with 50 mL of 10% sodium sulfite solution, 3 × 50 mL of saturated sodium bicarbonate solution, and 100 mL of water. The organic phase was then dried over anhydrous magnesium sulfate, filtered, and evaporated under reduced pressure to afford 0.148 g of crude product. The product was purified by dissolving it in 3 mL of hot chloroform and subsequently precipitating it with 9 mL of petroleum ether: yield 0.116 g of near-colorless needles; mp 151.5–153.0 °C (73.2%).

Anal. Calcd for $C_{15}H_{16}N_2O_3S$: C, 59.19; H, 5.30; N, 9.20; S, 10.53. Found: C, 59.18; H, 5.38; N, 9.02; S, 10.58.

5a: 70.9% yield; mp 148.5–149.5 °C, lit.[8b] mp 150–151 °C. **5b:** 73.9% yield, mp 138.5–139.5 °C; Anal. Calcd for $C_{15}H_{16}N_2O_3S$: C, 59.19; H, 5.30; N, 9.20; S, 10.53. Found: C, 59.05; H, 5.39; N, 8.95; S, 10.75. **5d:** 63.9% yield; mp 182.3–183.8 °C; Anal. Calcd for $C_{14}H_{13}FN_2O_3S$: C, 54.54; H, 4.25; N, 9.08; S, 10.40. Found: C, 54.41; H, 4.32; N, 8.89; S, 10.56. **5e:** 64.5% yield; mp 223.5–225.5 °C; Anal. Calcd for $C_{15}H_{13}F_3N_2O_3S$: C, 50.28; H, 3.66; N, 7.82; S, 8.95. Found: C, 50.33; H, 3.71; N, 7.81. **5g:** 50.1% yield; mp 165.5–167.5 °C; Anal. Calcd for $C_{15}H_{14}N_2O_5S$: C, 53.89; H, 4.22; N, 8.38; S, 9.59. Found: C, 53.70; H, 4.25; N, 8.19; S, 9.61.

Registry No.—**1**, 463-51-4; **2**, 1122-83-4; **3**, 40328-82-3; **4a**, 23990-58-1; **4b**, 40328-83-4; **4c**, 66538-80-5; **4d**, 66538-81-6; **4e**, 66538-82-7; **4f**, 66538-83-8; **4g**, 66538-84-9; **5a**, 7117-27-3; **5b**, 66538-85-0; **5c**, 66538-86-1; **5d**, 66538-87-2; **5e**, 66538-88-3; **5f**, 66538-89-4; **5g**, 66538-69-0; *m*-toluidine, 108-44-1; aniline, 62-53-3; *p*-toluidine; 106-49-0; *p*-fluoroaniline, 371-40-4; *p*-trifluoromethylaniline, 455-14-1; 3,4,5-trimethoxyaniline, 24313-88-0; 5-amino-1,3-benzodioxole, 14268-66-7.

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Synthesis of Unsymmetrical Biphenyls via Aryl-Substituted 1,4-Cyclohexadienes

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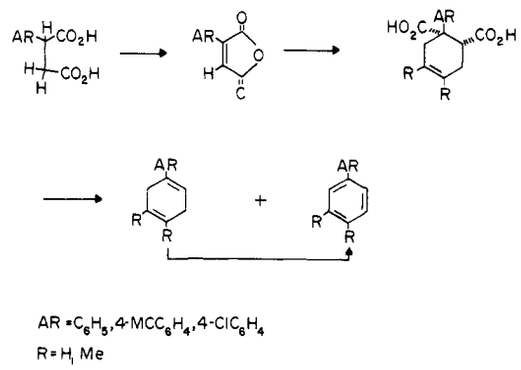
Because of a continuing interest in the chemistry and biological fate of biphenyl and especially unsymmetrically substituted biphenyls,[1] we had the need for a convenient synthesis of these compounds as well as the reduced 1-aryl-1,4-cyclohexadiene derivatives. The obvious use of the Birch reduction for the preparation of the dienes, in analogy with the successful reduction of simple substituted benzenes, has been discussed in the literature[2-4] and described to yield a difficultly separable mixture of dihydrophenyls and starting biphenyl. More recent investigation[5] of this process showed that the initially formed product of the Birch reduction of biphenyl is 1-phenyl-2,5-cyclohexadiene and that with appropriate care the compound could be isolated.

Since it appeared that this reductive type process was not efficient and would be even less so for more complex derivatives as well as suffering from the disadvantage of requiring as starting material the difficultly accessible unsymmetrical biphenyls, an alternative route was considered (Scheme I). This pathway involved the synthesis of a biphenyl nucleus incorporating functionality suitable for the regiospecific introduction of the unconjugated olefin. The bis dicarboxylic acid moiety may be considered a latent olefin function and transformation of this group to an olefin has been accomplished by the use of lead tetraacetate.[6] Although this process has been exploited most often in bicyclic systems, which preclude the possibility of further oxidation, it has been mentioned in passing that Δ^4-cyclohexene-1,2-dicarboxylic acid could be converted to 1,4-cyclohexadiene in 40% yield.[7]

Scheme I



Arylmaleic anhydrides, readily prepared from the appropriate substituted benzaldehydes via the succinic acid[8] followed in course by dehydrogenation[9] with selenium dioxide, condense readily with butadiene and 2,3-dimethylbutadiene. The products of this reaction have the substituted cyclohexene dicarboxylic acid function ready for conversion to the desired diene. Bis decarboxylation of these intermediates using lead tetracetate yeilded a mixture of diene and more completely oxidized biphenyl. Except for the parent, 1-phenyl-1,4-cyclohexadiene which yields a diene/biphenyl ratio of 5, the other derivatives all produce mixtures where the diene to biphenyl ratio is three or less. The identity of the diene component of these mixtures was determined by GC/MS which confirmed that the gross structure was indeed that of a biphenyl plus two hydrogens. In addition, the somewhat impure 1-phenylcyclohexadiene-1,4 had a melting point of 84–86 °C compared with the reported mp of 89 °C for this compound.[3]

The production of the fully aromatic biphenyl may arise by two different paths. The decarboxylation of the vicinal dicarboxylic group may occur either stepwise or in a concerted manner. The intermediate resulting from the loss of one carboxyl group may then lose a proton to yield a cyclodiene carboxylic acid which upon further decarboxylation would produce the biphenyl. A second possible route to the biphenyl is oxidation by lead tetracetate of the cyclodiene to the fully aromatic species, a process which has been shown to occur.[10]

Although this route is of only limited usefulness for the preparation of the aryl-substituted cyclodienes, it does suggest an entry into unsymmetrically substituted biphenyls. Oxidation of the diene/biphenyl mixture with DDQ occurs rapidly and cleanly, converting the mixture into homogeneous biphenyl. After simple chromatography of the reaction mixture analytically pure biphenyl is obtained.

Experimental Section

Melting points were determined with a Thomas-Hoover capillary melting point apparatus and are uncorrected. IR spectra were taken on a Model 621 Perkin-Elmer spectrometer. GLC analyses were done on a Varian series 2800 instrument equipped with a flame ionization detector and a 6 ft × ⅛ in. glass column packed with 3% OV 101 on 100/120 mesh Supelcoport. Mass spectra were obtained with a Fin-

Table I

AR	R	Yield, %	Biphenyl/diene
Ph	H	70	15[a]/85[b]
Ph	Me	54	40[c]/60[d]
4-MeC_6H_4	H	37	25[e]/75[f]
4-ClC_6H_4	H	32	30[g]/70[h]
4-MeC_6H_4	Me	60	60[i]/40[j]
4-ClC_6H_4	Me	85	50[k]/50[l]

[a] Registry no. 92-52-4. [b] Registry no. 4433-11-8. [c] Registry no. 644-08-6. [d] Registry no. 2051-62-9. [e] Registry no. 66483-38-3. [f] Registry no. 66483-39-4. [g] Registry no. 13703-52-1. [h] Registry no. 66483-33-8. [i] Registry no. 66483-34-9. [j] Registry no. 66483-35-0. [k] Registry no. 66483-36-1. [l] Registry no. 66483-37-2.

nigan Model 1015 spectrometer interfaced with a gas chromatograph.

Aryl-Substituted Succinic Acids. Except for phenylsuccinic acid which is commercially available, these compounds were prepared as described in the literature.[8]

Arylmaleic Acids. These compounds were prepared by the method of Hill[9] using the appropriate arylsuccinic acid. A mixture of 0.1 mol of succinic acid, 12.5 g of selenium dioxide, and 100 mL of acetic anhydride was heated to reflux. A vigorous but controlled reaction occurred at this point. Reflux was continued while stirring for 1 h. The hot dark solution was filtered and the solvent was removed under reduced pressure. The residue was recrystallized from CCl_4.

4-Chlorophenylmaleic anhydride: 42% yield; mp 143–144 °C; IR (KBr) ν_{max} 1850, 1835, 1820, 1760, 1610, 1215, 1095, 960, 840, 770 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.01 (s, 1 H, vinyl H), 7.75 (m, 4 H, aromatic). Anal. Calcd for $C_{10}H_5O_3Cl$: C, 57.57; H, 2.42. Found: C, 57.45; H, 2.31.

4-Methylphenylmaleic anhydride: 58% yield; mp 108–110 °C; IR (KBr) ν_{max} 3100, 1840, 1750, 1610, 1230, 1190, 1060, 910, 870, 820 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.42 (s, 3 H, CH_3), 6.95 (s, 1 H, vinyl H), 7.64 (m, 4 H, aromatic). Anal. Calcd for $C_{11}H_8O_3$: C, 70.21; H, 4.28. Found: C, 70.06; H, 4.11.

Diels–Alder Cycloaddition of Arylmaleic Anhydrides with Butadienes. A typical procedure is as follows: In a thick-walled-vessel equipped with a neck suitable for closure with a crown cap was placed 0.035 mol of aryl maleic anhydride, 30 mL of diene, 30 mL of toluene, and a magnetic stirring bar. The vessel was sealed and placed in an oil bath at 70 °C and kept there for 3 days. The toluene was then removed at reduced pressure and the resulting product was dissolved in 20 mL of 5 N aqueous KOH. The solution was decanted from a small amount of sticky residue and then washed with ether. Acidification of the solution resulted in immediate precipitation of the product.

1-(4-Chlorophenyl)-*cis*-1,2-dicarboxycyclohexene-4: 86% yield; mp 208–210 °C. The dimethyl ester was prepared (CH_2N_2) for analysis: mp 78–79 °C (ether/hexane); IR (KBr) ν_{max} 3040, 2960, 2940, 1735, 1725, 1490, 1440, 1250, 1235, 1225, 1175, 955, 920, 825, 820, 755 cm^{-1}. Anal. Calcd for $C_{16}H_{17}ClO_4$: C, 62.24; H, 5.56. Found: C, 61.95; H, 5.44.

1-(4-Methylphenyl)-*cis*-1,2-dicarboxycyclohexene-4: 81% yield; mp 188–190 °C. The dimethyl ester was prepared (CH_2N_2) for analysis: mp 100–101 °C (ether/hexane); IR (KBr) ν_{max} 3030, 2940, 1720, 1510, 1450, 1435, 1250, 1230, 1200, 1005, 950, 820, 730 cm^{-1}. Anal. Calcd for $C_{17}H_{20}O_4$: C, 70.81; H, 6.99. Found: C, 70.58; H, 6.96.

1-Phenyl-*cis*-1,2-dicarboxy-4,5-dimethylcyclohexene-4: 74% yield; mp 227–230 °C. The dimethyl ester prepared for analysis had mp 94–95 °C (MeOH): IR (KBr) ν_{max} 3050, 3000, 2955, 1740, 1720, 1500, 1450, 1440, 1250, 1200, 785, 740, 600 cm^{-1}. Anal. Calcd for $C_{18}H_{22}O_4$: C, 71.49; H, 7.34. Found: C, 71.90; H, 7.28.

1-(4-Chlorophenyl)-*cis*-1,2-dicarboxy-4,5-dimethylcyclohexene-4: 89% yield; mp 212–215 °C. The dimethyl ester prepared for analysis had mp 75–76 °C (benzene): IR (KBr) ν_{max} 3030, 2950, 1725, 1490, 1250, 1195, 1075, 1010, 830, 810, 760 cm^{-1}. Anal. Calcd for $C_{18}H_{21}ClO_4$: C, 77.59; H, 6.05; Cl, 16.36. Found: C, 77.71; H, 6.06; Cl, 16.15.

1-(4-Methylphenyl)-*cis*-1,2-dicarboxy-4,5-dimethylcyclohexene-4: 91% yield; mp 222–224 °C. The dimethyl ester had mp 97–99 °C: IR (KBr) ν_{max} 3020, 2980, 2940, 2920, 1730, 1715, 1516, 1440, 1250, 1200, 1125, 820, 810, 750 cm^{-1}. Anal. Calcd for $C_{19}H_{24}O_4$: C, 72.13; H, 7.65. Found: C, 71.97; H, 7.76.

Decarboxylation of *vic*-Dicarboxylic Acids. A solution of 10 mmol of dicarboxylic acid in 20 mL of Me_2SO and 1.8 mL of pyridine was cooled in an ice bath. Stirring was provided by a magnetic stirrer and the flask was left open to the atmosphere. To this mixture was added, all at once, 4.5 g of lead tetracetate. Within minutes gas evolution started and continued for ca. 5 min. The reaction mixture was stirred for an additional 2 h at which time the clear solution was poured into 75 mL of water. The resulting solid was filtered and extracted with benzene. After drying the extract and removal of the solvent the product was obtained as a mixture of biphenyl and arylsubstituted cyclohexadiene as determined by GC (Table I).

Oxidation of the Biphenyl/Diene Mixture to Homogeneous Biphenyl. To a solution of 7.5 mmol of biphenyl/cyclodiene mixture in 15 mL of benzene was added 5.0 mmol of dichloro-5,6-dicyanoquinone (DDQ). The solution turned green instantaneously. GLC analysis at this time indicated complete conversion of the aryl cyclohexadiene to the biphenyl. The reaction mixture was filtered and the filtrate was chromatographed on a short column of alumina. Elution with benzene yielded analytically pure biphenyl.

3,4-Dimethylbiphenyl: 68% yield; mp 22–24 °C (the literature reports this compound as a liquid[11]); IR (film) ν_{max} 3020, 1600, 1480, 1440, 1360, 870, 840, 760, 740, 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.23 (s, 3 H, CH_3), 2.25 (s, 3 H, CH_3), 7.36 (m, 8 H, aromatic). Anal. Calcd for $C_{14}H_{14}$: C, 92.26; H, 7.74. Found: C, 91.92; H, 7.75.

3,4,4′-Trimethylbiphenyl: 48% yield; mp 75–76 °C; IR (KBr) ν_{max} 3070, 1600, 1490, 1440, 1305, 1110, 1015, 1010, 980, 880, 830, 810, 720, 715 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.33 (s, 3 H, CH_3), 2.35 (s, 3 H, CH_3), 2.40 (s, 3 H, CH_3), 7.34 (m, 7 H, aromatic). Anal. Calcd for $C_{15}H_{16}$: C, 91.78; H, 8.22. Found: C, 91.88; H, 8.10.

3,4-Dimethyl-4′-chlorobiphenyl: 48% yield; mp 75–76 °C; IR (KBr) ν_{max} 3020, 1465, 1380, 1130, 1105, 1095, 1010, 885, 840, 820, 740, 770 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.30 (s, 3 H, CH_3), 2.32 (s, 3 H, CH_3), 7.32 (m, 7 H, aromatic). Anal. Calcd for $C_{14}H_{13}Cl$: C, 77.59; H, 6.05. Found: C, 77.71; H, 6.06.

Registry No.—4-chlorophenylsuccinic acid, 58755-91-2; 4-chlorophenylmaleic anhydride, 3152-15-6; 4-methylphenylsuccinic acid, 66483-40-7; 4-methylphenylmaleic anhydride, 3152-16-7; 1,3-butadiene, 106-99-0; 1-(4-chlorophenyl)-*cis*-1,2-dicarboxycyclohexene-4, 66483-41-8; 1-(4-chlorophenyl)-*cis*-1,2-dicarbomethoxycyclohexene-4, 66483-42-9; 1-(4-methylphenyl)-*cis*-1,2-dicarboxycyclohexene-4, 66483-43-0; 1(4-methylphenyl)-*cis*-1,2-dicarbomethoxycyclohexene-4, 66483-44-1; phenylmaleic anhydride, 36122-35-7; 2,3-dimethylbuta-1,3-diene, 513-81-5; 1-phenyl-*cis*-1,2-dicarboxy-4,5-dimethylcyclohexene-4, 66483-45-2; 1-phenyl-*cis*-1,2-dicarbomethoxy-4,5-dimethylcyclohexene-4, 66483-46-3; 1-(4-chlorophenyl)-*cis*-1,2-dicarboxy-4,5-dimethylcyclohexene-4, 66483-47-4; 1-(4-chlorophenyl)-*cis*-1,2-dicarbomethoxy-4,5-dimethylcyclohexene-4, 66483-48-5; 1-(4-methylphenyl)-*cis*-1,2-dicarboxy-4,5-dimethylcyclohexene-4, 66483-49-6; 1-(4-methylphenyl)-*cis*-1,2-dicarbomethoxy-4,5-dimethylcyclohexene-4, 66483-50-9; 1-phenyl-*cis*-1,2-dicarboxycyclohex-4-ene, 66483-51-0; phenylsuccinic acid, 635-51-8.

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