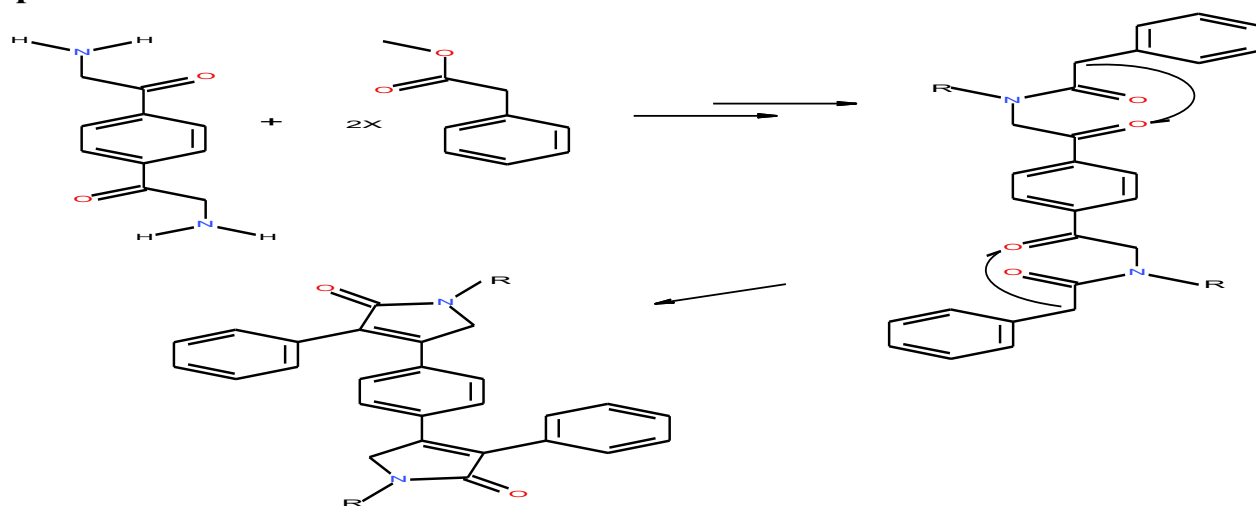


New Synthesis of Separated DPP, DPP and isoDPP derivatives

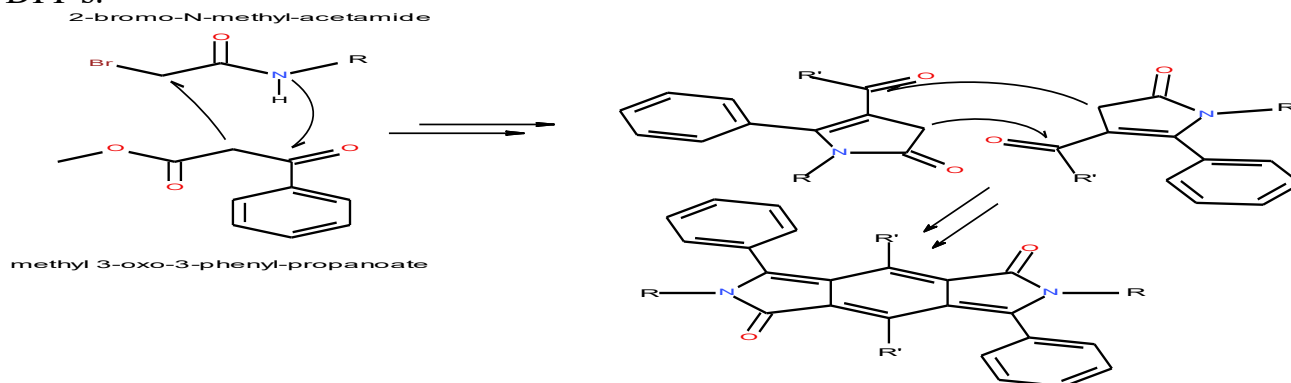
By Robert B. Login rloginconsulting.com

Recently I proposed a synthetic route to DPP analogs based on alpha-amino ketones (see rloginconsulting.com. Pdf). Since then, I continued to think about DPP and now I have new proposals to put forward. Before I present my newer ideas, I want to go back to the alpha-amino ketones and show another idea based on it.

Separated DPP



Scheme 1: As pointed out in my previous proposals, the alpha-amino ketone is protected as a ketal which is hydrolyzed after amide formation. A strong base and heat would probably be required for this ring closure. Here the unsaturated lactams are separated and conjugated through an aromatic ring. Can they still function as dyes? If so then there are many variants of the starting materials such as heterocyclic aromatics, substituents on the aromatics, bromine derivatives that can be coupled by typical coupling reactions, and so forth. The lactam R groups can be the typical ones usually employed with the DPP's.



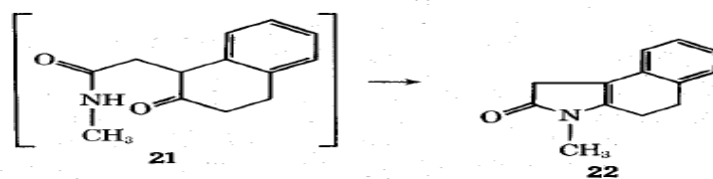
Scheme 2: The above reactions seem very feasible, activated methylene reacts with a reactive bromo-derivative followed by ring closure to the unsaturated lactam. The resulting ester is converted to the ketone which can be accomplished in several ways.

Followed by base catalyzed ring closure. Should the amide prove difficult then similar reactions can afford the corresponding lactone(butenolide).

Grzybowski, Marek, and Daniel T. Gryko. "Diketopyrrolopyrroles: Synthesis, reactivity, and optical properties." *Advanced Optical Materials*, 3.3 (2015): 280-320.

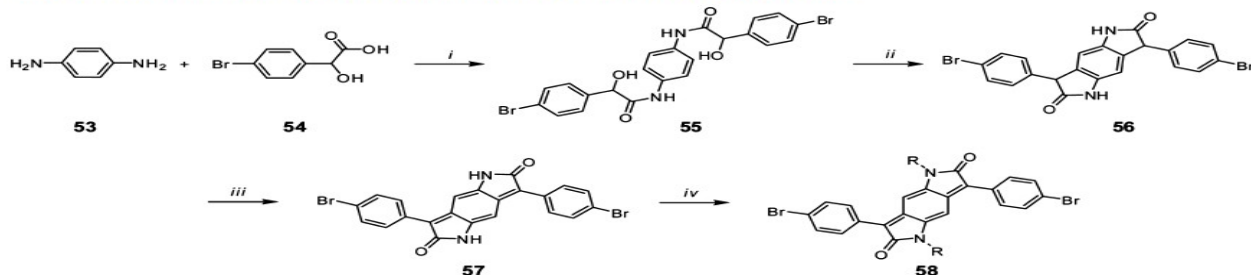
Can these lactams also be separated but conjugated and also function as dyes? As I mentioned, the ester is converted to a carbonyl by a variety of reactions. See:

Evans, David, Carl Bryan, and Geoffrey Wahl. "Total Synthesis of Naturally Occurring Substances. II. The Synthesis of the Hasubanan Carbocyclic System." *The Journal of Organic Chemistry*, 35.12 (1970): 4122-4127. for the following example somewhat related to scheme 2.



The product of scheme 2 is isomeric with a whole series of related structures, for example:

Scheme 13. Synthetic Route to the Dibrominated Phenyl-Flanked Benzodipyrrolidone⁴⁷



⁴⁷Reagents and conditions: (i) chlorobenzene, reflux; (ii) H₂SO₄, room temperature; (iii) K₂S₂O₈, NaOH (aq), EtOH; (iv) RI (or RBr), *t*-BuOK, DMF, 80 °C.

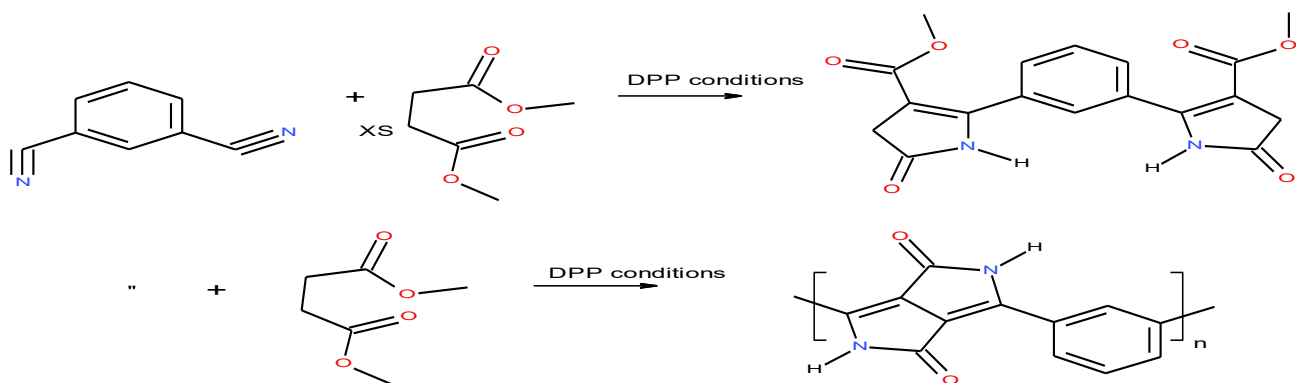
tronics. The chromophore was originally prepared as disperse dyes in the mid-1970s owing to its brilliant color and excellent photochemical stability.⁴³⁷ Benzodipyrrolidone can be viewed as an "extended" DPP by fusing two pyrrolinones to cyclohexa-1,4-diene, which should provide stronger intermolecular interactions and larger π - π overlapping. Moreover, the quinodimethane moiety in benzodipyrrolidone, in analogy to the tetracyanoquinodimethane (TCNQ), is expected to exhibit extensive π - π stacking. On the basis of the molecular geometry and electronic structure, benzodipyrrolidone should be a promising building block for organic electronics. The benzodipyrrolidone-based polymer semiconductors were developed recently and show encouraging performance in both OTFTs and OSCs.

The above scheme and quote comes from this extensive review:

Guo, Xugang, Antonio Facchetti, and Tobin J. Marks. "Imide-and amide-functionalized polymer semiconductors." *Chemical reviews*, 114.18 (2014): 8943-9021.

My idea has the lactam nitrogen in the same position as its in DPP while the above is

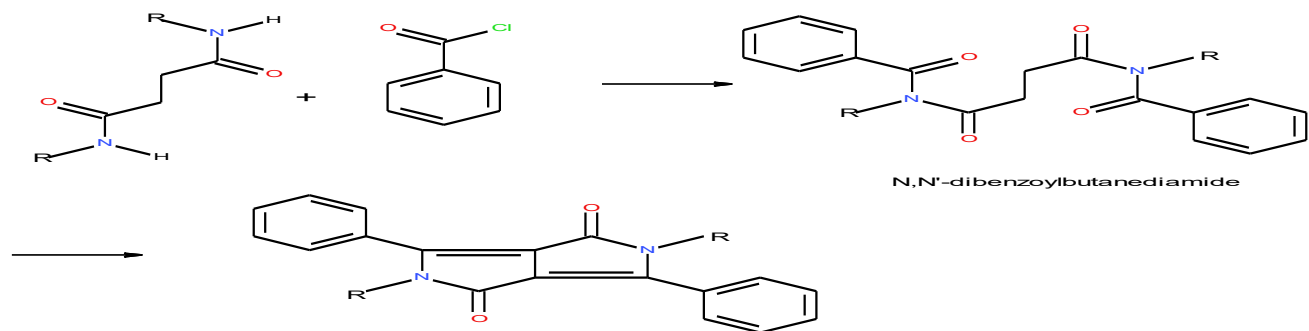
really a separated isoDPP.



Scheme3: Can difunctional CN aromatics lead to separated and polymeric DPP's? Using DPP condensation conditions (hindered strong base/ heat); I propose that polymeric DPP would result when the reagents are balanced and the separated monomer idea would require excess succinate ester but the product could be post condensation polymerized through the carboxyl groups or the esters can be converted to ketones and condensed as in scheme 2. The lactam nitrogens can be derivatized as usual. The separated DPP's lactam nitrogens can also be chain extended if derivatized with difunctional coupling groups (this is possible with all of these ideas resulting in polymers or oligomers, if so desired). Otherwise, typical N-R groups employed in DPP technology can be used.

Bis-imides

Basically, reaction of succinate esters with primary amines to form N,N'-bis-amides which can be treated with acid halides as follows:



Scheme 4: Cyclization of the bis-imide would require a very strong hindered base like LiOtBu and probably acid catalyst and/or heat to dehydrate the intermediate. Should this synthesis be facile then this would be a simpler DPP synthesis because synthesis of the lactam R group would not be a separate step after cyclization as it is now.

My problem is that references to this type of reaction of imide enolates with imide carbonyls has so far been limited. The following references are worth considering, however:

Collado, M. Isabel, et al. "Metalation vs nucleophilic addition in the reactions of N-phenethylimides with organolithium reagents. Ready access to isoquinoline derivatives via N-acyliminium ions and Parham-type cyclizations." *The Journal of organic chemistry*, 62.7 (1997): 2080-2092.

Hauck Jr, Fred P., and Jane T. Fan. "Arylsuccinimides. I. Alkylation and acylation studies." *The Journal of Organic Chemistry*, 34.6 (1969): 1703-1708. (actually shows that imides can self-condensate).

Leading me to think that it is not well known? There are references to the addition of Grignards to the imide carbonyl so I think other nucleophiles would also add especially if ring formation is also a driving force.

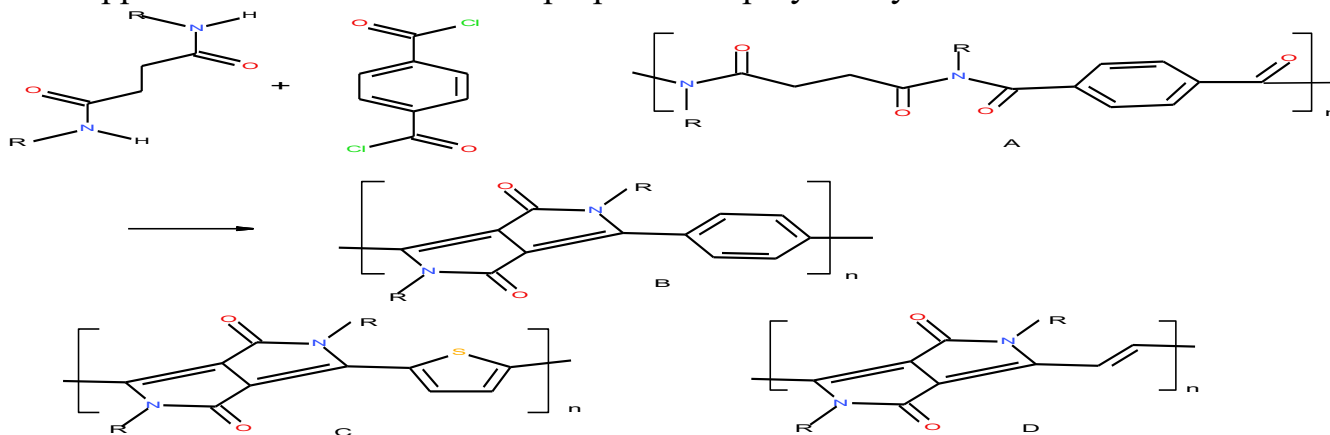
FLITSCH, Wilhelm, and Stefan R. SCHINDLER. "Alkenylation of Imides and Activated Amides." *Synthesis*, 1975.11 (1975): 685-700.

Zabicky, Jacob. "chemistry of amides." (1970). Wiley Functional Groups, p.368-369.

I also believe these proposals do not conflict with Baldwin's rules.

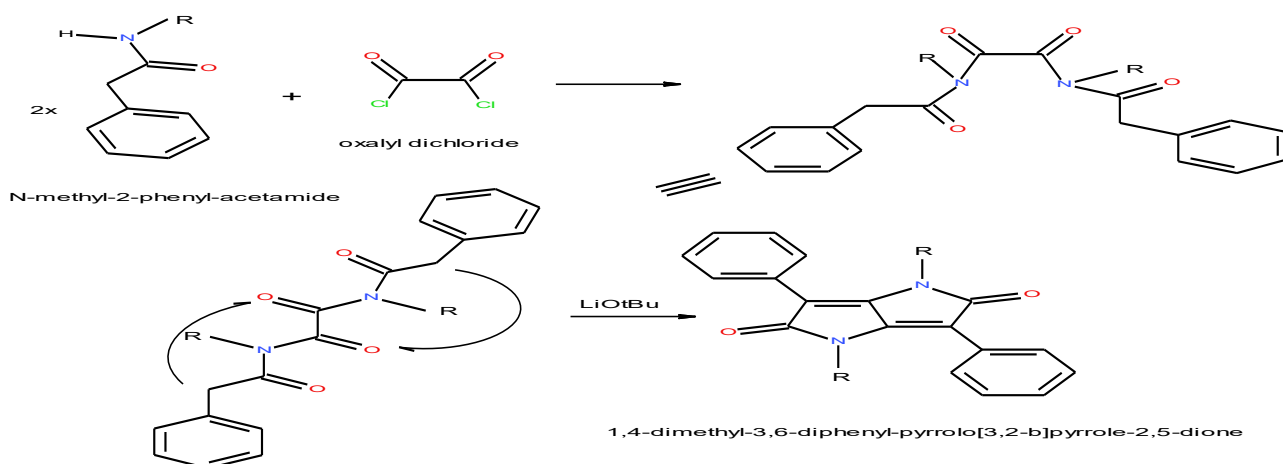
Gilmore, Kerry, Rana K. Mohamed, and Igor V. Alabugin. "The Baldwin rules: revised and extended." *Wiley Interdisciplinary Reviews: Computational Molecular Science*, 6.5 (2016): 487-514.

This approach to DPP's can also be proposed for polymer synthesis:



Scheme 5: C & D are alternative structure illustrating the flexibility of this idea. Should this route prove unreliable then the most probable route to polymeric derivatives; however, is to put a coupling moiety on the phenyl or other heterocyclic aromatic groups and to post react them with a suitable electron donating oligomers or polymers similar to those employed in the extensive DPP literature (see US 8,946,376 B2 for many examples), with Suzuki or other coupling reactions, for example.

IsoDPP derivatives:

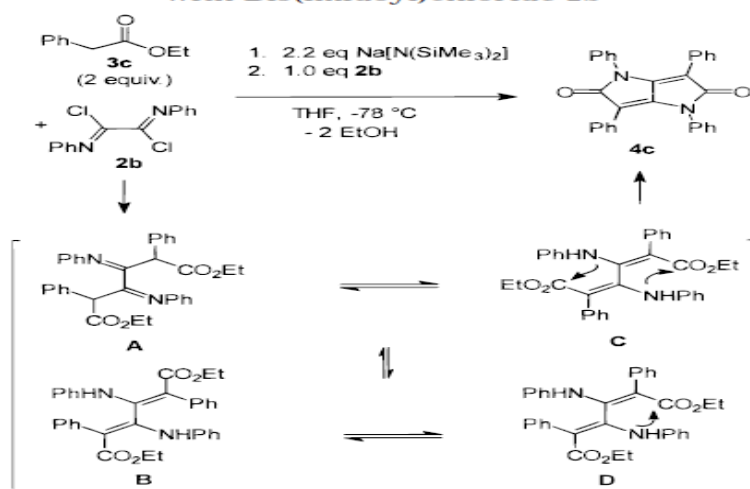


Scheme 6: Imide route to isoDPP derivatives. Here as before the aromatic moieties can be functionalized with typical coupling groups.

This idea like the previous one depends on the ability of imide enolates to add to other imide carbonyls. A strong hindered base such as LiOtBu and possibly a subsequent acid catalyst and/or heat to facilitate dehydration maybe required.

IsoDPP's have been synthesized by several routes. For example:

Scheme 3. Reaction of Ethyl Phenylacetate 3c with Bis(imidoyl)chloride 2b



Langer, Peter, Jörg Wuckelt, and Manfred Döring. "New and efficient synthesis of pyrrolo [3, 2-b] pyrrole-2, 5-diones by double-anion-capture reactions of ester carbanions with bis (imidoyl) chlorides of oxalic acid." *The Journal of Organic Chemistry*, 65.3 (2000): 729-734. (see their references for earlier procedures).

Helmholz, Falko, Rita Schroeder, and Peter Langer. "Synthesis of unsymmetrical bis (imidoyl) dichlorides of oxalic acid." *Zeitschrift für Naturforschung B*, 60.11 (2005): 1192-1196.

Welterlich, Irina, Olga Charov, and Bernd Tieke. "Deeply colored polymers containing 1, 3, 4, 6-tetraarylpyrrolo [3,

2-b] pyrrole-2, 5-dione (IsoDPP) units in the main chain." *Macromolecules*", 45.11 (2012): 4511-4519.

I showed these references to indicate that there is real interest in isoDPP's.

And that my approach would be worth considering.

Thanks for reading these proposals!

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Claims:(examples of possible claims, not meant to be limiting)

1. The reaction of N,N'-dialkyl amides of succinic acid with aromatic acid halides to form the corresponding imides.
2. The imides of claim 1 wherein the aromatic moieties are capable by suitable derivation to undergo coupling reactions.
3. The imides of claim 1 wherein said compounds are treated with hindered alkoxide bases resulting in DPP compounds.
4. The reaction of oxalyl dihalides with 2-phenylacetamides to form N,N'-bis imides.
5. The imides of claim 4 wherein, in a suitable solvent that they and bases such as LiOtBu are soluble in, are treated with said bases to form isoDPP.