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Coupling Reaction of Alkynyliodonium Salts with Alkynylcopper Reagents. A New Access to Liquid-Crystalline 1,3-Butadiynes

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1,4-Disubstituted 1,3-butadiynes bearing long alkyl and alkoxy chains are seletively prepared by the coupling reaction of alkynyliodonium salts with alkylcopper reagents. The length of the alkyl chains both in the alkynyliodonium salts and in the copper reagents is not the significant factor of the coupling reaction and the coupling reaction affords unsymmetrical 1,4-disubstituted 1,3-butadiynes bearing long alkyl chains in good yields. The 1,3-butadiynes prepared in the present study exhibit mesogenic properties.

Keywords: Coupling reaction, alkynyliodonium salts, 1,4-disubstituted 1,3-butadiynes, liquid crystals

INTRODUCTION

Recently it has been recognized that hypervalent iodine reagents are useful in organic synthesis.[1] Alkynyl(phenyl)iodonium salts **1**, especially, are valuable because they contain a synthetically significant carbon–carbon triple bond and are accessible as a synthon (synthetic equivalent) of alkynyl cations.[1c,2] Several alkynylation reactions with alkynyliodonium salts have been recently developed.[1c,2]

We have found that alkynyliodonium salts react with organocopper reagents[3,4] such as alkynl, alkenyl, alkynyl, and aryl copper reagents. These coupling reactions proceed stereoselectively and provide the products with the retention of the configuration of the reagents.[3] Furthermore, the coupling reaction with alkynylcopper reagents affords unsymmetrical diacetylenes selectively.[4]

On the other hand, 1,4-disubstituted 1,3-butadiynes have been recently found to display liquid-crystalline and non-linear optical properties.[5–11] Conjugated 1,3-butadiynes are a useful linkage for mesogens and non-linear optics. Long-chained alkyl

groups play an important role in the generation of such properties and are also essential for the formation of the molecular assembly which is applied to cyrstal engineering and molecular devices.[12]

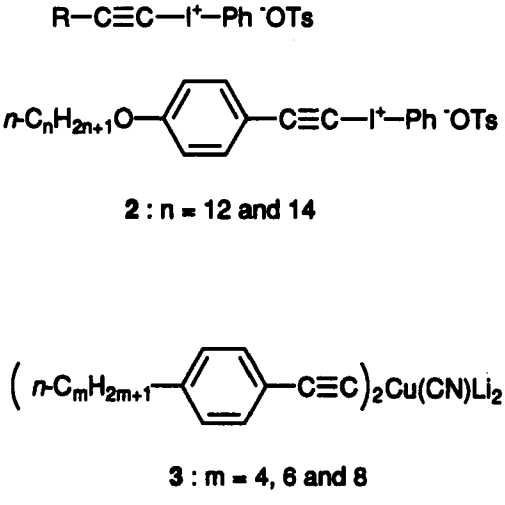
In view of the increasing importance of 1,4-disubstituted 1,3-butadiynes, it was thought that the coupling reactions using alkynyliodonium salts and organocopper reagents were useful for synthesis of the substrates for such purpose. Thus, we have extended to show mesogenic properties. In this paper we report on the synthesis of liquid-crystalline 1,3-butadiynes substituted with long-chained alkyl groups by the reaction of alkynyl(phenyl)iodonium salts **2** with organocopper reagents **3**.

RESULTS AND DISCUSSION

Coupling Reaction of Long-Chained Alkynyl(phenyl)iodonium Salts 2 with Long-Chained Alkynylcopper Reagents 3

Alkynyl(phenyl)iodonium tosylates **2** bearing long chains ($R^1 = n\text{-}C_{12}H_{25}$ and $n\text{-}C_{14}H_{29}$) were readily prepared from hydroxy(tosyloxy)iodobenzene and aryl acetylenes.[13] Treatment of *p*-alkoxyphenylacetylenes with hydroxy(tosyloxy)iodobenzene in CH_2CI_2 in the presence of a desiccant gave crystalline alkynyl(phenyl)iodonium tosylates (**2a**: $R^1 = n\text{-}C_{12}H_{25}$ and **2b**: $R^1 = n\text{-}C_{14}H_{29}$) in 37–41% yields. Alkynyl(phenyl)iodonium tosylates **2** were stable to air and moisture and could be used without any special precautions.

Coupling reactions were conducted in THF under N_2 atmosphere. Alkynyl (phenyl) iodonium tosylate **2a** ($R^1 = n\text{-}C_{12}H_{25}$) was added, in THF at $-70°C$, to a solution of mixed alkynyl-substituted organocopper reagent **3** prepared from a lithium acetylide and CuCN, and the reaction mixture was left to come to room temperature. After the



SCHEME I.

workup of the reaction mixture, diacetylenes **4** and **5** were obtained either by column chromatography on silica gel with hexane-CH_2Cl_2 or by recrystallization from ethanol. The major products were unsymmetrical 1,3-butadiynes **4**. Similarly, coupling reactions of alkynyliodonium salt **2b** were conducted. The results are given in Table I. Table I indicates that the coupling reaction proceeds well even in the case where both the substrates and the copper reagents bear long-chained alkyl groups, and the long alkyl chains do not affect the coupling reactions.

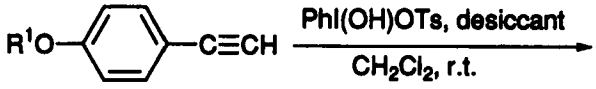
Mesogenic Properties of 1,4-Disubstituted 1,3-Butadiynes

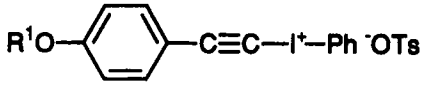
The liquid phase transition temperatures and the phase types of the 1,3-butadiynes **4** newly prepared in the present work have been examined by optical microscopy and confirmed by differential scanning calorimetry (DSC). The results are given in Table II. The 1,3-butadiynes **4** having long alkyl chains are all enantiotropic liquid crystals and

TABLE I

Coupling reactions of alkynyliodonium tosylates **2** with alkynylcopper reagents **3**

2 R^1	**3** R^2	1,3-diynes (isolated yield, %) **4**	**5**
n-$C_{12}H_{25}$	n-C_4H_9	65(**4a**)	18(**5a**)
	n-C_6H_{13}	54(**4b**)	22(**5a**)
	n-C_8H_{17}	56(**4c**)	25(**5a**)
n-$C_{14}H_{29}$	n-C_4H_9	61(**4d**)	16(**5b**)
	n-C_6H_{13}	56(**4e**)	32(**5b**)
	n-C_8H_{17}	56(**4f**)	25(**5b**)

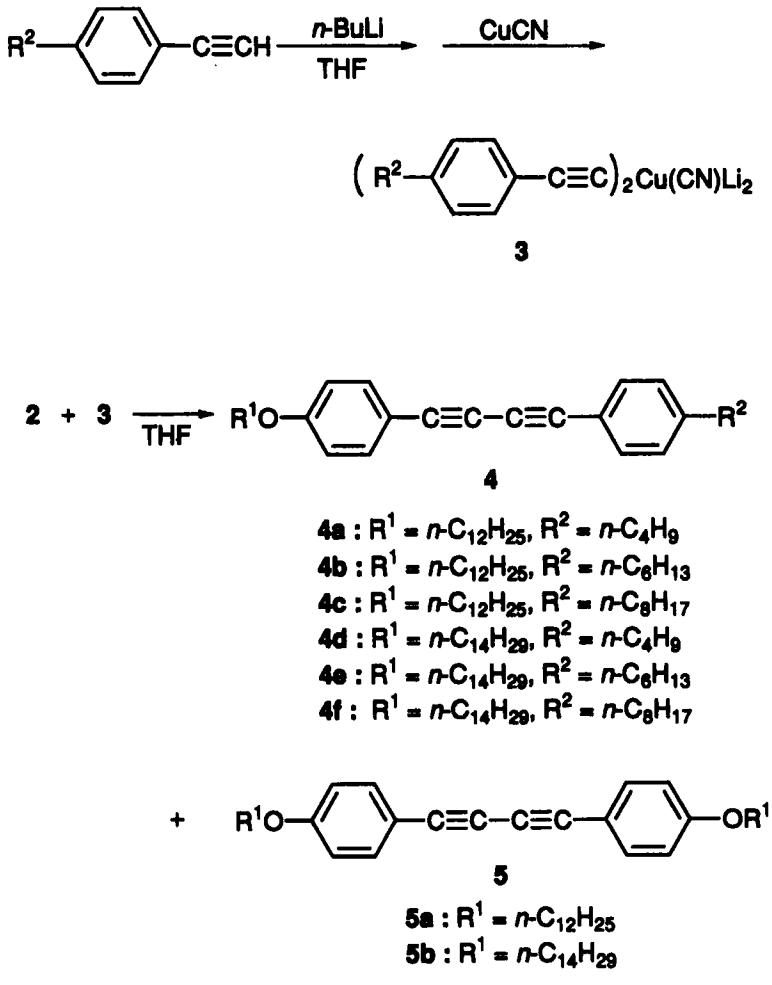




2

2a ; $R^1 = n\text{-}C_{12}H_{25}$
b ; $R^1 = n\text{-}C_{14}H_{29}$

SCHEME 1 Preparation of alkynyliodonium salts **2**.



SCHEME 2 Preparation of 1,4-disubstituted 1,3-butadiynes.

show similar mesoganic regions at 50–100°C. The 1,3-butadiynes **4a** and **4d** exhibit only the nematic phase but other 1,3-butadiynes display both nematic and smectic phases.

CONCLUSION

The long-chained alkyl groups both in the alkynyliodonium salts **2** and in the alkynylcopper reagents **3** do not affect the coupling reaction. The utility of long alkyl groups as the spacer of liquid crystals is generally recognized. Therefore, the present procedure using alkynylidonium salts and alkynylcopper reagents provides a new access to 1,3-butadiynes which display liquid-crystalline properties.

TABLE II

Liquid crystal phase and transition temperatures of unsymmetrical 1,3-dinyes **4**[a]

4a	$K \underset{50.7}{\overset{51.2}{\rightleftharpoons}} N \underset{96.7}{\overset{96.9}{\rightleftharpoons}} I$
4b	$K \underset{63.3}{\overset{63.4}{\rightleftharpoons}} S \underset{65.7}{\overset{66.9}{\rightleftharpoons}} N \underset{104.0}{\overset{108.0}{\rightleftharpoons}} I$
4c	$K \underset{60.0}{\overset{61.0}{\rightleftharpoons}} S_1 \underset{65.7}{\overset{71.2}{\rightleftharpoons}} S_2 \underset{75.0}{\overset{78.2}{\rightleftharpoons}} N \underset{102.0}{\overset{106.1}{\rightleftharpoons}} I$
4d	$K \underset{61.6}{\overset{66.0}{\rightleftharpoons}} N \underset{97.0}{\overset{97.8}{\rightleftharpoons}} I$
4e	$K \underset{55.0}{\overset{60.0}{\rightleftharpoons}} S_1 \underset{71.9}{\overset{74.3}{\rightleftharpoons}} S_2 \underset{73.8}{\overset{77.6}{\rightleftharpoons}} N \underset{100.5}{\overset{103.8}{\rightleftharpoons}} I$
4f	$K \underset{65.0}{\overset{68.5}{\rightleftharpoons}} S_1 \underset{76.7}{\overset{78.7}{\rightleftharpoons}} S_2 \underset{77.7}{\overset{81.8}{\rightleftharpoons}} S_c \underset{83.0}{\overset{85.6}{\rightleftharpoons}} N \underset{101.1}{\overset{104.2}{\rightleftharpoons}} I$

[a] key; K: crystal, S: smectic, S_c: smectic C, S_1 and S_2: higher order smectic, N: nematic, and I: isotropic

The coupling reaction of alkynyliodonium salts with alkynylcopper reagents is effective even in the cases of the substrates bearing long alkyl chains. The most mesogenic 1,3-butadiynes prepared in the present study display smectic and nematic phases suitable for use in liquid-crystal display devices. Therefore, the present coupling reaction possesses possible wide applications for liquid crystals, electronic, and nonlinear optical materials.

EXPERIMENTAL

Melting points were measured with a YANACO micro melting apparatus and are uncorrected. ^{1}H NMR spectra were obtained with HITACHI R-600 (60 MHz) and BRUKER AC-250P (250 MHz) spectrometers and ^{13}C NMR spectra with a BRUKER AC-250P (62.9 MHz) spectrometer. Chemical shifts are given in ppm. IR spectra were recorded with a HORIBA FT-200 spectrometer. Microanalyses were performed by the Service Center of the Elementary Analysis of Organic Compound, Faculty of Science, Kyushu University. Alkynyl(phenyl)iodonium tosylates **2** were prepared according to the reported procedure.[4]

Preparation of Long-Chained Arylacetylenes

To a solution of CH_2CI_2 (40 ml) and DMF (12 ml) at 0°C was added $POCl_3$ (12 ml) dropwise, and the mixture was stirred until the solution turned red. *p*-Alkylacetophenone (50 mmol) prepared from *p*-*n*-alkylbenzene, acetyl chloride, and aluminium chloride was added dropwise to the reaction mixture. The mixture was

refluxed for 3 h with stirring and poured onto a mixture of ice and water. The mixture was hydrolyzed with $CH_3COONa \cdot 3H_2O$ until the solution became neutral, and then the product was extracted with ether. The ethereal extract was washed with water and brine, dried over anhydrous Na_2SO_4, and concentrated. The crude product was dissolved in 1,4-dioxane (40 ml) and the dioxane solution was added dropwise to a refluxing solution of 0.2 M NaOH (25 ml) in 1,4-dioxane (20 ml). The mixture was refluxed for an additional 4 h, poured into water and extracted with ether. The ethereal extract was washed with water and brine, dried over anhydrous Na_2SO_4, and concentrated. The colorless liquid was purified by column chromatography on silica gel with ether-hexane (1:2) as the eluent.

4-(Butylphenyl)acetylene[10] (57%), colorless liquid; δ_H (60 MHz; $CDCl_3$) 0.91 (3H, br s, Me), 1.25 (4 H, br s, CH_2), 2.60 (2 H, t, *J*7.2, $ArCH_2$), 3.00 (1 H, s, C≡CH), 7.10 (2 H, d, *J*7.8, ArH) and 7.37 (2 H, d, *P*7.8, ArH).

4-(Hexylphenyl)acetylene[10] (74%), colorless liquid; δ_H (60 MHz, $CDCl_3$) 0.87 (3 H, br s, Me) 1.25 (8 H, br s, CH_2), 2.61 (2 H, t, *J* 7.8, $ArCH_2$), (1 H, s, C≡CH), 7.10 (2 H, d, *J*7.8, ArH) and 7.37 (2 H, d, *J*7.8, ArH).

4-(Octylphenyl)acetylene[10] (60%), colorless liquid; δ_H (60 MHz, $CDCl_3$) 0.87 (3 H, br s, Me), 1.26 (12 H, br s, CH_2), 2.60 (2 H, t, *J* 7.2, $ArCH_2$), 3.00 (1 H, s, C≡CH), 7.10 (2 H, d, *J*7.8, ArH) and 7.38 (2 H, d, *J*7.8 ArH).

Coupling Reaction of Long-Chained Alkynyl(phenyl)iodonium Tosylates 2 with Long-Chained Alkynylcopper Reagents 3. General Procedure

To a solution of an arylacetylene (1.0 mmol) in THF (25 ml) at −70°C was added dropwise *n*-BuLi in hexane (0.625 ml, 1.0 mmol) under a nitrogen atmosphere. CuCN (44.5 mg, 0.5 mmol) was then added at −70°C, and the mixture was stirred at −40°C for 2 h. The mixture was cooled to −70°C, and a solution of [(*p*-alkoxyphenyl)ethynyl]iodonium tosylate **2** (0.5 mmol) in CH_2Cl_2 (2 ml) was added dropwise to the cooled mixture, which was then allowed to warm to room temperature. The whole was poured into saturated aqueous ammonium chloride, and the resulting precipitate was filtered off. The filtrate was extracted with ether, and the ethereal extract was washed with brine, dried over anhydrous Na_2SO_4, and concentrated. The products were separated by column chromatography on silica gel with hexane-CH_2Cl_2 as the eluent and recrystallized from ethanol.

1-[4-(Dodecyloxy)phenyl]-4-(4-butylphenyl)-1,3-butadiyne **(4a)** (Found: C, 86.79; H, 9.41. Calcd for $C_{32}H_{42}O$:C, 86.89; H, 9.49%); ν_{max}(Nujol)/cm^{-1} 2212.0 and 2139.6 (C≡C); δ_H (250 MHz; $CDCl_3$) 0.92 (3 H, t, *J*6.7, Me), 1.26 – 1.54 (26 H, m, CH_2), 1.78 (2 H, quint, *J*6.7, CH_2), 2.61 (2 H, t, *J*7.5 $ArCH_2$), 3.96 (2 H, t, *J*6.5, OCH_2), 6.83 (2 H, d, *J*7.5, ArH), 7.13 (2 H, d, *J*7.5, ArH) and 7.44 (4 H, q, *J*5.5, ArH).

1-[4-(Dodecyloxy)phenyl]-4-(4-hexylphynyl)-1,3-butadiyne **(4b)** (Found: C, 86.80; H, 10.05. Calcd for $C_{34}H_{46}O$:C, 86.82; H, 9.78%); ν_{max} (Nujol)/cm^{-1} 2210.0 and 2138.0 (C≡C); δ_H (250 MHz, $CDCl_3$) 0.88 (3 H, t, *J*6.7, Me), 1.27 – 1.57 (30 H, m, CH_2), 1.76

(2 H, quint, *J*6.7, CH_2), 2.60 (2 H, t, *J*7.5, $ArCH_2$), 3.95 (2 H, t, *J*6.5, OCH_2), 6.83 (2 H, d, *J*7.5, ArH), 7.12 (2 H, d, *J*7.5, ArH) and 7.44 (4 H, q, *J*5.5, ArH).

1-[4-(Dodecyloxy)phenyl]-4-(4-octyphenyl)-1,3-butadiyne **(4c)** (Found: C,86.58; H, 10.10 Calcd for $C_{36}H_{50}O$: C, 86.76; H, 10.03%); ν_{max} (Nujol)/cm^{-1} 2210.0 and 2138.0 (C≡C); δ_H (250 MHz, $CDCl_3$) 0.88 (3 H, t, *J*6.7, Me), 1.26–1.57 (34 H, m, CH_2), 1.75 (2 H, quint, *J*6.6, CH_2), 2.60 (2 H, t, *J*7.5, $ArCH_2$), 3.95 (2 H, t, *J*6.5, OCH_2), 6.83 (2 H, d, *J*7.5, ArH), 7.13 (2 H, d, *J*7.5, ArH) and 7.44 (4 H, q, *J*5.5, ArH).

1-[4-(Tetradecyloxy)phenyl]-4-(4-butylphenyl)-1,3-butadiyne **(4d)** Found: C, 86.86; H, 10.03. Calcd for $C_{34}H_{46}O$: C, 86.82; H, 9.78%); ν_{max} (Nujol)/cm^{-1} 2212.0 and 2139.6 (C≡C); δ_H (250 MHz, $CDCl_3$) 0.89 (3 H, t, *J*6.7, Me), 1.26–1.57 (30 H, m, CH_2), 1.74 (2 H, quint, *J*7.2, CH_2), 2.60 (2 H, t, *J*7.4, $ArCH_2$), 3.95 (2 H, t, *J*6.5, OCH_2), 6.83 (2 H, d, *J*7.5, ArH), 7.13 (2 H, d, *J*7.5, ArH) and 7.44 (4 H, q, *J*5.5, ArH).

1-[4-(Tetradecyloxy)phenyl]-4-(4-hexylphenyl)-1,3-butadiyne **(4e)** (Found: C, 86.59; H, 10.09. Calcd for $C_{36}H_{50}O$: C, 86.76; H, 10.03%); ν_{max} (Nujol)/cm^{-1} 2210.0 and 2138.0 (C≡C); δ_H (250 MHz, $CDCl_3$), 0.88 (3 H, t, *J*6.7, Me), 1.26–1.57 (34 H, m, CH_2), 1.76 (2 H, quint, *J*7.2, CH_2), 2.60 (2 H, t, *J*7.4, $ArCH_2$), 3.95 (2 H, t, *J*6.5, OCH_2), 6.83 (2 H, d, *J*7.5, ArH), 7.13 (2 H, d, *J*7.5, ArH) and 7,44 (4 H, q, *J*5.5, ArH).

1-[4-(Tetradecyloxy)phenyl]-4-(4-octylphenyl)-1,3-butadiyne **(4f)** (Found: C, 86.53; H, 10.36. Calcd for $C_{38}H_{54}O$: C, 86.70; H, 10.26%) ν_{max} (Nujol)/cm^{-1} 2210.0 and 2138.0 (C≡C); δ_H (250 MHz, $CDCl_3$) 0.88 (3 H, t, *J* 6.7, Me), 1.26–1.57 (38 H, m, CH_2), 1.77 (2 H, quint, *J* 6.7, CH_2), 2.60 (2 H, t, *J* 7.4, $ArCH_2$), 3.95 (2 H, t, *J*6.5, OCH_2), 6.83 (2 H, d, *J*7.5, ArH), 7.13 (2 H, d, *J*7.5, ArH) and 7.44 (4 H, q, *J*5.0, ArH).

1,4-Bis[4-(dodecyloxy)phenyl]-1,3-butadiyne **(5a)**[4] δ_H (250 MHz, $CDCl_3$) 0.8 8 (3 H, t, *J*6.6, Me), 1.26–1.41 (36 H, m, CH_2), 1.75 (4 H, quint, *J*6.8, CH_2), 3.95 (4 H, t, *J*6.5, OCH_2), 6.83 (4 H,d, *J*8.6, ArH) and 7.43 (4 H, d, *J*8.6, ArH). δ_C (62.9 MHz $CDCl_3$) 14.13, 22.69, 25.98, 29.12, 29.36 (× 2), 29.58 (× 2), 29.64 (× 2), 31.92, 68.08, 72.84 81.29, 113.60, 114.58, 133.99 and 159.80.

1,4-Bis[4-(tetradecyloxy)phenyl]-1,3-butadiyne **(5b)**[4,10] δ_H (250 MHz, $CDCl_3$) 0.88 (6 H, t, *J*6.8, Me), 1.26–1.45 (44 H, m, CH_2), 1.78 (4 H, quint, *J*6.8, CH_2), 3.95 (4 H, t, *J*6,5, OCH_2), 6.83 (4 H, d, *J*8.7, ArH) and 7.44 (4 H, d, *J*8.7, ArH). δ_C NMR (62.9 MHz, $CDCl_3$) 14.15, 22.71, 25.99, 29.13, 29.37 (× 2), 29.60 (× 2), 29.64 (× 2), 31.93, 68.10, 72.86, 81.30, 113.64, 114.60, 134.00 and 159.82.

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