High Birefringent Bisdiynes and Hexatriynes Based on Double Elimination of β-Substituted Sulfones

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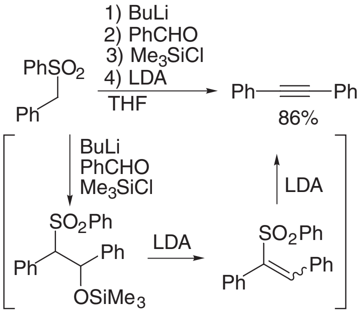
In order to realize high birefringence, acetylenes with long molecular size such as bis(phenyldiynyl)benzenes **1** and diphenylhexatriynes **4** are synthesized successfully on the basis of double elimination of the β-substituted sulfones which can be prepared easily by reaction of benzyl or propargyl sulfones with propynal derivatives.

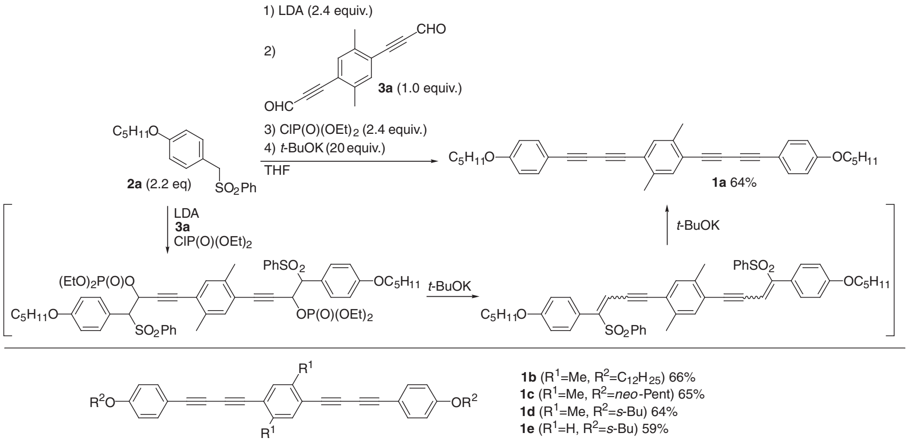
High birefringence (Δn) liquid crystals play a pivotal role in the field of display technology, and they have been utilized widely in spatial light modulators and in compensation films for the viewing angle, reflectors and polarizers.[1] A number of high birefringent liquid crystalline compounds have been studied so far,[2] and high Δn phenylacetylenes have been prepared successfully by taking advantage of high conjugation along the molecular long axis.[3] For preparation of phenylacetylenes and butadiynes which bring about high birefringence (Δn), Sonogashira reaction[4] is used frequently for the coupling of terminal acetylenes with aryl and acetylenic halides, respectively. Although it is known that unsaturated compounds with high conjugation along the molecular long axis could be potential high birefringence materials, synthetic methods for butadiynes and hexatriynes are still in demand.[5] We have developed a new methodology for access to acetylenes based on double elimination of β-substituted sulfones which can be prepared easily from the reaction of benzyl sulfones with benzaldehydes. This protocol is composed of a number of reactions such as aldol reaction, protection of the aldolate and double elimination of the resulting β-substituted sulfone, and all the operation can be carried out in one-pot (Scheme 1).[6] By taking advantage of this protocol, we succeeded to prepare various phenylene-ethynylenes.

We postulated that when propynal derivatives are subjected to this reaction with benzylic and propargylic sulfones, highly conjugated acetylenes such as bisdiynes and hexatriynes which are expected as a new category of high Δn compounds would be accessible. This is indeed the case, and the desired acetylenes were obtained successfully. Herein are described these preliminary results of the preparation of highly conjugated acetylenes and their birefringence properties.



Scheme 1.

We chose bisdiynes **1** as the first target, and tackled the reaction of benzyl sulfone **2** with dipropynal **3**. Starting compound such as benzylic sulfone **2a** was prepared easily by the reaction of the 4-pentyloxybenzyl bromide with $PhSO_2Na$, and dipropynal **3a** was produced by Sonogashira coupling between diiododimethylbenzene and propargyl alcohol followed by Swern oxidation. The operation of the double elimination was straightforward. When benzylic sulfone **2a** was treated successively with LDA, **3a**, $ClP(O)(OEt)_2$ and *t*-BuOK, the desired bis(phenylbutadiynyl)benzene **1a** was obtained in 64% yield (Scheme 2).[7] The 64% yield reveals that this acetylene formation took place in 80% yield at both formyl groups in **3a**. When the different combination of sulfone **2** and dialdehyde **3** was subjected to this protocol, the corresponding bis(diynyl)benzenes **1**



Scheme 2.

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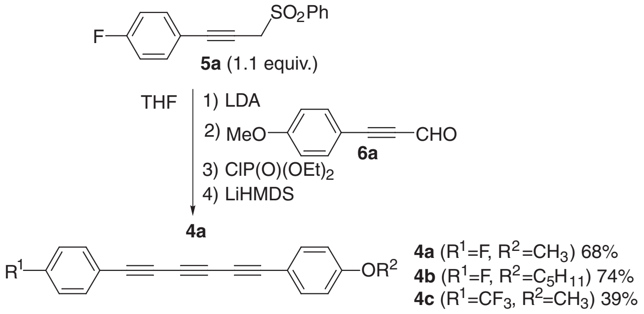
were obtained in reasonable yields.

We next challenged to synthesize hexatriynes **4** by use of propargyl sulfone **5** with electron-withdrawing group and aldehyde **6** with electron-donating group as starting compounds (Scheme 3). Hexatriynes **4** are expected to bring about high birefringence because of long conjugation along the molecular long axis as well. Fluorophenylpropargyl sulfone **5a** was prepared by H_2O_2-oxidation of the corresponding sulfide which was derived from Sonogashira coupling between fluoroiodobenzene and phenyl propargyl sulfide. Aldehyde **6a** was prepared by MnO_2-oxidation of 4-methoxyphenylpropargyl alcohol which was produced from Sonogashira coupling between iodomethoxybenzene and propargyl alcohol.

When (4-fluorophenyl)propargyl sulfone **5a** was treated consecutively with LDA, 4-methoxyphenylpropynal **6a**, ClP(O)-$(OEt)_2$ and LiHMDS, the one-pot protocol for acetylene synthesis proceeded smoothly to give the desired fluorophenyl(methoxyphenyl)hexatriyne **4a** in 68% yield. This process can be utilized for access to other hexatriyne derivatives substituted by pentyloxy and trifluoromethyl groups **4b** and **4c**.

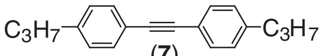


Scheme 3.

With new acetylenes, **1** and **4**, in hand, we measured birefringences of these compounds, and the refractive indices of several of them were evaluated as extrapolated values from mixtures containing 10wt % of each test compounds in MJ931381 (Merck, Japan) by use of Abbe refractometer (2T, Atago) (Table 1). As we expected, refractive indices of bis(diynyl)benzenes **1a**, **b**, and **e** were found considerably larger in comparison with other simpler aromatic acetylenes such as **7**. Hexatriyne **4b** showed a remarkably high birefringence value larger than 0.5, and it has been disclosed that hexatriyne **4** is a promising compound for high birefringent organic material.

In summary, we have succeeded in the convenient syntheses of bis(diynyl)benzenes **1** and hexatriynes **4**, and disclosed that these compounds are promising for high birefringence (Δn) organic materials. Further investigation on the relation between substituents on **1** and **4** and refractive indices is underway in our laboratory.

Table 1. Refractive indices of **1** and **4**

compound	Refractive Index
1a	0.44 (185 °C, 633 nm)
1b	0.31 (135 °C, 633 nm)
1e	0.46 (210 °C, 633 nm)
4b	0.52 (90 °C, 633 nm)
 **(7)**	0.26 (20 °C, 589 nm)[a]

[a] Ref 8.

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7 To a THF solution (10 mL) of 4-pentyloxybenzyl phenyl sulfone (**2a**) (280 mg, 0.88 mmol) was added BuLi (0.60 mL, 1.6 M THF solution, 0.97 mmol) at −78 °C, and the mixture was stirred for 0.5 h. To this solution was added a THF solution (2 mL) of 2,5-dimethylbenzene-1,4-dipropynal (**3a**) (84 mg, 0.4 mmol), and the mixture was stirred for 5 min. After $ClP(O)(OEt)_2$ (0.14 mL, 0.96 mmol) had been added, the reaction mixture was stirred at RT for 2 h. After *t*-BuOK (896 mg, 8.0 mmol) had been added at 0 °C, the mixture was stirred at RT for 3 h. After usual workup with sat. NH_4Cl aq/CH_2Cl_2, the combined organic layer was washed with brine and dried over anhydrous magnesium sulfate. The organic layer was evaporated under vacuum, and the residue was subjected to column chromatography to give **1a** (135 mg, 64%). **1a**: ^1H NMR (500 MHz, CD_2Cl_2): δ 0.93 (t, $J = 7.0$ Hz, 6H), 1.34–1.46 (m, 8H), 1.75–1.81 (m, 4H), 2.40 (s, 6H), 3.96 (t, $J = 6.6$ Hz, 4H), 6.84 (d, $J = 8.5$ Hz, 4H), 7.32 (s, 2H), 7.46 (d, $J = 8.5$ Hz, 4H); ^{13}C NMR (125 MHz, CD_2Cl_2): δ 14.0, 20.0, 22.4, 28.1, 28.8, 68.1, 72.7, 79.5, 79.7, 83.6, 113.3, 114.6, 122.5, 133.5, 134.1, 138.7, 160.0. Elemental analysis calcd (%) for $C_{38}H_{38}O_2$: C 86.65, H 7.27; found: C 86.62, H 7.29.

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