# THE PHOTOREACTIONS OF SOME ARYL ESTERS PHOTO-FRIES REARRANGEMENT VS PHOTODECARBOXYLATION— SUBSTITUENT AND SOLVENT EFFECTS

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Abstract—A number of substituted phenyl acetates have been irradiated by UV light. The reactions observed are: (1) cleavage of the O-acyl bond, leading to phenols, (2) photo-Fries rearrangements, leading to toluene derivatives. Methoxy substituents at the o- and/or p-positions were found to be displaced by the acyl moiety. The decarboxylation reaction is considerably enhanced by substitution at the o- and/or m-positions. In i-propanol and in cyclohexane no (or hardly any) decarboxylation is observed. In ether, however, the decarboxylation is pronounced. All these reactions proceed from the same excited state, the first excited singlet.

### INTRODUCTION

RECENTLY<sup>1</sup> we described the photoreactions of an aryloxyaryl ester (I) in various solvents. The major primary photoproduct was found to be the diaryl ether (IV), which must have resulted from the starting ester by the loss of carbon dioxide. This photodecarboxylation was found to be solvent-dependent, ether being the favoured



solvent. However, the reaction was complicated by another primary reaction namely, cleavage of the central ether-bond and subsequent processes.<sup>2</sup>

From the literature<sup>3</sup> it is known that the major photoreaction of aryl esters, the photo-Fries rearrangement is accompanied by several minor side reactions, one of which is a decarboxylation reaction.<sup>4, 5a, bc</sup>

$$ArOCOR \rightarrow ArR + CO_2$$

Only recently, Finnegan and Knutson<sup>6</sup> reported a dramatic solvent-dependence of this reaction, again ether being the favoured solvent.

In order to gain some insight into possible factors governing the course of the photoreactions of aryl esters, particularly with respect to the rearrangement and the decarboxylation, a number of substituted phenyl acetates was subjected to irradiation with UV light in various solvents.

## RESULTS

All the acetates irradiated in this study were synthesized from the corresponding phenols by either of two procedures. The Me substituted phenyl acetates were obtained by reacting the phenols with acetic anhydride catalysed by perchloric acid. In the case of the OMe substituted phenols this method led to acylation of the aromatic ring as well. Therefore, the OMe substituted phenyl acetates were obtained by reacting the phenols with acetic anhydride in pyridine.

Solutions of the acetates were irradiated with the unfiltered light of a high pressure mercury lamp (Hanau TQ 81) at 25°. Before and during the irradiation the solutions were flushed with nitrogen.

In some cases the expected irradiation products were prepared by thermal reactions such as the Fries-rearrangement and the methylation of the phenols. In some cases the irradiation products were isolated by means of chromatography. Characterization was achieved by spectroscopic methods (IR and NMR).

It can be seen from Table 1 that the conversion after 8 hr irradiation (ether solution) varies considerably for the different esters. By withdrawing samples from the irradiated mixtures at regular intervals, it was noted that some irradiation products (phenols)\* passed through a maximum with time. The product yield vs time plots proved to be linear through 20% conversion in most cases. Therefore, it seemed more reasonable to compare product distributions at 20% conversion of the starting ester. These results are collected in Table 2.

Generally, cleavage products (phenols),<sup>†</sup> products arising from a photo-Fries rearrangement to o- and/or p-positions, and decarboxylation products were found. The photo-Fries rearrangement did not take place when the o- and/or p-positions were substituted by Me groups as has been observed before. However, when OMe groups occupied the o- and/or p-positions, these substituents were found to be displaced by the acyl moiety. The displacement of the OMe group during the photo-Fries rearrangement was recently reported for the first time by Bradshaw *et al.*‡ Very little or no rearrangement to the p-position was found to take place when both o-positions were occupied by Me or OMe groups, e.g. 2,6-dimethylphenyl acetate

<sup>\*</sup> The photo-Fries and decarboxylation products were stable to the irradiation conditions.

<sup>†</sup> The fate of the free acyl radical is not known and has not been looked at.

<sup>&</sup>lt;sup>‡</sup> Our thanks are due to Professor J. S. Bradshaw for communicating his results prior to publication.<sup>7</sup>

	Ya	etate	1			Solvent	Сопуп	Phenol		+Frics	p-Frics	Decarbox
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	<u>ک</u>	$\langle \rangle$	Ŗ				- <b>2</b>	n 1	- <b>2</b> *	- <b>*</b>	0 <sup>C</sup> ™e	- <b>~</b>
	ы	<u>,</u>	4	S	9							
F		I	1	I	I	Ether	47-7	25-4		23-9	13-6	1-7
						i-PrOH	89-2	28.5		9-1	13-3	z
						C <sub>6</sub> H <sub>12</sub>	21.8	trace		43-0	11-4	ક
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						i-PrOH	72·1	36-2		32·1	ż	ድ
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•	Mc	1	Me	ļ	Me	Ether	0-06	5.6	I	I	ł	24-8
2	Mc	I	OMe	ł	Me	Ether	<b>93</b> .8	3-4	I	ł	g	31-4
90	OMe		I	I		Ether	68·1	19-3	19-9	3.9	11-8	8·8
0	OMe	ł			OMe	Ether	42-9	13-7	l	£	i	21-0
9	I	I	OMe	Ι	I	Ether	64·5	16-3		<b>38</b> ·1	7-3°	5.8
П		OMe	I	OMe	ļ	Ether	0-66	19.3		31-7	ċ	2·1
						i-PrOH	<b>69-3</b>	15.1		45:3	¢.	ይ
						C <sub>6</sub> H <sub>12</sub>	26-0	8·2		61.5	ć	ይ

TABLE 1. THE IRRADIATION "OF SOME ARYL ACETATES PRODUCT VIELDS" AFTER AN 8 HR DRRADIATION PERIOD

<sup>•</sup> The unfiltered light of an HP Mercury lamp (Hanau TQ 81) was used throughout. Irradiations were carried out at 25° under N<sub>2</sub>. All concentrations were 10<sup>-2</sup>M.

\* Product yields were determined by GLC and are expressed in mole % based on consumed starting ester. The consumed starting ester is not completely accounted for, partly because of inevitable tar-formation.

Displacement of an OMe group.

Decarbox	Re Me	R <sub>3</sub>		6 6	S	8.5	17-0	6-8	15-7	8	30	34-1	28-9	9.4	20-5	6.1	6.4	8	90
p-Fries	R <sub>6</sub> H	R <sub>s</sub> Me		14-3 25-2	12.7	10-4	3.8	ł	ć	¢.,	د.	I	9	16-7	i	3.7	¢.	ć	6
o-Fries		R <sub>5</sub> R <sub>4</sub> R <sub>3</sub>		25-9 31-4	42.2	I	ļ	S0-4	4·5	19-4	30-1	1	-	2.75	90	32-9	40-9	63-6	61-3
						17-0	I					1	I	17.6					
nol	H R <sub>2</sub>			214 18:2	trace	22-7	21-3	39-7	26-5	20-3	14-5	19-2	6·8	26-0	16.2	17-5	27-3	20-5	10-6
Solvent Phe	2	, , , , ,	i	Ether i-PrOH	C <sub>6</sub> H <sub>12</sub>	Ether	Ether	Ether	Ether	i-PrOH	C <sub>6</sub> H <sub>12</sub>	Ether	Ether	Ether	Ether	Ether	Ether	i-PrOH	C <sub>6</sub> H <sub>12</sub>
	ļ		9	ł		1	Me	Ι				Mc	Me		OMe	1	ł		
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	ж- <sup>1</sup> /2-ж	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	4	I		ł	1	Me	I			Mc	OMe	I	Ι	OMe	 •		
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Acetate	ļ		~	 		2 Me	3 Me	4	<b>S</b>			6 Mc	7 Me	8 OM	9 OM	10			
1	L																		

6018

Table 2. The irradiation of some aryl acetates product yields  $^{\rm A}$  t 20 % conversion of starting ester

<sup>e</sup> See Table 1. <sup>b</sup> See Table 1.

' See Table 1.

Table 3. The irradiation" of some arve acetates in ether substituent effect on product yields<sup>4</sup> at 20% conversion of starting ester

Decarboxylation	Мс	R <sub>6</sub> K <sub>1</sub>	R, R, R,			1-0	12-1	24:3	9-7	22-4	48-7	41-3	13-4	29-3	8-7	9-1
p-Frics	H, O	R <sup>4</sup>	R K K	U Me		1-0	0-7	0-3	I	¢.	ł	8	1-2	i	0-3	ċ
rics	о <sup>н</sup>	R <sub>6</sub> C Me	R, R, R,			1-0		I	1-9	0-2	1		0-2	9	1.3	1.6
0-Fi	о́н Ю	Me <sup>-C</sup> <sup>C</sup> <sup>R</sup> <sup>2</sup>	R <sub>5</sub> R <sub>5</sub> R <sub>5</sub>				1:3	I			I	1	14			
Phenol	H_O	R <sub>6</sub> R	R <sub>5</sub> R <sub>5</sub>			1-0	1.1	10	1-9	1:2	<b>6</b> -0	0-3	1-2	0-8	0.8	1:3
					6	I	Ì	Me	ł	I	Me	Me	I	OMe	I	ł
	   o_u	، ۲۳ (	K		S	1	I	I	Ι	Mc	Ι		I	ļ		OMe
		`~{\		. <b>~</b> *	4	I	ł	Ì	Mc	ļ	Me	OMe	I	ļ	OMe	 
Acetate		2 2	2		'n		I	I	1	. Mc	ł	1	 	 		WO .
•					7	-	2 Me	3 Me	4	 10	6 Mc	7 Me	8 0 V	9 ON	10	- 11

See Table 1.
Product yields were determined by GLC and are expressed in mole % based on consumed starting ester, and relative to the unsubstituted ester (1).
See Table 1.

(Table 2 ester 3:  $3\cdot8\%$ ), 2,6-dimethoxyphenyl acetate (Table 2 ester 9: uncertain)<sup>\*</sup> and 4-methoxy-2,6-dimethylphenyl acetate (Table 2 ester 7:  $0\cdot0\%$ ). In these cases a relatively high proportion of decarboxylation was observed. No OMe displaced product was found in the case of 2,6-dimethoxyphenyl acetate, again decarboxylation being the major reaction. No *p*-rearrangement was observed when both *m*-positions were substituted by Me or OMe groups. We have not been able to detect any decarbonylation products.<sup>7</sup> No indications were found for a phototransposition of the ring C atoms.

Three esters have been irradiated in ether as well as in i-propanol and cyclohexane. It may be noted that the photo-Fries rearrangement is favoured in i-propanol and the decarboxylation in ether. The rearrangement is the only reaction observed in cyclohexane, not counting the phenol forming reaction. This solvent-effect confirms previously reported results.<sup>1,6,7</sup>

#### DISCUSSION

Two mechanisms have been advanced for the photo-Fries rearrangement, the one postulated by Anderson and Reese<sup>8</sup> proceeding through a bridged biradical intermediate, and the other by Kobsa<sup>9</sup> starting with a dissociation of the O-acyl bond into a radical pair held in a solvent-cage.

All experimental evidence obtained so far points to the rearrangement being an intramolecular process. Kobsa<sup>9</sup> reached this conclusion from the absence of crossproducts in his irradiation experiments. Schutte and Havinga<sup>10</sup> concluded from isotopic studies that in the photo-Fries rearrangement of *p*-methoxyphenol acetate, the dissociating bond is still largely intact in the transition state (no isotope-effect). Sandner and Trecker<sup>11</sup> reached a similar conclusion for the photo-Fries rearrangement of *p*-tolyl acetate.

Finnegan and Knutson<sup>5c</sup> recently demonstrated that the photodecarboxylation also proceeds by an intramolecular process, via a transition state illustrated below (S)-(+)-3,5-di-t-butylphenyl 2-methylbutanoate giving decarboxylation with retention of configuration.



Two major effects on the ratio photo-Fries rearrangement vs decarboxylation have to be explained: the solvent-effect and the substituent-effect.

The remarkable solvent-effect has been suggested to be due to solvent-polarity.<sup>6</sup> The first factor to consider now is the multiplicity of the excited state(s) involved in these reactions. There is evidence that the photo-Fries rearrangement starts from an upper singlet state. Stratenus<sup>12</sup> found that the rearrangement of 1-naphthyl acetate  $(E_T = 60 \text{ Kcal/mole})$  was unaffected by triplet quenchers (anthracene,  $E_T = 42 \text{ Kcal/mole})$  and sensitisers (benzophenone,  $E_T = 68.5 \text{ Kcal/mole}$ , and triphenylene,  $E_T = 66.6 \text{ Kcal/mole}$ ). Sandner and Trecker<sup>11</sup> reported similar results for the rearrangement of *p*-tolyl acetate. If starting from a different excited state, the decarboxylation might result from the (lowest) excited triplet state. The solvent-effect according to Finnegan and Knutson<sup>6</sup> should then be, that polar solvents like alcohols favour

• The *p*-rearranged product could not be prepared nor isolated. However, no large unidentified peaks remained in the gaschromatograms.

reaction from an upper singlet, and less polar solvents like ethers favour reaction from the (lowest) excited triplet. If that were true, however, one would expect the yield of decarboxylated product to be highest in cyclohexane, and this is in contrast with the results. Therefore, information concerning the multiplicity of the excited state(s) involved in these reactions was needed.

The phosphorescence spectra of phenyl and of 3,5-dimethylphenyl acetate\* in EPA and in THF were broad and the structureless apart from a few shoulders. Nevertheless, the triplet energies could be approximated from the shoulder on the low wavelength side: phenyl acetate  $E_T = 83$  Kcal/mole, and 3,5-dimethylphenyl acetate  $E_T = 80$  Kcal/mole, both values representing lower limits. Sensitization experiments with acetophenone, which had already been done were unsuccessful, which is readily understood in the light of the triplet energies of the respective aryl acetates.<sup>†</sup> Therefore, quenching experiments with 1,3-cyclohexadiene<sup>13</sup> ( $E_T = 54$  Kcal/mole)<sup>14,15</sup> were carried out.

No change in product distribution was observed and no cyclohexadiene dimers<sup>16</sup> could be detected by GLC. It is therefore concluded that the excited state involved in the photodecarboxylation is not the (lowest) excited triplet<sup>‡</sup> but most likley an upper singlet state (possibly the same excited state involved in the photo-Fries rearrangement). Consequently, the solvent must have its effect at another stage of the process.

Substitution in the aromatic ring has its effects on the product distribution (Table 3). The amount of phenol formed varies from 0.3 to 1.9 relative to the unsubstituted case in a rather unpredictable way. The photo-Fries rearrangement is the major reaction when the *ortho* positions are free, with the exception of 3,5-dimethylphenyl acetate. The amount of *o*-Fries product varies from 0.2 to 1.9 again relative to the unsubstituted case. The amount of *p*-Fries product was invariably found to be lower than in the unsubstituted case (range: 0.0 to 0.73) with the exception of 2-methoxy-phenyl acetate.

The effect of substituents at the *o*-positions may be twofold. First, *o*-substituents prevent the rearrangement to the *o*-position by their mere presence. Furthermore, the effect may have also a steric character. From dipole moment data and the Kerr constant it has been concluded<sup>17</sup> that the ester group is not coplanar with the benzene ring, the angle of twist being ca. 90° for phenyl acetate. Accepting the non-coplanarity, there remain two possible conformations:



It is readily seen that the transition state in the decarboxylation reaction as suggested by Finnegan and Knutson<sup>5c</sup> requires the structural arrangement of the s-cis \* Our thanks are due to Dr. N. G. Minnaard, Dept. of Org. Chem. University of Leiden, for recording

and interpreting the phosphorescence spectra.

<sup>†</sup> The absence of a sensitising effect by acetophenone ( $E_T = 73.6$  Kcal/mole) on the photo-Fries rearrangement of *p*-tolyl acetate<sup>11</sup> may also be due to the fact that the  $E_T$  of *p*-tolyl acetate is perhaps some 80 Kcal/mole.

<sup>‡</sup> The involvement of a very short-lived triplet state can be ruled out on account of the observed phosphorescence lifetime.

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conformation. That the s-cis conformation is the favoured conformation for decarboxylation, is suggested by the reported photoreactions of  $\beta$ -propiolactone<sup>18</sup> and by recent results reported by Chapman anL Adams.<sup>19</sup> The irradiation of 2,3-diphenyl- $\beta$ -propiolactone in ether (!) was found to lead to some phenanthrene, which was presumably formed by decarboxylation to (c + t)-stilbene and subsequent cyclization and oxidation by the well known process.<sup>20</sup>



The structures of carboxylic esters have been investigated by many physical methods.<sup>21</sup> The s-*trans* conformation is generally accepted to be the favoured conformation. As for aryl esters, Lee and Wilmshurst<sup>22</sup> ascribed the solvent-, and temperature-dependent doubling of the carbonyl band in the IR spectra of some aryl acetates to Fermi resonance rather than to coexisting conformers. The relatively low dipole moments reported for aryl esters<sup>23</sup> may also point to the s-*trans* conformation being the favoured conformation.

Recently, Kessler and Rieker<sup>24</sup> proved the existence of an equilibrium between s-trans and s-cis conformations in substituted acetanilides by means of NMR spectroscopy. They found an increasing population of the s-cis conformation with increasing size of the substituent in 2-, 2,6-di, and 2,4,6-trialkylacetanilides. The NMR spectra of some suitable esters (1, 3, and 5) were recorded in different solvents and at different temperatures, in order to detect a similar equilibrium for aryl acetates. Indeed, the low-temperature NMR spectra of these aryl acetates showed signs of a possible s-trans  $\Rightarrow$  s-cis equilibrium. The signals of the ring protons as well as those for the o-, and m-Me groups showed a down-field shift similar to those reported for the acetanilides. The signal of the signals was observed, the temperature probably not being sufficiently low ( $-80^\circ$ ).

On the basis of the present evidence, the following possible reaction scheme<sup>†</sup> is proposed:



\* The acetyl-protons in the corresponding acetanilides<sup>24</sup> showed an up-field shift. The difference may be due to a slightly different spatial arrangement relative to the benzene ring.<sup>23</sup>

 $\dagger$  In our case it is unnecessary to consider benzvalene type intermediates, <sup>7</sup> since no phototransposition reaction was observed.

‡ In this scheme no difference is made for o-, and p-rearrangement.

The substituents and solvents studied must affect the energy difference between transition states I and II, e.g. ethers must decrease the energy difference between transition states I and II, particularly in the case of o-, and/or m-substituted esters. Perhaps ether molecules participate somehow or other in transition state II. It might be interesting to test this steric substituent-effect with an ester having "fixed" s-trans and s-cis conformations. 2,6-Di-t-butylphenyl acetate might serve this purpose.

From the effect, although smaller, of *p*-Me and *p*-OMe substituents, it may be concluded, that other than steric factors play a role also.<sup>26</sup> However, owing to the limited number of substituents studied, we are not in the position to say more about this at present.

After completion of this manuscript, Planck<sup>27</sup> reported some preliminary results of a study on the mechanism of the photo-Fries rearrangement of phenyl benzoate and phenyl *o*-toluate in various solvents. Any possible relation between his results and ours, however, must await further experiments.

#### EXPERIMENTAL

*Materials.* 4-Methoxy-2,6-dimethylphenol<sup>\*</sup> was prepared from 2,6-dimethyl-*p*-benzoquinone. A 10% soln of the quinone in MeOH was hydrogenated (15 min) at 20° and 50 atm using a Pt/C (0·1%) catalyst. The catalyst was removed by filtration and 6·5% (by volume) of conc H<sub>2</sub>SO<sub>4</sub> was added to the filtrate. After standing for 24 hr, the 4-methoxy-2,6-dimethylphenol was precipitated on the addition of 5 vols of a sat NaClaq. The crude product was filtered off, dissolved in ether, and the soln dried over Na<sub>2</sub>SO<sub>4</sub>. After fractionation, b.p. 133-134°/12 mm, the product was recrystallized from pet. ether (40-60°), m.p. 77·8-78·2° (reported<sup>29</sup> m.p. 76-77°). The yield was 80% based on starting quinone.

3,5-Dimethoxyphenol was prepared from phloroglucinol according to Pratt and Robinson.<sup>30</sup> All other phenols were commercially available. The phenols were purified by fractionation or crystallization before use. The purity was checked by GLC and 2-dimensional TLC.

Preparation of the esters. The esters 1-6 were prepared by reacting  $Ac_2O$  and the phenol in CHCl<sub>3</sub> with catalytic amounts of HClO<sub>4</sub> (70%). The esters 7-11 were prepared by reacting  $Ac_2O$  and the phenol in a mixture of benzene and pyridine (1:1)† The esters were purified by fractionation or crystallization. In all cases the purity was checked by GLC 2-dimensional TLC and spectroscopic methods (IR and NMR). Two new esters are: 4-methoxy-2,6-dimethylphenyl acetate (7), m.p. 41.5-42.5° (from pentane) and 3,5-dimethylphenyl acetate (11), m.p. 33-33.5° (from pentane).

Reference compounds. The hydroxyketones were prepared by the thermal Fries reaction. These compounds were purified by column chromatography and crystallization. The purity was checked as before.

The decarboxylation products<sup>‡</sup> toluene, o-, and p-xylene and mesitylene were commercial samples. o-Methoxy-, p-methoxy-, and 2,6-dimethoxytoluene and 3,4,5-trimethylanisole were prepared by reacting the corresponding phenols (commercially available) with Me<sub>2</sub>SO<sub>4</sub>. 1,2,3,5-Tetramethylbenzene and 3,5dimethoxytoluene were isolated from the irradiation mixtures of the corresponding esters (esters 6 and 11 respectively) by chromatography on silica.

\* This compound was prepared by Mr. A. H. Bijkerk. The 2,6-dimethyl-p-benzoquinone was obtained by the salcomine-catalysed oxidation of 2,6-dimethylphenol.<sup>28</sup>

 $\dagger$  The esterification using HClO<sub>4</sub> as catalyst led to ring-acylation in the case of OMe-substituted phenols. 4-Methoxy-2,6-dimethylphenol gave as the main product 3-aceto-2,6-dimethyl-4-methoxyphenyl acetate, m.p. 55-56° (pentane), IR: CO (ester), 1765 cm<sup>-1</sup>; CO (ketone), 1700 cm<sup>-1</sup>; NMR: four different Me signals (S) at 114.5, 123, 132 and 140 c/s (each 3H), 221.5 c/s (S, 3H, OMe group) and 390 c/s (S, 1H, one aromatic proton).

2,6-Dimethoxyphenol gave 3-aceto-2,6-dimethoxyphenyl acetate, m.p.  $108-110^{\circ}$  (pet. ether  $80-100^{\circ}$ ); IR: CO (ester), 1775 cm<sup>-1</sup>; CO (ketone), 1680 cm<sup>-1</sup>; NMR: 137 c/s (S, 3H, ester Me), 150 c/s (S, 3H, ketone Me), 228 and 229 c/s (total 6H, two non-equivalent OMe groups) and two doublets centred at 400 and 454 c/s (AB-system, J = 9 c/s).

<sup>‡</sup> Our thanks are due to Professor D. Ir. B. M. Wepster, Dept. of Org. Chem., Technical University, Delft, for a gift of 1,2,3-trimethylbenzene.