Pergamon

Tetrahedron Letters, Vol. 36, No. 25, pp. 4393-4396, 1995
Elsevier Science Ltd
Printed in Great Britain
0040-4039/95 $9.50+0.00

0040-4039(95)00858-6

The Preparation of Aromatic NLO Amine and Diamine Monomers for Polymerization: A Mild Mitsunobu Coupling Technique for the Tethering of Sensitive NLO Chromophores

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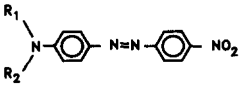
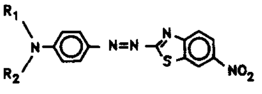
SUMMARY: Polymerizable NLO monomers, including those containing highly nonlinear, reagent sensitive chromophores, are prepared under very mild conditions using a deprotection strategy, coupled with Mitsunobu chemistry.

Recently there has been an explosion of interest in poled polymers for nonlinear optical (NLO) applications such as frequency doubling and electro-optical modulation and switching.[1] Performance requirements for integrated devices dictate that the materials must operate continuously at 80 – 100°C and may experience brief excursions to 250°C or more during fabrication. These demands require both orientational stability of the poled order as well as intrinsic thermal stability for the NLO chromophore and polymer.[1b,2] While it has been shown that certain NLO polyimide derivatives have the high glass transition temperatures[3] necessary to maintain the polar order at elevated temperatures, the incorporation of highly nonlinear, yet thermally stable,[4] chromophores into polymerizable monomers has proved troublesome. In this report, we describe a novel synthetic strategy for the preparation of highly nonlinear, yet thermally stable, dye functionalized monomers. The routes described allow the preparation of a variety of NLO functionalized aromatic amines and diamines including some bearing particularly reagent sensitive functionality, which, to our knowledge, are inaccessible by existing methods.

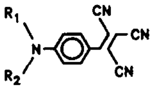


2a R_1=Et, R_2=$-(CH_2)_2OH$

2b R_1=Ph, R_2=$-C_6H_4-O(CH_2)_2OH$

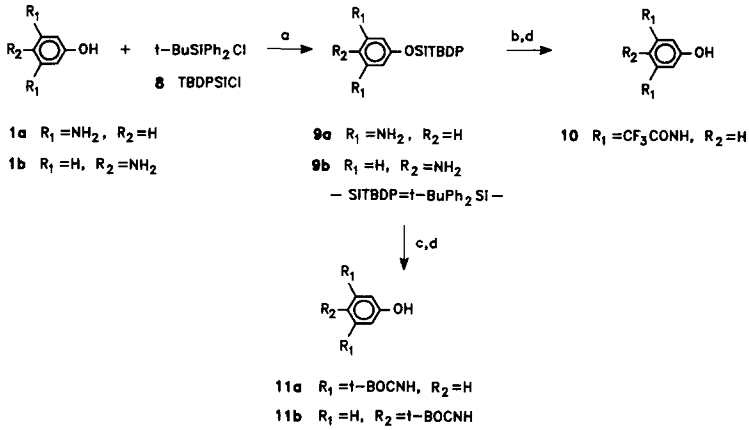


3 R_1=Ph, R_2=$-C_6H_4-(CH_2)_2OH$



4 R=Et, R_2=$-(CH_2)_2OH$

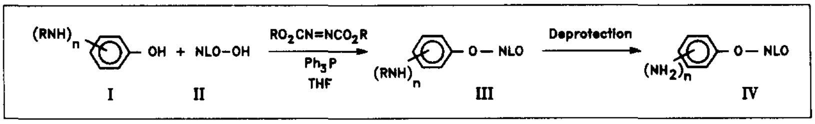
We have recently described in preliminary fashion a viable nucleophilic displacement route to certain nitro substituted nonlinear optical (NLO) functionalized aromatic diamines.[5] This procedure utilizes nucleophilic displacement on the tosylates derivatives of the dyes **2a** and **2b** by the phenoxy anion of 3,5-diaminophenol **1a** generated with strong base. While this technique is operationally simple (no prior protection of the amino functionality is necessary) and good chemoselectivity results in strongly basic solution, the product yields are moderate (see Table I) and the technique is limited to those chromophores which are stable in strongly basic media. Unfortunately, this is not the case for many NLO chromophores, particularly examples with powerful electron acceptor functionality. Two cases in point are provided by the complete failure of the nucleophilic displacement route to provide aromatic diamines from the corresponding tosylate derivatives of **3** and **4**. In each case, the basic solutions decolorize almost instantly upon contact with the phenoxide reagent, and complex product mixtures result. This is unfortunate, since both 6-nitrobenzothiazole[4,6] and tricyanovinyl[5b,7] acceptor functionality have been shown to provide exceptionally nonlinear chromophores with surprising thermal stability.[5b] The thermal stability of chromophores containing the latter functionality was unexpected in light of the extreme sensitivity of the tricyanovinyl group to attack by nucleophiles.[8] This is believed to be the reason why derivatives of 4 decompose when subjected to the basic conditions. The extreme sensitivity of the tricyanovinyl group to nucleophilic or basic reagents was further illustrated by the unexpected observation that attempts to desilylate the protected t-butyldiphenylsilyl ether of 4 (prepared by electrophilic substitution of N-(2′-t-butyldiphenylsiloxyethyl)- N-ethyl)aniline 5 with tetracyanoethylene (TCNE)[8b] in DMF at 70°C) using tetrabutylammonium fluoride in THF(1M) resulted initially in low yields and complex product mixtures. The problem arises from competitive attack of the naked fluoride nucleophile on the strongly electrophilic substituent and subsequent reactions. Fortunately, this undesired side reaction can be suppressed completely by the addition of two equivalents (based on available fluoride ion) of a weak proton acid such as glacial acetic acid, which apparently mediates the nucleophilicity of the reagent without hindering its reactivity toward the silylated protecting group.



Scheme 1: Selective protection of aminophenols
a. t-BuPh$_2$SiCl, triethylamine, CH$_3$CN, reflux, 2h; b. (CF$_3$CO)$_2$O, pyridine, reflux, 2h; c. tert-butylpyrocarbonate, pyridine, 25°C, 18h; d. Bu$_4$NF-THF(1M), 25°C, 1h.

To overcome the limitations discussed, we have developed an exceedingly mild coupling procedure, generally applicable to all chromophores but particularly useful for those containing reagent-sensitive acceptor functionality, capable of producing substituted aromatic amine and diamine monomers for subsequent polyamide and polyimide formation. This new procedure employs a novel selective deprotection strategy in concert with Mitsunobu coupling chemistry.[9] Typical starting materials for the Mitsunobu coupling study were the NLO chromophores **2a,b**, **3**, **4**, each containing either a hydroxyethyl or hydroxyalkoxy tether group. The alcohol **2b** was prepared as described in Ref. 5b. The 6-nitrobenzothiazole derivative 3 was generated by azo coupling[10] of 6-nitrobenzothiazole-2-diazonium tetrafluoroborate 6 to N-(4′-hydroxyethylphenyl) diphenylamine 7. The two nitro-substituted azobenzene dyes **2a** and **2b** are included in this study for direct comparison of the results of the Mitsunobu method with those obtained using the tosylate displacement route.

All attempts to perform the Mitsunobu coupling using the free aminophenols failed. Although examples of phenolic ether formation under Mitsunobu conditions abound in the literature,[9] we are unaware of any example directly utilizing an aminophenol. For this reason, the selective protection procedure shown in Scheme I was developed. We have demonstrated that both trifluoroacetamido and t-butoxycarbonylamido functionality can selectively be introduced into the aminophenols by the preparation of **10** and **11a,b**. In practice, the conversion of **1a** and **1b** to the completely protected derivatives may be combined into a one-pot procedure. Desilylation occurs readily by treatment with Bu_4NF in THF at room temperature to produce **10** and **11a,b**. The amino protecting groups[11] do not interfere with the Mitsunobu coupling reaction and are easily removed subsequently under mild conditions to unmask the free amino substituents without affecting the NLO functionality. This is a critical feature given the demonstrated reactivity of certain acceptor substituents. The trifluoroacetamido group is readily hydrolyzed using either K_2CO_3 in MeOH – H_2O or, less conveniently, with aqueous acid (6N, HCl, THF, reflux). The t-BOC protecting group can be removed selectively either by thermolysis or, preferably, by treatment with acid at room temperature.



Protected Phenol I	NLO–OH II	Coupling Yield (%) (Protected Amine) III	Deprotection Yield (%) [Method] IV
10	**2a**	**12** (55)	**18** (73) [A][a] ⟨54⟩[d]
10	**2b**	**13** (65)	**19** (90) [A][a] ⟨27⟩[d]
10	**3**	**14** (76)	**20** (60) [A][a] ⟨0⟩[d]
10	**4**	**15** (71)	**21** (17) [B][b] ⟨0⟩[d]
11a	**4**	**16** (64)	**21** (82) [C][c] ⟨0⟩[d]
11b	**4**	**17** (76)	**22** (88) [C][c] ⟨0⟩[d]

Table 1: The Preparation of NLO Substituted Aromatic Amines and Diamines by Mitsunobu Coupling
a. Method A = K_2CO_3, $MeOH-H_2O$, 40 °C, 14h; b. Method B = 6NHCl–THF, reflux; c. Method C = trifluoroacetic acid–CH_2Cl_2, 25°C, 2h; d. Yield from tosylate displacement (reference 5a).

The data in Table I show that the desired coupling products are generated in reasonable yields. In most cases, trifluoroacetamido group is hydrolyzed in aqueous base as described (e.g., **18 – 20**). Under these conditions, the 6-nitrobenzothiazole chromophore **20** survives and the yield of the substituted azo dye **19** is much improved relative to that obtained using tosylate displacement chemistry (59% overall versus 27%). Since the tricyanovinyl substituent is not stable even under these mild conditions, acidic hydrolysis was used to produce **21** from **15**, albeit the yield is poor (17%). For derivatives of this type, the use of the t-butoxycarbonyl protecting group was much preferred, since it could be completely removed at room temperature with trifluoroacetic acid in methylene chloride. With this procedure, the diamine **21** was produced in 82% yield versus 17% obtained by the acidic hydrolysis of the bis-trifluoroacetamido derivative **15**. Surprisingly, the functionalized amines **20**−**22** are reasonably stable both in solution and in the solid state (prolonged storage at room temperature in the light results in some decomposition). No evidence of self-condensation of the amino derivatives **21** and **22** was observed under the conditions of isolation and purification.

In summary, the use of Mitsunobu chemistry, coupled with a selective deprotection strategy, for the preparation of a variety of NLO substituted aromatic amines and diamines has been demonstrated to be a valuable synthetic procedure. The technique is versatile and works well for a number of cases where direct nucleophilic displacement on functionalized tosylate derivatives either fails completely or gives low product yields. For chromophores containing reagent sensitive functionality, the procedure provides a high yield route to new functionalized dye monomers.

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(*Received in USA* 15 *February* 1995; *revised* 25 *April* 1995; *accepted* 3 *May* 1995)