Functionalized Azo Dyes by Direct Ullmann Coupling

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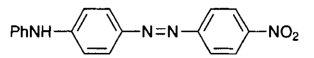
A variety of thermally stable 4-(*N*,*N*-diarylamino)-4′-nitroazobenzene dyes can be produced by direct copper-mediated C–N bond formation on preformed amino substituted azo dyes, thus avoiding a troublesome azo coupling step; the products are useful chromophores for high temperature nonlinear optical applications.

Integrated polymeric electro-optic switches and modulators may operate continuously at elevated temperatures (80–100 °C) and experience brief excursions to much higher temperatures (>250 °C) during semiconductor fabrication.[1] Useful polymeric devices will require thermal stability of both the polymers and the nonlinear optical (NLO) chromophores as well as a stabilized induced polar order at elevated temperatures. While the latter topic has received considerable attention,[2] the design of very thermally stable NLO chromophores of uncompromised nonlinearity is a relatively recent concern. In this regard, we have reported[3] that the use of diarylamino electron donor substituents in extended donor–acceptor substituted chromophores results in significant improvement in thermal stability relative to dialkylamino substituted derivatives without compromising the nonlinearity. Since donor–acceptor substituted azobenzene derivatives are attractive NLO chromophores for poled-polymer applications because of their large dipole moments, long wavelength charge-transfer absorptions and large intrinsic molecular hyperpolarizabilities,[4] we have sought a general synthetic route to 4-*N*,*N*-diarylamino-4′-nitroazobenzene derivatives, particularly those containing additional functionality appropriate for subsequent polymer attachment.

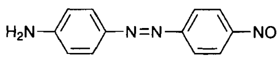
In principle, the most straightforward route to such materials is the azo coupling of diazonium salts of *p*-nitroaniline[5] with appropriately substituted triphenylamines. However, since diarylamino substituents are relatively poor electron donors, diazo coupling reactions on substituted triphenylamines are slow and side reactions often occur leading to poor product yields. Phase transfer techniques using amphiphilic alkylsulfonate salts sometimes increase the rate of azo coupling,[6] and we have found that 4-*N*,*N*-diphenyl-4′-nitroazobenzene can be prepared in 47% yield using this method. However, all diazo coupling procedures are inapplicable for triarylamine derivatives containing additional strongly electron donating (alkoxy, alkylamino, *etc.*) substituents. For example, the attempted azo coupling of *p*-nitrobenzene diazonium salts with *N*-(*p*-methoxyphenyl)-diphenylamine results unexpectedly in dearylation and the isolation of 4-(*N*-phenylamino)-4′-nitroazobenzene (Disperse Orange 1, **DO1**) as the major product. Similar difficulties were encountered with triphenylamine derivatives substituted with other strongly electron donating substituents.

We now report that a wide variety of functionalized 4-*N*,*N*-diarylamino-4′-nitroazobenzene derivatives can be prepared directly in fair to good yields by the Ullmann coupling of

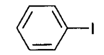
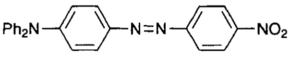
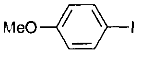
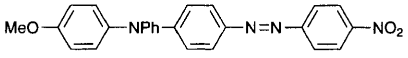
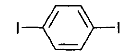
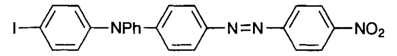
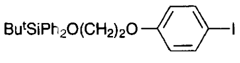
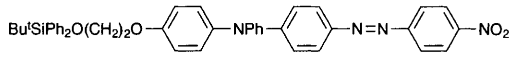
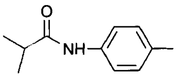
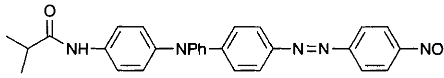
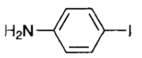
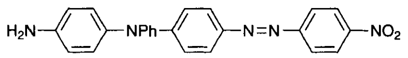
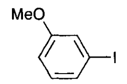
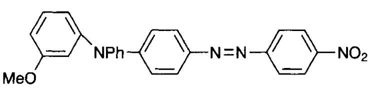
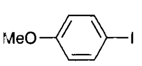
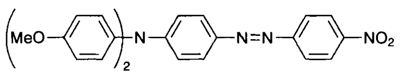
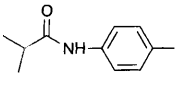
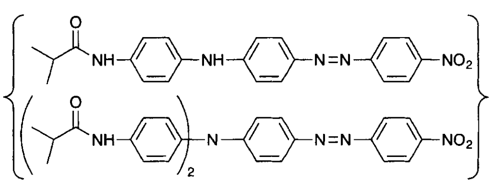
Table 1 NLO triphenyl amine derivatives by direct Ullmann coupling



DO1



DO3

Entry	Dye	Aryl halide	Procedure	Product	Yield (%)	Mp / °C	λ_{max} / nm
1	**DO1**		A[a]		81	144–145	486
2	**DO1**		A		68	154–155	498
3	**DO1**		A		74	171–173	486
4	**DO1**		A		50	– – –[b]	496
5	**DO1**		A		56	169–171	496
6	**DO1**		A		61	155–157	498
7	**DO1**		B[c]		55	116–118	492
8	**DO3**		B		40	168–169	510
9	**DO3**		A		19 40	210–212 255–257	448 502

[a] Phase transfer, 180 °C. [b] Oil. [c] Triglyme, 210 °C.

substituted aryl halides with commercially available preformed azo dyes such as **DO1** and the primary amino substituted derivative 4-amino-4′-nitroazobenzene (Disperse Orange 3, **DO3**). This procedure provides a direct, straightforward route to a variety of useful, thermally stable NLO chromophores.

The Ullmann coupling procedure, including phase transfer variants,[7] is a well known synthetic route to simple, substituted di- and tri-arylamines.[8–10] To our knowledge, this reaction has not been used for the generation of substituted nitroazobenzene derivatives. We have successfully utilized two synthetic variants for the functionalization of the orange dyes **DO1** and **DO3**. The first (Method A) involves a phase transfer procedure utilizing 18-crown-6, potassium carbonate, copper or copper bronze and a high boiling aromatic solvent such as *o*-dichlorobenzene. The second technique (Method B) utilizes triethylene glycol dimethyl ether as the solvent and no crown ether. The latter permits higher reaction temperatures of 200–220 °C and is useful for stubborn reactions. In all cases, the reactions were monitored continuously by TLC. Representative results from these studies are shown in Table 1. In spite of the elevated reaction temperatures, the functionalized azo products survive and are easily isolated, often in moderate to good yields. Using Method A, the products were isolated by removal of the solvent under vacuum followed by flash column chromatography[11] on silica gel. Using Method B, the filtered reaction was diluted with water and extracted with either dichloromethane or ethyl acetate prior to chromatographic purification. We observed no significant differences in yield using either commercial copper powder (1 μm, Alfa Chemical) or activated copper–bronze. The structures of the azo products are secured by their spectral and analytical data. The yield of the Ullmann-type coupling to produce the simple diphenyl derivative (entry 1) is almost twice that obtained by the phase transfer azo coupling route. This material is also isolated in 74% yield using bromobenzene as the starting material, although a longer reaction time (48 h) was required. When aryl diiodides are used in excess, monoarylation products (entry 3) can be isolated in reasonable yield. All of the yields reported are for chromatographically pure materials, but are otherwise unoptimized. Primary aminoaryl functionality can be bis-arylated in a one pot reaction using larger excesses of iodide starting materials (3–4 mmol per mmol amine) and/or higher reaction temperatures. This is illustrated in entries 8 and 9 for the amino substituted dye **DO3**.

Given the harsh conditions, the reaction is remarkably tolerant of functionality. For example, it has been suggested that the classical intermolecular Ullmann coupling reaction fails for primary aryl amides containing *para*-halogen substituents,[12] presumably due to competitive condensation (polymerization) involving the acetamido nitrogen and the aryl halide. This is not the case with the aminonitroazobenzene derivatives studied here (entries 5 and 9). Presumably the enhanced acidity of the NH protons of the azo dyes directs the coupling reaction in the desired fashion. The reaction is not limited to the preparation of the relatively sterically hindered isobutyroamide starting materials, since the coupling reaction also works for *p*-iodoacetanilide, although the yields are somewhat lower and relatively more of the monoadduct is isolated. Likewise, the results in entry 4 show that protection of pendant hydroxy functionality as the *tert*-butyldiphenylsilylether yields the desired coupling product and avoids the undesirable side reactions which occur if the free hydroxy containing material is used directly. The protecting group is easily removed quantitatively at room temperature by the subsequent treatment with 1 mol dm^{-3} tetrabutylammonium fluoride in THF.

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