent diazo compound to give azine, reaction (3), but dimerized to give olefin, reaction (4). This result was explained<sup>15</sup> by proposing that the triplet ground-state<sup>16</sup> could not convert into the singlet state so that reaction with the singlet diazo compound could not take place, *cf.* reactions

