Electron Transfer Activation - A Selective Photooxidation Method for the Preparation of Aromatic Aldehydes and Ketones

Jean Santamaria* and Rachid Jroundi

Laboratoire de Recherches Organiques associé au CNRS, Ecole Supérieure de Physique et Chimie Industrielles, 10 rue Vauquelin 75231 Paris Cedex 05.

Key words : Singlet Electron Transfer ; benzylic oxidation ; hydroperoxides

Abstract : A selective and mild photocatalytic procedure for benzylic oxydations with 9,10-dicyanoanthracene (DCA), an usual electron acceptor, in presence of methyl viologen (MV^{2+}) and FeCl₂ has been developed.

In spite of numerous reports, there is still a paucity of efficient methods to perform benzylic oxidations ending into carbonylated derivatives, aromatic aldehydes and ketones. The first row transition metal complexes most often proposed to realize such oxidations suffer from several drawbacks¹. For instance, the reactions require a large excess of the metal reagents which are expensive and present a hazardous environmental impact.

We report a selective and mild photocatalytic procedure for converting polyalkylated aromatic hydrocarbons into mono-aldehydes or -ketones in good to excellent yields (61-87 %). These carbonyl derivatives arise from an iron(II)-photocatalyzed decomposition of the corresponding hydroperoxides, selectively generated *in situ* by a photo-induced electron transfer oxidation, using catalytic amounts of 9,10-dicyanoanthracene (DCA) in the presence of methylviologen (MV²⁺) and FeCl₂.

Ar-CH₂R $\frac{hv/O_2}{DCA-MV^{2+}/Fe^{2+}}$ Ar-CO-R 61-87 % visible light R = H or alkyl

Typical procedure

The irradiation of an acetonitrile-methanol (9:1) solution ² (50 ml) of the aromatic compound (5 mmol) in presence of catalytic amounts of DCA (0.02 mmol), MV^{2+} (0.02 mmol) and FeCl₂ (0.005 mmol) is carried out with a 500 W high-pressure mercury lamp through a U.V. cut-off glass filter ($\lambda \ge 420$ nm) at 20 °C under oxygen bubbling. The progress of the photoreaction if monitored by TLC and HPLC. After consumption of the substrate, the solvent is removed and the residue analyzed by ¹H NMR. The carbonyl derivatives are isolated by flash chromatography on silica gel.

Table 1 summarizes the results obtained with various aromatic compounds. With polymethylated substrates, only one methyl group is oxidized in these conditions; in the naphthalene series selective oxidation of the α -methyl group is observed. As it could be expected, the reaction could not be performed when the aromatic ring bears electron-withdrawing substituents such as NO₂ or CN (entries 7 to 11). Conversely, the effect of electron-donating groups increases both the overall rate and the yield of photooxidation (entries 15 and 16). Besides, it is noteworthy that no alcoholic derivatives are obtained as by

D	Substants	Carbonal and usta	Boaction time (h)	Vield	(%)
Kun	Substrate	Carbonyl products	Reaction time (ii)	h	(70)
	. 1	сно ~ 人		U	Č .
1			4	90	69(14) ^d
	\sim	CHO CHO			
	$\sim \downarrow$				
2	(KL	(Kl	3	87	71(22) ^d
	• • •	сно			
	\downarrow	<i>►</i>			
3			8	97	61(26) ^d
	_				
	R - <	R{}−Сно			
4	$R = C_c H_s$		3	88	58(28) ^d
5	= OCH3		3.30	97	78(15) ^d
6	= tBu		8	80	63(24) ^d
7-11	$R = NO_2$, CN, CO_2CH_2	3, Cl, Br unreactive			
	\sim	, Å			
12	(J	(J	1.30	98	85
	_ ~ _ /	~			
13			7	79	69
			0		
	\sim				<i></i>
14			4	93	75
	•	✓ 0 Ⅱ			
15			2	01	92
15			3	91	05
	• •				
16			2	98	87
	сн30	сн ₃ о			
		<u>م</u> للم			
17	(I)		3.30	92	81
	\sim \sim	$\sim \sim$			
	$\sim \sim \sim$	~Ľ~			
18		(LI)	4	98	82
	\sim \sim	\sim \sim			

Table 1. Carbonyl products resulting from DCA- MV^{2+}/Fe^{2+} - sensitized photooxidation of various aromatic compounds^a.

a. At room temperature and at total consumption of the substrate ; b. Evaluated from ${}^{1}H$ NMR data ; c. Isolated by flash chromatography ;

d. The corresponding acid was obtained as by products.

products. Finally, from the Rehm-Weller equation for an electron-transfer mechanism ⁴ and from the reduction potential and singlet excitation energy data (2.89 eV, 278.38 kJ/mol) ³ of DCA, this system can oxidize aromatic compounds such as those having $E_{oxy} \le 2 V$.

These oxidations show the general catalytic character of this new benzylic oxidation procedure.

One electron photocatalytic oxidations of methyl aromatic compounds using many sensitizers such as cyanoaromatics ⁵, cerium(IV) ammonium ⁶ or TiO₂⁷ have been reported. In the presence of O₂, a sequence of electron-transfer, proton-transfer steps as shown in Scheme 1 are postulated, and both an alkylperoxide radical (eq. 2) and a hydroperoxide (eq. 3) are probable intermediates in the products formation.



Scheme 1. S = sensitizer

We have recently discovered that the DCA- MV^{2+} system, when irradiated in acetonitrile, leads to the corresponding hydroperoxides isolated as such ⁸ in excellent yields.

Ar-CH₂-R $\frac{hv/O_2}{DCA-MV^{2+}}$ Ar-CH(OOH)-R R = H or alkyl

We have established now, from photochemical experiments performed at room temperature with these hydroperoxides ⁹ that :

- in the absence of Fe^{2+} the hydroperoxides are stable (d).

- both light and addition of catalytic amounts of Fe^{2+} are essential for the hydroperoxide decomposition (a)(Scheme 2).



Scheme 2

Therefore, in the overall reaction process the carbonyl derivatives arise from an iron(II)-photocatalytic decomposition of the intermediate hydroperoxides, selectively generated *in situ*.

This work has thus shown that the general mechanism displayed on scheme 1 can be now more precisely described; in effect, the existence of intermediate hydroperoxide is proved and also it is established that eq. 3 necessitates the catalytic action of ions such as Fe^{2+} .

Further studies are underway on this selective "photo-Fenton" decomposition.

Acknowledgments : We thank Prof. J. Rigaudy for his interest in this work.

References and Notes

- 1. For reviews, see : Sheldon, R.A.; Kochi, J.K., Metal-Catalyzed Oxidations of Organic Compounds ; Academic Press : New York, 1981. Organic Syntheses by Oxidation with Metal Compounds ; Mijs, W.J.; De Jonge, C.R.H.T.; Eds, Plenum Press : New York, London, 1986.
- 2. Solvents were distilled prior to use.
- 3. Eriksen, J.; Foote, C.S.; Parker, T.L., J. Amer. Chem. Soc., 1977, 99, 6455-6456.
- 4. Rehm, D.; Weller, A., Isr. J. Chem., 1970, 8, 259-271.
- Saito, I.; Tamoto, K.; Matsuura, T., *Tetrahedron Lett.*, **1979**, *31*, 2889-2892; Santamaria, J.; Gabillet, P.; Bokobza, L., *Tetrahedron Lett.*, **1984**, *25*, 2139-2142; Santamaria, J.; Ouchabane, R., *Tetrahedron*, **1986**, *42*, 5559-5566; Lewis, F.D.; Petisce, J., *Tetrahedron*, **1986**, *42*, 6207-6217; Baciocchi, E.; Piermattei, A.; Rol, C.; Ruzziconi, R.; Sebastiani, G.V., *Tetrahedron*, **1989**, *45*, 7049-7062; Albini, A.; Spreti, S., *Z. Naturforsch*, **1986**, *41b*, 1286-1292, Julliard, M.; Galadi, A.; Chanon, M., *J. Photochem. Photobiol. A : Chem.*, **1990**, *54*, 79-90.
- 6. Baciocchi, E.; Del Giacco, T.; Rol, C.; Sebastiani, G.V., Tetrahedron Lett., 1985, 26, 3353-3356.
- 7. Pichat, P.; Disdier, J.; Hermann, J.M.; Vaudano, P., Nouv. J. Chem., 1986, 10, 545-551.
- 8. Santamaria, J.; Jroundi, R.; Rigaudy, J., Tetrahedron Lett., 1989, 30, 4677-4680.
- 9. All these hydroperoxides are isolated and characterized.

(Received in France 9 April 1991)