acid chloride (4) will undergo a Friedel–Crafts reaction to result in the cyclic phenylated pyromellitides (1). This could be predicted on the basis of work reported by Bhatt et al.[6]

All reactions occur readily to result in overall yields of the pyromellitides of 23% for the cis and 27% for the trans isomers from the dianhydride. For all compounds the cis form is more soluble but the trans isomers are more reactive.

NMR spectra serve to distinguish between the cis and trans structures, 1 and 2. The central aromatic hydrogens in the trans structure are in identical environments and therefore give rise to just one singlet at δ 8.08, whereas two singlets are observed for the nonidentical, central hydrogens in the cis structure: one at δ 7.58, the other at δ 8.29.

Experimental Section

Dibenzoyliso-(and tere-) phthalic Acids (5 and 6). The Friedel–Crafts addition of benzene to pyromellitic dianhydride was carried out as described previously[4,5] with the exception of the procedure used for purification of the products. The 71.2 g of crude mixture of dibenzoylphthalic acids from reaction of 73 g (0.333 mol) of pyromellitic dianhydride was dissolved in 2500 mL of boiling 6 M aqueous KOH, filtered hot, and cooled overnight in a refrigerator to precipitate the potassium salt of 2,5-dibenzoylterephthalic acid. The precipitate was collected by suction filtration and dissolved in water, and the solution was filtered again. The filtrate was acidified with dilute HCl to precipitate the diacid which was recrystallized from glacial acetic acid, mp 324 °C (lit.[5] 319–320 °C), yield 39.2 g (31.5% based on pyromellitic dianhydride).

The aqueous basic solution from which the above salt precipitated was then acidified with 600 mL of dilute HCl. To this, 500 mL of water was added and the solution was cooled in ice to precipitate 36.2 g of crude 4,6-dibenzoylisophthalic acid. The acid was dissolved in a minimum amount of 6 M aqueous NaOH and dilute HCl was added to lower the pH to less than 1. The precipitate was isolated by filtration, washed briefly with cold water, and dried to yield 31.2 g (25% based on pyromellitic dianhydride), mp 278–280 °C (lit.[5] 277–278 °C).

3,3,5,5-Tetraphenylpyromellitide (1). A solution of 24.0 g (0.07 mol) of 4,6-dibenzoylisophthalic acid and 120 mL of thionyl chloride was heated to reflux for 3 h to give a clear yellow solution. A vacuum line was attached to the flask, and the excess thionyl chloride was removed with the aid of an aspirator until the pseudo acid chloride was left as an off-white paste in the bottom of the flask. Radiant heat from an infrared lamp was useful in this last step. The last vestiges of thionyl chloride need not be removed. To the paste of pseudo acid chloride was added 1 L of dry benzene followed by slow addition with stirring of 70.09 g (0.52 mol) of aluminum chloride. The resulting heterogeneous mixture was refluxed for 16 h, and then the benzene layer was concentrated to about 500 mL by distillation. After cooling, the aluminum chloride complex was destroyed by addition of 500 g of ice and 200 mL of 6 M HCl. The benzene layer was separated from the resulting mixture, filtered, and dried over Na_2SO_4. After filtering again, the benzene solution was concentrated to 200 mL and 800 mL of absolute alcohol was added. Upon cooling 3,3,5,5-tetraphenylpyromellitide precipitated. The precipitate was collected, dried, and dissolved in a minimum amount of boiling benzene. To this was added an equal amount of absolute alcohol and the solution was cooled to yield white platelets: mp 280–282 °C (lit.[2] 275–276 °C); yield 14.9 g (47.0%); NMR ($CDCl_3$) δ 7.16 (20 H), 7.58 (1 H), and 8.29 (1 H). Anal. Calcd for $C_{34}H_{22}O_4$: C, 80.57; H, 4.45. Found: C, 80.02; H, 4.44.

3,3,7,7-Tetraphenylpyromellitide (2). The process described above was repeated except that 2,5-dibenzoylterephthalic acid was used. The reaction mixture workup was changed as described below.

The final reaction mixture (after $AlCl_3$ addition) was steam distilled to remove the benzene and the solid residue was isolated by filtration and dried. The filtrate was extracted twice with 100-mL portions of benzene and twice with 100-mL portions of chloroform. The extracts were evaporated on a steam bath and the residue was added to that solid removed directly from the steam distillation residue. The combined solids were subjected to Soxhlet extraction by benzene for 3 days. The benzene solution was reduced in volume to 200–300 mL and an equal amount of absolute alcohol was added to precipitate the tetraphenylpyromellitide. The solid was recrystallized from benzene or benzene–ethanol to yield 15.4 g (48.6%): mp 354–356 °C; NMR ($CDCl_3$) δ 7.31 (20 H, s), 8.08 (2 H, s).

Anal. Calcd for $C_{34}H_{22}O_4$: C, 80.57; H, 4.45. Found: C, 80.50; H, 4.64.

3,3,5,5-Tetraphenyltetrathiopyromellitide (7). A solution of 3.0 g (0.006 mol) of 3,3,5,5-tetraphenylpyromellitide and 0.80 g (0.012 mol) of phosphorus pentasulfide in 50 mL of xylene was heated at reflux for 36 h. The resulting clear red solution was filtered hot and steam distilled until a red residue precipitated in the still pot. After the residue was cooled to room temperature it was collected by vacuum filtration and dissolved in a minimum amount of hot chloroform, filtered, and cooled. The yellow precipitate, probably the dithio derivative, was removed by filtration and the filtrate was concentrated to one-half of its original volume. An equal amount of alcohol was then added and the solution was cooled to 0 °C to facilitate precipitation of the tetrathio compound. The fine, red precipitate that forms was collected by vacuum filtration and dried in a vacuum desiccator overnight to yield 3.1 g (90%) of 3,3,5,5-tetraphenyltetrathiopyromellitide, mp 338–340 °C.

Anal. Calcd for $C_{34}H_{22}S_4$: C, 73.11; H, 3.94; S, 22.94. Found: C, 73.13; H, 3.88; S, 22.89.

3,3,7,7-Tetraphenyltetrathiopyromellitide. The reaction as described above was carried out on the trans isomer except that the reaction was complete in less than 12 h. The crude product was obtained in 90% yield and was extracted with boiling $CHCl_3$. The solution was concentrated and cooled to yield beautiful, deep-maroon crystals, mp 357 ± 2 °C. (Slow heating results in polymerization and no melting point. The value reported was obtained by inserting capillaries into a preheated block.)

Anal. Calcd for $C_{34}H_{22}S_4$: C, 73.11; H, 3.94; S, 22.94. Found: C, 72.95; H, 4.05; S, 22.68.

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Registry No.—**1,** 59914-21-5; **2,** 3886-00-8; **4,** 52496-56-7; **5,** 52497-38-8; **6,** 52497-37-7; **7,** 60095-15-0; phosphorus pentasulfide, 1314-80-3; 3,3,7,7-tetraphenyltetrathiopyromellitide, 62586-46-3.

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Diels–Alder Synthesis of Hindered Aromatic Amines

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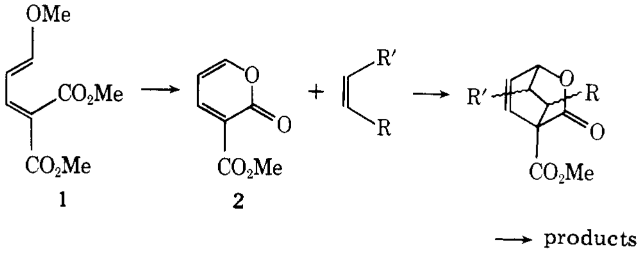
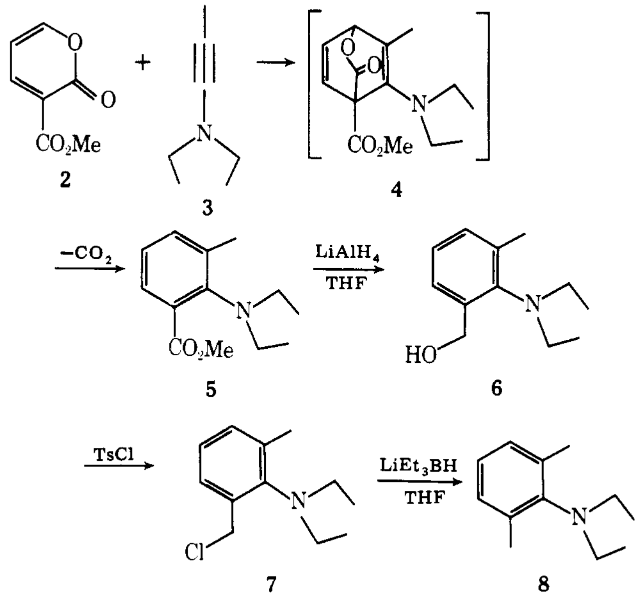
Recent interest in this laboratory in highly functionalized butadienes for use as synthons for natural product synthesis has led us to a simple preparation of symmetrical and unsymmetrical, highly hindered aromatic amines. Studies with butadiene 1[1] have shown that it will undergo a variety of ad-

Scheme I



Scheme II



dition reactions,[2] but it has proved to be a poor Diels–Alder reagent. However, diene 2, derived from 1,[3] readily undergoes cycloaddition (Diels–Alder) reactions as demonstrated previously by Corey[4] and others as illustrated in Scheme I.

When ynamine 3 is added to a benzene solution of 2, an exothermic reaction occurs affording adduct 5 (Scheme II). The initial assumption as to the favored orientation of the diene (2) and dienophile (3), based on the polarization of these reagents, proved to be correct. The reaction proceeds in a unidirectional cycloaddition process, presumably through an adduct such as 4, that spontaneously loses CO_2 resulting in formation of 5. Amino ester 5 exhibits the physical and spectral properties expected for an aromatic amine with hindered rotation about the nitrogen–aromatic ring carbon bond.

Reduction of ester 5 affords a second unsymmetrical hindered amine 6 which is further transformed to chloride 7 on treatment with *p*-toluenesulfonyl chloride. Although it is not unusual to form chlorides from the reaction of an alcohol with tosyl chloride, it is suspected that the severe crowding present in the tosylate 6 probably accelerates the formation of chloride 7. Symmetrical diethylamino-*o*-xylene 8 is readily available from lithium triethylborohydride ($LiEt_3BH$/THF) reduction of 7. As in the case for amines 5 and 6, the steric crowding about the *N*,*N*-diethylamino group in 7 and 8 seems to preclude any effective overlap of the nitrogen lone pair with the aromatic ring. Clearly alterations in the ynamine to be added to butadiene 2 would conveniently provide other hindered amines in this series that are of some theoretical interest.

Experimental Section

Methyl 2-(*N*,*N*-Diethylamino)-3-methylbenzoate (5). 1-Diethylamino-1-propyne (3, 1.08 g, 9.73 mmol) was added to α-pyrone 2[6] (1.49 g, 9.73 mmol) in dry benzene (35 mL at room temperature). After addition the reaction mixture was stirred and heated under reflux overnight, cooled, poured into CH_2Cl_2 (50 mL), washed with H_2O (50 mL), and dried ($MgSO_4$). The solvent was removed at reduced pressure and distillation (Kugelrohr oven, 80–90 °C, 0.5 mmHg) afforded 1.70 g (79%) of substituted 5: ^1H NMR δ_{CDCl_3} (Me_4Si) 7.43–6.90 (m, 3 H, PhH), 3.88 (s, 3 H, $-OCH_3$), 3.07 (q, J = 7 Hz, 4 H, $-CH_2-$), 2.31 (s, 3 H, $PhCH_3$), 1.02 (t, J = 7 Hz, 6 H, $-CH_3$); ^{13}C NMR (relative to Me_4Si, $CDCl_3$) 169.89 (carbonyl), 148.58, 138.70, 132.11 (fully substituted aromatic carbons), 133.63, 127.23, 123.93 (aromatic methynes), 51.96 ($-OCH_3$), 47.53 (R_2NCH_2-), 19.26 ($PhCH_3$), 14.68 ppm ($-CH_3$'s); IR (film) 1735, 1650, 1590 cm^{-1}; λ_{max} (EtOH) 235 nm; *m/e* 221. Anal. Calcd for $C_{13}H_{19}NO_2$: C, 70.56; H, 8.65. Found: C, 70.63; H, 8.59.

***N*,*N*-Diethyl-2-hydroxymethyl-6-methylaniline (6).** Aminomethyl benzoate 5 (0.5 g, 2.26 mmol) in THF (10 mL) was added to lithium aluminum hydride (0.08 g, 2.26 mmol) in THF (20 mL) at 0 °C. The suspension was stirred at room temperature (1 h) and excess hydride was quenched with 10% NaOH. The reaction mixture was filtered and the aluminum salts were washed with cold THF (25 mL) and H_2O (25 mL). The filtrate was dissolved in CH_2Cl_2 (75 mL), washed with H_2O (50 mL) and saturated NaCl (75 mL), and dried ($MgSO_4$). The solvent was removed at reduced pressure and the reaction mixture was distilled (Kugelrohr oven, 90–100 °C, 0.5 mmHg) affording 0.30 g (71%) of amino alcohol 6: ^1H NMR δ_{CDCl_3} (Me_4Si) 7.01 (s, 3 H, PhH), 5.06 (s, broad, 1 H, −OH), 4.75 (s, 2 H, $-CH_2-$), 3.10 (q, J = 7 Hz, 4 H, $-CH_2-$), 2.29 (s, 3 H, $-CH_3$), 1.04 (t, J = 7 Hz, 6 H, $-CH_3$); IR (film) 3380 cm^{-1}; *m/e* 193.

***N*,*N*-Diethyl-2-chloromethyl-6-methylaniline (7).** Tosyl chloride (1.48 g, 7.77 mmol) in CH_2Cl_2 (15 mL) was added at room temperature to amino alcohol 6 (1.50 g, 7.77 mmol) and triethylamine (0.78 g, 7.77 mmol) in CH_2Cl_2 (75 mL). After stirring for 12 h, the reaction mixture was diluted with CH_2Cl_2 (75 mL), washed with H_2O (100 mL) and saturated aqueous NaCl (100 mL), and dried ($MgSO_4$). The solvent was removed at reduced pressure and distilled (Kugelrohr oven, 60–70 °C, 0.5 mmHg) yielding 1.20 g (73%) of amino chloride 7: ^1H NMR δ_{CDCl_3} (Me_4Si) 7.38–6.97 (m, 3 H, PhH), 4.77 (s, 2 H, $-CH_2Cl$), 3.08 (q, J = 8 Hz, 4 H, $-CH_2-$), 2.25 (s, 3 H, $PhCH_3$), 1.01 (t, J = 8 Hz, 6 H, $-CH_3$); IR (film) 1590 cm^{-1}; *m/e* 211.

***N*,*N*-Diethyl-2,6-dimethylaniline[5] (8).** Lithium triethylborohydride (2.38 mmol, 1 M in THF) was added to amino chloride (0.25 g, 1.18 mmol) in THF (20 mL) at 0 °C. The reaction mixture was allowed to equilibrate to room temperature and stirred for 2 h. Excess hydride was destroyed by the addition of H_2O, and the organoborane intermediates were oxidized by stirring at room temperature overnight with 10% NaOH (10 mL) and H_2O_2 (30%, 10 mL). The reaction mixture was poured into $CHCl_3$ (25 mL) and extracted with $CHCl_3$ (3 × 25 mL). The organic extracts were washed with H_2O (50 mL) and saturated NaCl (50 mL) and dried ($MgSO_4$). The solvent was removed at room temperature and distillation (Kugelrohr oven, 50–75 °C, 0.5 mmHg) afforded 0.17 g (81%) of the desired substituted aniline 8: ^1H NMR δ_{CDCl_3} (Me_4Si) 6.95 (s, 3 H, PhH), 3.07 (q, J = 8 Hz, 4 H, $-CH_2-$), 2.27 (s, 6 H, $PhCH_3$), 0.99 (t, J = 8 Hz, 6 H, $-CH_3$); ^{13}C NMR (relative to Me_4Si, $CDCl_3$) 138.30, 128.8, 128.62, 124.84 (aromatic carbons), 47.37 (R_2NCH_2), 19.54 ($PhCH_3$), 14.77 ppm ($-CH_3$); IR (film) 1590 cm^{-1}; *m/e* 177.

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Registry No.—**2**, 25991-27-9; **3**, 4231-35-0; **5**, 41895-85-6; **6**, 62601-02-9; **7**, 62601-03-0; **8**, 3995-38-8.

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Intramolecular Decomposition of Isopropylidene Diazomalonate (Diazo Meldrum's Acid)[1c]

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In a discussion of the nonstereospecific addition to olefins of the carbene 1 derived from Meldrum's acid via the diazo compound 2, it was noted that direct irradiation of 2 led, in addition to 1–2% of addition products, to "very little product of any kind".[2] We report here on the fate of 1 generated by pyrolysis and photolysis of 2.

Pyrolysis of 2 at 320 °C was carried out under vacuum in