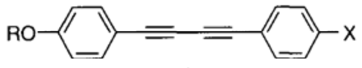
Synthesis of Liquid-Crystalline Enynes by Palladium-Catalyzed Cross-Coupling Reaction

Tsugio Kitamura,* Yasutaka Aoyagi, and Yuzo Fujiwara
Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Hakozaki, Fukuoka 812-8581

(Received September 18, 1998; CL-980722)

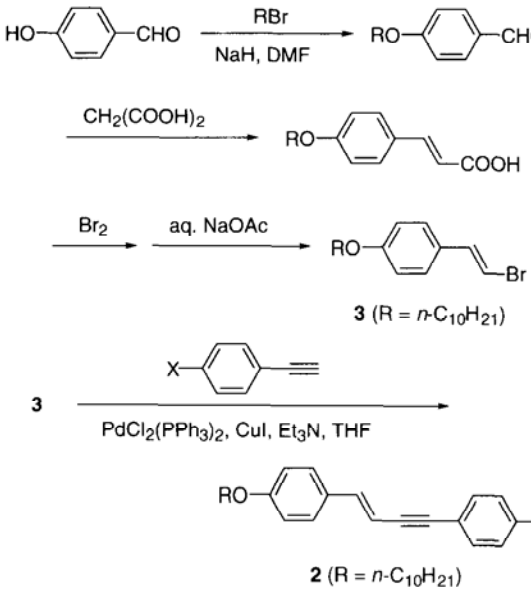
An arylvinyl bromide bearing a long-chain alkoxy group reacts with arylacetylenes in the presence of a palladium catalyst to give liquid-crystalline 1,4-diaryl-1-buten-3-yne derivatives. The new liquid-crystalline compounds with a conjugated enyne core show mesogenic phases at a wide range of temperature.

Recently we have found that diaryldiacetylenes (**1**) bearing long-chain substituents are prepared by the reaction of alkynyliodonium salts with alkynylcopper reagents and show mesogenic properties.[1] These diaryldiacetylenic compounds **1** have a rod-like core of diacetylene structure and are suitable for liquid crystals, electronic, and nonlinear optical materials.[2] In order to find further a new property of acetylenic liquid crystals, we have examined enyne structures in which one triple bond of the diaryldiacetylenes is displaced by a double bond. We report here the synthesis of the first group of (*E*)-1,4-diaryl-1-buten-3-ynes (**2**) for utilization in liquid crystal display devices. Although a conjugated rod-like group is suggested as a useful linking group for mesogens, we believe that the reported compounds represent the first group of 1,4-disubstituted 1-buten-3-yne liquid crystals.



1

The enynes **2** were prepared by the convergent route shown in Scheme 1. First, 4-decyloxyphenylvinyl bromide (**3**) was prepared according to the literature.[3] 4-Decyloxybenzaldehyde was prepared from 4-hydroxybenzaldehyde and 1-bromodecane by use of NaH in DMF. Condensation of 4-decyloxybenzaldehyde with malonic acid gave 4-decyloxycinnamic acid, which was converted into the corresponding 4-decyloxyphenylvinyl bromide **3** by bromination followed by decarboxylation and dehydrobromination. The ^{1}H NMR spectrum of **3** showed vinylic signals at δ 6.63 (d, J = 14 Hz) and 6.96 (d, J = 14 Hz), clearly indicating the (*E*)-configuration.



Scheme 1.

Next, the coupling reaction of 4-decyloxyphenylvinyl bromide **3** with arylacetylenes was conducted with a palladium catalyst.[4] To a mixture of **3**, an amine, and CuI in THF were added a palladium catalyst and 4-methoxyphenylacetylene. After stirring for 24 h at room temperature, 1-(4-decyloxyphenyl)-4-(4-methoxyphenyl)-1-buten-3-yne (**2a**) was separated and purified. As shown in Table 1, both $Pd(PPh_3)_4$ and $PdCl_2(PPh_3)_2$ catalysts worked well in this coupling reaction to give the same yield (70%) of the product **2a**. Piperidine as the additive was almost the same as triethylamine. Thus, we chose $PdCl_2(PPh_3)_2$ as the catalyst and Et_3N as the additive for the convenience for conducting the next coupling reactions.

Table 1. Palladium-catalyzed coupling reaction of **3** with 4-methoxyphenylacetylene[a]

Pd cat.	Amine	Yield/%
$Pd(PPh_3)_4$	Et_3N	70
$PdCl_2(PPh_3)_2$	Et_3N	70
$PdCl_2(PPh_3)_2$	Piperidine	73

[a] All reactions were conducted with Pd cat. (0.05 mmol), **3** (1 mmol), an amine (1.5 mL), CuI (0.1 mmol), and 4-methoxyphenylacetylene (2 mmol) in THF (10 mL).

The palladium-catalyzed coupling reaction of 4-decyloxyphenylvinyl bromide **3** with several arylacetylenes was conducted as follows. To a suspension of $PdCl_2(PPh_3)_2$ in THF were added **3**, Et_3N, CuI, and an arylacetylene, and the reaction mixture was stirred at room temperature for 24 h. After workup of the reaction mixture, the product, 1,4-diaryl-1-buten-3-yne **2**, was separated by column chromatography on silica gel and then purified by a preparative HPLC. The results are given in Table 2. As shown in Table 2, the coupling reaction with arylacetylenes bearing electron-donating groups such as butyl, methoxy, and methyl substituents gave high yields (68-70%) of the coupling products. Although the same reaction of arylacetylenes bearing electron-withdrawing cyano and nitro groups resulted in a slightly decrease in the yield of the products, the palladium-catalyzed coupling reactions giving 1,4-diaryl-1-buten-3-ynes **2** proceeded well in the cases of arylacetylenes with any kind of substituents. The geometry of the 1,4-diaryl-1-buten-3-ynes **2** was (*E*) configuration with respect to the double bond, showing that the vinylic protons were appeared at δ 6.22-6.23 (d, J = 16 Hz) and 6.85-6.88 (d, J = 16 Hz). The (*E*) configuration was completely retained during the coupling reaction.

Table 2. Palladium-catalyzed coupling reaction of **3** with arylacetylenes[a]

Arylacetylene, X	Product	Yield/%
CH_3O	**2a**	70
CH_3	**2b**	69
C_4H_9	**2c**	68
CN	**2d**	65
NO_2	**2e**	61

[a] All reactions were conducted with $PdCl_2(PPh_3)_2$. (0.05 mmol), **3** (1 mmol), Et_3N (1.5 mL), CuI (0.1 mmol), and an arylacetylene (2 mmol) in THF (10 mL).

Table 3. Liquid crystal phases and transition temperatures of 1,4-diaryl-1-buten-3-ynes **2**

Compound	Liquid Crystal Phase and Transition Temperature/°C[a]
2a: X = OMe	$K \underset{83.9}{\overset{95.0}{\rightleftharpoons}} N \underset{142.1}{\overset{143.9}{\rightleftharpoons}} I$
1a: X = OMe	$K \underset{81.4}{\overset{81.9}{\rightleftharpoons}} S_X \underset{89.7}{\overset{93.1}{\rightleftharpoons}} S_C \underset{127.2}{\overset{127.8}{\rightleftharpoons}} I$
2d: X = CN	$\begin{tikzcd} K \arrow[rr, "84.9"] & & S_A \arrow[r, shift left, "150.7"] \arrow[dl, "65.7"] & I \arrow[l, shift left, "146.3"] \\ & S_B \arrow[ul, "53.9"] & & \end{tikzcd}$
1b: X = CN	$\begin{tikzcd} K \arrow[rrr, "149.8"] & & & I \arrow[dl, "148.3"] \\ & S_X \arrow[ul, "131.7"] & S_A \arrow[l, "145.3"] & \end{tikzcd}$

[a] Key: K, crystal; N, nematic; S, smectic, S_A, smectic A; S_B, smectic B; S_C, smectic C, S_X, high order smectic, and I, isotropic.

The 1,4-diaryl-1-buten-3-ynes **2** thus prepared are mesogenic. The liquid crystal phase transition temperatures and the phase types of the 1-buten-3-ynes **2** were examined by optical microscopy on the basis of the texture[5] and confirmed by DSC. The representative examples and the comparison with the corresponding diacetylenes **1** are listed in Table 3. The 1,4-diaryl-1-buten-3-ynes **2** obtained in this study were enantiotropic liquid crystals. Compared with the corresponding 1,4-diaryldiacetylene **1**, the 1,4-diaryl-1-buten-3-ynes **2** showed a wide mesogenic range of temperature.

In summary, we have found that 1,4-diaryl-1-buten-3-ynes **2** bearing long-chain substituents can be prepared by the palladium-catalyzed coupling reaction in high yields and show mesogenic phases at a wide range of temperature. Especially, the enyne **2d** with an electron-withdrawing cyano group exhibits a smectic A phase at a surprisingly wide range of temperature compared with the diacetylene **1b**.

We thank Prof. M. Matsumoto and Mr. Y. Sano of Kyushu Sangyo University for experimental support. This work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture of Japan.

References

1 T. Kitamura, C. H. Lee, H. Taniguchi, M. Matsumoto, and Y. Sano, *J. Org. Chem.*, **59**, 8053 (1994); T. Kitamura, C. H. Lee, H. Taniguchi, Y. Fujiwara, M. Matsumoto, and Y. Sano, *Mol. Cryst. Liq. Cryst.*, **287**, 93 (1996); T. Kitamura, C. H. Lee, Y. Taniguchi, Y. Fujiwara, M. Matsumoto, and Y. Sano, *J. Am. Chem. Soc.*, **119**, 619 (1997).
2 M. D. Wand and S. Monahan, *SPIE* **1911**, 29 (1993); S. T. Wu, J. D. Margerum, C. S. Hsu, and S. H. Lung, *Appl. Phys. Lett.*, **61**, 630 (1992); A. E. Stiegman, E. Graham, K. J. Perry, L. R. Khundkar, L.-T. Cheng, and J. W. Perry, *J. Am. Chem. Soc.*, **113**, 7658 (1991); G. H. W. Milburn, C. Campbell, A. J. Shand, and A. R. Werninick, *Liq. Cryst.*, **8**, 623 (1990); J. Tsibouklis, A. R. Werninck, A. J. Shand, and G. H. W. Milburn, *Liq. Cryst.*, **3**, 1393 (1988); C. Fouquey, J.-M. Lehn, and J. Malthete, *J. Chem. Soc., Chem. Commun.*, **1987**, 1424; P. S. Vincett and G. G. Roberts, *Thin Solid Films*, **68**, 135 (1980); B. Grant, *Mol. Cryst. Liq. Cryst.*, **48**, 175 (1978); G. M. J. Schmidt, *Pure Appl. Chem.*, **27**, 647 (1971).
3 G. Eigel, *Ber.*, **20**, 2527 (1887).
4 K. Sonogashira, Y. Tohda, and N. Hagihara, *Tetrahedron Lett.*, **1975**, 4467.
5 D. Demus and L. Richter, "Textures of Liquid Crystals," Verlag Chemie, Weinheim (1978); G. W. Gray and J. W. G. Goodby, "Smectic Liquids Crystals–Textures and Structures," Leonard Hill, Glasgow (1984).