

Photochemical Fries Rearrangement of Phenyl Phenylacetate

by

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Compounds 2-hydroxyphenyl benzyl ketone (2) and 4-hydroxyphenyl benzyl ketone (3) were given by irradiation of phenyl phenylacetate (1) with low pressure UV lamp. The reaction seems to proceed via both inter- and intramolecular pathway. When benzene solution of 1 with trichloroacetic acid was irradiated with high pressure UV lamp, a maximum yield of 3 were found in a acid-substrate ratio ($\text{CCl}_3\text{COOH}/1=6.0$). In this reaction, the yield of 2 increased with concentration of the acid.

Key words : Phenyl phenylacetate, Fries rearrangement, Trichloroacetic acid.

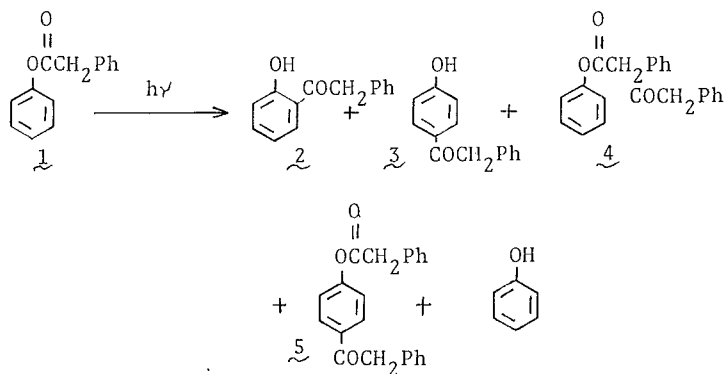
1 Introduction

Since 2-hydroxy-5-*t*-butylbenzophenone was caused under UV irradiation of *p*-*t*-butylphenyl benzoate,¹⁾ photochemical Fries rearrangement of several phenyl esters have tried and the mechanism of the reaction was also discussed.²⁾

In the AlCl_3 -catalyzed Fries rearrangement of phenyl phenylacetate (1), the reaction conditions were examined to get high yield of 2-hydroxyphenyl benzyl ketone (2) and 4-hydroxyphenyl benzyl ketone (3).³⁾ We also discussed the mechanism of the Fries rearrangement of 1 under various conditions (reaction temperature, reaction time, solvent and catalyst).⁴⁾

The present work deals with photochemical Fries rearrangement of 1 under irradiation with low pressure UV lamp and with high pressure UV lamp in the presence of trichloroacetic acid.

After methanol solution of 1 was irradiated with low pressure UV lamp, rearrangement products 2 and 3 were detected along with 2-(phenylacetyl)phenyl benzyl ketone (4), 4-(phenylacetyl)phenyl benzyl ketone (5) and phenol (GC and TLC).



The increasing product ratio (2/3) was observed in higher concentration of trichloroacetic acid under irradiation with high pressure UV lamp.

2 Experimental

2.1 Synthesis of phenyl phenylacetate 1. Compound 1 was prepared by heating of phenol and phenylacetyl chloride.³⁾ Products 4 and 5 were also prepared by condensation of 2 and 3 with phenylacetyl chloride, respectively. Pure compounds were obtained by repeated recrystallization from ethanol.

2.2 UV irradiation of phenyl phenylacetate 1 with low pressure UV lamp.

Each methanol solution of 1 0.53 g (2.5 mmol/1 ml) was irradiated with low pressure UV lamp (2537 Å) in the prescribed time interval. Each quartz text tube was arranged on a circuit apart 3 cm from centered light source. At the end of irradiation, the reaction mixture was analyzed by GC and TLC. When DMF, DMSO, carbon tetrachloride and cyclohexane were used as solvent, GC was used only in analysis of these reaction mixture. Gas chromatography was used Type GCG-30 mode in Yanagimoto Co. Ltd., Column : Apiezon Greese, Carrier gas : He, Column temperature : 283 °C, Gas flow rate : 50 ml/min., Sensitivity : 2.64 mV. TLC : silicagel-(toluene:benzene:methanol = 50:25:1). Each spot of the product on TLC was detected using iodine as color development.

2.3 UV irradiation of a mixture of 2-hydroxyphenyl benzyl ketone 2 and 4-hydroxyphenyl benzyl ketone 3 with low pressure UV lamp. Anhydrous ethanol solution (3 ml) containing 2 0.053 g (0.25 mmol) and 3 0.530 g (2.5 mmol) was irradiated with low pressure UV lamp for 80 h. Products 1, 4 and 5 were detected with 3 with TLC. In this reaction, a starting material 2 disappeared. The same procedure was also applied to the UV irradiation of 1. Each Rf value of products agreed with them of authentic samples.

2.4 UV irradiation of phenyl phenylacetate 1 with high pressure UV lamp in the presence of trichloroacetic acid. Benzene solution of 1 0.01 g (0.47 mmol/20 ml) containing trichloroacetic acid was irradiated with high pressure UV lamp (3700 Å) in merrygoround for 50 h. After the reaction mixture was washed with water and dried, 2 and 3 were separated each other with TLC (silicagel-benzene).

3 Results and discussion

When ethanol solution of 1 was irradiated with low pressure UV lamp for 20 h, a maximum yield of 3 and a minimum recovery of 1 were found, respectively. On the other hand, the yield of 2 decreased with irradiation time (Fig. 1). These results suggest that photochemical reverse Fries rearrangement of 2 and 3 may occur during UV irradiation.

After UV irradiation of ethanol solution of 3 with a trace of 2, was carried out for 80 h, products 1, 4 and 5 were detected with starting material 3 and without 2 (TLC) (Fig. 2, a). When ethanol solution of 1 was irradiated with low pressure UV lamp for 80 h, products 2, 3, 4, 5 and phenol were detected with unchanged 1 (TLC) (Fig. 2, b). The same result was also given by analysis using gas chromatography.

Products 2, 3 and 4 were also detected in the photochemical Fries rearrangement of 1 using DMSO, DMF, cyclohexane and carbon tetrachloride as solvent. The result shows that the photochemical Fries rearrangement of 1 proceeds with some intermolecularity.

Excited 1 with UV irradiation (a) re-arranges 2 and 3 intramolecularly (b).

A part of excited 1 dissociates into phenyl radical and phenylacetyl

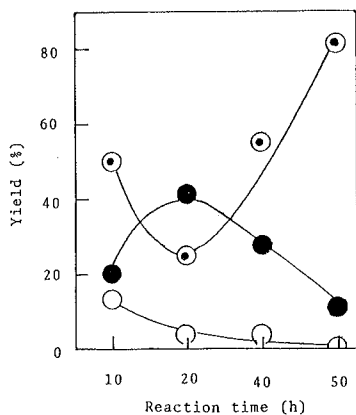


Fig. 1 Photochemical Fries rearrangement of phenyl phenylacetate 1

Each methanol solution of 1 0.53 g (2.5 mmol/1 ml) was irradiated with low pressure (2537 Å).

- ◐: Phenyl phenylacetate 1
- : 2-Hydroxyphenyl benzyl ketone 2
- : 4-Hydroxyphenyl benzyl ketone 3

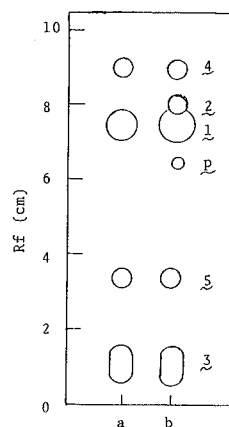
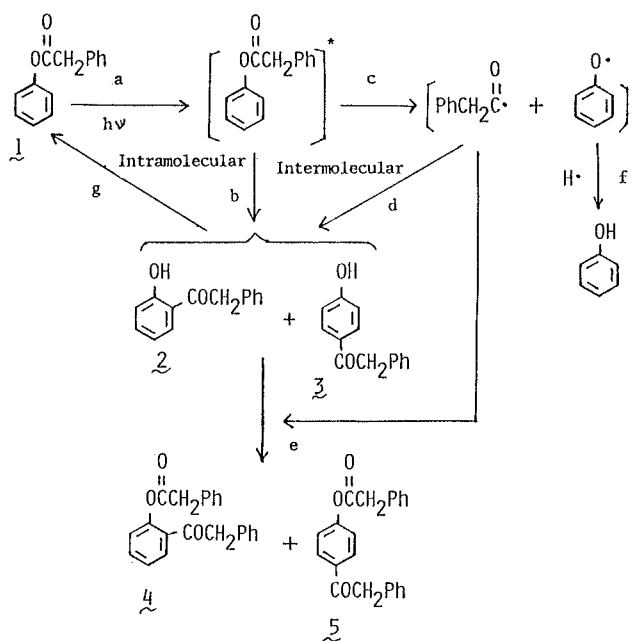


Fig. 2 TLC of a mixture of reaction products (2 and 3) (a) and 1 (b) after low pressure lamp irradiation for 80 h.

- 1: Phenyl phenylacetate
- 2: 2-Hydroxyphenyl benzyl ketone
- 3: 4-Hydroxyphenyl benzyl ketone
- 4: 2-(Phenylacetyl)phenyl benzyl ketone
- 5: 4-(Phenylacetyl)phenyl benzyl ketone
- P: Phenol



Scheme 1

radical (c), in which they cause 3 and 4 intermolecularly by recombination (d). On the other hand, secondary products 4 and 5 are given by attack on 2 and 3 with phenyl acetyl radical, respectively (e). Phenyl radical changes to phenol by getting hydrogen radical derived from process e (f), and photochemical reverse Fries rearrangement from 2 and 3 to 1 seems to proceed via intramolecular pathway (g) (Scheme 1).

A few benzene solutions of **1** containing trichloroacetic acid were irradiated with high pressure UV lamp for 20 h. A highest yield of **3** was given at a acid-substrate ratio ($\text{CCl}_3\text{COOH}/1=6$). Since the yield of **2** increased with added amounts of trichloroacetic acid, higher ortho-para ratio ($2/3$) was observed (Fig.3).

Photochemical Fries rearrangement of **1**, o-tolyl, m-tolyl and p-tolyl phenylacetate were carried out in benzene solution containing trichloroacetic acid and in neutral solvent. In general, lower yield of rearrangement products were found in benzene solution containing trichloroacetic acid. No regularity of ortho-para ratio was observed in these reactions (Table 1). The photochemical Fries rearrangement of protonated phenyl esters should await further investigation.

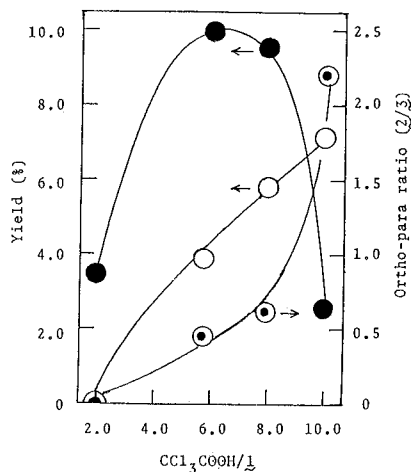


Fig. 3 Photochemical Fries rearrangement of: phenyl phenylacetate **1** in the presence of trichloroacetic acid

Each benzene solution of 1 0.10 g (0.47 mmol/20 ml) was irradiated with high pressure lamp (3700 Å) for 50 h.

○ : 2-Hydroxyphenyl benzyl ketone **2**
 ● : 4-Hydroxyphenyl benzyl ketone **3**
 ◐ : Ortho-para ratio ($2/3$)

Table 1 Photochemical Fries rearrangement of phenyl phenylacetates

X	CCl_3COOH (mmol)	Product yield (%)		o/p Ratio
		o-Hydroxy ketone	p-Hydroxy ketone	
H	No addition	7.7	14.0	0.55
	1.44	Not detected	6.7	0
	2.35	4.3	3.5	1.23
o-CH ₃	No addition	10.5	17.0	0.62
	1.42	7.9	8.6	0.92
m-CH ₃	No addition	18.8	7.6	2.47
	1.42	4.4	3.7	1.20
p-CH ₃	No addition	12.8	—	—
	1.42	4.9	—	—

Each benzene solution of phenyl phenylacetates (0.47 mmol/20 ml) was irradiated with high pressure lamp (3700 Å) for 20 h.

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