

PHOTOCHEMICAL REARRANGEMENT OF PHENYL BENZOATE IN THE PRESENCE OF
CYCLODEXTRINS AND AMYLOSE

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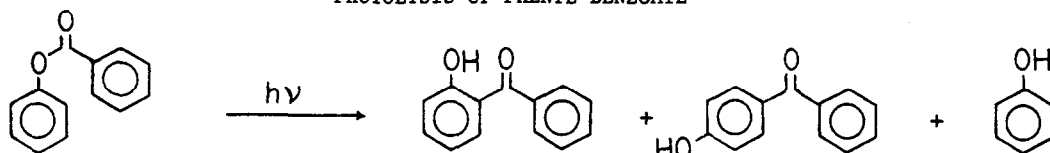
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Abstract: The photorearrangement of phenyl benzoate in aqueous medium is changed in the presence of cyclodextrins or amylose; the ortho/para migration ratio is altered in favor of the para position.

Cyclodextrins form inclusion compounds in aqueous solution with a variety of substrates and can catalyse several reactions. These systems are considered to be enzymes models and some interesting rate enhancement have been found¹. More recently, studies on the cyclodextrin reactions have been focused on their selectivity².

It is now established that amylose [linear (1→4)- α -D-glucose] can adopt a helical conformation and forms complexes with iodine and many organic molecules³. Unlike cyclodextrins, amylose has never been used to catalyse organic reactions. We wish to report here the influence of amylose or cyclodextrins on the photorearrangement of phenyl benzoate. Irradiation were performed in an immersion type quartz reactor with a 450 watts Ace-Hanovia UV lamp, medium pressure mercury arc. Phenyl benzoate (1 mmol) was stirred in 450 ml of distilled water in the presence of a host compound (α and β -cyclodextrin: 1 mmole, amylose⁴: 1 g, soluble starch⁵: 2 g) for 1h before the photoreaction (24h). The product mixtures were analysed by quantitative vapor phase chromatography (flame ionisation detector, Silicone oil SE-30 column, relative response ratio method). The results are summarized in the Figure. Both cyclodextrins have a similar effect, shifting the ortho/para ratio to 1.8 - 1.9 from the 4.0 value in pure water. Amylose and soluble starch⁵ (which contains 27% amylose and 73% amylopectin) also favorise the para over the ortho migration with a ratio of 2.4 and 3.3 respectively. These data can be explained by assuming that the substrates form organized assemblies with cyclodextrins or amylose, and react according to the mechanism proposed for the photo-Fries reaction which involves fragmentation to give free radicals followed by extensive geminal recombination. The change in the migration pattern can be explained as the result of the geometric blocking role of the cyclodextrin or the amylose α helix chain. An aromatic nucleus bonded to the host may have its ortho positions well shielded while the para position may be more accessible and might be involved in the reaction. Another explanation involves the non-polar micro-environment provided by the cavity of cyclodextrins and amylose^{3,6}. Plank *et al.*⁷ found an influence of solvent polarity on the photorearrangement of phenyl benzoate. A polar solvent such as methanol gave a o/p ratio of 0.75, whereas a less polar solvent such as ether gave a o/p ratio of 0.50. We are presently studying the influence of amylose on the selectivity of other organic reactions.

PHOTOLYSIS OF PHENYL BENZOATE



SOLVENT	RELATIVE YIELDS ⁸ (%)			CONVERSION OF ESTER (%)	ORTHO/PARA RATIO
	HYDROXYBENZOPHENONE				
	ORTHO	PARA	PHENOL		
H ₂ O	80	20	0	62.8	4.0
H ₂ O + STARCH	73	22	5	92.0	3.3
H ₂ O + AMYLOSE	68	28	4	66.4	2.4
H ₂ O + α-CDX (EQUIMOLAR RATIO)	63	34	3	55.1	1.9
H ₂ O + β-CDX (EQUIMOLAR RATIO)	64	36	0	28.4	1.8

Acknowledgements

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References and notes

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4. Amylose was purchased from Sigma Chem. Co. and was free of amylopectin. The viscosity-average molecular weight was found to be 4.35×10^5 from viscosity measurements in dimethyl sulfoxide.
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8. The averages of the values for triplicate runs, which coincide with each other within 5%.

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