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Diphenylmethylchlorocarbene: comparison of experiment and theory

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Abstract

Diphenylmethylchlorocarbene (5) exhibits minimal 1,2-Ph migration ($k_{Ph}=1.5\times10^6$ s^{-1}); 1,2-H migration ($k_H=2.1\times10^7$ s^{-1}) is 14 times faster in pentane at 25°C. © 1999 Elsevier Science Ltd. All rights reserved.

The kinetics and energetics of the 1,2-rearrangements of alkylchlorocarbenes have been intensively scrutinized,[1] especially carbenes with representative alkyl groups such as methylchlorocarbene (**1**), *i*-propylchlorocarbene (**2**), benzylchlorocarbene (**3**), and α-methylbenzylchlorocarbene (**4**).[2] The exceptionally rapid 1,2-H shifts ($k_H>10^8$ s^{-1}) observed[2a,c,i] for **2** and **4** led us to examine the corresponding alkylacetoxycarbenes, where the electron-donating effect of the acetoxy 'spectator' substituent[3] stabilized the carbenes,[4] and depressed their 1,2-H shifts to a readily measurable kinetic range (10^5–10^6 s^{-1}).[5]

Most recently, Keating, Garcia-Garibay, and Houk (KGH) provided an elegant and thorough theoretical survey of the 1,2-H and 1,2-Ph rearrangements of 7 alkylchlorocarbenes (including **1**–**4**) at the B3LYP/6-311G**//B3LYP/6-31G* level.[6] Not only did KGH describe the ground state and rearrangement transition state geometries and energies of the carbenes, but their study also differentiated the intrinsic migratory aptitudes of H and Ph from the 'bystander' effects of Ph and Me substituents[7] which modulate the migratory aptitudes.[8]

Highlights of the KGH analysis[6] include: (a) The generally accepted migratory aptitude in 1,2-carbenic rearrangements is H>Ph>Me, although bystander effects[8,9] strongly influence the observed aptitudes. (b) The *innate* barrier opposing 1,2-Ph (calculated at 9.5 kcal/mol in **3**) is *lower* than that for 1,2-H (calculated at 11.5 kcal/mol in **1**); i.e., the intrinsic migratory aptitude is Ph>H. One observes 'exclusive' 1,2-H migration[10] in **3** because the Ph bystander lowers E_a for the 1,2-H shift from 11.5 kcal/mol (in **1**) to 5.5 kcal/mol in **3**, which then dominates 1,2-Ph (E_a ~9.5 kcal/mol). (c) As bystander substituents, Ph>Me at promoting a 1,2-H shift, but only if steric factors do not prevent Ph conjugation with the developing C=C; steric inhibition of resonance renders Ph less effective than Me.[6,9] (d) The desired alignment of Ph can be disrupted by a second C_α substituent; a *gem*-Me would prevent Ph from achieving planarity with

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the incipient C=C, and mitigate its effect. Substituent effects at C_α are therefore not additive, and 2 Me groups promote the 1,2-H shift more than 1 Ph and 1 Me.

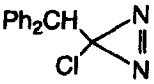
$CH_3\ddot{C}Cl$ **1**

$(CH_3)_2CH\ddot{C}Cl$ **2**

$PhCH_2\ddot{C}Cl$ **3**

$PhCH(CH_3)\ddot{C}Cl$ **4**

$Ph_2CH\ddot{C}Cl$ **5**



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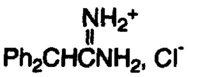
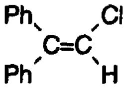


$Ph_2CH\overset{\overset{NH_2^+}{\|}}{C}NH_2,\ Cl^-$

7



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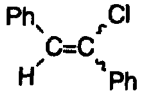

(*E,Z*)-**9**

These considerations lead KGH to suggest that it is "possible that the rearrangement of 2,2-diphenylmethylchlorocarbene (**5**) might give significant amounts of 1,2-Ph shift... steric interactions between *gem*-C_2 phenyl groups would prevent effective stabilization of a 1,2-H shift transition state, while good alignment of a single Ph bystander substituent with the forming π-system could accelerate the phenyl rearrangement significantly."[6] Here we report an experimental study of this suggestion.

Carbene **5** was generated either photochemically or thermally from diazirine **6**. The latter was obtained by HOCl oxidation[11] of diphenylmethylamidinium chloride, **7**, prepared from diphenylacetonitrile by reaction with methylchloroaluminum amide.[12] Diazirine **6** (36%) was purified by silica gel chromatography (1:2 CH_2Cl_2:pentane) and characterized by UV (342, 358 nm) and NMR spectroscopy.

Solutions of **6** in pentane or tetrachloroethane (TCE) were photolyzed in a Rayonet reactor (A_{342}=0.5, 350 nm, 25°C) or thermally decomposed (78°C, 12 h), affording 1,2-H shift product 1-chloro-2,2-diphenylethene (**8**), and 1,2-Ph shift products (*E,Z*)-1-chloro-1,2-diphenylethene (**9**). These were identified by isolation (**8**)[13] or by capillary GC spiking experiments with a synthesized sample (**9**).[14] Appropriate NMR and MS data validated the structural assignments.

H-shift exceeded Ph-shift in all cases, with pentane solvent particularly favoring 1,2-H. Product distributions (1,2-H:1,2-Ph) were, in pentane, 14.2:1 (hν) or 13.7:1 (Δ), and, in TCE, 3.3:1 (hν) or 7.3:1 (Δ). The photochemical results, however, are likely to be contaminated by rearrangements directly from the excited diazirine,[15] so that the thermal product distributions should be more representative of carbene **5**. The thermal 1,2-Ph shift ranges from 7% (pentane) to 12% (TCE) of the total 1,2-rearrangement. The 2:1 statistical advantage of Ph vs H in **5** means that these values should be halved to reflect the weight of Ph migration.

Absolute rate constants (reproducibility ±5%) for the rearrangements of **5** were measured at 25°C by laser flash photolysis (LFP)[4] at 351 nm of diazirine **6** in pentane or TCE (A_{342}=0.5). Data were obtained using the pyridine ylide method,[4,5,16] monitoring the growth of the **5**/pyridine ylide at 390 nm, with [pyr]=0.012–0.054 M. Details of this methodology as applied to carbenic rearrangements have been described.[4,5] We thus obtained $k_T=2.2\times10^7$ s^{-1} (pentane) and $k_T=2.6\times10^7$ s^{-1} (TCE) for the sum of 1,2-H and 1,2-Ph shifts of **5**. Partitioning these rate constants according to the 78°C product distributions (without statistical correction) affords estimates of $k_H=2.1\times10^7$ (pentane) or 2.3×10^7 s^{-1} (TCE), and $k_{Ph}=1.5\times10^6$ (pentane) or 3.1×10^6 s^{-1} (TCE). An Arrhenius study of k_T from −40 to 25°C in TCE gave E_a=1.65 kcal/mol and log A=8.6 s^{-1} (7 points, r=0.99).

How do these results compare with the KGH[6] predictions? In Table 1 the kinetic data for the 1,2-rearrangements of carbenes **1**–**5** and EtCCl are shown. It is striking that k_H for **5** is slow enough to be readily measurable by our LFP apparatus which requires an intermediate lifetime >10 ns. In pentane, $\tau_5\sim48$ ns, and $k_H=2.1\times10^7$ s^{-1}, which is ~24 times *slower* than k_H for **4**. Indeed, k_H(**5**) is even less than k_H(**3**). Thus, α-Me substitution on $PhCH_2CCl$, affording PhCHMeCCl (**3** → **4**) enhances k_H by ~10-fold, but α-Ph substitution (**3** → **5**) decreases k_H by ~2.6 times. Moreover, 2 α-Me groups (as in **2**) are at least five times better at promoting a 1,2-H shift than the 2 α-Ph groups of **5**.

Table 1
Kinetic data for alkylchlorocarbene 1,2-rearrangements[a]

Carbene	k_H (s^{-1})	k_{Ph} (s^{-1})	E_a (kcal/mol)	log A (s^{-1})	References
MeCCl (**1**)	3 x 10^6		4.9	9.7	2a,b,c,i
EtCCl	> 10^8		2.4	9.7	2a,c
$PhCH_2CCl$ (**3**)	5.4 x 10^7 [b]		4.5 – 4.8	11.1 – 11.3	2d
Me_2CHCCl (**2**)	> 10^8		~2[c]	~10.3[c]	2a,c,i
PhCHMeCCl (**4**)	~5 x 10^8 [c]				2a,i
Ph_2CHCCl (**5**)	2 x 10^7 [d]	1.5 x 10^6 [d]	1.65[e]	8.6[e]	*f*

[a] In hydrocarbon solvents at 25 °C. [b] In TCE,[2h] k_H = 4.5 x 10^7 s^{-1}, E_a = 3.2 kcal/mol, log A = 10.0 s^{-1}. [c] Estimated value. [d] In TCE, k_H = 2.3 x 10^7 s^{-1} and k_{Ph} = 3.1 x 10^6 s^{-1}. [e] In TCE. [f] This work.

These results are in general agreement with both the KGH analysis[6] (points a–d, above) and with Nickon.[8,9] However, the KGH suggestion that Ph_2CHCCl might exhibit 1,2-Ph migration[6] is not strongly supported: k_{Ph} is ~14 times smaller than k_H (7.3 times smaller in TCE). The activation parameters in Table 1 reveal a low E_a for the 1,2-H shift of **5**. However, the underlying compensation[5b] of E_a and log A generates a very unfavorable A factor, leading to the low k_H for **5**. This again illustrates the entropically unfavorable, geometry-dependent nature of phenyl resonance donation.[5b,6]

The minimal phenyl migration observed with Ph_2CHCCl is echoed in the case of $Ph_2CCHOAc$. Thus, our preliminary studies (in TCE) of the acetoxy analogue of **5**, $Ph_2CHCOAc$, reveal only 1,2-H (k_H=7.2×10^5 s^{-1}) and 1,2-acetyl (k_{Ac}=5.6×10^6 s^{-1}) migrations; no 1,2-Ph shift is observed upon photochemical generation of the carbene from the diazirine at 25°C. Moreover, comparisons with previously obtained kinetic data (in TCE)[5b] reveal that k_H for $Ph_2CHCOAc$ (7.2×10^5 s^{-1}), exceeds k_H for both PhCHMeCOAc (1.6×10^5 s^{-1}) and $PhCH_2COAc$ (5.7×10^4 s^{-1}), although it remains inferior to $Me_2CHCOAc$ (1.9×10^6 s^{-1}). Thus, for RCOAc, 2 α-Me substituents promote the 1,2-H shift more than 2 α-Ph groups, but 1 α-Me and 1 α-Ph are less effective than 2 α-Ph substituents.

Acknowledgement

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