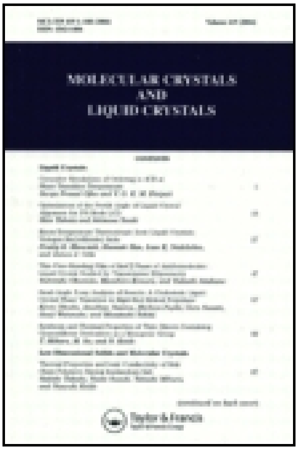

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A Convenient and General Synthetic Method for Photochromic Fulgides by Palladium-Catalyzed Carbonylation of 2-Butyne-1,4-Diols

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A Convenient and General Synthetic Method for Photochromic Fulgides by Palladium-Catalyzed Carbonylation of 2-Butyne-1,4–Diols

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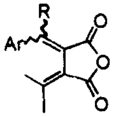
Palladium-catalyzed carbonylation of substituted 2-butyne-1,4-diols affords a variety of photochromic fulgides in one step. This methodology provides an alternative to the traditional method based on the Stobbe condensation.

Keywords: Photochromic fulgide; Palladium-catalyzed carbonylation

INTRODUCTION

Thermally irreversible, photochromic fulgides (**1**, Ar; heteroaromatic) exhibit useful properties making them applicable to photochemical devices [1]. One of the most important research in this field is the synthesis of a variety of photochromic fulgides to establish basic correlation between their structures and properties. In general,



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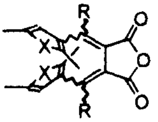

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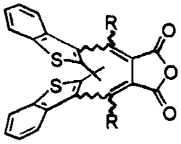

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fulgides have been synthesized by successive condensations of two ketones with succinate in the presence of base (the Stobbe condensation). This method, however, requires many steps and the yield of each step is not always high. Therefore, to establish a convenient synthetic method is instrumental in the development of this field of study. We have already demonstrated a route to photochromic fulgies (**1**) based on the palladium-catalyzed carbonylation of substituted 2-butyne-1,4-diols (**4**) [2-4]. This paper is concerned with the survey of this method and the synthesis of fulgides (**2**,**3**).

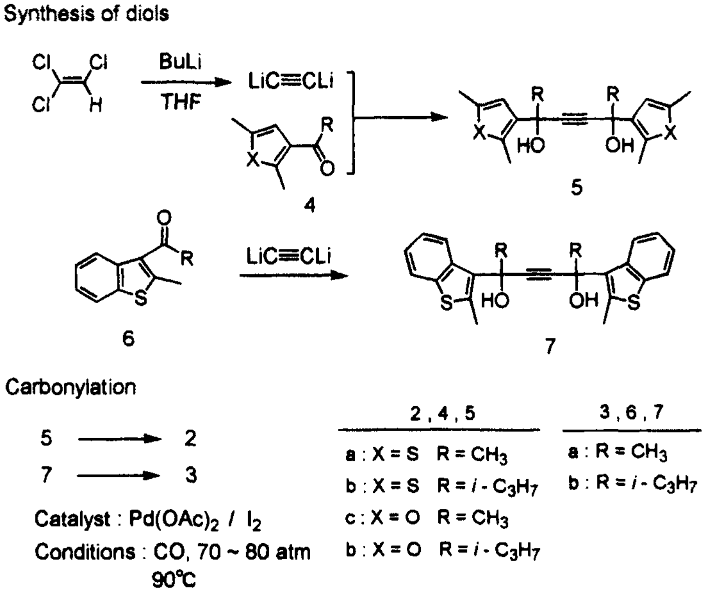
RESULTS

In 1969 Tsuji and Nogi [5] found that the palladium-catalyzed carbonylation of 2,5-dimethyl-3-hexyne-2,5-diol affords bis(isopropylidene)succinic anhydride as the major product. With their finding as a start, we approached this reaction in various ways. It has been found that the combined use of equimolar amounts of $Pd(OAc)_2$ and I_2 in benzene gave the most satisfactory catalyst [2]. We applied this catalytic system to the carbonylation of substituted 2-butyne-1,4-diols and succeeded in one-pot synthesis of photochromic fulgides (**1**) having substituents such as furyl, thienyl, and indolyl [3]. The fulgides are obtained generally in good yields. It should be noted that the furyl or thienylfulgides (1) having *t*-butyl (R; *t*-C_4H_9) can be synthesized in 40-75% yields, while they have not yet been synthesized by the conventional method.

Photochromic fulgides possessing heteroaromatic substituents on each methylene are expected to show interesting properties on photoirradiation due to the steric congestion. At the present stage, however, little is known about this type of fulgides [6]. To further explore the scope of this carbonylation method, we turned attention to bis(furyl, thienyl, or benzothienyl)fulgides (**2**, **3**). We applied this method to the synthesis of these fulgides as illustrated in Scheme 1.

The diols (**5** and **7**) were synthesized according to the reported method [7,8] and carbonylated under pressure. Compared with the synthesis of **1**, the yields of **2** and **3** were low (< 10%) in general. In their ^1H NMR spectra of the major constituents of **2a** and **2c** there appear three peaks due to the methyl groups in the range of δ1.8-2.5. This fact indicates the formation of symmetrically substituted fulgides.

Scheme 1



From the chemical shifts the major constituents of **2a** and **c** were concluded to be the ZZ isomers, in which the thienyl and furyl groups are located in the cis configuration with respect to the carbonyl groups. The product **3a**, which was obtained by the carbonylation of **7a**, exhibited four ^{1}H NMR peaks due to the four methyl groups in the range of δ1.3-2.9. In this reaction the EZ isomer was formed

EXPERIMENTAL

Synthesis of diols (5 and 7). Dilithioacetylene was generated by the reported method [7] and was allowed to react with the ketones [8].

General procedure for the carbonylation. In a 50 ml stainless steel autoclave were placed benzene, diol, catalyst (5 mol%), and a stirring bar. The air was purged with CO and the autoclave was pressurized at 70-80 atm and heated at 90℃. After the reaction benzene was evaporated under reduced pressure. The oily, viscous residue was chromatographed on Wakogel C-200 using, hexane, hexane/toluene, toluene, toluene/ chloroform, chloroform, and methanol as the eluent in this order. The eluate of hexane/toluene and toluene gave the fulgides. The following examples are representative.

Synthesis of 2c. Diol **5c** (1.01 g, 2.59 mmol) was carbonylated under 75 atm of CO for 15h. The eluate of 1:2 - hexane/toluene gave dark brown oily substances (0.13 g) which was allowed to stand until a crystalline solid appeared. The solid was repeatedly recrystallized from pentane to give the pale yellow ZZ isomer ; mp 150-152℃ ; IR (KBr) 1802(m), 1756(s) cm^{-1}; ^1H NMR ($CDCl_3$) δ1.90, 2.12, 2.52, 5.49 ; HRMS calcd for $C_{20}H_{20}O_5$ 340.1311, found 340.1322.

Synthesis 2a. Diol **5a** (0.53, 1.58 mmol) was carbonylated under 80 atm for 14h. On standing the eluate (0.113 g) from toluene afforded the solid ZZ isomer and oily EZ isomer (ca. 5% yield). The solid was recrystallized from hexane gave the ZZ isomer in a pure form (0.012 g, ca. 2% yield) ; mp 201-204℃ ; IR (KBr) 1808(m), 1763(s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ2.19, 2.36, 2.43, 6.58.

Synthesis of 3a. Diol **7a** (0.51 g, 1.25 mmol) was carbonylated under 80 atm for 14h to give **3a**. The eluate from 1:2 - hexane/ toluene gave the EZ isomer (0.010 g, ca. 2% yield); IR (KBr), 1814(m), 1769(s)cm^{-1}; ^{1}H NMR ($CDCl_3$) δ1.39, 1.85, 2.62, 2.82, 7.2-7.9 (aromatic H) ; HRMS calcd for $C_{26}H_{20}S_2O_3$ 444.0854, found 444.0864.

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