

Photochemical *ortho*-acylation of phenols with 1,1,1-trichloroethane

Francisco Galindo, M. Consuelo Jiménez, Miguel A. Miranda, Rosa Tormos

Departamento de Química—Instituto de Tecnología Química UPV-CSIC, Universidad Politécnica de Valencia, Camino de Vera s/n. Apdo. 22012, E-46071 Valencia, Spain

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Abstract

Photolysis of phenols in the presence of 1,1,1-trichloroethane, using wet methanol as solvent, leads to *o*-acetylphenols. These products are accounted for in terms of HCl elimination and subsequent recombination of the resulting phenoxy–dichloroethyl radical pairs. Direct spectroscopic evidence for the involvement of *o*-dichloroethylphenols as intermediates is provided.

Keywords: *ortho*-Acylation; Phenol; 1,1,1-Trichloroethane; Photolysis

1. Introduction

o-acetylphenols are useful synthetic intermediates for the preparation of drugs, industrial chemicals and natural products. They can be obtained either by direct acylation of phenols under Friedel–Crafts conditions or, in a two-step process, by Fries rearrangement of phenyl esters. Such rearrangement can be effected by means of Lewis acid catalysis or on photochemical activation [1–6].

In the present work, a synthetic equivalent of Friedel–Crafts acylation has been achieved by simple irradiation of phenols (**1**) in the presence of a 20-fold molar excess of 1,1,1-trichloroethane, using wet methanol (0.5% water content) as solvent.

2. Experimental details

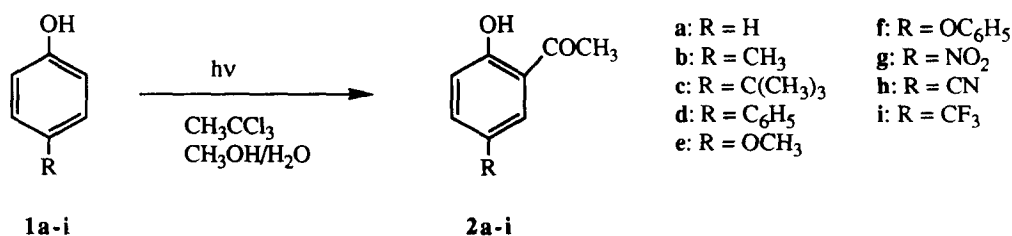
2.1. General irradiation procedure

Solutions of the corresponding phenol (0.15 mmol) in 15 ml of CH₃OH containing 0.3 ml of CH₃CCl₃ were irradiated

for 1 h with the quartz-filtered light of a 125 W medium pressure mercury lamp, under Ar atmosphere. The photomixtures were analysed by gas chromatography (GC) as well as by GC–mass spectrometry (MS). *o*-Hydroxypropiophenone was added as internal standard for quantitative determination.

3. Results and discussion

The efficiency of this procedure was found to depend on the nature of the ring substituent (Scheme 1 and Table 1). The parent phenol as well as the compounds with alkyl, phenyl or alkoxy groups at the *para* position (**1a–1f**) gave rise to the *ortho*-acylated products **2a–2f** with moderate yields (entries 1–6 in Table 1). The reaction failed in the case of the electron-withdrawing NO₂, CN or CF₃ substituents (entries 7–9). This would be compatible with a mechanism involving photoionization of phenols, to give their radical cations plus solvated electrons [7], followed by capture of the latter by 1,1,1-trichloroethane (Scheme 2). (Direct electron transfer from excited phenols to CH₃CCl₃ would be thermodynamically favoured; however, the reaction



Scheme 1.

Table 1
Preparation of *o*-acetylphenols (**2**) by photolysis of phenols (**1**) in the presence of 1,1,1-trichloroethane

Entry	Phenol	Composition of the photomixtures (%) ^a	
		1	2
1	1a	66	34
2	1b	62	38
3	1c	46	54
4	1d	56	44
5	1e	35	65
6	1f	59	41
7	1g	100	Traces
8	1h	100	Traces
9	1i	100	Traces

^a Significant amounts of polymers were formed (25% as an average).

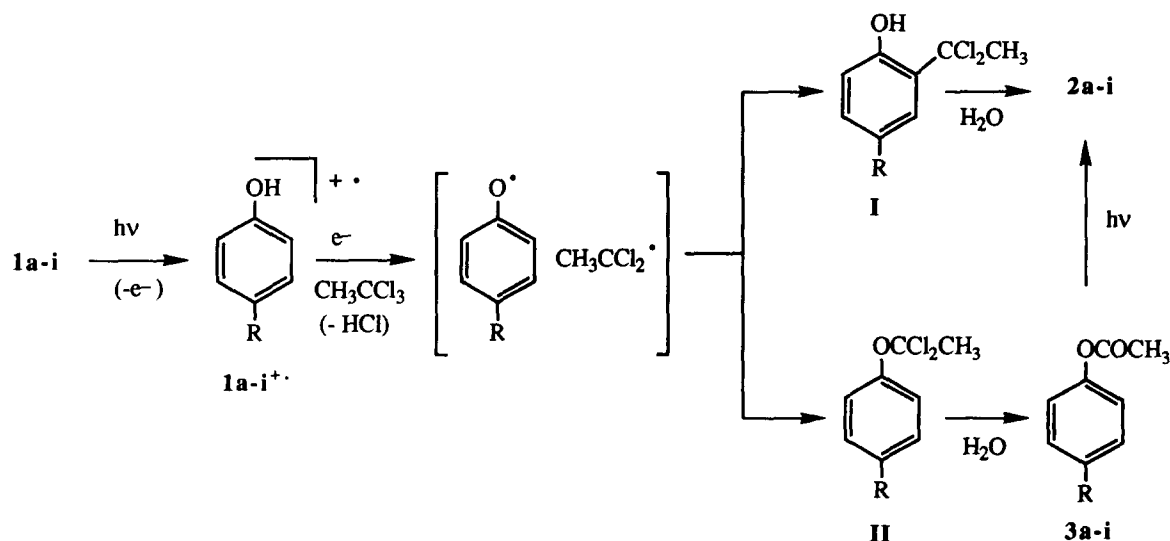
should be slow in view of the high exothermicity (Marcus inverted region [8]). For instance, $E_{D/D^{+}}$ of phenol is 0.6 V vs. saturated calomel electrode (SCE) [9] and $E_{A^{+}/A}$ of CH_3CCl_3 is -1.5 V vs SCE [10], while the singlet energy of phenol is $103 \text{ kcal mol}^{-1}$ [11]. According to the Rehm-Weller equation [12], ΔG_{FIS} would be ca. $-55 \text{ kcal mol}^{-1}$.

Dichloroethylphenols **I** are logical precursors of acylphenols **2**. They must arise via HCl elimination and C–C recombination of the resulting phenoxy–dichloroethyl radical pairs.

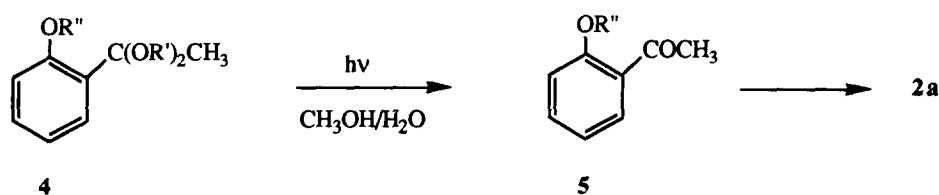
Intermediates **I** were not detected under the reaction conditions employed ($\text{MeOH-H}_2\text{O}$), probably because of a rapid hydrolysis to the final products. In order to confirm this hypothesis, phenols **1** were irradiated in net CH_3CCl_3 without added solvent. Analysis of the reaction mixtures by GC–MS and GC–Fourier transform IR (FTIR) spectroscopy revealed indeed the presence of **I** together with the dichloroethyl ethers **II**, which are obviously the C–O radical recombination products (**I**, FTIR 3588, 3053, 1609, 1484, 1227 cm^{-1} , MS 190 (M^+ , 5), 157 (30), 155 ($M^+ - \text{Cl}$, 100), 119 ($M^+ - \text{Cl} - \text{HCl}$, 71), 94 (33), 77 (12); **II**, FTIR 3080, 1632, 1593, 1492, 1379, 1207, 1150, 1022, 972, 849, 754 cm^{-1} , MS 190 (M^+ , 1), 154 ($M^+ - \text{HCl}$, 12), 119 ($M^+ - \text{HCl} - \text{Cl}$, 100), 112 (16), 91 (10), 77 (10)).

In view of the large excess of methanol as compared with water under the employed photolysis conditions, formation of methyl acetals **4** ($R' = \text{Me}$, $R'' = \text{H}$) by solvolysis of the dichloroethylphenols **I** was in principle expected. However, these compounds were not detectable by GC–MS or GC–FTIR. The presence of phenolic hydroxy groups at the *ortho* position must facilitate the acetal hydrolysis through an intramolecular mechanism of acid catalysis [13–15]. As a matter of fact, compound **4** ($R' = \text{Me}$, $R'' = \text{H}$) is very sensitive to hydrolysis, and all attempts to prepare it by different methods in the presence of acids have been unsuccessful [16].

In order to check whether these types of intermediates, if formed, are readily converted into *o*-acetylphenols, the corre-



Scheme 2.



Scheme 3.

sponding ethylene acetal with a protected phenolic hydroxy group (**4**, OR', OR' = OCH₂CH₂O, R'' = COCH₃) [17] was submitted to photolysis under the conditions of Table 1. As expected, large amounts of **2a** were obtained, together with its acetate. Again, the methyl acetals were not present in the reaction mixture (Scheme 3).

Not even traces of acetates **3** were detected after photolysis of **1** in MeOH–CH₂CCl₃. As these products might in principle be formed on partial hydrolysis of the ethers **II**, phenyl acetate (**3a**) was irradiated in methanol containing traces of HCl. In this control experiment, **3a** was completely converted into a mixture of phenol (**1a**, 80%) and its *o*-acetyl derivative (**2a**, 20%), which is the expected photo-Fries rearrangement product.

In summary, the photolysis of phenols in the presence of 1,1,1-trichloroethane affords the corresponding *o*-acetylphenols as single products. The preparative yields are similar to those achieved in the widely used two-step process involving conversion of the phenols into their acetates, followed by photo-Fries rearrangement of the latter. Extension of this methodology to the introduction of other acyl rests on phenolic rings (using 1,1,1-trichloro compounds obtained by treatment of acyl chlorides with PCl₅) is currently under study.

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