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ARE PHENYLHALOCARBENES AMBIPHILIC?

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Summary. In additions to simple alkenes and styrenes at 25°C, the selectivities of PhCF and PhCCl are best described as electrophilic.

Our 1979/80 classification of carbenes as electrophilic, ambiphilic, or nucleophilic placed the phenylhalocarbenes, PhCX, with the electrophiles.[2,3] Their selectivity indices, $\underline{m}_{CXY}$,[2] were lower than that of CCl_2, the classic electrophilic carbene, and the available relative reactivities were appropriate.[2,4] We pointed out that calculated HOMO/LUMO differential orbital energies for PhCX/alkene additions predicted ambiphilicity for (e.g.) PhCF, but considered this offset by an "early" transition state, where the geometry strongly favored p/π over σ/π^* carbene/alkene orbital interactions.[2]

Six years later, there are reasons to reexamine the earlier classification: (a) PhCCl is reported to readily add to electron deficient olefins at 80°C.[5] (b) The absolute rate constants for the additions of PhCCl (and its p-MeO and p-Me derivatives) to several p-substituted styrenes give curved Hammett correlations, consistent with ambiphilic selectivity.[6] Now we report new results that reaffirm the electrophilicity of PhCF and PhCCl.

We first determined the selectivities of PhCF and PhCCl toward p-X-substitued styrenes (X = MeO, Me, H, Cl, and CF_3) at 25°C. The carbenes were photolytically generated ($\lambda > 300$ nm) from the appropriate 3-aryl-3-halodiazirines,[7] and the relative reactivities were obtained from standard[4] competitive reactions between pairs of alkenes, with analysis by calibrated hplc or gc.[8] All product cyclopropanes were isolated and fully characterized. The resultant Hammett correlations for PhCF ($\rho = -0.22$) and PhCCl ($\rho = -0.32$) appear in Fig. 1, where the carbenes are clearly seen to be electrophiles. There is no evidence of the curvature that appears in the correlations of the ambiphilic carbenes PhOCCl[9] or MeOCCl.[10] Additionally, the ρ value we observe for photolytically generated PhCCl at 25°C (-0.32) agrees with $\rho = -0.33$ for the thermally generated species [$PhCHCl_2$/KO-t-Bu/18-Crown-6, 7°C].[11]

It is unclear why these product-based Hammett correlations are linear, whereas the intermediate-based (i.e. on k_{abs} for PhCX itself) correlations are curved.[6] Any process that quenches PhCX competitively with addition to styrenes will contribute to "$\underline{k}_{abs}$" when the carbene itself is followed, so that these Hammett correlations could be affected by unknown or adventitious quenchers. A referee suggests that the curved $\underline{k}_{abs}$ Hammett correlations may reflect association between the carbene and the styrene prior to addition but independent of addition selectivity. For selectivity studies, the product-based results are probably more trustworthy because they account for the fate of the carbenes.

We next determined the relative reactivities (vs. isobutene) of PhCX toward the electron deficient alkenes methyl acrylate and acrylonitrile. Again, the carbenes were generated photolytically at 25°C, and the cyclopropane adducts were isolated and fully characterized. Product ratios were measured by calibrated capiltary gc. The results,[12] adjusted to a trans-2-butene standard, appear in Table I, where they are compared with data for MeCCl,[3] PhOCCl,[13] and MeOCCl[14] (all generated from diazirines).

Examination of Table I, where the substrate set is designed to detect ambiphilicity,[2] shows PhCF and PhCCl to be electrophiles. Their selectivity patterns resemble those of electrophilic MeCCl (Table I) and CCl_2 (not shown: cf., refs 2 and 3). However, compared to MeCCl, where the electron deficient alkenes are much less reactive than trans-butene, there is some indication that nucleophilic (σ-π^*) interactions play a stronger role in the corresponding reactions of PhCF and PhCCl. Even so, methyl acrylate and acrylonitrile are less reactive than trans-butene and we do not see the patent pattern of ambiphilicity exhibited by MeOCCl or PhOCCl.[18] By operational (experimental) criteria,[2] we should continue to characterize PhCCl and PhCF as "electrophilic."

All carbenes have the potential for nucleophilic reactions with olefins; the crucial factor is whether the HOMO(carbene)/LUMO(alkene) interaction is comparable to or stronger than the LUMO(carbene)/HOMO(alkene) interaction in the transition state.[2] In this context, we find that $\underline{k}_{abs}$, measured by laser flash photolytic spectroscopy,[19] for the additions of either PhCF on PhCCl to methyl acrylate or acrylonitrile show these alkenes to be more reactive than 1-hexene: $10^{-6}\underline{k}_{abs}^{PhCF}$ (L/mol-sec) = 0.93,[6] 1.4 and 1.2 for quenching by 1-hexene, methyl acrylate, or acrylonitrile, respectively (in isooctane); and similarly $10^{-6}\underline{k}_{abs}^{PhCCl}$ = 2.2,[6] 5.1, and 5.4 in isooctane (0.94, 1.3, and 1.7 in acetonitrile). From the perspective of the unreactive monoalkylethylene, 1-hexene, therefore, the nucleophilic potentials of PhCF or PhCCl are apparent.[20] Nevertheless, the most apposite experimental description of the empirical selectivity of the phenylhalocarbenes toward alkenes remains "electrophilic," at least at 25°C, where the quantitative data has been obtained.[21] It is, of course, possible that further structural alteration of PhCX by substitution of a p-methoxy group would produce an ambiphilic carbene.[6] This possibility remains to be rigorously tested.

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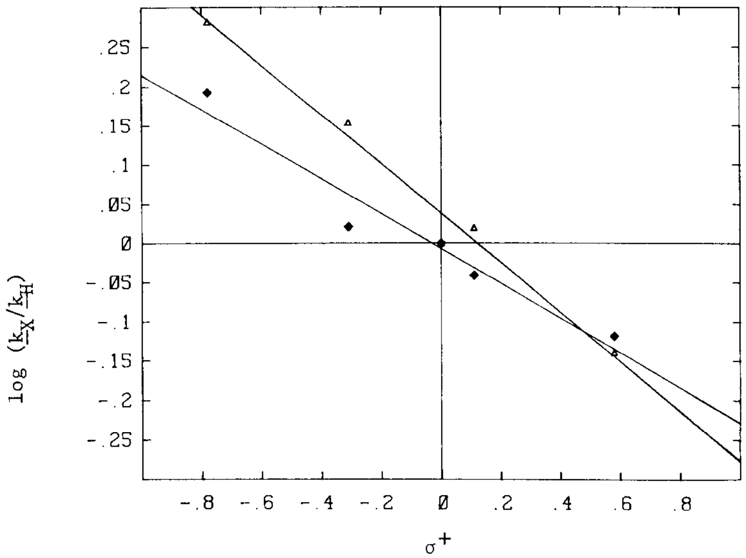

Figure 1. Log(k_X/k_H) vs. σ^+ for the additions of PhCCl (Δ) and PhCF (◈) to *p*-X-$C_6H_4CH{=}CH_2$ at 25°C. The substituents are MeO, Me, H, Cl, and CF_3; see ref. 8. The slopes and correlation coefficients are -0.32, 0.99 and -0.22, 0.97 for PhCCl and PhCF, respectively. Both correlations are significant at the 99% confidence level.

Table I. Carbene/Alkene Relative Reactivities at 25°C

	Carbene				
Alkene	PhCF[a]	PhCCl[b]	MeCCl[c]	PhOCCl[d]	MeOCCl[e]
$Me_2C{=}CMe_2$	33.2	25.5	7.44	3.0	12.6
$Me_2C{=}CHMe$	12.0	16.0	4.69		
$Me_2C{=}CH_2$	6.67	5.0	1.92	7.3	5.43
trans-MeCH=CHR	1.00[f]	1.00[f]	1.00[f]	1.0[g]	1.00[f]
$CH_2{=}CHCOOMe$	0.74[h]	0.50[h]	0.078	3.7	29.7
$CH_2{=}CHCN$	0.80[h]	0.55[h]	0.074	5.5	54.6

[a] Data from ref. 15, renormalized to *trans*-butene. [b] Data from ref. 16, renormalized to *trans*-butene. [c] Data from refs. 3 and 17. [d] Data from ref. 13. [e] Data from ref. 14. [f] R=Me. [g] R=Et. [h] New data, normalized to *trans*-butene; *cf.*, ref. 12.

References and Notes

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(8) k_{rel} for additions to p-X-$C_6H_4CH{=}CH_2$; For PhCF; (X=) MeO, 1.56 ± .12; Me, 1.05 ± .01; H, 1.00; Cl, 0.90 ± .10; CF_3, 0.72 ± .01. For PhCCl; MeO, 1.92 ± .01; Me, 1.43 ± .01; H, 1.00; Cl, 1.05 ± .02; CF_3, 0.72 ± .02.

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(12) k_{rel} (vs. isobutene) for additions to $CH_2{=}CHX$; For PhCF; (X=) COOMe, 0.11 ± .01; CN, 0.12 ± .02. For PhCCl; COOMe, 0.10 ± .01; CN, 0.11 ± .01.

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(20) However k_{abs} for PhCF or PhCCl additions to trans-pentene[6] are larger than for additions to methyl acrylate or acrylonitrile, in qualitative agreement with the relative rate constants of Table I.

(21) It is conceivable that selectivity alterations at higher temperatures could change the philicities of carbenes. See, for example, Giese's studies reviewed in: R.A. Moss and M. Jones, Jr., "Reactive Intermediates," Vol. 3, M. Jones, Jr., and R.A. Moss, Ed., Wiley, New York, 1985, pp. 75-78.

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