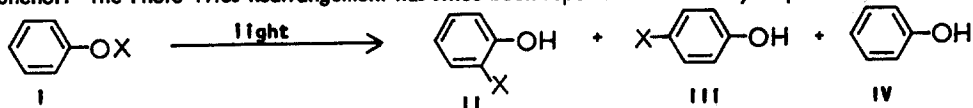


A MECHANISTIC STUDY OF THE PHOTO-FRIES REARRANGEMENT

C.E. Kalmus<sup>1</sup> and David M. Hercules  
 Department of Chemistry  
 University of Georgia  
 Athens, Georgia 30601 USA

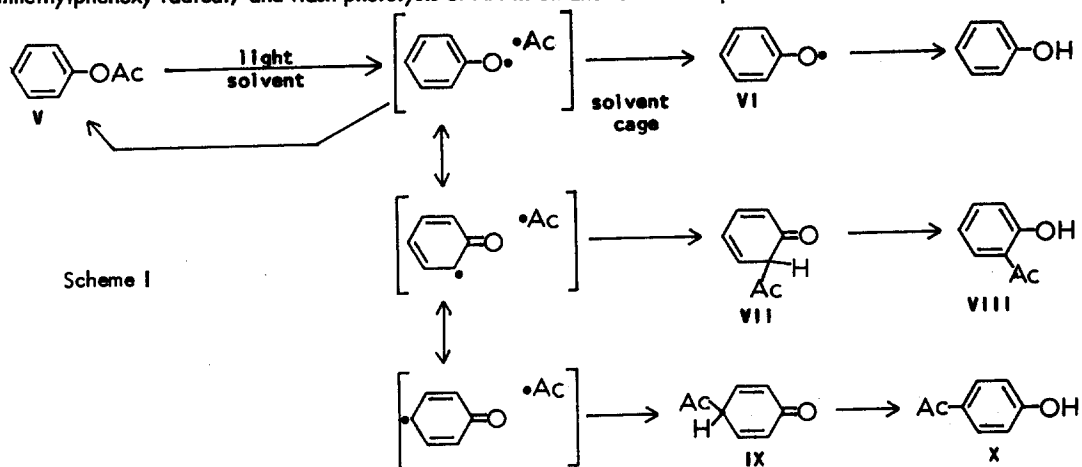
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The Photo-Fries Rearrangement, analogous to the classical Fries Rearrangement, was first reported in 1960.<sup>2</sup> Irradiation of phenyl esters was observed to produce both ortho and para rearrangement products and phenol. The Photo-Fries Rearrangement has since been reported for a variety of phenol derivatives



having a carbonyl group adjacent to the phenoxy oxygen.<sup>3</sup> Several phenyl ethers have also been observed to both rearrange and form phenols.<sup>4,5</sup> Similarly, nitrogen analogues of phenyl esters have been observed to rearrange and to form aniline. We have studied the photo-reactions of phenyl acetate (PA), 2,6-dimethylphenyl acetate (DMPA), acetanilide (AA), and 2,6-dimethylacetanilide (DMAA) in ethanol, hexane and 1,1,2-trichlorotrifluoroethane (Freon).

Flash photolysis of PA in each of the solvents produced a transient absorption spectrum of the neutral phenoxy radical (VI) with a lifetime of about 100  $\mu$ sec. A transient absorption spectrum of (VII) was also observed which decayed unimolecularly into 6-hydroxyacetophenone (VIII); first order rate constant of  $1.25 \pm .10 \text{ sec}^{-1}$ , in hexane at 25<sup>o</sup> C. Flash photolysis of DMPA in ethanol produced the 2,6-dimethylphenoxy radical, and flash photolysis of AA in ethanol and Freon produced the anilino radical.



Flash photolysis of DMPA in either hexane or Freon produced a transient absorption spectrum of a benzylic radical and not of a phenoxy radical. Analysis of the photoproducts of DMPA in ethanol, hexane, and Freon showed that benzylic addition was a major reaction pathway. Photolysis of oxygenated solutions of DMPA in ethanol, hexane, and Freon resulted in the formation of 2-formyl-6-methylphenyl acetate in 5%, 50% and 90% yields, respectively. The formation of the expected Photo-Fries products, 2,6-dimethylphenol and 3,5-dimethyl-4-hydroxyacetophenone, decreased from 90% in ethanol, to 40% in hexane and 5% in Freon. Similar results were found for photolysis of DMAA in ethanol and Freon.

In order to determine if the rearrangement and phenol-forming reactions were occurring from two different excited states, PA in ethanol was irradiated at several wavelengths from 230-270 nm. This wavelength region spanned the lowest energy uv absorption band for PA. No differences in the product ratios were observed as a function of wavelength.

The relative fluorescence intensities (RI) of a series of phenol derivatives were obtained in hexane: phenol (RI = 100), 2,6-dimethylanisole (RI = 79), phenyl ether (RI = 41), allyl phenyl ether (RI = 9), and phenyl acetate (RI = 0). These fluorescence intensities show an inverse relationship compared to the respective Photo-Fries reactivity; i.e. a greater degree of reactivity resulted in less intense fluorescence. Since the uv absorption spectra for the compounds are similar, this constitutes evidence that the Photo-Fries Rearrangement probably occurs from the lowest excited singlet state.

The similarity of photolysis products of phenyl esters and phenyl ethers implies that the same mechanism occurs for each reaction. This is further indicated by the similarity of the uv absorption spectra of the phenols, phenyl ethers, and phenyl esters studied. The uv absorption of compound I is characteristic of the ArO moiety and independent of the nature of the X-group. The lowest energy transition for phenol is  $\pi \rightarrow \pi^*$  with a charge transfer from the oxygen into the ring.<sup>6</sup> The loss of charge from the oxygen weakens the O-X bond and could result in its eventual cleavage. Irradiation of phenols has in fact been observed to cause bond cleavage. Flash photolysis of phenols in non-polar solvents has been observed to produce homolytic cleavage of the O-H bond.<sup>7</sup> Also the first excited singlet state of phenol has a pKa of 4.0 compared to a ground state pKa of 10.0.<sup>8</sup>

This suggests that the mechanism of the Photo-Fries Rearrangement consists of the homolytic bond cleavage and cage recombination in Scheme I. This is the simplest of the mechanisms that have been previously proposed. The initially formed radical pair is either held together by a solvent cage until they react, or the two radicals drift apart and the phenoxy radical abstracts a hydrogen atom to form phenol.

In the case of phenyl ethers, strong evidence for the mechanism of Scheme I can be seen in the photoreaction of trans-but-2-enylphenyl ether in ethanol. The ortho and para photolysis products consisted of a mixture of cis and trans isomers and also of primary and secondary adducts of the alkyl chain.<sup>5</sup> The resonance structures of the alkyl radical fragment show how the cis/trans isomerization and the reactions at the primary and secondary sites can occur.



In addition to the uv absorption and reaction product similarities of phenyl esters to phenyl ethers, the observations of the phenoxy radical VI and of the cyclohexadienone VII are further

evidence for the mechanism of Scheme 1. The cyclohexadienone is a necessary intermediate in a radical recombination mechanism.

The unusual reactions observed with DMPA provide an insight into the role of the carbonyl group in the Photo-Fries Rearrangement. Since the initial excitation produces an electron deficiency at the aryl oxygen, the adjacent electron rich carbonyl provides a source of charge to make up some of the deficiency. Donation of charge from the carbonyl to the aryl oxygen would serve to strengthen the otherwise weakened O-CO bond. This would reduce the probability of bond cleavage and activate the carbonyl. It is this activation of the carbonyl that produces the benzylic radical by an intramolecular benzylic hydrogen atom abstraction.

The degree of carbonyl participation in excited state reactions is affected by substituents and solvents. Situations that reduce the possibility of carbonyl participation, increase the Photo-Fries reactivity of a compound. For example, electron withdrawing groups substituted on the carbonyl have been observed to increase Photo-Fries reactivity.<sup>9</sup> This occurs because the electron withdrawing group causes the carbonyl to bond its electrons more tightly, thereby reducing the probability of carbonyl participation in the excited state. The lack of carbonyl participation allows the weakened O-CO bond to cleave. Ethanol has often been observed to increase Photo-Fries reactivity. The ethanol can hydrogen bond to the carbonyl oxygen electrons, and again a reduced participation in the excited state produces an increased reactivity. Conversely, electron withdrawing groups on the ring increase the possibility of charge transfer from the carbonyl to the aryl oxygen and serve to decrease reactivity.<sup>9</sup>

The similarities of the photolysis products and flash photolysis observations from AA and DMAA imply that a similar mechanism is occurring with the nitrogen analogues.

In summary, we feel that the Photo-Fries Rearrangement is primarily a reaction of the aryloxy functional group. Excitation of this group leads to a homolytic cleavage of the ArO-X bond, and subsequent radical recombination produces the rearrangement products. The radical stabilizing ability and other characteristics of the X-group also affect the reaction.

A more detailed discussion of the results and mechanism will be reported elsewhere.

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