1660, 1630, 1605 cm^{-1}; NMR ($CDCl_3$) δ 5.57 (s, 2 H, C_2- and C_6-H), 3.78 (s, 6 H, C_3- and C_5-OCH_3), 3.40 (q, 2 H, J = 7 Hz, OCH_2CH_3), 3.24 (s, 3 H, C_4-OCH_3), 1.21 (t, 3 H, J = 7 Hz, OCH_2CH_3). Anal. Calcd for $C_{11}H_{16}O_5$: C, 57.88; H, 7.07. Found: C, 57.54; H, 7.20.

4-Isopropoxy-3,4,5-trimethoxycyclohexa-2,5-dienone (16c). This (117 mg) was obtained from **6** (0.5 mmol), PIFA (0.5 mmol), and K_2CO_3 (1 mmol) in isopropyl alcohol–acetonitrile as colorless crystals. Recrystallization from ethyl acetate–hexane gave pure **16c**: mp 125.5–127 °C (lit.[8a] no physical and spectral data); IR ($CHCl_3$) 1660, 1630, 1600 cm^{-1}; NMR ($CDCl_3$) δ 5.58 (s, 2 H, C_2- and C_6-H), 4.1–3.7 (m, 1 H, C*H*<), 3.77 (s, 6 H, C_3- and C_5-OCH_3), 3.20 (s, 3 H, C_4-OCH_3), 1.12 (d, 6 H, J = 6 Hz, $CHMe_2$); exact mass calcd for $C_{12}H_{18}O_5$ 242.1153, found 242.1153.

4-Ethoxy-4-methoxycyclohexa-2,5-dienone (17). This (151 mg) was obtained from **7** (138 mg, 1 mmol), PIFA (1 mmol), and K_2CO_3 (2 mmol) in methanol–acetonitrile as a colorless syrup: IR ($CHCl_3$) 1690, 1675, 1640 cm^{-1}; NMR ($CDCl_3$) δ 6.79 (d, 2 H, J = 10 Hz, C_3- and C_5-H), 6.22 (d, 2 H, J = 10 Hz, C_2- and C_6-H), 3.62 (q, 2 H, J = 7 Hz, OCH_2CH_3), 3.34 (s, 3 H, C_4-OCH_3), 1.22 (t, 3 H, J = 7 Hz, OCH_2CH_3); exact mass calcd for $C_9H_{12}O_3$ 168.0787, found 168.0798.

1-Oxaspiro[4,5]deca-6,9-diene-2,8-dione (18). (i) This (142 mg) was obtained from **8a** (166 mg, 1 mmol) and PIFA (1 mmol) in acetonitrile as colorless crystals. Recrystallization from benzene–hexane gave pure **18**: mp 106.5–108 °C (lit.[20] mp 100–102 °C, lit.[21] mp 106 °C); IR ($CHCl_3$) 1785, 1675, 1635 cm^{-1}; NMR ($CDCl_3$) δ 6.84 (d, 2 H, J = 10 Hz, C_6- and C_{10}-H), 6.24 (d, 2 H, J = 10 Hz, C_7- and C_9-H), 2.9–2.2 (m, 4 H, $CH_2 \times 2$). (ii) This (53 mg) was obtained from **8b** (121 mg, 0.47 mmol), PIFA (0.47 mmol), and pyridine (0.16 mL) in acetonitrile.

1,4-Dioxaspiro[4,5]deca-6,9-diene-2,8-dione (19). This (134 mg) was obtained from **9** (168 mg, 1 mmol) and PIFA (1 mmol) in acetonitrile as pale yellow crystals; mp 57–60 °C. Recrystallization from benzene–pentane gave pure **19** as colorless needles: mp 66–67 °C (lit.[22] mp 62–64 °C); IR ($CHCl_3$) 1820, 1680, 1640 cm^{-1}; NMR ($CDCl_3$) δ 6.71 (d, 2 H, J = 10 Hz, C_6- and C_{10}-H), 6.28 (d, 2 H, J = 10 Hz, C_7- and C_9-H), 4.46 (s, 2 H, CH_2).

1-Oxaspiro[4,5]deca-6,9-dien-8-one (20). This (89 mg) was obtained from **10** (152 mg, 1 mmol), PIFA (1 mmol), and pyridine (0.3 mL) in acetonitrile as a syrup:[23] IR ($CHCl_3$) 1690, 1670, 1630 cm^{-1}; NMR ($CDCl_3$) δ 6.76 (d, 2 H, J = 10 Hz, C_6- and C_{10}-H), 6.08 (d, 2 H, J = 10 Hz, C_7- and C_9-H), 4.06 (t, 2 H, J = 6 Hz, CH_2), 2.4–2.0 (m, 4 H, $CH_2 \times 2$); exact mass calcd for $C_9H_{10}O_2$ 150.0678, found 150.0677.

Registry No. **1**, 533-31-3; **2**, 2033-89-8; **3**, 66967-26-8; **4**, 72312-07-3; **5**, 20491-91-2; **6**, 642-71-7; **7**, 622-62-8; **8a**, 501-97-3; **8b**, 74454-78-7; **9**, 1878-84-8; **10**, 10210-17-0; **11a**, 57197-23-6; **11b**, 57197-24-7; **11c**, 109183-15-5; **12**, 64701-03-7; **13**, 66967-27-9; **14**, 72312-08-4; **15**, 67271-97-0; **16a**, 57197-13-4; **16b**, 57197-20-3; **16c**, 57197-21-4; **17**, 73010-52-3; **18**, 4572-26-3; **19**, 4385-47-1; **20**, 67856-28-4; $PhI(OCOCF_3)_2$, 2712-78-9.

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New Syntheses of Acridin-9-ones, Benzo[*c*]quinolizin-6-ones, Pyrrolo[1,2-*a*]quinoline-1,5-diones, and Some Related Tetracyclic Compounds

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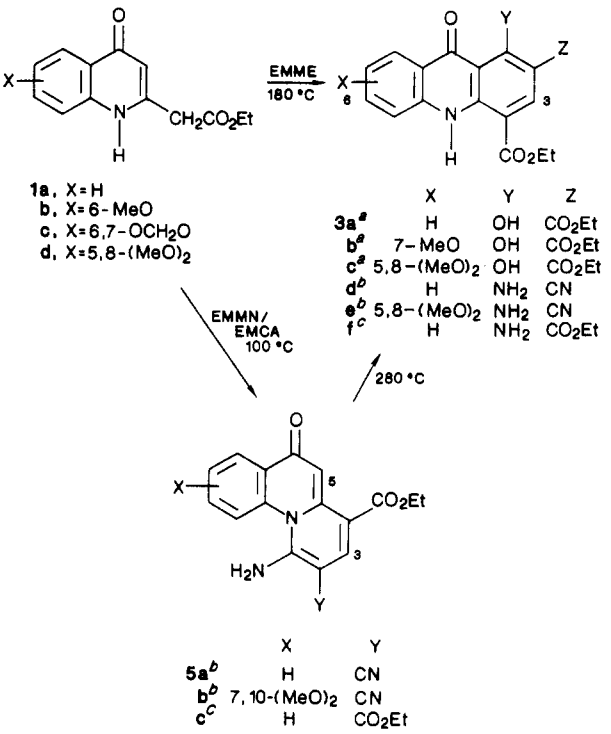
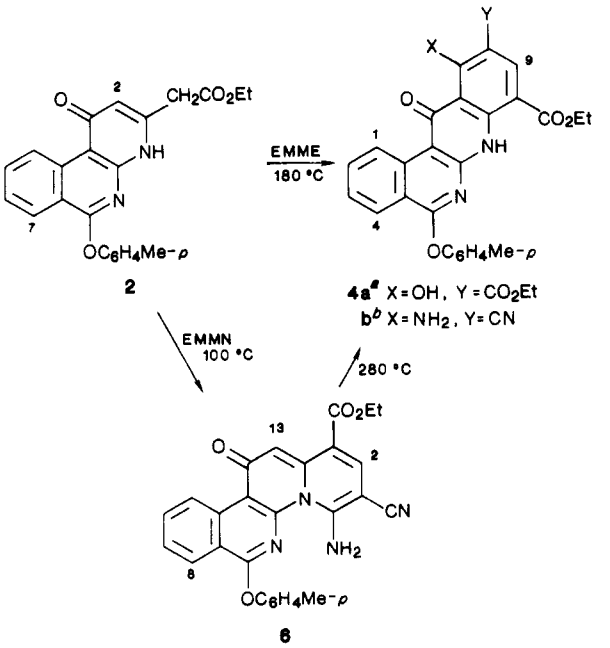
In work on possible DNA interacalating heterocycles, we were interested in the products resulting from annulation of the acetic esters **1** (Scheme I) and **2** (Scheme II).

Scheme I



[a] From EMME. [b] From EMMN. [c] From EMCA.

Scheme II



[a] From EMME. [b] From EMMN.

Compounds **1** were prepared from the anilines and diethyl 3-oxoglutarate, by an improvement on a published Conrad–Limpach synthesis.[1] The tricyclic ester **2** was obtained from 1-(*p*-methylphenoxy)isoquinolin-3-amine.[2]

Condensation reactions were then carried out with diethyl(ethoxymethylene)malonate (EMME), (ethoxymethyl)malononitrile (EMMN), ethyl (ethoxymethylene)cyanoacetate (EMCA), and diethyl acetylenedicarboxylate (DEAD).

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0022-3263/87/1952-3930$01.50/0

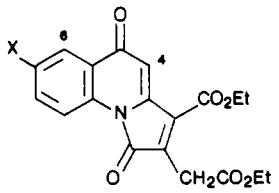
Reaction of compounds **1** with EMME at 180 °C gave the acridinones **3a–c** in 70–80% yield, with none of the isomers which would result from cyclization on N. Structures **3** were indicated by the absence of a signal in the ^{1}H NMR spectra corresponding to that for H-3 in **1**. At lower reaction temperatures, mixtures of **3** and unreacted **1** were obtained, and there was no indication of an intermediate. Cyclization of **2** gave the analogous tetracycle **4a**.

The nitrile EMMN reacted more rapidly with **1a,d**, and at 100 °C, the benzoquinolizinones **5** were produced in >90% yield. This structure was assigned from the characteristic singlets for H-3 and H-5 and downfield shift of the doublet for H-10 in **5a** relative to that for H-5 in **3d**, in the ^{1}H NMR spectrum. In paraffin oil at 280 °C, the N-cyclized products isomerized to the acridinones **3d,e**. Compound **2** reacted likewise to give **6** and **4b**.

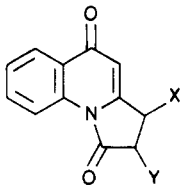
The reaction of **1a** with EMCA followed the EMMN pathway with cyclization through the nitrile group throughout the range 100–180 °C (i.e., even where EMME reacted) and **5c** was formed, which was isomerized to **3f** at 280 °C.

In the literature reports of reactions of these malonic acid derivatives with some related heterocycle acetic acid esters,[3] cyclization was invariably onto the ring N. Our finding of cyclization onto C-3 of **1** was therefore of particular interest in leading to a simple, new synthesis of highly substituted acridin-9-ones.

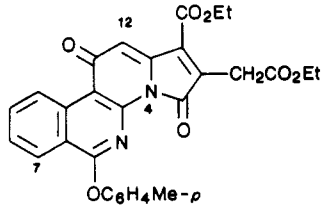
Compounds **1a,b** reacted readily with DEAD at 100 °C to give the pyrrolo[1,2-*a*]quinolinediones **7a,b** in >50% yield. Ring closure onto the N was evident from the signal for H-4 in the ^{1}H NMR spectrum. Carbonyl group ^{13}C NMR data of a reduced product provided evidence for a five-membered ring. Thus, hydrogenation of **7a** readily removed the 2,3-double bond to give **8a** [δ 178.8 (C-5), 174.5 (C-1), 170.4, 168.3 (esters)]. This is a derivative of **8b** [δ 178.8 (C-5), 175.3 (C-1)], which was available from other work.[4] The lactam carbonyl shifts are almost the same and typical of γ-lactams, whereas a six-membered ring would be expected to have this signal at a higher field.[5]



7a, X = H
b, X = MeO



8a, X = CO_2Et, Y = CH_2CO_2Et
b, X = Y = H



9

The products obtained from reactions of acetylenic esters with pyridin-2-yl[6] and quinolin-2-yl[7] acetic esters are quite different to those above, and our results therefore illustrate a novel synthesis of the pyrrolo[1,2-*a*]quinoline system. In the same way, **2** gave the aromatic 7,14-diaza steroid system **9**.

Both maleate- and fumarate-type intermediates are known in Michael addition reactions with acetylenic esters.[8] The formation of an initial maleate adduct could explain the present result. The geometry of this is such that the end ester group cannot attain the required closeness to C-3 or N for six-membered ring formation. The other ester group from DEAD is accessible for ring closure onto the N, however. We found that ethyl propiolate failed to react with **1a**, a result in accord with this explanation.

Experimental Section

General. ^{1}H NMR spectra were recorded on a Perkin-Elmer R32 90-MHz spectrometer. In addition to the data listed below, all spectra contained ethyl group signals centered at δ 1.1 (t, J = 7 Hz, CH_3) and 4.2 (q, J = 7 Hz, CH_2), in the correct integral ratios for the suggested structures. ^{13}C NMR spectra were recorded on a JEOL PFT-100FT (25 MHz) spectrometer.

Preparation of Compounds 1 and 2. Equimolar quantities of the appropriate amine and diethyl 3-oxoglutarate, in $CHCl_3$ containing a drop of concentrated HCl, were heated under Dean–Stark conditions for 24 h. The solvent was removed and the residue dissolved in hot light petroleum (bp 90–110 °C). The solution was stirred in an ice–salt bath, and the intermediate which crystallized (>80% yield) was collected.

This was mixed with 5 times its weight of PPA and heated at 110–120 °C for 2 h. Ice–water was added to the cooled mixture, the pH was taken to 5–6 with 10% NaOH (pH 4 for **1c**), and the product (>70% yield) was filtered ($CHCl_3$ extraction necessary for **1d**) and washed with water. In this way the following were prepared.

1a: mp 202–203 °C (from EtOH) (lit.[1] mp 202–204 °C); ^{1}H NMR ($CDCl_3$) δ 3.75 (s, 2 H, CH_2), 6.2 (s, 1 H, H-3), 7.2–7.6 (m, 3 H, H-6,7,8), 8.2 (d, J = 8 Hz, 1 H, H-5).

1b: mp 181–183 °C (from EtOH) (lit.[1] mp 181–184 °C); ^{1}H NMR [$CDCl_3$/$(CD_3)_2SO$] δ 3.7 (s, 2 H, CH_2), 3.9 (s, 3 H, MeO), 6.1 (s, 1 H, H-3), 7.2 (dd, J = 9, 3 Hz, 1 H, H-7), 7.45 (d, J = 9 Hz, 1 H, H-8), 7.55 (d, J = 3 Hz, 1 H, H-5).

1c: mp 251–253 °C (from MeOH); ^{1}H NMR [$(CD_3)_2SO$] δ 3.55 (s, 2 H, CH_2), 5.85 (s, 1 H, H-3), 5.9 (s, 2 H, OCH_2O), 6.8 (s, 1 H, H-8), 7.3 (s, 1 H, H-5).

1d: mp 63–65 °C (from toluene); ^{1}H NMR ($CDCl_3$) δ 3.7 (s, 2 H, CH_2), 3.9 (s, 6 H, MeO), 6.2 (s, 1 H, H-3), 6.5, 6.85 (d + d, J = 9 Hz, 2 H, H-6,7), 8.65 (br s, 1 H, NH).

2: mp 157–159 °C (from toluene); ^{1}H NMR ($CDCl_3$) δ 2.4 (s, 3 H, Me), 3.6 (s, 2 H, CH_2), 6.3 (s, 1 H, H-2), 7.2 (s, 4 H, OAr), 7.4–8.1 (m, 2 H, H-8,9), 8.5 (d, J = 8 Hz, 1 H, H-7), 10.1 (d, J = 8 Hz, 1 H, H-10).

General Reaction Method. A mixture of the compounds **1** or **2** and 1.1 molar equiv of EMME (180 °C), EMMN (100 °C), EMCA (100 °C), or DEAD (100 °C) was heated for 1 h. The mixture initially liquified and then solid formed. After cooling, the solid was filtered with the aid of a little acetone. The following products were thereby obtained.

A. From EMME. 3a (78%): mp 215–216 °C (from toluene); ^{1}H NMR ($CDCl_3$) δ 7.15–7.75 (m, 3 H, H-5,6,7), 8.2 (d, J = 8 Hz, 1 H, H-8), 8.8 (s, 1 H, H-3), 12.4 (br s, 1 H, OH). Anal. Calcd for $C_{19}H_{17}NO_6$: C, 64.2; H, 4.8; N, 3.9. Found: C, 64.3; H, 4.7; N, 3.9.

3b (68%): mp 220–221 °C (from toluene); ^{1}H NMR ($CDCl_3$) δ 3.83 (s, 3 H, MeO), 7.1–7.3 (m, 2 H, H-5,6), 7.4 (d, J = 2 Hz, 1 H, H-8), 8.7 (s, 1 H, H-3), 12.1 (s, 1 H, OH).

3c (73%): mp 202–203 °C (from toluene); ^{1}H NMR ($CDCl_3$) δ 3.92, 3.95 (s + s, 6 H, MeO), 6.5, 7.0 (d + d, J = 9 Hz, 2 H, H-6,7), 8.9 (s, 1 H, H-3), 12.3 (br s, 1 H, OH).

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(8) George, M. V.; Khetan, S. K.; Gupta, R. K. *Adv. Heterocycl. Chem.* **1976**, *19*, 279.

4a (56%): mp 309–311 °C (from toluene); ^{1}H NMR ($CDCl_3$) δ 2.45 (s, 3 H, Me), 7.2 (s, 4 H, OArH), 7.4–8.0 (m, 2 H, H-2,3), 8.4 (d, J = 8 Hz, 1 H, H-4), 8.8 (s, 1 H, H-9), 9.7 (d, J = 8 Hz, 1 H, H-1), 12.3 (br s, 1 H, OH).

B. From EMMN. 5a (94%): mp 220–221 °C (from MeOH); ^{1}H NMR [$(CD_3)_2SO$] δ 7.0 (s, 1 H, H-5), 7.2–7.6 (m, 2 H, H-8,9), 7.75 (s, 1 H, H-3), 7.8–8.2 (m, 2 H, H-7,10). Anal. Calcd for $C_{17}H_{13}N_3O_3$: C, 66.5; H, 4.2; N, 13.6. Found: C, 66.2; H,4.4; N,13.8.

5b (96%): mp 256–258 °C (from dioxane); ^{1}H NMR (CF_3CO_2H) δ 3.74, 3.79 (s + s, 6 H, MeO), 6.7, 7.0 (d + d, J = 8 Hz, 2 H, H-8,9), 6.9 (s, 1 H, H-5), 7.6 (br s, 2 H, NH_2), 8.2 (s, 1 H, H-3).

6 (73%): mp 225–227 °C (from a large volume of EtOH); ^{1}H NMR [$(CD_3)_2SO/CF_3CO_2H$] δ 2.4 (s, 3 H, Me), 7.1–7.4 (d + d, J = 8 Hz, 4 H, Ar H), 7.6–8.05 (m, 2 H, H-9,10), 8.1, 8.45 (s + s, 2 H, H-2,13), 8.5 (d, J = 8 Hz, 1 H, H-8), 9.4 (br s, 2 H, NH_2), 9.6 (d, J = 8 Hz, 1 H, H-11).

These compounds were isomerized by adding to stirring paraffin oil at 280–290 °C and heating for 0.5 h. Light petroleum (bp 60–90 °C) was added to the cooled mixture, and the product was filtered off, dried, and recrystallized from toluene.

3d (79% from **5a**): mp 263–265 °C; ^{1}H NMR (CF_3CO_2H) δ 6.9–7.6 (m, 3 H, H-5,6,7), 7.75 (d, J = 8 Hz, 1 H, H-8), 8.0 (s, 1 H, H-3). Anal. Calcd for $C_{17}H_{13}N_3O_3$: C, 66.5; H, 4.2; N, 13.6. Found: C, 66.4; H, 4.5; N, 13.5.

3e (79% from **5b**): mp 270–272 °C; ^{1}H NMR (CF_3CO_2H) δ 3.8, 3.92 (s + s, 6 H, MeO), 6.8, 7.2 (d + d, J = 9 Hz, 2 H, H-6,7), 8.5 (s, 1 H, H-3).

4b (67% from **6**): mp 273–275 °C; ^{1}H NMR (200 MHz/CF_3CO_2H) δ 2.6 (s, 3 H, Me), 7.4, 7.6 (d + d, J = 8 Hz, 4 H, Ar H), 8.0, 8.35 (t + t, J = 8 Hz, 2 H, H-2,3), 8.5 (s, 1 H, H-9), 8.87 (d, J = 8 Hz, 1 H, H-4), 10.0 (d, J = 8 Hz, 1 H, H-1).

C. From EMCA. 5c (90%): mp 201–203 °C (from toluene); ^{1}H NMR [$(CD_3)_2SO/CF_3CO_2H$] δ 7.3–7.5 (m, 2 H), 7.4 (s, 1 H, H-5), 7.9–8.3 (m, 2 H), 8.3 (s, 1 H, H-3).

3f (64%) was then obtained by thermal isomerization as for the EMMN reactions above and had mp 200–201 °C (from toluene): ^{1}H NMR (CF_3CO_2H) δ 7.0–7.6 (m, 3 H, H-5,6,7), 7.75 (d, J = 8 Hz, 1 H, H-8), 8.5 (s, 1 H, H-3). A sample for analysis was further purified by eluting through a short alumina column with $CHCl_3$ (R_f 0.95). Anal. Calcd for $C_{19}H_{18}N_2O_5$: C, 64.4; H, 5.1; N, 7.9. Found: C, 64.4; H, 5.0; N, 7.9.

D. From DEAD. 7a (50%): mp 140–141 °C (from acetone); ^{1}H NMR ($CDCl_3$) δ 3.84 (s, 2 H, CH_2), 7.0 (s, 1 H, H-4), 7.3, 7.6 (t + t, J = 8 Hz, 2 H, H-7,8), 8.1 (d, J = 8 Hz, 1 H, H-6), 8.64 (d, J = 8 Hz, 1 H, H-9); ^{13}C NMR ($CDCl_3$) δ 14.0, 30.5, 61.6, 62.3, 113.2, 117.0, 123.2, 125.5, 126.7, 134.6, 136.9, 139.4, 144.1, 160.7, 166.2, 167.9, 180.0. Anal. Calcd for $C_{19}H_{17}NO_6$: C, 64.2; H, 4.8; N, 3.9. Found: C, 64.3; H, 5.0; N, 4.1.

A sample of this compound, when hydrogenated in EtOH over 10% Pd/carbon, rapidly took up 1 mol of hydrogen. Removal of catalyst and solvent gave **8a** as a yellow glass: ^{1}H NMR ($CDCl_3$) δ 2.9–3.1 (m, 2 H, CH_2CO_2Et), 3.5–3.8 (m, 1 H, $CHCH_2CO_2Et$), 4.1 (with ester CH_2, 1 H, $CHCO_2Et$), 6.4 (d, J = 1.5 Hz, 1 H, H-4), 7.25–7.7 (m, 2 H, H-7,8), 8.15 (dd, J = 8,2 Hz, 1 H, H-6), 8.95 (d, J = 8 Hz, 1 H, H-9); ^{13}C NMR ($CDCl_3$) δ 14.0, 33.4, 40.0, 46.4, 61.3, 62.7, 109.0, 117.8, 124.9, 126.1, 126.5, 133.2, 136.3, 150.1, 168.3, 170.4, 174.5, 178.8.

7b (55%): mp 139–140 °C (from acetone); ^{1}H NMR (200 MHz/$CDCl_3$) δ 3.84 (s, 2 H, CH_2), 3.9 (s, 3 H, MeO), 7.0 (s, 1 H, H-4), 7.2 (dd, J = 9, 3 Hz, 1 H, H-8), 7.5 (d, J = 3 Hz, 1 H, H-6), 8.6 (d, J = 9 Hz, 1 H, H-9).

9 (59%): mp 210–212 °C (from acetone); ^{1}H NMR ($CDCl_3$) δ 2.45 (s, 3 H, Me), 3.8 (s, 2 H, CH_2), 7.1 (s, 1 H, H-12), 7.3 (d + d, J = 8 Hz, 4 H, Ar H), 7.5–8.0 (m, 2 H, H-8,9), 8.45 (d, J = 8 Hz, 1 H, H-7), 9.8 (d, J = 8 Hz, 1 H, H-10).

Registry No. **1a**, 109152-04-7; **1b**, 109152-05-8; **1c**, 109152-06-9; **1d**, 109152-07-0; **2**, 109152-08-1; **3a**, 109152-09-2; **3b**, 109152-10-5; **3c**, 109152-11-6; **3d**, 109152-12-7; **3e**, 109152-13-8; **3f**, 109152-14-9; **4a**, 109152-15-0; **4b**, 109152-16-1; **5a**, 109152-17-2; **5b**, 109152-18-3; **5c**, 109152-19-4; **6**, 109152-20-7; **7a**, 109152-21-8; **7b**, 109152-22-9; **8a**, 109152-23-0; **9**, 109152-24-1; EMME, 87-13-8; EMMN, 123-06-8; EMCA, 94-05-3; DEAD, 762-21-0; aniline, 62-53-3; 1-(*p*-methylphenoxy)isoquinoline-3-amine, 106051-96-1; diethyl 3-oxoglutarate, 105-50-0; 4-methoxyaniline, 104-94-9; 5-aminobenzodioxole, 14268-66-7; 2,5-dimethoxyaniline, 102-56-7.

Synthesis and Stereochemistry of Novel Triarylmesitylenes. Bases for Rigid Tridentate Ligands

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Syn–anti stereochemistry is rarely encountered in substituted benzenoid aromatic compounds, even though it is a fundamental consideration for saturated carbocycles. It has been previously noted[1] that relative orientation of substituents on benzene rings gives rise to only a small subset of the limited number of geometrically isomeric aromatics. In the past year, however, three papers have appeared[1,2] in which the relative conformations of substituents on hexasubstituted benzenes have been at issue. In all of those cases, the six substituents about the central benzene ring have been identical. Also, it was not apparent that any of the compounds were intended for further derivitization.

Recent advances in the construction of strong binders for cations,[3] anions[4], and transition metals[5] have been aided by the availability of rigid, bidentate subunits, including orthodisubstituted benzenes, *peri*-naphthalenes, and 1,8-disubstituted biphenylenes. On the other hand, there are no higher order (tridentate, etc.) binding units that are rigidly oriented, convergent, and amenable to functional group transformation, although the interesting special case of *all-cis*-1,3,5-trimethylcyclohexane-1,3,5-tricarboxylic acid has been cleverly exploited[6] in the synthesis of more elaborate binders.

If substituents at the 1, 3, and 5 positions of a benzene ring could be held at 60–90° angles and all-syn with respect to the plane of the benzene ring, the result would be a useful well-oriented tridentate binding unit. In the hope that 2-, 4-, and 6-methyl groups would enforce the necessary stereochemistry, we investigated compounds of general structure A. Before incorporating the actual ligating groups, two preliminary questions needed to be addressed: the synthesis of the structural unit and the ability of the methyl groups to hold the other substituents in place. These two issues are the subject of the present investigation.

Experimental Section

Solvents and reagents were commercially available except as noted and were used without further purification. Boronic acids were prepared when necessary from the corresponding lithium reagents and trialkylborates by using standard methodology. Tribromomesitylene was prepared[7] from mesitylene and Br_2/Fe. Separations were performed on a Beckman HPLC apparatus with variable wavelength UV detection; the preparative column was 1.5 × 50 cm packed with silica gel, and the analytical column was 1 × 25 cm C_{18}-silicate. Proton and carbon NMR spectra (vs. Me_4Si) were obtained on a Bruker 360-MHz spectrometer; ^{13}C spectra were fully decoupled. Analytical data were obtained by

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