Photochemistry of α-Carbonylferrocenes and Related Compounds

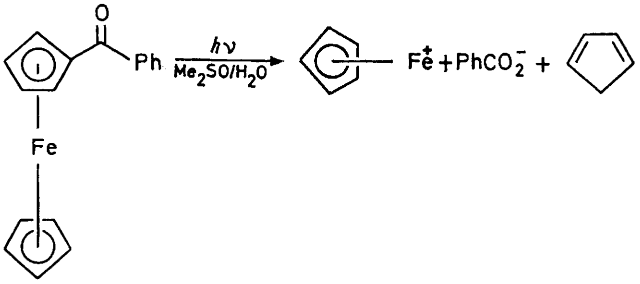
By L. H. Ali, A. Cox, and T. J. Kemp*

(*School of Molecular Sciences, University of Warwick, Coventry* CV4 7AL)

Summary Benzoylferrocene photoreacts with water in solvents such as dimethyl sulphoxide and pyridine to yield cyclopentadienyliron benzoate and free cyclopentadiene identified by i.r., u.v., and n.m.r. spectroscopy; a variety of other α-carbonylferrocenes are photoreactive in these solvent systems to give products which may also contain carboxylate groups.

IN contrast to benzophenone, benzoylferrocence (I) is remarkably inert on photo-irradiation in reducing solvents such as isopropyl alcohol,[1] although some photoreaction has been briefly noted[2] in solvents such as dimethyl sulphoxide, pyridine, and dimethylformamide (DMF), affording a purple colouration in each case, but no further characterisation was attempted.

We find that (I) undergoes an efficient photoreaction with a molar excess of water in Me_2SO or pyridine to give cyclopentadienyliron benzoate and free cyclopentadiene (see Scheme).



(I)

SCHEME.

The reaction, which was not quenched in the presence of 10^{-2}M-naphthalene and which failed to proceed in dry solvents, was carried out in a Pyrex vessel, being effected by both the 466 and 359 nm bands, absorptions which are associated with electronic transitions in the metal–carbon bonds.[3]

Solutions of benzoylferrocene in C_5D_5N show signals at τ 6·06 (s, 5H, unsubstituted ring), 5·70, 5·25 (m, 2H each, substituted ring), and 2·65, 2·10 (m, 5H, C_6H_5), and on photolysis in the same solvent, new peaks appear at τ 6·2 (s, 5H, unsubstituted ring), 2·6, 2·2 (m, 5H, C_6H_5), and 3·8 (m, 4H), 7·5 (m, 2H) (free cyclopentadiene), (s, 5H, unsubstituted ring), 2·6, 2·2 (m, 5HC_6H_5,), and 3·8 (m, 4H), 7·5 (m, 2H) (free cyclopentadiene). Concurrently, the optical absorption band characteristic of ferrocenes, λ_{max} 466 nm, is destroyed and the other band, λ_{max} 359 nm, gradually shifts to 340 nm. The i.r. spectrum of the starting material in Me_2SO shows ν_{max} 1638 cm^{-1} (C=O) which absorption disappears on photolysis leading to a build-up of the characteristic absorption at 1538 cm^{-1} (vs). In pyridine or $(CD_3)_2SO$ an absorption at 1365 cm^{-1} (s) is evident which also indicates the presence of a carboxylate group. Acidification (dilute HCl) of the solution results in destruction of the absorption at 1538 cm^{-1} and the appearance of a new band at 1710 cm^{-1} ($PhCO_2H$) from which solution benzoic acid was successfully isolated.

Admission of oxygen to the solution before acidification produces the purple colouration noted before[2] (λ_{max} 550 nm) which was not identified but which displays the characteristic e.s.r. spectrum of high-spin Fe^{III}. The same material is also generated by admission of oxygen to the product of photolysis of benzoylferrocene in pyridine, or by irradiating benzoylferrocene in Me_2SO solution in a quartz vessel in which case Me_2S is also produced.[4]

N.m.r. studies on the photoreaction of t-butyl-substituted benzoylferrocenes in C_5D_5N strongly indicated that it is the originally unsubstituted ring which remains bound to the iron atom.

The Table lists the compounds which have also been irradiated and give rise to strong i.r. absorptions.

Compound	ν_{max} (C = O) in starting material	ν_{max} (CO_2^-) in product
Formylferrocene	1663	1593
Acetylferrocene..	1666	1562
1,1′-Dibenzoylferrocene ..	1641	1538
p-Methoxybenzoylferrocene ..	1630	1530
Ferrocenoic acid	1692	1582
Methyl ferrocenoate	1712	1550
Ferrocenoyl chloride	1766	1585
Ferrocenoic amide	1664	1527
1-Ferrocenylbut-1-en-3-one ..	1660	1553
1-Benzoyl-2-t-butylferrocene ..	1638	1537

Ferrocenylacetone, ferrocenylmethyl acetate, and ferrrocenylacetic acid are photochemically unreactive under these conditions and both benzophenone and *p*-aminobenzophenone are similarly stable. The i.r. frequencies suggest the presence of carboxylate species as products but experiments are in hand to clarify this point and also the mechanistic details of these reactions.

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