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Cyclopropanation Transition States. The Electronic Effect

Sir:

The stereochemistry of olefin cyclopropanation by carbenes and carbenoids has been a particularly active topic for the past several years.[1] Possible influences include electronic effects,[1,2] steric effects,[1b] and specific complexation effects involving metal ions[3] or substituted olefins.[4] Electronic effects have been attributed to dispersion forces,[5] secondary electrostatic interactions,[6,7] or, more generally, secondary electronic interactions viewed in molecular orbital terms.[8] These suggestions are based on experiments involving unsymmetrical carbenes or carbenoids in which the two groups differ in size as well as electronics. Only if one assumes a very early transition state, can steric differences be ignored. Such an assumption is probably justified in Closs's substituent work on the reactive monoarylcarbenes[6] and monoarylcarbenoids,[6,9] but the endo-aryl and endo-hydrogen transition states probably occur at different separation distances which could change electronic effect magnitudes.

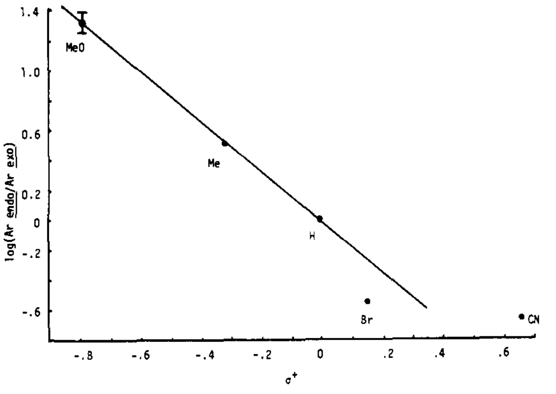
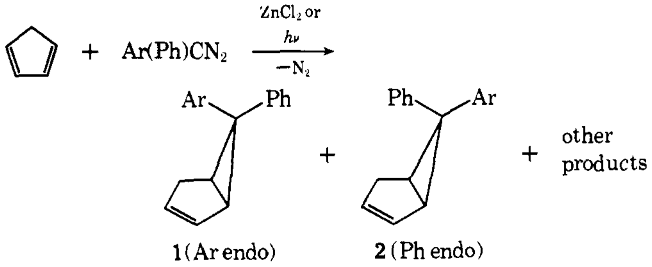


Figure 1. σ^+ ρ plot of diarylcarbenoid cyclopropanation stereoselectivity at 0 °C.

We felt that examining the effect of para substitution on diarylcarbenoid and diarylcarbene cyclopropanations would clarify the electronic effect since the transition states leading to **1** (Ar endo) and **2** (Ph endo) should occur at the same carbene-olefin separation distance and would therefore have the same steric hindrance between the endo-group and the olefin substrate. Furthermore, the low reactivity of the diaryl species implies a relatively product-like transition state with only small carbene-olefin separation[10] where both steric and electronic effects might be maximized. The appropriate diaryldiazomethanes were added to cyclopentadiene in the usual fashion[11] using both zinc chloride catalysis and Pyrex filtered irradiation. Reverse-phase high pressure liquid chromatography[12] allows analytical separation of the isomeric olefin products[13] without fear of isomerization so that reliable kinetic stereoselectivities can be obtained. The stereochemistry of the 6,6-diarylbicyclo[3.1.0]hex-2-enes (**1**) and (**2**) can be determined by application of europium shift reagents[14,15] to the hydroboration derived 6,6-diarylbicyclo[3.1.0]hexan-3-*exo*-ols.



The results for both the carbene and carbenoid reactions are shown in Table I. Note that in all cases the major prod-

Table I. Substituent Effects on Diarylcarbene and Diarylcarbenoid Reactions

$Ar(Ph)CN_2$	Conditions (°C)	Cyclopropane	Ar_{endo}/Ar_{exo}[a]	Benzophenone	Ketazine[b]
p-C_6H_4CN	$ZnCl_2$ (25)	37	1/2.5	15	35
	$ZnCl_2$ (0–5)	9	1/4.5	20	50
	hν (0–5)	32	1/3.2	20	4 (24)[c]
p-C_6H_4Br	$ZnCl_2$ (25)	31	1/3.5	68	5
	$ZnCl_2$ (0–5)	21	1/3.6	17	24
	hν (0–5)	25	1/3.5	26	— —(25)[c]
Ph[d]	$ZnCl_2$ (25)	35	— —	29	24
Ph[d]	$ZnCl_2$ (0–5)	23	— —	15	51
Ph[d]	*hν* (0–5)	19	— —	25	1 (36)[c]
p-$C_6H_4CH_3$	$ZnCl_2$ (25)	12	2/1	5	60
	$ZnCl_2$ (0–5)	20	3/1	24	25
	hν (0–5)	14	1.1/1	35	20 (10)[c]
p-$C_6H_4OCH_3$	$ZnCl_2$ (25)	11	$\geqslant$20/1[e]	46	10
	$ZnCl_2$ (0–5)	5	$\geqslant$20/1[e]	47	30
	hν (0–5)	15	$\geqslant$20/1[e]	21	(22)[c]

[a] Isomer ratio determined by recycling reversed phase HPLC with 254-nm detector. [b] Ketazine = tetraarylketazine. [c] Yield of 1,1,2,2,-tetraarylethane. [d] From ref 8. [e] No second isomer could be seen by NMR or recycling HPLC on the crystalline isomer mother liquors. We estimate a maximum of 5% of a second isomer could be present.

Table II. σ^+ ρ Results for Carbenoid Cyclopropanation Stereoselectivity

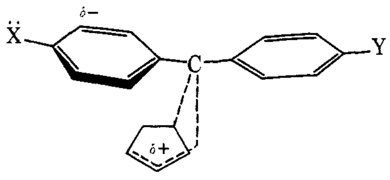
System	Temp, °C	ρ^a
Ar(Ph)CN$_2$ + ZnCl$_2$ + cyclopentadiene	0	−1.45
Ar(Ph)CN$_2$ + ZnCl$_2$ + cyclopentadiene	25	−1.23
Ar(Ph)CN$_2$ + hν + cyclopentadiene	0	−1.24
ArCHLiBr + *cis*-2-butene	−10	−0.35 (ref 6b)
ArCHN$_2$ + hν + *cis*-2-butene	−10	−0.35 (ref 6b)
ArCHN$_2$ + ZnCl$_2$ + 1,4-butadiene	−10	−0.46 (ref 9, 2 pts only)
ArCHN$_2$ + ZnCl$_2$ + cyclohexene	−10	−1.3 (ref 9, 2 2 pts only)

[a] Represents a least-squares fit to the data.

uct has the electron rich aryl group endo to the 5-ring, the carbenoid results are temperature dependent, the electron donating groups have generally lower cyclopropane yields, and the stereoselectivities of the carbene and carbenoid are quite similar.

A plot of log (isomer ratio)[16] vs. σ^+ (Figure 1) gives a fairly good correlation with some deviation for the electron deficient substituents and a $\rho = -1.45$ for the carbenoid reaction at 0 °C. In the transition state, the electron deficient carbene lobe is clearly conjugated with the electron rich aryl ring and little rehybridization and mixing with the electron rich lobe has occurred. We have made similar plots of Closs's data[6,9] for comparison purposes (Table II), and find that the more reactive monoarylcarbenoids show similar behavior but are much less perturbed by the substituents as one would expect for relatively earlier transition states. Only for the unreactive cyclohexene which has the steric problem of ring methylene groups does the monoarylcarbenoid show electron demand similar to the diarylcarbenoid.

Although the surprising similarity of the diarylcarbene and diarylcarbenoid stereoselectivities could be merely fortuitous, the weight of the data suggests that some common mechanistic features occur. One possibility is that the actual cyclopropanation transition state represented here by structures 3 and 4 is very similar for both reactions.[17] We note that the model 3 suggested by electrostatic theory[6,7] correctly predicts for both cases that the more electron rich endo-aryl group controls the stereochemistry through secondary interactions in the major transition state. The correlation for electron withdrawing groups is poor because the unsubstituted phenyl ring is endo in the predominant transition state, and the lack of correlation with σ^+ for the phenyl moiety indicates that some orbital mixing and rehybridization is occurring in these cases. Model 4 better represents the disposition of orbitals in the transition state.



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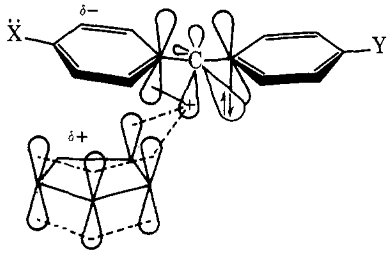

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One could imagine that these relatively late transition states are so stabilized by resonance donation from the rings and by secondary interactions with the diene substrate, that nearly all "memory" of the precursors has been lost.[18] We note that the methyl system which is least able to provide resonance stabilization shows the greatest stereoselectivity difference. Moss's results on phenyl-halo carbenes[21] led him to speculate that carbenoid and carbene selectivities tend to become more similar as the species become more stable. Although our reasoning is different,[22] our results support this generalization. A more detailed discussion of the mechanistic problems involved in equating transition states derived from diarylcarbenoids and triplet diarylcarbenes must wait for the full paper. We are continuing our investigations of the details of cyclopropanation transition states.

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(16) If this is a kinetic process, then the isomer ratio equals the kinetic ratio of endo-aryl attack to exo-aryl attack.

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(18) Although diarylcarbenes are triplets[19] in rigid media, mixtures of triplet and singlet states have been implicated[20] in various diphenylcyclopropanations. The precursor seems to have little effect on the stereoselectivity.

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