

Terminally Substituted Linear Conjugated Polyenes : Precursors of Molecular Wires.

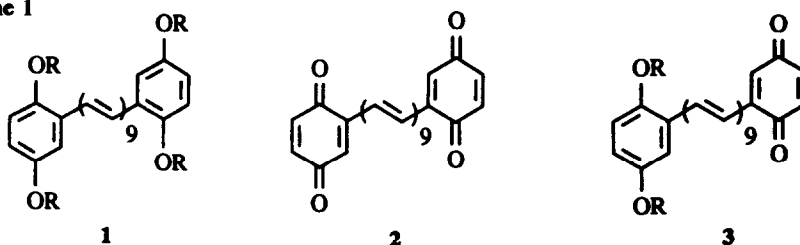
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Abstract : As precursors of molecular wires, linear conjugated polyenes with protected hydroquinone terminal groups **1a-c** have been obtained from gentisic aldehyde by condensation with 1-ethoxy-6-lithiohexa-1,3,5-triene **6**, followed by reacting the resultant aldehydes **5** with the dianion of the bis-phosphonate **7**.

During the last ten years, molecules with long polyenic chains have been prepared and studied as potential organic non-linear optical materials.^{1, 2} Some of them with terminal electroactive groups (4-N-methylpyridinium) and an adequate number of conjugated double bonds have been investigated by J.M. Lehn and Coll. as membrane electron channels.² We planned to synthesize molecules **1-3** (R=H) with nine conjugated double bonds, as in carotenoids, but with a quinone or hydroquinone terminal group and without an angular methyl group. The all *trans* configuration of the polyenic chain must be favoured owing to the lack of substituents. These molecules could be able to conduct electrons and by their redox properties transfer them from a reducing medium to an oxidizing medium separated by a lipid membrane.²

Scheme 1

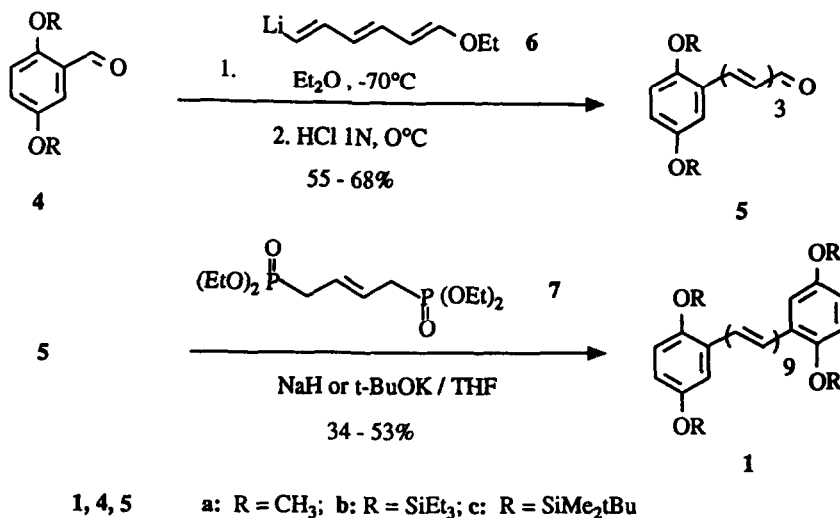


We report herein a short synthesis of polyenes **1a-c**, in two steps starting from aldehydes **4**. The key step is the direct transformation of aldehydes **4** into trienals **5** (R = Me, SiEt₃, SiMe₂tBu), using a powerful polyvinylation reagent 1-ethoxy-6-lithiohexa-1,3,5-triene **6**.³ After protection of the phenolic groups of gentisic aldehyde **4**, the aldehydes **4** were condensed, in ether at -70°C, with the lithio enol ether **6**, prepared *in situ* by bromine lithium exchange.³ The adducts, after a mildly acidic work-up yielded, by a hydrolysis-dehydration sequence, the trienals **5** (**5a** : 55 % ; **5b** : 60 % and **5c** : 68 % yield from **4**). The structures and configurations of the compounds **5** have been determined by mass spectrometry and high field NMR spectroscopy. All the trienals **5** exhibit only one isomer with an all *trans* configuration (14,1 Hz < J_{2,3}; J_{4,5}; J_{6,7} < 15,2 Hz). The coupling reaction of two moles of aldehydes **5** with the bis-diethylphosphonates **7**⁵,

leading to the polyenes **1** was performed in THF, using NaH (**1a** and **1b**) or tBuOK (**1c**) for the formation of the dianion. After purification (recrystallization from CH₂Cl₂ for **1a** and chromatography on silica gel for **1b** and **1c**), the polyenes **1a-c** (melting point : **1a** : 215°C ; **1b** : 165 °C and **1c** : 167 °C) were obtained in 53, 34 and 41% yield respectively. All the compounds **1** and **5** are new, and gave spectral data and microanalyses consistent with the proposed structures.

We are now studying the deprotection of the phenolic groups.

Scheme 2



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