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THE PHOTOLYSIS OF η^6-*o*-, *m*- OR *p*-AZIDOTOLUENE-η^5-CYCLOPENTADIENYLIRON HEXAFLUOROPHOSPHATE

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Summary

Photolysis studies were carried out using dilute solutions of η^6-*o*-, *m*- or *p*-azidotoluene-η^5-cyclopentadienyliron hexafluorophosphate (I, II or III, respectively) in cyclohexane or CH_2Cl_2 as solvent. From I, the only ring contraction product was 1-cyano-2-methylferrocene (IV) while the analogous product from III was 1-cyano-3-methylferrocene (V). With II as substrate, a 1:3 mixture of IV and V was obtained. When the solvent was CH_2Cl_2, some ferrocene was also formed. Mechanistic interpretations of these results are discussed.

Introduction

Recently we have studied the thermolysis and photolysis of η^6-azidobenzene-η^5-cyclopentadienyliron hexafluorophosphate and found that both reactions gave cyanoferrocene as one of the products [1]. It was suggested that this ring contraction resulted from processes involving the formation of the phenylnitrene complex as a reaction intermediate. A similar ring contraction for the free ligand was first reported by Crow and Wentrup [2] and by Hedaya and coworkers [3] in the gas phase pyrolysis of phenyl azide, while such a reaction in an organometallic system was first observed by Munro and Pauson [4] in the thermolysis of azidobenzenetricarbonylmanganese hexafluorophosphate to give cyanocyclopentadienyltricarbonylmanganese. Munro and Pauson [4] also found that the thermolysis of the *p*-azidotoluenetricarbonylmanganese complex gave only 1-cyano-3-methylcyclopentadienyltricarbonylmanganese. In the present work, we have investigated the photolysis of the three isomeric η^6-azidotoluene-η^5-cyclopentadienyliron hexafluorophosphates.

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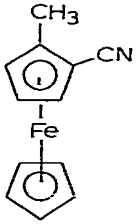
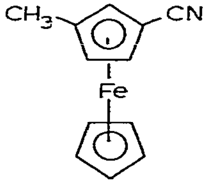
Results and discussion

The preparation of η^6-*o*-, *m*- or *p*-azidotoluene-η^5-cyclopentadienyliron hexafluorophosphate (I, II or III, respectively) was effected by the reaction of η^6-*o*-, *m*- or *p*-chlorotoluene-η^5-cyclopentadienyliron hexafluorophosphate with NaN_3 as previously described for the analogous preparation of the azidobenzene complex [1], the isomeric *o*-, *m*- or *p*-chlorotoluene complex required in these reactions being obtained from ligand exchanges between ferrocene and the chloroarene as reported in the literature [5—7]. The yields of these azidotoluene complexes and their ^1H NMR data are summarized in Table 1.

The photolysis was carried out in a Rayonet photochemical reactor equipped with 3000 Å lamps. Dilute solutions of I, II or III in cyclohexane or in methylene chloride were irradiated at ambient temperature ($30 \pm 1°C$) for 4 h. From the *o*-azidotoluene complex I, the ring contraction product was 1-cyano-2-methylferrocene (IV), while from the *p*-azidotoluene complex III, the analogous product was 1-cyano-3-methylferrocene (V) *. With the *m*-azidotoluene complex II, both IV and V, in a ratio of about 1:3, were obtained. When the photolysis was carried out in cyclohexane as solvent, besides IV and/or V, some unreacted starting material was recovered. On the other hand, with CH_2Cl_2 as solvent, there was no recovered azidotoluene complex, but some ferrocene was formed. The results are given in Table 2.



(IV)



(V)

In the earlier study on the photolysis of η^6-azidobenzene-η^5-cyclopentadienyliron hexafluorophosphate [1], some ferrocene was also obtained when CH_2Cl_2 was used as solvent. Because the yield of cyanoferrocene was lower in CH_2Cl_2 than in cyclohexane, it was mentioned briefly that further photolytic decomposition might occur in CH_2Cl_2 and the ferrocene possibly might be derived from cleavage of cyanoferrocene. From Table 2, it is seen that ferrocene was obtained in the photolysis in CH_2Cl_2 of I, II or III. It would be highly unlikely that both the cyano and the methyl groups could be lost from cyanomethylferrocenes IV and V to give ferrocene, and the previous suggestion [1] that ferrocene might be derived from cyanoferrocene is probably incorrect. Nesmeyanov and coworkers [8] have reported that the photolysis of $C_6H_6FeCp^+BF_4^-$ gave rise to ferrocene, benzene and $Fe(BF_4)_2$ and this photodisproportionation was found to be highly dependent on the nature of the solvent. It was noted that the solvents in which photodisproportionation could

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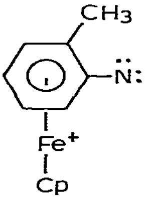
* Preliminary work by C.I. Azogu in this laboratory showed that thermolysis of I or III also gave IV or V, respectively. No thermolysis study has yet been carried out on complex II.

take place to give appreciable yields of ferrocene all contained atoms with unshared pairs of electrons [8]. The present finding that ferrocene was formed in photolysis in CH_2Cl_2 and not in cyclohexane is in agreement with this observed solvent effect, and photodisproportionation thus provides a plausible explanation for the formation of ferrocene as recorded in Table 2.

Wentrup and Crow [9,10] have shown that in the pyrolysis of substituted phenyl azides or benzotriazoles at high temperature, sigmatropic shifts of the cyano group took place in the resulting substituted cyanocyclopentadiene product. For example, the pyrolysis of *m*- or *p*-tolyl azide at 450°C and 1.0 Torr gave rise to the same mixture of 1-cyano-2-methylcyclopentadiene and 1-cyano-4-methylcyclopentadiene [9]. As already pointed out in the introductory paragraph, Munro and Pauson [4] have observed the formation of 1-cyano-3-methylcyclopentadienyltricarbonylmanganese as the only product in the thermolysis at 132°C and 0.5 Torr of *p*-azidotoluenetricarbonylmanganese hexafluorophosphate. It was concluded that under the milder thermolysis conditions, there was no sigmatropic migration of the cyano group [4]. The presently observed formation of IV from I and V from III also supports this conclusion and that under the relatively mild photolysis conditions, again there was no migration of the cyano group in the reaction product.



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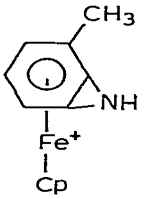

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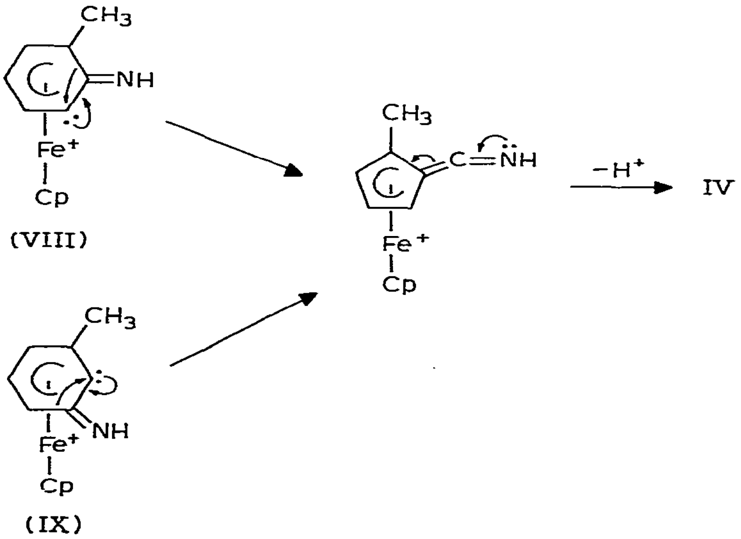
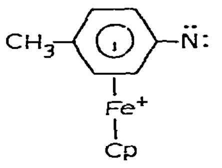


In analogy with the mechanism suggested by Thetaz and Wentrup [11] for the ring contraction from phenylnitrene to give 1-cyanocyclopentadiene, for the thermolysis or photolysis of η^6-azidobenzene-η^5-cyclopentadienyliron hexafluorophosphate, it was proposed that the phenylnitrene complex that was formed would undergo intramolecular insertion and then isomerization to an iminocarbene complex, which in turn would proceed by a Wolff-type of rearrangement to give the ring contraction product, cyanoferrocene [1]. Utilizing the same processes, with the *o*-azidotoluene complex I as substrate, the *o*-tolylnitrene complex VI that is formed will give rise to insertion product VII. Isomerization of VII will lead to iminocarbene complexes VIII and IX, but a Wolff-type of rearrangement with either VIII or IX gives only 1-cyano-2-methylferrocene (IV) as product.

Similarly, from the *p*-azidotoluene complex III, insertion with the *p*-tolylnitrene complex X will give XI which in turn may isomerize to iminocarbene complexes XII and XIII. Again a Wolff-type rearrangement with either XII or XIII gives only one product, 1-cyano-3-methylferrocene (V).



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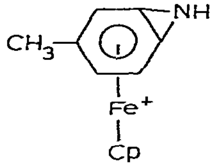

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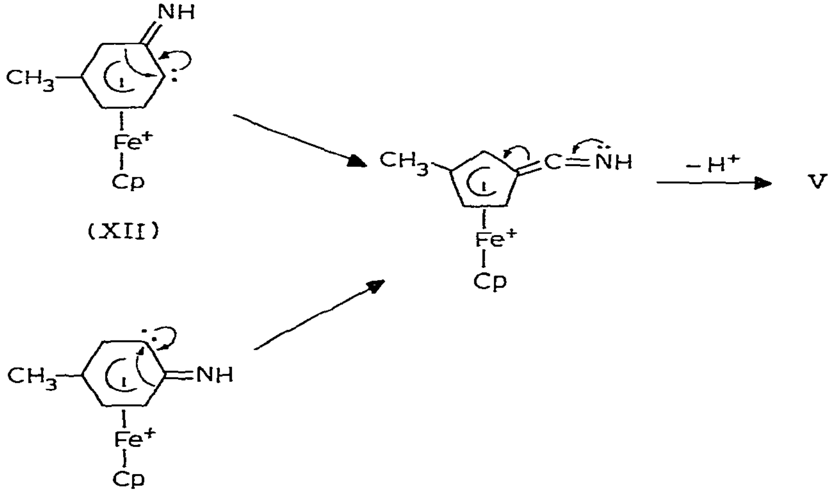

(XII)

(XIII)

From the photolysis of the *m*-azidotoluene complex II, the *m*-tolylnitrene complex will give rise to both insertion products VII and XI which will lead to the formation of IV and V, respectively. Apparently VII is formed to a lesser extent than XI possibly because of the steric effect of the *o*-methyl substituent.

Thus in the photolysis of II, a mixture of IV and V is obtained, with IV being formed in a lesser amount than V. From the above considerations, therefore, it may be concluded that the previously proposed mechanism for the ring contraction [1] can also adequately explain the presently observed results from the photolysis of the azidotoluene complexes I, II and III.

Experimental

Preparation of η^6-o-, m- and p-azidotoluene-η^5-cyclopentadienyliron hexafluorophosphates (I, II and III).

The azidotoluene complexes I, II and III were prepared from the reaction of the *o*-, *m*- or *p*-chlorotoluene complex with NaN_3 in a similar manner as already described for the synthesis of the azidobenzene complex [1]. Typically, treatment of 7.60 g (19.4 mmol) of η^6-*o*-chlorotoluene-η^5-cyclopentadienyliron hexafluorophosphate with 10.0 g (154 mmol) of NaN_3 in 25 ml of dry DMF at room temperature for 48 h followed by work up as described previously [1] gave 6.20 g (80%) of product I. The yields of I, II and III and their NMR data are given in Table 1.

Photolysis reactions

The procedures used in the various photolysis reactions are also similar to those previously employed in the photolysis of the azidobenzene complex [1]. Some typical experiments are described below.

(a) Photolysis of I. A solution of 1.00 g (25 mmol) of the *o*-azidotoluene complex I in 500 ml of CH_2Cl_2 in a pyrex reaction vessel was irradiated for 4 h in a Rayonet photochemical reactor equipped with 3000 Å lamps. The solvent was then removed in a rotary evaporator and the dark brown residue was extracted with ether to separate the non-ionic materials. After removal of the ether from the extract, the yellow-orange crystalline residue was redissolved in ether and 2.0 g of adsorption alumina was added. The ether was again evaporated off and the alumina, with its adsorbed products, was placed on top of an alumina column (25 cm × 2.5 cm dia) for chromatographing. The first yellowish-orange band was eluted with Skelly B to give 55 mg (12%) of a crystalline product, the IR and NMR spectra of which were identical with those of an authentic sample of ferrocene. A second orange band was eluted with CH_2Cl_2, giving 27 mg (5%) of a product which was identified as 1-cyano-2-methylferrocene (IV) ^{1}H NMR δ(acetone-d_6) 2.2(s, 3H, CH_3), 4.2(s, 5H, Cp), and 4.3—

TABLE 1

YIELDS AND ^{1}H NMR DATA FOR η^6-*o*, *m*, AND *p*-AZIDOTOLUENE-η^5-CYCLOPENTADIENYLIRON HEXAFLUOROPHOSPHATES

Product	Yield (%)	^{1}H NMR (δ(acetone-d_6)ppm from TMS)		
		CH_3	Cp	Aromatic
o-$CH_3(N_3)C_6H_4FeCp^+ PF_6^-$ (I)	80	2.5(s)	5.3(s)	6.2—2.7(m)
m-$CH_3(N_3)C_6H_4FeCp^+ PF_6^-$ (II)	80	2.6(s)	5.2(s)	6.2—6.6(m)
p-$CH_3(N_3)C_6H_4FeCp^+ PF_6^-$ (III)	86	2.5(s)	5.3(s)	6.3—6.6(m)

4.6(m, 3H, substituted Cp)ppm. Its characteristic IR absorption for C≡N appeared at 2240 cm^{-1}, and its ^{13}C NMR spectrum showed the CH_3 peak at 13.59 ppm and an intense unsubstituted Cp peak at 71.15 ppm. A third band, purplish brown in color, was eluted with a 1:10 mixture of acetone/CH_2Cl_2 to give an unidentified liquid; however, among the peaks in its mass spectrum were *m/e* peaks at 107 and 133, suggesting the presence of $CH_3C_6H_4NH_2$ and $CH_3C_6H_4N_3$.

The ionic residue from the photolysis reaction in CH_2Cl_2 that remained after the ether extraction was dissolved in a small amount of CH_3NO_2 and chromatographed through another alumina column. Only one band was eluted with a 5:1 mixture of CH_2Cl_2/CH_3NO_2, giving 50 mg of a brown solid which appeared to be an impure sample of the *o*-toluidine complex, *o*-$CH_3(NH_2)C_6H_4FeCp^+PF_6^-$.

When 1.00 g (25 mmol) of I in 500 ml of cyclohexane (as a slurry since I was not completely dissolved) was irradiated for 4 h and worked up as described above, the photolysis products were again separated into non-ionic and ionic fractions by ether extraction and each fraction chromatographed through an alumina column. For the non-ionic material, there was no ferrocene upon elution with Skelly B, but elution with CH_2Cl_2 gave 97 mg (17%) of IV as the only non-ionic product. From the ionic residue, the first band was eluted with CH_2Cl_2 to give 342 mg (34%) of recovered reactant I. A second band was eluted with a 5/1 mixture of CH_2Cl_2/CH_3NO_2 to give 240 mg of a brown solid which appear to be a mixture of I and the *o*-toluidine complex, *o*-$CH_3(NH_2)C_6H_4FeCp^+PF_6^-$.

(b) Photolysis of III. A solution of 1.00 g (25 mmol) of the *p*-azidotoluene complex III in 500 ml of CH_2Cl_2 or cyclohexane was irradiated for 4 h and worked up as described in the preceding section. For the reaction of CH_2Cl_2, from the non-ionic fraction, the pure products obtained were 31 mg (7%) of ferrocene and 55 mg (10%) of 1-cyano-3-methylferrocene (V). The ^{1}H NMR of V gave δ(acetone-d_6) 2.0(s, 3H, CH_3), 4.2(s, 5H, Cp) and 4.3—4.6(m, 3H, substituted Cp)ppm. Its C≡N IR absorption appeared at 2250 cm^{-1} and its ^{13}C NMR showed a CH_3 peak at 14.53 ppm and an intense unsubstituted Cp peak at 71.22 ppm. From the ionic residue for the reaction in CH_2Cl_2, only an impure product (147 mg) containing some *p*-toluidine complex,

TABLE 2

YIELDS OF PRODUCTS FROM THE PHOTOLYSIS OF η^6-*o*, *m* OR *p*-AZIDOTOLUENE-η^5-CYCLOPENTADIENYLIRON HEXAFLUOROPHOSPHATE (I, II OR III, RESPECTIVELY)

Reactant	Solvent	Yield (%) [a]			
		IV [b]	V [c]	Ferrocene	Recovered I, II or III
I	Cyclohexane	17	—	—	34
	CH_2Cl_2	5	—	12	—
II	Cyclohexane	11 (IV + V) [d]		—	32
	CH_2Cl_2	7 (IV + V) [d]		13	—
III	cyclohexane	—	13	—	32
	CH_2Cl_2	—	10	7	—

[a] Besides these pure products, impure, unidentified materials were also present. [b] IV is 1-cyano-2-methylferrocene. [c] V is 1-cyano-3-methylferrocene. [d] Ratio of IV/V is about 1/3.

p-$CH_3(NH_2)C_6H_4FeCp^+PF_6^-$, was obtained. For the reaction in cyclohexane, the non-ionic fraction gave 75 mg (13%) of V as the only product, and from the ionic fraction, 318 mg (32%) of unreacted III was recovered.

(c) Photolysis of II. Similar photolysis reactions were carried out on 1.00 g (25 mmol) of the *m*-azidotoluene complex II in 500 ml of CH_2Cl_2 or cyclohexane. After the usual work up, from the reaction in CH_2Cl_2, the non-ionic fraction gave 60 mg (13%) of ferrocene and 40 mg (7%) of a mixture of IV and V. From the reaction in cyclohexane, the non-ionic fraction gave 61 mg (11%) of a mixture of IV and V, and the ionic residue gave 324 mg (32%) of recovered II. The presence of both IV and V in these products was shown by the ^{13}C NMR spectrum which gave CH_3 absorptions at 13.59 and 14.53 ppm as well as Cp absorptions at 71.15 and 71.22 ppm for IV and V, respectively. The ^1H NMR spectrum also showed two CH_3 peaks at 2.2 and 2.0 ppm, respectively, for IV and V, the relative areas for these peaks being about 1:3, indicating that the ratio of IV to V was about 1:3.

Acknowledgement

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