Tetrahedron Letters,Vol.25,No.47,pp 5415-5418,1984 0040-4039/84 $3.00 + .00
Printed in Great Britain

THE PHILICITY OF A TRIPLET CARBENE: ADDITIONS OF DIPHENYLCARBENE TO STYRENE SUBSTRATES

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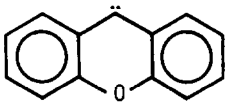
Summary. Triplet diphenylcarbene adds to ring-substituted styrenes as an ambiphile, reacting more rapidly with electron-rich or electron-poor styrenes than with styrene itself.

The selectivity of carbenes toward alkenes has been intensively studied.[1] The results operationally define a carbene's philicity; i.e., whether it reacts with olefinic substrates as an electrophile, ambiphile, or nucleophile.[2] Singlet carbene-alkene cycloaddition reactions are known that exemplify each kind of carbenic philicity, and the dependence of the expressed philicity on the carbenic substituents is reasonably well rationalized by frontier molecular orbital theory.[2]

In marked contrast, however, very little is known about the philicity of triplet carbenes. Shechter *et al.*[3] reported that 9-xanthylidene (**1**) added to a series of ring-substituted styrenes with what we would define[2] as ambiphilic selectivity. The carbene was suggested to be largely in its triplet state during the addition reactions.[3]



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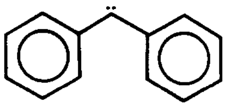

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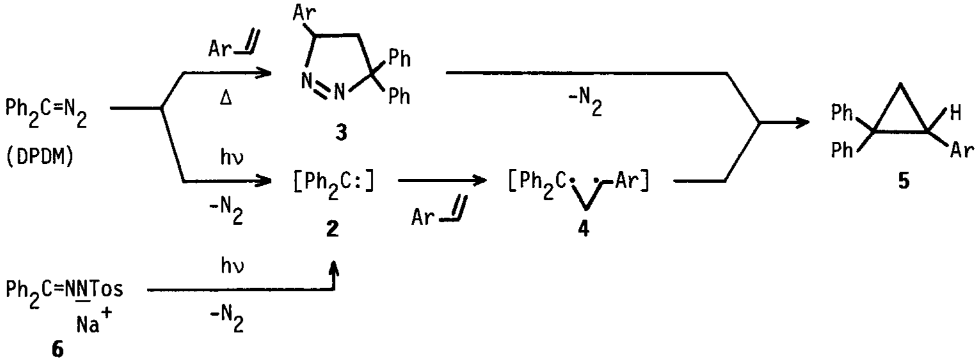
9-Xanthylidene can be regarded as a perturbed diphenylcarbene. Diphenylcarbene (**2**) and methylene are the carbenic species whose triplet states have been most thoroughly characterized. It is therefore of considerable interest to know whether the archtypal triplet diarylcarbene, 2, also adds ambiphilically to alkenes. Although additions of triplet **2** to alkylethylenes are frequently complicated by concurrent hydrogen abstraction reactions, cyclopropanation of styrene is clean.[4] Product studies[4] and absolute kinetic measurements[5] indicate that the addition of **2** to styrene proceeds via the triplet carbene. Moreover, Hammett studies of singlet carbene additions to styrenes have revealed the ambiphilic behavior of methoxychlorocarbene[6] and phenoxychlorocarbene.[7] Taken together, these considerations led us to examine the philicity of diphenylcarbene in additions to styrenes.

Although conceptually simple, a Hammett study of **2** and styrenes is complicated by the thermal 1,3-dipolar cycloaddition of diphenyldiazomethane (DPDM), a choice precursor for 2, to the styrenes, affording pyrazolines (**3**) that spontaneously decompose in 70-80% yields to triarylcyclopropanes (**5**);[4,8] cf., Scheme I. The reactivities of the various styrenes (Table I) toward DPDM in CH_3CN at 50 °C were measured, and afford a satisfactory log ($\underline{k}_{rel}$) vs. σ correlation with ρ = +1.68 ($\underline{r}$ = 0.99), indicating nucleophilic addition of the diazoalkane.[9,10]



Scheme I

Rate constants ($\underline{k}_2$) were determined[11] for thermal DPDM additions to several styrenes, at various temperatures, in order to determine a temperature low enough so that the thermal DPDM/styrene reaction would be too slow to compete with a photolytic decomposition of DPDM to **2**. The results (Table I) can be extrapolated to show that thermal reactions of DPDM will be insignificant (<1%), even in the presence of the most reactive styrene derivative, when the photolysis of DPDM is carried out at -78 °C within a 4 hr period.

Thus, we photolyzed[12] DPDM in binary mixtures of excess styrenes at -78 °C, and obtained the latter's relative reactivities toward carbene **2** ($\underline{k}_{rel}$ = 1.00 for styrene) from the cyclopropane product ratios[8] determined by hplc.[13] The data appear in Table II. We also generated **2** by irradiation of sodium benzophenone tosylhydrazonate (**6**)[14] suspended in styrene/THF mixtures at 0 °C. Under these conditions, thermal additions of DPDM appear to be minimized, and the relative reactivities thus obtained (Table II) are in good agreement with those derived from the DPDM photolyses at -78 °C. The absence of a temperature effect on the relative reactivities suggests that $\Delta\Delta S^{\ddagger} \sim 0$ for the competitive Ph_2C additions.

The results summarized in Table II indicate that Ph_2C behaves as an ambiphile, reacting more rapidly with electron-rich or electron-poor styrenes than with styrene itself. The ambiphilicity of **2** appears to be somewhat "compressed" relative to that reported[3] for carbene **1**. The latter shows stronger kinetic discrimination in response to substituent variation of the substrates (Table II).

Hammett analysis of the Ph_2C relative reactivities (-78 °C) for the $\underline{p}$-CH_3O, $\underline{p}$-CH_3, and H substrates affords $\rho \sim -0.48$ ($\underline{r}$ = 0.99) vs. σ and -0.17 ($\underline{r}$ = 0.99) vs. σ^+. A linear correlation is not observed with the entire subset of electron-poor styrenes, but the data for the $\underline{m}$-substituted substrates do correlate with σ, ρ = +0.34 ($\underline{r}$ = 0.99).

The expressed ambiphilicity of Ph_2C is mechanistically distinct from that of CH_3OCCl[6] or $PhOCCl$.[7] These (singlet) carbenes are ambiphilic because of the specific interactions of their HO and LU molecular orbitals with the LU and HO molecular orbitals of the substrates in concerted cycloaddition reactions.[2,6,7] In contrast, the ambiphilicity of **2** can be reasonably attributed to electron donating or electron withdrawing substituent stabilization of the benzylic radical center in (triplet) 1,3-diradical **4**, an obligatory intermediate in this triplet carbene addition (Scheme I). This rationalization parallels that given by Shechter for

Table I. Rate Constants ($\underline{k}_2$) at 50.0 °C and Arrhenius Parameters for Thermal Additions of Diphenyldiazomethane to Substituted Styrenes in Acetonitrile

X in $X-C_6H_4-CH=CH_2$	$\underline{k}_2 \times 10^5$ $(sec^{-1} \cdot M^{-1})^a$	$\Delta H^{\ddagger}$ $(kcal \cdot mol^{-1})^b$	$\Delta S^{\ddagger}$ $(cal \cdot deg^{-1} \cdot mol^{-1})^b$
p-Me	1.84 ± 0.02	13.9	-52.7
H	2.52 ± 0.03	17.3	-55.5
m-Cl	4.73 ± 0.04	13.5	-52.8
m-NO_2	10.0 ± 0.1	10.1	-50.6

[a] Reported average deviations are for 2 to 4 runs. [b] These values are each based on 3 runs at temperatures between 50° and 60 °C. Estimated errors are ±1 $kcal \cdot mol^{-1}$ and ±5 $cal \cdot deg^{-1} \cdot mol^{-1}$.

Table II. Relative Reactivities of Substituted Styrenes toward Diphenylcarbene

X in $X-C_6H_4-CH=CH_2$	$\underline{k}_X/\underline{k}_H$ for **2**[a] (i)	(ii)	$\underline{k}_X/\underline{k}_H$ for **1**[b]
p-MeO	1.36±0.02	1.35±0.02	1.56
p-Me	1.16±0.02	1.15±0.02	1.33
H	1.00	1.00	1.00
p-Cl	1.59±0.03	1.25±0.09	1.52
m-Cl	1.25±0.03	1.23±0.02	
p-Br	1.46±0.03	1.45±0.02	2.62
m-Br	1.36±0.10	1.27±0.09	3.48
m-NO_2	1.73±0.07		

[a] Deviations listed are for two to five runs. Diphenylcarbene was generated either (i) by photolysis of DPDM at -78 °C or (ii) by photolysis of **6** at 0 °C. Yields of cyclopropanes were 70 - 80% for all styrenes studied under either experimental condition. [b] Data from reference 3, normalized to H = 1.00; -25 °C.

reactions of **1**,[3] and is in accord with indications that benzylic radicals[15] and benzylic 1,3-diradicals[16] can be stabilized by either electron donating or electron withdrawing substituent. We caution, however, that substituent effects on radical reactions are still not completely understood[17] and that examples counter to our rationalization could be cited.

Nevertheless, in an operational sense, triplet diphenylcarbene adds to styrenes as an ambiphile. Taken together with Shechter's results for 9-xanthylidene,[3] our findings suggest that ambiphilicity in triplet carbene additions may be a relatively general phenomenon, at least with arylalkene substrates.[18]

Acknowledgments. The authors at Mie University acknowledge with thanks grants-in-aid from the Ministry of Education, Science, and Culture of Japan. The authors at Rutgers University gratefully acknowledge the support of the National Science Foundation. We thank Professor Leonard Kaplan for helpful discussions.

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(12) DPDM (10 mg) was added to carefully weighed binary mixtures of the styrenes (∿1 g) in 1.0 ml of ether or pentane. Reaction mixtures were degassed and irradited for ∿3 hrs in Pyrex tubes at -78 °C, until all DPDM was destroyed (uv). No appreciable dependence of k_{rel} on solvent was observed.

(13) A C-18 reverse phase column was used and was eluted with MeOH/water.

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(Received in Japan 16 August 1984)