

Tetrahedron Letters 40 (1999) 5101-5104

TETRAHEDRON LETTERS

Diphenylmethylchlorocarbene: comparison of experiment and theory

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Received 8 March 1999; revised 28 April 1999; accepted 1 May 1999

Abstract

Diphenylmethylchlorocarbene (5) exhibits minimal 1,2-Ph migration ($k_{Ph}=1.5\times10^6 \text{ s}^{-1}$); 1,2-H migration ($k_{H}=2.1\times10^7 \text{ s}^{-1}$) 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 ($k_{\rm H} > 10^8 \, {\rm s}^{-1}$) observed^{2a,c,i} for 2 and 4 led us to examine the corresponding alkylacetoxycarbenes, where the electron-donating effect of the acetoxy 'spectator' substituent³ stabilized the carbenes,⁴ and depressed their 1,2-H shifts to a readily measurable kinetic range (10⁵-10⁶ 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 substituents⁷ which modulate the migratory aptitudes.⁸

Highlights of the KGH analysis⁶ 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 migration¹⁰ 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 ($E_a \sim 9.5$ 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.



These considerations lead KGH to suggest that it is "possible that the rearrangement of 2,2diphenylmethylchlorocarbene (5) might give significant amounts of 1,2-Ph shift... steric interactions between *gem*-C₂ 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 oxidation¹¹ of diphenylmethylamidinium chloride, 7, prepared from diphenylacetonitrile by reaction with methylchloroaluminum amide.¹² Diazirine 6 (36%) was purified by silica gel chromatography (1:2 CH₂Cl₂: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 (hv) or 13.7:1 (Δ), and, in TCE, 3.3:1 (hv) 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 $\pm 5\%$) 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 KGH⁶ predictions? In Table 1 the kinetic data for the 1,2rearrangements of carbenes 1–5 and EtCCl are shown. It is striking that $k_{\rm H}$ for 5 is slow enough to be readily measurable by our LFP apparatus which requires an intermediate lifetime >10 ns. In pentane, $\tau_5 \sim 48$ ns, and $k_{\rm H}=2.1\times10^7$ s⁻¹, which is ~24 times *slower* than $k_{\rm H}$ for 4. Indeed, $k_{\rm H}(5)$ is even less than $k_{\rm H}(3)$. Thus, α -Me substitution on PhCH₂CCl, affording PhCHMeCCl (3 \rightarrow 4) enhances $k_{\rm H}$ by ~10-fold, but α -Ph substitution (3 \rightarrow 5) decreases $k_{\rm H}$ 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.

Carbene	<i>k</i> _H (s ⁻¹)	$k_{\rm Ph}({\rm s}^{-1})$	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 ₂ CCl (3)	5.4 x 10 ^{7 b}		4.5 - 4.8	11.1 – 11.3	2d
Me ₂ CHCCl (2)	> 10 ⁸		~2°	~10.3°	2a,c,i
PhCHMeCCl (4)	~5 x 10 ^{8 c}				2a,i
Ph ₂ CHCCl (5)	$2 \times 10^{7} d$	1.5 x 10 ^{6 d}	1.65 ^e	8.6 ^e	f

 Table 1

 Kinetic data for alkylchlorocarbene 1,2-rearrangements^a

^aIn hydrocarbon solvents at 25 °C. ^bIn TCE, ^{2h} $k_{\rm H} = 4.5 \times 10^7 \, {\rm s}^{-1}$, $E_{\rm a} = 3.2 \, {\rm kcal/mol}$, log $A = 10.0 \, {\rm s}^{-1}$. ^cEstimated value. ^dIn TCE, $k_{\rm H} = 2.3 \times 10^7 \, {\rm s}^{-1}$ and $k_{\rm Ph} = 3.1 \times 10^6 \, {\rm s}^{-1}$. ^cIn TCE. ^fThis work.

These results are in general agreement with both the KGH analysis⁶ (points a-d, above) and with Nickon.^{8,9} However, the KGH suggestion that Ph₂CHCCl might exhibit 1,2-Ph migration⁶ 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 Ph₂CHCCl is echoed in the case of Ph₂CCHOAc. Thus, our preliminary studies (in TCE) of the acetoxy analogue of **5**, Ph₂CHCOAc, reveal only 1,2-H ($k_{\rm H}$ =7.2×10⁵ s⁻¹) and 1,2-acetyl ($k_{\rm Ac}$ =5.6×10⁶ 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 $k_{\rm H}$ for Ph₂CHCOAc (7.2×10⁵ s⁻¹), exceeds $k_{\rm H}$ for both PhCHMeCOAc (1.6×10⁵ s⁻¹) and PhCH₂COAc (5.7×10⁴ s⁻¹), although it remains inferior to Me₂CHCOAc (1.9×10⁶ 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

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

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