



Pergamon

Tetrahedron Letters 40 (1999) 6923–6926

TETRAHEDRON  
LETTERS

## A convenient synthesis of push–pull polyenes designed for the elaboration of efficient nonlinear optical materials

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Received 1 July 1999; accepted 26 July 1999

### Abstract

We present a convenient and versatile synthetic approach towards push–pull phenylpolyenes and diphenylpolyenes bearing a hydroxyl functional group. These chromophores are of particular interest for the design of efficient nonlinear optics materials due to their large optical nonlinearities, their transparency in the near IR and their capacity to be incorporated into polymeric materials. © 1999 Elsevier Science Ltd. All rights reserved.

*Keywords:* attachable push–pull chromophores; polyenes; Horner–Emmons–Wittig reaction; Knoevenagel condensation; solid–liquid phase transfer; nonlinear optical materials.

Interest in the design of nonlinear optical (NLO) organic materials has kept growing for the past two decades due to potential applications in various fields such as telecommunications, optical data storage and optical information processing.<sup>1</sup> A large effort has been devoted to the search of polymeric materials for electro-optical modulation.<sup>2</sup> Such materials, which are based on the incorporation of push–pull chromophores (i.e. combining electron-releasing and electron-withdrawing groups interacting via a conjugated linker) in a polymeric matrix are interesting in view of both their processability and their chemical flexibility. The design of competitive materials requires an optimization approach both at the molecular level and at the supramolecular level.

In this connection, we have been interested in the synthesis of push–pull chromophores showing very large molecular nonlinearities and liable to be incorporated in a controlled manner in polymeric or hybrid organic–inorganic materials.<sup>3</sup> A number of studies have shown that molecular engineering of polyenic chains provides an effective route towards giant quadratic ( $\beta$ )<sup>4</sup> or cubic ( $\gamma$ )<sup>5</sup> hyperpolarizabilities. We have thus decided to prepare push–pull polyenes combining an enhanced hyperpolarizability  $\beta$ , a suitable thermal stability, transparency in the near IR, and the presence of a functional group allowing for covalent linkage to a polymeric backbone. Based on these criteria which are required for the elaboration of optimized polymeric materials for electro-optical modulation, we have focussed on the synthesis

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of push–pull phenylpolyenes of series **A** and diphenylpolyenes of series **B** (Scheme 1). The specific donor/acceptor pairs have been chosen to maintain satisfactory thermal stability.<sup>6</sup>

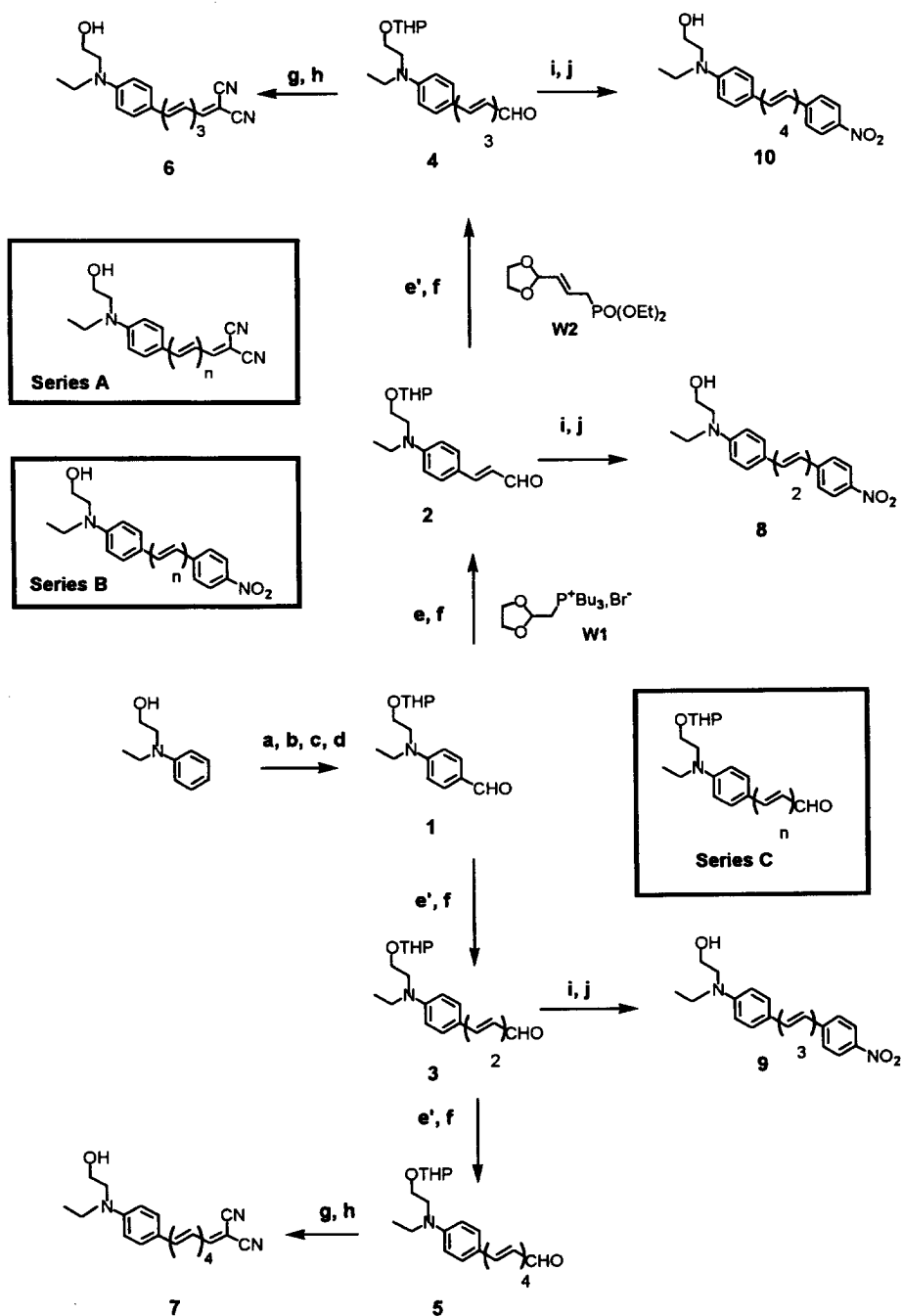
The synthesis is based on a sequential protection–vinylic extension–condensation–deprotection strategy which allows for the preparation of elongated push–pull phenylpolyenes and diphenylpolyenes of various length, in significant yields and high stereochemical purity. The key compounds in the synthetic scheme are extended polyenals of series **C** bearing the hydroxyl group protected as a tetrahydropyranyl (THP) ether. These polyenals can be prepared in high efficiency using vinylic homologations based upon Wittig (or Horner–Emmons–Wittig) condensations followed by a selective deprotection of an acetonide intermediate. Aldehyde **2** can be prepared in quantitative yield by reacting **1** with 1,3-dioxolan-2-ylmethyl-tributylphosphonium bromide (**W1**)<sup>7</sup> in solid–liquid phase transfer conditions, then converting the intermediary acetonide into aldehyde **2** using mild conditions (Scheme 1). Similarly, aldehyde **3** can be obtained in quantitative yield from **1** by using diethyl [3-(1,3-dioxolan-2-yl)-prop-2-enyl] phosphonate (**W2**)<sup>8</sup> in solid–liquid phase transfer conditions instead of phosphonium salt **W1**. This methodology allows to prepare in almost quantitative yield aldehydes **4** and **5** from, respectively, **2** and **3** as pure all-*E* derivatives.

The generic aldehyde **1** was prepared in good overall yield (75%) starting from the commercially available 2-(*N*-ethylanilino)-ethanol according to a four-step procedure including benzylation of the hydroxy function, formylation of the aromatic ring via a Vilsmeier–Haack reaction, saponification then protection of the released hydroxyl group as a tetrahydropyranyl (THP) ether.

Although conjugated polyenals of series **C** are significantly deactivated due to the electron-releasing effect of the donor moiety, synthesis of push–pull derivatives of series **A** and **B** could be achieved by using convenient reactions. Push–pull phenylpolyenes **6** and **7** of series **A** were prepared by a Knoevenagel condensation of the corresponding polyenal precursors with malonodinitrile with 70–85% yield. Caution has to be taken to ensure formation of the pure push–pull derivative and to avoid formation of shorter homologues. Push–pull diphenylpolyenes **8–10** were prepared with 70–95% yield by reaction of the polyenals **2–4** with diethyl *p*-nitrobenzylphosphonate in solid–liquid phase transfer conditions at room temperature,<sup>6a</sup> followed by acidic cleavage of the tetrahydropyranyl protection.

All push–pull phenylpolyenes and diphenylpolyenes were isolated as pure compounds with all-*E* stereochemistry as evidenced by <sup>1</sup>H NMR study, <sup>13</sup>C NMR, and high resolution MS. Their UV–visible spectra show an intense absorption band in the visible region and a typical positive solvatochromism. The maximum absorption wavelength depends both on the length of the polyenic chain and on the donor/acceptor pair. As expected, increasing the polyenic chain length leads to a bathochromic shift of the absorption band (as well as to an enhancement of the molecular optical nonlinearities).<sup>6</sup> Nevertheless, all compounds described in the present work remain transparent in the near IR region, as required for application of electro-optical modulation for telecommunications. These molecules are therefore excellent candidates for the elaboration of functionalized materials for electro-optical modulation. Recent studies indicate that incorporation of such optimized push–pull chromophores can lead to stable hybrid organic–inorganic thin film materials with very large electro-optical coefficients.<sup>3</sup>

We have implemented a convenient and versatile synthetic methodology that allows for the preparation with excellent stereochemical purity and mild reaction conditions of various push–pull phenylpolyenes and diphenylpolyenes of interest for NLO. These NLO chromophores hold promise for the design of efficient materials for electro-optical modulation and photorefractive applications.<sup>2b,3</sup>



Scheme 1. (a)  $\text{PhCOCl}$  (1 equiv.),  $\text{Et}_3\text{N}$  (1.1 equiv.), anhydrous THF, rt, 2 h; (b)  $\text{POCl}_3$  (1 equiv.), anhydrous DMF (3.5 equiv.),  $90^\circ\text{C}$ , 6 h; (c) 5% NaOH in MeOH– $\text{H}_2\text{O}$ , reflux, 1 h; (d) dihydropyran (2 equiv.), PPTS (0.2 equiv.), anhydrous  $\text{CH}_2\text{Cl}_2$ , rt, 24 h; (e) **W1** (1 equiv.), anhydrous  $\text{CH}_2\text{Cl}_2$ , *t*-BuOK (1.2 equiv.), cat. 18-O-6, rt, 20 h; (e') **W2** (1.5 equiv.), anhydrous  $\text{CH}_2\text{Cl}_2$ , *t*-BuOK (1.2 equiv.), cat. 18-O-6, rt, 20 h; (f)  $\text{SiO}_2/\text{CH}_2\text{Cl}_2\text{--EtOH}$ ; (g) THF– $\text{H}_2\text{O}$ , 10% HCl, rt, 1 h; (h) malonodinitrile, 1 equiv., anhydrous ethanol, reflux 4h; (i) diethyl *p*-nitro-benzylphosphonate (1 equiv.), anhydrous THF, NaH (2 equiv.), cat. 18-O-6, rt, 6 h; (j)  $\text{CH}_2\text{Cl}_2\text{--EtOH}$ , 10% HCl, reflux, 1 h

## Acknowledgements

We thank the Ministère de l'Éducation Nationale, de la Recherche et de la Technologie for a PAST position to M.M. We also wish to thank Mrs. Sophie Cerceau for assistance in synthesizing the starting materials.

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