

UV LASER PHOTOCHEMISTRY: EVIDENCE FOR "THROUGH-BOND COUPLING" EFFECTS IN THE LIFETIMES OF 2,2-DIMETHYL-1,3-CYCLOPENTADIYL TRIPLET DIRADICALS.

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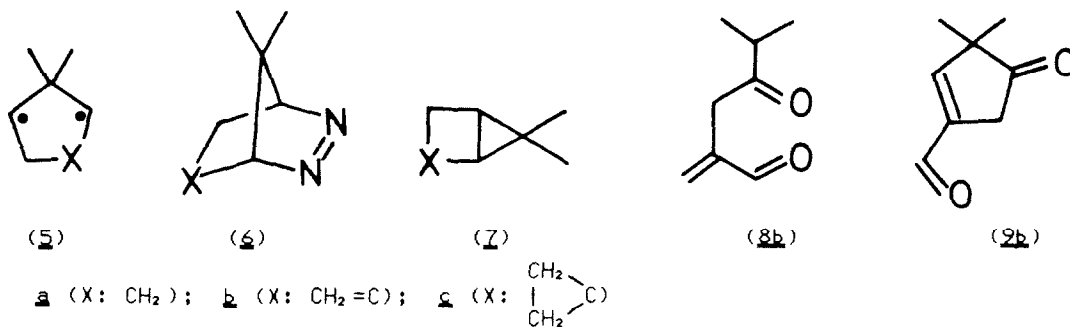
SUMMARY: The 2,2-dimethyl substituted 1,3-diradicals 5a-c possess significantly shorter triplet lifetimes (τ_T) than the parent 1,3-cyclopentadiyl 3, which is being rationalized on the basis of changes in the "through-bond" coupling and thus singlet-triplet energy splitting between the radical sites.

The short lifetime ($\tau_T < 0.1$ ns) of the triplet 1,3-diradical 1 (no trapping



by molecular oxygen) was explained in terms of facile spirocyclopropane ring opening to the allyl-stabilized triplet 1,4-diradical 2 ($\tau_T \sim 10$ ns).^{2*} The fact that this resonance-stabilized diradical is, however, about 10-fold shorter lived than the parent triplet 1,3-cyclopentadiyl (3), for which $\tau_T \sim 100$ ns,^{2b,c} was rationalized on the grounds that 2 is a flexible species (free rotation about the radical site in the side chain) while 3 is a rigid planar structure. Conformational effects were predicted by Salem³ to be important for efficient spin-orbital coupling in intersystem-crossing processes.

On the basis of these lifetime data, one would anticipate that the triplet diradical 4, which possesses allylic stabilization as in 2 and the conformational rigidity as in 3, should be a long lived ($\tau_T > 1000$ ns) entity. Unfortunately, it was so far not possible to prepare the azoalkane precursor to the triplet diradical 4, but the 2,2-dimethyl derivative 5b exhibited in the oxygen trapping method a lifetime much shorter than the flexible diradical 2. To discount steric impediments towards oxygen trapping by gem-dimethyl substitution, the related diradicals 5a and 5c were investigated. The spirocyclopropane moiety



in the latter was to serve as "free radical clock"⁴, which should lead to cyclopropylcarbinyl rearrangement products if $\tau_T > 10$ ns.⁵

All three gem-dimethyl substituted 1,3-diradicals 5a-c possess triplet lifetimes significantly shorter (about at least 100-fold!) than the parent 1,3-cyclopentadiyl (3). We take this as evidence that gem-dimethyl substitution perturbs the singlet-triplet energy gap (ΔE_{ST}) by changes in the "through-bond" coupling between the radical sites in these triplet species. An optimal condition for long-lived triplet ground state 1,3-diradicals is an exact balance between "through bond" and "through space" interactions.⁶ In such cases a relatively large energy gap ($\Delta E_{ST} > 2$ kJ/mol) in favour of its triplet state prevails, so that spin-orbital coupling (ca. 1 kJ/mol) is too weak for efficient inter-system-crossing and consequently a longer lived triplet diradical species results, for example, the parent 1,3-cyclopentadiyl (3).

The unknown azoalkanes 6b,c were prepared by acid-catalyzed cycloaddition of 4,4-dimethyl-4H-pyrazole trimer⁷ with allene and methylenecyclopropane, respectively⁸. The benzophenone-sensitized laser photolyses (Coherent, Innova 18) of azoalkanes 6a-c at 364 nm in CCl₄, n-tetradecane and n-hexadecane under argon atmosphere led exclusively to the corresponding bicyclo[2.1.0]pentanes 7a-c. No spirocyclopropane ring-opened products could be detected for azoalkane 6c. The unknown hydrocarbon products 7b,c were fully characterized.⁸ Moreover, laser photolyses of the azoalkanes 6a-c were conducted according to the above conditions, but under an oxygen atmosphere (10 atm). In the case of azoalkane 6b, the KI/CH₃CO₂H or Fe(SCN)₃ tests⁹ indicated that only traces (too little for isolation) of peroxidic products were present, but the oxygenated products 8b and 9b, presumably derived from the decomposition of intermediary peroxides, were isolated in ca. 11% total yield.⁸ When benzophenone triplet sensitizer was omitted, no such oxygenated products were formed. Only traces (too small for isolation) of oxygenated products were observed in the triplet sensitized photolysis of azoalkane 6c under 10 atm O₂ pressure, while for 6a the exclusive product was the bicyclopentane 7a. Control experiments confirmed that the hydrocarbons 7a-c were stable towards the photolysis conditions in the presence of oxygen.

Steric factors cannot be the dominating feature responsible for the inefficient oxygen trapping of the gem-dimethyl substituted 1,3-diradicals 5a-c compared to the parent 1,3-cyclopentadiyl (3), for which trapping under 10 atm oxygen pressure is ca. 100%!⁹ Had the triplet lifetime of the 1,3-diradical 5c been similar to 3, spirocyclopropane ring-opened products should have been detected in the laser photolysis under argon atmosphere.³ Thus, the lifetime of 5c must be more than 100-fold (upper limit) lower than that of the parent triplet 1,3-cyclopentadiyl (3), but not less than 1000-fold (lower limit) since traces of oxygenated products were detected, i.e. $0.1 \text{ ns} \leq \tau_T(\text{5c}) \leq 1 \text{ ns}$. The lifetime of 5a must be below the diffusion limit, i.e. $\tau_T(\text{5a}) < 0.1 \text{ ns}$, because not even traces of oxygenated products could be detected in the triplet-sensitized photolysis of azoalkane 6a under 10 atm O_2 . For the allyl-stabilized 1,3-diradical 5b we estimate a triplet lifetime of $\tau_T(\text{5b}) \geq 1 \text{ ns}$ lower limit, because appreciable quantities (ca. 11%) of oxygen trapping products were isolated. Unfortunately it was not possible to perform quantitative product studies as a function of $[\text{O}_2]$ in view of the thermal instability of the azoalkane 6b during capillary GC analysis. However, even these crude lifetime data clearly express that gem-dimethyl substitution in the 1,3-diradicals 5a-c leads to at least a 100-fold diminution of the triplet lifetimes compared to the parent 1,3-cyclopentadiyl (3).

What is responsible for this increased intersystem-crossing rate in these diradicals? The reasons must be sought in the gem-dimethyl substitution, a common feature in the diradicals 5a-c in contrast to the parent one 3. Since steric effects seem not to be appreciable (no spirocyclopropane ring-opening in 5c) and since conformational effects are essentially constant (planar structures according to molecular mechanics calculations¹¹), we postulate that the $\Delta E_{S,T}$ energy gap is reduced as a result of perturbations in the balance of "through-bond" and "through-space" couplings. For the parent 1,3-cyclopentadiyl (3) this balance appears optimal since the energy gap is $\Delta E_{S,T} = 3.8 \text{ kJ/mol}$ in favor of a triplet ground state¹². However, for the gem-dimethyl substituted derivatives 5a-c $\Delta E_{S,T}$ must be substantially less if spin-orbital coupling (ca. 1 kJ/mol)³ is to be efficient, in order to account for the fast intersystem-crossing and thus their short triplet lifetimes. In fact, the 1,3-diradicals 5a-c might have singlet ground states. In this context, it should be relevant to probe effects of other geminal substituents between the radical sites on the lifetime of triplet trimethylene diradicals.

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