

The Tri- π -methane Rearrangement: Mechanistic and Exploratory Organic Photochemistry¹

Howard E. Zimmerman* and Vladimír Církva

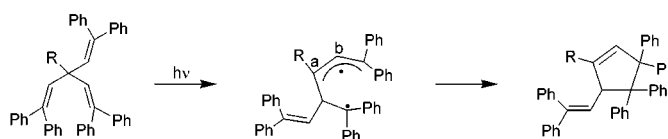
Chemistry Department, University of Wisconsin, Madison, Wisconsin 53706

zimmerman@bert.chem.wisc.edu

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ABSTRACT

THE TRI- π -METHANE REARRANGEMENT

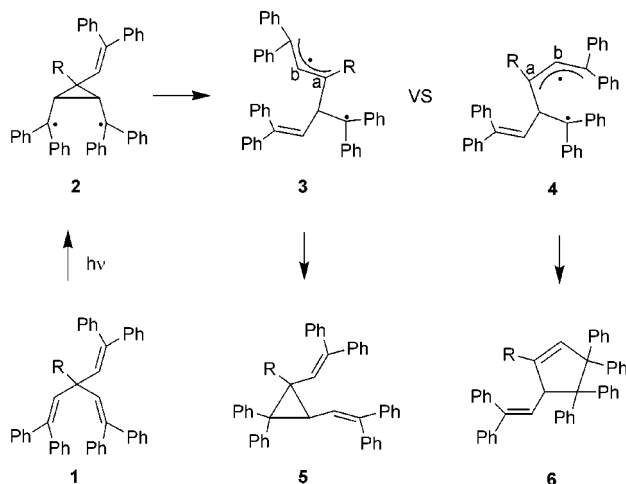


The di- π -methane rearrangement is firmly established as a mode of synthesizing three-membered-ring compounds. We now report the tri- π -methane counterpart.

The di- π -methane rearrangement has become a well-understood organic reaction that is of considerable value in the synthesis of three-membered-ring compounds. We now report the tri- π -methane counterpart. Scheme 1 shows the

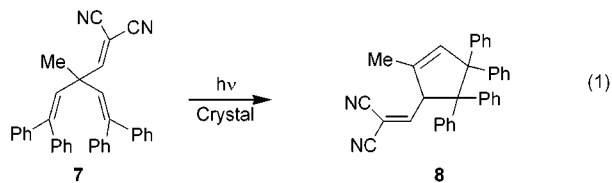
mechanism of the di- π -methane rearrangement and its potential diversion to a tri- π -methane pathway. In this, on excitation, the singlet or triplet bridges to give cyclopropyl dicarbonyl diradical **2**. Opening of this species tends to give transoid (bond a–b) allylic diradical **3** as a consequence of less steric interference. This species closes to afford π -substituted cyclopropane product **5** characteristic of a di- π -methane rearrangement, but closure to form a five-membered ring would result in a trans double bond in that ring. In contrast, if cyclopropyl dicarbonyl diradical opening were to lead to cisoid allylic diradical **4**, closure to tri- π -methane product **6** may compete with 1,3-closure to di- π -methane product **5**. We can document two instances of tri- π -methane rearrangement. In one case we successfully employed crystal lattice photochemistry,² wherein the lattice enforced the cisoid conformation in the cyclopropyl dicarbonyl diradical; note eq 1. The only solution example, curiously, is found in the barrelene to semibullvalene rearrangement, where in the final step of the mechanism symmetry resulted in equal proximity of the two ends of the allylic moiety to the single odd-electron carbon. The consequence was a di- π -methane

Scheme 1. Competition between Di- π -methane and Tri- π -methane Rearrangements. Note That the Allylic Diradical May Be Transoid Above Bond a–b as in **3** or Cisoid as in **4**



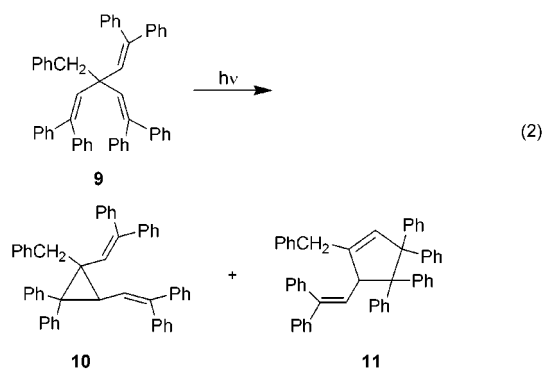
(1) This is Paper 256 of our general series. For paper 255, see: Zimmerman, H. E.; Nesterov, E. E. *Org. Lett.* **2000**, *2*, 1169–1171.

(2) Zimmerman, H. E.; Zuraw, M. J. *J. Am. Chem. Soc.* **1989**, *111*, 7974–7989.



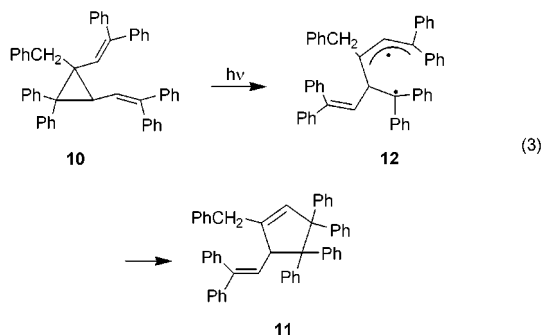
rearrangement which could be construed as arising by two routes—the di- π and the tri- π .³

However, now we report finding a solution tri- π -methane rearrangement, depicted in eq 2. This occurs in competition



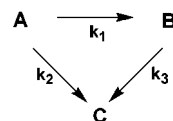
with the di- π -methane rearrangement. On direct irradiation, tris-diphenylvinyl methane **9** led to 52% of tri- π -methane product **11** in addition to the ordinary di- π -methane photoproduct **10**, with both *cis* and *trans* isomers being formed (31 and 17%, respectively).

However, a complication soon became apparent. It was observed that di- π -methane photoproduct **10** rearranged photochemically to afford five-membered-ring isomer **11**. The consequent question then was whether there really was a direct pathway to tri- π -methane product **11** or, instead, just an indirect route via the well-known di- π -methane rearrangement followed by a 1,3-sigmatropic shift, via diradical **12** or its concerted equivalent; note eq 3.



The kinetic situation is depicted in Scheme 2. The question is just how large is the direct rate constant k_2 relative to the constant k_3 for the indirect formation of the five-membered-ring product? It seems that although the kinetics of $A \rightarrow B$

Scheme 2. Kinetic Problem. **A** Represents the Tri- π Reactant, **B** Is the Di- π -methane Three-Membered-Ring Compound, and **C** Is the Tri- π -methane Five-Membered-Ring Photoproduct



$\rightarrow C$ are well-known, the kinetics have not been solved analytically for the situation in Scheme 2. The solution is given^{4a} in eq 4. It needs to be recognized that the three rate

$$B = (k_1 A_0) [e^{-(k_1+k_2)t} - e^{-k_3 t}] / (k_3 - k_1 - k_2) \quad (4)$$

constants, in actuality, are operational values which give the rate at which each process occurs under the photolysis conditions employed. Each constant is proportional to the product of the quantum efficiency of that reaction multiplied by the efficiency of formation of the reacting excited state. Because of differential light absorption, **A** and **B** compete unequally for light. From the operational viewpoint, this is irrelevant, but the relative utilization of the two pathways is a function of the reaction conditions.

As a second mode of excitation, it was of interest to use singlet sensitization by naphthalene, since in this case energy transfer rather than relative light absorption is a factor.

Fitting the expression for the concentration of **B** as a function of time, as given in eq 4, to the experimentally obtained^{4b} values leads to relative values for k_1 , k_2 , and k_3 .

Table 1 gives the relative rate constants obtained for direct

Table 1. Relative Rate Constants

sensitizer	k_1	k_2	k_3
none	0.223	0.143	0.024
naphthalene	0.099	0.028	0.014

irradiation and for naphthalene sensitization. Under both conditions the direct tri- π -methane pathway dominates relative to the indirect route. For direct irradiation there is a factor of 6 while in the naphthalene-sensitized runs there is a factor of 2. The sources of the differences in utilization of the two pathways seem likely to be greater light absorption by the tri- π -methane reactant in the direct irradiations and a potentially lower efficiency of singlet energy transfer to the di- π -methane three-membered-ring photoproduct in the sensitized runs.

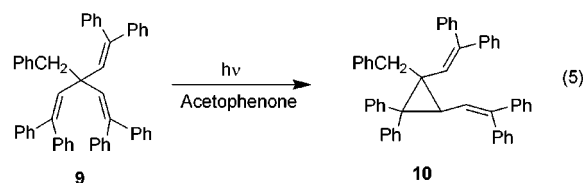
Hence the direct route, the tri- π -methane rearrangement, is dominant and the indirect, two-step mechanism plays a lesser role.

(3) (a) Zimmerman, Binkley, R. W.; Givens, R. S.; Sherwin, M. A. *J. Am. Chem. Soc.* **1967**, *89*, 3932–3933. (b) There is a reaction utilizing all three π -bonds in a different way in a barrelene derivative; note Pokkuluri, P. R.; Scheffer, J. R.; Trotter, J. *J. Am. Chem. Soc.* **1990**, *112*, 3676–3677.

(4) (a) The kinetic derivation is given in the Supporting Information. (b) The details of curve fitting and the programming involved will be described in our full paper.

Additionally, from the preparative viewpoint, at extended photolysis times, the five-membered-ring photoproduct dominates as a consequence of both routes affording this product.

Another interesting facet is the multiplicity dependence. On acetophenone sensitization, tri- π -methane reactant **9** afforded only di- π -methane rearrangement (eq 5). One

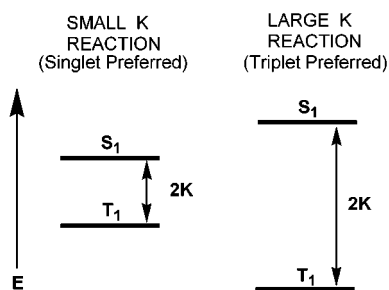


interpretation is that triplet cyclopropyl dicarbonyl diradical **2T** opens selectively to transoid allylic carbonyl diradical **3** while singlet cyclopropyl dicarbonyl diradical **2S** opens to afford cisoid allylic carbonyl diradical **4**. Multiplicity dependence in organic photochemistry is common, and a theoretical basis has been provided⁵ in terms of “exchange integral control”.

The exchange integral K in SCF-MO theory gives a measure of the energetic splitting between S_1 and T_1 . The generalization has been suggested that triplets prefer “large K ” reaction routes while singlets prefer “small K ” reactions. Scheme 3 shows the source of the preference, namely each reacting excited state selecting the lower energy of two

(5) (a) Zimmerman, H. E.; Penn, J. H.; Johnson, M. R. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 2021–2025. (b) Zimmerman, H. E.; Armesto, D.; Amezua, M. G.; Gannett, T. P.; Johnson, R. P. *J. Am. Chem. Soc.* **1979**, *101*, 6367–6383. (c) Zimmerman, H. E.; Factor, R. E. *Tetrahedron* **1981**, *37*, Supplement 1, 125–141.

Scheme 3. Multiplicity Dependence



pathways. Relevant to the present reactions, homopolar diradicals have been categorized as a “large K ” type with K increasing as the odd-electron centers become more separated as in the transoid diradicals.

In conclusion, it now is apparent that a five-membered-ring counterpart, the tri- π -methane rearrangement, of the established di- π -methane rearrangement is present. We are pursuing the reaction to determine its generality and mechanisms.

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Supporting Information Available: The derivation of eq 4 is given along with information on some of the details of irradiation wavelength. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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