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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 ¹³C NMR examination proved to be benzotriazole 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 80 °C for 15 min, and the solvent was evaporated under water-pump pressure on a rotary evaporator. The ¹H and ¹³C 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 Barrio¹⁰ 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 ¹³C 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. PhNH₂, 62-53-3; *o*-NO₂C₆H₄NH₂, 88-74-4; *p*-MeOC₆H₄NH₂, 104-94-9; *p*-NO₂C₆H₄NH₂, 100-01-6; *o*-NH₂C₆H₄C₂H₄NH₂-*o*, 1454-80-4; *o*-NH₂C₆H₄NH₂, 95-54-5; PhNHCOCH₃, 103-84-4; PhI, 591-50-4; *o*-NO₂C₆H₄I, 609-73-4; *p*-IC₆H₄OME, 696-62-8; *p*-NO₂C₆H₄I, 636-98-6; *o*-IC₆H₄C₆H₄I-*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; benzotriazole, 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 biaryls² 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 ylidenemalononitriles⁴ 1 with dienamines⁵ 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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