Monatshefte für Chemie 124, 209–215 (1993)

Monatshefte für Chemie
Chemical Monthly

Direct Photolysis and Electron Transfer Photooxygenation of Enol Acetates of 3-Phenylpropiophenones

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Summary. Direct photolysis of enol acetates of 3-phenylpropiophenones **1a–c** gives rise to the parent propiophenones **2a–c** and the 1,3-acyl shift products **3a–c**. By contrast, 2,4,6-triphenylpyrylium tetrafluoroborate sensitized photolysis of substrates **1a–c** affords the α-acetyloxypropiophenones **7a–c** as the most general products. These results have been rationalized according to the generation of radical pairs in the direct photolysis and radical cations in the photoinduced electron transfer processes.

Keywords. Enol acetates of 3-phenylpropiophenones; 1,3-Acyl migration; Photoinduced electron transfer; 2,4,6-Triphenylpyrylium tetrafluoroborate.

Direkte Photolyse und Elektron-Transfer-Photooxygenierung von Enolacetaten von 3-Phenylpropiophenonen

Zusammenfassung. Die direkte Photolyse von Enolacetaten der 3-Phenylpropiophenone **1a–c** ergab die zugrundeliegenden Propiophenone **2a–c** und die 1,3-acyl-verschobenen Produkte **3a–c**. Im Gegensatz dazu ergab die 2,4,6-Triphenylpyrylium-tetrafluorborat-sensitivierte Photolyse der Substrate **1a–c** die α-Acetyloxypropiophenone **7a–c** als generelle Produkte. Diese Ergebnisse sind mit der Erzeugung von Radikalpaaren bei der direkten Photolyse und der Bildung von Radikalkationen beim photoinduzierten Elektronen-Transfer-Prozess zu erklären.

Introduction

The most characteristic feature of the photochemistry of enol esters is 1,3-acyl migration, occurring through recombination of the radical pair generated by homolytic CO–O bond cleavage [1]. However, we have recently shown [2] that enol acetates of cyclic aromatic ketones give rise to small amounts of oxygenated photoproducts, there being some coincidence between the results achieved upon direct irradiation and those achieved under photoinduced electron transfer (PET).

In order to explore the behaviour of other structurally related enol esters, we have studied the photoreactivity of three 1-acetyloxy-1,3-diphenylpropenes (**1a–c**)

in the presence or absence of 2,4,6-triphenylpyrylium tetrafluoroborate (*TPT*), a well-known PET sensitizer [3].

Results and Discussion

Starting materials **1a–c** were prepared by enol acetylation of the corresponding ketones **2a–c**, using acetic anhydride in pyridine or, alternatively, isopropenyl acetate in the presence of *p*-toluenesulfonic acid as catalyst. In all cases, a stationary mixture of both stereoisomers of **1** and the initial propiophenone was obtained. Only the predominant *Z*-isomer was submitted to irradiation in this study.

Direct photolysis of enol acetates **1a–c** were performed through quartz in hexane solutions (10^{-2} *M*) for 2 h. The results achieved are summarized in Table 1. Besides small amounts of the starting material, the corresponding 3-phenylpropiophenones **2a–c** and the 1,3-butanediones **3a–c** were present in the reaction mixtures [4]. Diphenylmethane **4** and benzophenone **5** were also detected in the irradiation of the benzhydryl derivative **1c**.

By contrast with the parent benzoylacetone, where the tautomeric equilibrium is shifted to the enol form [4], a remarkable structural feature of β-diketones **3a–c** was the total predominance of the dicarbonylic tautomer, the enol form of **3a–c** being not detected by ^{1}H-NMR spectroscopy [5]. Related precedents for the lack of enolization of these α-substituted β-diketones **3** can be found in the literature [7].

The formation of compounds **2** and **3** corresponds to the usual photoreactivity of enol esters (Scheme 1). Thus, after light absorption the starting material **1** undergoes homolytic CO–O bond rupture to give an acetyl/vinyloxy radical pair. Recombination of the latter would form the starting enol ester **1** or the β-diketone **3**. Alternatively, hydrogen abstraction from the medium would afford the propiophenone **2**.

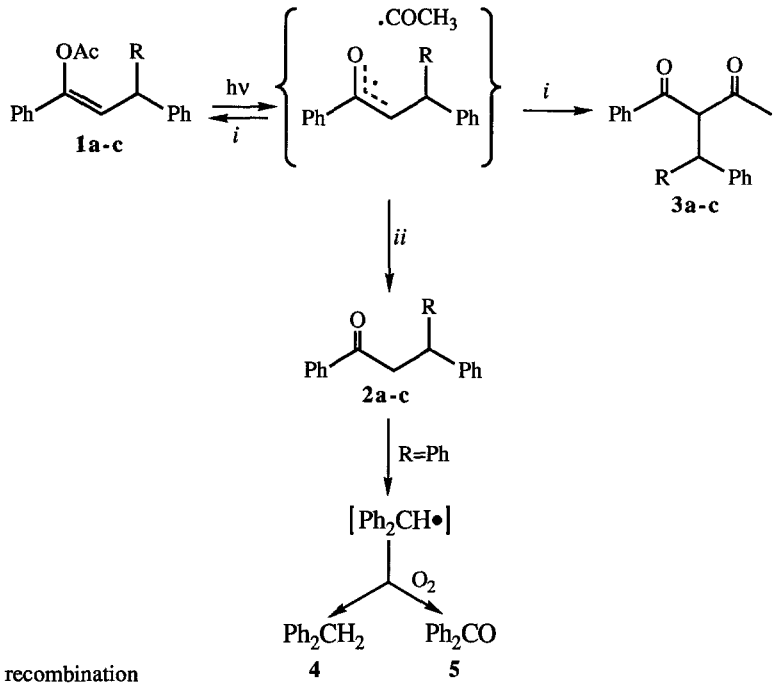
Finally, the small amounts of diphenylmethane and benzophenone observed in the irradiation of the 3,3-diphenyl derivative **1c** must arise from the diphenylmethyl radical, via hydrogen abstraction and oxygen trapping respectively.

TPT sensitized irradiations of enol acetates **1a–c** were carried out in dichloromethane solutions (10^{-3} *M*) through pyrex. An aqueous potassium chromate solution was used as radiation filter to ensure that no direct excitation

Table 1. Results of the photolysis of enol acetates **1a–c** in the absence or presence of *TPT*

Substrate	Conditions*	Products (Yields, %)
1a	D	**2a** (34), **3a** (26)
	TPT	**2a** (13), **6a** (4), **7a** (74)
1b	D	**2b** (54), **3b** (30)
	TPT	**2b** (31), **7b** (54)
1c	D	**2c** (32), **3c** (38), **4** (8), **5** (4)
	TPT	**6** (72), **7c** (7)

* D = Direct photolysis; TPT = *TPT* photosensitization



i : recombination
ii : H abstraction

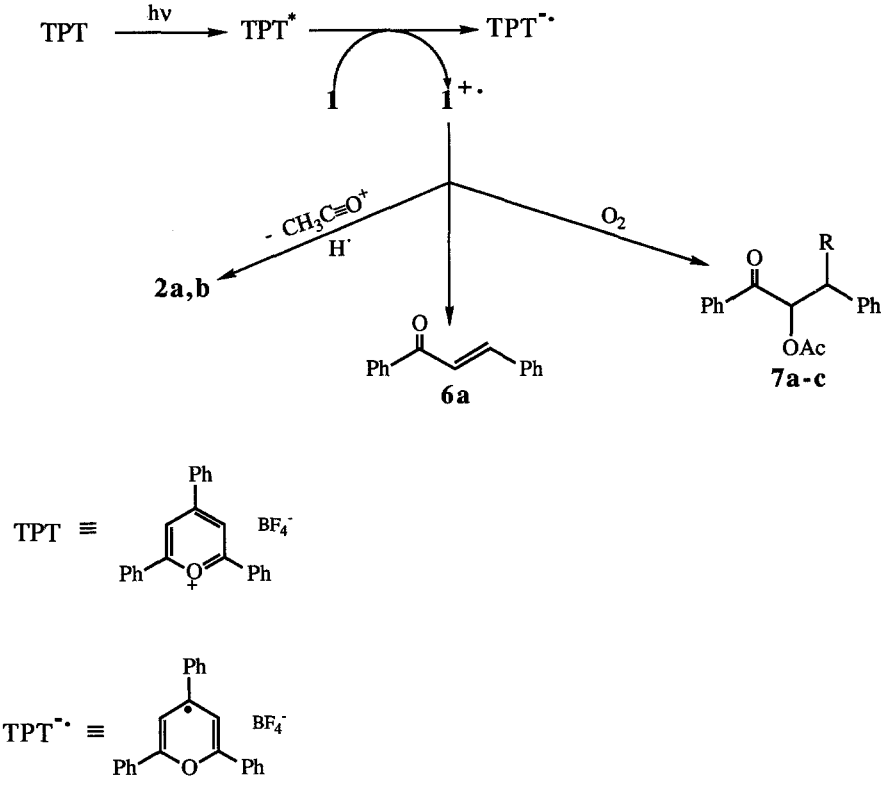
R	
a	H
b	Me
c	Ph

Scheme 1. Mechanism of the direct photolysis of enol acetates **1a–c**

of substrates **1** might occur [8]. The results obtained under these conditions are also included in Table 1; they are quite different from those achieved in the direct photolysis. Thus, **1a–c** were converted into mixtures of α-acetyloxypropiophenones **7a–c**, the corresponding 3-phenylpropiophenones **2a, b**, minor amounts of chalcone **6a**, and degradation products.

The structure of compounds **7b** and **7c** was confirmed by alternative synthesis. Thus, treatment of the enol acetate **1b** with *m*-chloroperoxybenzoic acid in dichloromethane at room temperature afforded the α-acetyloxyketone **7b**, while **7c** was obtained by bromination of **2c** in the presence of $AlCl_3$ followed by nucleophilic substitution of bromine by acetate.

A reasonable explanation for these results is presented in Scheme 2. The key intermediates are the radical cations $\mathbf{1}^{+\bullet}$ generated through a PET process from the styrenic moiety of **1** to *TPT* in its excited state. From these species, the formation of α-substituted propiophenones **7a–c** and chalcone **6a** would imply the same steps as those operating in the anodic oxidation of enol acetates of aliphatic ketones, which also involves radical cations as intermediates and affords α-acetyloxyketones and α,β-enones as final products [9]. On the other hand, loss of acylium ion from $\mathbf{1}^{+\bullet}$ followed by hydrogen abstraction would form the propiophenones **2a, b**. Finally, in the case of the benzhydryl derivative, oxidative β-photofragmentation of **2c** [10], **6c** or **7c** would lead to benzophenone.



Scheme 2. Mechanism of the *TPT* sensitized photolysis of enol acetates **1a–c**

In conclusion, photolysis of enol acetates of 3-phenylpropiophenones **1** gives rise to a product distribution dependent upon the absence or presence of *TPT* as photosensitizer. The most characteristic products arise from radical pair recombination (β-diketones **3a, c**) or oxygenation of the radical cation **1a–c**$^{+\cdot}$ (α-acetyloxypropiophenones **7a, c**).

Experimental Part

The melting points are uncorrected and were measured with a Büchi 510 apparatus. IR spectra of pure compounds were obtained in CCl_4 solutions or KBr disc (**3c**) with a Perkin–Elmer 851 spectrophotometer. Alternatively (and also to analyse some reaction mixtures) an FT-IR Hewlett–Packard 5965A detector coupled with a GC Hewlett–Packard 5890 fitted with a 25 m capillary column of crosslinked 5% phenylmethylsilicone was used. Wave number absorptions (cm^{-1}) are given only for the carbonyl bands. ^{1}H-NMR spectra were recorded in CCl_4 with a 60 MHz Varian 360 EM instrument. In the case of 1,3-diketones **7b, c**, the ^{1}H-NMR spectra were measured in $CDCl_3$ using a 200 MHz Jeol spectrometer. Chemical shifts are reported in δ values (ppm), using $(CH_3)_4Si$ as internal standard; coupling constants are given in Hz. MS were measured with a GC/MS Hewlett–Packard 5988 A spectrometer provided with a capillary column like the GC/FTIR; *m/z* ratio and their relative abundances in percentages (in brackets) are given only for the most significant peaks. Elemental analyses were performed at the Instituto de Química Bio-Orgánica of the C.S.I.C. in Barcelona. Purification of the reaction mixtures was carried out by flash column chromatography on silica gel Merck 60, 70-230 mesh using mixtures of hexane-dichloromethane as eluent. Analytical

samples of pure compounds were accomplished using a Waters isocratic HPLC apparatus equipped with a semipreparative Microporasil™ column, with a mixture 95/5 *v/v* of hexane/ethyl acetate as eluent.

TPT was prepared by condensation of chalcone (2.08 g, 10 mmol) with acetophenone (1.20 g, 10 mmol) in 1,2-dichloroethane (350 ml) using a 50% ethereal solution of tetrafluoroboric acid (160 ml) at 70° following the procedure described previously [11].

Preparation of the Enol Acetates **1a–c**

A mixture of the corresponding 3-phenylpropiophenone (1.00 g), acetic anhydride (10 ml) and pyridine (15 ml) was heated at reflux temperature for 12 h. After this time, the reaction mixture was poured into ice/water (100 ml) and extracted with CH_2Cl_2. The organic phase was washed with 5% aqueous HCl, 5% aqueous $NaHCO_3$, and finally with water. After drying with anhydrous Na_2SO_4, the solvent was concentrated and the residue submitted to flash chromatography. The following yields were obtained: **1a** 18%, **1b** 23% and **1c** 38%.

Alternatively, enol acetylation was accomplished by heating (at about 100°) a solution of the 3-phenylpropiophenone (1.00 g) in isopropenyl acetate (20 ml) in the presence of catalytic amounts 4-toluenesulfonic acid under continuous removal of the resulting acetone. Periodic distillation of the isopropenyl acetate and addition of a fresh feed of this acylating reagent results in greater enhancement of the reaction conversion. After several addition-distillation cycles, the reaction mixtures were washed with water, dried over Na_2SO_4 and the solvent removed under vaccum. Isolation by flash column chromatography gave rise to the corresponding enol acetates **1a** 37%, **1b** 45%, and **1c** 65%.

Direct Irradiation Procedure

A solution of the enol acetate **1a–c** (5 mmol) in 450 ml of distilled hexane was irradiated for 2 h at room temperature with a 125 W medium pressure mercury lamp inside a quartz immersion well photoreactor. After removal of the solvent, the photolysis residue was submitted to purification. The resulting products and their yields are summarized in Table 1.

TPT Sensitized Photolysis

A solution of the enol acetates **1a–c** (0.5 mmol) and *TPT* (40 mg) in CH_2Cl_2 (450 ml) was irradiated for 4 h at room temperature using a 125 W medium pressure mercury lamp as a light source and pyrex and aqueous potassium chromate solution (0.5 g/l) as filters. After removal of the solvent, the photolysis mixtures were submitted to purification. The results are presented in Table 1.

Synthesis of 2-Acetyloxy-1,3-diphenyl-1-butanone (**7b**)

m-Chloroperoxybenzoic acid (70 mg, 0.4 mmol) was added to a solution of the enol acetate **1b** (100 mg, 0.38 mmol) in CH_2Cl_2 (25 ml) and the mixture heated at reflux temperature for 2 h. After this time, the organic layer was washed with 5% $NaHCO_3$, dried over anhydrous Na_2SO_4 and concentrated in vaccum. Analysis of the reaction mixture by GC and GC-MS established that one of the two diastereomers (30 + 35%) present in the epoxidation-rearrangement mixture of **1b** was the same as compound **7b** obtained in the *TPT* sensitized photolysis of **1b**.

Synthesis of 2-Acetyloxy-1,3,3-triphenyl-1-propanone (**7c**)

Bromine (60 mg, 0.38 mmol) in CCl_4 (5 ml) was added under continuous magnetic stirring at room temperature to a solution of 3,3-diphenylpropiophenone (100 mg, 0.35 mmol) in CCl_4 (5 ml) containing

catalytic amounts of anhydrous $AlCl_3$. The progress of the reaction was followed by the decrease of the methylene doublet at δ 3.6 ppm and the appearance of a new one at δ 5.9 ppm. After the addition was completed, the suspension was filtered, the solvent removed and the 2-bromo-1,3,3-triphenyl-1-propanone (100 mg, 78%) isolated by column chromatography [12].

This α-bromopropiophenone (70 mg, 0.2 mmol) was treated with sodium acetate (1.00 g) in *DMSO* (10 ml) at room temperature for 2 h. Subsequent addition of water (100 ml) and extraction with CH_2Cl_2 allowed to obtain after purification 2-acetyloxy-3,3-diphenylpropiophenone (40 mg, 58%), which showed the same spectroscopic properties as compound **7c** isolated from *TPT* sensitized photolysis of **1c**.

Spectral and Analytical Data of the Compounds

(Z)-1-Acetyloxy-1,3-diphenylpropene (**1a**)

IR 1750. ^{1}H-NMR 7.53–7.29 (m, 5 H, C_6H_5C=C), 7.18 (s, 5 H, $C_6\mathbf{H}_5CH_2$), 5.83 (t, J = 7, 1 H, CH=C), 3.43 (d, J = 7, 2 H, CH_2), 2.23 (s, 3 H, CH_3). MS 252 (M^+, 2), 210 (20), 209 (5), 192 (10), 105 (100), 77 (37), 43 (40). Anal. calcd. for $C_{17}H_{16}O_2$: C 80.93, H 6.30; found C 80.62, H 6.44%.

(Z)-1-Acetyloxy-1,3-diphenyl-1-butene (**1b**)

IR 1750. ^{1}H-NMR 7.59–7.02 (m, 5 H, C_6H_5C=C), 7.22 (s, 5 H, $C_6\mathbf{H}_5CH$), 5.75 (d, J = 9, 1 H, CH=C), 3.93–3.52 (m, 1 H, $CHCH_3$), 2.21 (s, 3 H, CH_3CO), 1.47 (d, J = 7, 3 H, CH_3CH). MS 266 (M^+, O), 224 (10), 209 (38), 191 (5), 167 (19), 131 (30), 120 (10), 105 (75), 77 (84), 43 (100). Anal. calcd. for $C_{18}H_{18}O_2$: C 81.18, H 6.81; found C 82.02, H 7.00%.

(Z)-1-Acetyloxy-1,3,3-triphenyl-1-propene (**1c**)

IR 1750. ^{1}H-NMR 7.58–7.09 (m, 5 H, C_6H_5C=C), 7.25 [s, 10 H, $(C_6\mathbf{H}_5)_2CH$], 6.12 (d, J = 9, 1 H, CH=C), 4.91 (d, J = 9, 1 H, $CHPh_2$), 2.12 (s, 3 H, CH_3). MS 328 (M^+, 1), 286 (7), 268 (25), 191 (5), 167 (9), 105 (100), 77 (20), 43 (40). Anal. calcd. for $C_{23}H_{20}O_2$: C 84.12, H 6.14; found C 84.07, H 6.21%.

1-Phenyl-2-(phenylmethyl)-1,3-butanedione (**3a**) [7]

M.p. 46–51 °C. IR 1715, 1691. ^{1}H-NMR 8.10–7.32 (m, 5 H, C_6H_5CO), 7.13 (s, 5 H, $C_6\mathbf{H}_5CH$), 4.63 (t, J = 7, 1 H, CHCO), 3.31 (d, J = 7, 2 H, CH_2), 2.06 (s, 3 H, CH_3). MS 252 (M^+, 2), 251 (1), 209 (66), 147 (24), 131 (12), 105 (100), 77 (87), 43 (56).

1-Phenyl-2-(1-phenylethyl)-1,3-butanedione (**3b**) [13]

M.p. 80–83 °C. IR 1719, 1690, ^{1}H-NMR 7.78–7.04 (m, 5 H, C_6H_5CO), 7.19 (br. s, 5 H, $C_6\mathbf{H}_5CH$), 4.79 (d, J = 11, 1 H, CHCO), 2.22 (s, 3 H, CH_3CO), 1.28 (d, J = 7, 3 H, CH_3CH). MS 266 (M^+, 0), 223 (40), 209 (8), 161 (22), 131 (5), 105 (100), 77 (58), 43 (10). Anal. calcd. for $C_{18}H_{18}O_2$: C 81.18, H 6.81; found C 81.71, H 6.53%.

1-Phenyl-2-(diphenylmethyl)-1,3-butanedione (**3c**) [13]

M.p. 133–137 °C. IR 1715, 1689. ^{1}H-NMR 7.96–7.01 (m, 5 H, C_6H_5CO), 7.27 [s, 10 H, $(C_6\mathbf{H}_5)_2CH$], 5.60 (d, J = 12, 1 H, CHCO), 5.09 (d, J = 12, 1 H, $CHPh_2$) 2.04 (s, 3 H, CH_3). MS 328 (M^+, 0), 285 (98), 223 (32), 178 (10), 167 (18), 105 (100), 43 (20). Anal. calcd. for $C_{23}H_{20}O_2$: C 84.12, H 6.14; found C 83.55, H 6.50%.

2-Acetyloxy-1,3-diphenyl-1-propanone (**7a**) [14]

IR 1740, 1705. ^{1}H-NMR 8.06–7.31 (m, 5H, C_6H_5CO), 7.24 (s, 5H, $C_6H_5CH_2$), 6.01 (ABX, $J_{AX}=9$, $J_{BX}=5$, 1H, CHO*Ac*), 3.04 (ABX, 2H, CH_2), 2.05 (s, 3H, CH_3). MS 268 (M^+, 1), 208 (55), 207 (30), 131 (5), 105 (90), 91 (10), 77 (30), 43 (100).

2-Acetyloxy-1,3-diphenyl-1-butanone (**7b**) [15]

FT-IR 1762, 1710. ^{1}H-NMR 7.89–7.06 (m, 5H, C_6H_5CO), 7.18 (s, 5H, C_6H_5CH), 5.92 (d, $J=5$, CHO*Ac*), 3.48–3.13 (m, 1H, $CHCH_3$), 2.09 (s, 3H, CH_3CO), 1.24 (d, $J=7$, 3H, CH_3CH). MS 282 (M^+, 0), 222 (7), 221 (3), 178 (1), 136 (6), 105 (100), 77 (33), 43 (25).

2-Acetyloxy-1,3,3-triphenyl-1-propanone (**7c**)

M.p. 89–92 °C. FT-IR 1740, 1715. ^{1}H-NMR 8.05–7.30 (m, 5H, C_6H_5CO), 7.25+7.16 [(br s)+(br s), 2×5H, $(C_6H_5)_2CH$], 6.64 (d, $J=9$, 1H, CHO*Ac*), 4.64 (d, $J=9$, 1H, $CHPh_2$), 1.93 (s, 3H, CH_3CO). MS 344 (M^+, 0), 284 (72), 283 (50), 197 (10), 167 (84), 152 (14), 105 (76), 77 (50), 43 (100).

Acknowledgement

Financial support by the Spanish DGCYT (Grant No. 88-0494) is gratefully acknowledged.

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Received April 13, 1992. Accepted May 15, 1992