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Probing charge alteration in the π-mediated rearrangement of 1-indanylchlorocarbene

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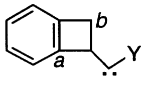
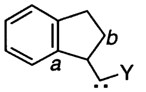
Abstract—The 'phenyl' carbon migration of 1-indanylchlorocarbene is accelerated by appropriate aromatic methoxyl substitution in accord with a π-mediated rearrangement mechanism. © 2001 Elsevier Science Ltd. All rights reserved.

The 1,2-C migration of 'phenyl' carbon *a* is kinetically preferred to that of 'benzyl' carbon *b* in the rearrangements of both benzocyclobutenylcarbenes **1-Y** (Y = Cl, OAc or F)[1] and benzocyclopentenyl[indanyl]carbenes **2-Y** (Y = Cl or OAc).[2] These rearrangements are π-mediated and can be formulated as an electrophilic attack of the carbenic carbon on the aromatic ring,[1,2] illustrated for **2-Cl** (X = H) in Eq. (1).[3]



1-Y

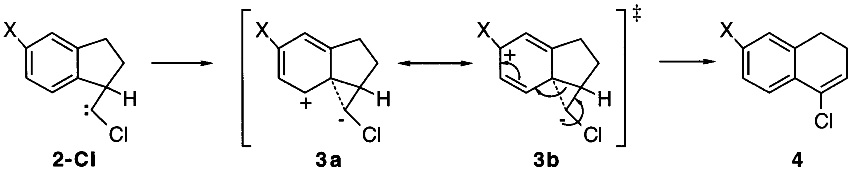


2-Y

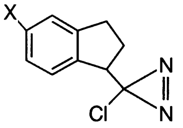
In this formulation, transition state **3** bears a partial positive charge on the appropriate aromatic carbon atoms. In particular, some positive charge will be imposed on the carbon *para* to the site of carbenic attack; cf. **3b**. Accordingly, observation of a significant substituent effect at the '*para*' carbon (e.g. for X = MeO) would support the π-mediation/electrophilic attack mechanism. Here we present pertinent computational and experimental probes.

Ab initio and DFT calculations[4a] of the rearrangement of **2-Cl** to **4-Cl** (X = H) afforded the ground and transition states illustrated in Fig. 1. The B3LYP/6-31G* activation parameters (298 K, gas phase) were $\Delta H^{\ddagger} = 4.2$ kcal/mol, $\Delta S^{\ddagger} = -5.07$ eu, and $\Delta G^{\ddagger} = 5.7$ kcal/mol. A 0.76 Å contraction between the GS and TS separations of the carbene and proximal aromatic carbon atoms is apparent as the new C–C bond of **4-Cl** begins to form. Concurrently, there is a 0.16 Å expansion of the C–C bond that is destined to break. Most importantly, the computed charges[4b] indicate the imposition of 0.03–0.16 unit of positive charge on the '*para*' carbon as GS **2-Cl** advances to TS **3**.

An experimental probe of charge alteration is possible by comparison of the absolute kinetics and product distributions for the rearrangements of the indanylchlorocarbenes **2-Cl** (X = H),[2] and **2-Cl** (X = MeO). These carbenes were generated from diazirines **5**, where the preparative sequence for **5** (X = MeO) followed that described[2] for **5** (X = H).[5] Thus, 5-methoxy-1-indanone



(1)



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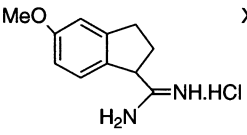

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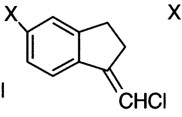

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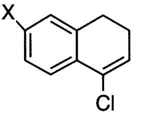

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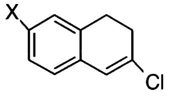

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Keywords: carbenes; diazirines; kinetics.

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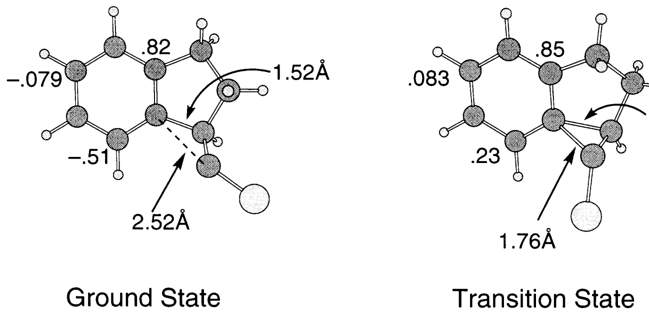

Figure 1. B3LYP/6-31G* geometries and Mullikin charges computed for the ground state (GS) and transition state (TS) in the rearrangement of **2-Cl** to **4-Cl**.[4]

was converted (42%) to 5-methoxy-1-cyanoindane with tosylmethyl isocynanide and NaOEt in DME/EtOH. The cyanoindane afforded 50% of 5-methoxyindane-1-carboximidamide, **6** upon reaction with $MeClAlNH_2$ (toluene, 80°C, 3 h).[6] Amidine **6** was then oxidized to 3-chloro-3-(5-methoxyindan-1-yl)diazirine, **5** (X = MeO) (30%, λ_{max} 346, 362 nm, pentane) with 12% aqueous NaOCl in DMSO at 30–35°C.[7] The diazirine was purified by short path chromatography on silica gel with pentane eluent, and characterized by UV and NMR spectroscopy.

Thermolysis of **5** (X = MeO) in pentane (78°C, sealed tube, 12 h) gave 66.7% of *E*,*Z*-1-chloromethylene-5-methoxyindane, **7** (X = MeO) by 1,2-H shift of carbene **2-Cl** (X = MeO), and 33.3% of 1-chloro-3,4-dihydro-6-methoxynaphthalene, **8** (X = MeO) by 1,2-C_a shift of **2-Cl** (X = MeO); less than 1% of 1,2-C_b shift to **9** (X = MeO) was observed (GC).

Products were identified by GC-MS and GC-coinjection with authentic samples. *Z*,*E*-**7** were prepared by a Wittig reaction of 5-methoxy-1-indanone and $Ph_3P{=}CHCl$, whereas **8** and **9** were obtained from reactions of 6-methoxy-1-tetralone or 6-methoxy-2-tetralone, respectively, with PCl_5.

Photolysis of diazirine **5** (X = MeO) in a pentane solution ($A_{346} = 0.5$, $\lambda > 320$ nm, 25°C, 2 h) gave alkenes **7** and 1,2-C_a shift product **8** in a ratio of 1.67±0.10, similar to the product ratio obtained by thermolysis (2.00±0.05).

The absolute rate constant (k_{re}) for rearrangement of carbene **2-Cl** (X = MeO) was determined at 25°C by laser flash photolyis (LFP) at 351 nm of diazirine **5** (X = MeO) in pentane.[8] We employed the pyridine ylide methodology,[9] observing a strong absorption at 390 nm for the carbene/pyridine ylide. A correlation of the apparent rate constants for ylide formation (2.33–2.62×10^7 s^{-1}) versus pyridine concentration (19–49 mM) was linear (five points, $r = 0.997$), with a slope of 9.1×10^7 M^{-1} s^{-1}, equivalent to the rate constant for ylide formation from **2-Cl** (X = MeO), and a Y-intercept of 2.16×10^7 s^{-1}, which we take as k_{re}, the composite rate constant for carbene rearrangements to **7** and **8**.

We can partition k_{re} for **2-Cl** (X = MeO) into k_H and k_{Ca} in accord with the product distribution. The photochemical result (**7**/**8** = 1.67) may be biased by rearrangement directly from the electronically excited diazirine,[1,10] so that we employ[2] the 78°C thermal distribution (**7**/**8** = 2.00). We thus obtain $k_H = 1.44 \times 10^7$ s^{-1} and $k_{Ca} = 7.2 \times 10^6$ s^{-1} for the rearrangements of **2-Cl** (X = MeO) to **7** and **8**, respectively.[11] In Table 1, we compare these rate constants to analogous and similarly derived data for the rearrangements of **2-Cl** (X = H)[2] and cyclopentylchlorocarbene.[2] The latter affords only the 1,2-H shift product, chloromethylenecyclopentane.

The kinetics results paint a clear picture. Whereas the rate constants for the 1,2-H shifts of all three carbenes are similar, indeed, identical for **2-Cl** (X = H or MeO), the rate constant for the 1,2-C_a rearrangement of **2-Cl** (X = MeO) is 4.8 times greater than k_{Ca} for **2-Cl** (X = H). C_a migration is accelerated by substitution of the electron donating MeO group on the aromatic ring carbon *para* to the migrant carbon atom, i.e. a ring carbon computed to become more positive during the π-mediated rearrangement of **2-Cl** to **4** (cf. Fig. 1).[12] Additionally, 1,2-C_b migration, already at a 33-fold kinetic disadvantage in **2-Cl** (X = H), is no longer observable with **2-Cl** (X = MeO), where the 1,2-C_a process is enhanced ~fivefold.

The present results provide strong support for the formulation of these 1,2-aryl carbon shifts[1,2] as electrophilic attacks of the carbenic centers on the *ipso* carbon atoms of the phenyl groups (cf. Eq. (1)).

Table 1. Absolute rate constants (s^{-1}) of carbenic rearrangements

Carbene	k_H (1,2-H)	k_{Ca} (1,2-C_a)	k_{Cb} (1,2-C_b)
2-Cl (X = H)[a]	1.4×10^7	1.5×10^6	4.5×10^4
2-Cl (X = MeO)[b]	1.4×10^7	7.2×10^6	[c]
C_5H_9CCl[a,d]	2.2×10^7	[c]	[c]

[a] Data from Ref. 2.

[b] This work.

[c] Not observed.

[d] Cyclopentylchlorocarbene.

Acknowledgements

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4. (a) Gaussian 98, Revision A7. Gaussian, Inc.; Pittsburgh, PA, 1998. DFT calculations used Becke's three parameter hybrid method with the LYP correlation functional: Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. ZPE and thermal corrections were obtained from HF/6-31G* gas phase results; (b) Similar qualitative alterations in charge were computed by two other methods incorporated in Gaussian 98: natural population analysis ($\Delta\delta = +0.031$) and the CHelpG method ($\Delta\delta = +0.044$). The Mulliken charge alteration (Fig. 1) is +0.16 for the '*para*' carbon, and +0.03 and +0.74 for the '*ortho*' carbons.
5. Details may be found in the Ph.D. Thesis of W. Ma, Rutgers University, New Brunswick, NJ, May, 2000.
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11. We estimate errors of ±15% in these absolute rate constants.
12. In a related comparison, 1,2-C_a migration, which is ~10 times slower than 1,2-H migration in **2-Cl** (X = H), is only twice as slow in **2-Cl** (X = MeO).