Monatshefte für Chemie 121, 371–375 (1990)

Monatshefte für Chemie
Chemical Monthly
© by Springer-Verlag 1990

Electron Transfer Photofragmentations of 3-Phenylpropiophenones

María V. Baldoví[a], **Hermenegildo García**[a], **Miguel A. Miranda**[b,*], and **Jaime Primo**[a]

[a] Departamento de Química, E.T.S.I.I., Universidad Politécnica, E-46071 Valencia, Spain
[b] Departamento de Química Orgánica, Facultad de Farmacia, E-46010 Valencia, Spain

Summary. Photolysis of 3-phenylpropiophenones **1 a–d** in the presence of 2,4,6-triphenylpyrylium tetrafluoroborate (*TPT*) yields the corresponding α,β-unsaturated ketones **2 a–c** and **1 d** (from **1 c**), together with acetophenone (**3**), benzophenone (**4**), benzoic acid (**5**) and benzaldehyde (**6**), presumably by fragmentations of the radical cation $\mathbf{1}^{+\cdot}$, generated via a single electron transfer process from **1** to the excited *TPT*.

Keywords. Photosensibilization; Electron transfer; 2,4,6-Triphenylpyrylium tetrafluoroborate; 3-Phenylpropiophenones.

Photofragmentierung von 3-Phenylpropiophenonen via Elektronenübertragung

Zusammenfassung. Photolyse der 3-Phenylpropiophenone **1 a–d** in Gegenwart von 2,4,6-Triphenylpyrylium-tetrafluoroborat (*TPT*) ergeben die entsprechenden α,β-ungesättigten Ketone **2 a–c** und **1 d** (aus **1 c**), neben Acetophenon (**3**), Benzophenon (**4**), Benzoesäure (**5**) und Benzaldehyd (**6**), vermutlich durch Fragmentierung des Radikal-Kations $\mathbf{1}^{+\cdot}$, das mittels Übertragung eines Elektrons von **1** zu *TPT* im angeregten Zustand erzeugt wird.

Introduction

Photosensitized electron transfer constitutes a well established methodology for the generation of radical cations in solution [1], which we have recently applied to the dehydrogenation of flavanones to flavones [2]. As an extension of this work, we were interested in the electron transfer photochemistry of 3-phenylpropiophenones of the type **1**, whose structures have in common with flavanones the two aryl rings linked by the 1-propanone bridge, although they lack the heterocyclic moiety.

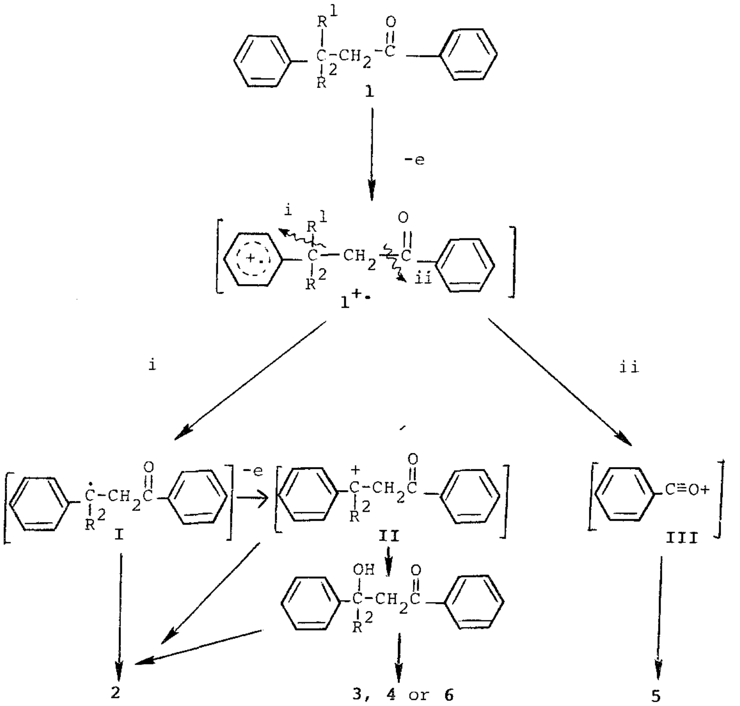
Results and Discussion

Irradiations were carried out at room temperature in the presence of catalytic amounts of the electron transfer photosensitizer 2,4,6-triphenylpyrylium tetrafluoroborate (*TPT*) [3] in aerated solutions of dichloromethane containing 0.1% water. The resulting products and their yields, expressed in percentages of the compound in the final crude mixture of photolysis, are given in Table 1.

Table 1. *TPT* photocatalyzed electron transfer reactions of 3-phenylpropiophenones in aerated CH_2Cl_2 solutions

Starting material				Yields (%)					
$Ph\mathrm{CR}^1\mathrm{R}^2-\mathrm{CH}_2\mathrm{CO}Ph$		Reference	Recovered %	$Ph\mathrm{CR}^1=\mathrm{CHCO}Ph$		$Ph\mathrm{COCH}_3$ **3**	$Ph_2\mathrm{CO}$ **4**	$Ph\mathrm{CO}_2\mathrm{H}$ **5**	Other products %
1: R^1	R^2			**2**	Reference				
a: H	H	8	72	4	8	–	–	12	*Ph*CHO (**6**) 3
b: *Me*	H	9	24	14	10	17	–	36	–
c: *Ph*	H	10	7	35	11	15	16	6	**1d** 14
d: *Ph*	OH	12	4	–		43	45	4	–

These results indicate that the radical cations **1**$^{+\cdot}$, formed by single electron transfer (SET) from the electron rich phenyl ring of **1** to excited *TPT*, undergo C – H or C – C bond cleavage to give intermediates **I** or **II**, as illustrated in Scheme 1. Further oxidation of the benzylic radicals **I** under the reaction conditions, affords the corresponding cations **II**. The feasibility of these processes is strongly supported by the well established behaviour of alkylaromatics following electron transfer oxidation [1, 4]. Formation of α,β-unsaturated ketones **2** from the intermediates **I** or **II** through disproportionation or deprotonation, respectively, or also via trapping of the benzylic cations **II** by water and subsequent dehydration of the resulting hydroxyketones is thus easily explained. (It must be emphasized that in fact **1 d** is a photoproduct of **1 c**.)



Scheme 1

Electron transfer photofragmentation of hydroxyketones such as **1 d** must be the origin of the isolated benzaldehyde (**6**) (starting form **1 a**) acetophenone (**3**) (from **1 b, c, d**) and benzophenone (**4**) (from **1 c** or **1 d**). This process is formally a retro-aldol reaction, and its correlation with the McLafferty rearrangement of analogous radical cations in the gas phase (electron impact mass spectrometry) is evident. Furthermore, the fact that the reaction mixtures of **1 c** and **1 d** contain equimolar amounts of acetophenone and benzophenone constitutes a further support in favour of the hypothesis that both compounds are formed as a consequence of the same cleavage process.

Finally, benzoic acid is presumably the product of nucleophilic attack by water to the benzoyl cation (**V**), generated after breaking of the carbonyl-methylene bond (process ii). This fragmentation is similar to that undergone by the radical cations of the 3-phenylpropiophenones **1** in the gas phase (electron impact mass spectrometry), where the benzoyl cation (*m*/*z* 105 amu) constitutes the base peak.

The fact that only catalytic amounts of *TPT* are required to accomplish these transformations indicates that oxygen must be acting as the electron sink. In this context, it is interesting that during electron transfer photooxygenations sensitized by 9,10-dicyanoanthracene (*DCA*), the radical anion of this compound reduces ground state oxygen to superoxide, regenerating in this way the photosensitizer [5]. The reduction potential of *TPT* does not allow the analogous process directly [6], but it is possible that electron transfer is assisted by oxygen [7].

Experimental

Preparation of 2,4,6-Triphenylpyrylium Tetrafluoroborate (*TPT*)

An equimolar mixture of chalcone (21.0 g, 100 mmol), acetophenone (12.0 g, 100 mmol), and tetrafluoroboric acid (8.7 g, 100 mmol) were heated at 60°C under magnetic stirring for 3 h. After this time, ethyl ether (1 l) was added and the resulting suspension was filtered. Additional amounts of *TPT* could be collected from the mother liquor by standing overnight in the refrigerator. The total yield was 64%. *TPT* samples employed as photosensitizer were recrystallized from dichloromethane before their use.

Irradiation Procedure

A solution of the corresponding 3-phenylpropiophenone **1** (250 g) and *TPT* (50 mg) in dichloromethane (300 ml, water constant 0.1%) were irradiated under continuous magnetic stirring in an open vessel through a potassium chromate filter (100 mg/l), using a 125 W medium pressure mercury lamp. The time of photolysis was in all cases 6 h. The irradiation mixture was kept at 10°C by a circulating cooling bath. Control experiments showed that no products were formed if the solutions were kept in the dark for 24 h or if the irradiations were carried out in the absence of *TPT*. The reaction mixtures were analyzed by GC/MS (HP 5988 A), GC coupled with a FT-IR detector (HP 5965 A) and ^{1}H-NMR (Varian 360 EM).

Physical and spectroscopic properties of compounds **1 a–d** and **2 a–c** were in good agreement with the values reported in the literature [8–12].

Acknowledgement

Financial support by the DGICYT, Spain (Grant No. PB .88-0494) is gratefully acknowledged.

References

[1] a) Julliard M., Chanon M. (1983) Chem. Rev. **83**: 425; b) Mariano P. S. (1985) in: Synthetic Organic Photochemistry (Horspool W. M., ed.). Plenum Press, New York, p. 145; c) Kavarnos G. J., Turro N. J. (1986) Chem. Rev. **86**: 401; d) Mattay J. (1987) Angew. Chem. Int. Ed. Engl. **26**: 825

[2] Climent M. J., García H., Iborra S., Miranda M. A., Primo J. (1989) Heterocycles **29**: 115

[3] For applications of *TPT* as electron transfer photosensitizer see: a) Farid S., Shealer S. E. (1973) J. Chem. Soc. Chem. Commun.: 677; b) Okada K., Hisamitsu K., Miyashi T., Mukai T. (1982) J. Chem. Soc. Chem. Commun.: 974; c) Mattay J., Gersdorf J., Mertes J. (1986) J. Chem. Soc. Chem. Commun.: 1088; d) Adam W., Dorr M. (1987) J. Am. Chem. Soc. **109**: 1570

[4] Lewis F. D., Petisce J. R. (1986) Tetrahedron **42**: 6207

[5] Okamoto A., Snow M. S., Arnold D. R. (1986) Tetrahedron **42**: 6175

[6] Mattes S. L., Farid S. (1983) Org. Photochem. **6**: 233

[7] In this case, superoxide ion would be a logical by-product and its participation to a certain extent in the formation of some of the products could not be rigorously ruled out

[8] Dhar D. N. (1981) The Chemistry of Chalcones and Related Compounds. J. Wiley, New York
[9] Filler R., Beaucare V. D., Kang H. H. (1975) J. Org. Chem. **40**: 935
[10] Freeman J. P. (1957) J. Org. Chem. **22**: 1608
[11] Southwick P. L., Pursglove L. A., Numerof P. J. (1950) J. Am. Chem. Soc. **72**: 1600
[12] Matsumura N., Kunugihara A., Yoneda S. (1983) Tetrahedron Lett. **24**: 3239

Received July 18, 1989. Accepted December 21, 1989