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Hammett Studies of Aryldichloromethide Carbanion Reactions

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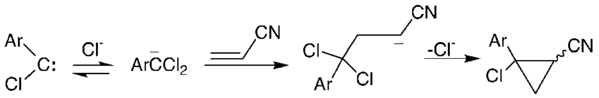
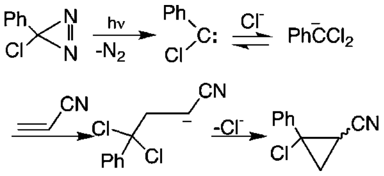
ABSTRACT



Rate constants were measured for the capture of para-substituted phenylchlorocarbenes by chloride ions to form aryldichloromethide carbanions and for the additions of these carbanions to acrylonitrile. Hammett analyses give $\rho = +0.86$ for the former reaction and $\rho = -2.65$ for the latter reaction.

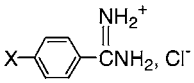
We recently reported that phenylhalocarbenes are captured by halide ions, generating phenyldihalomethide carbanions. Moreover, the carbanions can be visualized by laser flash photolysis (LFP), and their additions to, e.g., acrylonitrile, affording cyclopropanes, can be kinetically monitored.[1] We illustrate the reaction sequence for phenylchlorocarbene and phenyldichloromethide carbanion in Scheme 1, where the carbanion adds to acrylonitrile in a Michael fashion, affording a new carbanion which closes to the 1-chloro-1-phenyl-2-cyanocyclopropane isomers with the expulsion of chloride.[1] LFP reveals an absorption for $PhCCl_2^-$ at 410 nm which we monitored in the presence of varying quantities of added acrylonitrile. We thus obtained $k = 2.5 \times 10^7$ M^{-1} s^{-1} for the quenching of the carbanion by acrylonitrile.

Scheme 1



Mayr noted that "only few kinetic data on addition reactions of carbanions to electron-deficient π-electron systems have been reported."[2,3] Accordingly, we examined the kinetics of aryldichloromethide additions to acrylonitrile in the context of a Hammett analysis. The results are reported here.

Arylamidine hydrochlorides **1a**−**e** were prepared from the corresponding arylnitriles by reaction with NaOMe/MeOH, followed by NH_4Cl. Procedures for **1a**,[4] **1b**,[4] **1c**,[4] and **1e**[5] have been published; new amidine **1d** was similarly prepared (see the Supporting Information). The amidines were oxidized to arylchlorodiazirines **2a**−**e** with NaOCl according to Graham's procedure.[4−6] The diazirines were characterized



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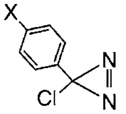

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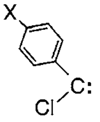

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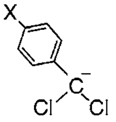

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a, X=H; **b**, X=Cl; **c**, X=CF_3; **d**, X=CN; **e**, X=NO_2

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[1] Moss, R. A.; Tian, J. *J. Am. Chem. Soc.* **2005**, *127*, 8960.

[2] Lucius, R.; Mayr, H. *Angew. Chem., Int. Ed.* **2000**, *39*, 1995.

[3] Review: Bernasconi, C. F. *Tetrahedron* **1989**, *45*, 4017.

[4] Moss, R. A.; Terpinski, J.; Cox, D. P.; Denney, D. Z.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1985**, *107*, 2743.

[5] Creary, X.; Sky, A. F.; Phillips, G. *J. Org. Chem.* **1990**, *55*, 2005 and references therein.

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by ^{1}H and ^{13}C NMR spectroscopy and by UV spectroscopy. All of the diazirines had UV absorptions in the 325−390 nm region. They have been previously described,[5] except for **2d** (see the Supporting Information). LFP of diazirines **2a**−**e** with a xenon fluoride excimer laser at 351 nm ($A_{\mathbf{2a-e}}$ = 0.5 at 310 nm) generated carbenes **3a**−**e**. The UV spectra of **3a** and **3b** in 1 M MeCN−THF and of **3c**−**e** in CCl_4 are shown in Figure S1 of the Supporting Information; their absorption maxima are collected in Table 1.[7]

Table 1. UV Absorptions of Carbenes (**3**) and Carbanions (**4**)[a]

X	solvent	λ_{max} (**3**)	λ_{max} (**4**)
H	MeCN−THF	320	410
Cl	MeCN−THF	320	408
CF_3	CCl_4	312	400
CN	CCl_4	312	400
NO_2	CCl_4	312	416

[a] Reported in nm at 25 °C in 1 M MeCN−THF (**a** and **b**) and in CCl_4 (**c**−**e**).

In the presence of added tetrabutylammonium chloride (TBACl), LFP of the diazirines revealed not only carbenes **3a**−**e** but also carbanions **4a**−**e** formed by reactions of the carbenes with chloride[1] (see Scheme 1). Figure 1 shows the UV spectra of carbene **3b** and carbanion **4b** formed upon LFP of diazirine **2b** in the presence of 0.2 M TBACl in 1 M MeCN−THF. Analogous LFP−UV spectra of carbene **3a** and carbanion **4a** appear in Figure S2 (Supporting Information); absorption maxima of the carbanions appear in Table 1.

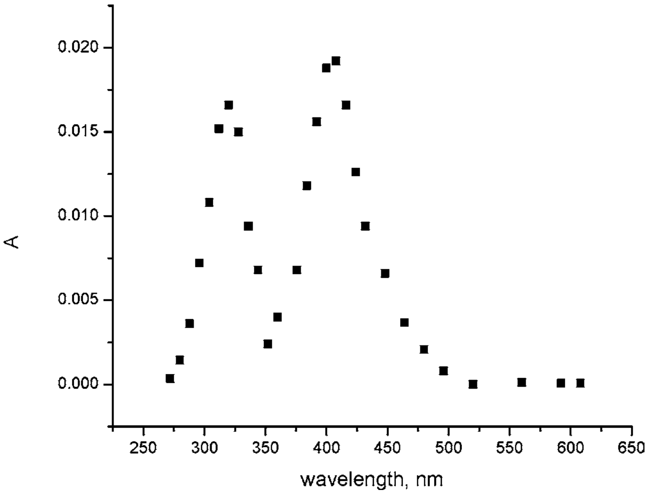

Figure 1. UV absorptions of carbene **3b** (320 nm) and carbanion **4b** (408 nm) in 1 M MeCN−THF. The data points were recorded 400 ns after the laser pulse.

MeCN−THF was not an appropriate solvent for similar reactions of carbenes **3c**−**e** because these form transient ylides with THF (see Figure S3, Supporting Information). The THF ylide of carbene **3e** has been reported previously.[8] On the other hand, reactions of carbenes **3c**−**e** with TBACl could be visualized by LFP in CCl_4.[9] Figure S2 (Supporting Information) shows the LFP−UV spectra of carbenes **3c**−**e** and carbanions **4c**−**e** in CCl_4; absorption maxima appear in Table 1. Although phenylchlorocarbene abstracts Cl from CCl_4, the reaction is rather slow ($k = 3.8 \times 10^4$ M^{-1} s^{-1} in MeCN)[10] and does not interfere with the much more rapid (μs to ns) processes that we examine here.

Kinetics of the carbene−chloride reactions were followed by LFP, monitoring the apparent rate of decay of each carbene with added TBACl. Rate constants for the carbene−chloride reactions were obtained from the slopes of correlations of the apparent quenching rate constants as a function of the concentration of TBACl. The rate constants (k_{Cl}) are collected in Table 2; Figure S4 of the Supporting Information depicts the correlations.

Table 2. Rate Constants for Reactions of Carbenes and Carbanions

carbene	k_{Cl} (M^{-1} s^{-1})	carbanion	k_{ACN} (M^{-1} s^{-1})
3a[a]	1.61×10^8	**4a**[a]	2.50×10^7
3b[a]	3.45×10^8	**4b**[a]	1.07×10^7
3c[b]	5.45×10^8	**4c**[b]	1.62×10^6
3d[b]	7.00×10^8	**4d**[b]	9.18×10^5
3e[b]	8.68×10^8	**4e**[b]	1.16×10^4

[a] Solvent 1 M MeCN−THF, 25 °C. [b] Solvent CCl_4, 25 °C.

The capture of carbenes **3a**−**e** by chloride ion to form carbanions **4a**−**e** is rapid, with k_{Cl} ranging from 1.6×10^8 M^{-1} s^{-1} for **3a** to 8.7×10^8 M^{-1} s^{-1} for **3e**. The rate constants increase with increasing electron-withdrawing power of the carbene's para-substituent; i.e., as the carbene is destabilized and the carbanion product is stabilized.[11] However, the range of the rate constants is small, with k_{Cl} (**3e**)/k_{Cl} (**3a**) = 5.4. A Hammett correlation of log k_{Cl} vs σ_P[12] (Figure 2) affords $\rho = +0.86$ ($r = 0.985$).

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[6] Graham, W. H. *J. Am. Chem. Soc.* **1965**, *87*, 4396.

[7] UV spectra of **3a**−**c** at 77 K (3-methylpentane glass) and at ambient temperature (isooctane solution) are described in: Gould, I. R.; Turro, N. J.; Butcher, J., Jr.; Doubleday, C., Jr.; Hacker, N. P.; Lehr, G. F.; Moss, R. A.; Cox, D. P.; Guo, W.; Munjal, R. C.; Perez, L. A.; Fedorynski, M. *Tetrahedron* **1985**, *41*, 1587.

[8] Celebi, S.; Tsao, M.-L.; Platz, M. S. *J. Phys. Chem. A* **2001**, *105*, 1158.

[9] Carbanions **4a** and **4b**, however, were unstable in CCl_4 and not readily visualized in this solvent.

[10] Jones, M. B.; Maloney, V. M.; Platz, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 2163. Electron-withdrawing substituents on ArCCl further slow Cl abstraction.

[11] *p*-Methylphenylchlorocarbene did not appear to give the corresponding dichloromethide carbanion (LFP−UV)) with TBACl.

[12] Substituent constants are taken from: Smith, M. B.; March, J. *March's Advanced Organic Chemistry, Reactions, Mechanisms, and Stucture*, 5th ed.; Wiley: New York, 2001; p 370. σ_p^- is used in the Hammett correlation of Figure 3 for the *p*-nitro substituent because there is direct resonance interaction of the carbanionic charge and the substituent (cf. this reference, p 375). In this case, the use of σ_p leads to a poor correlation. Surprisingly, however, the rate data for the cyano-substituted carbanion correlates much better with σ_p than with σ_p^-.

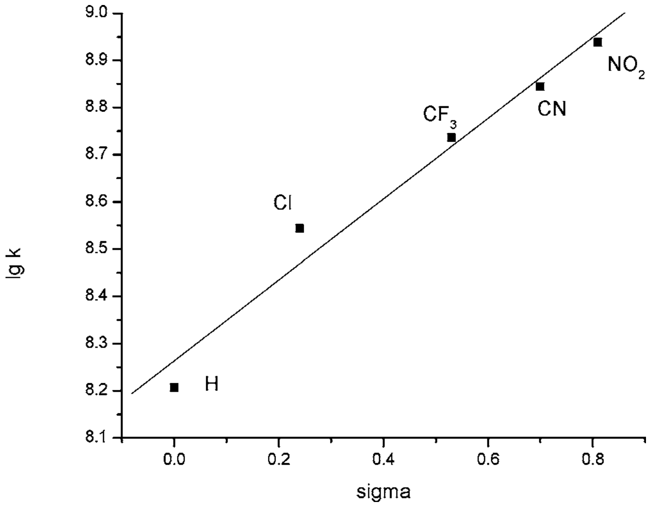

Figure 2. Hammett correlation of log k_{Cl} vs σ_P for the reactions of carbenes **3a**−**e** with TBACl; see Table 2 and text.

Carbanions **4a**−**e** were formed from carbenes **3a**−**e** in the presence of 0.2 M TBACl. The kinetics of the carbanions' additions to acrylonitrile (ACN) were monitored by following the apparent rate of decay of the carbanions with added ACN. Rate constants (k_{ACN}) were obtained from slopes of correlations of the apparent quenching constants as a function of ACN concentration. The values of k_{ACN} are collected in Table 2; Figure S5 of the Supporting Information shows the individual correlations. GC−MS demonstrated that the appropriate cyclopropanes (see Scheme 1) were formed in the additions of carbanions **4a**−**e** to acrylonitrile.

The rate constants for additions of carbanions **4a**−**e** to acrylonitrile (k_{ACN}) are considerably more sensitive to substituents than k_{Cl} for the carbene−chloride reactions. Thus, k_{ACN} decreases from a high of 2.5×10^7 M^{-1} s^{-1} for **4a** to a low of 1.2×10^4 M^{-1} s^{-1} for **4e**, a ratio of 2155. The rate constants decrease with increasing electron-withdrawing power of the carbanion's para substituent, i.e., as the carbanion is increasingly stabilized and the loss of stabilization upon addition to ACN becomes more substantial. A Hammett correlation of log k_{ACN} vs σ_P (σ_P^- for NO_2)[12] appears in Figure 3, where $\rho = -2.65$ ($r = 0.991$).

A conventional interpretation of the Hammett correlations suggests that the reactions of carbenes **3** with Cl^- to give carbanions **4** traverse "early" transition states. Minimal negative charge is imposed on the α carbon atom, leading to high rate constants, relatively little dependence on the para substituent, and a small positive Hammett ρ value. On the other hand, the substantial rate constant range, significant substituent dependence, and relatively large negative ρ observed for the additions of carbanions **4** to ACN suggest that these reactions involve "late" transition states in which there is substantial bonding between the carbanion's α carbon and the β carbon of the ACN. The implication is that Michael-type additions of $ArCX_2^-$ to electron-deficient alkenes will generally be selective processes, quite sensitive to substrate structure, and possibly subject to asymmetric induction in appropriate cases.[13] These are intriguing synthetic possibilities which we intend to explore.

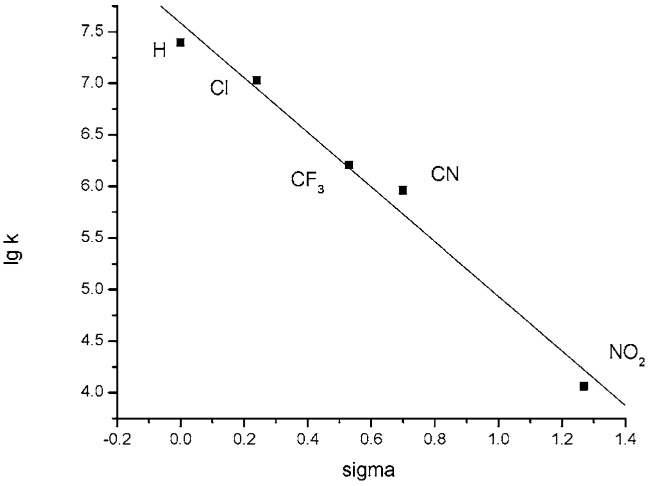

Figure 3. Hammett correlation of log k_{ACN} vs σ_P (σ_P^- for NO_2) for the reactions of carbanions **4a**−**e** with ACN; see Table 2 and text.

Acknowledgment. We are grateful to the National Science Foundation for financial support.

Supporting Information Available: Preparations of **1d** and **2d**; Figures S1−S5, showing UV spectra of carbenes, carbanions, and THF-ylides; and rate constant determinations for carbene−chloride and carbanion−acrylonitrile reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) For example, chloride ion could be partnered by a chiral quaternary ammonium ion instead of the achiral tetrabutylammonium ion, thus generating $ArCCl_2^-$ paired with a chiral cation. See for examples of asymmetric phase-transfer catalysis by chiral ammonium ions: Maruoka, K.; Ooi, T. *Chem. Rev.* **2003**, *103*, 3013.