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Preliminary communication

NOVEL PHOTOREACTION PRODUCTS OF *N*-SUBSTITUTED FERROCENYLIMINES

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Summary

Ferrocene-aldimines and -ketimines undergo benzophenone sensitized photochemical hydrolysis to give the corresponding ferrocene-carbaldehydes or -ketones.

Although the photochemistry of ferrocene derivatives has attracted increasing attention over the last few years [1] no photochemical reactions of ferrocenylimines have been described. This is surprising since the irradiation of arylimines leads to several products [2]. We now report the sensitized photochemical hydrolysis of ferrocene-aldimines and -ketimines on irradiation for 2 h with a medium-pressure mercury lamp. The results obtained from the photolysis of thirteen compounds are collected in Table 1, in each case the dominant product was ferrocenecarbaldehyde or a ferrocenylketone and in most cases it was the only product.

Under the conditions that we have used, benzaldehyde-*N*-substituted imines undergo either reductive dimerization [3] or give the corresponding nitriles [4] as the principal products. Benzaldehyde was only obtained by irradiation of benzaldehyde-*N*-alkylimines when oxygen was bubbled through the reaction mixture [5] and as a minor product from the irradiation of benzylidene-t-butylamine in benzene [4].

Products isolated from the photolysis of phenylhydrazones include hydrocarbons, nitriles, amines and benzaldehyde with the aldehyde usually present as a minor component [6]. The photolysis of ketimines leads to reduction [7,8] or reductive dimerization [8] and the formation of ketones in these reactions does not appear to have been reported.

Several mechanistic pathways have been proposed to account for the formation of aldehydes from imines. Furey and Kan [5] have suggested that the carbon—nitrogen double bond is attacked by photochemically generated

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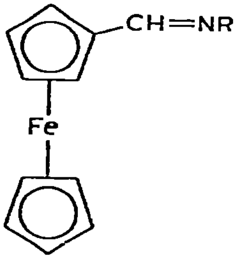
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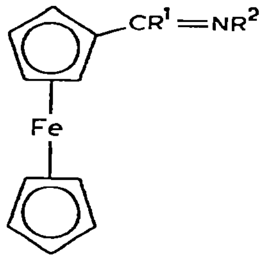
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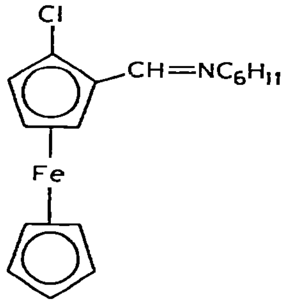
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TABLE 1

CARBONYL PRODUCTS, YIELDS AND EXPERIMENTAL CONDITIONS FOR THE PHOTOLYSIS OF UNSATURATED NITROGEN DERIVATIVES OF FERROCENE

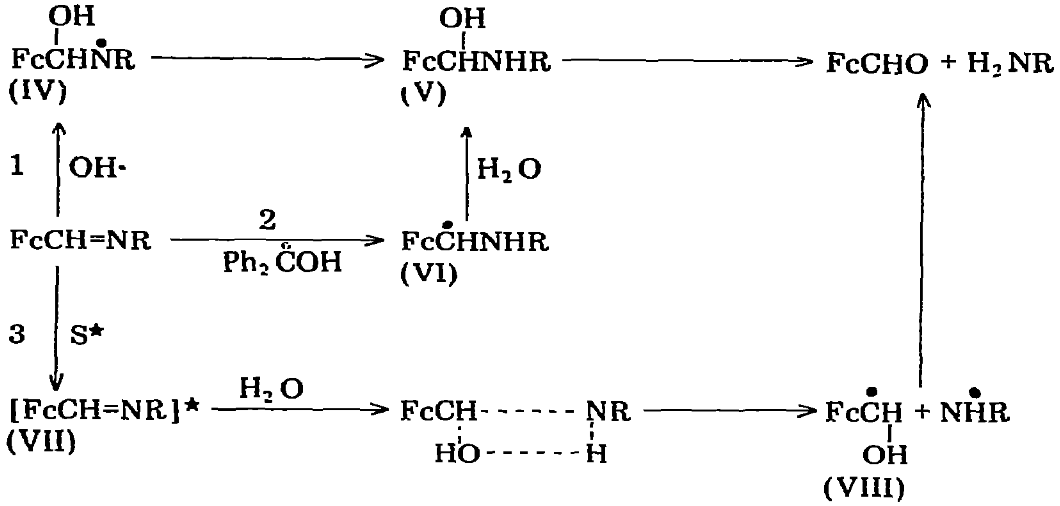
Reactant	Sensitizer	Solvent	Product	Yield (%)
I; R = C_6H_{11}	Ph_2CO(NpH)	EtOH	FcCHO [a]	42 (42)
I; R = C_6H_{11}	Ph_2CO	i-PrOH	FcCHO	28
I; R = C_6H_{11}	Ph_2CO	Me_2SO	FcCHO	45
I; R = C_6H_{11}	Ph_2CO	PhH	FcCHO	73
I; R = C_6H_{11}	Ph_2CO	C_6H_{12}	FcCHO	20
I; R = CH_2Ph	Ph_2CO(NpH)	EtOH	FcCHO	45 (43)
I; R = Ph	Ph_2CO	EtOH	FcCHO	18
I; R = Np	Ph_2CO	EtOH	FcCHO	42
I; R = NHPh	Ph_2CO	EtOH	FcCHO	20
I; R = $NHCONH_2$	Ph_2CO	EtOH	—	0
I; R = OH	Ph_2CO	EtOH	FcCHO	7
II; R^1 = Me R^2 = Ph	Ph_2CO	EtOH	FcCOMe	53
II; R^1 = Ph, R^2 = *p*-tolyl	Ph_2CO	EtOH	FcCOPh	30
III	Ph_2CO	EtOH	FcCHO	30
I; R = C_6H_4-CF_3-*p*	Ph_2CO	EtOH	FcCHO	15
I; R = NHCOMe	Ph_2CO	EtOH	—	0
FcCN	Ph_2CO	EtOH	—	0

[a] Fc = π-C_5H_5Fe-π-C_5H_4

hydroxyl radicals (Scheme 1, reaction 1) to give the radical IV which abstracts hydrogen to form the secondary amine V. A reaction proceeding by this path would not be expected to show the sensitivity to electron-withdrawing groups that we have observed. Alternatively [3] a hydrogen atom may be transferred to the imine from benzophenone ketyl to form the intermediate VI which abstracts hydroxyl from water or peroxide [5] to give the amine V (reaction 2). This mechanism is not compatible with our observed results in non-hydroxylic solvents and with naphthalene as sensitizer. The concerted mechanism (reaction 3) [5] in which the excited imine VII is attacked by water to yield the cleavage product VIII directly is consistent with our results although it is not possible to exclude the alternative pathways mentioned above.

All new compounds prepared were characterized by elemental analysis and spectroscopy.

SCHEME 1



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