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THE PHOTO-FRIES REACTION OF ARYL ESTERS: EFFECT OF SOLVENT ON PRODUCT DISTRIBUTION

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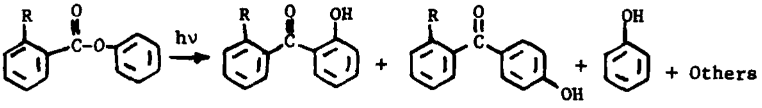
The mechanism of the photo-Fries rearrangement of aryl esters has been investigated by a number of workers.(1) In this regard, it has been reported by some workers that the rearrangement is unaffected by the nature of the solvent.(2) It has also been reported that the rearrangement is influenced by the solvent.(3,4)

Pertaining to this problem, we would like to report some of the results of our studies on the mechanism of this rearrangement. The photo-rearrangements of phenyl benzoate (R=H) and phenyl *o*-toluate (R=Me) have been studied in several solvents. The reactions were run in sealed Vycor tubes using a Rayonet "Merry-Go-Round" reactor employing 3000 A lamps. The reactions were carried out to 50-90% completion and the yields of products II and III (R=H,Me) were determined. In each case, various amounts of phenol (IV) were detected (VPC). The results are compiled in Table I.



I II III IV

It is apparent from these data that the yields of rearrangement products are dependent on the nature of the solvent. Additional experiments with phenyl benzoate in ether-methanol solvent mixtures indicated that the yield of phenol was also solvent dependent. In these experiments the yield of rearrangement products increased from 36% in ether to 79% in methanol. The yield of phenol was found to decrease with increasing concentration of methanol (Table II).

Table I

Photolysis of Phenyl Benzoate and Phenyl _o_-Toluate in Various Solvents

Solvent[a]	% Conversion	Fries Product[b], % Yield	$\frac{II}{II + III} \times 10^2$
Phenyl Benzoate:[c]			
cyclohexane[d]	4	40	28
ether	99	33	33
dioxane[d]	4	36	36
benzene[d]	4	33	39
isopropanol	81	77	46
methanol	79	76	47
methanol[e]	98	76	55
ethanol[f]	38	78	53
_t_-butanol[e]	98	84	57
Phenyl _o_-Toluate:[g]			
benzene	30	30	73
ether	72	28	78
methanol	80	57	63
isopropanol	72	60	65

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[a] The solvent, benzene & methanol, were spectral grade. The others were of reagent grade and were redistilled and dried before use.

[b] The % Fries product is the sum of the yields of II & III.

[c] The yields of products were determined by vapor phase chromatography (internal standard method) and are based on consumed ester. Ester concentration was 0.100 ± 0.005 M in each run.

[d] R. A. Finnegan and J. J. Mattice, _Tetrahedron_, **21**, 1015 (1965).

[e] In these runs 2537 A lamps were used.

[f] W. M. Horspool and P. L. Pauson, _J. Chem. Soc._, 5162 (1965).

[g] The yields of products were determined by NMR (internal standard method) using the relative intensity of CH_3 peaks and are based on consumed ester. Ester concentration was 0.090 ± .002 M in each run.

Table II

Photolysis of Phenyl Benzoate in Ether-Methanol Solvent Mixtures[a]

Methanol Vol. %	% Conversion	Fries Product[b], Yield Mole %	II/III	Phenol Yield Mole %
0	92	36	0.50	44
30	93	48	0.55	32
50	96	58	0.65	23
70	98	67	0.71	17
100	99	79	0.75	13

[a] The yields of products were determined by vapor phase chromatography (internal standard method) and are based on consumed ester. Ester concentration was 0.10 M in each run.

[b] The % Fries product is the sum of the yields of II & III.

These results indicate that the photo-Fries reaction of these compounds is markedly affected by the nature of the solvent.* The solvents can be divided into two types, non-polar and polar, according to their effects. The polar solvents favor rearrangement and the non-polar solvents favor phenol formation. It is readily apparent that this effect is not merely a solvent dependent partitioning between an intramolecular rearrangement process and an intermolecular hydrogen abstraction process which leads to the formation of phenol. Both benzene and ether (non-polar solvents) give essentially the same results, but are vastly different in their H-donating ability. The possibility that this solvent effect is due to changes in the viscosity of the solvent media must also be discounted. Sandner and Trecker(2) have found that the quantum yield for the rearrangement of p-tolyl acetate was unaffected by a 100-fold change in viscosity of the reaction media.

However, these results are consistent with a mechanism involving two reactive excited states: one leading to the rearrangement products and the other to the formation of phenol. It is suggested that the relative stabilities of these two states respond to changes in the polarity of the solvent.(5) Coppinger and Bell(6) have recently suggested the intermediacy of a charge-transfer complex in these rearrangement reactions.

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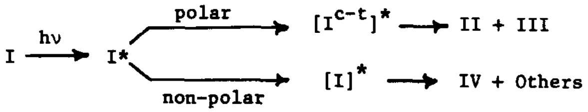
* The apparent increase in yield of II relative to III for the phenyl benzoate reaction is surprising and this aspect of the solvent effect is under investigation.



Although the present results can be rationalized on the basis of a charge-transfer intermediate, we have no direct evidence for its existence.

Experiments designed to determine the exact nature of the intermediates and the reactive excited states involved in this reaction are currently in progress.

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References

(1) For recent reviews: (a) D. Bellus and P. Hrdlovic, *Chem. Rev.* **67**, 599 (1967); (b) V. I. Stenberg, in "Organic Photochemistry," O. L. Chapman, Ed., Marcel Dekker, Inc., New York, N. Y., 1967, p. 127ff.

(2) M. R. Sandner and D. J. Trecker, *J. Am. Chem. Soc.*, **89**, 5725 (1967)

(3) E. D. A. Plank, Ph.D. Thesis, Purdue University, 1966; *Dissertation Abstr.*, **B27**, 415 (1966).

(4) After this was work completed , Finnegan and Knutson reported a similar solvent effect on the product distribution in the photorearrangement of 3,5-di-*t*-butylphenyl benzoate: R. A. Finnegan and D. Knutson, *Tetrahedron Letters* 3429 (1968).

(5) A similar explanation has been proposed to account for the solvent effects found in butyrophenone photochemistry: P. A. Leermakers and R. D. Rauk, *J. Am. Chem. Soc.*, **90**, 2246 (1968).

(6) G. M. Coppinger and E. R. Bell, J. Phys. Chem., 70, 3479 (1966).