

Communications

Synthesis of Spiropyran Substituted 2,3-Dicyanopyrazines

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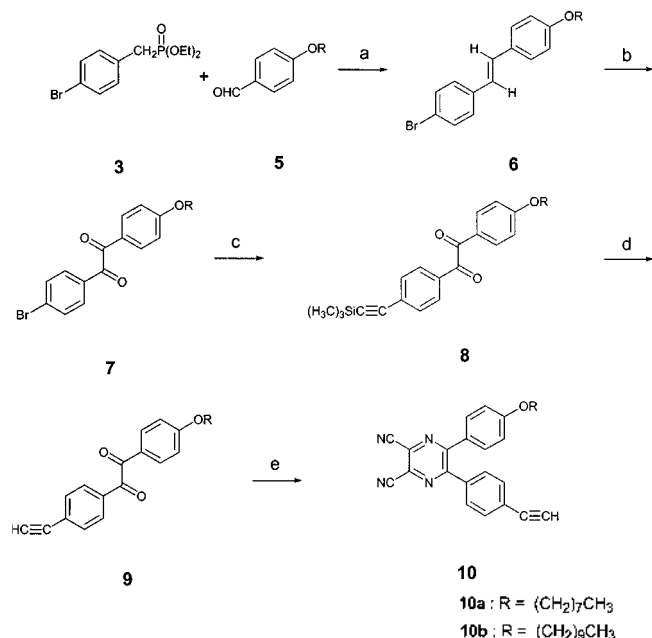
With the development of the electronics and information industries, the importance of functional dyes has increased. Many research papers have been published concerning new synthetic methods and mechanisms of functional dyes. Since their discovery, pyrazine and spiropyran have been two of the most popular materials due to their potential applications in many technical fields. 2,3-Dicyanopyrazine derivatives have some specific properties resulting from the two strong electron withdrawing cyanogroups on the pyrazine ring. Highly functionalized 2,3-dicyanopyrazine derivatives can be used as fluorescent dyestuffs, emitters for electroluminescent devices etc.¹⁻³ Spiroyrans have photochromic properties so they are useful for data storage, electronic devices, optical filters and so on. Moreover, it is easy to control their physical and chemical properties by modifying their molecular structures.^{4,5}

This adaptation of their functionality can be applied to many fields, so we designed spiropyran substituted 2,3-dicyanopyrazine derivatives. Novel compounds **15** were synthesized by the direct coupling reaction of 6-iodospiropyran **14** and 2,3-dicyanopyrazine derivatives with a long alkyl chain **10**.

Firstly, we synthesized the 2,3-dicyanopyrazine compounds with a terminal acetyl functional group to react with aryl halide. 1-(4-alkoxyphenyl)-2-(4-bromophenyl) ethenes **6** were prepared in good yield (82-85%) by the Wittig reaction of 4-bromobenzyl-phosphonic acid diethylester **3** and 4-alkoxybenzaldehydes **5** in tetrahydrofuran using sodium hydride as a base under refluxing conditions. The ¹H NMR spectra of **6** indicated that the ethylene protons appeared two doublets at

7.07-6.91 ppm ($J = 16.2$). According to the coupling constant, compound **6** should exist in the *trans*-configuration. The terminal -CH₃ of the long alkyl chain group appeared as a triplet at 0.89 ppm, and the O-CH₂ protons were split as a triplet at 3.97 ppm. Oxidation of **6** in the presence of 0.5 equiv. iodine in DMSO under reflux conditions gave 1-(4-Alkoxy phenyl)-2-(4-bromophenyl)-ethanediones **7** in moderate yield (45-47%). The crude product was purified by column chromatography in silica gel, eluting with hexane-ethylacetate (5:1). Treatment of **7** with an excess amount of trimethylsilylacetylene in triethylamine as a solvent in the presence of catalytic amounts of palladium(II)acetate and triphenylphosphine under an argon atmosphere led to the production of 1-(4-Alkoxyphenyl)-2-(4-trimethylsilyl ethynyl phenyl) ethanediones **8** in good yield (89-92%). Treatment of **8** with potassium carbonate using a mixture of dichloromethane and methanol under mild conditions resulted in a very high rate of conversion to 1-(4-alkoxy phenyl)-2-(4-ethynyl phenyl) ethanediones **9**.⁶ In the FT-IR spectra of compound **9**, a terminal acetylene absorption band at 3301 cm⁻¹ was observed, while the internal acetylene absorption band of compound **8** had disappeared. 2,3-Dicyanopyrazine derivatives have been readily synthesized by condensation of diaminomaleonitrile (DAMN) and α -diketone compounds. DAMN is well known as a tetramer of hydrogen cyanide and is a useful compound in the chemical industry, being used as a starting material for the synthesis of various heterocyclic compounds. 2,3-Dicyano-5-(4-ethynyl phenyl)-6-(4-alkoxy phenyl) pyrazines **10** were obtained by the condensation reaction of DAMN with compound **9** in the presence of a catalytic amount of *p*-toluenesulfonic acid (Scheme 1). The stretching vibrations of cyano groups for **10** were observed, appearing at 2227 cm⁻¹.

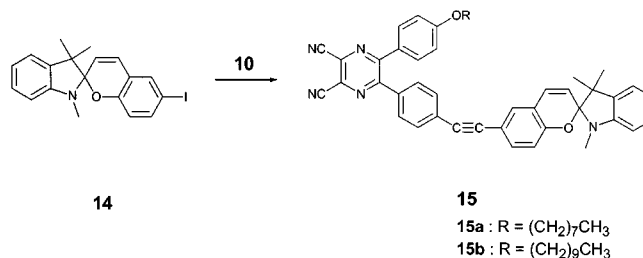
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Scheme 1. Reagents and conditions: (a) NaH, THF; (b) 0.5 equiv. iodine, DMSO; (c) excess trimethylsilylacetylene, palladium(II) acetate, P(Ph)₃, NEt₃; (d) K₂CO₃, Cl₂/C₂H₂; O₂-free MeOH (2:1); (e) DAMN, *p*-toluenesulfonic acid, MeOH.

Next, we synthesized spiroopyran including a halide group to react with the terminal acetylene group. 1,3,3-Trimethyl-6'-iodo-spiro[2*H*-benzopyran-2,2'-indoline] **14** was prepared by a literature process.⁷

Finally, we made a compound having the functionalities of 2,3-dicyanopyrazine and spiroopyran by a coupling reaction. The palladium-catalyzed coupling reaction of **14** with **10** was carried out by refluxing the reaction mixture in tetrahydrofuran in the presence of triphenylphosphine, cuprous iodide and triethylamine and gave 2,3-dicyano-5-{4-[2-(1,3,3-trimethyl spiro [2*H*-benzopyran-2,2'-indoline]-6'-yl)ethynyl phenyl]-6-(4-octyloxy phenyl) pyrazine **15a** and 2,3-dicyano-5-{4-[2-(1,3,3-trimethyl spiro [2*H*-benzopyran-2,2'-indoline]-6'-yl)ethynyl phenyl]-6-(4-octyloxy phenyl) pyrazine **15b** in 45-50% yield.⁸ The reaction routes were summarized in Scheme 2. In the case of compound **15**, the N-CH₃ group of spiroopyran appeared as a singlet at 2.17 ppm and two -CH₃



Scheme 2. Reagents and conditions: P(Ph)₃, CuI, NEt₃, THF.

signals partially overlapped at the range of 1.45-1.26 ppm, principally with the long alkyl chain group of the 2,3-dicyanopyrazine.

In conclusion, we have demonstrated that 2,3-dicyanopyrazines containing a terminal acetylene group **10** can be used as intermediates, in order to combine with iodide substituted spiroopyran **14**. It is expected that this procedure will be useful for combining two functional dye compounds that have totally different functionalities.

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- A mixture of **14** (5 mmol), PdCl₂ (5 mol%), P(Ph)₃ (10 mol%), CuI (2.5 mol%), and triethylamine (15 mmol) in THF (10 mL) was refluxed. To the refluxing solution was added a **10** (5 mmol) over 10 minute. After the solution was refluxed for 2 hr, the precipitate was filtered off. The crude product was purified by column chromatography in silica gel, eluting with hexane-ethylacetate (5:1).