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

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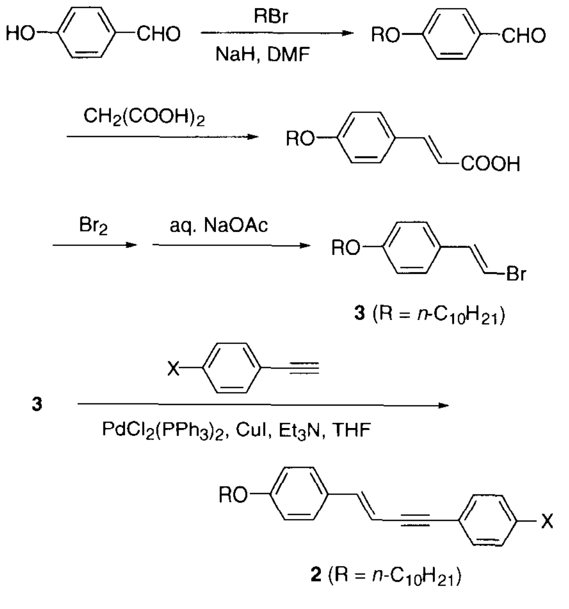
An arylvinyl bromide bearing a long-chain alkoxy group reacts with arylacetylenes in the presence of a palladium catalyst to give liquid-crystalline 1,4-diaryl-1-buten-3-yne derivatives. The new liquid-crystalline compounds with a conjugated enyne core show mesogenic phases at a wide range of temperature.

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 ^1H 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	$\begin{tikzcd} K \arrow[rrrr, "149.8"] & & & & I \arrow[dl, "148.3"] \\ & S_X \arrow[ul, "131.7"] & & S_A \arrow[ll, "145.3"] & \end{tikzcd}$

[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**.

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