Ortho Methyl Group Effects in Cumyl Systems

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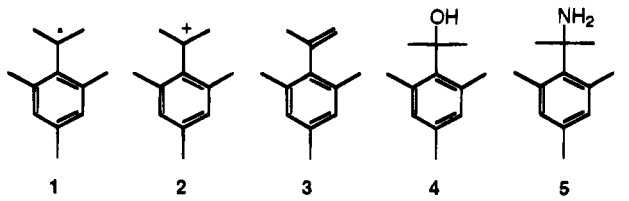
Received January 23, 1995®

In an attempt to evaluate the steric effect of ortho methyl groups on the stability of the cumyl radical, 2,2′,4,4′,6,6′-hexamethylazocumene (**6**) was synthesized and its rate of decomposition was measured. The fact that **6** decomposes 40 times faster than azocumene is attributed to a ground state steric effect. Calculations on the mesitylcumyl radical **1** and cation **2** show both systems to be substantially nonplanar with dihedral angles of 48° and 35°, respectively. Calculated charge distributions for cation **2** corroborate previously obtained NMR results which showed substantial loss of charge delocalization.[1]

Introduction

We were interested in the extent to which ortho methyl groups disrupt conjugation in cumyl systems. To this end we decided to examine radical **1**, cation **2**, and alkene **3**.[1,2] A common precursor to each was considered to be 2-(2,4,6-trimethylphenyl)-2-propanol (**4**) which could be converted to amine **5**, to azoalkane **6**, and then to radical **1** or with magic acid to cation **2** or by elimination to olefin **3**.



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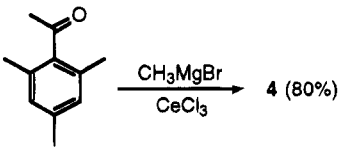
Results and Discussion

Our initial attempts to prepare 2-(2,4,6-trimethylphenyl)-2-propanol (**4**) by Grignard or lithium reagent addition to ketone **7** gave very low yields. However, with CH_3CeCl_2, **4** (eq 2) was obtained in 80% yield.[3] We assume this to be the result of steric hindrance to carbonyl addition resulting in the formation of enolate anion, and indeed, 2,4,6-trimethylacetophenone (**7**), recovered from attempted methyllithium addition, is deuterated in the α-position when the workup is completed with D_2O. Furthermore, addition of methyllithium to 2,2′,4,4′,6,6′-hexamethylbenzophenone (**8**), which is undoubtedly more hindered than **7**, occurs smoothly to give alcohol **9** in absence of $CeCl_3$. Both sterically hindered alcohols **4** and **9** are readily converted into their corresponding alkenes **3** and **10**, respectively. These alkenes are very unreactive and, as a result of their steric effects, display some unusual chemistry.[1,4]



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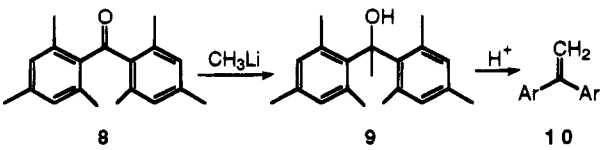
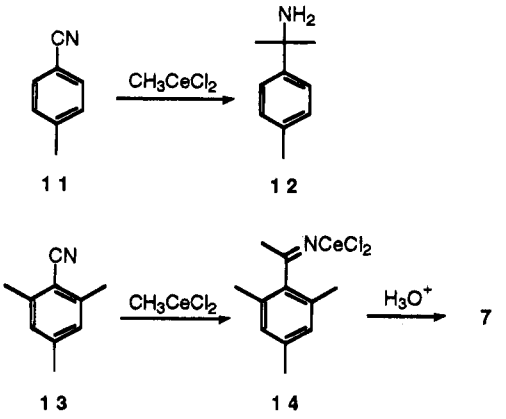


Synthesis of the prerequisite amine **5**, which was to be used to make azoalkane **6**, proved to be more difficult than initially expected. A variety of Ritter type conditions with alcohol **4** (HN_3, NaCN, INCO) led only to elimination to alkene **3** or, at best, gave a 1% yield of 5.[5]

Following the interesting results reported by Ciganek,[6] we find that while CH_3CeCl_2 will add twice to *p*-methylbenzonitrile (**11**, eq 3) to give amine **12**, only a single addition to 2,4,6-trimethylbenzonitrile (**13**) occurs giving imine **14**, as indicated by isolation of ketone **7** from hydrolysis. The second addition is apparently sterically impeded.



(3)

® Abstract published in *Advance ACS Abstracts,* July 15, 1995.

(1) For a preliminary account see Evilia, R. F.; Pan, D.; Timberlake, J. W.; Whittenburg, S. L. *Tetrahedron Lett.* **1991**, *32*, 871.

(2) The para methyl derivatives were used for synthetic simplicity.

(3) Imamoto, T.; Takiyama, N.; Nakamura, K.; Hatajima T.; Kamiya, Y. *J. Am. Chem. Soc.* **1989**, *111*, 4392.

(4) The chemistry of alkanes **3** and **10** will be published separately.

(5) Other unsuccessful attempts included mesityl copper lithium plus 2-bromo-2-nitropropane, NaH plus NaOCN which was expected to give isocyanate (Timberlake, J. W.; Martin, J. C. *J. Org. Chem.* **1968**, *33*, 4054.), mesityllithium plus $ArSN{=}C(CH_3)$ (Davis, F. A.; Mancinelli, P. A. *J. Org. Chem.* **1977**, *42*, 398.), preparation of various leaving groups from **4** which could be solvolyzed in presence of N_3^- or NH_3, and preparation of azine from ketone **7** followed by addition of Cl_2 then MeMgBr (after Timberlake and Martin in ref above).

(6) Ciganek, E. *J. Org. Chem.* **1992**, *57*, 4321.

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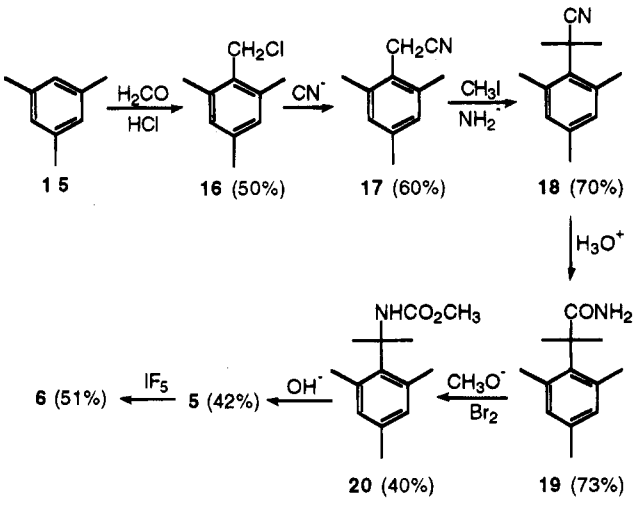
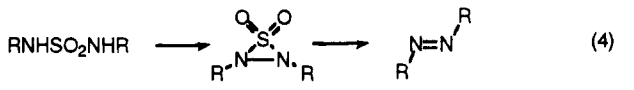
Ultimately, 2-mesityl-2-propylamine (**5**) was prepared by the following sequence (Scheme 1). Direct Hoffmann degradation of amide **19** to amine **5** resulted in formation of byproducts that made purification difficult. Modified conditions gave carbamate **20** which, upon hydrolysis, gave purer samples of **5**.

Scheme 1



A common method of preparation of azoalkanes from amines involves cyclization of sulfamides to thiadiaziridine dioxides with subsequent oxidation (eq 4).[7] However, treatment of amine **5** with SO_2Cl_2 again led to



(4)

alkene **3** via elimination. Alternatively, azo compounds can be prepared by the direct oxidation of amines with iodine pentafluoride.[8] Indeed, **6** was obtained by this procedure in 50% yield.

The fact that the completed synthesis of **6** was accomplished in an overall yield of only 1.3% required that the normal methods of rate analysis be revised.[9] It was found that FT-NMR could be used with excellent results with as little as a 4 mg sample per kinetic run. However, initially we found that trace amounts of acid present in the $CDCl_3$ solvent catalyzed the decomposition as evidenced by irreproducible results and the observation, by NMR, that alkene **3** was the only decomposition product. This could be avoided by use of pyridine-d_5 as solvent, acid scavenger, internal lock, and internal standard (integration was accomplished by using the residual pyridine protons).

The rate of decomposition of 2,2′,4,4′,6,6′-hexamethylazocumene was cleanly first order and the only observable products were alkene **3** and isopropylmesitylene, in equal amounts, which undoubtedly arise from disproportionation of radical **1**. As expected for this sterically hindered radical with the para position blocked, no dimers are formed. The rate constants for thermal decomposition are listed in Table 1 along with those for azocumene[10] (redetermined in pyridine), and *p*,*p*′-dimethylazocumene for comparison. There appears to be some specific solvation effect[12] as evidenced by the diminution of the rate of decomposition in pyridine relative to toluene (a factor of three for azocumene). This is also evident from the much smaller, and in one case, **6**, a negative $\Delta S^{\ddagger}$. This is not the norm for thermolysis of azoalkanes, but there is some precedent.[11] While azoalkanes usually show only small solvent effects, this may not be true here and the small $\Delta S^{\ddagger}$ values could be the result of geometric restrictions placed on the transition state.

Table 1. Rates of Thermal Decomposition in Pyridine-d_5

2,2′,4,4′,6,6′-hexamethylazocumene		azocumene	
temp. °C	$k \times 10^5$ s^{-1}	temp, °C	$k \times 10^5$ s^{-1}
21.0	1.66	49.5	1.26
25.0	2.81	55.3	2.28
30.0	5.32	59.4	4.24
35.0	9.85	64.5	8.39
40.0	17.9	69.5	14.8
45.0	31.9		
$\Delta H^{\ddagger}$ (kcal/mol)	22.3 ± 0.6	$\Delta H^{\ddagger}$ (kcal/mol)	27.1 ± 0.5
$\Delta S^{\ddagger}$ (eu)	−4.6 ± 1.2	$\Delta S^{\ddagger}$ (eu)	2.7 ± 1.3

Table 2. Rates of Decomposition of Azocumene Systems at 50 °C

	$k \times 10^5$ s^{-1}	rel rate
azocumene	3.87 (toluene)[a]	
	1.26 (pyridine)[b]	1.0
p,*p*-dimethylazocumene	4.96 (toluene)[c]	
	1.61 (pyridine)[d]	1.28
2,2′,4,4′,6,6′-hexamethylazocumene	56.3 (pyridine)[b]	44.7

[a] From ref 10. [b] This work. [c] From ref 13. [d] Extrapolated from azocumene data.

We had originally expected that the rate of decomposition of 2,2′,4,4′,6,6′-hexamethylazocumene (**6**) would be slower than that of azocumene (or *p*,*p*′-dimethylazocumene) and would thus reflect, to some extent, the effect of the ortho methyl groups in diminishing the delocalization of the odd electron. Clearly this is not the case. While it is probably true (*vide infra*) that **1** is not planar and so also the transition state for the incipient radical from thermolysis of **6**, our results do not confirm this. Even after correction for solvent effects, the mesitylazo compound **6** decomposes 35 times faster than the para methyl derivative (Table 2). If one assumes planarity for radical **1** and that each ortho methyl group contributes to stabilization to the same extent that a para methyl group does, the cumulative effect gives a calculated rate of 4.12 (Table 2, 1.28 × 2 × 1.61).[14] The rate enhancement of the mesityl derivative is still nearly 14 times faster. We believe these results are best explained by the larger steric contributions of the ortho methyl groups in the ground state than in the transition state.[15]

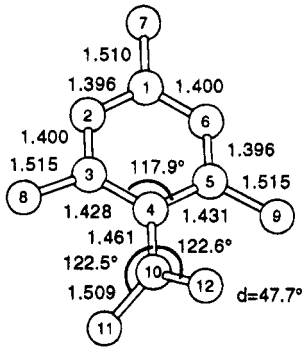
We have previously reported ^{13}C NMR results for cation **2** that established a significant loss of charge delocalization by comparison of calculated versus ob-

(7) Timberlake, J. W.; Alender, J. A.; Garner, A. W.; Hodges, M. L.; Ozmeral, C.; Szilagyi, S.; Jacobus, J. O. *J. Org. Chem.* **1981**, *45*, 2082. Ohme, R.; Schmitz, E. *Justus Liebigs Ann. Chem.* **1968**, *713*, 74.
(8) Stevens, T. E. *J. Org. Chem.* **1961**, *26*, 2531.
(9) (a) Engel, P. S. *Chem. Rev.* **1980**, *80*, 99. (b) Timberlake, J. W.; Martin, J. C. *Rev. Sci. Instrum.* **1973**, *44*, 151.
(10) Nelsen, S. F.; Bartlet, P. D. *J. Am. Chem. Soc.* **1966**, *88*, 137.
(11) Engel, P. S.; Wu, W.-X. *J. Org. Chem.* **1990**, *55*, 2720.
(12) Luedtke, A.; Meng, K.; Timberlake, J. W. *Tetrahedron Lett.* **1987**, *28*, 4255.
(13) Shelton, J. R.; Liang, C. K. *J. Org. Chem.* **1973**, *38*, 2301.
(14) This calculation would be the same regardless of the mechanism of decomposition, concerted or stepwise, as long as the mechanism is the same for the para methyl and the mesitylazocumene derivatives. For discussions on the decomposition mechanism, which are not pertinent to this paper, see ref 9a.
(15) Steric contributions to azoalkane decompositions have been extensively evaluated, see, for example, Timberlake, J. W.; Garner, A. W. *J. Org. Chem.* **1976**, *41*, 1666 and references listed therein.

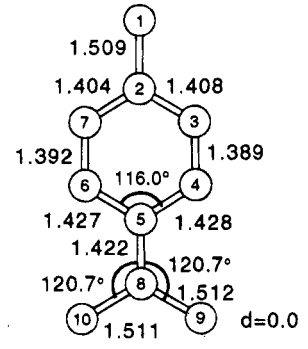
Table 3. Calculations of Charge at the Tertiary Center Carbon

	p-methylcumyl cation	mesitylcumyl cation
Mulliken	+0.137	+0.143
electrostatic potential	+0.418	+0.677
dihedral angle	0.0°	35.0°

Table 4. *Ab Initio* Calculations on Cumyl Radicals



carbon	spin densities:
C(1)	0.014745
C(2)	0.001063
C(3)	0.027555
C(4)	0.002886
C(5)	0.025634
C(6)	0.001045
C(7)	0.000166
C(8)	0.001021
C(9)	0.001021
C(10)	0.861082
C(11)	0.002066
C(12)	0.002057



carbon	spin densities:
C(1)	0.000433
C(2)	0.040525
C(3)	0.000740
C(4)	0.054438
C(5)	0.004077
C(6)	0.059880
C(7)	0.000778
C(8)	0.773843
C(9)	0.003699
C(10)	0.003711

served chemical shifts.[1,16] *Ab initio* calculations at the 3-21G level indicate a similar loss of delocalization and lack of planarity resulting from the steric influence of the ortho methyl groups. The electrostatic potential at the cationic carbon of **2**, +0.677, is much less than that for the planar *p*-methylcumyl cation, +0.418,[17] and the dihedral angle of 35° for **2** establishes the extent of orthogonality (Table 3). Creary found the rate of solvolysis of an ortho disubstituted cumyl system to be 86 times faster than the unsubstituted cumyl case.[18] This is consistent with our calculations and NMR data. Parenthetically, attempts to optimize the structure of **2** at the 6-31+G* level gave problems with convergence, although the *p*-methylcumyl cation did not. However, since the dihedral angles for the radicals were essentially the same at the 3-21 G and 6-31 G* levels, we assume they would be similarly close for the cations at the two levels and a single point 6-31+G* charge calculation gave nearly identical results to that of the 3-21 G calculation.

Calculations on **1** and the *p*-methylcumyl radical (Table 4) were done with geometry optimization at the 6-31G* level (UHF) and spin densities were determined with a single point calculation at the 6-31G* ROHF level. While spin contamination is obvious, S^2 is 1.397 and 1.323, respectively, for the two systems, slight improvement is noted with spin annihilation (1.144 and 1.110). Still it is assumed that the best geometries for these radicals come from the UHF calculations and the best spin densities from ROHF, and the results are as expected. The *p*-methylcumyl radical is planar with 77.4% of the odd electron at the cumyl carbon (C-5) and **1** has a dihedral angle of 48° with 86% of the spin density at the cumyl carbon (C-10). Further evidence of the difference in extent of delocalization is found at the para position, 1.5% of the spin density for **1** and 4.1% for *p*-methylcumyl radical. There is also a much shorter bond, 1.422 Å (C5–C8), for the *p*-methylcumyl than for **1**, 1.461 Å (C4–C10). It is, of course, impossible to proportion these differences quantitatively between ground state versus transition state energies of the azo compounds, but they do support our qualitative explanations offered herein.

Conclusions

In an attempt to evaluate the steric effects of ortho methyl groups on the stability of the cumyl radical, the rate of decomposition of 2,2′,4,4′,6,6′-hexamethylazocumene (**6**) was compared to other azocumene systems. The rate acceleration of **6** is attributed to a ground state steric effect. *Ab initio* calculations of the geometrics of the ortho methylated cumyl radical and cation show that they are substantially nonplanar.

Experimental Section

The kinetics were determined in pyridine-d_5 (99.5%) using the residual proton signal as an internal standard. The decay of the methyl groups of the "isopropyl methyl" signals were followed over time with a calibrated probe temperature for both the mesitylazocumene (**6**) and azocumene. Good linearity for all kinetic runs were obtained ($r > 0.99$) with excellent reproducibility.

The decomposition of mesitylazocumene (**6**) showed buildup of only two products in equal amounts and were identified as 2,4,6-trimethylcumene and 2-mesityl-1-propene (**3**).

2,4,6-Trimethylcumene. To a mixture of 36 g (0.3 mol) of mesitylene and 100 mL of 85% H_2SO_4 was added dropwise 18.0 g (0.3 mol) of isopropyl alcohol over 1 h while the temperature was kept at 40–50 °C. The temperature was increased to 80 °C for 5 h. The organic layer was separated, washed with water and 10% Na_2CO_3, and dried over $MgSO_4$. Fractional distillation yielded 28 g (58%); bp 128–130 °C/6 mm. The product was ~95% pure by GC and an additional distillation gave 99% purity: ^{1}H NMR ($CDCl_3$) δ 1.31 (6H, d), 2.22 (3H, s), 2.34 (6H, s), 3.40 (1H, m), 6.82 (2H, s). Anal. Calcd for $C_{12}H_{18}$: C, 88.80; H, 11.20. Found: C, 88.71; H, 11.09.

2-Mesityl-1-propene (3). 2-Mesityl-2-propanol (**4**) (1.78 g, 10.0 mmol) in 50 mL of THF was shaken vigorously with 20 mL of 10% aq HCl for 10 min. The solution was saturated with salt and extracted with ether. The ether was washed with water, aq $NaHCO_3$, and water and dried over $MgSO_4$. After concentration the liquid was chromatographed twice over silica gel to yield 580 mg (36%) of 2-mesityl-1-propene as a clear liquid. Flash distillation provided an analytically pure sample: ^{1}H NMR ($CDCl_3$) δ 1.91(3H, dd), 2.20 (6H, s), 2.23 (3H, s), 4.73 (1H, m), 5.22 (1H, m), 6.82 (2H, s); ^{13}C NMR ($CDCl_3$) δ 19.4 (q), 20.7 (q), 23.5 (q)), 114.6 (t), 128.0 (d), 134.3 (s), 135.5 (s), 140.3 (s), 144.8 (s). Anal. Calcd for $C_{12}H_{16}$: C, 89.92; H, 10.08. Found: C, 89.80; H, 10.00.

α²-Chloroisodurene (16) was prepared according to the literature in 50% yield. From 120 g of mesitylene was obtained 84.5 g of **16**: mp 37 °C (lit.[19] mp 35–37 °C); ^{1}H NMR ($CDCl_3$) δ 2.27 (3H, s), 2.40 (6H, s), 4.64 (2H, s), 6.88 (2H, s).

(16) In ref 1, p 871, the next to the last line should read C-3, not C-1.

(17) Politzer, P. A.; Murray, J. S. *Rev. Comput. Chem.*, Lipkowitz, K. B.; Boyd, D. B., Eds., Academic Press: New York, 1991; Vol. 2, Ch. 4. Chirlian, L. E.; Francl, M. M. *J. Comput. Chem.* **1987**, *8*, 894. Williams, D. E.; Yan, J.-M. *Adv. At. Mol. Phys.* **1988**, *23*, 87.

(18) Creary, X.; Casingal, V. P.; Leahy, C. E. *J. Am. Chem. Soc.* **1993**, *115*, 1734, and private communication with Professor Creary.

(19) Lindberg, U. H.; Jakupovic, E.; Nylen, B.; Ulff, B.; Akerman, B. *Acta Pharm. Suec.* **1968**, *7*, 531.

Mesitylacetonitrile (17) was prepared according to the literature in 60.3% yield.[19] From 50.0 g of **16** was obtained 28.4 g of **17**: mp 73–74 °C (lit.[19] mp 79–80 °C); ^{1}H NMR ($CDCl_3$) δ 2.25 (3H, s), 2.33 (6H, s), 3.57 (2H, s), 6.87 (2H, s); ^{13}C NMR ($CDCl_3$) δ 17.41, 19.96, 20.90, 117.48, 124.46, 129.41, 136.50, 137.90.

2-Methyl-2-mesitylpropionitrile (18) was prepared according to the literature in 70.6% yield.[19] From 8.0 g of **17** was obtained after recrystallization from ethanol 6.6 g of **18**: ^{1}H NMR ($CDCl_3$) δ 1.90 (6H, s), 2.20 (3H, s), 2.58 (6H, s), 6.80 (2H, s); ^{13}C NMR ($CDCl_3$) δ 20.33, 24.18, 29.62, 37.56, 126.45, 132.32, 133.92, 136.07, 136.67.

2-Methyl-2-mesitylpropionamide (19) was prepared in 73% yield according to the literature.[19] From 1.5 g of **18** was obtained 1.2 g of **19**: mp 126.5–127.5 °C (lit.[19] mp 125–127 °C); ^{1}H NMR ($CDCl_3$) δ 1.67 (6H, s), 2.22 (3H, s), 2.40 (6H, s), 6.79 (2H, s); ^{13}C NMR ($CDCl_3$) δ 20.37, 23.51, 28.06, 48.07, 131.95, 135.89, 137.65, 138.07, 182.65.

Methyl-2-mesityl-2-propylcarbamate (20). A solution of 5.0 g (24 mmol) of 2-methyl-2-mesitylpropionamide (**19**) in 22 mL of methanol was mixed with 1.1 g (48 mmol) of sodium methoxide. Bromine (10.5 g, 48 mmol) was added until the solution turned yellow, and white sodium bromide appeared simultaneously. The solution was heated to 50 °C in a water bath for 10 min, cooled, and diluted with water and the precipitate collected. Recrystallization from methanol yielded 2.3 g (40.1%) of **20**: mp > 200 °C dec; ^{1}H NMR ($CDCl_3$) δ 1.78 (6H, s), 2.20 (3H, s), 2.45 (6H, s), 3.60 (3H, s), 5.05 (1H, s), 6.80 (2H, s). Anal. Calcd for $C_{14}H_{21}NO_2$: C, 71.46; H, 8.99; N, 5.95. Found: C, 71.16; H, 9.11; N, 5.61.

2-Mesityl-2-propylamine (5). To a solution of 50 g of potassium hydroxide in 117 mL of methanol and 33 mL of water was added 14.5 g (61.7 mmol) of **20**, and the solution was heated at reflux for 8 h. The product was isolated by dilution with water and extraction with ether. The ether solution was dried, and the hydrochloride salt was isolated by passing dry HCl over the ether solution to yield 7.6 g (42%) of amine hydrochloride of **5**. An analytical sample was prepared by recrystallization from ethanol–ethyl acetate: mp > 200 °C dec; ^{1}H NMR ($CDCl_3$, of free amine) δ 1.63 (8H, s), 2.20 (3H, s), 2.58 (6H, s), 6.82 (2H, s); ^{13}C NMR ($CDCl_3$) δ 20.20, 25.82, 33.81, 56.09, 132.30, 134.87, 136.20, 143.00. Anal. Calcd for $C_{12}H_{26}ClN$: C, 67.42; H, 9.45; N, 6.55. Found: C, 67.44; H, 9.30; N, 6.36.

2,2′,4,4′,6,6′-Hexamethylazocumene (6). To a 25 mL round-bottomed flask equipped with a condenser attached to a drying tube, a magnetic stirring bar, and a dropping funnel were added 3 mL of dry CH_2Cl_2 and 1.06 mL (13 mmol) of pyridine previously distilled from BaO. Under Ar 0.07 mL (1 mmol) of IF_5 (iodine pentafluoride) was added at once to the flask which was kept at −78 °C by a dry ice–acetone bath. The mixture was stirred for 30 min, and then 0.177 g (1 mmol) of 2-mesityl-2-propylamine in 5 mL of CH_2Cl_2 was added dropwise while the temperature was kept at −78 °C. After 1 h the solution was warmed to room temperature and water was added. The organic layer was washed successively with 5% HCl, 5% $NaHSO_3$, and brine and dried over $MgSO_4$. A yellow solid was obtained after the removal of CH_2Cl_2 which was recrystallized from CH_2Cl_2 to give 0.09 g of **6** (51% yield); mp ~30 °C dec; ($CDCl_3$) δ 1.58 (6H, s), 2.26 (3H, s), 2.30 (6H, s), 6.85 (2H, s); UV (C_6H_6) 366 nm, ϵ = 42.

2-Mesityl-2-propanol (4). A 2 L three-neck flask charged with 74.4 g (0.20 mol) of cerium chloride heptahydrate was connected to a vacuum pump. The contents were heated to 130–140 °C with vigorous stirring until the water was completely removed from the cerium chloride. Dry THF (200 mL) was added and with stirring the mixture was again pumped to dryness. The flask was fitted with a gas inlet, a dropping funnel, and a condenser. Under Ar flow, 500 mL of freshly dried THF was added followed by addition of 70 mL (0.224 mol) of MeMgBr at 0 °C and it was stirred for 2 h. 2,4,6-Trimethylacetophenone (21.6 g, 0.133 mol) in 100 mL of freshly dried THF was added, and the reaction was stirred for 1 h at 0 C. The reaction mixture was treated with 10% aqueous acetic acid to destroy the excess MeMgBr, and the product was extracted into ether, successively washed with brine, $NaHCO_3$, and brine, and dried over $MgSO_4$. The solvent was evaporated, and the solid was recrystallized from ethanol to give 19.0 g of **4** (80%): mp 111.5–112.5 °C (lit.[3] mp 110–111 °C); ^{1}H NMR ($CDCl_3$) δ 1.68 (7H, s), 2.21 (3H, s), 2.44 (6H, s), 6.75 (2H, s); ^{13}C NMR ($CDCl_3$) δ 20.20, 25.82, 33.81, 56.09, 132.30, 134.87, 136.20, 143.00.

1,1-Dimesitylethanol (9). To 1.06 g (4.00 mmol) of dimesityl ketone (**8**) in 80 mL of hexane at 0 °C under an Ar atmosphere was added 4 mL of 1.5 M methyllithium (6.0 mmol). The mixture was heated at reflux for 2 h and then quenched with 50 mL of water. The hexane layer was removed and combined with an ether extract of the water and dried over $MgSO_4$. The solid remaining after removal of solvents was recrystallized from hexane to give 742 mg (65%) of alcohol **9**: mp 123.5–124 °C; ^{1}H NMR (C_3D_6O) δ 2.04 (6H, s), 2.17 (12H, s), 2.92 (3H, s), 6.67 (4H, s); ^{13}C NMR (C_3D_6O) δ 20.47, 24.06, 33.36, 81.78, 132.13, 135.35, 136.22, 144.41. Anal. Calcd for $C_{20}H_{26}O$: C, 85.04; H, 9.30. Found: C, 85.21; H, 9.16.

1,1-Dimesitylethene (10). To a solution of 88 mg (0.31 mmol) of dimesitylethanol **9** in 20 mL of THF was added 20 mL of 5% HCl. The mixture was shaken vigorously, extracted with ether, and dried over $CaCl_2$. After removal of solvent and recrystallization from hexane, there was obtained 61 mg of white crystals (74%): mp 97.5–98 °C; ^{1}H NMR ($CDCl_3$) δ 2.14 (12H, s), 2.25 (6H, s), 5.51 (2H, s), 6.83 (4H, s); ^{13}C NMR ($CDCl_3$) δ 20.94, 21.49, 124.37, 129.45, 136.03, 136.47, 139.58, 143.92. Anal. Calcd for $C_{20}H_{24}$: C, 90.83; H, 9.17. Found: C, 90.60; H, 9.12.

***p*-Methylcumylamine (12).** $CeCl_3 \cdot 7H_2O$ (10 g, 26.6 mmol) was dried under vacuum at 140 °C overnight. Under an Ar atmosphere at −50 °C, 50 mL of dry THF was added followed by 17.7 mL of 1.5 M solution of methyllithium (26.7 mmol). The mixture was stirred at −50 °C for 1 h followed by the addition of 0.52 g (4.45 mmol) of *p*-methylbenzonitrile in 2 mL of THF. The mixture was stirred for 3 h at −50 °C followed by the addition of 25 mL of aq NH_4Cl. The organic layer was separated, washed with water, dried, and concentrated to give 0.44 g (66%) of crude amine:[20] ^{1}H NMR ($CDCl_3$) δ 1.58 (6H, s), 2.64 (3H, s), 7.33 (4H, m).

2,4,6-Trimethylbenzonitrile with $MeCeCl_2$. The reaction was conducted as for **12** above except hydrolysis after the addition was conducted with 10% aq HCl, which led to isolation of 2,4,6-trimethylacetophenone identified by spectral comparison with an authentic sample.

Computational Methodology. All calculations were carried out using GAUSSIAN 92.[21] Geometries of cations were optimized at the restricted Hartree–Fock theory[22] level with 3-21G[23] bases set while atomic charges were calculated with 6-31+G*[24] by using pop=chelpg key word.[25] Geometries of radicals were optimized at unrestricted Hartree–Fock theory with spin density calculations at restricted open shell[26] Hartree-Fock theory with the 6-31G* basis set.

Acknowledgment. The authors thank Professors Ken Houk and Dan Pasto for helpful comments.

JO950128C

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