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Solid solutions have been reported for numerous classes of organic pigments, but quinacridones have enjoyed the most success as commercial products and patented technologies. Quinacridone solid solutions are often characterized by their perform-

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Synthesis of Polycyclic Arenes Involving Nitrile Anion and Dipolar Nucleophilic Additions to Arynes

Edward R. Biehl*

We report here three quick and efficient polycyclic syntheses which involve a nucleophilic addition to an aryne in the key step.

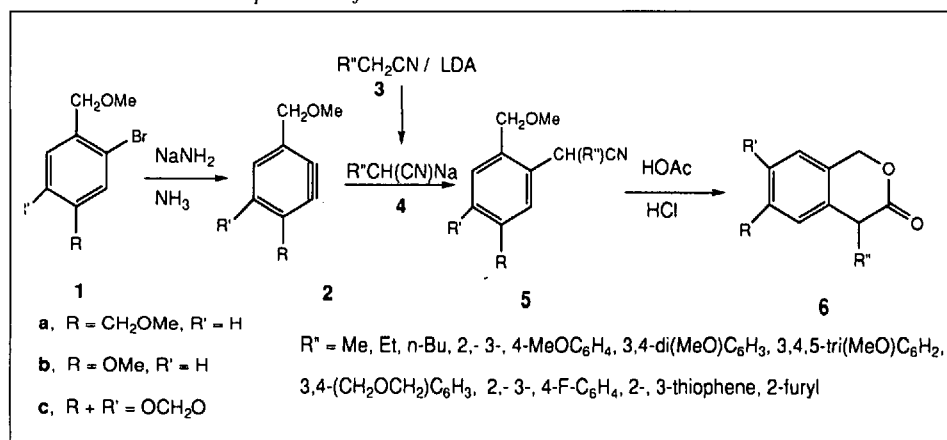
Method 1. This method involves the preparation of 4-substituted isochromanones **6**, valuable *ortho*-diquinomethane precursors, by the intermolecular nucleophilic addition of α -sodio nitriles **4** to arynes **2a–c**, generated by the reaction of the appropriate aryne precursors **1a–c** with sodamide in liquid ammonia (*Scheme 1*). The resulting *ortho* methoxy-methylarylacetonitriles **5a–c** then undergo acid catalyzed cyclization to 4-alkyl- and 4-aryl-isochromanones **6a–c** [1]. The overall yields of 4-alkyl derivatives are much higher (40–70%) than those of 4-aryl derivatives (15–50%) due to extensive aryne amination by ammonia in the α -sodioarylacetonitrile reactions.

Method 2. Since *Method 1* is the method of choice for 4-arylisochranones, we attempted to increase their yields by substituting lithium diisopropylamide (LDA) and THF for sodamide and ammonia in the first aryne addition step [2]. However, these reactions give rearranged 2-aryl-methylbenzonitriles, likely by a tandem addition-rearrangement pathway [3]. This unexpected result led to the development

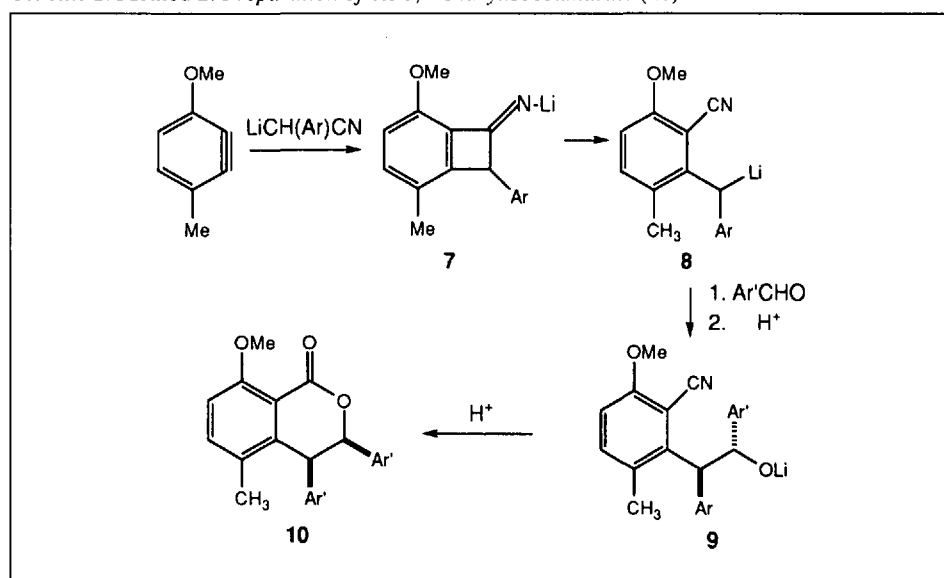
of a second aryne-nucleophilic annelation method (*Scheme 2, Method 2*), in which rearranged 2-(α -lithioaryl)methyl benzonitriles **8** formed by the ring opening of benzocyclobutenium aryne-nucleophile adduct **7**, are diastereomerically trapped with aromatic aldehyde producing *anti*-3,4-diaryl alcoholates **9** which cyclized smoothly to *cis*-3,4-diarylisocoumarins **10** in overall yields generally > 60% [4].

Method 3. *Sammes* [5] showed initially that anthraquinones can be prepared conveniently by the [2+4] cycloaddition of 3-lithiophthalides to arynes, which we designate as *Method 3*. We have extended this

Scheme 1. Method 1: Preparation of Isochromanones



Scheme 2. Method 2: Preparation of *cis*-3,4-Diarylisocoumarins (**10**)



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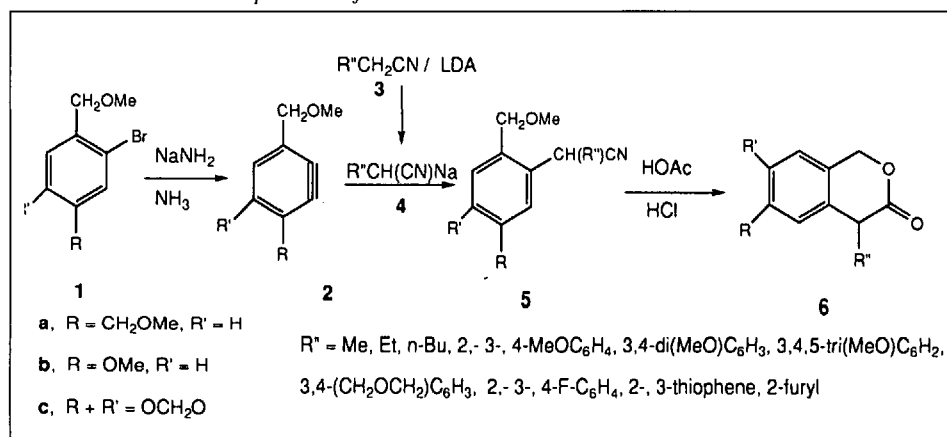
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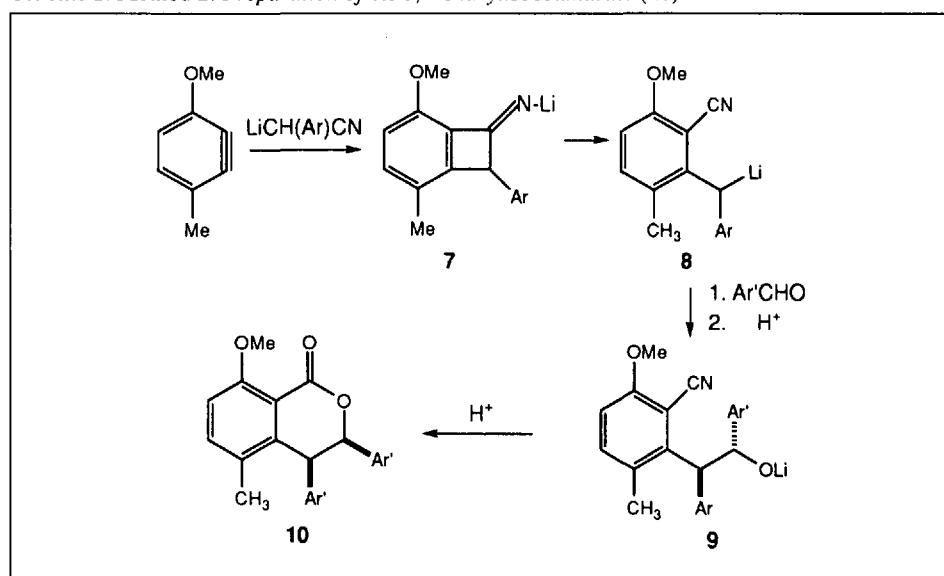
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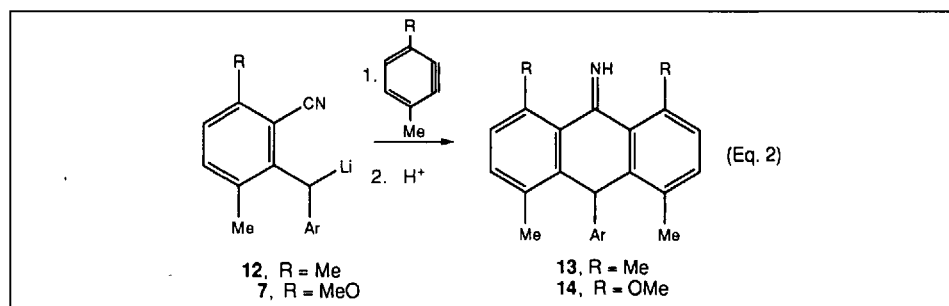
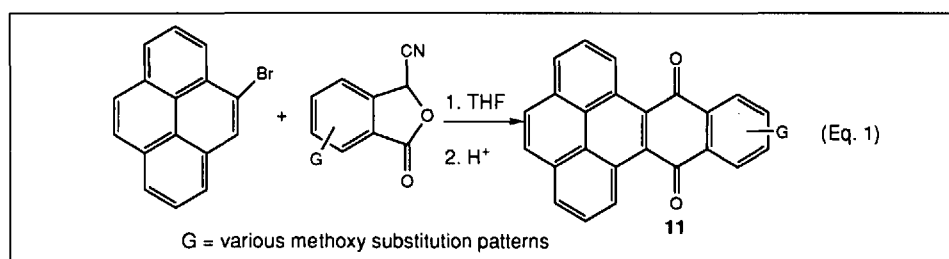
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methodology by using 3-lithiated 3-cyanophthalides which not only greatly increased the reaction workup time (< 1 h compared to overnight in the case of Sammes lithiumphthalide-mediate reaction), but also because of readily availability using Swenton's elegant methodology [6], enables one to prepare a wide variety of anthraquinones, such as methyl ethers of anthraquinones, such as chrysophanol [7], helmintho-sporin [7], morindaparvin [8], and biologically active azaanthraquinones [9]. Recently, we have prepared hexacene quinones **11** by the reaction of 4-bromopyrene and cyanophthalides [10] (Scheme 3).

Other dipolar nucleophiles have been discovered that react with arynes to give polycyclics. E.g., as shown in Scheme 4, the generation of another equiv. of aryne in the presence of α -lithiated rearranged nitriles **12** and **7** from the reaction of 2-bromo-1,4-dimethylbenzene and 2-bromo-4-methylanisole yields the respective 9-imino derivatives of 10-arylanthrones **13** [11] and **14** [12]. 10-Hydroxy-9-anthracenecarbonitriles [13] can be prepared similarly by generating arynes in the presence of α -lithiated *o*-(methoxycarbonyl)arylacetonitriles, with no apparent restriction on the nature of the aryne. 10-Amino-9-anthracenecarbonitriles can also be prepared by the reaction of α -lithiated α -cyano-*o*-tolunitrile with methoxy substituted arynes [14], 1-naphthalynes [15] and 1-pyrynes [12]. However, it yields rearranged dinitriles when treated with 3,6-dimethoxybenzynes, 9-phenanthryne [16] and 4-pyryne [12]. The 10-amino- and 10-aminoanthracenes are powerful fluores-



cent materials, whose excitation wavelengths occur from 320 to 360 nm and emission wavelengths range from 520 to 560 nm [12].

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Novel Perylene Derivatives as Highly Photostable Fluorescent Dyes

Heinz Langhals*

Abstract. Perylene-3,4-dicarboxylic imides are prepared by a new decarboxylizing condensation with moderately sterically hindered primary amines. Perylene-3,4-dicarboxylic anhydride is prepared *via* a saponification reaction of the dicarboximide and is a starting material for a number of new types of chromophores. A second route to novel perylene derivatives is a partial hydrolysis of perylene dyes and a condensation with diamines. The dyes thus obtained are orange to red fluorescing in solution.

1. Introduction

Perylene-3,4:9,10-tetracarboxylic bis-anhydride (**1**, C.I. No. 71127) is prepared in an analytically pure state on technical scale and it is the starting material for the preparation of perylene dyes (perylene-3,4:9,10-tetracarboxylic bisimides, **2**) [1]. The perylenes **2** are well-known as highly photostable pigments and fluorescent dyes; for a review see [2]. An essential point for the lightfastness and inertness of **2** is the

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