Examination of Models for Carbocationic Polymerization: Influence of Chain Length on Carbocation Reactivities

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ABSTRACT: The kinetics of the reactions of the carbocations $CH_3[C(CH_3)_2CH_2]_nC^+Ph_2$ (**1a**$^+$−**1d**$^+$, $n = 0$, 1, 2, 34) with allyltrimethylsilane (**4**) and dimethylphenylsilane (**5**) have been investigated. It is found that the carbocation **1a**$^+$ ($n = 0$) is 10^2 times more reactive than the more highly substituted analogues **1b**$^+$−**1d**$^+$, which hardly differ in their electrophilic reactivity. We, therefore, conclude that the $(CH_3)_3$-CCH_2 and $(CH_3)_3CCH_2C(CH_3)_2CH_2$ groups are suitable to mimic the polyisobutylene chain in a growing carbocation.

Introduction

In order to understand the mechanism of carbocationic polymerization, we have performed kinetic experiments with low molecular weight model compounds which possess the same structure as the carbocations involved in polymerization.[1−6] The question arises, however, whether the model systems really reflect the situation in a growing carbocationic chain. We have addressed this problem by comparing the reactivities of persistent low molecular weight carbocations with those of higher molecular weight homologues. Our approach thus differs from related earlier work, which has been based on apparent propagation rate constants.[7,8]

One of us has recently demonstrated that living polyisobutylene polymers can be terminated with 1,1-diphenylethene and quenched with methanol.[9] This method has now been improved and modified to synthesize the compounds **1b**-OMe and **1c**-OMe, precursors of the cations **1b**$^+$ and **1c**$^+$, the reactivities of which have been compared with that of **1d**$^+$.

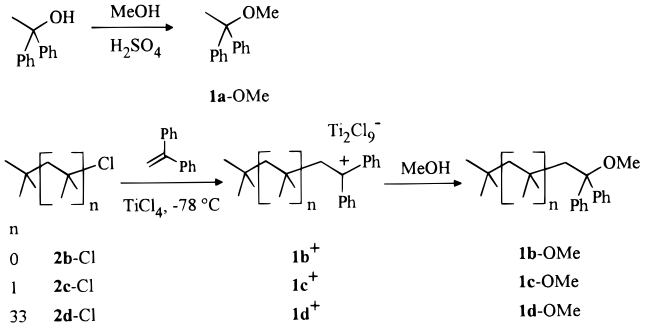
Syntheses of the Alkyldiphenylmethyl Methyl Ethers 1-OMe

While 1,1-diphenylethyl methyl ether **1a**-OMe was prepared from 1,1-diphenylethanol and methanol according to a literature procedure,[10] compounds **1b**-OMe through **1d**-OMe were synthesized by methanolysis of the 1,1-diphenyl-substituted carbenium ions obtained by $TiCl_4$-promoted reactions of the tertiary alkyl chlorides **2b**-Cl - **2d**-Cl with 1,1-diphenylethene (Scheme 1).

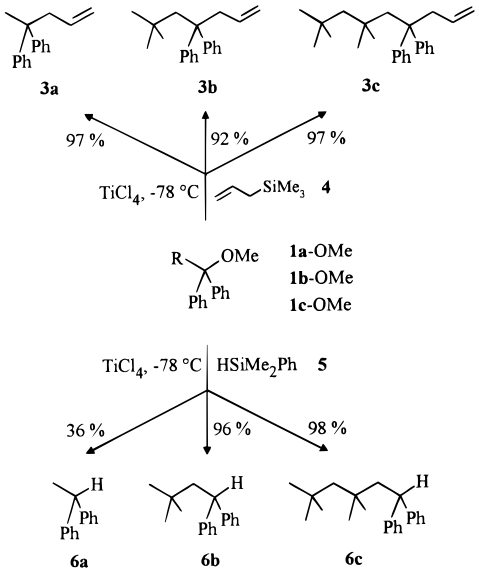
Lewis Acid Promoted Reactions of the Ethers 1-OMe

Treatment of the alkyldiphenylmethyl methyl ethers **1a**-OMe through **1c**-OMe with 1−2 equiv of $TiCl_4$ and 2−3 equiv of allyltrimethylsilane (**4**) gave the terminal olefins **3a**−**3c** (and chlorotrimethylsilane) in almost quantitative yield (Scheme 2). Analogous reactions with

Scheme 1



Scheme 2



dimethylphenylsilane (**5**) yielded the hydrocarbons **6a**−**c**. The low isolated yield of **6a** is due to the problems of separation from silicon-containing side products.

Kinetic Investigations

The ionization of **1b**-OMe with $TiCl_4$ at −50 °C in CH_2Cl_2 gave a solution of **1b**$^+$ with an absorption maximum at $\lambda = 441$ nm ($\log \epsilon = 4.29$), similar to that reported for other alkyldiphenylmethylium ions in sulfuric acid (e.g., **1a**$^+$, $\lambda = 430$ nm, $\log \epsilon = 4.35$) by Deno.[11] For the determination of the kinetics of the

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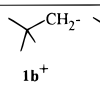
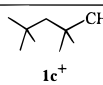
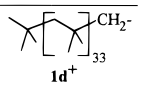
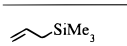
Table 1. Rate Constants and Eyring Activation Parameters of the Reactions of Carbenium Ions $1a^+$−$1d^+$ with Allyltrimethylsilane (4) and Dimethylphenylsilane (5) (CH_2Cl_2)

benzhydryl cation	$\Delta H^‡$ (kJ mol^{-1})	$\Delta S^‡$ (J mol^{-1} K^{-1})	k_2(−70 °C) (L mol^{-1} s^{-1})	k_2(20 °C)$_{calc}$[a] (L mol^{-1} s^{-1})
		Allyltrimethylsilane (**4**)		
1a$^+$			(2−6) × 10^1	
1b$^+$	25.0 ± 0.3	−137 ± 2	1.10 × 10^{-1}	1.49 × 10^1
1c$^+$	30.9 ± 0.7	−118 ± 3	3.38 × 10^{-2}	1.33 × 10^1
1d$^+$	32.8 ± 0.7	−108 ± 4	3.41 × 10^{-2}	1.91 × 10^1
		Dimethylphenylsilane (**5**)		
1b$^+$	20.9 ± 0.4	−97.2 ± 2	1.48 × 10^2	9.58 × 10^3
1c$^+$	25.9 ± 0.8	−77.0 ± 4	8.74 × 10^1	1.40 × 10^4
1d$^+$	26.4 ± 1.0	−74.9 ± 5	8.16 × 10^1	1.44 × 10^4

[a] Calculated from the activation parameters.

Scheme 3. Relative Reactivities of Carbocations toward Nucleophiles (CH_2Cl_2, −70 °C)

R =	H-	H_3C-			
		1a$^+$	**1b**$^+$	**1c**$^+$	**1d**$^+$
 **4**	9.5×10^7 [a]	(2 - 5)×10^2	1.00	0.31	0.31
$PhMe_2SiH$ **5**	4.5×10^3 [a]	-	1.00	0.59	0.55

[a] Extrapolated from the correlation of log(k(−70 °C)) for the reactions of Ar_2CH^+ with allyltrimethylsilane (**4**)[18] or dimethylphenylsilane (**5**)[19] versus the E parameters.[20]

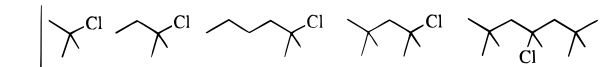
reactions of the carbocations $1a^+$−$1d^+$ with nucleophiles, compounds **1a**-OMe through **1d**-OMe were ionized with 50−90 equiv of $TiCl_4$, and the concentrations of the resulting carbocations were detected photometrically (λ_{filter} = 440 ± 5 nm) using fiber optics and the work station described previously.[12] Addition of the nucleophiles **4** or **5** resulted in a decay of the carbocation absorbance, which followed a second-order rate law, first order with respect to carbocation and first order with respect to the nucleophiles **4** or **5**. As discussed previously, the carbocation concentration in the rate equation corresponds to the sum of paired and nonpaired carbocations, for which identical reactivities have been derived.[1,12,13] Since the carbocations 1^+ decompose at elevated temperatures, the kinetic studies with **1c**$^+$ and **1d**$^+$ had to be carried out below −60 °C while **1b**$^+$ could be studied up to −45 °C. The experiments with **1a**$^+$ were poorly reproducible, and only an approximate value at −70 °C could be determined (Table 1).

Discussion

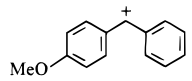
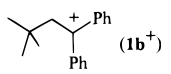
Comparison of the cations $1a^+$−$1d^+$ shows that replacement of methyl by the neopentyl group (**1a**$^+$ → **1b**$^+$) reduces the reactivity toward allyltrimethylsilane (**4**) by more than 2 orders of magnitude (k_2(−70 °C), Table 1, Scheme 3). A reduction of only a factor of 3 is found when another C_4 unit is inserted (**1b**$^+$ → **1c**$^+$), but further extension of the oligoisobutylene chain (**1c**$^+$ → **1d**$^+$) does not affect the reactivity. While **1a**$^+$ is too electrophilic for direct determination of its reactivity toward dimethylphenylsilane (**5**), the relative reactivities of $1b^+$−$1d^+$ toward **5** show the same pattern as discussed for **4**; i.e., cations **1c**$^+$ and **1d**$^+$ react with similar rates, 2 times more slowly than **1b**$^+$.

The remarkably large difference in reactivity between the methyl- (**1a**$^+$) and neopentyl-substituted carbocation (**1b**$^+$) reflects a well-known phenomenon in carbocation chemistry. In 1953 Brown reported that the solvolysis rates of *tert*-alkyl chlorides remained almost constant

Scheme 4. Relative Solvolysis Rates (80% EtOH/20% H_2O, 25 °C)[16]

					
k_{rel}	1	1.7	1.4	21	580

Scheme 5. Second-Order Rate Constants for the Reactions of Carbocations with the Hydride Donor 5 and the π-Nucleophile 4 (L mol^{-1} s^{-1}, CH_2Cl_2, −70 °C)

	$HSiMe_2Ph$ **5**	**4**
	149	187
 (**1b**$^+$)	148	0.11

when methyl groups were replaced by *n*-alkyl groups. A strong acceleration of the rate of the S_N1 reaction was observed, however, when branched alkyl groups were introduced (Scheme 4).[14−16]

Back strain, i.e., the release of steric strain during rehybridization from sp^3 to sp^2, has been shown to be the main reason for these differences in solvolysis rates. When the reactivities of the carbocations **1a**$^+$ and **1b**$^+$ with nucleophiles are compared, the opposite change of hybridization has to be considered, and it is not surprising that **1b**$^+$ is noticeably less reactive than **1a**$^+$. A similar rate ratio has been derived for the reactions of the *tert*-butyl cation and 2,4,4-trimethyl-2-pentyl cation with allylsilanes from their selectivities.[17]

The activation entropies of the reactions of $1b^+$−$1d^+$ with the π-nucleophile **4** and the hydride donor **5** are similar to those previously reported for the analogous reactions of these nucleophiles with benzhydryl cations.[18,19] Consequently the replacement of hydrogen by a neopentyl group in the benzhydryl cation (Ph_2CH^+ → **1b**$^+$) reduces the reactivity toward **4** and **5** by 8 and 4 orders of magnitude, respectively, due to an increase of $\Delta H^‡$. The reduced electrophilicities of $1a^+$−$1d^+$ compared to Ph_2CH^+ thus reflect a combination of electronic and steric effects.

In previous work, we have shown that the rates of reactions of carbocations with noncharged π-, σ-, and *n*-nucleophiles can be described by a three-parameter equation where steric effects are neglected.[20] We have stressed the point, however, that this simple model will fail when systems with great steric hindrance are included.[20] Cations $1b^+$−$1d^+$ are the first examples where this phenomenon can be described quantitatively: The tertiary carbocation **1b**$^+$ and the *p*-anisylphenylcarbenium ion show equal reactivities toward the hydride donor **5** (Scheme 5), where steric effects play a minor role in the transition state.[19] Considerable steric strain is developed in the transition state of the reaction of the tertiary cations $1a^+$−$1d^+$ with π-nucleophiles, however, and allyltrimethylsilane (**4**) reacts 10^3 times more slowly with **1b**$^+$ than with the *p*-methoxy substituted benzhydryl cation though both cations show the same electrophilicity toward the hydride donor **5**.

Conclusion

The reactivity difference between the cations **1a**$^+$ and $1b^+$−$1d^+$ indicates that the alkyl chain in carbocationic isobutylene polymerizations cannot be approximated by

a methyl group. The solvolysis rate constants listed in Scheme 4 indicate that other *n*-alkyl groups are not suitable either.[14−16] Comparison of **1b**$^+$ and **1d**$^+$ shows that a neopentyl group is already a reasonable model for the polyisobutenyl group, and the identities of the rate constants for **1c**$^+$ and **1d**$^+$ reveal that two isobutenyl units are sufficient to model the long chain. It remains to be clarified whether the independence of carbocation reactivities from the length of the polymer chain also holds for very fast reactions which are getting close to diffusion control.

Experimental Section

Dichloromethane (Merck, p.a.) was stirred over sulfuric acid for 3 days, then washed with water, aqueous $NaHCO_3$ solution, and again with water, dried over $CaCl_2$, and distilled from CaH_2 before use. Titanium tetrachloride (Fluka) was distilled and stored under nitrogen. Allyltrimethylsilane (Fluka, >99%) was distilled from $LiAlH_4$ and stored under nitrogen. Dimethylphenylsilane (Fluka, >98%) was used without further purification.

The reaction products were dried in vacuo before identification or purified by bulb-to-bulb distillation (Büchi KGR-50). The reported boiling points correspond to the temperature of the oven. The kinetic experiments were carried out photometrically using fiber optics ($\lambda_{filter} = 440 \pm 5$ nm) and the work station described previously.[12] The mass spectra were determined on a Finnigan MAT 311A spectrometer with a combined EI/FD source (70 eV). The ^{1}H and ^{13}C NMR spectra were obtained on Bruker WM 300 spectrometer with $CDCl_3$ as solvent and tetramethylsilane (δ = 0.00 ppm) as internal standard.

1-Methoxy-1,1-diphenylethane (1a-OMe). 1-Methoxy-1,1-diphenylethane was prepared according to the literature.[10] Recrystallization from MeOH yielded **1a**-OMe as colorless needles (42%, mp 31−31.5 °C (lit.[10] mp 35−36 °C (MeOH))); ^{1}H NMR δ = 1.86 (s, 3 H, 2-H), 3.15 (s, 3 H, OMe), 7.19−7.37 (m, 10 H, phenyl); ^{13}C NMR δ = 25.1 (q, C-2), 50.6 (q, OMe), 80.8 (s, C-1), 126.8, 128.0 (2 d, aromat CH), 146.4 (s, C_{ipso}, phenyl); MS *m*/*z* (%) = 213, 212 (1.9, 16, $M^+ + 1$, M^+), 197 (100), 181 (18), 135 (42), 105 (20), 77 (29).

Syntheses of the Methyl Ethers 1b-OMe and 1c-OMe. General Procedure. A solution of $TiCl_4$ and 2,6-di-*tert*-butylpyridine in dry methylene chloride/*n*-hexane (6:4) was cooled in a dry ice bath. After adding a solution of alkyl chloride and 1,1-diphenylethene in 5 mL of the solvent during 1 h, the dark red solution was stirred for another 2 h at −78 °C. The mixture was combined with precooled methanol (10 mL) and filtered over Celite, and the aqueous layer was extracted with *n*-hexane. The combined organic fractions were dried over $MgSO_4$, the solvent was removed in vacuo, and the crude reaction products were recrystallized from *n*-pentane.

1-Methoxy-3,3-dimethyl-1,1-diphenylbutane (1b-OMe). Compounds **2b**-Cl (0.46 g, 5.0 mmol) and 1,1-diphenylethene (0.92 g, 5.1 mmol) were added to a solution of $TiCl_4$ (1.1 mL, 10 mmol) and 2,6-di-*tert*-butylpyridine (45 μL, 0.20 mmol) in dry solvent (35 mL). Recrystallization yielded **1b**-OMe as colorless needles (700 mg, 52%, mp = 84.5−86 °C); ^{1}H NMR δ = 0.80 (s, 9 H, ^{t}Bu), 2.41 (s, 2 H, 2-H), 3.05 (s, 3 H, OMe), 7.16−7.21, 7.24−7.30, 7.36−7.40 (3 m, 10 H, phenyl); ^{13}C NMR δ = 31.1 (q, C-4), 31.5 (s, C-3), 44.6 (t, C-2), 50.6 (q, OMe), 82.4 (s, C-1), 126.3 (d, C_{para}, phenyl), 127.1, 127.7 (2 d, C_{ortho}, C_{meta}, phenyl), 146.9 (s, C_{ipso}, phenyl); MS *m*/*z* (%) = 197 (100, $M^+ - C_5H_{11}$), 180 (1.9), 165 (3.8), 105 (28), 91 (3.2), 77 (26), 57 (11).

1-Methoxy-3,3,5,5-tetramethyl-1,1-diphenylhexane (1c-OMe). Compounds **2c**-Cl (1.49 g, 10.0 mmol) and 1,1-diphenylethene (1.80 g, 10.0 mmol) were added to a solution of $TiCl_4$ (2.0 mL, 18 mmol) and 2,6-di-*tert*-butylpyridine (60 μL, 0.27 mmol) in dry solvent (80 mL). Recrystallization yielded **1c**-OMe as colorless needles (2.24 g, 69%, mp = 84−85 °C); ^{1}H NMR[9] δ = 0.79 (s, 6 H, 3-Me), 0.98 (s, 9 H, ^{t}Bu), 1.24 (s, 2 H, 4-H), 2.46 (s, 2 H, 2-H), 3.01 (s, 3 H, OMe), 7.11−7.17, 7.21−7.26, 7.33−7.36 (3 m, 10 H, phenyl); ^{13}C NMR δ = 29.2 (q, 3-Me), 32.4 (q, C-6), 36.7 (s, C-3, C-5), 45.1 (t, C-2), 50.7 (q, OMe), 58.7 (t, C-4), 82.8 (s, C-1), 126.2 (d, C_{para}, phenyl), 127.2, 127.7 (2 d, C_{ortho}, C_{meta}, phenyl), 147.1 (s, C_{ipso}, phenyl); MS *m*/*z* (%) = 197 (100, $M^+ - C_9H_{19}$), 180 (1.5), 165 (1.5), 105 (13), 91 (2.2), 77 (8.2), 57 (7.5).

1d-OMe was prepared as previously described in ref 9.

Reaction of the Methyl Ethers 1a-OMe through 1c-OMe with the Nucleophiles 4 and 5. General Procedure. A solution of the methyl ether in dry methylene chloride (20 mL) was cooled in a dry ice bath. Subsequently $TiCl_4$ was added and the nucleophile was dropped slowly into the dark red solution. After stirring for another 1 h at −78 °C, aqueous ammonia (30 mL) was added, and the mixture was filtered over Celite. The aqueous layer was extracted with CH_2Cl_2, the combined organic fractions were dried over $MgSO_4$, the solvent was removed, and the reaction products were dried or distilled in vacuo.

4,4-Diphenyl-1-pentene (3a). Treatment of **1a**-OMe (0.425 g, 2.00 mmol) with $TiCl_4$ (0.30 mL, 2.7 mmol) and allylsilane **4** (0.571 g, 5.00 mmol) yielded **3a** as a colorless oil (430 mg, 97%); ^{1}H NMR δ = 1.61 (s, 3 H, 5-H), 2.88 (br d, *J* = 7.0 Hz, 2 H, 3-H), 4.93−5.06 (m, 2 H, 1-H), 5.39−5.53 (m, 1 H, 2-H), 7.13−7.29 (m, 10 H, phenyl); ^{13}C NMR δ = 27.5 (q, C-5), 45.8 (s, C-4), 46.2 (t, C-3), 117.5 (t, C-1), 125.7 (d, C_{para}, phenyl), 127.3, 127.9 (2 d, C_{ortho}, C_{meta}, phenyl), 135.1 (d, C-2), 149.3 (s, C_{ipso}, phenyl); MS *m*/*z* (%) = 181 (100, $M^+ - C_3H_5$), 166 (13), 165 (14), 103 (27), 91 (3.2), 77 (13).

6,6-Dimethyl-4,4-diphenyl-1-heptene (3b). Treatment of **1b**-OMe (0.268 g, 1.00 mmol) with $TiCl_4$ (0.25 mL, 2.3 mmol) and allylsilane **4** (0.343 g, 3.00 mmol) yielded **3b** as a colorless oil (255 mg, 92%); ^{1}H NMR δ = 0.62 (s, 9 H, ^{t}Bu), 2.13 (s, 2 H, 5-H), 2.99 (d, *J* = 6.9 Hz, 2 H, 3-H), 4.83−4.88 (m, 2 H, 1-H), 5.27−5.38 (m, 1 H, 2-H), 7.03−7.18 (m, 10 H, phenyl); ^{13}C NMR δ = 31.8 (q, C-7), 32.4 (s, C-6), 43.2 (t, C-3), 48.7 (t, C-5), 49.5 (s, C-4), 117.5 (t, C-1), 125.5 (d, C_{para}, phenyl), 127.5, 128.4 (2 d, C_{ortho}, C_{meta}, phenyl), 135.4 (d, C-2), 149.6 (s, C_{ipso}, phenyl); MS *m*/*z* (%) = 237 (29, $M^+ - C_3H_5$), 181 (40), 165 (7.0), 129 (29), 91 (29), 77 (5.1), 57 (100).

6,6,8,8-Tetramethyl-4,4-diphenyl-1-nonene (3c). Treatment of **1c**-OMe (0.65 g, 2.0 mmol) with $TiCl_4$ (0.50 mL, 4.6 mmol) and allylsilane **4** (0.570 g, 5.00 mmol) yielded **3c** as a colorless oil (650 mg, 97%); ^{1}H NMR δ = 0.64 (s, 6 H, 6-Me), 0.88 (s, 9 H, ^{t}Bu), 1.08 (s, 2 H, 7-H), 2.23 (s, 2 H, 5-H), 3.00 (d, *J* = 6.9 Hz, 2 H, 3-H), 4.83−4.88 (m, 2 H, 1-H), 5.25−5.38 (m, 1 H, 2-H), 7.02−7.17 (m, 10 H, phenyl); ^{13}C NMR δ = 29.9 (q, 6-Me), 32.4 (q, C-9), 37.7 (s, C-6, C-8), 43.7 (t, C-3), 49.3 (t, C-5), 50.0 (s, C-4), 59.3 (t, C-7), 117.6 (t, C-1), 125.5 (d, C_{para}, phenyl), 127.5, 128.5 (2 d, C_{ortho}, C_{meta}, phenyl), 135.5 (d, C-2), 149.9 (s, C_{ipso}, phenyl); MS *m*/*z* (%) = 293 (16, $M^+ - C_3H_5$), 208 (16), 181 (28), 165 (15), 129 (49), 113 (25), 103 (8.2), 91 (52), 77 (11), 73 (17), 57 (100).

1,1-Diphenylethane (6a). Compound **1a**-OMe (0.425 g, 2.00 mmol) was ionized with $TiCl_4$ (0.30 mL, 2.7 mmol) and treated with dimethylphenylsilane (**5**) (0.545 g, 4.00 mmol). Distillation (40−50 °C/3 × 10^{-3} mbar) yielded **6a** as a colorless liquid (130 mg, 36%, (lit.[21] 136 °C/12 mmHg)); ^{1}H NMR δ = 1.64 (d, *J* = 7.2 Hz, 3 H, 2-H), 4.15 (q, *J* = 7.2 Hz, 1 H, 1-H), 7.14−7.31 (m, 10 H, phenyl); ^{13}C NMR δ = 21.8 (q, C-2), 44.7 (d, C-1), 126.0 (d, C_{para}, phenyl), 127.6, 128.3 (2 d, C_{ortho}, C_{meta}, phenyl), 146.4 (s, C_{ipso}, phenyl): MS *m*/*z* (%) = 183, 182 (4.5, 37, $M^+ + 1$, M^+), 167 (100), 165 (21), 152 (12), 103 (5.1), 77 (8.9).

3,3-Dimethyl-1,1-diphenylbutane (6b). Compound **1b**-OMe (0.268 g, 1.00 mmol) was ionized with $TiCl_4$ (0.25 mL, 2.3 mmol) and treated with dimethylphenylsilane (**5**) (0.409 g, 3.00 mmol) to give **6b** as a colorless liquid (230 mg, 96%); ^{1}H NMR δ = 0.91 (s, 9 H, ^{t}Bu), 2.18 (d, *J* = 6.7 Hz, 2 H, 2-H), 4.13 (t, *J* = 6.6 Hz, 1 H, 1-H), 7.17−7.22, 7.26−7.47 (2 m, 10 H, phenyl); ^{13}C NMR δ = 30.2 (q, C-4), 31.5 (s, C-3), 48.4 (d, C-1), 49.4 (t, C-2), 125.8 (d, C_{para}, phenyl), 127.8, 128.4 (2 d, C_{ortho}, C_{meta}, phenyl), 146.7 (s, C_{ipso}, phenyl); MS *m*/*z* (%) = 239, 238 (1.9, 13, $M^+ + 1$, M^+), 168 (14), 167 (100), 165 (16), 152 (9.0), 103 (3.0), 91 (1.9), 77 (4.7).

3,3,5,5-Tetramethyl-1,1-diphenylhexane (6c). Compound **1c**-OMe (0.649 g, 2.00 mmol) was ionized with $TiCl_4$ (0.50 mL, 4.6 mmol) and treated with dimethylphenylsilane

(**5**) (0.681 g, 5.00 mmol) to give **6c** as a colorless liquid (580 mg, 98%); ^{1}H NMR δ = 0.80 (s, 6 H, 3-Me), 0.87 (s, 9 H, ^{t}Bu), 1.20 (s, 2 H, 4-H), 2.11 (d, J = 6.5 Hz, 2 H, 2-H), 4.00 (t, J = 6.5 Hz, 1 H, 1-H), 7.00−7.06, 7.12−7.23 (2 m, 10 H, phenyl); ^{13}C NMR δ = 29.3 (q, 3-Me), 32.2 (q, C-6), 32.3, 36.2 (s, C-3, C-5), 48.1 (d, C-1), 50.3 (t, C-2), 55.4 (t, C-4), 125.7 (d, C_{para}, phenyl), 127.8, 128.4 (2 d, C_{ortho}, C_{meta}, phenyl), 147.1 (s, C_{ipso}, phenyl); MS m/z (%) = 295, 294 (1.9, 11, $M^+ + 1$, M^+), 167 (100), 91 (3.2), 71 (5.7), 57 (23).

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Supporting Information Available: Data tables containing details of the kinetic experiments, e.g., concentrations, rate constants at variable temperatures, and activation parameters (4 pages). Ordering information is given on any current masthead page.

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