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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 performance properties in paint, i.e. higher fastness properties and more brilliant colors. Miles is pursuing a program to study solid solutions and to infer from solid solution crystal homogeneity, specific performance improvements in organic pigments.

**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-methylacetonitriles 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 aryneamination by ammonia in the α-sodioarylacetonitrile reactions.

**Method 2.** Since Method 1 is the method of choice for 4-arylisochromanones, 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 lead 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 diasteroisomerically trapped with aromatic aldehyde producing anti-3,4-diaryl alcohates 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- lithiumphthalides to arynes, which we designate as Method 3. We have extended this
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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 lithiumphthalimide-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 the natural products chrysophanol [7], helminthosporin [7], morindaparvin [8], and biologically active azanthraquinones [9]. Recently, we have prepared hexacene quinones 11 by the reaction of 4-bromopyrene and cyananthophthalides [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 arynes 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- and 11-arynes of 10-arylanthrones 13 [11] and 14 [12]. 10-Hydroxy-9-anthracene carbonitriles [13] can be prepared similarly by generating arynes in the presence of α-lithiated o-(methoxycarbonyl)arylacetanitrides, with no apparent restriction on the nature of the aryne. 10-Amino-9-anthracene carbonitriles can also be prepared by the reaction of α-lithiated α-cyano-α-tolunitrile with methoxy substituted arynes [14], 1-naphthalenes [15] and 1-pyrynes [12]. However, it yields rearranged dirimines when treated with 3,6-dimethoxybenzene, 9-phenanthryne [16] and 4-pyryne [12]. The 10-amino- and 10-aminoanthracenes are powerful fluorescent materials, whose excitation wavelengths occur from 320 to 360 nm and emission wavelengths range from 520 to 560 nm [12].

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1. Introduction

Perylene-3,4,9,10-tetracarboxylic bisanhydride (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 (perylenes-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

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.

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