C_{13}: ^1H NMR ($CDCl_3$) δ 7.81 (d, J = 8.34 Hz, 2 H), 7.29 (d, J = 8.34 Hz, 2 H), 2.91 (t, J = 6.57 Hz, 2 H), 2.71 (t, J = 6.12 Hz, 2 H), 1.70 (m, 4 H), 1.35–0.60 (m, 16 H); ^{13}C NMR ($CDCl_3$) δ 203.7, 148.4, 135.5, 129.2, 128.3, 38.6, 35.8, 29.1, 28.7, 28.3, 28.1, 27.7, 27.6, 27.0, 26.6, 26.5, 26.3; IR (CCl_4) 2930, 2857, 1681 cm^{-1}; UV (hexane) λ_{max} = 250 nm, $\epsilon = 1.4 \times 10^4$; MS m/z (relative intensity) 118 (37), 131 (100), 146 (81), 147 (31), 272 (M^+, 49).

C_{14}: ^1H NMR ($CDCl_3$) δ 7.81 (d, J = 8.06 Hz, 2 H), 7.26 (d, J = 8.06 Hz, 2 H), 2.89 (t, J = 6.69 Hz, 2 H), (t, J = 6.09 Hz, 2 H), 1.70 (m, 2 H), 1.60 (m, 2 H), 1.40–0.70 (m, 18 H); ^{13}C ($CDCl_3$) δ 203.0, 148.1, 134.7, 129.2, 128.3, 39.0, 35.5, 29.1, 28.4, 28.1, 27.6, 27.4, 27.2, 27.0, 26.8 (2 C's), 25.6, 25.2; IR (CCl_4) 2929, 2857, 1682 cm^{-1}; UV (hexane) λ_{max} = 250 nm, $\epsilon = 1.6 \times 10^4$; MS m/z (relative intensity) 118 (31), 131 (46), 146 (100), 147 (44), 286 (M^+, 64).

C_{15}: ^1H NMR ($CDCl_3$) δ 7.88 (d, J = 6.80 Hz, 2 H), 7.27 (d, J = 6.80 Hz, 2 H), 2.90 (t, J = 8.10 Hz, 2 H), 2.70 (t, J = 6.00 Hz, 2 H), 1.75 (m, 2 H), 1.66 (m, 2 H), 1.4–0.8 (m, 20 H); ^{13}C NMR ($CDCl_3$) δ 202.6, 148.2, 135.0, 129.1, 128.4, 37.6, 35.2, 29.2, 29.1, 28.3, 28.14, 28.09, 27.7, 27.5, 27.4, 27.3, 27.2, 26.4, 25.7; IR (CCl_4) 2930, 2857, 1680 cm^{-1}; UV (hexane) λ_{max} = 251 nm, $\epsilon = 1.5 \times 10^4$; MS m/z (relative intensity) 118 (23) 131 (69), 146 (100), 147 (45), 300 (M^+, 59).

***trans*-EA_{11}**: ^1H NMR ($CDCl_3$) δ 9.77 (t, J = 1.8 Hz, 1 H), 7.30 (m, 5 H), 6.38 (d, J = 15.8 Hz, 1 H), 6.22 (dt, J = 15.8 Hz, 6.8 Hz, 1 H), 2.43 (td, J = 7.3 Hz, 1.8 Hz, 2 H), 2.20 (m, 2 H), 1.64 (m, 2 H), 1.46 (m, 2 H), 1.40–1.20 (m, 8 H); IR (CCl_4) 1729 cm^{-1}; MS m/z 244 (M^+).

***cis*-EA_{11}**: ^1H NMR ($CDCl_3$) δ 9.76 (t, J = 1.8 Hz, 1 H), 7.30 (m, 5 H), 6.41 (d, J = 11.6 Hz, 1 H), 5.66 (dt, J = 11.6 Hz, 7.2 Hz, 1 H), 2.42 (td, J = 7.3 Hz, 1.8 Hz, 2 H), 2.34 (m, 2 H), 1.64 (m, 2 H), 1.46 (m, 2 H), 1.20–1.40 (m, 8 H); IR (CCl_4) 1729 cm^{-1}; MS m/z 244 (M^+).

***trans*-EA_{12}**: ^1H NMR ($CDCl_3$) δ 9.75 (t, J = 1.8 Hz, 1 H), 7.30 (m, 5 H), 6.37 (d, J = 15.8 Hz, 1 H), 6.20 (dt, J = 15.8 Hz), 7.0 Hz, 1 H), 2.41 (td, J = 7.2 Hz, 1.8 Hz, 2 H), 2.19 (dt, J = 7.0 Hz, 7.2 Hz, 2 H), 1.8–1.1 (m, 14 H); IR (CCl_4) 1729 cm^{-1}; MS m/z 258 (M^+).

***cis*-EA_{12}**: ^1H NMR ($CDCl_3$) δ 9.75 (t, J = 1.8 Hz, 1 H), 7.30 (m, 5 H), 6.35 (d, J = 11.6 Hz, 1 H), 5.65 (dt, J = 11.6 Hz, 7.2 Hz, 1 H), 2.41 (dt, J = 7.2 Hz, 1.8 Hz, 2 H), 2.31 (m, 2 H), 1.8–1.1 (m, 14 H); IR (CCl_4) 1729 cm^{-1}; MS m/z 258 (M^+).

***trans*-EA_{13}**: ^1H NMR ($CDCl_3$) δ 9.76 (t, J = 1.8 Hz, 1 H), 7.30 (m, 5 H), 6.38 (d, J = 15.7 Hz, 1 H), 6.23 (dt, J = 15.7 Hz, 6.9 Hz, 1 H), 2.42 (td, J = 7.4 Hz, 1.8 Hz, 2 H), 2.21 (m, 2 H), 1.64 (m, 2 H), 1.46 (m, 2 H), 1.40–1.20 (m, 12 H); IR (CCl_4) 1729 cm^{-1}; MS m/z 272 (M^+).

***cis*-EA_{13}**: ^1H NMR ($CDCl_3$) δ 9.76 (t, J = 1.8 Hz, 1 H), 7.30 (m, 5 H), 6.41 (d, J = 11.7 Hz, 1 H), 5.67 (dt, J = 11.7 Hz, 7.2 Hz, 1 H), 2.42 (td, J = 7.4 Hz, 1.8 Hz, 2 H), 2.33 (m, 2 H), 1.64 (m, 2 H), 1.46 (m, 2 H), 1.40–1.20 (m, 12 H); IR (CCl_4) 1729 cm^{-1}; MS m/z 272 (M^+).

***trans*-EA_{14}**: ^1H NMR ($CDCl_3$) δ 9.76 (t, J = 1.9 Hz, 1 H), 7.30 (m, 5 H), 6.38 (d, J = 15.9 Hz, 1 H), 6.23 (dt, J = 15.9 Hz, 6.8 Hz, 1 H), other hydrogens are overlapped with the hydrogens from the starting ketone and cyclophane; IR (CCl_4) 1729 cm^{-1}; MS m/z 286 (M^+).

***cis*-EA_{14}**: ^1H NMR ($CDCl_3$) δ 9.76 (t, J = 1.9 Hz, 1 H), 7.30 (m, 5 H), 6.41 (d, J = 11.7 Hz, 1 H), 5.67 (dt, J = 11.7 Hz, 7.3 Hz, 1 H), other hydrogens are overlapped with the hydrogens from the starting ketone and cyclophane; IR (CCl_4) 1729 cm^{-1}; MS m/z 286 (M^+).

***trans*-EA_{15}**: ^1H NMR ($CDCl_3$) δ 9.76 (t, J = 1.9 Hz, 1 H), 7.30 (m, 5 H), 6.37 (d, J = 15.9 Hz, 1 H), 6.23 (dt, J = 15.9 Hz, 6.9 Hz, 1 H), other hydrogens are overlapped with the hydrogens from the starting ketone and cyclophane; IR (CCl_4) 1728 cm^{-1}; MS m/z 300 (M^+).

***cis*-EA_{15}**: ^1H NMR ($CDCl_3$) δ 9.76 (t, J = 1.9 Hz, 1 H), 7.30 (m, 5 H), 6.40 (d, J = 11.6 Hz, 1 H), 5.67 (dt, J = 11.6 Hz, 7.4 Hz, 1 H), other hydrogens are overlapped with the hydrogens from the starting ketone and cyclophane; IR (CCl_4) 1728 cm^{-1}; MS m/z 300 (M^+).

Acknowledgment. We thank the NSF, DOE, and AFOSR for their generous support of this research and Dr. C. E. Doubleday, Jr., for helpful discussions in the preparation of the K_n.

Supplementary Material Available: ^1H NMR spectra of compounds K_{11}–K_{15}, *cis*- and *trans*-EA_{11}–*cis*- and *trans*-EA_{15}, and C_{11}–C_{15}, ^{13}C and two-dimensional ^1H–^1H homonuclear chemical shift correlated NMR of compounds C_{11}–C_{15} (31 pages). Ordering information is given on any current masthead page.

Unexpected Behavior of Limonene in the Oxidative Aminomercuration Reaction with HgO/HBF_4 and Aromatic Amines: Stereospecific Synthesis of 1,2-Diamines

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Solvomercuration–demercuration of alkenes provides a very general and useful method for Markovnikov functionalization of carbon–carbon double bonds.[1] Moreover, by using some mercury salts, an oxidative–demercuration process can occur, leading, in the presence of a nucleophile, to bifunctionalized compounds.[2] Although some attempts directed toward asymmetric induction have been performed by using chiral mercury salts, the enantiomeric excess was low in all cases.[3] The synthetic utility of the above mentioned reaction decreases when unconjugated dienic systems are used because of the competition reaction between the two double bonds; furthermore, side reactions are usually observed when the two double bonds are not equivalent, e.g., in the case of limonene. The monohydroxymercuration of limonene can only be achieved with high chemoselectivity with aqueous micelles,[4] the mercuration always taking place at the less hindered exocyclic double bond.

We report here our preliminary results on the aminomercuration reaction of limonene with HgO/HBF_4 as the mercuration reagent.

Thus, (*R*)-(+)-limonene (1) reacted with HgO/HBF_4 (1 equiv of HgO and 2 equiv of HBF_4, 40% v/v) in the presence of primary aromatic amines (molar ratio 1:1:5) in THF at −20 °C to give rise to mercurial **3**. Heating of **3** at 80 °C for 5 h did not afford the expected diamine **8**,[2] but diamine **4** was obtained as the major product, along with monoamines **5**, **6**, and *p*-cymene (**7**)[5] (Scheme I). Diamine **4** was obtained by high-vacuum distillation of the reaction crude as a very viscous red-orange oil. The ^{13}C NMR and ^1H NMR data show the presence of only one enantiomer.

Single-crystal X-ray analysis established unequivocally the complete structure and absolute 1*R*,2*R*,4*R* configuration for **4a**[6] (Figure 1). The 1*S*,2*S*,4*S* enantiomer **4a'** was obtained from (*S*)-(−)-limonene under the same reaction conditions (see the previous text).

When the mercurial intermediate **3a** was reduced in situ with $NaBH_4/OH^-$, the β-elimination reaction was the most

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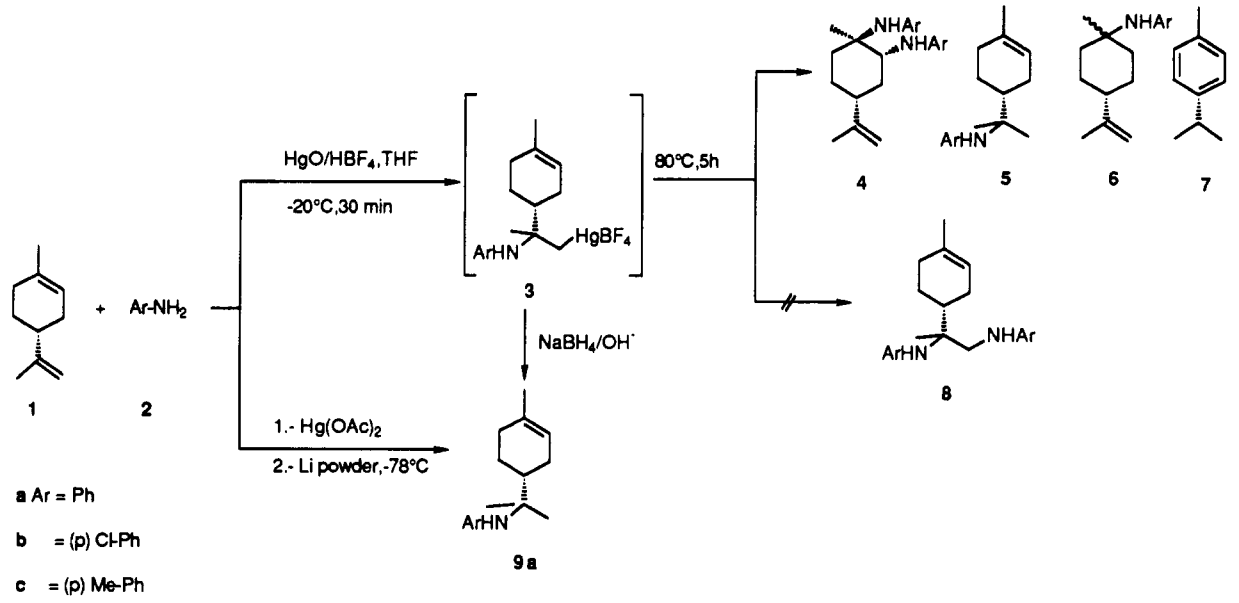
Scheme I



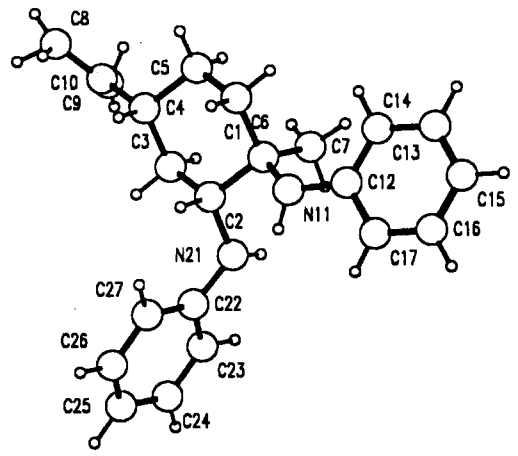


Figure 1. Molecular structure and labeling scheme for **4** ($C_{22}H_{28}N_2$).

important process and the monoamine **9a** was obtained in only 10% yield. In order to improve the synthesis of **9a**, the aminomercuration reaction was carried out with $Hg(OAc)_2$ as mercuric salt and the mercurial was reduced in situ with excess of Li powder at −78 °C,[7] furnishing amine **9a** in 65% yield (Scheme I). The previous results show that the aminomercuration process first involves the exocyclic double bond of the limonene as in the hydroxymercuration process.[4] Therefore, the formation of diamines **4** can be explained by means of a mercurinium ion exchange through the sequence **3**–**10**–**11**–**12** (Scheme II).

Scheme II

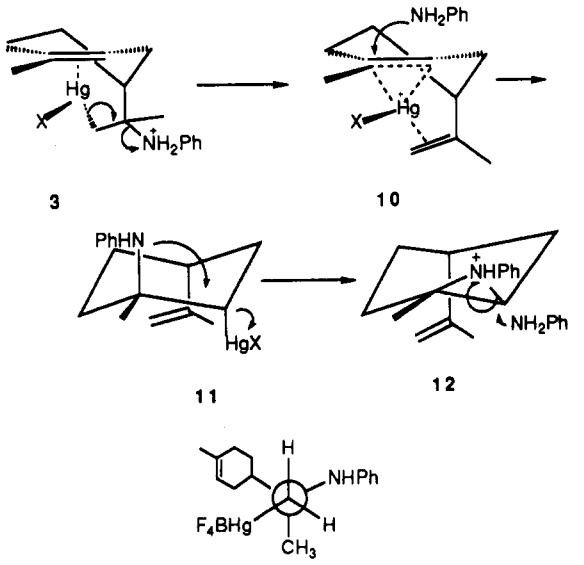


Figure 2.

Thus, formation of the mercurinium ion **10**[8] through a β-elimination reaction of the protonated aminomercurial **3** followed by attack of amine would lead to a new aminomercurial compound **11**, which is known to afford diamine and Hg^0.[2] The exclusive formation of a single enantiomer can be understood by assuming the formation of an aziridinium intermediate **12**, followed by nucleophilic attack of a second equivalent of amine at the less hindered carbon atom.

The fact that the diamine **8** (Scheme II) was not formed can be explained in terms of steric interaction between the cyclohexyl ring and the bulky Hg in the antiperiplanar Hg–N conformation of the aminomercurial **3** (Figure 2): therefore, the departure[9] of Hg^0 assisted by the nitrogen

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(5) Detected by GC–MS from the reaction volatiles.

(6) See supplementary material.

(7) Barluenga, J.; Ara, A.; Asensio, G. *Synthesis* **1975**, 116.

(8) When the reaction was carried out with methyl α-terpinyl ether or α-terpinyl acetate as starting material under the same reaction conditions as for limonene, a mixture of two diastereoisomers was obtained in ~3:1 molar ratio.

(9) Cires, L. A. Thesis, Oxido de mercurio (II)/acido tetrafluoroborico. Aplicaciones en síntesis Orgánica; 1,2-difuncionalización de olefinas y reacciones de alquilacion. Thesis, Universidad de Oviedo, 1982.

atom via an aziridinium intermediate cannot occur. Since the aminomercuration is a reversible process,[10] especially in a strong acid media, the β-elimination is a much more favorable process.

Experimental Section

General Procedures. Melting points were determined in an open capillary on a Büchi hot-stage apparatus and are uncorrected. Optical rotations were recorded at room temperature on a Perkin-Elmer Model 241 polarimeter. ^1H (300-MHz) and ^{13}C NMR (75-MHz) spectra were recorded on a Brücker AC-300 spectrometer with tetramethylsilane as internal standard. GC-Mass spectra were recorded on a Hewlett-Packard 5930 A mass spectrometer. Microanalyses were performed on a Perkin-Elmer Model 240 instrument.

General Procedure for Preparation of 1,2-Diaminocyclohexanes (4). To a THF solution (20 mL) of limonene (1.36 g, 10 mmol) and the corresponding arylamine (50 mmol) was added dropwise a water solution of HgO (2.1 g, 10 mmol) and HBF_4 (4.05 mL, 40% v/v, 20 mmol). The reaction mixture was stirred for 30 min at −20 °C, and then it was heated to reflux for 5 h, during which time the yellow solution changed to red and Hg^0 was formed. The flask was then cooled to room temperature, and the Hg^0 was filtered off (1.8 g, 90%). The organic layer was poured into 3 M NaOH (20 mL) and extracted with ether (3 × 20 mL). The ethereal layer was washed with water (2 × 20 mL), dried (Na_2SO_4), and evaporated at reduced pressure. The excess of amine was eliminated at 10^{-2} Torr, and the resulting oil was distilled at 10^{-6} Torr. A mixture of monoamines 5 and 6 distilled at 120–130 °C, while diamines 4 were collected at 150–160 °C as a viscous yellow-orange oil in 45–50% yield. **4a** crystallized on standing and was then recrystallized from ethanol, giving a white crystalline solid; mp 101–102 °C.

(−)-(1*R*,2*R*,4*R*)-*N*,*N*′-Diphenyl-1-methyl-4-(1-methylethenyl)-1,2-diaminocyclohexane (4a): $[\alpha]_D$ −54.6° (*c* 1.00, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.2–1.5 (m + s, 5 H), 1.7–1.9 (m + s, 6 H), 2.1 (m, 2 H), 2.3 (m, 1 H), 3.5 (s, 2 H, NH), 4.8 (s, 2 H), 7.2–6.8 (m, 10 H, Ar); ^{13}C NMR ($CDCl_3$) δ 17.2, 20.6, 27.5, 33.6, 38.0, 43.8, 56.8, 59.6, 108.7, 114.2, 118.0, 119.8, 120.3, 128.5, 129.1, 145.6, 147.4, 148.3 MS *m*/*z* 320 (M^+). Anal. Calcd for $C_{22}H_{28}N_2$: C, 82.50; H, 8.75; N, 8.75. Found: C, 82.45; H, 8.75; N, 8.70. Anal. Calcd for $C_{22}H_{28}N_2$: C, 82.50; H, 8.75; N, 8.75. Found: C, 82.45; H, 8.75; N, 8.70.

(−)-(1*R*,2*R*,4*R*)-*N*,*N*′-Bis(*p*-chlorophenyl)-1-methyl-4-(1-methylethenyl)-1,2-diaminocyclohexane (4b): $[\alpha]_D$ −38.3° (*c* 1.00, $CHCl_3$); ^{13}C NMR ($CDCl_3$) δ 17.5, 20.7, 27.5, 33.6, 37.9, 43.8, 57.1, 59.7, 108.9, 115.3, 121.7, 122.6, 125.0, 128.5, 129.0, 144.1, 145.9, 148.2; MS *m*/*z* 388 (M^+). Anal. Calcd for $C_{22}H_{26}N_2Cl_2$: C, 67.86; H, 6.68; N, 7.19; Cl, 18.25. Found: C, 67.78; H, 6.61; N, 7.11; Cl, 18.17.

(−)-(1*R*,2*R*,4*R*)-*N*,*N*′-Di-*p*-tolyl-1-methyl-4-(1-methylethenyl)-1,2-diaminocyclohexane (4c): $[\alpha]_D$ −36.2° (*c* 1.00, $CHCl_3$); ^{13}C NMR ($CDCl_3$) δ 17.4, 20.0, 20.2, 20.5, 27.4, 33.5, 37.9, 43.7, 56.8, 59.6, 108.5, 114.4, 121.7, 126.9, 128.9, 129.0, 129.4, 129.6, 142.6, 145.0, 148.3; MS *m*/*z* 348 (M^+). Anal. Calcd for $C_{24}H_{32}N_2$: C, 82.76; H, 9.19: N, 8.04. Found: C, 82.68; H, 9.07; N, 7.96.

(−)-*N*-α-Terpinyl-*N*-phenylamine (9). To a THF solution (20 mL) of limonene (1.36 g, 10 mmol) and aniline (4.7 g, 50 mmol) was added $Hg(OAc)_2$ (3.18 g, 10 mmol) and the mixture stirred at room temperature for 30 min. Then, NaOH (20 mL, 0.5 M) and $NaBH_4$ (0.38 g, 10 mmol)/NaOH (10 mL, 3 M) were consecutively added. After 2 h, diethyl ether (20 mL) was added and the solution washed with water (3 × 20 mL) (Hg^0, 1.9 g, 95%). The organic layer was dried with Na_2SO_4 and concentrated under vacuum and the residual oil purified by flash column chromatography with CH_2Cl_2 as the eluent: yield 1.48 g, 65%; yellowish oil; [α] −12° (*c* 1, $CHCl_3$): ^1H NMR ($CDCl_3$) δ 1.2–2.0 (m, 16 H), 3.4 (br, 1 H), 5.4 (s, 1 H), 7.2–6.8 (m, 5 H); ^{13}C NMR δ 23.0 (q), 24.0 (t), 24.8 (q), 25.3 (q), 26.5 (t), 31.0 (t), 41.7 (d), 55.6 (s), 116.5 (d), 117.4 (d), 120.7 (d), 128.5 (d) 133.3 (s), 146.5 (s); MS *m*/*z* 229 (M^+). Anal. Calcd for $C_{16}H_{23}N$: C, 83.84; H, 10.04; N, 6.11. Found: C, 83.80; H, 10.00; N, 6.06.

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Acknowledgment. Financial support of this work by Direccion General de Investigacion Cientifica y Tecnica (DGICYT PB86-0254) is greatfully acknowledged. M. C.S.M. thanks the RHAE program of the Secretaria de Ciencia e Tecnologia and the Conselho Nacional de Desenvolvimento Cientifico e Technológico of Brazil for a fellowship.

Supplementary Material Available: X-ray data for compound 4 (8 pages). Ordering information is given on any current masthead page.

C-N Rotational Barriers in Ferrocenecarboxamides

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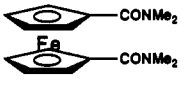
Introduction

The barrier to rotation about the C-N bond of amides is lowered by the presence of electron-donating groups attached to the amide carbonyl.[1-3] For example, the ΔG^* for C-N bond rotation in *N*,*N*-dimethyl-4-methoxybenzamide is 14.5 kcal mol^{-1}, while the corresponding barrier in *N*,*N*-dimethyl-4-nitrobenzamide is 16.4 kcal mol^{-1}.[2,3] This effect has been attributed to competitive delocalization (cross-conjugation) whereby electron donation diminishes the C-N bond order relative to a more electron-deficient system. In view of the striking facility for electron donation exhibited by ferrocenes,[4] the rotational barriers for ferrocenecarboxamides might be expected to be rather low in comparison to other arenecarboxamides. Specifically, one might expect comparatively free rotation of the NR_1R_2 group in the fulvene-like resonance for **2a** shown in Scheme I. Though ferrocenecarboxamides have been known for some time,[5] we know of no study of their rotational barriers. We find that the ΔG^* for C-N bond rotation in the simple ferrocenecarboxamides **3** and **4** is also about 14.4 kcal mol^{-1}. These results and a possible explanation are recounted below.



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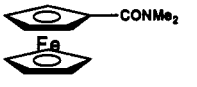

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Results and Discussion

Ferrocenecarboxamides **3** and **4** were prepared without incident from their corresponding acid chlorides by exposure to the appropriate amines in dichloromethane,

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