Reaction of 2,3-Diphenyl-5,6-dihydropyrazine and Malononitrile to Give 2,6-Diamino-3,5-dicyano-4,10-diphenyl-1,7-diazatricyclo[5.2.1.$0^{4,10}$]deca-2,5-diene. A Novel Synthesis of a Substituted Diazadihydrotriquinacene

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The reactions of 2,3-diphenyl-5,6-dihydropyrazine (1) and 2,3-di(*p*-fluorophenyl)-5,6-dihydropyrazine with malononitrile to give 2,6-diamino-3,5-dicyano-4,10-diphenyl-1,7-diazatricyclo[5.2.1.$0^{4,10}$]deca-2,5-diene (2) and 2,6-diamino-3,5-dicyano-4,10-di(*p*-fluorophenyl)-1,7-diazatricyclo[5.2.1.$0^{4,10}$]deca-2,5-diene (6) in 70 and 61% yield, respectively, are reported. The structure proofs for 2 and 6 are based on spectral properties and hydrolytic and decarboxylative conversions to 3 and 7 as well as x-ray structure analysis of 3. The mechanism of the rearrangement involved in the formation of 2 is discussed and 2 is noted to be a readily available precursor to a substituted diazatriquinacene system.

Investigation of an alleged heterophilic addition to nitrogen has prompted reports that the reaction of hydrogen cyanide with 2,3-diphenyl-5,6-dihydropyrazine (1) is, in fact, normal.[1,2] Accordingly, the heterophilic course suggested for the reaction of 1 with malononitrile[3] seems unlikely and has been reinvestigated. We now wish to report that the product of this reaction is 2,6-diamino-3,5-dicyano-4,10-diphenyl-1,7-diazatricyclo[5.2.1.$0^{4,10}$]deca-2,5-diene (2) and to note that this rearrangement may provide a novel and efficient entry to the diazatriquinacene systems.

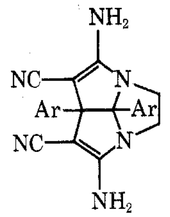
Results and Discussion

Reaction of 1 with 2 equiv of malononitrile in 20 ml of 95% ethanol at reflux for 1 h provides a 70% yield of material with an empirical formula of $C_{22}N_6H_{18}$ as shown by analysis and mass spectrometry. The presence of an enaminonitrile function in this compound is revealed by its infrared and ultraviolet spectra. The former has absorptions attributable to amino and nitrile functions at 3226–3300 cm^{-1} and 2174 cm^{-1}, while the latter has a chromophore for the enaminonitrile at λ_{max} 256 nm (ϵ 22 000).[4-6] The NMR spectrum of this material indicates the presence of two phenyl groups, four exchangeable protons, and two methylene groups. The latter are in an apparent AA′BB′ system.

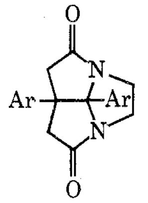
Treatment of $C_{22}N_6H_{18}$ with 50% sulfuric acid provides in 27% yield a compound $C_{20}H_{18}N_2O_2$, as expected for hydrolytic and decarboxylative conversion of an enaminonitrile to a carbonyl derivative.[4] The infrared spectrum of this hydrolytic product shows strong carbonyl absorption at 1718 and 1698 cm^{-1} (sh) consistent with a ring fused γ-lactam, while the NMR spectrum shows four new protons in two equivalent methylene groups (J_{AB} = 17 Hz) as well as ten aromatic and four AA′BB′ protons.

Of the possible structures we consider to be mechanistically reasonable for the above reactions, 2 and 3 provide the best agreement to the above data for the enaminonitrile and the lactam, respectively. Of the many alternatives[6] only 4 and its hydrolytic product 5 require further consideration.

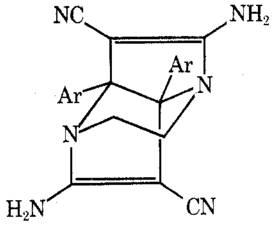
The principal difference in the structures under consideration lies in the symmetry of the carbons bearing the phenyl groups. In the case of 2 and 3, these carbons are located on the molecular mirror plane and are nonequivalent. For structures 4 and 5, however, these carbons are located symmetrically about a C_2 axis and are formally equivalent. The ^{13}C NMR of the enaminonitrile product shows two peaks at δ 66.2 and 99.1 ppm which are attributable to nonequivalent carbons bearing phenyls in accord with structure 2. The hydrolytic product, 3, shows peaks at δ 49.7 and 97.1 ppm, which can be similarly assigned.



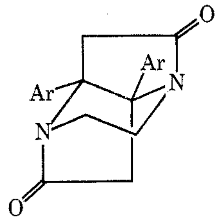
2, Ar = C_6H_5
6, Ar = p-FC_6H_4



3, Ar = C_6H_5
7, Ar = p-FC_6H_4



4, Ar = C_6H_5



5, Ar = C_6H_5

In order to make certain of the nonequivalence of the aromatic rings, 2,3-di(*p*-fluorophenyl)-5,6-dihydropyrazine was prepared and allowed to react with 2 equiv of malononitrile to provide a compound $C_{22}H_{16}F_2N_6$. This material had infrared, ultraviolet, and NMR spectral properties which, except for the bands associated with the phenyl groups, were very similar to those of 2. The ^{19}F spectrum of this material showed two peaks at δ 112.9 and 115.0 ppm consistent with structure 6. Hydrolysis of 6 with sulfuric acid gave 7, a compound which also showed nonequivalence of the phenyl groups in its ^{13}C and ^{19}F spectra. To confirm these assignments the structure of 3 was determined by x-ray structure analysis.

The crystals of 3 are orthorhombic, the space group is *Pbca*, and there are eight molecules of $C_{20}H_{18}N_2O_2$ in the unit cell. The structure was solved by direct methods[7] and has been refined to values of R and R_w of 0.066 and 0.060 on 1355 nonzero reflections. The final model was obtained by least-squares refinement of the positional and anisotropic thermal parameters for the nonhydrogen atoms and the positional and isotropic thermal parameters for the hydrogen atoms. A stereoscopic view of the molecular structure of 3 is shown in Figure 1.

The final atomic coordinates and full list of bond lengths and angles will appear in the microfilm edition. The individual values do not require extensive comment although the C(4)–C(10) bond [1.587 (7) Å] appears to be lengthened owing to the overcrowding of the three nonhydrogen substituents on each atom. The departure of the molecule in the solid from formal C_s symmetry is quite striking. While part of the reason for this effect may be due to intermolecular forces, the steric

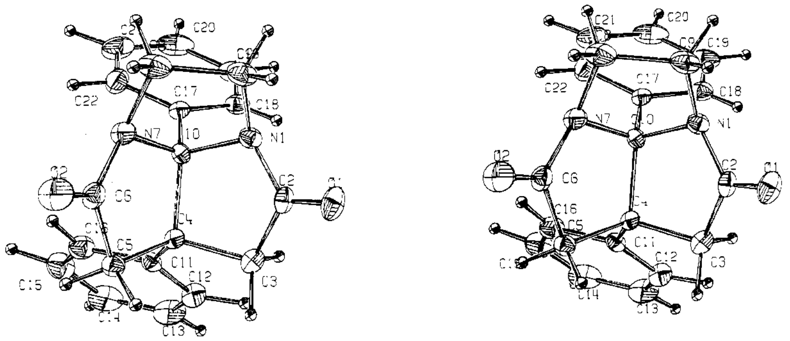
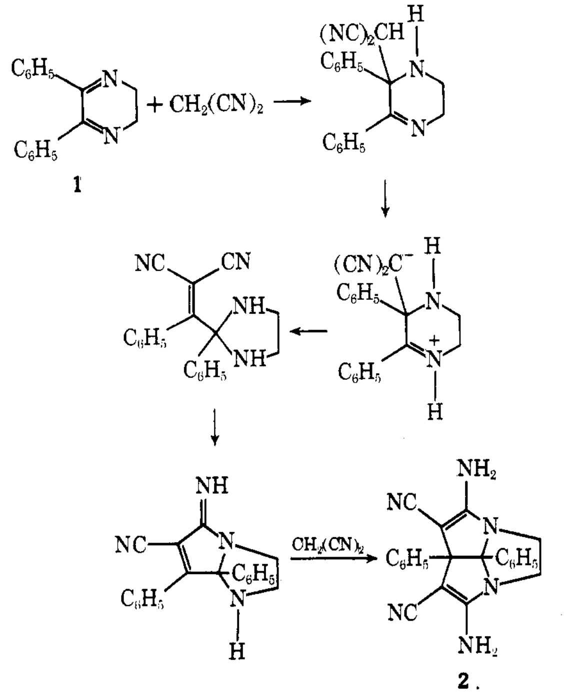


Figure 1. Stereo pair showing a single molecule of **3**.

overcrowding due to the fully substituted central C(4)–C(10) bond causes very significant departures from the fully eclipsed conformation of substituents around that bond; the C(11)–C(4)–C(10)–C(17), C(3)–C(4)–C(10)–N(1), and C(5)–C(4)–C(10)–N(7) torsion angles are −12.4, −11.3, and −5.4°, respectively. This twist of substituents about C(4)–C(10) will induce dissymmetry in the molecule and cause minor variations in the conformations of the two nitrogen-containing rings and in the spatial dispositions of the attached phenyl groups (Figure 1).

There are no unusually short intermolecular contacts; a feature of the packing is the number of contacts in the range 3.34–3.60 Å involving a carbonyl oxygen atom. A list of the shorter contacts will appear in the microfilm edition.

The structural assignments to **2** and **6** as products of the reaction of diaryldihydropyrazines and malononitrile raise the question as to how this rearrangement proceeds. A formal proposal is shown in which addition of the malononitrile to the imine bond provides a zwitterion in which ring contraction of the tetrahydropyrazine ring is promoted by formation of a double bond which is conjugated with a phenyl ring and two nitrile groups. The rearrangement finds formal analogy in the benzilic acid rearrangement[8a] and amino groups migrations to electron-deficient centers.[8b] Analogous additions involving malononitrile are well known.[8c] The simplicity of this synthesis and its potential for the synthesis of a diazatriquinacene are noted.[9]



Experimental Section[10]

p,p′-Difluorobenzil was prepared from 7.89 g of *p*-fluorobenzaldehyde (Aldrich Chemical Co.) and a solution of 0.75 g of potassium cyanide in 24 ml of 2:1 ethanol–water in a manner analogous to the preparation of benzil.[11] Extractive workup with benzene gave 7.39 g of an orange-yellow oil, which was heated on a steam bath with 40 ml of glacial acetic acid and 20 ml of concentrated nitric acid for 2 h. Dilution with 150 ml of water gave *p,p′*-difluorobenzil as a light yellow precipitate. Recrystallization from methanol provided 2.65 g (34%) of yellow needles: mp 120–121 °C; ir (Nujol) 1670 s, 1600 s, 1502 m, 1235 s, 1210 m, 1155 s, 888 s, 843 s, 798 m, 760 m, 746 cm^{-1} m; ^{1}H NMR ($CDCl_3$) δ 7.00–7.46 (m, 4, meta H's), 7.84–8.10 (m, 4, ortho H's); ^{19}F NMR ($CDCl_3$) δ 101.7 (t of t, *J* = 8.5 and 5.5 Hz); mass spectrum (70 eV) *m/e* (rel intensity) 246 (3.9, M^+), 123 (100.0), 95 (35.2), 75 (12.9).

Anal. Calcd for $C_{14}H_8F_2O_2$: C, 68.29; H, 3.28; F, 15.43. Found: C, 68.07; H, 3.01; F, 15.28.

A second crop of 702 mg (9%) of material with mp 118–120 °C was also collected.

2,3-Di(*p*-fluorophenyl)-5,6-dihydropyrazine was synthesized by heating 3.20 g (0.013 mol) of *p,p′*-difluorobenzil and 0.811 g (0.013 mol) of 98% ethylenediamine in 25 ml of ethanol at reflux for 1 h.[12] The 1.81 g (52%) of yellow crystals obtained in cooling the reaction mixture had mp 103–106 °C; ir (Nujol) 1590 s, 1560 m, 1500 s, 1310 m, 1265 m, 1230 s, 1210 s, 1155 s, 983 s, 860 m, 842 s, 833 s, 817 m, 809 cm^{-1} m; ^{1}H NMR ($CDCl_3$) δ 7.43–6.73 (m, 8, *p*-FC_6H_4), 3.62 (s, 4, $-CH_2CH_2-$); ^{19}F NMR ($CDCl_3$) δ 110.9 (t of t, *J* = 8.5 and 5.5 Hz); mass spectrum (70 eV) *m/e* (rel intensity) 270 (25.4, M^+), 122 (13.7), 121 (100.0).

Anal. Calcd for $C_{16}H_{12}N_2F_2$: C, 71.10; H, 4.48; N, 10.37; F, 14.06. Found: C, 70.95; H, 4.53; N, 10.34; F, 14.02.

Synthesis of 2,6-Diamino-3,5-dicyano-4,10-diphenyl-1,7-diazatricyclo[5.2.1.0^{4,10}]deca-2,5-diene (2). A mixture of 4.68 g (0.02 mol) of 2,3-diphenyl-5,6-dihydropyrazine and 2.65 g (0.04 mol) of malononitrile in 20 ml of 95% ethanol was heated at reflux for 1 h.[3] After cooling, the crystals which precipitated were collected by filtration and washed with ethanol. Trituration with hot ethanol afforded 5.87 g of faintly brown fluffy material which was a 1:1 solvate[3] of **2** with ethanol according to the NMR spectrum (Me_2SO-d_6). This material was dried in vacuo at 78 °C overnight to give 5.07 g (70%) of **2:** mp 341 °C dec (lit.[3] 340 °C dec); ir (Nujol) 3436, 3300, 3226, 3165, 2174, 1637, and 1585 cm^{-1}; uv max (95% ethanol) 256 nm (ε 22 000) and 214 (10 500); ^{1}H NMR (Me_2SO-d_6) δ 6.98 (br s, 10, C_6H_5), 6.83 (s, 4, NH_2, exchanges with deuterium oxide), 3.33 (AA′BB′, 4, $-CH_2CH_2-$); ^{13}C NMR (Me_2SO-d_6) δ 164.0 ($C_{2,6}$), 138.9, 138.2, 128.5, 126.8, 126.1 (ArC), 119.7 (CN), 99.1 (C_{10}), 66.2 (C_4), 63.4 ($C_{3,5}$), 48.2 ($C_{8,9}$); mass spectrum (70 eV) *m/e* (rel intensity) 366 (11.5, M^+), 229 (90.2), 126 (68.3), 91 (35.4), 84 (33.4), 82 (31.8), 62 (42.3), 60 (49.5), 43 (72.5), 30 (100.0).

Anal. Calcd for $C_{22}N_6H_{18}$: C, 72.11; H, 4.95; N, 22.93. Found: C, 71.86; H, 4.93; N, 22.90.

Synthesis of 2,6-Diamino-3,5-dicyano-4,10-di(*p*-fluorophenyl)-1,7-diazatricyclo[5.2.1.0^{4,10}]deca-2,5-diene (6). A mixture of 2.14 g (7.9 mmol) of 2,3-di(*p*-fluorophenyl)-5,6-dihydropyrazine and 1.06 g (16 mmol) of malononitrile in 7 ml of ethanol was heated at reflux for 2 h. The precipitate which appeared was collected by filtration, washed with ethanol, and dried at 78 °C (0.1 mm) overnight to give 2.464 g (61%) of **6:** mp 341 °C dec; ir (Nujol) 3322 m, 2179 vs, 1660 m, 1631 vs, 1590 s, 1500 vs, sh, 1230 s, 1154 s, 868 m, 830 cm^{-1} m; uv max (95% ethanol) 212 nm (ε 15 300), 257 (19 800); ^{1}H NMR (Me_2SO-d_6) δ 2.32–3.85 (AA′BB′, 4, $-CH_2CH_2-$), 6.67–7.22 (m, 12,

C_6H_4F and NH_2, addition of deuterium oxide reduces integration to 8 H); ^{19}F NMR (Me_2SO-d_6) δ 114.9 (t of t, 1 F, J = 8.5 and 5.5 Hz),[13] 116.1 (t of t, 1 F, J = 8.5 and 5.5 Hz); mass spectrum (70 eV) *m/e* (rel intensity) 403 (27.6), 402 (100.0, M^+), 359 (11.1), 332 (19.1), 331 (20.6), 319 (13.3), 242 (50.4), 241 (45.6), 122 (14.2), 43 (12.7).

Anal. Calcd for $C_{22}H_{16}F_2N_6$: C, 65.66; H, 4.01; N, 20.89; F, 9.44. Found: C, 65.42; H, 4.00; N, 21.16; F, 9.66.

Hydrolysis of 2,6-Diamino-3,5-dicyano-4,10-diphenyl-1,7-diazatricyclo[5.2.1.0^{4,10}]deca-2,5-diene. Formation of 3. A suspension of 2.01 g (5.5 mmol) of **2** in 90 ml of 50% sulfuric acid was heated at gentle reflux for 3 h. The yellow reaction mixture was allowed to cool to room temperature, poured onto 100 g of crushed ice, and neutralized with ammonium hydroxide. Extraction with chloroform provided 1.33 g of slightly yellow-brown solid. Chromatography on 50 g of alumina with benzene and chloroform–benzene provided 0.767 g of crude dilactam **3**, mp 225–230 °C. Rechromatography on 40 g of silica gel with chloroform as eluent gave 663 mg of material, mp 234–239 °C. Recrystallization from aqueous ethanol gave 464 mg (27%) of **3** as white plates: mp 239–240 °C; ir (KBr) 1722 vs, 1703 sh, 1380 s, 1312 m, 1260 m, 1017 m, 957 m, 772 m, 760 m, 703 s, and 498 cm^{-1} m; ^1H NMR ($CDCl_3$) δ 7.02 (m, 10, C_6H_5), 3.62 (AA′BB′, 4, $-CH_2CH_2-$), 3.25 (AB, 4, $-CH_2-$, J = 17 Hz, $\Delta\nu_{AB}$ = 53 Hz); ^{13}C NMR ($CDCl_3$) δ 177.9 ($C_{2,6}$), 140.3, 135.4, 128.1, 127.8, 127.7, 127.0 (ArC), 97.1 (C_{10}), 49.7 (C_4), 48.1 ($C_{8,9}$), 44.3 ($C_{3,5}$); mass spectrum (70 eV) *m/e* (rel intensity) 319 (22.5), 318 (100.0, M^+), 317 (22.6), 262 (19.9), 260 (18.8), 248 (17.9), 247 (41.9), 246 (27.5), 241 (10.1), 220 (10.1), 117 (28.2), 115 (20.3), 104 (12.6), 103 (10.9), 91 (21.1), 77 (16.0), 70 (23.6), 43 (14.6), 42 (18.8), 32 (14.8), 31 (19.0), 28 (21.6).

Anal. Calcd for $C_{20}H_{18}N_2O_2$: C, 75.45; H, 5.70; N, 8.80. Found: C, 75.55; H, 5.88; N, 8.97.

Hydrolysis of 1,7-Diazatricyclo[5.2.1.0^{4,10}]-4,10-di(*p*-fluorophenyl)-2,6-diamino-3,5-dicyanodeca-2-5-diene. Formation of 7. A suspension of 1.039 g (2.6 mmol) of **6** in 45 ml of 50% sulfuric acid was heated at reflux for 4 h. Workup by extraction with chloroform and chromatography on alumina provided 322 mg of a faintly brown solid, mp 201–207 °C. Recrystallization of this material from aqueous ethanol afforded 242 mg (26%) of dilactam **7** as colorless needles: mp 206–208 °c; ir (Nujol) 1726 vs, 1710 vs, 1600 m, 1500 s, 1360 s, 1300 m, 1224 s, 1165 m, 1156 m, 1015 m, 928 m, 850 m, 833 m, and 702 cm^{-1} m; ^1H NMR ($CDCl_3$) δ 7.28–6.62 (m, 8, *p*-FC_6H_4), 3.23 (AB, 4, $-CH_2-$, J = 17.5 Hz), 3.62 (AA′BB′, 4, $-CH_2CH_2-$); ^{13}C NMR ($CDCl_3$) 177.6 ($C_{2,6}$), 162.7, 161.6, 136.0, 131.4, 128.7, 128.6, 115.5, 115.3 (ArC), 96.7 (C_{10}) 49.3 (C_4), 48.0 ($C_{8,9}$), 44.4 ($C_{3,5}$); ^{19}F NMR ($CDCl_3$) δ 112.9 (t of t, 1 F, J = 5.2 and 8.3 Hz), 115.0 (t of t, 1 F, J = 5.2 and 8.3 Hz); mass spectrum (70 eV) *m/e* (rel intensity) 355 (24.7), 354 (100.0, M^+), 353 (22.9), 298 (31.5), 297 (11.8), 296 (19.6), 284 (26.6), 283 (50.4), 282 (29.0), 256 (31.7), 254 (12.3), 205 (14.1), 136 (12.7), 135 (50.0), 134 (11.0), 133 (25.1), 122 (18.7), 121 (13.0), 115 (14.2), 95 (15.4), 70 (39.0), 42 (26.9).

Anal. Calcd for $C_{20}H_{16}N_2O_2F_2$: C, 67.79; H, 4.55; N, 7.91; F, 10.72. Found: C, 67.51; H, 4.47; N, 7.86; F, 10.32.

X-Ray Analysis of 4,10-Diphenyl-2,6-dioxo-1,7-diazatricyclo[5.2.1.0^{4,10}]decane (3). Crystals of **3** as white, transparent needles elongated in the *c* direction were obtained from absolute ethanol. An untwinned crystal with dimensions ca. 0.2 × 0.1 × 0.3 mm was used for data collection. Crystal data: $C_{20}H_{18}N_2O_2$, mol wt 318.4, orthorhombic, $a = 24.229$ (9), $b = 15.449$ (7), $c = 8.796$ (3), $U = 3292.4 \times 10^{-24}$ cm^3, $Z = 8$, $D_c = 1.28$ g/cm^3, μ (Cu Kα) = 6.82 cm^{-1}, F (000) = 1344, systematic absences $0kl$, when $k = 2n + 1$, $h0l$, when $l = 2n + 1$, and $hk0$, when $h = 2n + 1$ establish the space group as *Pbca*, λ (Cu Kα) = 1.54178 Å.

The intensity data were collected on a computer-controlled four-angle Syntex $P2_1$ diffractometer using a 2θ scan mode with variable scan speeds. Scan speeds ranging from 2°/min to 10°/min were determined for individual reflections by a fast scan of the peak maximum. The background to scan time ratio used was 0.25. A total of 2814 independent reflections was scanned in the 2θ sphere from 0° to 130° with graphite-monochromatized Cu Kα radiation (λ = 1.54178 Å). Out of these reflections, 1355 were considered to be significantly above zero at the 2σ level, as determined by counting statistics.

The structure was solved by direct methods.[7] Several cycles of full-matrix least-squares refinement of the positional and anisotropic thermal parameters for the nonhydrogen atom converged to an R factor of 0.103 and R_w of 0.106. The weights were taken as $1/[\sigma(F_o)^2 + (0.02F_o)^2]$, where $\sigma(F_o)$ is the standard deviation based on counting statistics. All the hydrogen atoms were located from a difference map and then included in the refinement with isotropic thermal parameters. The final R factor was 0.066 and R_w was 0.060. The value of $[\Sigma w \Delta^2/(m - n)]^{1/2}$ was 1.40. The scattering curves were taken from the analytical expressions used in "International Tables for X-Ray Crystallography".[14] The final values for the thermal parameters and the list of structure factors will appear in the microfilm edition.

Acknowledgment. This work was supported by the National Institutes of Health and the National Science Foundation. The x-ray work was carried out on a Syntex $P2_1$ diffractometer, EXTL computer system, and XD3 Structure Graphics system whose purchase was made possible by an NSF Major Equipment Chemistry Departmental Grant (MPS 75-05911) to the University of Illinois. We are grateful for the support. The structure determination was part of a class project and we acknowledge the contributions and participation of William Baker, Monique Hinterberger, Philip Urnezis, and John Zeigler.

Registry No.—**1,** 1489-06-1; **2,** 59873-34-6; **3,** 59873-35-7; **6,** 59873-36-8; **7,** 59873-37-9; *p,p′*-difluorobenzil, 579-39-5; *p*-fluorobenzaldehyde, 459-57-4; 2,3-di(*p*-fluorophenyl)-5,6-dihydropyrazine, 59873-38-0; ethylenediamine, 107-15-3; malononitrile, 109-77-3.

Supplementary Material Available. Full details of the x-ray determination (7 pages). Ordering information is given on any current masthead page.

References and Notes

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(10) Melting points were determined on a Büchi or Nalge melting point apparatus and are uncorrected; boiling points are uncorrected. The ^1H NMR spectra were recorded on Varian spectrometers and the chemical shifts are reported in δ (ppm) relative to Me_4Si as internal standard. The ^{19}F NMR spectra were measured on a Varian A-56/60 or HA-100 spectrometer, and the chemical shifts are reported on the δ scale, upfield from internal fluorotrichloromethane standard. The ^{13}C NMR spectra were recorded on a Varian XL-100-15 spectrometer, operated at 25.2 MHz and equipped with a Digit Lab FTS-NMR/3 Model Fourier transform system. All the ^{13}C spectra were measured in the proton-decoupled mode, and the chemical shifts are reported in δ (ppm) downfield from internal Me_4Si. NMR spectrometers were operated by the author or by Mr. R. L. Thrift and associates. The infrared spectra were measured on a Perkin-Elmer Model 137, 237B, or 521 spectrophotometer as a Nujol mull or a KBr pellet, and the frequencies were calibrated against polystyrene. The uv spectra were measured on a Perkin-Elmer 202 ultraviolet–visible spectrometer. The mass spectra were obtained on a Varian MAT CH-5 spectrometer under the supervision of Mr. J. C. Cook by Mr. J. Wrona.

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