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THE DI-π-METHANE REARRANGEMENT. INTERESTING OBSERVATIONS FROM THE PHOTOCHEMISTRY OF 1,3-DIMETHYL-3-(β-STYRYL)CYCLOHEXENE.

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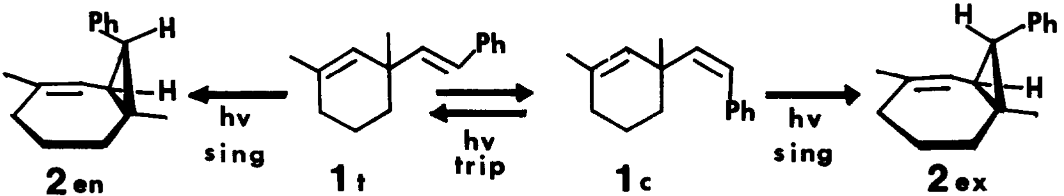
Results from previous studies pertaining to the stereochemical course of the singlet and triplet di-π-methane rearrangement of unconstrained 1,4-dienes have been obtained and discussed in terms of orbital topology and least motion control.[1-3] In more recent investigations,[4] we have shown how structure influences the stereochemistry of the singlet reaction and efficiency of the triplet process. These observations, when combined, indicate that the singlet rearrangement of 1,4-dienes to vinylcyclopropanes is concerted and possesses two possible, low energy transition states, having the syn and anti-disrotatory orbital geometries. In addition, an interesting interdependence of di-π-methane structure, excited state multiplicity and reaction efficiency has been noted.[3] Zimmerman and Pratt[2a] have offered a rationale for the lack of di-π-methane reactivity of triplet acyclic 1,4-dienes in terms of the competitive and efficient free-rotor deactivation from bridged cyclopropyldicarbinyl triplet diradicals.

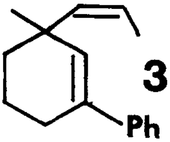
Our continuing interests in this area of photochemistry are focused on these aspects of the rearrangement. The study of the photochemistry of the isomeric 1,3-dimethyl-3-(β-styryl)cyclohexenes (**1c** and **1t**), reported below, has yielded results which pertain to the influence of di-π-methane conformation on the singlet rearrangement stereochemistry, and the nature of the structure-multiplicity-rearrangement efficiency relationship.

The styrylcyclohexenes, **1c** and **1t**, required for this study were prepared from 2-methylcyclohexanone by the general route we have employed earlier.[1] The isomeric dienes, obtained from a final Wittig reaction of benzylidene triphenylphosphorane with 1,3-dimethylcyclohexene-3-carboxaldehyde, were cleanly separated by silica gel chromatography. Structrual and stereochemical assignments to the pure isomers (>96%) were made on the basis of spectral and analytical data.[5] Direct irradiation (3.6 mM, acetonitrile, corex filter) of **1c** and **1t**, independently, gave rearrangement to two photoproducts along with cis-trans isomerization to a mixture of the stereoisomeric dienes. The relative ratio of the two rearrangement products, identified (*vide infra*) as the exo- and endo-isomers of 3,7-dimethyl-8-phenylbicyclo[5.1.0]oct-2-enes (2ex and 2en), was found to be a sensitive function of irradiation time (28% recovered 1c, 7% 1t, 31% 2en and 29% 2ex for 45 min from 1c; 21% recovered 1t, 9% 1c, 32% 2en and 18% 2ex for 45 min from 1t),[6] a result of rapid cis-trans isomerization of the starting materials. In order to determine if the direct irradiation reactions of 1c and 1t are stereoselective, low conversion irradiations were conducted using flint glass filtered light. Interestingly, at 25% conversion of 1c the exo to endo product ratio was 10:2.6,[7] while at up to 50% conversion of 1t only the endo product is present in the reaction mixture. Triplet sensitized photolyses of 1c and 1t, using a host of triplet sensitizers[8] of triplet energy >57 kcal/mol led only to cis-trans isomerization of the reactants.

Assignment of structure and stereochemistry to both of the photoproducts, 2ex and 2en, was made on the basis of their analytical and spectral properties. The relative chemical shifts of the C-7 methyl and C-1 methine protons were of particular utility.[8] In 2ex the phenyl substituent at C-8 should exist predominantly in a conformation having the plane of aromatic ring tilted to the C-1 proton side of the bisected geometry in order to minimize the nonbonded interactions between phenyl and methyl. As a result the C-1 proton is located in the deshielding region of the aromatic ring and has the unusual chemical shift of 3.47 ppm. This effect also explains the relative chemical shifts of 0.79 and 1.25 ppm for the C-7 methyl protons in 2ex and 2en, respectively.[8]



The triplet photochemistry of 1c and 1t, in comparison to that of a close structural analog, 1-phenyl-3-methyl-3-(1-*cis*-propenyl)cyclohexene (3),[1] which undergoes di-π-methane rearrangement from its triplet, seems particularly interesting in light of earlier observations on the nature of free-rotor deactivation of 1,4-diene systems. Since the triplets of both 1 and 3 appear equally capable of forming their corresponding bridged cyclopropyldicarbinyl diradicals 4 and 5 and, yet display differing reactivities, free-rotor deactivation from this type of triplet diradical does not appear to account for the lack of triplet rearrangement of acyclic 1,4-dienes. Thus, the important feature in controlling the di-π-methane triplet reactivity of 1,4-dienes is perhaps only the structural contraints placed on the π-chromophore of lowest triplet energy.[9] Accordingly, when the lowest triplet energy chromophore is unconstrained, di-π-methane rearrangement is inefficient



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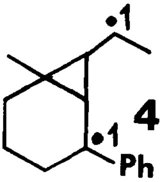

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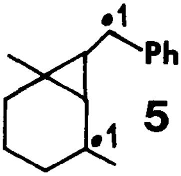

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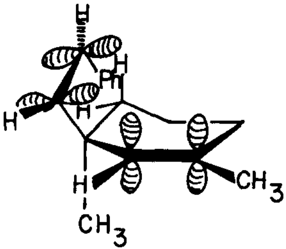
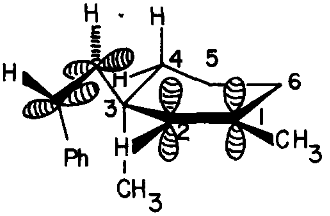
due to the rapid and efficient free-rotor deactivation by π-bond isomerization. The results and conclusions nicely parallel those of Hixson[10] on aromatic analogs.

Another interesting aspect of the observations presented above concerns the stereoselectivities of the singlet reactions of 1c and 1t, which yield 2ex and 2en, respectively, and their interpretation in terms of the effect of 1,4-diene conformation on the stereochemical mode chosen for the reaction. Although much is known about the effect of conformation on the stereochemistry of the cyclohexadiene-hexatriene photointerconversion,[11] little attention has been given to conformational control of the di-π-methane reaction. In 1c, for example, two low energy conformations (s-cis (1cc) and s-trans (1ct)), which place the styryl moiety in correct alignment for migration[12] of the endocyclic vinyl moiety, are possible. Clearly, the lower energy of the two is 1cc, due to its minimization of repulsive interactions between the C-4 axial hydrogen and the styryl moiety



1ct



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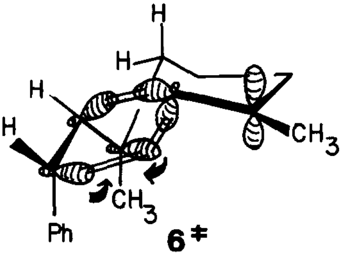

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Reaction of this conformer[13] by a concerted anti-disrotatory pathway would be prevented by its conversion to a high energy trans-fused bicyclo[5.1.0]hexane system. Additionally, anti- and syn-disrotatory modes in reaction of the s-trans conformer, 1ct, would generate 2en and another highly strained bicyclic octene, respectively. Thus, the selective formation of 2ex from 1c appears to indicate that the reaction occurs predominantly from the lower energy conformer, 1cc, and through the syn-disrotatory transition state orbital geometry, 6.[‡] A similar analysis of the reaction of the trans-isomer 1t shows that rearrangement to 2en is again from the s-cis conformation and via the syn-disrotatory mode. These observations demonstrate that 1,4-diene conformation is important in controlling the stereochemistry of the di-π-methane rearrangement. Also, they suggest that the inherent energy differences between the syn- and anti-disrotatory concerted modes must be small enough such that interactions, which control conformation, are of overriding importance.

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(3) For a general review of these aspects of the di-π-methane rearrangement see, S. S. Hixson, P. S. Mariano and H. E. Zimmerman, *Chem. Rev.*, **73**, 531 (1973).

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(5) The vinyl regions in the proton nmr's of **1c** (AB quartet, J-13Hz) and **1t** (AB quartet, J=16Hz) along with uv spectral properties easily establish the stereochemistries of these dienes.

(6) Analyses were conducted by glc using a 1.5% OV-101 packed column at 140° and phenanthrene as an internal standard.

(7) Rapid isomerization of **1c** to **1t** would account for the small quantity of **2en** in the reaction mixture since, with flint glass, the trans-isomer is more strongly absorbing.

(8) Nmr spectroscopic observations on phenylcyclopropanes by Closs and Moss, are fully in accord with our observations; G. L. Closs and R. A. Moss, *J. Amer. Chem. Soc.*, **86**, 4042 (1964).

(9) We have shown previously[4] that one other factor controlling triplet di-π-methane reactivity is the prevention of collapse of cyclopropyldicarbinyl diradicals to vinylcyclopropanes by structural constraints.

(10) S. S. Hixson and J. C. Tausta, *Tetrahedron Lett.*, 2007 (1974).

(11) *Cf.* W. G. Dauben, M. S. Kellog, J. I. Seeman, N. D. Vietmeyer and P. H. Wendschuh, *Pure Appl. Chem.*, **33**, 197 (1973); J. E. Baldwin and S. M. Krueger, *J. Amer. Chem. Soc.*, **91**, 6444 (1969); and C. W. spangler and R. P. Hennis, *Chem. Commun.*, 24 (1972).

(12) Migration of this bond is expected on the basis of early observations on the regiochemistry of the general reaction; H. E. Zimmerman and A. C. Pratt, *J. Amer. Chem. Soc.*, **92**, 6259 (1970)

(13) If reaction from the singlet excited states of **1c** and **1t** is faster than conformational interconversion of the s-cis and s-trans conformers, then the ground state populations, relative absorption characteristics and quantum yields for reaction of both conformers will be important in determining the product ratio. If not, ground state population along with relative absorption characteristics of the two conformers will not be influential. Thus, in the latter situation the well-known Curtin-Hammett principle should operate.