Tetrahedron Letters No.30, pp. 3429-3432, 1968. Pergamon Press. Printed in Great Britain.

PHOTOCHEMICAL STUDIES, VII.[1] SOLVENT EFFECTS ON THE PHOTOLYSIS OF ARYL ESTERS: FRIES REARRANGEMENT *vs*. DECARBOXYLATION

R. A. Finnegan and D. Knutson
Department of Medicinal Chemistry, School of Pharmacy
State University of New York at Buffalo, Buffalo, N. Y., 14214, U. S. A.

(Received in USA 25 March 1968; received in UK for publication 2 May 1968)

An aryl ester (I), depending on its particular structure, gives rise to one or more of a variety of reaction products when irradiated with ultraviolet light. Although Fries rearrangement products are most commonly encountered[2,3] several examples of decarboxylation[4,5] and decarbonylation[5b,c-7] have been observed. In addition, solvolysis reactions[1a,8] (*e.g.*, when ethanol is used as solvent) as well as other processes leading to the corresponding phenol or to the carboxylic acid[4,9] are known. Finally, a special case of aryl-oxygen cleavage has also been reported.[10] These transformations are summarized in Figure 1.

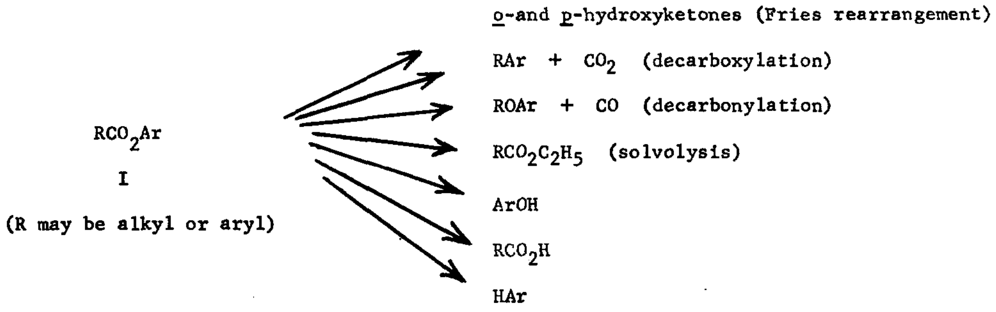


FIG. 1

We have been interested particularly in the decarboxylation process[5] and have sought means by which the product distribution could be controlled to preparative advantage. After initial unsuccessful attempts to exert such control by employing filters or sensitizers, we discovered that dramatic differences in product distribution could be observed by the simple expedient of changing the solvent. In Table I are collected gas chromatographic composition data for the reaction mixtures obtained after three hours irradiation of solutions of 3,5-di-*t*-butylphenyl benzoate (II) in various solvents. The reaction, which is outlined in Equation

TABLE I

Irradiation of 3,5-Di-t-butylphenyl Benzoate:[a] Solvent Effect on the Product Distribution.

Solvent	Composition of Reaction Mixture[b]			
	Starting Ester	3,5-Di-t-butylphenol	Hydroxy-ketone	Total Biaryl (ratio 3,5/2,5)
ethanol	22	30	48	--
2-propanol	29	34	37[d]	--
dimethylformamide	35	51	9[e]	--
n-hexane	10	55	8	15 (0.5)
tetrahydrofuran	6	53	12	28 (0.65)
glyme	2	41	5	51 (0.70)
dioxane	9	42	2	48 (0.60)
ether	--	56	--	44 (0.52)
ether-ethanol(9:1)	8	43	34	15 (0.67)

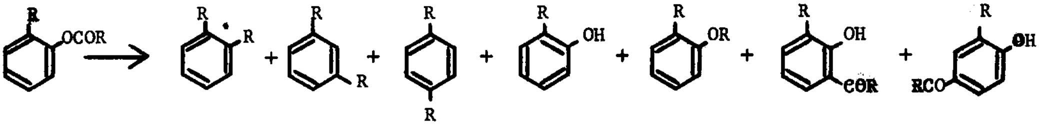
a) A 450 watt, medium pressure mercury lamp housed in a double-walled quartz immersion well was used.

b) The reactions were followed by gas chromatographic analysis and the figures listed represent the weight percentages after three hours reaction time.

c) The initial concentration of starting ester was 0.021 M.

d) This figure increased to 52% after 6 hours. After 17 hours, it had decreased to 16%, suggesting that the Fries product undergoes further change.

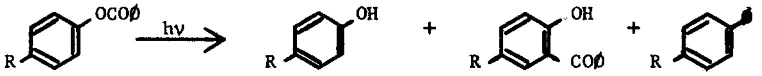
e) This figure had reached its maximum value (16%) after 1 hour. After 4 hours, the Fries product was no longer detected and a new product having a longer retention time was present instead.



(2)

of a 7:7:3 mixture of o-, m-, and p-di-t-butylbenzenes was then effected by chromatography on an alumina column.

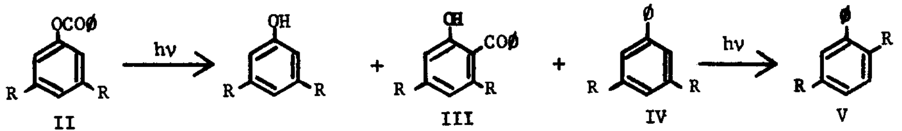
An additional example will suffice to illustrate this solvent effect. Irradiation of an ethanol solution of 4-t-butylphenyl benzoate (Equation 3, R = t-Butyl) for 10 hours provided a reaction mixture consisting of a 3:1 mixture of the Fries rearrangement product and the



(3)

corresponding phenol as the sole products detected by gas chromatography. This reaction had been studied previously by Kobsa;[12] however, we now find that when ether is used as the solvent, the decarboxylation product, 4-t-butylbiphenyl, m.p. 50-51° (lit.[11] m.p. 52.2°) is formed in

1, (R = t-Butyl) has been described previously[5a] excepting that the 2,5-di-*t*-butylbiphenyl (V), a product of secondary photochemical change,[5a,b] had not been detected. The results in Table I indicate that in polar solvents such as ethanol, the decarboxylation process is minimized while the formation of the Fries rearrangement product is enhanced. The reverse appears to be true when the non-polar, ethereal solvents are used. In addition, the reaction proceeds at a greater rate in these latter solvents as judged by the relative amounts of starting material remaining at the end of the arbitrarily chosen three hour reaction period. The final entry in the Table shows that the use of a mixed solvent system provided results consistent with the demonstrated effect.



(1)

To illustrate the preparative utility of this discovery, the crude mixture obtained after irradiation of an ethanol solution of II was chromatographed on an alumina column thus allowing the isolation of the Fries product, III, in 51% yield. Similar work-up of the mixture obtained after irradiation of a glyme solution of II led to the isolation in 41% yield of a 3:7 mixture of the biaryls IV and V. The properties of pure IV have been recorded earlier[5a] and the identification of V (which eluted first from the alumina column and was recrystallized from methanol) followed from its melting point, 93.5° (lit.[11] m.p. 94.2°), infrared bands at 889 and 826 cm^{-1} (1,2,4-trisubstituted pattern), ultraviolet maximum at 264 mμ, ϵ 850 (*ortho*-substituted biphenyl), and its 100 mc nmr spectrum which revealed the uniquely shielded *ortho* proton (3.02τ) to be a doublet with J=2.3 cps. The use of a Corex filter, while slowing the reaction down, serves to suppress the secondary rearrangement of IV to V without influencing the overall product distribution.

An interesting use of the photo-decarboxylation reaction was made in the preparation of hindered alkylbenzenes such as *o*-di-*t*-butylbenzene and *t*-butylmesitylene by the irradiation of the appropriate aryl pivaloate.[5b] We reported, for example, that *o*-di-*t*-butylbenzene could be prepared and isolated in 1% yield (along with lesser amounts of its *meta* and *para* isomers) by photolysis of benzene solutions of *o*-*t*-butylphenyl pivaloate (Equation 2, R = t-Butyl). This reaction has now been repeated using dioxane as a solvent and after 23 hours irradiation, gas chromatography showed the formation of the dialkylbenzenes in 17% yield! Isolation in 11% yield

12% yield along with the other products.

In conclusion, we suggest that the presently observed effects are due to solvent polarity rather than to the hydrogen-bonding ability[13] or viscosity[14] of the solvent.

REFERENCES

1. (a) For part VI, see R. A. Finnegan and D. Knutson, J. Am. Chem. Soc., **90**, 1670 (1968). (b) This investigation was supported by Grant GP-5785 from the National Science Foundation.
2. V. I. Stenberg, in "Organic Photochemistry," Vol. 1., O. L. Chapman, Ed., Marcel Dekker, Inc., New York, N.Y., 1967, p 127.
3. D. Bellus and P. Hrdlovic, Chem. Rev., **67**, 599 (1967).
4. R. A. Finnegan and J. J. Mattice, Tetrahedron, **21**, 1015 (1965).
5. R. A. Finnegan and D. Knutson, a) Chem. and Industry, 1837 (1965); b) Chem. Commun., 172 (1966); c) J. Am. Chem. Soc., **89**, 1970 (1967).
6. W. M. Horspool and P. L. Pauson, J. Chem. Soc., 5162 (1965).
7. D. H. R. Barton, Y. L. Chow, A. Cox, and G. W. Kirby, J. Chem. Soc., 3571 (1965).
8. J. C. Anderson and C. B. Reese, J. Chem. Soc., 1781 (1963).
9. D. Taub, C. H. Kuo, H. L. Slates, and N. L. Wendler, Tetrahedron, **19**, 1 (1963).
10. S. T. Reid and G. Subramanian, Chem. Commun., 245 (1966).
11. J. I. G. Cadogan, D. H. Hey, and G. H. Williams, J. Chem. Soc., 3352 (1954).
12. H. Kobsa, J. Org. Chem., **27**, 2393 (1962).
13. D. V. Rao and V. Lamberti, J. Org. Chem., **32**, 2896 (1967).
14. M. R. Sandner and D. J. Trecker, J. Am. Chem. Soc., **89**, 5725 (1967).