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PHOTOCHEMICAL REACTIONS OF FERROCENYL KETONES

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SUMMARY

Ultraviolet irradiation of formyl-, acetyl- and benzoyl-ferrocene in the presence of hydrogen- and electron-donors, leads to photoreduction only with tin(IV) hydrides. The photoreaction of the ketones with water or methanol was also studied.

INTRODUCTION

Earlier work[1] has suggested that ferrocenyl ketones are not susceptible to photochemical reduction by 2-propanol. This is in contrast to the corresponding benzene derivatives such as benzophenone, which is photoreduced efficiently to pinacol [eqn. (1)][2].

$$Ph_2C{=}O+(CH_3)_2CHOH \xrightarrow{h\nu} Ph_2C(OH)CPh_2(OH)+(CH_3)_2C{=}O \qquad (1)$$

Naphthyl ketones, however, require either a better hydrogen-donor such as tri-n-butyltin(IV) hydride[3] or an electron-donor such as a tertiary amine[4] for efficient reduction. In the hydrogen abstraction process this difference is attributed to the lower energy of the first excited state of a naphthyl ketone ($\approx$245 kJ·mol^{-1}) as compared to that of a phenyl ketone (285–300 kJ·mol^{-1}), and to the difference of electron distribution in the excited states. For the phenyl ketone the excited state is (n,π^*) and the oxygen atom has radical character, whilst for the naphthyl ketone the excited state is (π,π^*). With the tertiary amine the mechanism of the reduction is different, and the amine acts initially as an electron-donor rather than as a hydrogen-donor to the excited state of the ketone in the first step of the reaction [eqn. (2)].

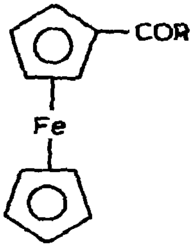
$$[C_{10}H_7C(O)CH_3]^*+(C_2H_5)_3N \rightarrow [C_{10}H_7C(O)CH_3]^{\dot{-}}+(C_2H_5)_3N^{\dot{+}} \qquad (2)$$
$$(C_{10}H_7 = \text{2-naphthyl})$$

In ferrocenyl ketones the lowest excited state is thought to be charge-transfer in nature[5] and less than 170 kJ·mol^{-1} in energy. This led us to investigate the photochemical behaviour of ferrocenyl ketones in the presence of different reducing agents.

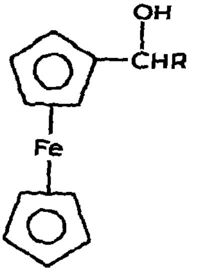
RESULTS AND DISCUSSION

Solutions of formyl-[(I); R=H], acetyl-[(I); R=CH_3], and benzoyl-[(I);

R = Ph] ferrocene were irradiated in the presence of reducing agents with light from a medium pressure mercury arc filtered through quartz or Pyrex glass. The hydrogen donors were chosen for their differing bond strengths to hydrogen: 2-propanol (C–H bond strength ≈370 kJ·mol^{-1}), triphenylmethane (C–H≈300 kJ·mol^{-1}), triphenylsilane (Si–H 295–310 kJ·mol^{-1}), triphenyltin(IV) hydride and tri-n-butyltin(IV) hydride (Sn–H < 290 kJ·mol^{-1}).



(I)



(II)

For the ferrocenyl ketones (I) photoreduction was observed only with the tin(IV) hydrides to give the corresponding alcohols (II) as the major product. These products were not formed by thermal reduction, as shown by monitoring control samples in the absence of an ultra-violet source. The quantum yields for photoreduction were low, and values could not be estimated accurately because the radiation used was polychromatic and because a solid deposit formed on the wall of the vessel nearest to the lamp in most reactions. Values of quantum yield (Φ) for the photoreduction of acetylferrocene are shown in the Table 1. Where no reduction was observed estimates of the upper limit for Φ are given.

TABLE 1

	2-Propanol	*Ph$_3$CH*	*Ph$_3$SiH*	*Bu$_3$SnH*	*Ph$_3$SnH*
Φ	< 0.0002	< 0.0001	< 0.0001	≈0.002	≈0.002

Irradiation of acetylferrocene with 2-propanol using either quartz- or Pyrex-filtered light at a reaction temperature of either 25° or 70° gave no detectable reduction products and no acetone. With triphenylmethane, triphenylsilane and triphenyltin(IV) hydride products were formed by photochemical decomposition of the reducing agent[6].

The lowest excited states of acylferrocenes, like those of acylnaphthalenes, are not (n,π^*) and the oxygen atom has little radical character. The reduced efficiency of the reactions for acylferrocenes is probably a result of the lower energy of the excited states. Estimates of the enthalpy changes in the primary reaction step [eqn. (3)] suggest that the inefficiency of the photoreduction of ferrocenyl ketones even by tin(IV) hydrides arises because the initial step is relatively slow and physical decay of the excited state competes effectively with chemical reaction.

$$[C_{10}H_7C(O)R]^* + R'_3SnH \rightarrow C_{10}H_7\dot{C}R(OH) + R'_3\dot{S}n \qquad \Delta H \approx -60\ \mathrm{kJ \cdot mol^{-1}}$$

$$[FcC(O)R]^* + R'_3SnH \rightarrow Fc\dot{C}R(OH) + R'_3\dot{S}n \qquad \Delta H \approx +15\ \mathrm{kJ \cdot mol^{-1}} \quad (3)$$

$(Fc = C_{10}H_9Fe)$

By analogy with acylnaphthalenes, the acylferrocenes might undergo photoreduction with tertiary amines by way of electron transfer to the ferrocene. We therefore irradiated acylferrocenes [(I); R = H, CH_3, Ph] in 2-propanol in the presence of triethylamine (up to 25% v/v). Although the solution darkened a little on prolonged irradiation, no reduction products of the ferrocenes were detected. This implies that electron transfer to the excited state of the acylferrocene from the tertiary amine is not a fast reaction.

Whenever a ferrocenyl ketone was irradiated in methanol as solvent a rapid change in colour of the solution was observed. This effect was investigated further, particularly in view of the inertness of 2-propanol. Acylferrocenes [(I); R = CH_3, Ph] irradiated in methanol were consumed with a quantum yield of 0.02 or greater. In the absence of oxygen the colour faded to a pale yellow-brown, and the solution was very sensitive to oxidation, darkening and depositing a brown precipitate on exposure to air or more rapidly on addition of manganese dioxide. The precipitate contained over 70% of the original iron. In the solution cyclopentadiene was identified by GLC. A less volatile, colourless product was observed as a major component on thin layer chromatography (TLC) of the reaction mixture. This product survived treatment with acid, but decomposed slowly on standing and could not be isolated. A different product of this type (as indicated by TLC) was obtained from each ketone, and was probably derived from the substituted ring of the acylferrocene.

The effect of methanol and of water in this reaction was investigated by irradiation of acetylferrocene in 30% v/v methanol in dioxane and in 30% v/v water in dioxane (the photoreaction is much slower in dioxan than in the mixed solvents). With the methanolic solvent photoreaction occurred with a quantum yield of 0.01–0.02, and in the aqueous solvent reaction was about five times as efficient. Infra-red analysis of the products from the aqueous solution indicated the presence of carboxylate, and is in agreement with the findings of Ali, Cox and Kemp[7].

The effectiveness of methanol and water in bringing about photoreaction, and the relative ineffectiveness of triethylamine, support the proposal of Tarr and Wiles[8] that electron transfer occurs from the excited state of the ferrocenyl ketone to the other reagent [eqn. (4)]. Ferricinium ions break down in the presence of radicals, which accounts for the precipitation of iron compounds and the production of cyclopentadiene[9].

$$[FcC(O)R]^* + CH_3OH \rightarrow Fc^+C(O)R + \dot{C}H_3 + OH^- \qquad (4)$$

EXPERIMENTAL

Formyl[10]-, acetyl[11]- and benzoyl[12]-ferrocene, tri-n-butyltin(IV) hydride[13] and triphenyltin(IV) hydride[6] were prepared via standard procedures. Commercial samples of triphenylsilane (B.D.H.) and triphenylmethane (B.D.H.) were used. Light petroleum (b.p. 40–60°) was used as solvent unless otherwise stated. Methanol and

2-propanol were dried via the Grignard procedure and distilled prior to use. Dioxane was dried with sodium and distilled.

Irradiation procedure

Oxygen-free nitrogen was bubbled through all the solutions prior to irradiation. A 500 watt medium pressure mercury arc tube (Hanovia 6744) was used with a quartz filter, and a 100 watt medium pressure mercury arc tube (Hanovia 12277) with a Pyrex glass filter. Quantum yields were estimated by comparison with valerophenone in benzene[14] as a secondary standard actinometer, with corrections for the differences in absorption characteristics.

In the methanol experiments cyclopentadiene was identified and estimated by gas-liquid chromatography with a Pye series 104 chromatograph using a 0.004 x 1.5 m column packed with 10% polyethylene glycol on Kieselguhr. The absence of acetone in the experiments using 2-propanol was confirmed using gas-liquid chromatography (conditions as above) by comparison with an authentic sample.

All the reactions were monitored by thin-layer chromatography using Eastman Chromagram Sheet 6060 (silica gel with fluorescent indicator) and 15% ether/light petroleum mixture. The R_f values of the alcohols [(II); R = H, CH_3, Ph] were checked against those of authentic samples.

In the aqueous dioxane experiment the solvent was removed under reduced pressure, and the infra-red spectrum of the crude product was recorded. A strong absorption band at 1540 cm^{-1} was taken to indicate the presence of carboxylate.

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