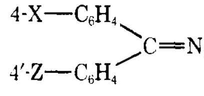
Orbital Preferences in Generation of Singlet Arylcarbenes

Sir:

We wish to report the effects of para substituents on (a) the rates of unimolecular decomposition of diphenyldiazomethanes (**1**) to the corresponding carbenes[1] (**2**) and (b) the structures of singlet para-substituted phenylcarbenes (**3**) as determined by MINDO/3 methods.[2] These investigations reveal the significance of substituent-induced conformational effects in the generation of **2** and in **3**, and suggest that various para-substituted phenyl groups discriminate between the orbitals of a singlet carbene.


$4\text{-X—C}_6\text{H}_4\text{(4'-Z—C}_6\text{H}_4\text{)C=N}_2$

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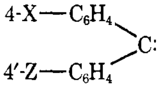
$4\text{-X—C}_6\text{H}_4\text{(4'-Z—C}_6\text{H}_4\text{)C:}$

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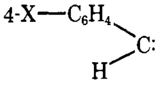
$4\text{-X—C}_6\text{H}_4\text{(H)C:}$

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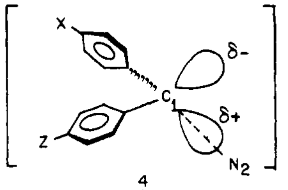
The unimolecular rate coefficients for thermolyses of **1** in water (2.18 M)/1,2-dimethoxyethane (Table I)[3] indicate that incorporation of any single para substituent, be it electron-donating or electron-withdrawing, facilitates decomposition relative to diphenyldiazomethane. Similarly, 4-methyl-4'-nitrodiphenyldiazomethane, **1**, containing an electron-donor (X = CH_3) and an electron-withdrawing substituent (Z = NO_2), decays more rapidly than either of the corresponding monosubstituted (CH_3 or NO_2) derivatives. Symmetrically para-disubstituted diphenyldiazomethanes (**1**; X = Z = CH_3, NO_2), however, thermolyze more slowly than their monosubstituted analogues.

These observations raze transition states for decomposition of **1** with stereochemistries in which the aryl groups are effectively coplanar as might be inferred from previous evidence for symmetrically disubstituted systems (**1**; X = Z = H, Cl, CH_3, OCH_3).[1d] The results may be rationalized, however, with a decomposition mechanism in which there is extensive interaction of each phenyl group with an electron-deficient or an electron-rich orbital developing within a tetrahedral-like transition state (**4**). The mechanistic process demands extensive cleavage of the carbon–nitrogen bond in **4** and is consistent with the activation parameters ($\Delta H^{\ddagger}$ = 27.2 ± 0.2 kcal/mol, $\Delta S^{\ddagger}$ = 0.0 ± 0.4 eu) reported for thermolysis of diphenyldiazomethane in acetonitrile at 85 °C.[1a]

Table I. Rate Coefficients, k_1, for Unimolecular Decomposition of Para-Substituted Diphenyldiazomethanes (**1**)

Substituent	10^3k_1[a] (min^{-1})	Substituent	10^3k_1[a] (min^{-1})
H	1.55 ± 0.06[b]	4-CN	3.90 ± 0.12[b]
4-Cl	2.15 ± 0.07	4-NO_2	6.68 ± 0.28
4-CH_3	2.56 ± 0.16	4-CH_3/4'-CH_3	2.05 ± 0.11
4-OCH_3	8.14 ± 0.23	4-CH_3/4'-NO_2	11.10 ± 0.33
4-CF_3	2.68 ± 0.10	4-NO_2/4'-NO_2	1.38 ± 0.12
4-SO_2CH_3	3.58 ± 0.08		

[a] Water (2.18 M)/1,2-dimethoxyethane at 75.0 ± 0.05 °C. [b] Standard deviation.



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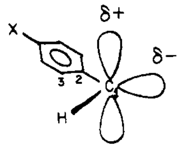
Structural factors in **3** were then investigated by MINDO/3 methods (Table II) to determine whether such singlet carbenes might express stereochemical orbital preferences.[2,4,5] The C_2C_1 bond length in **5** and the dihedral angle, θ, of the aromatic ring in **6** reveal that any substituent at the para position of a singlet phenylcarbene (**5**) results in shortening of the C_2C_1 bond distance with concomitant ring rotation that is dependent upon the nature of the substituent. Thus rotation of the aryl group about the C_2C_1 bond to a planar conformation ($\theta \approx 0°$) allows stabilization of the electron deficient p orbital by electron-donating substituents. Twisting to a perpendicular conformation ($\theta \approx 90°$) leads to stabilization of the electron rich σ-orbital by electron-withdrawing substituents. The calculated net atomic charges (Table II) reinforce this interpretation. The ability of a para substituent to allow a phenyl group to discriminate between and conformationally react to the nonbonded orbitals of the singlet carbene gives support to the mechanism proposed for thermolyses of **1**.



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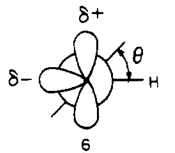

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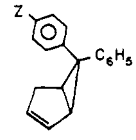
Conformational effects may be expected to influence the properties of **2** as singlets, especially in light of evidence indicating the importance of phenyl twisting on the chemistry of triplet diphenylcarbene.[6] Of note is that para-monosubstituted diphenylcarbenes add preferentially to cyclopentadiene to give 6,6-diphenylbicyclo[3.1.0]hex-2-enes in which the more electron rich aryl group is endo (**7**, Z = CH_3, OCH_3; **8**, Z = Br, CN) to the cyclopentene ring.[7] The selectivity has been rationalized in terms of a singlet-like transition state in which the aryl rings of the carbene are essentially coplanar and the only significant substituent effect is interaction with the ini-

Table II. Calculated Equilibrium Geometries (**5**, **6**) and Heats of Formation of Singlet Para-Substituted Phenylcarbenes (**3**)

Substituent 4-X (**5**)	C_1H bond length (Å)	C_2C_1 bond length (Å)	C_2C_1H bond angle (deg)	θ[a] (deg) (**6**)	(ΔH_f (kcal/mol)	Barrier to rotation[b] (kcal/mol)	Net atomic charge on C_1[c]
H	1.126	1.454	109.7	1.3	119.0	<0.1	−0.0046
Cl	1.126	1.452	109.5	0.4	109.7		0.0009
CH_3	1.126	1.453	109.9	4.2	113.9		−0.0060
OCH_3	1.127	1.445	109.8	−0.4	71.5		−0.0225
OH	1.127	1.445	109.8	−0.3	59.7	3.2	−0.0217
CF_3	1.121	1.447	109.6	89.9	−55.9		0.0725
CN	1.123	1.449	109.4	89.3	140.1	0.6	0.0669
COOH	1.122	1.449	109.4	89.5	19.0		0.0677
CHO	1.122	1.449	109.4	89.9	86.0		0.0677
NO_2	1.120	1.448	109.4	89.9	98.9		0.0745

[a] H:C_1:C_2:C_3 dihedral angle. [b] About C_2C_1 bond. [c] In units of electron charge.

tially vacant p orbital of the carbene.[7] It now appears that inclusion of large substituent-generated steric effects offers an alternative explanation of these observations. That is, when Z is electron withdrawing, the substituted aryl function aligns to maximize the overlap with the electron rich σ-orbital of the carbene. Assuming electrophilic attack upon the π-framework of the olefin, the transition state for endo addition (**9**) is



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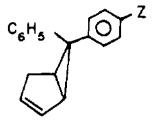

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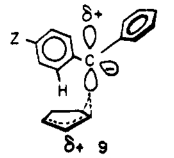

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therefore impeded by the steric repulsion between the olefin and an ortho ring hydrogen. Such congestion will be relieved for modes of addition in which the endo aryl ring is coplanar with the electron deficient carbenic orbital (exo addition for Z = electron withdrawer; endo addition for Z = electron donor).

Examination of the calculated minimum energy reaction profiles for decomposition of para-substituted phenyldiazomethanes is in progress.

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References and Notes

(1) (a) D. Bethell, D. Whittaker, and J. B. Callister, *J. Chem. Soc.*, 2466 (1965); (b) D. Bethell and R. D. Howard, *J. Chem. Soc. B*, 745 (1969); (c) D. Bethell, A. R. Newall, G. Stevens, and D. Whittaker, *ibid.*, 749 (1969); (d) D. Bethell, A. R. Newall, and D. Whittaker, *ibid.*, 23 (1971), have determined that diaryldiazomethanes decompose in aqueous and in alcoholic acetonitrile to diarylcarbenes which are then partitioned between the hydroxylic solvent and the diazo componds.

(2) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97**, 1285, 1294, 1302, 1307 (1975); M. J. S. Dewar, D. H. Lo, and C. A. Ramsden, *ibid.*, **97**, 1311 (1975).

(3) In the present system the diphenyldiazomethanes (**1**) thermolyze in water/1,2-dimethoxyethane to benzhydrols (95–99%) and benzophenone azines (0–5%). The kinetics indicate clearly that **1** decomposes unimolecularly in a rate limiting process to **2** which is then captured by water or **1** to yield the benzhydrol or the benzophenone azine. The details of this investigation will be described separately.

(4) M. J. S. Dewar, R. C. Haddon, W-K. Li, W. Thiel, and P. K. Weiner, *J. Am. Chem. Soc.*, **97**, 4540 (1975), have treated methylene in various electronic configurations by MINDO/3 methods.

(5) QCPE Program No. 279 was modified to double precision for use with the IBM 370/168 facility available at The Ohio State University. The phenylcarbene system was chosen as a theoretical model because it provided a working simplification within the chemical and budget requirements. Throughout the calculations, the aromatic ring was treated as a rigid, regular hexagon with carbon–carbon and carbon–hydrogen bond lengths of 1.400 and 1.080 Å, respectively. All remaining geometrical parameters were optimized as a function of energy.

(6) W. J. Baron, M. E. Henrick, and M. Jones, Jr., *J. Am. Chem. Soc.*, **95**, 6286 (1973), and references therein.

(7) D. Crumrine and H-H. B. Yen, *J. Am. Chem. Soc.*, **98**, 297 (1976).

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Metal Complexes of Poly(α-amino acids). Optical Rotatory Properties of Copper(II) Complexes of Poly-L-lysine, Poly-L-ornithine, and Poly-L-diaminobutyric Acid

Sir:

In the last few years a considerable amount of work has been carried out on metal complexes of poly(α-amino acids).[1] Such compounds can be considered useful models in order to understand the way of action of metalloproteins. It is known that all water soluble poly(α-amino acids), with the only exception of poly-L-proline, bind Cu(II) ions in alkaline aqueous solution, forming complexes of the biuret type.[2] Poly-L-histidine[3] and poly-L-lysine[4,5] bind copper ions even in the pH region below 8 forming other kinds of complexes in which imidazole and amino side-chains, respectively, are involved.

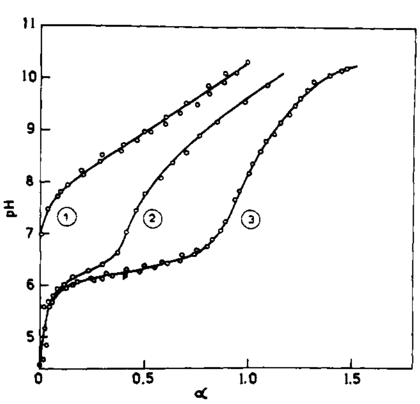

Figure 1. Titration curves of PDBA–Cu(II) aqueous solutions at different Cu(II)/PDBA molar ratios: (1) Cu(II)/PDBA = 0, (2) Cu(II)/PDBA = 0.1, (3) Cu(II)/PDBA = 0.25. In all cases [PDBA] was in the range (5.2–5.4) × 10^{-3} molar residue.

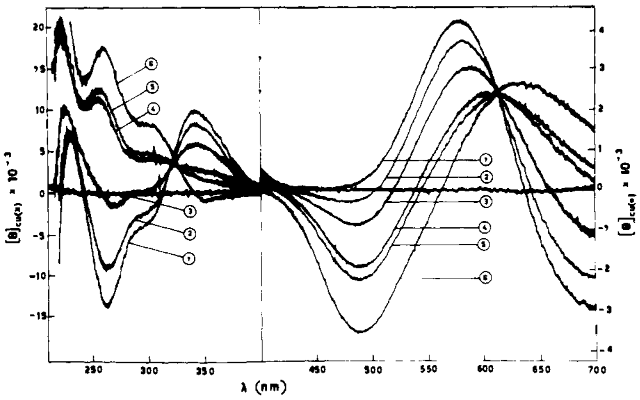

Figure 2. CD spectra of PDBA–Cu(II) aqueous solutions at different pH's. [PDBA] = 4.8 × 10^{-3} molar residue [Cu(II)] = 1.2 × 10^{-3} M: (1) pH 8.29, (2) pH 9.31, (3) pH 10.18, (4) pH 11.67, (5) pH 12.09, (6) pH >13. The ellipticity values are given per bound Cu(II).

In view of the importance of copper complexes of peptides and poly(α-amino acids) as models for copper proteins, and of the effects of stereospecific catalysis, we have reexamined the problem of complex formation of Cu(II) with poly-L-lysine (PLL), and the study has been extended to poly-L-ornithine (PLO) and poly(L-diaminobutyric acid) (PDBA). The specific purpose of our work was to ascertain the relationships between complex structure and conformation of the polypeptide backbone.

As an example the potentiometric titration curve of PDBA in absence and in presence of Cu(II) ions is shown in Figure 1. When cupric ions are present, two distinct buffer regions are observed, corresponding to the formation of two kinds of complexes. Type I complex is formed at pH <8, while type II complex is stable at very alkaline pH's. Inspection of the potentiometric titration data of PDBA with the Bjerrum method reveals that four protons are displaced per mole of bound Cu^{2+} at pH $\simeq 7.5$. This result is consistent with that previously reported by Matano et al.[4,5] on a type I complex of PLL, in which four amino nitrogens have been suggested to occupy square-planar coordination positions of Cu^{2+}. Type II complexes are formed at strongly basic pH values, and the hypothesis has been made that *amido* nitrogens are involved in complex formation.[4,5]