

## Novel Synthesis of Liquid-Crystalline Diaryldiacetylenes Bearing Long Chains

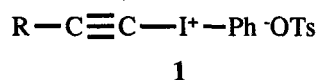
Tsugio Kitamura, Chi Han Lee, Yuki Taniguchi, Yuzo Fujiwara

Department of Chemical Science and Technology, Faculty of Engineering,  
Kyushu University, Hakozaki, Fukuoka 812-81, Japan

The coupling reaction of alkynyl(phenyl)iodonium salts with alkynylcopper reagents proceeds under mild conditions to provide unsymmetrical and symmetrical diacetylenes. The length of the alkyl chains both in the alkynyl(phenyl)iodonium salts and in the copper reagents is not a significant factor of the coupling reaction and the unsymmetrical diaryldiacetylenes are selectively prepared. But the selectivity of the formation of these diaryldiacetylenes depends on the substituent of the alkynylcopper reagents. The prepared diaryldiacetylenes exhibit mesogenic properties.

### 1. INTRODUCTION

Recently it has been recognized that hypervalent iodine reagents are useful in organic synthesis.<sup>1</sup> 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.<sup>1c,2</sup> Several alkynylation reactions with alkynyliodonium salts have been recently developed.<sup>1c,2</sup>

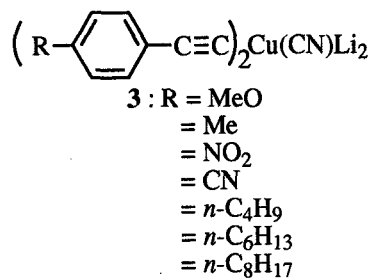
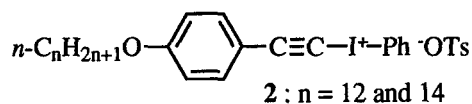


We have found that alkynyliodonium salts react with organocopper reagents<sup>3,4</sup> such as alkyl-, alkynyl-, and arylcopper reagents. These coupling reactions proceed stereoselectively and provide the products with the retention of the configuration of the vinylcopper reagents.<sup>3</sup> Furthermore, the coupling reaction with alkynylcopper reagents affords unsymmetrical diacetylenes selectively.<sup>4</sup>

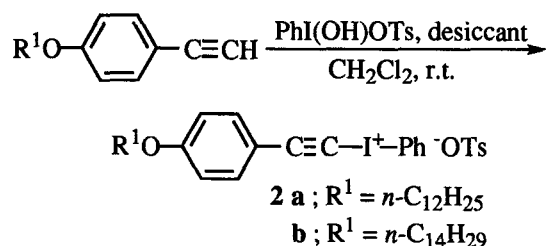
On the other hand, 1,4-disubstituted 1,3-

butadiynes have been recently found to display liquid-crystalline and non-linear optical properties.<sup>5-11</sup> Conjugated 1,3-butadiynes are 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 molecular assembly which is applied to crystal engineering and molecular devices.<sup>12</sup>

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 the synthesis of those compounds. Thus, we have extended the coupling reaction to the substrates bearing long alkyl and alkoxy chains which are expected to show mesogenic properties. Here we report synthesis of liquid-crystalline diaryldiacetylenes by means of the coupling reaction of alkynyl(phenyl)iodonium salts (2) with alkynylcopper reagents (3).



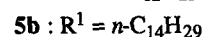
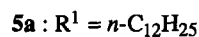
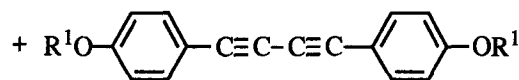
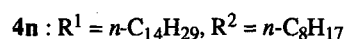
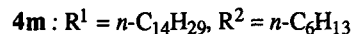
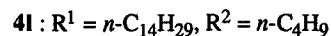
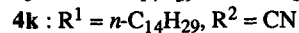
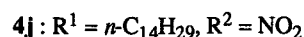
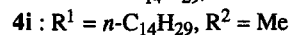
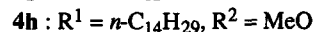
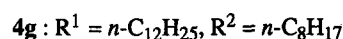
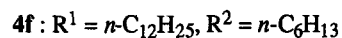
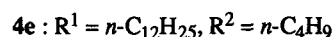
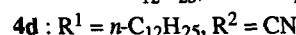
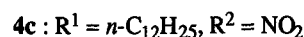
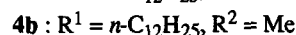
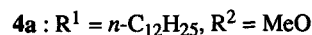
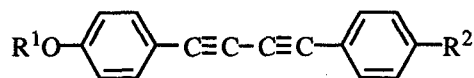
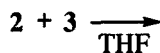
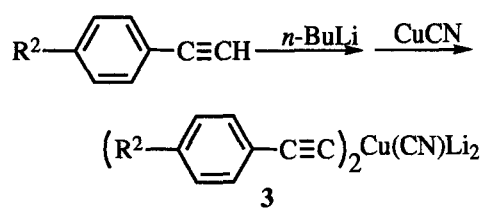
Scheme 1. Preparation of alkynyliodonium salts 2

## 2. RESULTS AND DISCUSSION

Alkynyl(phenyl)iodonium tosylates 2 bearing long chains (R<sup>1</sup> = *n*-C<sub>12</sub>H<sub>25</sub> and *n*-C<sub>14</sub>H<sub>29</sub>) were readily prepared from hydroxy(tosyloxy)iodobenzene and arylacetylenes.<sup>13</sup> Treatment of *p*-alkoxyphenylacetylenes with hydroxy(tosyloxy)iodobenzene in CH<sub>2</sub>Cl<sub>2</sub> in the presence of a desiccant gave crystalline alkynyl(phenyl)iodonium tosylates (2a: R<sup>1</sup> = *n*-C<sub>12</sub>H<sub>25</sub> and 2b: R<sup>1</sup> = *n*-C<sub>14</sub>H<sub>29</sub>) 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<sub>2</sub> atmosphere. Alkynyl(phenyl)iodonium tosylate 2a (R<sup>1</sup> = *n*-C<sub>12</sub>H<sub>25</sub>) was added, in THF at -70°C, to a solution of mixed organocopper reagent 3 prepared from a lithium acetylide and CuCN, and the reaction mixture was left to come to room temperature. After the workup of the reaction mixture, diacetylenes 4 and 5 were obtained either by column chromatogra-

phy on silica gel with hexane-CH<sub>2</sub>Cl<sub>2</sub> or by recrystallization from ethanol. The major products were coupling products, symmetrical and unsymmetrical diacetylenes (4 and 5), respectively. Similarly, coupling reactions of alkynyliodonium salt 2b were conducted. The results are given in Table 1. Table 1 indicates that the substituent on the aromatic ring affects the selectivity of the coupling reaction. The electron-



Scheme 2. Preparation of diaryldiacetylenes

donating groups on the aromatic ring preferentially give unsymmetrical diacetylenes **4** and increases that of symmetrical diacetylenes **5**. But the coupling reaction proceeds well even in the cases where both the substrates and copper reagents bear long-chained

Table 1. Yields of Diacetylenes **4** and **5** by Coupling Reaction of Iodonium Tosylates **2** with Alkynylcopper Reagents **3**

2 R <sup>1</sup>	3 R <sup>2</sup>	diacetylenes (isolated yield, %)	
		4	5
<i>n</i> -C <sub>12</sub> H <sub>25</sub>	MeO	90 ( <b>4a</b> )	7 ( <b>5a</b> )
	Me	63 ( <b>4b</b> )	32 ( <b>5a</b> )
	NO <sub>2</sub>	38 ( <b>4c</b> )	52 ( <b>5a</b> )
	CN	29 ( <b>4d</b> )	36 ( <b>5a</b> )
	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	65 ( <b>4e</b> )	18 ( <b>5a</b> )
	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	54 ( <b>4f</b> )	22 ( <b>5a</b> )
	<i>n</i> -C <sub>8</sub> H <sub>17</sub>	56 ( <b>4g</b> )	25 ( <b>5a</b> )
<i>n</i> -C <sub>14</sub> H <sub>29</sub>	MeO	67 ( <b>4h</b> )	12 ( <b>5b</b> )
	Me	59 ( <b>4i</b> )	12 ( <b>5b</b> )
	NO <sub>2</sub>	26 ( <b>4j</b> )	60 ( <b>5b</b> )
	CN	10 ( <b>4k</b> )	54 ( <b>5b</b> )
	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	61 ( <b>4l</b> )	16 ( <b>5b</b> )
	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	56 ( <b>4m</b> )	32 ( <b>5b</b> )
	<i>n</i> -C <sub>8</sub> H <sub>17</sub>	56 ( <b>4n</b> )	25 ( <b>5b</b> )

alkyl groups, and the long alkyl chains do not affect the coupling reactions.

The prepared diacetylenes **4** and **5** are mesogenic. The liquid crystal phase transition temperatures and the phase types of diaryldiacetylenes were examined by optical microscopy and were confirmed by differ-

Table 2. Liquid crystal phase and transition temperatures of unsymmetrical 1,3-diyne **4**<sup>a</sup>

<b>4 a</b>	K $\xrightleftharpoons[67.6]{78.0}$ S <sub>c</sub> $\xrightleftharpoons[84.2]{96.2}$ S <sub>1</sub> $\xrightleftharpoons[96.2]{125.5}$ N $\xrightleftharpoons[125.5]{125.5}$ I
<b>4 b</b>	K $\xrightleftharpoons[80.6]{83.7}$ S $\xrightleftharpoons[116.0]{87.1}$ N $\xrightleftharpoons[115.7]{115.7}$ I
<b>4 c</b>	K $\xrightleftharpoons[105.7]{95.9}$ S <sub>1</sub> $\xrightleftharpoons[119.3]{124.3}$ S <sub>c</sub> $\xrightleftharpoons[142.5]{145.1}$ I
<b>4 d</b>	K $\xrightleftharpoons[133.9]{149.8}$ S <sub>1</sub> $\xrightleftharpoons[134.9]{134.9}$ S <sub>A</sub> $\xrightleftharpoons[146.7]{146.7}$ I
<b>4 e</b>	K $\xrightleftharpoons[50.7]{51.2}$ N $\xrightleftharpoons[96.7]{96.9}$ I
<b>4 f</b>	K $\xrightleftharpoons[63.3]{63.4}$ S $\xrightleftharpoons[65.7]{66.9}$ N $\xrightleftharpoons[104.0]{108.0}$ I
<b>4 g</b>	K $\xrightleftharpoons[60.0]{61.0}$ S <sub>1</sub> $\xrightleftharpoons[65.7]{71.2}$ S <sub>2</sub> $\xrightleftharpoons[75.0]{78.2}$ N $\xrightleftharpoons[102.0]{106.1}$ I
<b>4 h</b>	K $\xrightleftharpoons[74.4]{78.3}$ S <sub>c</sub> $\xrightleftharpoons[121.3]{82.5}$ N $\xrightleftharpoons[121.8]{121.8}$ I
<b>4 i</b>	K $\xrightleftharpoons[76.2]{85.0}$ S $\xrightleftharpoons[81.5]{107.6}$ S <sub>C</sub> $\xrightleftharpoons[107.0]{107.0}$ I
<b>4 j</b>	K $\xrightleftharpoons[111.1]{129.9}$ S $\xrightleftharpoons[123.7]{123.7}$ S <sub>A</sub> $\xrightleftharpoons[146.3]{147.6}$ I
<b>4 k</b>	K $\xrightleftharpoons[130.3]{146.0}$ S <sub>A</sub> $\xrightleftharpoons[131.8]{131.8}$ I
<b>4 l</b>	K $\xrightleftharpoons[61.6]{66.0}$ N $\xrightleftharpoons[97.0]{97.8}$ I
<b>4 m</b>	K $\xrightleftharpoons[55.0]{60.0}$ S <sub>1</sub> $\xrightleftharpoons[71.9]{74.3}$ S $\xrightleftharpoons[73.8]{77.6}$ N $\xrightleftharpoons[100.5]{103.8}$ I
<b>4 n</b>	K $\xrightleftharpoons[65.0]{68.5}$ S <sub>1</sub> $\xrightleftharpoons[76.7]{78.7}$ S $\xrightleftharpoons[77.7]{81.8}$ S <sub>c</sub> $\xrightleftharpoons[83.0]{85.6}$ N $\xrightleftharpoons[101.1]{104.2}$ I

<sup>a</sup> key : K, crystal ; S, smectic ; S<sub>c</sub>, smectic C ; S<sub>A</sub>, smectic A ; S<sub>1</sub> and S<sub>2</sub>, higher order smectic ; N, nematic, and I, isotropic

ential scanning calorimetry (DSC). The smectic A phase was identified by a typical "fan-shaped" texture observed with a polarizing microscope, and the

smectic C phase was recognized by a typical Schlieren texture. The results are given in Table 2. Only cyano-substituted diacetylenes **4d** and **4k** were monotropic liquid crystals and showed smectic phases on cooling. Diarylacetylenes **4a**, **4b**, **4f**, **4g**, **4h**, **4i**, **4m**, and **4n** exhibited smectic and nematic phases. But **4e** and **4l** displayed only the nematic phase.

### 3. CONCLUSION

The long-chained alkyl groups both in the alkynyliodonium salts **2** and in the alkynylcopper reagents **3** do not affect the coupling reaction. But the substituent on the aromatic ring influences the selectivity of the coupling reaction. The present procedure using alkynyliodonium salts and alkynylcopper reagents provides a new access to diaryldiacetylenes which display liquid-crystalline properties.

The most mesogenic diarylacetylenes 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 non-linear optical materials.

### REFERENCES

1. For recent reviews and a book : (a) T. Kitamura, *J.Synth. Org. Chem. Jpn.*, **53**, 893 (1995). (b) A Varvoglis, *The Organic Chemistry of Polycoordinated Iodine*; VCH Publisher: New York, 1992. (c) R. M. Moriarty and R. K. Vaid, *Synthesis*, 1990, 431.
2. P. J. Stang, *Angew. Chem. Int. Ed. Engl.*, 1992, **31**, 274; *Acc. Chem. Res.*, 1991, **24**, 304.
3. P. J. Stang and T. Kitamura, *J. Am. Chem. Soc.*, 1987, **109**, 7561.
4. T. Kitamura, T. Tanaka, H. Taniguchi, and P. J. Stang, *J. Chem. Soc., Perkin Trans.1*, 1991, 2892; T. Kitamura, C. H. Lee, H. Taniguchi, M. Matsumoto, and Y. Sano, *J. Org. Chem.*, 1994, **59**, 8053.
5. M. D. Wand, S. Monahan, D. Liptak, and R. Vohra, *SPIE*, 1993, **1911**, 29.
6. S. T. Wu, J. D. Margerum, C. S. Hsu, and S.H. Lung, *Appl. Phys. Lett.*, 1992, **61**, 630.
7. A. E. Stiegman, E. Graham, K. J. Perry, L. R. Khundkar, L. -T. Cheng, and J. W. Perry, *J. Am. Chem. Soc.*, 1991, **113**, 7658.
8. G. H. W. Milburn, C. Campbell, A. J. Shand, and A. R. Werninck, *Liq. Crysts.*, 1990, **8**, 623.
9. C. Fouquey, J. -M. Lehn, and J. Malthete, *J. Chem. Soc., Chem. Commun.*, 1987, 1424.
10. B. Grant, *Mol. Cryst. Liq. Cryst.*, 1978, **48**, 175.
11. G. Schmidt, *Pure Appl. Chem.*, 1971, **27**, 647.; P. S. Vincett and G. G. Roberts, *Thin Solid Films*, 1980, **68**, 135.
12. P. J. Stang, B. W. Surber, Z. -C. Chen, K. A. Roberts, and A. G. Anderson, *J. Am. Chem. Soc.*, 1987, **109**, 228.; L. Rebrovic and G. F. Koser, *J. Org. Chem.*, 1984, **49**, 4700.
13. J. Van Der Veen, W. H. De Jeu, A. H. Grobber, and J. Boven, *Mol. Cryst. Liq. Cryst.*, 1972, **17**, 291.