Diels-Alder Trapping of Photochemically Generated o-Xylenols – Application in the Synthesis of Novel Organic Molecules and Polymers

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Introduction

Excited state intramolecular hydrogen abstractions are some of the best studied processes in organic photochemistry. Among this class of reactions, the photoenolization of o-methylphenyl ketones has received a considerable amount of attention from both a mechanistic and a synthetic perspective. This reaction, which typically occurs from the (n,π*) state, involves abstraction of an o-methyl hydrogen by the carbonyl oxygen to afford at triplet 1,4-biradical (Scheme 1). Decay of this biradical to the ground state affords two singlet biradicals, which are resonance equivalents of two o-hydroxy quinodimethanes or o-xylenols. These o-xylenols are designated E- and Z- to denote the relative positions of the –OH and exo-methylene groups. The Z-xylenol is short lived (a nanosecond or less, depending upon the solvent) and reverts to ketone via a 1,5-hydrogen shift. However, the E-xylenol cannot undergo this 1,5-hydrogen shift and has a significantly longer lifetime, up to microseconds in hydrogen bonding solvents. This is long enough to enable it to undergo chemistry – principally intramolecular cyclization to benzocyclobutanols or Diels-Alder cycloadditions.

In 1961, Yang and Rivas reported that o-xylenols generated by irradiation of either o-methylbenzophenone, 1a, or o-benzylbenzophenone, 1b, could be trapped via a Diels-Alder cycloaddition with dimethyl acetylenedicarboxylate to afford the corresponding tetralin derivatives, 2, in reasonable yields (Scheme 1). Since this early report, the Diels-Alder trapping of o-xylenols has been used extensively in the construction of fused 6-membered ring systems. With a few exceptions, these
Scheme 2. Generation and trapping of bis(o-xylenol)s from 2,5-dibenzoyl-p-xylenes.

**Trapping of o-Xylenols Generated from 2,5-Dibenzoyl-p-xylenes**

Our first entry into this chemistry dealt with the use of substituted 2,5-diaryloyl-p-xylenes, 3, as bis(o-xylenol) equivalents. These diketones are readily prepared by the reaction of the corresponding substituted arylmagnesium bromide with 2,5-dimethyl terephthalonitrile followed by acid hydrolysis of the resulting diimine. Irradiation of benzene solutions of 3 and a slight stoichiometric excess of representative dienophiles afforded the corresponding 1,5-dihydroxy-1,5-diaryloctahydroanthracenes, 4, in high yield (Scheme 3). These octahydroanthracenes can be converted into 1,5-diphenylanthracenes, 6, in two steps, catalyzed dehydration followed by dehydrogenation/aromatization with DDQ.
Scheme 4. Polymer formation from trapping of bis(o-xylenol)s with dimethyl acetylenedicarboxylate.

Diels-Alder trapping of o-xylenols generated from diketone 3 produced two isomeric bisadducts— one in which the two –OH groups are on the same face of the molecule, *syn*, and one in which they are on opposite faces, *anti* (Scheme 5). The structure of both isomers was confirmed by a combination of spectroscopy, X-ray crystallography, and chemical derivatization. The basic stereochemical and regiochemical outcome of this cycloaddition follows that observed by Block and Stevenson for o-xylenols derived from o-methylbenzophenone. Hydrogen bonding between the o-xylenol –OH and the ester group on the dienophile directs the cycloaddition process and results exclusively in bisadducts in which the –OH and ester are on vicinal carbons and are *cis* to each other.
Scheme 5. Stereochemical and regiochemical outcome for trapping of o-xylenols from 3.

The melting point of *anti*-4a is more than 150°C higher than that of *syn*-4a (295-296°C vs. 130-132°C). This large difference in melting points can be explained by the differences in modes of self-assembly between the two diastereomers. Intermolecular hydrogen bonding between *syn* bisadducts results in the formation of dimeric structures, since both –OH groups are on the same face of the molecule. However, the –OH groups of the *anti* bisadduct are on opposite faces and intermolecular hydrogen bonding produces columnar structures in which the bisadducts are directly superimposed on top of each other. A top-down view of the X-ray crystal structure of stacks formed from *anti*-4a (Figure 1) shows the perfect alignment of the phenyl substituents on each bisadduct. These pendant phenyls are separated by about 4Å (edge to edge distance). In essence, these columnar structures could serve as molecular scaffolds upon which certain functional groups could be attached to give materials with various properties such as
PTFE), but they are brittle. Efforts to improve the ductility of these films through the use of more flexible diketones are in progress.

\[
\begin{align*}
\text{Ar} &= \text{Ph, } 4-(\text{OC}_{12}\text{H}_{25})\text{Ph} \\
\text{Ar} &= \text{Ph, } 4-(\text{OC}_{12}\text{H}_{25})\text{Ph}
\end{align*}
\]

Scheme 6. Polyimides from trapping of o-xylenols from 3.

Similarly, polyesters 9 can be prepared both in solution (cyclohexanone or benzene) and in thin films by irradiation of diketones and a variety of commercially available bisacrylates having alkyl or oligo- (ethylene oxide) or (propylene oxide) spacing groups. As expected, these have lower glass transition temperatures (<160°C) than the polyimides described above. However the resulting films are significantly more
Scheme 7. Bisadducts from trapping of o-xylenols from 11.

Both *syn* and *anti* bisadducts are formed in this system as well, however, the *anti* isomer is formed in slightly higher yield than the *syn* – formation of anti 11a is favored 3:2 over *anti*-11a. This is in sharp contrast to bisadducts formed from 2,5-dibenzoyl-p-xylene, 3, where the *syn* isomer is the preferred photoproduct. The solubility behavior of bisadducts formed from these two isomeric diketones is also different. *Anti*-bisadducts produced from diketone 3, were insoluble in methanol and could be readily separated from photoproduct mixture by trituration. However, the *syn* bisadducts formed from diketone 10 were insoluble in methanol while the *anti* isomer was soluble. This suggests that *syn*-- and *anti*-- 11 may form different structures in the crystal than do *syn*-- and *anti*-- 4. X-ray crystallographic studies are underway to test this hypothesis.
Scheme 10. Polyimides from trapping of o-xylenols from diketone 10.

**Summary**

Bis(o-xylenol) equivalents are useful synthetic intermediates in the construction of polymers and hydroxyl substituted organic molecules which can organize by hydrogen bonded self-assembly into unique supramolecular structures. These polymers and supramolecular materials have potential use as coatings and thin films in aerospace, electronic and biomedical applications.

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