Solvent-free synthesis of diketopyrrolo [3,4-c] pyrrole pigments

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Article

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Solvent-free synthesis of diketopyrrolo [3,4-c] pyrrole pigments

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Abstract

The paper describes environmentally friendly and cost effective solvent-free multistep & multi-reagent process of the synthesis of.diketopyrrolo[3,4-c]pyrrole/2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (DPP) pigments, a new class of most recently introduced high-performance pigments, now in use for a variety of applications, beyond colour appearance , such as liquid crystal displays (LCD) of electronic equipments & TV monitors. Silent features of the process versus state-of-the-art of process, reaction mechanism of the in-situ multistep synthesis and mechanism of the formation of by-products are discussed. Moreover, the process provides the only approach to the stepwise synthesis of unsymmetrical diketopyrrolo pyrrole molecules. The process is particularly aimed at reducing carbon emissions and for energy saving in chemical processes.

Introduction

With concerns of the reduction of carbon emissions and for the sake of energy saving the green chemistry is getting increasingly important. We believe that the factors enumerated underneath would be the pointers of the chemical technologies of tomorrow:

- ✓ Energy efficiency: in which the exothermies/endothermies of the reactions are efficiently exploited for driving the reactions.
- ✓ Cost efficiency: higher productivity with same or less resources (energy, equipment, man power and other investments).
- ✓ Waste efficiency: less waste & pollution (better yields).
- ✓ Safety efficiency: Taming the chemical reactions (i.e. infinity reactions, micro reactors).
- ✓ Over-all better value addition.

We strongly believe that many of the said objectives can be achieved by adapting any or many of the following technologies:

- ✓ Solvent-free processes[1)]
- ✓ Surface chemistry reactions (including homo- & heterogeneous catalysis and phase transfer reactions[2)]
- ✓ Solid-state reactions[3)]
- ✓ Continuous/semi-continuous process (micro reactors, extrusions)
- ✓ Automation i.e. electronically remote-controlled processes

The focus of this publication , however, is on the solvent-free multistep multi-reagent synthesis of diketopyrrolo[3;4-c]pyrrole pigments_, a new class of most recently introduced high-performance pigments, used for wide range of applications, including liquid crystal displays of electronic materials [4)] . Moreover, the process also provides the only approach to the stepwise synthesis of unsymmetrical diketopyrrolo pyrrole molecules, in general.

Discussion

Many organic reactions have traditionally been carried out, and are still being carried out in organic solvents, without concern for their real necessity, reaction efficiency, energy demand and pollution. We are of the opinion that many chemical reactions now being practiced in solvents can in fact be carried out in the absence of a solvent, particularly where at least one of the reactants is a liquid, and/or the liquids are transiently or permanently formed in the reaction. We believe that in many such cases, the reaction could proceed more easily and efficiently, and even more selectively than solvent-based reactions. Also, the solvent-free reactions could be more economical and ecologically favourable.

In pursuit of this idea we have investigated solvent-free synthesis of many specialty chemicals. We particularly wish to describe our proprietary solvent-free technology of the high performance diketopyrrolopyrrole pigments (Figure1), to demonstrate the advantages of a solvent–free technology over a solvent based technology.

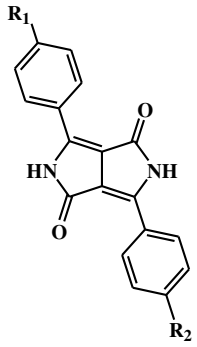

Figure 1: Diketopyrrolopyrrole pigments

State-of-the-art Diketopyrrolopyrrole (DPP) pigment technology

Diketopyrrolopyrrole pigments, also called DPP pigments, have been an unrelated chance discovery like the discovery of phthalocyanine pigments by de Diesbach in 1927 [5)].

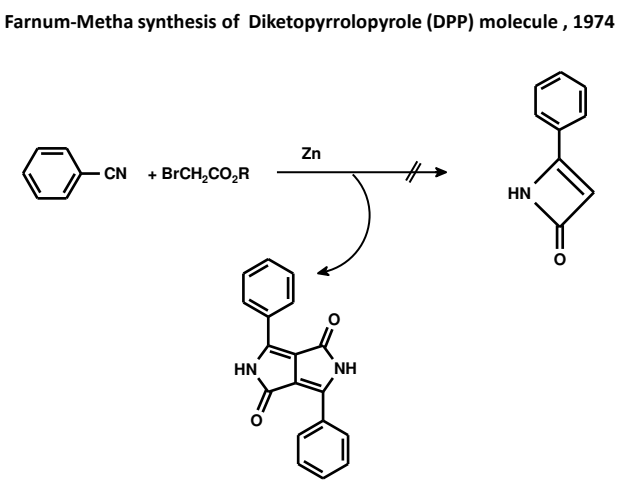

Figure 2: Farnum-Metha synthesis of diketopyrrolopyrole molucule

In 1974 Farnum and Metha[6)] attempted the synthesis of 2-azetinone by reacting benzonitrile with bromoacetic acid ester (Figure 2). Instead, diketopyrrolopyrrole chromophore was formed as a red compound in small yields. The potential of this molecule for organic pigment applications was exploited by Ciba in general and Abul Iqbal in particular in the mid-80s thereby employing the synthesis shown in Figure 3.

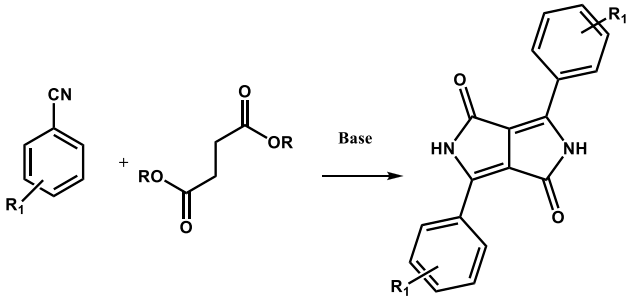

Figure 3: State-of-the-art technology of DPP pigments, Iqbal et al (Ciba)

The process involves the reaction of two moles of a nitrile with one of diisoalkyl succinate in the presence of more than two moles of an exotic sodium tertiary-alcoholate, in an absolutely inert and anhydrous solvent, followed by the hydrolysis and finishing of the resulting pigment in a different solvent[7,8)].

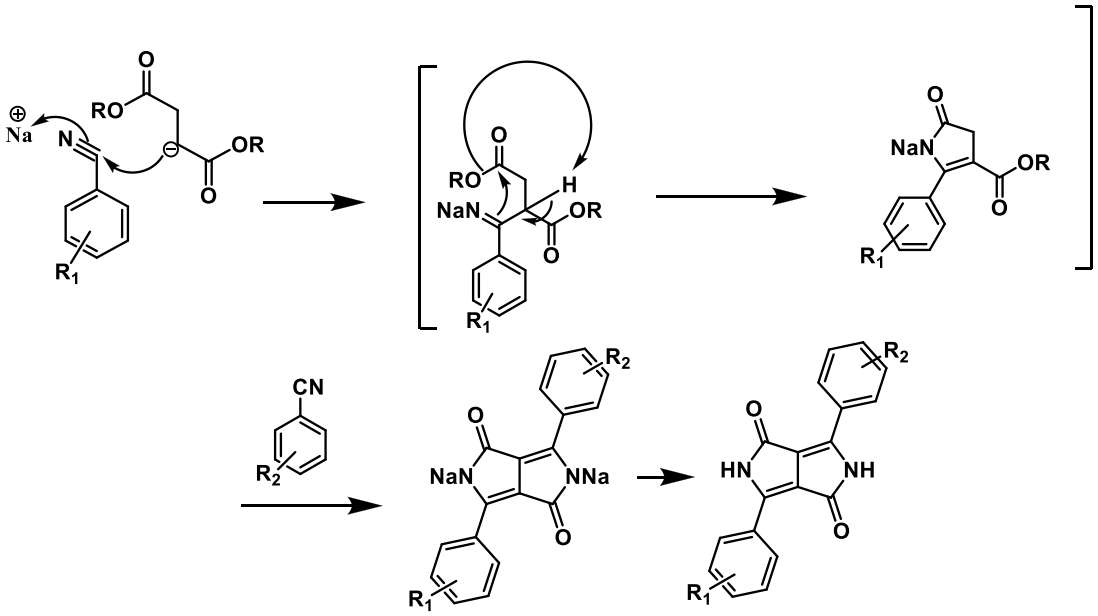

Figure 4: Reaction scheme and mechanism of the formation of DPP pigments

Mechanistically, the reaction takes place in many steps in situ (Figure 4) Starting with the reaction of the anion of one of the two methylenic groups of the succinic diester with a nitrile moiety. The imino group generated as a result of this attack, undergoes cyclisation with the neighbouring ester group to form the first pyrrole ring. We have observed that the formation of the yellow coloured mono-condensation/mono-cyclisation product already takes place at 40 ^{o}C e resulting pyrrole then reacts with the second mole of the same or different nitrile to form the pyrrolopyrrole structure in which two pyrrole moieties are fused to each other, back to back [3,4-c] position. Since the reaction can also be carried out stepwise, it is also possible to obtain unsymmetrical DPP molecule pigments under carefully controlled reactions, particularly employing the new solvent-free process. Such pigments show unique properties.

By-products of the DPP Pigment synthesis

By-products of the reaction are usually the aldehydes (Figgure.5, A) and the dialkyl succinyl succinate (Figure 5, B).

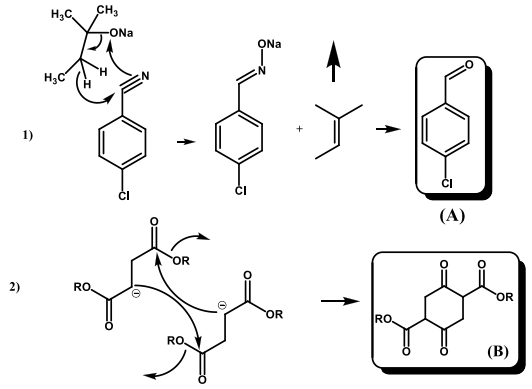

Figure 5: By-products of the DPP synthesis

Mechanisms of formation of the said by-products are outlined in Figure 5.

It is assumed that the formation of the aldehyde (A) is initiated by the hydride transfer from the solvent *tert*-alcohol to the nitrile, following the reversal process of the synthesis of the corresponding *tert*-alcohols. Dialkyl succinyl succinate (B) is formed by the self condensation of the dialkyl succinate as a result of Dieckmann reaction.

Novel solvent-free DPP pigment technology[9,10)]

We have now developed an alternative technology for the production of DPP pigments which excludes the use of the exotic inert and high- purity solvent, responsible both for the inefficiency and sensitivity of the DPP synthesis. In our technology the alcohols formed as by-products of the reaction are fully utilized to keep the reaction mass stirrable throughout the reaction. Moreover, the reaction is carried out in a special reactor (Fig.7) jointly designed with the German engineering company Drais (now Loedige) for employing the Froude Number > 1.
Table 2 enumerates the salient features of new solvent-free DPP pigment technology.

We have also found that the solvent-free synthesis can generate fewer by-products and particularly eliminate the formation of the hazardous and toxic aldehydes such as p-chlorobenzaldehyde in the synthesis of Pigment Red 254, the reason being that the aldehyde is formed by the reaction of the solvent with the nitrile.

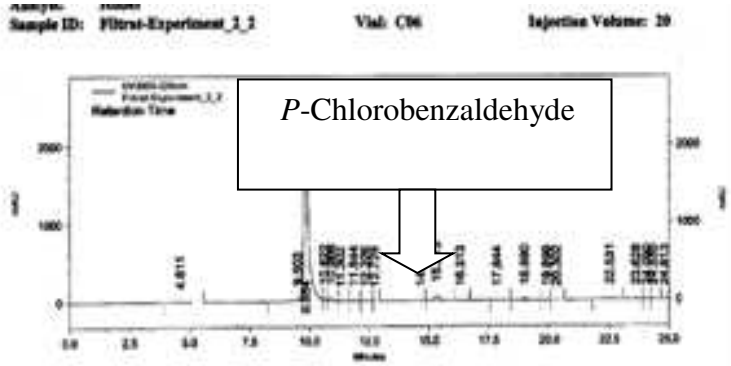

Figure 6: HPLC analysis for the absence of p-chlorobenzaldehyde

Figure 6 shows the HPLC analysis of a typical reaction mixture in the synthesis of Pigment Red 254 employing solvent-free technology, confirming the absence of p-chlorobenzaldehyde.

Experimental details

Figure 7: Zero emission pilot plant for novel solvent-free technologies

Figure 7 shows the 'zero' emission pilot plant used for the development of solvent-free technologies, and particularly the solvent-free DPP synthesis. This technology has since been extended to other specialty chemicals and pigments[11)].

The process is described in detail in U.S. Pat. 7,728,139 (MCA Technologies GmbH, 2010) as a preprint

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