perature and then heated for 2 h at 80 °C. The volatile materials were removed by gentle heating at ca. 1 mm. Examination of the product by NMR showed only unreacted starting material.

Subsequently, the reaction was repeated at 105 °C with 2 mmol of the aniline. The standard workup gave 0.21 g (36%) of yellow crystalline NMR-pure 2,6-dinitroiodobenzene: mp 113 °C (lit.[16] mp 113 °C).

Reaction of *o*-Phenylenediamine. A mixture of *o*-phenylenediamine (0.216 g, 2 mmol), isoamyl nitrite (1.2 g, 10 mmol), and 5 mL of diiodomethane was heated with stirring at 80 °C for 2 h. The standard workup produced a dark residue (0.27 g), which upon ^1H and ^{13}C NMR examination proved to be benztriazole by comparison with the spectra of an authentic sample. An entirely similar result was obtained when the reaction was carried out at 110 °C.

Ancillary Experiments. 1. Reaction of Diazoaminobenzene with Trimethylsilyl Iodide. To a mixture of 0.75 g (5 mmol) of sodium iodide and 0.39 g (2 mmol) of diazoaminobenzene in 10 mL of acetonitrile was added 0.55 g (5 mmol) of trimethylsilyl chloride. The mixture turned dark, and gas evolution began immediately. The mixture was heated to 60 °C for 15 min, and the solvent was evaporated under water-pump pressure on a rotary evaporator. The ^1H and ^{13}C NMR spectra of the crude mixture showed a complex mix of products. It was estimated from these spectra that approximately 20% starting material remained and that a similar amount of iodobenzene had been formed. No further analysis was carried out. A duplicate reaction gave the same result.

2. Reaction of 1-Phenyl-3,3-diethyltriazene with Isoamyl Nitrite. The method of Ku and Barrio[10] was used to prepare 1-phenyl-3,3-diethyltriazene from benzenediazonium chloride. A mixture of 0.89 g (5 mmol of triazene was dissolved in 10 mL of diiodomethane, and 1.17 g (10 mmol) of isoamyl nitrite was added. The reaction mixture was allowed to stand at room temperature for 30 min and then heated to 80 °C for 2 h. A small portion of the solution was dissolved in deuteriochloroform and examined directly by ^1H and ^{13}C NMR. The composition of the mixture was 44% iodobenzene and 56% unreacted starting material. This could be increased to 63% iodobenzene–37% starting material by the addition of a second 10 mmol of isoamyl nitrite and a further 2 h of heating at 80 °C.

Several attempts were made to prepare the triazene directly by the reaction of isoamyl nitrite on mixtures of aniline and diethylamine in chloroform. These reactions were followed by NMR, which indicated that the isoamyl nitrite reacted much more rapidly with the diethylamine than with the aniline. Presumably *N*-nitrosodiethylamine was being formed, though this matter was not further investigated.

3. Reaction of Acetanilide with Isoamyl Nitrite. Acetanilide (0.75 g, 5 mmol) was dissolved in 10 mL of diiodomethane, and 1.17 g (10 mmol) of isoamyl nitrite was added. The mixture was heated at 80 °C for 1.5 h. An additional 1.17 g of isoamyl nitrite was added, and the heating was continued for another hour. The aromatic regions of the proton and carbon spectra showed absorptions due only to iodobenzene. An estimated yield based on both NMR and GC analysis were 30–40%.

In a similar experiment, the diacetyl derivative of 2,2′-diaminobiphenyl was reacted with an excess of isoamyl nitrite in diiodomethane. Examination of the product by NMR showed no starting material remaining after 1.5 h at 80 °C. There was no spectral evidence for the formation of 2,2′-diiodobiphenyl.

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Registry No. $PhNH_2$, 62-53-3; o-$NO_2C_6H_4NH_2$, 88-74-4; p-$MeOC_6H_4NH_2$, 104-94-9; p-$NO_2C_6H_4NH_2$, 100-01-6; o-$NH_2C_6H_4C_6H_4NH_2$-o, 1454-80-4; o-$NH_2C_6H_4NH_2$, 95-54-5; $PhNHCOCH_3$, 103-84-4; PhI, 591-50-4; o-$NO_2C_6H_4I$, 609-73-4; p-IC_6H_4OMe, 696-62-8; p-$NO_2C_6H_4I$, 636-98-6; o-$IC_6H_4C_6H_4I$-o, 2236-52-4; 2,6-dinitroaniline, 606-22-4; 1-phenyl-3,3-diethyltriazene, 13056-98-9; diazoaminobenzene, 136-35-6; 2,6-dinitroiodobenzene, 26516-42-7; benztriazole, 95-14-7.

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A Facile One-Pot Synthesis of Unsymmetrical Biaryl-2-carbonitriles by Novel Reaction of Ylidenemalononitriles with Dienamines

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Although symmetrical biaryl can be prepared by many aryl–aryl carbon bond formation reactions,[1] the known methods for the synthesis of unsymmetrical biaryls[2] are limited. The synthetic value of these methods is further diminished by poor yields of the products and the formation of an intricate mixture of the isomers which are not readily separable.

In continuation to our studies on cycloaddition reactions of dienamines,[3] herein we report a novel reaction of readily accessible ylidenemalononitriles[4] **1** with dienamines[5] **2** to afford unsymmetrical biaryl-2-carbonitriles **3** in good yields (Scheme I). This method constitutes a very convenient and facile one-pot synthesis for the preparation of unsymmetrical biaryls **3**, which are not readily obtainable by conventional aryl–aryl coupling reactions.[1,2]

Reaction of 2-thienylidenemalononitrile (**1a**) and 4-(1,3-butadienyl)morpholine (**2a**) in equimolar quantities gave bright red crystals, mp 160–161 °C. This product is assigned biaryl-2-carbonitrile structure **3a** on the basis of elemental analyses and spectral data. Reaction of 2-thienylidenemalononitrile (**1a**) with *N*,*N*-diethyl-1,3-butadienylamine **2b** also yielded biaryl **3a** in comparable yield. The versatility of this method was demonstrated by the synthesis of biaryl-2-carbonitriles **3b–g** from ylidenemalononitriles **1b–g** derived from aldehydes having electron-withdrawing as well as electron-releasing groups.

A plausible mechanism for the formation of biaryl-2-carbonitriles by this reaction could be (4 + 2) cycloaddition of ylidenemalononitriles **1** and dienamine **2** followed by concomitant elimination of HCN and amine moieties from the adduct. The formation of the adducts of type **4** and **5** which would have been the result of the addition of one molecule of ylidenemalononitrile onto the intermediate product was not observed in these reactions (Scheme I).

In conclusion this method appears to be very convenient and fairly general for the synthesis of unsymmetrical biaryl-2-carbonitriles which could be difficult to reach otherwise. The easy availability of a variety of ylidenemalononitriles and diene partners significantly extends the scope of this methodology and more particularly ylidenemalononitriles derived from polycyclic, aromatic, and hetero aromatic aldehydes are likely to afford interesting novel biaryls.

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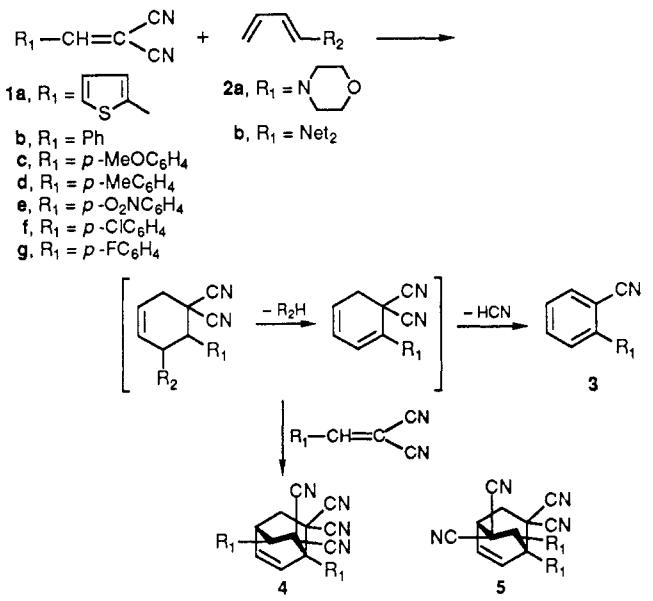
Scheme I



Experimental Section

Melting points were determined in open capillary tubes on a Büchi apparatus and are uncorrected. The ^1H NMR spectra were recorded on a Bruker 300-MHz and Varian 60-MHz spectrometers, and chemical shift values are recorded in δ units (parts per million) relative to tetramethylsilane as internal standard. ^{13}C NMR spectra were obtained with proton-noise decoupling and proton-coupling on Bruker 300-MHz instrument, and chemical shifts are expressed relative to internal standard tetramethylsilane in $CDCl_3$. Infrared spectra were recorded on a Perkin-Elmer 237B IR spectrometer in potassium bromide disks. Mass spectra were recorded on a AEI MS30 instrument.

Ylidenemalononitriles **1** were prepared by condensing corresponding aldehyde with malononitrile.[6]

Dienamines **2** were prepared by condensing freshly distilled crotonaldehyde with freshly distilled corresponding secondary amine.

General Procedure for the Synthesis of Biaryl-2-carbonitriles. 2-(2-Thienyl)benzonitrile (3a). The solution of 2-thienylidenemalononitrile (**1a**) (1.60 g, 10 mmol) in dry benzene (20 mL) was added dropwise to the stirred solution of 4-(1,3-butadienyl)morpholine (**2a**) (1.39 g, 10 mmol) in dry benzene (10 mL) at room temperature under nitrogen blanket. Stirring was continued further for 24 h at room temperature. Benzene was then removed under reduced pressure, and the pasty material left was purified by column chromatography (silica gel, benzene) and recrystallized (hexane–benzene, 5:1) to afford 1.48 g (80%) of **3a** as bright red crystals, mp 160–161 °C. Reaction of **1a** with *N,N*-diethyl-1,3-butadienylamine (**2b**) under similar conditions yielded **3a** in 75% yield: IR (KBr) 2240 (C≡N), 1480, 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.85–7.60 (m, 7 H); ^{13}C NMR ($CDCl_3$) δ 112.0, 118.7, 126.0, 126.2, 127.7, 127.9, 128.0, 132.5, 132.8, 137.8, 155.4; mass (M^+) 185. Anal. Calcd for $C_{11}H_7NS$: C, 71.32; H, 3.81; N, 7.56. Found: C, 71.40; H, 3.80; N, 7.50.

1,1′-Biphenyl-2-carbonitrile (3b). Benzylidenemalononitrile (**1b**) (1.54 g, 10 mmol) reacted with 4-(1,3-butadienyl)morpholine **2a** (1.39 g, 10 mmol) in benzene (as above). Chromatography (hexane) yielded 1,1′-biphenyl-2-carbonitrile (**3b**) (1.16 g, 65%) as light yellow oil, which crystallized on storing in cooling condition, mp 35–37 °C (lit.[2a] mp 26–36.5 °C).

4′-Methoxy-1,1′-biphenyl-2-carbonitrile (3c). (4′-Methoxybenzylidene)malononitrile (**1c**) (1.84 g, 10 mmol) reacted with 4-(1,3-butadienyl)morpholine (**2a**) (1.39 g, 10 mmol) in dry benzene (as above). Chromtographic purification (hexane) afforded biphenyl-2-carbonitrile (**3c**) (1.57 g, 75%) as crystalline solid: mp 156–157 °C; IR 2235, 1580, 1450, 755 cm^{-1}; ^1H NMR δ 3.82 (s, 3 H), 6.86–7.68 (m, 8 H); mass (M^+) 209. Anal. Calcd for $C_{14}H_{11}NO$: C, 80.36; H, 5.29; N, 6.69. Found: C, 80.30; H, 5.31; N, 6.60.

4′-Methyl-1,1′-biphenyl-2-carbonitrile (3d). (4′-Methylbenzylidene)malononitrile (**1d**) (1.68 g, 10 mmol) reacted with 4-(1,3-butadienyl)morpholine (**2a**) (1.39 g, 10 mmol) in dry benzene (as above) to afford biphenyl-2-carbonitrile (**3d**) (1.43 g, 74%) as a crystalline solid, mp 120–121 °C, after chromatographic purification (hexane): IR 2240, 1590, 1465, 750 cm^{-1}; ^1H NMR δ 2.36 (s, 3 H), 6.85–7.70 (m, 8 H); mass (M^+) 193. Anal. Calcd for $C_{14}H_{11}N$: C, 87.01; H, 5.74; N, 7.25. Found: C, 87.19; H, 5.70; N, 7.40.

4′-Nitro-1,1′-biphenyl-2-carbonitrile (3e). (4-Nitrobenzylidene)malononitrile (**1e**) (1.99 g, 10 mmol) reacted with 4-(1,3-butadienyl)morpholine (**2a**) (1.39 g, 10 mmol) in dry benzene (as above) to afford biphenyl-2-carbonitrile (**3e**) (1.45 g, 65%) as crystalline solid, mp 179–180 °C, after chromatographic purification (hexane–benzene, 10:1): IR 2240, 1600, 1520, 755 cm^{-1}; ^1H NMR δ 7.25–7.63 (m, 6 H), 8.22 (m, 2 H); mass (M^+) 224. Anal. Calcd for $C_{13}H_8N_2O_2$: C, 69.64; H, 3.59; N, 12.49. Found: C, 69.80; H, 3.47; N, 12.53.

4′-Chloro-1,1′-biphenyl-2-carbonitrile (3f). Reaction of (4-chlorobenzylidene)malononitrile (**1f**) (1.88 g, 10 mmol) with 4-(1,3-butadienyl)morpholine (**2a**) (1.39 g, 10 mmol) in dry benzene (as above), after chromatographic purification, yielded biphenyl-2-carbonitrile (**3f**) (1.66 g, 78%) as crystalline solid, mp 115–116 °C (lit.[2a] mp 113–115 °C) and IR, NMR dcata same as reported.

4′-Fluoro-1,1′-biphenyl-2-carbonitrile (3g). Reaction of (4-fluorobenzylidene)malononitrile (**1g**) (1.72 g, 10 mmol) with 4-(1,3-butadienyl)morpholine **2a** (1.39 g, 10 mmol) in dry benzene (as above) after chromatographic purification yielded biphenyl-2-carbonitrile (**3g**) (1.38 g, 70%) as crystalline solid. The melting point and IR, NMR data are the same as reported.[2a]

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Registry No. **1a**, 28162-32-5; **1b**, 2700-22-3; **1c**, 2826-26-8; **1d**, 2826-25-7; **1e**, 2700-23-4; **1f**, 1867-38-5; **1g**, 2826-22-4; **2a**, 19352-93-3; **2b**, 14958-13-5; **3a**, 125610-77-7; **3b**, 24973-49-7; **3c**, 125610-78-8; **3d**, 114772-53-1; **3e**, 17254-19-2; **3f**, 89346-58-7; **3g**, 89346-55-4.

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Reversal of the Order of Catalytic Efficiency of Primary and Secondary Amines in the Ionization of a Sterically Hindered Carbon Acid

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It is now generally recognized that base-catalyzed proton abstraction from carbon acids by primary and secondary amine bases follows the order of effectiveness, 2° amines > 1° amines, when comparing bases with the same pK_a value.[1,2] This differing catalytic effectiveness is easily observed in statistically corrected Brönsted plots for proton abstraction (or anion protonation) where these classes of amines normally fall on separate, though frequently parallel, linear plots. The observed trend has been attributed to a decrease in hydrogen-bonded solvation of the protonated amines with increasing N-substitution coupled with a lag in the development of this solvation in the

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