

Photo-Fries Reaction of Biphenyl System Crossover Photo-Fries Migration

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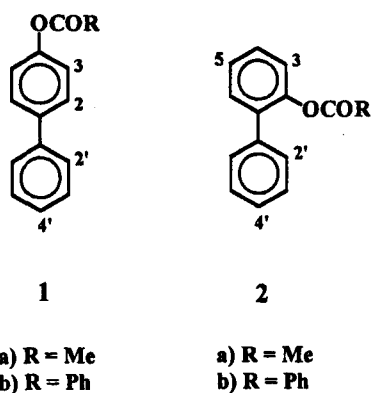
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Many reports¹ have appeared during the last decade in connection with the mechanism of the photo-Fries reaction. These contributions have confirmed that photo-Fries rearrangement occurs through homolytic cleavage of the carbonyl-oxygen bond from its singlet excited state to give a caged radical pair. In-cage recombination affords the migration products while hydrogen abstraction by the aryloxy radical leads to the formation of phenols, which are by-products.

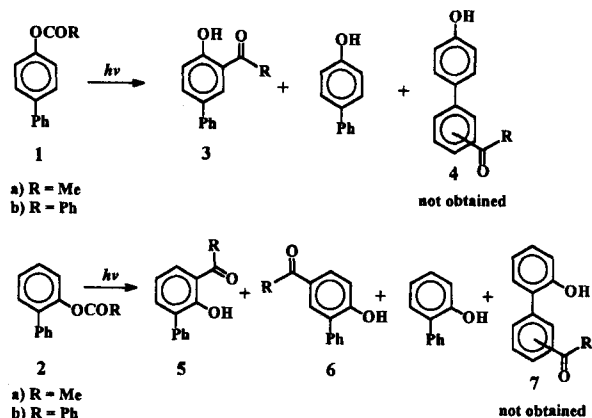
However, no reports have been made relating to the course of photochemical reaction of biphenyl system such as biphenyl acetate which is an active metabolite² of fenbuphen. In spite of the considerable interest attracted by the photochemistry of the phenol derivatives³ not only from the fundamental but also from the applied point of view,⁴ a little is known about the reaction processes in the presence of these compounds.

We have undertaken the photolysis of biphenyl acetate (**1a**, **2a**) and biphenyl benzoate (**1b**, **2b**) in order to investigate the possibility of carbonyl transfer not only to *ortho*- and *para*-position but also to the carbon-2' and carbon-4' position. Irradiation of these compounds was also performed in the presence of phenylphenol to investigate intermolecular photo-Fries reaction which gives crossover products.

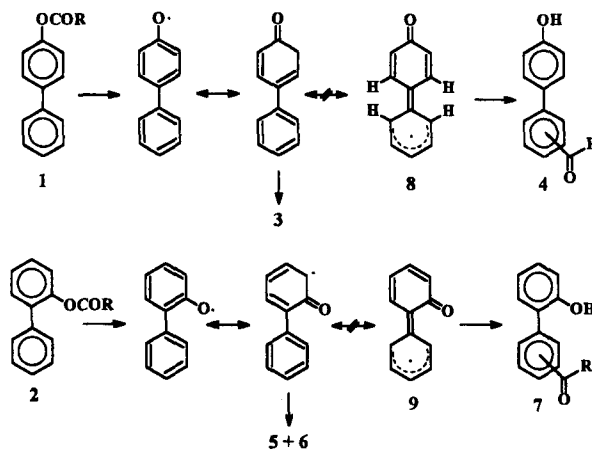


Irradiation of **1** with 254 nm-light in benzene produced a common Fries products, **3** (**3a**: 61%, **3b**: 54%) and irradiation of **2** in the same condition produced **5** (**5a**: 11%, **5b**: 23%) and **6** (**6a**: 6%, **6b**: 27%). However, the products (**4** and **7**) from acetyl and benzoyl transfer to the carbon-2' and carbon-4' position were not afforded presumably due to the restricted geometry of the intermediate **8** and **9** (Scheme 1 and 2).

Irradiation of 2-biphenyl acetate (**2a**) with 254 nm-light in the presence of 4-phenylphenol⁵ produced crossover products **1a** (<1%) and **3a** (<1%) as minor products. Irradiation of phenyl acetate (**10**) in the presence of 4-phenylphenol



Scheme 1.

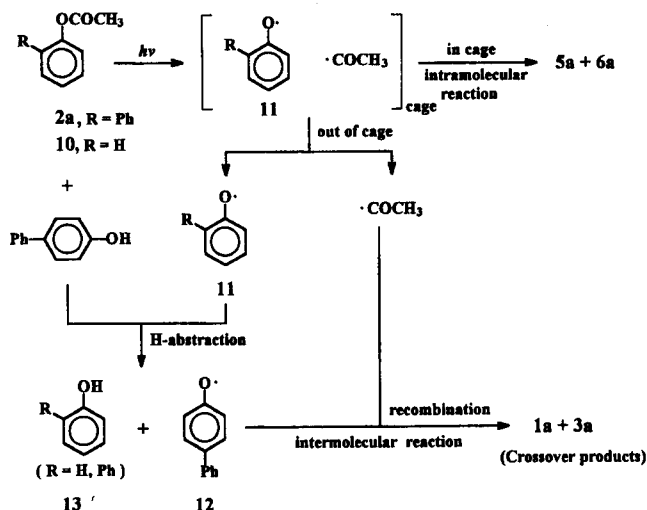


Scheme 2.

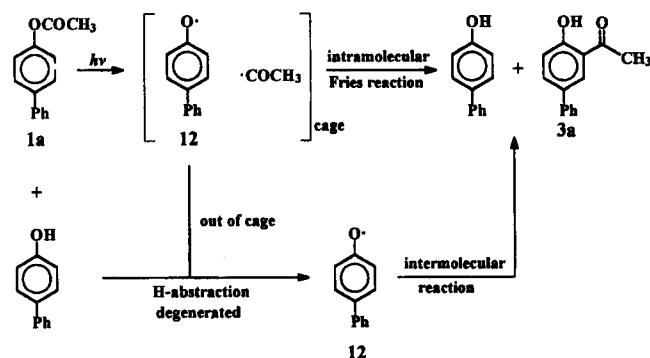
also produced **1a** (<1%) and **3a** (<1%) as minor products (Scheme 3).

Scheme 3 summarizes the photo-reaction of **2a** and **10** in the presence of 4-phenylphenol. After absorption of light by **2a** or **10**, a homolytic cleavage of the excited molecules occur at carbonyl and oxygen bond. The resulting pair of aryloxy and carbonyl radical would be restrained by a solvent cage until they combine to form rearrangement products **5a** (11%) and **6a** (6%). Some of the aryloxy radical (**11**) in solvent cage would eventually abstract hydrogen from 4-phenylphenol to form 4-phenylphenoxy radical (**12**) and **13**. This phenoxy radical, **12** combines with carbonyl radical to produce **1a** and **3a**.

Irradiation of 4-biphenyl acetate (**1a**) in the presence of 4-phenylphenol was not performed because intramolecular and intermolecular Fries products would be degenerated



Scheme 3.



Scheme 4.

(Scheme 4).

Though Fries product 3a would be mostly produced by intramolecular reaction, intermolecular reaction procedure must be considered as a trivial mechanism (Scheme 4).

We are trying to find the optimum reaction condition for

better yield of 3a by trivial mechanism and Fries reaction of phenyl acetate in the presence of deuterated phenol is under investigation to confirm trivial mechanism of photo-Fries reaction.

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- The mole ratio of the ester to phenylphenol in the irradiation mixture was 4 to 1.
- Structural identification of the compounds was performed by comparison of NMR spectra with those of authentic samples.

Synthesis of (-)-Macronecine via Condensation Reaction between Malate Enolate and Imine

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Pyrrrolizidine alkaloids, found in the diverse plant species, have long been the targets of many synthetic efforts due to their interesting biological activities with relatively simple structures.¹ Necine bases, having 1-hydroxymethyl group in the pyrrolizidine ring system, compose the majority of the pyrrolizidine alkaloids. Many synthetic methodologies have been developed for the efficient construction of this struc-

ture and, mostly, 2-pyrrolidinones have served as useful intermediates for the synthesis of the polyhydroxylated pyrrolizidine alkaloids.

Recently, we reported the diastereoselective condensation between the enolate dianion of diethyl malate and nonenolizable imine and showed diastereoselectivity in the 2-pyrrolidinone formation could be controlled with addition of