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THE PHILICITY OF PHENOXYCHLOROCARBENE TOWARD STYRENES

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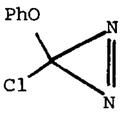
Summary. When generated by the thermolysis of 3-phenoxy-3-chlorodiazirine, phenoxychlorocarbene is an ambiphile in addition reactions with styrene derivatives.

Methoxychlorocarbene behaved as an ambiphile in addition to alkenes; *i.e.*, as an electrophile toward electron-rich olefins and as a nucleophile toward electron-poor olefins.[1] Ambiphilicity persisted whether the substrates were ethene derivatives[1] or styrene derivatives,[2] and we found that the ambiphilicity of CH_3OCCl could be rationalized by inspection of the carbene/alkene frontier molecular orbital (FMO) interactions.[1-3] These studies were extended to phenoxychlorocarbene, 1, which was thermally generated from 3-phenoxy-3-chlorodiazirine, 2, and also found to be ambiphilic in additions to ethene derivatives.[4]

$PhO\ddot{C}Cl$

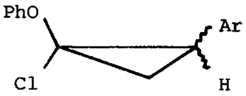
1



2

$PhOCHCl_2$

3



4

$PhO\bar{\ddot{C}}Cl_2$

5

Very recently, it was reported that PhOCCl generated by phase transfer catalytic (aq. NaOH, $PhCH_2\overset{+}{N}Et_3$, Cl^-) α-elimination from α,α-dichloroanisole, 3, added in poor yields ($\leq$11%) to styrenes as a *nucleophile*, with ρ (vs. σ) = 0.40 at 27°C.[5] *A priori*, it is not impossible that PhOCCl could be an ambiphile toward ethene substrates but a nucleophile toward styrenes; after all, the FMO energies of the substrates are different. However, combining *ab initio* HOMO and LUMO energies of PhOCCl[4] with semi-empirical HOMO and LUMO energies of $X\text{-}C_6H_4CH{=}CH_2$,[2] we find that PhOCCl is "predicted" to be an *ambiphile* toward representative styrenes.[6] Because of the disparity between our (admittedly crude) FMO prediction[6] and the reported[5] nucleophilicity of PhOCCl toward styrenes, we determined the styrene philicity of PhOCCl (thermally generated from 2). We now report that the observed *ambiphilicity* is in accord with FMO predictions[6] and consistent with the behavior of PhOCCl toward ethenes.[4]

Phenoxychlorodiazirine (2)[4] was thermally decomposed (25°C, 72h)[7] in each of six substituted styrenes (*cf.*, Table I), affording *syn*/*anti* mixtures of 1-chloro-1-phenoxy-2-arylcyclopropanes, 4. Products were isolated in 34-75% yields (based on 2), and purified either by chromatography on silica gel or kugelrohr distillation (~85°C/0.02 mm-Hg). Product identities followed from structurally-consonant nmr spectra and acceptable elemental analyses.

The relative reactivities of PhOCCl toward the styrenes were determined in the normal manner. Diazirine 2 (1-3 mmol) was decomposed (25°C, dark, 72 h)[7] in carefully weighed binary mixtures of the styrenes (each present in $\geq$10-fold excess). After reaction, styrenes were removed under vacuum ($T \leq 40°C$) and the cyclopropane product ratios were determined by hplc (Waters Associates instrument, C-18 reverse phase RCM column, eluents CH_3OH/H_2O or CH_3CN/H_2O), using a calibrated uv detector and electronic integration. Relative reactivities were calculated from $k_A/k_B = (O_B/O_A) \times (P_A/P_B)$, where O_B/O_A represents the initial styrene mole ratio, and P_A/P_B is the measured product ratio. Results appear in Table I. Normalizing the experimental reactivities to styrene (k_{rel} = 1.00), we obtain the relative reactivities shown in Table II, where we include, for comparison, related data for MeOCCl[2] and for "PhOCCl" generated from 3.[5]

The results in Table II clearly establish diazirine-generated PhOCCl as an ambiphile, electrophilic toward the electron-rich styrenes and nucleophilic toward the electron-poor styrenes. These trends are particularly clear in Figure 1, where log (k_{rel}) is plotted against σ^+ (for donor substituents) or σ (for withdrawing substituents).[8] Toward the p-CH_3O, p-CH_3, H subset, PhOCCl shows $\rho^+ = -0.37$ ($r = 0.9997$); toward the p-CF_3, p-Cl, H subset, $\rho = +0.28$ ($r = 0.9997$). We do not understand why m-nitrostyrene appears to be less reactive than expected from the latter correlation, but we note that this olefin is the only meta-substituted substrate in the set.

The ambiphilicity of PhOCCl resembles that of MeOCCl[2] (Table II), as anticipated from FMO considerations.[6] It remains to explain the differing philicities of the PhOCCl species generated from 2 or 3. We believe that the species thermally generated from 2 is free PhOCCl. As in the case of methoxychlorodiazirine,[1a] absolute rate constants for thermolysis of 2 at 25°C displayed little solvent dependence. In particular, the rate constants were very similar in an electron-rich or an electron-poor alkene, consistent with cyclopropanation by olefinic capture of PhOCCl rather than by (e.g.) the decomposition of an initially-formed pyrazoline (with electron-poor alkenes).[9]

Perhaps the species initially generated by the basic decomposition of 3[5] is carbanion 5. Rate determining addition of 5 to styrenes, followed by rapid cyclization to 4 with loss of chloride ion, would be expected to show $\rho > 0$ (nucleophilic behavior) in a Hammett correlation.

In conclusion, when generated by the thermolysis of diazirine 2, a method expected[10] to generate the free carbene, PhOCCl behaves as an ambiphile in additions to $ArCH=CH_2$. These results are in accord with FMO predictions.[6,11]

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References and Notes

(1) (a) R.A. Moss, M. Fedorynski, and W-C. Shieh, J. Am. Chem. Soc., 101, 4736 (1979); R.A. Moss and R.C. Munjal, Tetrahedron Lett., 4721 (1979). (b) Review: R.A. Moss, Acc. Chem. Res., 13, 58 (1980).

(2) R.A. Moss, W. Guo, and K. Krogh-Jespersen, Tetrahedron Lett., 23, 15 (1982).

(3) R.A. Moss, C.M. Young, L.A. Perez, and K. Krogh-Jespersen, J. Am. Chem. Soc., 103, 2413 (1981).

(4) R.A. Moss, L.A. Perez, J. Włostowska, W. Guo, and K. Krogh-Jespersen, J. Org. Chem., 47, 4177 (1982).

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Table I. Experimental Relative Reactivities for CH_3OCCl + X-$C_6H_4CH{=}CH_2$, 25°C.

	Competing alkenes		
Entry	A[a]	B[a]	$\underline{k}_A/\underline{k}_B$[b]
1	*m*-NO_2	H	1.33 ± 0.05
2	*p*-Cl	H	1.17 ± 0.02
3	*p*-CH_3	H	1.32 ± 0.06
4	*p*-CF_3	H	1.42[c]
5	*p*-OCH_3	*p*-CF_3	1.37[c]
6	*p*-OCH_3	*p*-Cl	1.69[c]
7	*p*-OCH_3	*p*-CH_3	1.45[c]

[a] X in X-$C_6H_4CH{=}CH_2$. [b] Errors are average deviations of 2 independent competitions. [c] Single competition.

Table II. Relative Reactivities for Additions of CZY to X-$C_6H_4CH{=}CH_2$.

	$\underline{k}_X/\underline{k}_H$		
X in X-$C_6H_4CH{=}CH_2$	PhOCCl[a]	PhOCCl[b]	MeOCCl[c]
p-CH_3O	1.95[d]	0.74	1.50
p-CH_3	1.32	0.88	1.07
H	1.00	1.00	1.00
p-Cl	1.17	1.12	1.04
p-CF_3	1.42		
m-NO_2	1.33		1.27

[a] This work; thermal decomposition of 2, 25°C. [b] Reference 5; NaOH-phase transfer catalyzed decomposition of 3, 27°C. [c] Reference 2; thermal decomposition of methoxychlorodiazirine, 25°C. [d] Calculated from Table I as the average of the products of entries 4x5 (1.95), 6x2 (1.98), and 7x3 (1.91).

References and Notes (continued)

(6) Taking $\varepsilon_{\underline{1}}^{HO}$ = -10.78 (eV), $\varepsilon_{\underline{1}}^{LU}$ = 2.02,[4] and $\varepsilon^{HO}_{X\text{-}C_6H_4CH=CH_2}$ = -7.74 (*p*-CH_3O), -8.20 (*p*-CH_3), -8.43 (H), -8.90 (*m*-Cl), -9.11 (*m*-NO_2),[2] and $\varepsilon^{LU}_{X\text{-}C_6H_4CH=CH_2}$ = 0.48 (*p*-CH_3O), 0.34 (*p*-CH_3), 0.25 (H), -0.27 (*m*-Cl), -0.34 (*m*-NO_2),[2] we obtain[1,2] the differential orbital energies $\underline{E}$ = $(\varepsilon^{LU}_{PhOCCl} - \varepsilon^{HO}_{X\text{-}C_6H_4CH=CH_2})$ and $\underline{N}$ = $(\varepsilon^{LU}_{X\text{-}C_6H_4CH=CH_2} - \varepsilon^{HO}_{PhOCCl})$ (in eV) for the reaction of PhOCCl with each styrene:

	X in X-$C_6H_4CH{=}CH_2$				
Differential Energy	*p*-CH_3O	*p*-CH_3	H	*m*-Cl	*m*-NO_2
$\underline{E}$	9.76	10.22	10.45	10.92	11.13
$\underline{N}$	11.26	11.12	11.03	10.51	10.44

$\underline{E}$ is the energetically dominant FMO interaction with *p*-CH_3O and *p*-CH_3 styrenes, whereas $\underline{N}$

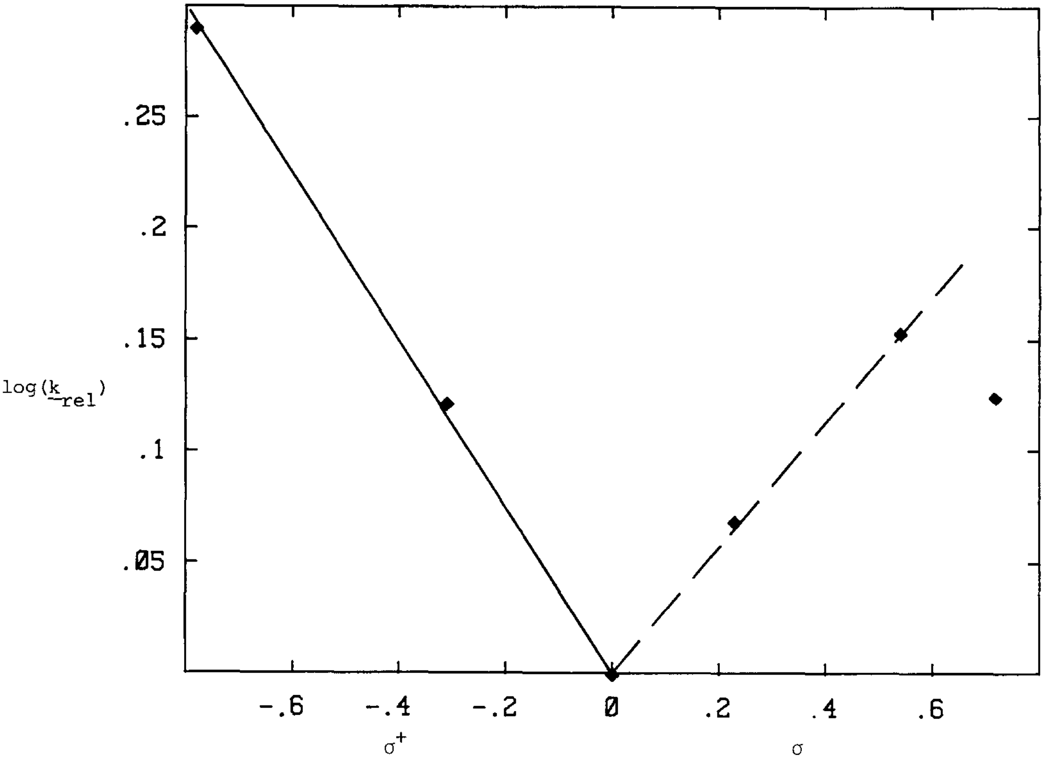

Figure 1. log($\underline{k}_{rel}$) vs. σ^+ or σ for additions of PhOCCl to X-$C_6H_4CH{=}CH_2$; cf., Table II. The solid line correlates data for X=p-CH_3O, p-CH_3, and H; the broken line correlates data for H, p-Cl, and p-CF_3. The point for X=m-NO_2 has been arbitrarily excluded.

References and Notes (continued)

(6) (continued) dominates with the m-Cl and m-NO_2 derivatives. The inversion, centered at styrene itself, "predicts" that PhOCCl should be ambiphilic toward this substrate set. In particular, PhOCCl should be electrophilic toward the p-CH_3O, p-CH_3, H subset.

(7) The half-life of 2 is ~19 h under these conditions; see below.

(8) Sigma values are taken from C.D. Ritchie and W.F. Sager, Prog. Phys. Org. Chem., 2, 323 (1964)

(9) Intermittently monitoring the decay of 2 at 340 nm, we found good first order kinetics with $10^6\underline{k}$ (sec^{-1}) = 9.47 (in $Me_2C{=}CMe_2$), 11.1 (in $CH_2{=}CHCOOMe$), and 9.83 (in isooctane). Interference by styrene absorbances prevented us from carrying out these experiments with the actual substrates of Table I.

(10) N.P. Smith and I.D.R. Stevens, J. Chem. Soc., Perkin Trans., 2, 213 (1979); Tetrahedron Lett., 1931 (1978); R.A. Moss and W.-C. Shieh, ibid., 1935 (1978).

(11) A referee has asked whether the possible intervention of kinetically significant carbene/alken complexes during addition reactions could complicate interpretation of carbenic philicity. Th general occurrence of such complexes [cf., Tetrahedron Lett., 24, 685 (1983) for leading references] is by no means clear; their importance could be restricted to highly reactive carbene and alkenes (neither PhOCCl nor styrenes fit this description). Moreover, the electrophilicity of CCl_2, CF_2, and PhCCl, the nucleophilicity of $(CH_3O)_2C$, and the ambiphilicity of PhOCCl, are all as predicted by theoretical considerations (see above).[1b,4] If carbene/alkene complexes intervene in these reactions, they do not appear to create anomalies in linear free energy analyses.

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