Rapid Intramolecular Addition Reactions of Triplet Arylcarbenes

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Abstract: Triplet arylcarbenes react intramolecularly with unsaturated ortho substituents, while singlet arylcarbenes react preferentially with solvent methanol. Rotation about the exocyclic C–CH bond is necessary in order for cycloaddition of the singlet carbene to occur. Quantum chemical calculations show that the barrier to such a rotation is relatively high. By contrast, little or no rotation about the exocyclic C–CH bond is required for the triplet to react, and the barrier to rotation is quite low.

The chemistry of many arylcarbenes is reasonably interpreted in terms of rapid equilibration of the singlet and triplet states.[1] The reactions of arylcarbenes with olefins are largely stereospecific,[2–5] even though the ground states of arylcarbenes are triplets.[6] This implies that the singlets have much higher reactivities than the triplet states. We have found that there are dramatic changes in relative reactivities for *intramolecular* reactions of arylcarbenes with double bonds. These results have prompted ab initio molecular orbital calculations on the rotational barriers and reaction modes of the relevant intermediates.

Experimental Results

On photolysis of the tosylhydrazone sodium salts **1**[7–9] in methanol, intramolecular addition to the double bond and intermolecular O–H insertion of the carbenes **5** occurred competitively (Scheme I; for simplicity, only the *E* isomers are shown).[10] The results are summarized in Table I. Direct irradiation afforded >80% of the benzyl ether **4a**, but on sensitization the fraction of the ether decreased to ca. 10%. Cycloaddition of the *E* and *Z* isomers of **5a** was moderately stereoselective even in the direct photolyses of (*E*)-**1a** and (*Z*)-**1a**, but on sensitization the stereoisomeric precursors gave identical mixtures of cycloadducts **6a** (exo/endo 45:55).[11] The same *exo*-**6a**/*endo*-**6a** ratio resulted from sensitized photolyses of the epimeric pyrazolines **3a**, suggesting full rotational equilibration of a 1,3-diradical intermediate. Very similar results were obtained with the all-carbon analogues **1b**, **2b**, and **3b** (Table I).

Discussion

These data imply that the intramolecular cycloaddition reactions of the triplet arylcarbenes ^{3}**5** proceed more rapidly than triplet → singlet interconversion ($k_T > k_{TS}$). These observations stand in contrast to the intermolecular case, where $k_T < k_{TS}$, as described above. Furthermore, the relatively rapid intramolecular triplet cycloadditions contrast to the rather inefficient intramolecular cycloadditions of the singlet arylcarbenes ^{1}**5**[12] and additions of benzyl radicals. The cyclization of 2-allylbenzyl radicals (k_{250} = 0.2 s^{-1}, E_a = 16.3 kcal/mol, log A = 11.1)[14] is strongly retarded as compared to the cyclization of 5-hexenyl radicals (k_{250} = 2 × 10^5 s^{-1}, E_a = 6.9 kcal/mol, log A = 10.4).[15]

Rotation about the bond connecting the sp^2-hybridized carbon of the benzyl radical to the ring must occur to achieve interaction of the vacant p orbital with the π bond. Consequently, a substantial fraction of the benzyl resonance stabilization must be sacrificed in the transition state of the intramolecular addition. Analogous considerations apply to benzyl cations and singlet arylcarbenes.[16] We have recently rationalized the differences in intramolecular reactivities of these species in terms of rotational barriers.[17]

However, no analogous effect is observed for triplet arylcarbenes whose reaction rates with alkenes appear to be strongly enhanced by intramolecularity. Two interpretations are conceivable: (1) the rotational barrier for triplet phenylcarbene is much smaller
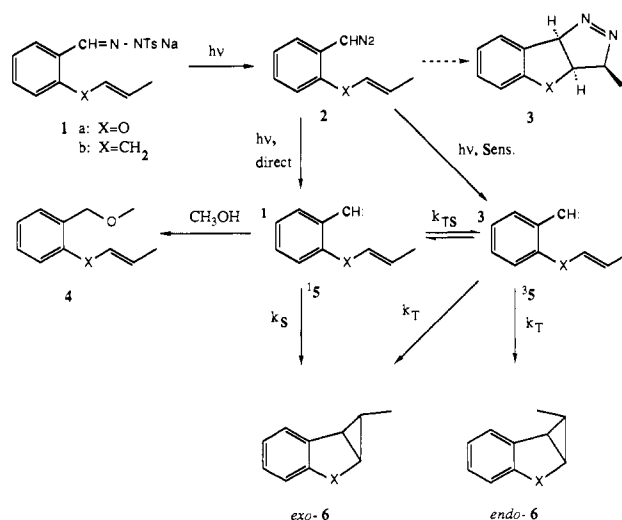
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Scheme I

Table I. Relative Yields of Products in Direct and Benzophenone-Sensitized Photolyses of **1** in Methanol

precursor	[Ph$_2$C=O], M	4	exo-6	endo-6
(*E*)-**1a**	0	83.7	11.0	5.3
(*E*)-**1a**	0.25	11.2	40.2	48.6
(*Z*)-**1a**	0	89.0	3.6	7.1
(*Z*)-**1a**	0.25	12.8	39.0	48.2
(*E*)-**1b**	0	69.8	27.3	2.9
(*E*)-**1b**	0.25	5.5	57.0	37.5
(*Z*)-**1b**	0	77.1	5.7	17.2
(*Z*)-**1b**	0.25	7.6	51.8	40.6

than that for the singlet so that the transition state of the former is achieved more readily or (2) the reaction proceeds with no

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(7) Isomerization of 2-allyloxybenzaldehyde with PdCl$_2$(PhCN)$_2$ (toluene, reflux) afforded an *E*/*Z* mixture of 2-(1-propenyloxy)benzaldehyde, separable by HPLC.
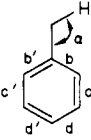
(8) The 2-(2-buten-1-yl)benzaldehydes and (*E*)-**1b** have been mentioned without reference to their synthesis.[9] Our route involved reactions of the Grignard reagent derived from O-protected 2-bromobenzyl alcohol with (*E*)-1-bromo-2-butene and 1-bromo-2-butyne, respectively.

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Table II. HF/3-21G-Optimized C–C Bond Lengths (Å) of Singlet and Triplet Phenylcarbene

species	a	b(b′)	c(c′)	d(d′)	α, deg
		S_1 Carbene			
planar	1.462	1.400 (1.398)	1.378 (1.381)	1.389 (1.385)	108
perpendicular	1.478	1.392	1.382	1.384	109
		T_0 Carbene			
planar	1.400	1.426 (1.429)	1.390 (1.390)	1.403 (1.402)	133
perpendicular	1.422	1.421	1.392	1.400	140

significant rotation but utilizes the half-filled σ orbital in the plane of the ring for attack on the neighboring π bond. Both alternatives have been explored here by ab initio molecular orbital calculations.[18]

Theoretical Results

We first explored the relative rotational barriers of singlet and triplet phenylcarbene. Radom et al.[19] previously calculated the barrier to rotation in T_0 and S_1 phenylcarbene. Ab initio molecular orbital calculations were performed with STO-3G-optimized geometries. The barriers found were 3.9 and 2.7 kcal/mol for the singlet and triplet, respectively.[19] We carried out geometry optimizations, with the 3-21G basis set, and the predicted rotational barriers for the singlet and triplet are 11.2 and 5.7 kcal/mol, respectively, at this theoretical level. The salient features of the optimized geometries of the two species are given in Table II. The rather large differences between our calculated rotational values and the ones previously reported[19] are due to the differences in the optimized geometries and energetic differences for different basis sets. Similar geometry differences occur in singlet vinylmethylene calculations.[20]

A comparison of the planar conformers shows that bond a is considerably longer in the singlet carbene. The value found in the singlet (1.46 Å) is similar to that (1.48 Å) found in polyenes for sp^2–sp^2 single bonds.[21] In the planar triplet carbene, on the other hand, the bond length is 1.40 Å, indicating substantial conjugation between the aromatic ring π system and the exocyclic
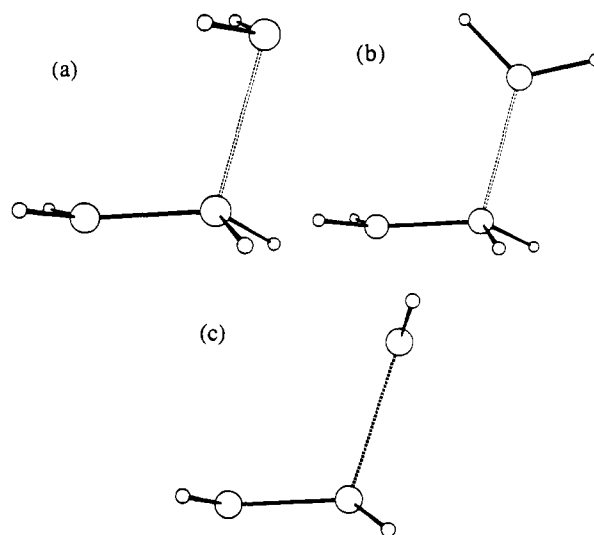
(10) Cyclization of the intermediate diazo compounds **2** to give the pyrazolines **3** proceeds slowly at room temperature.[9] A contribution of **3** to the formation of **6** has been excluded: (a) irradiation of **2** at >400 nm leaves **3** intact; (b) on irradiation of **1**, diazo compound **2** is generated and immediately photolyzed. In representative cases, procedures (a) and (b) gave identical **4:6** ratios.

(11) In order to avoid stereoisomerization of **1, 2,** and **6**, the sensitized photolyses of **1** were stopped after 2 min. Reisolation of unreacted tosylhydrazone and acid-catalyzed conversion of unreacted diazo compounds **2** and **4** confirmed the stereochemical integrity of the precursors. Sensitized exo/endo isomerization of **6** proceeded rather slowly even in the absence of **2**.

(12) Ratios of stereospecific intramolecular addition to intermolecular O–H insertion are the following: (Z)-**5a**, 0.037; (E)-**5a**, 0.080; (Z)-**5b**, 0.17; (E)-**5b**, 0.34. For phenylcarbene with 1 M 2-butene in methanol, the analogous intermolecular competition factor is ca. 0.2. Thus, the effective molarities (EM's) for the intramolecular addition reactions of [1]**5** range from ca. 0.2 to 2. Much higher EM's (10^3–10^8) are observed for the unbiased formation of five-membered rings.[13]

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Figure 1. 3-21G structures of the attack of triplet methylene on ethylene: (a) p orbital attack; (b and c) in-plane σ-orbital attack.

methine carbon. Nonetheless, the rotational barrier of the singlet is nearly double that of the triplet carbene. This is because an analogous interaction also exists in the perpendicular conformer of the triplet carbene, due to overlap between the ring π electrons and the half-filled hybrid orbital, as indicated by the relatively short bond a length of 1.422 Å in the perpendicular form. This type of π bonding is much less significant in the perpendicular conformer of singlet phenylcarbene, and it is not present in other benzylic systems;[22] in the singlet carbene, the exocyclic bond is 1.478 Å long. Thus, the low rotational barrier in the triplet is the consequence of the stabilization of the perpendicular conformer due to π delocalization.

This substantial conjugation suggests that perpendicular triplet phenylcarbene might be a local energy minimum, rather than a transition state for the interconversion of two planar conformers. However, we calculated the perpendicular conformer to be 0.2 kcal/mol less stable than the rotamer obtained by a 10° rotation about the exocyclic carbon–carbon bond to give a species with torsional angle equal to 80°. This indicates that perpendicular triplet phenylcarbene is truly a maximum with respect to the internal rotation. A similar result was found for singlet phenylcarbene. Here, we have found a difference of 0.3 kcal/mol between the perpendicular conformer and the rotamer in which the dihedral angle H–C(exocyclic)–C(ring)–C is equal to 80°.

The results of the triplet carbene calculations agree with the conclusions of a recent high-level study by Pacansky and Yoshimine[23a] on the related vinylmethylenes, but the singlet vinylmethylene was found to have a nonplanar geometry ($\omega_{H-C-C-C}$ = 147°).[23b]

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(22) Dorigo, A. E.; Houk, K. N., unpublished results.

(23) (a) Honjou, N.; Pacansky, J.; Yoshimine, M. *J. Am. Chem. Soc.* **1985**, *107*, 5332. (b) Pacansky, J.; Yoshimine, M.; Honjou, N., private communication.

The greater ease of rotation about the exocyclic C–C bond in triplet phenylcarbene implies that a reactive conformation can be achieved more readily than in the case of the singlet, which is in agreement with the observed relative intramolecular reactivities. Moreover, reaction of the triplet might take place with no rotation about the bond to the carbenic carbon. The minimum energy planar conformation also has an odd electron in the plane of the ring, suitably oriented for reaction with a neighboring double bond. In order to attempt to determine the relative ease of the two modes of attack between the two cases, we performed model HF/STO-3G and HF/3-21G calculations of the attack of triplet methylene on ethene.[24-26]   In these calculations two modes of approach were considered (parts a and b of Figure 1). In the first case, the methylene p orbital is attacking the double bond, whereas the second type of approach involves attack by the σ orbital, which lies in the methylene plane. The C···C forming bond was fixed at a distance of 2.0 Å, typical for C–C partially formed bonds in transition structures. All other parameters were optimized with a C_s symmetry constraint in both cases. Both sets of calculations suggest that attack by the in-plane orbital, as in Figure 1b, is significantly preferred (by 16.7 kcal/mol at the HF/STO-3G level and by 21.6 kcal/mol at the HF/3-21G level). The related

structure, Figure 1c, is only 0.3 kcal/mol higher in energy. Thus, the minimum energy conformation of **5** has the exocyclic CH group already suitably oriented for intramolecular insertion in the double bond. This model is obviously somewhat crude, but the qualitative conclusions should persist even if a higher level of theory were employed. The geometry of approach implied in Figure 1b resembles the transition structure, which Fueno and co-workers found from ab initio molecular orbital calculations (MRDCI/4-31G**//HF/4-31G**) for the analogous addition of triplet nitrene to ethylene.[27]

Conclusion

The calculations suggest that the rapid cycloaddition of a triplet methylene to a neighboring p bond results from the presence of the half-occupied in-plane σ orbital, which directly attacks the p system and also makes rotation out-of-plane much easier than for a singlet arylcarbene. More extensive comparison of rotational barriers in aromatic reactive intermediates will be reported in due course.[28]

Registry No. (*E*)-**1a**, 117607-41-7; (*Z*)-**1a**, 117607-42-8; (*E*)-**1b**, 74346-41-1; (*Z*)-**1b**, 117607-43-9; **3a** (isomer 1), 117607-53-1; **3a** (isomer 2), 117677-91-5; (*E*)-**4a**, 117607-48-4; (*Z*)-**4a**, 117607-49-5; (*E*)-**4b**, 117607-50-8; (*Z*)-**4b**, 117607-51-9; (*E*)-**5a**, 117607-44-0; (*Z*)-**5a**, 117607-45-1; (*E*)-**5b**, 117607-46-2; (*Z*)-**5b**, 117607-47-3; *exo*-**6a**, 117607-52-0; *endo*-**6a**, 117706-80-6; *exo*-**6b**, 63949-51-9; *endo*-**6b**, 30021-35-3; phenylcarbene, 3101-08-4; methylene, 2465-56-7; ethene, 74-85-1.

(24) No ab initio computational study of the addition of triplet methylene to ethylene has been reported in the literature. Dewar and co-workers[25] used the semiempirical MINDO/2 procedure with an extension of the "half-electron" method[26] for calculations of triplet states. These calculations suggest that the initial approach of methylene to the alkene takes place symmetrically and that the carbene subsequently veers to one side of the double bond and attacks one of the ethylene carbon atoms to form the diradical. In the transition state, the carbon atom of the methylene moiety is at a distance of 2.1 Å from the closer ethylene carbon and 2.3 Å away from the farther one.

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Electrolytes in Charged Micropores

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Abstract: We have studied a simple electrolyte enclosed within a charged cylindrical capillary and in thermodynamic equilibrium with an external solution, using the grand canonical Monte Carlo technique. Ionic correlation functions and mean activity coefficients have been evaluated at several charge densities and concentrations, and for several choices of capillary radius. Comparison with the results of the Poisson–Boltzmann equation is presented for all these quantities. The latter approximation is, as noticed previously, reasonably accurate if 1:1 electrolyte is present in a capillary. Important qualitative and quantitative differences are noticed for 2:2 simple electrolyte, even for moderate surface charge densities. Due to the interionic correlations, there is much more simple electrolyte present in the capillary than predicted by the mean-field theory. This affects the distribution of counterions and especially the mean activity coefficient of the electrolyte. Our simulations show that, at low charge densities, the mean activity coefficient of the electrolyte decreases with decreasing radius of the pore, while the Poisson–Boltzmann equation predicts the opposite behavior.

1. Introduction

The problem of adsorption of solute in liquid-filled pores has a number of important applications and is now being investigated intensively.[1,2]   In this work, the structural and thermodynamic properties of ionic solution enclosed within the charged micropores are studied by two different theoretical methods. A number of electrochemical systems can be modeled as a cylindrical capillary with a charge distributed on the inner surface, immersed in an electrolyte solution. This model has been used to explain electrokinetic phenomena,[3-11] to describe ion selectivity in certain types of ion-exchange resins,[12] and to evaluate the activity of electrolyte within a capillary,[13-17] which may be useful in engineering ap-

plications. In all these studies (except ref 16) the Poisson–Boltzmann equation (sometimes in a linearized form) has been

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