Supporting Information

Dicationic Intermediates Involving Protonated Amides: Dual Modes of Reactivity Including the Acylation of Arenes.

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¹H NMR Spectrum

¹³C NMR Spectrum

¹H NMR Spectrum

¹³C NMR Spectrum

¹H NMR Spectrum

¹³C NMR Spectrum

¹H NMR Spectrum

¹³C NMR Spectrum

General Methods, Spectroscopic and Analytical Data for New Compounds:

General Methods: Amides **1** and **5**, **8-11**, **13**, **15**, and **21** were purchased from commercial suppliers and used as received. Amides **23**, **25**, and **27** were prepared by acylation of the appropriate amines with cinnamoyl chloride, and their identities were established by ^1H and ^{13}C NMR and GCMS analyses. The trifluoromethanesulfonic acid (triflic acid) was purchased from 3M and it was distilled from an Ar atmosphere prior to use.²⁸ ^1H and ^{13}C NMR were recorded at 300 and 125 MHz, respectively.

General Synthetic Procedure (Products 2, 12, 14, 16, 22, 24, 26, 28): Approximately 0.2 g of the amide (ca. 1 mmol) is dissolved in 1 mL arene and 4 mL of triflic acid is added. The mixture is stirred for 6 hrs at 25°C and poured over about 15 g of ice. The resulting mixture is extracted twice with CHCl_3 and the organic extracts are washed with water, then brine, and dried over MgSO_4 . Concentration with reduced pressure then gives the products; if necessary, column chromatography is done over silica.

High Temperature Synthetic Procedure: In to an Ace-Thread glass, pressure tube, approximately 0.2 g of the amide (ca. 1 mmol) is dissolved in 1 mL C_6H_6 , and 4 mL of triflic acid is added. The mixture is stirred for 8 hrs at 100°C and poured over about 15 g of ice. The resulting mixture is extracted twice with CHCl_3 and the organic extracts are washed with water, then brine, and dried over MgSO_4 . Concentration with reduced pressure then gives the products; if necessary, column chromatography is done over silica.

Friedel-Crafts Acylations: Using the high temperature procedure described above, acetophenone and benzophenone were identified by GCMS analysis of the product mixtures. The product yields were determined by the addition of a measured amount of a standard to the product mixtures. The resulting mixtures were then analyzed by GC-FID. The yields were then determined by correcting for FID response factors.

1-Acetyl-4,4-diphenylpiperidine (3): MP (80% hexane:20% CHCl₃): 103-105°C; ¹H NMR (300 MHz, CHCl₃) δ, ppm 2.08 (s, 3H), 2.37-2.44 (m, 4H), 3.48-3.51 (m, 2H), 3.67-3.69 (m, 2H), 7.00 – 7.32 (m, 10H); ¹³C NMR (125 MHz, CHCl₃) δ, ppm 21.7, 36.0, 36.9, 38.8, 43.8, 45.2, 126.4, 127.2, 128.9, 146.5, 169.1; EI MS 279 (M⁺).

1-Benzoyl-4,4-diphenylpiperidone (12): MP (80% hexane:20% CHCl₃): 178-179°C; ¹H NMR (300 MHz, CHCl₃) δ, ppm: 2.30-2.40 (m, 2H), 2.40-2.55 (m, 2H), 3.35-3.52 (m, 2H), 3.76-3.91 (m, 2H), 7.04 – 7.40 (m, 15H); ¹³C NMR (125 MHz, CHCl₃) δ, ppm: 36.0, 37.0, 39.5, 45.2, 126.4, 127.1, 128.7, 128.9, 129.7, 136.4, 146.5, 170.5; EI MS 341 (M⁺).

3,3-Diphenyl-butylamide (16): MP (80% hexane:20% CHCl₃): 84-87°C; ¹H NMR (300 MHz, CHCl₃) δ, ppm 1.81 (s, 3H), 3.05 (s, 2H), 4.58 (s, 1H), 5.35 (s, 1H), 7.00-7.35 (m, 10H); ¹³C NMR (125 MHz, CHCl₃) δ, ppm 27.8, 45.7, 49.1, 126.6, 127.3, 128.6, 148.5, 173.7; EI MS 239 (M⁺).

3,3-Diphenyl-1-piperidin-1-yl-propan-1-one (24): MP (80% hexane:20% CHCl₃): 122-124°C; ¹H NMR (300 MHz, CHCl₃) δ, ppm 1.30-1.45 (m, 4H), 1.50-1.57 (m, 2H), 3.15 (d, *J* = 7.5 Hz, 2H), 3.32-3.45 (m, 4H), 4.72 (t, *J* = 7.8 Hz, 1H), 7.13-7.29 (m, 10H); ¹³C NMR (125 MHz, CHCl₃) δ, ppm 24.6, 26.1, 38.8, 45.1, 47.7, 126.6, 128.1, 128.7, 144.3, 170.0; EI MS 293 (M⁺).

Known Compounds:

Literature Citations:

Schaefer, H.; Hackmack, G.; Eistetter, K.; Krueger, U.; Menge, H. G.; Klosa, J. *Arzneimittel-Forschung*, **1984**, *34*(3), 233.

Gensler, W.; Rockett, J. C. *J. Am. Chem. Soc.* **1955**, *77*, 3262.

Ivanova, N.; Nikolova, M.; Zikolova, S. *Farmatsiya* **1976**, *26*(4), 10.

Method of Calculations:

Calculations were done using the *Gaussian98W* program package.¹ Geometry optimizations were done using density function theory (DFT) and the hybrid functional B3LYP at the 6-311G(d,p) level.^{2,3} Vibrational analyses were performed at the B3LYP/6-311G(d,p) level of theory and the optimized structure (**9a**) was found to have zero imaginary frequencies. Zero-point-energy correction was made to the single point energy for the structure. SCF GIAO nuclear magnetic shielding tensors were calculated at the B3LYP/6-311G(d,p) level and the ¹³C chemical shift values for **9a** were determined by comparison with tetramethylsilane (calculated at the same level of theory).

Literature Citations:

(1) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*; Gaussian Inc.: Pittsburgh, PA, 1998.

(2) (a) Becke, A. D. *Phys. Rev. A* **1988**, 38, 3098. (b) Becke, A. D. *J. Chem. Phys.* **1993**, 98, 5648. (c) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, 37, 785

(3) Raghavachari, K.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, 72, 650.

Structure:

B3LYP 6-311G (d,p) geometry:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	C	0.011981	1.214472	0.601318
2	1	H	0.199186	1.225312	1.678374
3	1	H	-0.589978	2.086189	0.362951
4	6	C	1.351425	1.301907	-0.171455
5	1	H	1.155487	1.518608	-1.235062
6	1	H	1.953847	2.132184	0.209797
7	6	C	2.112107	0.025557	-0.172791
8	6	C	1.399074	-1.270729	-0.205210
9	1	H	1.213291	-1.468599	-1.275141
10	1	H	2.055353	-2.073125	0.141358
11	6	C	0.065130	-1.261890	0.568566
12	1	H	0.245983	-1.293858	1.646110
13	1	H	-0.517122	-2.137358	0.299145
14	7	N	-0.709612	-0.029752	0.277097
15	6	C	-1.980778	-0.065702	-0.081660
16	8	O	-2.482958	-1.257298	-0.231841
17	6	C	-2.825202	1.148351	-0.284515
18	1	H	-3.783017	0.876544	-0.729463
19	1	H	-3.024204	1.631470	0.678350
20	1	H	-2.342709	1.874080	-0.941935
21	8	O	3.378573	-0.028610	-0.214486
22	1	H	3.851159	0.829476	-0.232590
23	1	H	-3.417327	-1.257190	-0.496467

Point Group : C₀₁

Energy + ZPE = - 479.066202 Hartrees

Number of Imaginary Frequencies : zero

¹³C NMR Spectrum

• acetone-external standard