

A New Route to Chiral Diaryldiacetylenic Liquid Crystals. Preparation of Iodonium Salts Bearing Chiral Alkynyl Ligands and Utility for Chiral Alkynyl Transfer Agents

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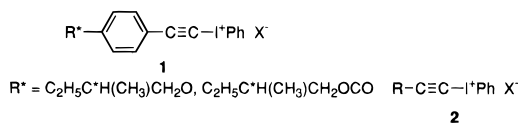
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1,4-Disubstituted diacetylenes display liquid-crystalline and nonlinear optical properties.¹ The extensive conjugation and polarity of these diacetylenes are associated with high nonlinear optical coefficients.² Long-chain alkyl groups play an important role in the generation of such properties and are essential for the molecular assembly that is useful for crystal engineering and molecular devices.³ Moreover, introduction of chiral units into liquid-crystalline materials creates new functionality; the generation of ferroelectricity is especially important for high-speed display devices. In view of the increasing importance of chiral materials, we thought that chiral alkynylphenyliodonium salts might be suitable transfer agents of chiral alkynyl components and applicable to the synthesis of novel chiral diaryldiacetylenes which are potent ferroelectric liquid crystals. We report here the novel chiral alkynylphenyliodonium tosylates **1** and their application as chiral alkynyl transfer agents for the synthesis of chiral diaryldiacetylenic liquid crystals.



Hypervalent iodine reagents are versatile reagents in oxidation and functionalization of organic compounds.⁴ However, despite their potential utility for asymmetric synthesis, the preparation

and use of iodanes with chiral ligands are still rare.^{5,6} Reported studies include asymmetric oxidation of sulfides to sulfoxides with chiral organoiodanes⁵ and the synthesis of organoiodanes bearing chiral binaphthyl ligands.⁶

Among hypervalent iodine compounds, the alkynylphenyliodonium salts **2** are especially valuable in organic reactions because they contain a synthetically significant carbon–carbon triple bond and can serve as synthons of alkynyl cations.^{4,7} We have found that reactions of alkynylphenyliodonium salts with organocopper reagents are useful for introduction of alkynyl components into various organosubstrates.^{8,9} Selective synthesis of unsymmetrical diaryldiacetylenes is particularly important from the standpoint of synthesis of functionalized materials.

Chiral alkynylphenyliodonium salts **1** were prepared by the following two methods (Scheme 1). Method A was conducted according to the procedures of Koser¹⁰ and Stang.¹¹ ((*S*)-(2-Methylbutoxy)phenyl)acetylene ($[\alpha]_D^{27} +12.3^\circ$ (*c* 1.0, CH₂Cl₂)) was treated with [hydroxy(tosyloxy)iodo]benzene in CH₂Cl₂ in the presence of a drying agent at room temperature. Evaporation of the solvent followed by trituration with hexane–ether afforded (((*S*)-2-methylbutoxy)phenyl)ethynyl)phenyliodonium tosylate (**1a**) ($[\alpha]_D^{27} +5.5^\circ$ (*c* 0.40, CH₂Cl₂)) as crystals in 30% yield. Method B is a modification of the procedure of Bachi and Stang.¹² 1-[4-(((*S*)-(2-Methylbutoxy)carbonyl)phenyl)-2-(trimethylsilyl)acetylene was treated with μ -oxobis((trifluoromethylsulfonyl)oxy)phenyliodine, prepared *in situ* from PhIO and triflic anhydride in CH₂Cl₂. However, the desired [[4-(((*S*)-2-methylbutoxy)carbonyl)phenyl]ethynyl]phenyliodonium triflate could not be obtained as crystals and was unstable. The CH₂Cl₂ solution of the crude iodonium triflate was then treated with aqueous NaOTs and stirred vigorously. Extraction with CH₂Cl₂ gave [[4-(((*S*)-2-methylbutoxy)carbonyl)phenyl]ethynyl]phenyliodonium tosylate (**1b**) as crystals in 38% yield. The chiral alkynylphenyliodonium tosylates **1** were stable to air and moisture and used without any special precautions.

Reactions of the chiral alkynylphenyliodonium salts **1** with the alkynylcopper reagents **3** were conducted under argon (Scheme 2). Addition of the chiral alkynylphenyliodonium tosylate **1a** to solutions of the lithium alkynylcuprates **3**, prepared from lithium arylacetylides and CuCN, in THF at -70°C and workup of the reaction mixture gave chiral diaryldiacetylenes (**4**) in good isolated yields (54–58%) after separation by column chromatography on silica gel or by recrystallization from ethanol. The lithium alkynylcuprates **3** bearing electron-withdrawing groups provide the unsymmetrical diaryldiacetylenes **4** selectively. For

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