Studies on the Formylation of the Tricarbonyl(monosubstituted cyclo-octatetraene)iron Derivatives $[Fe(CO)_3(C_8H_7X)]$ (X = Me, Ph, Br, or CPh_3)

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The products of formylation of the title compounds have been examined. The site of electrophilic attack ($CHCl{=}\overset{+}{N}Me_2$) appears to be governed largely by two *steric* factors, the bulk of both the substituent X and the $Fe(CO)_3$ unit, rather than substituent *inductive* effects.

HÜCKEL'S rule predicts that cyclo-octatetraene should be non-aromatic and this has been found experimentally.[1] The ' tub ' shape adopted by the molecule eliminates the possibility of conjugative stabilisation and a resonance energy of *ca.* -24 kJ mol^{-1} is found in contrast to *ca.* 144 kJ mol^{-1} for benzene.[1] Attempted acetylation of cyclo-octatetraene resulted largely in polymerisation; [2] however, it has been shown that co-ordination of cyclo-octatetraene to an iron tricarbonyl moiety confers an appreciable degree of aromaticity on the eight-membered ring.[3] Thus, formylation and acetylation proceed readily to give tricarbonyl(formylcyclo-octatetraene)iron and (acetylcyclo-octatetraene)tricarbonyliron respectively. We now report our observations on the formylation of some tricarbonyl(monosubstituted cyclo-octatetraene)iron derivatives, $[Fe(CO)_3(C_8H_7X)]$ (X = Me, Ph, Br, or CPh_3).

RESULTS

Following the earlier procedure,[3] treatment of $[Fe(CO)_3(C_8H_7Me)]$ with a mixture of phosphorus oxychloride and dimethylformamide (dmf) at 0 °C for 1 h, followed by hydrolysis, resulted in *ca.* 50% formylation of the C_8 ring. Separation on preparative silica plates resulted in the isolation of three products. Mass spectrometric and ^1H n.m.r. analysis (see Experimental section) indicated that these products were tricarbonyl(1-formyl-4-methylcyclo-octatetraene)iron, tricarbonyl(1-formyl-5-methylcyclo-octatetraene)iron, and tricarbonyl(1,3-diformyl-6-methylcyclo-octatetraene)iron in the ratio 20 : 9 : 4 respectively.

A similar reaction with $[Fe(CO)_3(C_8H_7Ph)]$ also resulted in the formation of three products: *viz.* tricarbonyl(1-formyl-7-phenylcyclo-octatetraene)iron, tricarbonyl(cyclo-octatetraene)iron, and tricarbonyl(1-formyl-5-phenylcyclo-octatetraene)iron in the ratio *ca.* 1 : 2 : 2 respectively.

In contrast, treatment of either $[Fe(CO)_3(C_8H_7Br)]$ with a phosphorus oxychloride–dmf mixture for 6 h or $[Fe(CO)_3(C_8H_7CPh_3)]$ for 1 h gave only one product in each instance (*ca.* 50% yield overall); (1-bromo-3-formylcyclo-octatetraene)tricarbonyliron and tricarbonyl(1-formyl-7-tritylcyclo-octatetraene)iron. No traces of the ' 1,4-' or ' 1,5-' disubstituted derivatives were observed in either case.

The isomers of the various disubstituted cyclo-octatetraene iron tricarbonyl derivatives were distinguished by ^1H n.m.r. spectra, on the basis of the number and type of multiplets exhibited. Thus, a ' 1,3 ' isomer, experiencing symmetry-averaging ' 1,2 ' tautomeric shifts, would show a singlet, two doublets, and three ' triplets ' for the cyclo-octatetraene ring protons, while a ' 1,5 ' isomer undergoing the same ' 1,2 ' shifts would show two doublets and a ' triplet '.

DISCUSSION

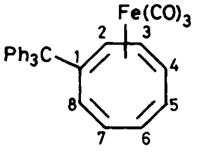
The position of attack in electrophilic substitution of monosubstituted benzenes has been well studied.[4] Thus, an electron-donating substituent, such as an alkyl group, directs the incoming electrophile towards the *ortho* and *para* positions, while electron-withdrawing groups, such as CN, are, in general, *meta* directing. However, although the inductive effect of the substituent is of paramount importance in determining the position of substitution, steric effects also play a part.[4-9]

The stereochemistry of electrophilic addition to co-ordinated oligo-olefins has been much studied, but no clear picture has yet emerged. Thus, while tricarbonyl(cyclohepta-2,4,6-trien-1-one)iron undergoes protonation on a co-ordinated double bond in CF_3CO_2H with the proton attacking the ring from the opposite side to the metal (M-*exo*),[10] tricarbonyl(cyclo-octatetraene)iron in H_2SO_4 is protonated on an unco-ordinated olefinic bond with the proton again attacking from the M-*exo* side of the ring.[11] However, M-*endo* protonation is experienced by the C_8H_8 ring in both $[Mo(CO)_3(C_8H_8)]$ [12] and $[Rh(C_5H_5)(C_8H_8)]$.[13]

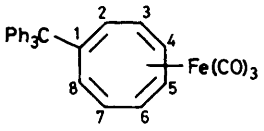
It has been suggested [14] that strong electrophiles such as the acylium ion tend to approach co-ordinated oligo-olefins from the M-*exo* side of the ring. However, contrary to this suggestion, it has been shown that acylation of tricarbonyl(cycloheptatriene)iron occurs on both sides of the ring. *endo* Addition proceeds with proton elimination to give (1-acetylcyclohepta-1,3,5-triene)tricarbonyliron, while *exo* addition does not lead to proton elimination and gives (2—6-η-1-acetylcycloheptadienium)tricarbonyliron hexafluorophosphate.[15] In contrast, Vilsmeir formylation gives only tricarbonyl(1-formylcyclohepta-1,3,5-triene)iron [15] and thus the evidence favours M-*endo* attack of the electrophile involved ($CHCl{=}\overset{+}{N}Me_2$).

A similar situation exists for $[Fe(CO)_3(C_8H_8)]$. Thus, Friedel–Crafts acylation gives two main products, (acetylcyclo-octatetraene)tricarbonyliron and (8-acetylbicyclo[5.1.0]octadienylium)tricarbonyliron hexafluorophosphate,[3] while Vilsmeir formylation gives only tricarbonyl(formylcyclo-octatetraene)iron.[3] Although evidence is lacking, it is not unreasonable to suggest M-*endo* attack of the electrophile ($CHCl{=}\overset{+}{N}Me_2$) in the case of Vilsmeir formylation of $[Fe(CO)_3(C_8H_8)]$.

Brookhart *et al.*[16] have shown that protonation of $[Fe(CO)_3(C_8H_7Me)]$ proceeds with M-*exo* attack at the 4- and 5-positions on the ring and argue that the proton attacks exclusively at the inner positions of the unbound diene in the ' frozen ' structure. We have now shown that Vilsmeir formylation of $[Fe(CO)_3(C_8H_7Me)]$ produces two monoformylated products, (1-formyl-4-methyl- and (1-formyl-5-methyl-cyclo-octatetraene)tricarbonyliron in a 20 : 9 ratio. This could be anticipated on the basis of Brookhart's results. The ^1H n.m.r. analysis of $[Fe(CO)_3(C_8H_7Me)]$ by Anet[17] suggests that positions 4, 5, and 6 on the eight-membered ring never become involved in co-ordination to the metal carbonyl moiety. If it is assumed that the electrophile involved, $CHCl{=}\overset{+}{N}Me_2$, approaches the ring from the same side as the tricarbonyliron moiety, then it is reasonable to expect attack at the least hindered positions, *i.e.* those not co-ordinated to the tricarbonyliron group. Whether attack occurs at an inner or outer unco-ordinated diene carbon atom is not obvious.



A



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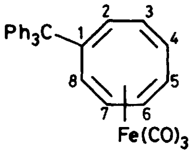
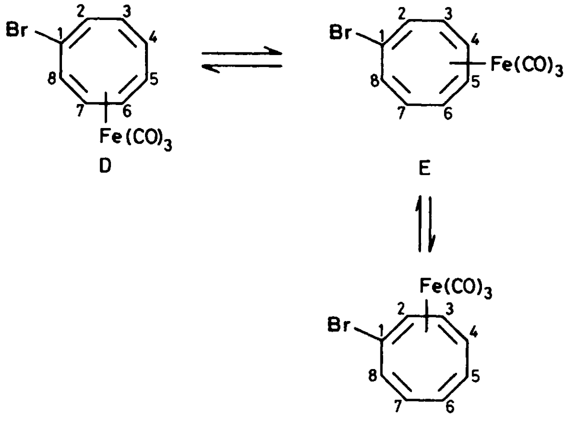


C

Investigation of the ^1H n.m.r. spectrum of $[Fe(CO)_3(C_8H_7CPh_3)]$ at various temperatures indicates that the ' frozen ' structure (at *ca.* −115 °C) involves the trityl group attached to an unco-ordinated carbon atom. On warming to room temperature, however, the ^1H n.m.r. spectrum adopts a pattern similar to that of $[Fe(CO)_3(C_8H_7Me)]$. Nevertheless, in the $[Fe(CO)_3(C_8H_7Me)]$ spectrum the doublet, due to the 2- and 8-positions, is at high field, while in the spectrum of the trityl derivative, this doublet appears at low field, implying that in the latter compound positions 2 and 8 do not become co-ordinated to the $Fe(CO)_3$ unit, thus neither can the carbon atom bearing the trityl group become co-ordinated. The most likely positions for the $Fe(CO)_3$ unit at room temperature on the basis of calculations made from the peak positions in the ' frozen ' spectrum are as in A—C. If the other two possible tautomers were involved to an appreciable degree, the individual proton would be averaged over a greater number of positions resulting in a ' closing-up ' of the spectrum.

If the assumption is made that the steric bulk of the trityl group precludes attack at the 2- and 8-positions then in this situation all carbon atoms in the cyclo-octatetraene ring are hindered either by the trityl group or by co-ordination to the iron tricarbonyl unit. However, positions 3 and 7 spend less time co-ordinated to the iron tricarbonyl unit than positions 4, 5, and 6, and are therefore less hindered. Hence, M-*endo* electrophilic attack may be expected to occur more readily at these positions, as observed.



An entirely similar situation exists for $[Fe(CO)_3(C_8H_7Br)]$. Analysis of the ^1H n.m.r. spectrum indicates that at room temperature, in a variety of solvents, tautomerism between the structures D—F exists. Therefore, exclusive electrophilic attack at the position 3 (or 7) is expected if position 2 is rendered sterically inaccessible by the Br group.

Unlike most other monosubstituted $[Fe(CO)_3(C_8H_8)]$ derivatives, $[Fe(CO)_3(C_8H_7Ph)]$ exhibits a ^1H n.m.r. spectrum in $CDCl_3$ displaying a single narrow multiplet due to the seven cyclo-octatetraene ring protons. Similar spectra are found in a range of other common solvents. The ' compactness ' of the n.m.r. spectrum implies complete fluxionality of the $Fe(CO)_3$ group around the PhC_8H_7 ring, as only in this case would the seven ring protons be averaged to such a degree that they resonated at almost the same frequency. At low temperature (*ca.* −115 °C) in CS_2, a ' frozen ' structure is found in which the Ph group is on a carbon atom of the co-ordinated diene.

If the $Fe(CO)_3$ unit is ' spinning ' around the ring, then it sterically hinders all points on the eight-membered ring equally. Consequently, *endo*-electrophilic attack would be expected to occur at those points least hindered by the substituent, *i.e.* 5, 4 (≡6), and 3 (≡7) positions in that order of reactivity. This is exactly as found experimentally.

It would appear, therefore, that the position of electrophilic attack by $CHCl{=}\overset{+}{N}Me_2$ on monosubstituted $[Fe(CO)_3(C_8H_8)]$ derivatives is governed largely by two steric factors rather than substituent inductive effects. First, the steric bulk of the substituent itself directs attack away from the 2- and 8-positions and secondly, when the electrophile approaches from the same side of the ring as the metal, the $Fe(CO)_3$ moiety hinders attack at those carbon atoms to which it is co-ordinated.

If, on the other hand, *exo* attack of the $CHCl{=}\overset{+}{N}Me_2$ electrophile occurs, then the above results can only be interpreted in terms of preferential attack at unco-ordinated olefinic sites, since steric hindrance by the tricarbonyliron group has now been removed. This is difficult to rationalise, since it would be expected that an olefinic carbon would be more nucleophilic when co-ordinated to tricarbonyliron moieties.

EXPERIMENTAL

The compounds $[Fe(CO)_3(C_8H_7Me)]$,[16] $[Fe(CO)_3(C_8H_7Ph)]$,[18] $[Fe(CO)_3(C_8H_7CPh_3)]$,[19] and C_8H_7Br [20] were prepared by literature methods. All other chemicals were commercial samples. Hydrogen-1 n.m.r. spectra were measured on a Varian Associates HA 100 machine. Mass spectra were obtained using an AEI MS 12 instrument while i.r. spectra were run on a Perkin-Elmer PE 257.

$[Fe(CO)_3(C_8H_7Br)]$.—The compounds $[Fe_2(CO)_9]$ (3.0 g) and C_8H_7Br (1.5 g) were stirred in refluxing pentane for 1 h under nitrogen. The mixture was then filtered and the filtrate evaporated. Chromatography of the residue on alumina (twice), eluting with a pentane–4% diethyl ether mixture, gave the product as deep red crystals (m.p. 54—56 °C) (46%). Mass spectrum: 324 M^+ (^{81}Br), 322 M^+ (^{79}Br), 296 $(M - CO)^+$ (^{81}Br), 294 $(M - CO)^+$ (^{79}Br), 268 $(M - 2CO)^+$ (^{81}Br), 266 $(M - 2CO)^+$ (^{79}Br), 240 $(M - 3CO)^+$ (^{81}Br), and 238 $(M - 3CO)^+$ (^{79}Br) (Found: C, 40.6; H, 2.05; Br, 24.8. Calc. for $C_{11}H_7BrFeO_3$: C, 40.9; H, 2.2; Br, 24.8%). I.r. (CCl_4): 2 057, 2 000, and 1 982 cm^{-1}. ^1H N.m.r. $\tau(C_6D_6)$: 4.34 (d, 2 H, *J* 10.0), 5.68 (m, 4 H), and 6.33 (t, 1 H, *J* 8.0 Hz).

Formylation of $[Fe(CO)_3(C_8H_7Me)]$.—The compound $[Fe(CO)_3(C_8H_7Me)]$ (2.0 g) in dmf (5 cm^3) was added to a mixture of dmf (40 cm^3) and phosphorus oxychloride (10 cm^3) at 0 °C. The mixture was stirred at 0 °C under nitrogen and then poured into ice-water and left overnight. The mixture was then extracted with diethyl ether (3 × 50 cm^3) and the ethereal layer separated, dried ($MgSO_4$), and evaporated to dryness. Chromatography of the residue on thick-layer silica plates, eluting with a benzene–pentane (1 : 1) mixture, gave a clean separation into five bands. The first band was unreacted starting material (890 mg, 45%).

The four product bands were removed and purified by further chromatography on silica plates. Thus, the second band gave a red oil (34 mg), *M* (mass spectrometry) = 284, which gave a very complicated ^1H n.m.r. spectrum and could not be identified. A third band gave a deep red oil (430 mg, 20%), which proved to be tricarbonyl(1-formyl-4-methylcyclo-octatetraene)iron. Mass spectrum: 286 M^+, 258 $(M - CO)^+$, 230 $(M - 2CO)^+$, and 202 $(M - 3CO)^+$. I.r. (CCl_4): 2 057, 1 999, 1 983, and 1 682 cm^{-1}. ^1H N.m.r., $\tau(CDCl_3)$: 0.64 (s, 1 H), 3.55 (d, 1 H, *J* 10.5), 3.92 (t, 1 H, *J* 10.5), 4.13 (d, 1 H, *J* 10.5), 4.37 (dd, 1 H, *J* 10.5 and 9.5), 5.18 (d, 1 H, *J* 10.5), and 5.61 (d, 1 H, *J* 9.5 Hz). The fourth band gave a red-orange oil (193 mg, 9%) which was shown to be tricarbonyl(1-formyl-5-methylcyclo-octatetraene)iron. Mass spectrum: 286 M^+, 258 $(M - CO)^+$, 230 $(M - 2CO)^+$, and 202 $(M - 3CO)^+$. I.r. (CCl_4): 2 057, 1 998, 1 984, and 1 684 cm^{-1}. ^1H N.m.r., $\tau(CDCl_3)$: 0.65 (s, 1 H), 3.26 (d, 2 H, *J* 11.5), 4.67 (dd, 2 H, *J* 11.5 and 10.0), and 5.49 (d, 2 H, *J* 9.0 Hz). A final band gave a deep red solid (m.p. 95—97 °C) (103 mg, 4%) which was shown to be tricarbonyl(1,3-diformyl-6-methylcyclo-octatetraene)iron. Mass spectrum: 314 M^+, 286 $(M - CO)^+$, 258 $(M - 2CO)^+$, and 230 $(M - 3CO)^+$. I.r. (CCl_3): 2 064, 2 009, 1 994, and 1 689 cm^{-1}. ^1H N.m.r., $\tau(CDCl_3)$: 0.52 (s, 2 H), 2.56 (s, 1 H), 3.77 (d, 2 H, *J* 10.5), and 5.35 (d, 2 H, *J* 10.5 Hz).

Formylation of $[Fe(CO)_3(C_8H_7Ph)]$.—The compound $[Fe(CO)_3(C_8H_7Ph)]$ (700 mg) in dmf (10 cm^3) was added to a solution of dmf (5 cm^3) and phosphorus oxychloride (3 cm^3) at 0 °C and stirred at this temperature under nitrogen for 1 h. The mixture was then poured onto ice and left overnight. The resulting suspension was extracted with diethyl ether and the ethereal layer was separated, dried ($MgSO_4$), and evaporated. Chromatography of the residue on thick-layer silica plates, eluting with a benzene–25% pentane mixture, gave four bands. The first band comprised unreacted starting material (210 mg, 51%). The product bands were then further purified by chromatography on silica plates. Thus, the second band gave a red oil (19 mg, 5%). Mass spectrum: 348 M^+, 320 $(M - CO)^+$, 292 $(M - 2CO)^+$, and 264 $(M - 3CO)^+$. I.r. (CCl_4): 2 058, 2 002, 1 986, and 1 679 cm^{-1}. ^1H N.m.r., $\tau(CDCl_3)$: 0.56 (s, 1 H), 2.72 (m, 5 H), 3.57 (d, 1 H, *J* 9.5), 3.87 (dd, 1 H, *J* 9.5 and 9.5), 4.08 (s, 1 H), 4.30 (d, 1 H, *J* 10.0), 4.66 (d, 1 H, *J* 9.5), and 5.74 (dd, 1 H, *J* 10.0 and 9.5 Hz). These data are consistent with this compound being tricarbonyl(1-formyl-7-phenylcyclo-octatetraene)iron. A third band gave a deep red oil (37 mg, 8.5%) which was shown to be tricarbonyl(1-formyl-4-phenylcyclo-octatetraene)iron. Mass spectrum: 348 M^+, 320 $(M - CO)^+$, 292 $(M - 2CO)^+$, and 264 $(M - 3CO)^+$. I.r. (CCl_4): 2 058, 2 002, 1 988, and 1 683 cm^{-1}. ^1H N.m.r., $\tau(CDCl_3)$: 0.60 (s, 1 H), 2.70 (m, 5 H), 3.74 (d, 1 H, *J* 10.0), 3.95 (d, 1 H, *J* 10.0), 4.06 (t, 1 H, *J* 10.0), 4.34 (t, 1 H, *J* 10.0), 4.69 (d, 1 H, *J* 10.0), and 5.28 (d, 1 H, *J* 10.0 Hz). The final band gave orange crystals (m.p. 96—97 °C) (39 mg, 9%), which proved to be tricarbonyl(1-formyl-5-phenylcyclo-octatetraene)iron. Mass spectrum: 348 M^+, 320 $(M - CO)^+$, 292 $(M - 2CO)^+$, and 264 $(M - 3CO)^+$. I.r. (CCl_4): 2 058, 2 002, 1 986, and 1 689 cm^{-1}. ^1H N.m.r., $\tau(CDCl_3)$: 0.66 (s, 1 H), 2.68 (m, 5 H), 3.16 (d, 2 H, *J* 11.5), 4.50 (dd, 2 H, *J* 11.5 and 9.0), and 5.10 (d, 2 H, *J* 9.0 Hz).

Formylation of $[Fe(CO)_3(C_8H_7Br)]$.—The compound $[Fe(CO)_3(C_8H_7Br)]$ (400 mg) in dmf (10 cm^3) was added to a mixture of dmf (5 cm^3) and phosphorus oxychloride (3 cm^3) at 0 °C and stirred at this temperature for 8 h. After hydrolysis (overnight) the mixture was extracted with diethyl ether. The ethereal layer was separated, dried ($MgSO_4$), and evaporated. The residue was chromatographed on thick-layer alumina plates and eluted with a pentane–30% diethyl ether mixture. The first band comprised unreacted starting material (190 mg, 48%), while the second band gave red-orange crystals (m.p. 111—112 °C) (110 mg, 25%) which were shown to be (1-

bromo-3-formylcyclo-octatetraene)tricarbonyliron. Mass spectrum: 352 M^+ (^{81}Br), 350 M^+ (^{79}Br), 324 $(M - CO)^+$ (^{81}Br), 322 $(M - CO)^+$ (^{79}Br), 296 $(M - 2CO)^+$ (^{81}Br), 294 $(M - 2CO)^+$ (^{79}Br), 268 $(M - 3CO)^+$ (^{81}Br), and 266 $(M - 3CO)^+$ (^{79}Br) (Found: C, 40.9; H, 2.05; Br, 22.9. Calc. for $C_{12}H_7BrFeO_4$: C, 41.1; H, 2.0; Br, 22.8%). I.r. (CCl_4): 2 065, 2 012, 1 994, and 1 687 cm^{-1}. ^{1}H N.m.r., τ(CS_2): 0.86 (s, 1 H), 3.22 (s, 1 H), 3.70 (d, 1 H, J 10.0), 4.70 (d, 1 H, J 10.0), 5.01 (dd, 1 H, J 8.0 and 10.0 Hz), and 5.45 (m, 2 H).

Formylation of [$Fe(CO)_3(C_8H_7CPh_3)$].—The compound [$Fe(CO)_3(C_8H_7CPh_3)$] (800 mg) in dmf (10 cm^3) was added to a mixture of phosphorus oxychloride (3 cm^3) and dmf (8 cm^3) at 0 °C. The mixture was stirred at this temperature for 1 h and then poured onto ice and left overnight. After work-up in the usual way, the residue was chromatographed on thick-layer silica plates to give two bands. The first was unreacted starting material (420 mg, 53%), while the second gave red crystals, m.p. 185 °C (decomp.) (150 mg, 18%) (Found: C, 72.7; H, 4.50. Calc. for $C_{31}H_{22}FeO_4$: C, 72.4; H, 4.30%). Mass spectrum: 430 $(M - 3CO)^+$ and 374 $[M - Fe(CO)_3]^+$. I.r. (CCl_4): 2 057, 1 998, 1 985, and 1 672 cm^{-1}. ^{1}H N.m.r., τ($CDCl_3$): 1.05 (s, 1 H), 2.81 (m, 15 H), 3.41 (s, 1 H), 3.76 (d, 1 H, J 10.0), 4.67 (d, 1 H, J 9.0), 5.25 (m, 2 H), and 5.76 (dd, 1 H, J 10.5 and 9.0 Hz). These data are consistent with this product being tricarbonyl(1-formyl-7-tritylcyclo-octatetraene)iron.

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