

## Biphasic Photochemistry: the Photo-Fries Rearrangement on Silica Gel

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**Summary** The photo-Fries rearrangement occurs when the substrate molecules are adsorbed on a silica gel-pentane slurry or on dry silica gel; the latter conditions are most effective when there is no free *ortho* position and substantial movement in the radical pair intermediate is required.

DESPITE extensive photochemical studies for many years, essentially all artificial systems studies have been in the liquid<sup>1</sup> or vapour phase. Studies in the crystalline state are an important exception and amongst these the work of Schmidt and his collaborators is especially notable.<sup>2</sup> In 1971, Leermakers showed,<sup>3</sup> in important preliminary studies, that some photochemical reactions could occur in molecules adsorbed on a silica gel surface in equilibrium with a liquid phase, a system in which there may, however, be complications.†

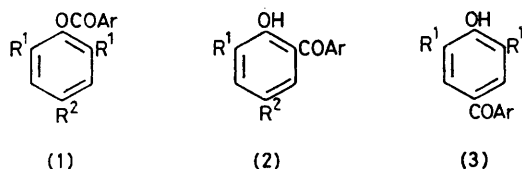
As part of a general study of photochemistry in biphasic systems we wished to know what restriction of molecular movement might be expected in radical pairs at a surface. We have used Leermakers' system (system B) and have also used dry silica gel<sup>4</sup> (system C) to study this question. The chemical system employed was the photo-Fries rearrangement [(1)→(2)/(3)] of aromatic esters since the mechanism

of this reaction in solution has, after some confusion, been established as involving homolysis in the excited singlet state, followed by recombination, in the solvent cage, of the radical pair.<sup>5</sup>

TABLE. Yield of photo-Fries rearrangement products<sup>a</sup>

Ester	System	Conversion (%) <sup>c</sup>	Yield <sup>b</sup> /%	
			(2)	(3)
(1a)	A	23	14 (3.5 <sup>d</sup> )	13 (42 <sup>d</sup> )
	B	27	12	10
	C	58	11	14
(1b)	A	22	19	24
	B	15	16	21
(1c)	A	29	37	—
	B	30	42	—
(1d)	A	22	35	—
	B	24	32	—
(1e)	A	40	—	5 (33 <sup>d</sup> )
	B	21	—	23
(1f)	A	20	—	9 (56 <sup>d</sup> )
	B	20	—	40
(1g)	C	31	—	70
	A	40	—	5
	B	31	—	18
	C	40	—	37

<sup>a</sup> Irradiations were carried out in quartz containers. The extent of the 'dark' reaction on silica gel was <<5%. All systems were nitrogen purged: (A) pentane, *ca.* 0.01 mmol ml<sup>-1</sup>; (B) slurry *ca.* 0.04 mmol per g silica gel and 3 ml of pentane; (C) dry, coated, silica gel, *ca.* 0.04 mmol g<sup>-1</sup>, agitated with nitrogen. The silica gel was 60–200 mesh heated to 210–230 °C (0.02 mmHg) for 24 h, and stored over phosphorus pentoxide before being coated. <sup>b</sup> Based on material consumed. <sup>c</sup> Based on recovered material, and determined spectroscopically or by g.l.c. <sup>d</sup> In propan-2-ol; see text.



- a**; R<sup>1</sup> = R<sup>2</sup> = H; Ar = Ph  
**b**; R<sup>1</sup> = R<sup>2</sup> = H; Ar = mesityl  
**c**; R<sup>1</sup> = H; R<sup>2</sup> = Me; Ar = Ph  
**d**; R<sup>1</sup> = H; R<sup>2</sup> = Pri; Ar = Ph  
**e**; R<sup>1</sup> = Me; R<sup>2</sup> = H; Ar = Ph  
**f**; R<sup>1</sup> = Pri; R<sup>2</sup> = H; Ar = Ph  
**g**; R<sup>1</sup> = Me; R<sup>2</sup> = H; Ar = mesityl‡

The results of the irradiation of the seven esters (1a–g) are shown in the Table. As a comparison the esters were also irradiated in pentane solution (system A), in which all yields are low. This is most probably a viscosity effect by comparison with literature determinations made in propan-2-ol which are given in parentheses in the Table.<sup>6</sup>

† We have shown that in certain cases more of the substance was in solution than previously suspected, and that there are problems in achieving an even distribution of the adsorbed molecules.

‡ Spectroscopic and precise mass data were in accord with this structure (3g). All others are known compounds.

In those molecules (**1a—d**) where there is a free *ortho* position and the amount of molecular movement required before recombination can occur is small, there is little difference amongst the three systems, *i.e.* photolysis and recombination can occur in the adsorbed molecule. It might be argued that in the biphasic system B reaction might still be occurring in solution; we estimate that *ca.* 1% of substrate is present in the pentane. Such a possibility is excluded for (**1a**) (system C) and the results are even clearer for those molecules (**1e—g**) having no free *ortho*

position. In these molecules, where the movement required is greater, the yields in system B are greater than in solution, and, more striking, even greater still in system C. In the case of compound (**1f**) the yield is greater than that reported in propan-2-ol.<sup>6</sup> These results are a preliminary indication of the restrictions imposed by dry silica gel, and studies are in hand to determine the 'walking distance' and its relation to structure and multiplicity.

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<sup>1</sup> The liquid phase includes the very viscous polymeric systems of considerable industrial importance.

<sup>2</sup> See, for example, "Solid State Photochemistry" in "Monographs in Modern Chemistry", Vol. 8 (Ed. D. Ginsburg), Verlag Chemie New York, 1976.

<sup>3</sup> C. H. Nicholls and P. A. Leermakers, *Adv. Photochem.*, 1971, **8**, 315. See also D. Fassler and W. Günther, *Z. Chem.*, 1978, **18**, 69; J. Griffiths and H. Hart, *J. Amer. Chem. Soc.*, 1968, **90**, 5296.

<sup>4</sup> H. Werbin and E. T. Strom, *J. Amer. Chem. Soc.*, 1968, **90**, 7296; G. Kortüm and W. Braun, *Ann.*, 1960, **632**, 104.

<sup>5</sup> W. Adam, *J.C.S. Chem. Comm.*, 1974, 289; C. E. Kalmus and D. M. Hercules, *J. Amer. Chem. Soc.*, 1974, **96**, 449; J. W. Meyer and G. S. Hammond, *ibid.*, 1970, **92**, 2189; J. S. Humphrey and R. S. Roller, *Mol. Photochem.*, 1971, **3**, 35; and refs. cited therein.

<sup>6</sup> H. Kobsa, *J. Org. Chem.*, 1962, **27**, 2293; D. A. Plank, *Tetrahedron Letts.*, 1968, 5423.