# Pentacarbonyliron-promoted Conversion of 3a,7a-Dihydroindenones into Indanones [1]

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Reactions of 3a-7a-dihydroindenones or 3a,4,7,7a-tetrahydro-4,7-methanoindene-1,8-diones with $Fe(CO)_5$ afford indanones as the sole products. No corresponding diene–$Fe(CO)_3$ complexes have been detected. The mechanisms for these reactions are established on the basis of deuterium-labelling experiments.

A NUMBER of transition-metal complexes are known to act as homogeneous catalysts for olefin isomerization.[2] This kind of reaction requires that the catalyst be substitution-labile in order to allow initial formation of the reactive, co-ordinatively unsaturated intermediate, and then to regenerate it by release of the isomerized olefin. Consequently, species which form stable complexes with dienes, such as tricarbonyliron, are not expected to exhibit catalytic activity. Thus the reaction of 3a,7a-dihydroindene with $Fe(CO)_5$ affords the stable tricarbonyliron complex (1), with no double-

(1)
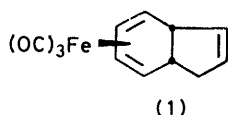
bond migration even at elevated temperatures.[3] A number of 5-vinylcyclohexadiene–tricarbonyliron complexes have also been prepared with hydrogen shifts.[4] In addition, 3a,7a-dihydrobenzofuran–tricarbonyliron complexes have been synthesized without isomerization.[5] These observations suggest that the bond energy between iron and the diene ligand may even offset the stabilization energy for an aromatic ring. In this paper we report what is, to the best of our knowledge, the first example of the pentacarbonyliron-catalysed rearrangement of a 5-alkenylcyclohexadiene system to a benzenoid derivative.

RESULTS AND DISCUSSION

3a,7a-Dihydroindenone (2a) and 2,4-dibromo-3a,7a-dihydroindenone (2b) were obtained by the thermolysis [6,7] of (3a) and (3b), respectively, which were prepared according to known methods.[8,9] We established that (2a) and (2b) were stable in refluxing xylene or dioxan.

Treatment of (2a) with an excess of pentacarbonyliron solution in refluxing dioxan (18 h) or xylene (14 h) afforded the indanone (10) in 66 and 74% yields, respectively. No corresponding carbonyliron complex (4a) was obtained. In addition, no skeletal rearrangements have been encountered. Similarly, treatment of (3a) with pentacarbonyliron or enneacarbonyldi-iron gave the same indanone in 44—54% yields under various conditions. There is no direct evidence to show that the decarbonylation process of (3a) does not involve the participation of iron carbonyls. However, the isolation of the adduct (5a) (74%) from the reaction in the presence

of maleic anhydride indicates that the transformation of (3a) to indanone occurred stepwisely via (2a) as an intermediate, which undergoes double-bond migration.

The general mechanism of the migration of double bonds catalysed by iron carbonyls has been proposed to proceed via the unstable (olefin)–$Fe(CO)_4$ intermediate.[10] By inspection of models, the cyclohexadiene moiety of (2), however, is planar or nearly so. This should provide a cis-diene system to accommodate iron carbonyls, leading to the corresponding organometallic intermediate (4a).[11] The fact that (4a) was not isolated from the reaction is striking, and contrasts with the isolation of the stable dihydroindene–tricarbonyliron complex (1) and related compounds.[3-5] The isolation of the adduct (5a) as described above may suggest that the rate of formation of the diene–carbonyliron complex (4a) is slow. Two pathways are proposed to account for isomerization reactions. In Scheme 1, the bridgehead

(2) a; X = H
b; X = Br

(3) a; X = H
b; X = Br

(4) a; X = H
b; X = Br

(5) a; X = H
b; X = Br
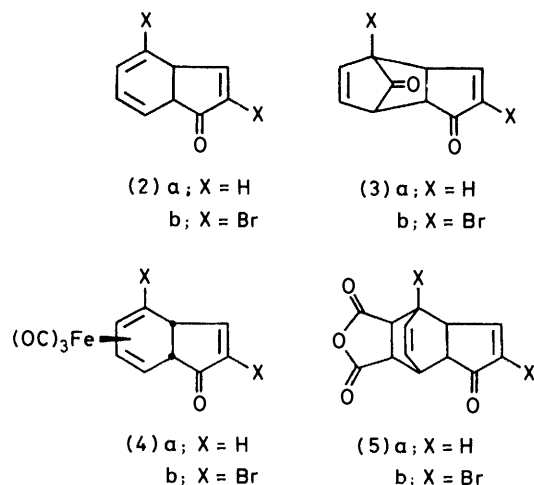
hydrogen in (4a) may be activated by the carbonyl group. Therefore, oxidative addition may lead to the allyl complex (5) which would be in equilibrium with (6). Reductive elimination of (6) may yield either (7), which would give (2a) after dissociation, or (8) which may repeat the above process via the allyl complex (9) to give indanone (10) after liberating the metallic moiety. Alternatively, the hydroxybenzocyclopentadienyl–carbonyliron complex (12),[12] which could be formed from the enol (11) and iron carbonyl, may also yield indanone (10) by reductive elimination followed by ketonization as summarized in Scheme 2.

Although the two mechanisms give the same end product, the distribution of migrating hydrogens in the final product should be different. Thus, the deuterium-labelled compound (13) was prepared from [2,2,5,5-$^2H_4$]-cyclopentanone [13] according to known methods.[8,9] On treatment of (13) with pentacarbonyliron in refluxing xylene, the [2,3,4,7-$^2H_4$]indanone (14) was obtained in 47% yield. The deuterium distribution in (14) was

deuterium-labelling experiment described above again rule out this possibility.

In a similar fashion, treatment of (2b) with an excess of pentacarbonyliron in refluxing xylene (8 h) afforded 4-bromoindanone (15a) in 38 and 35% yield, respectively. Again, the corresponding carbonyliron complex (4b) was not obtained. Furthermore, the expected rearrangement product, 2,4-dibromoindanone (15b) was not
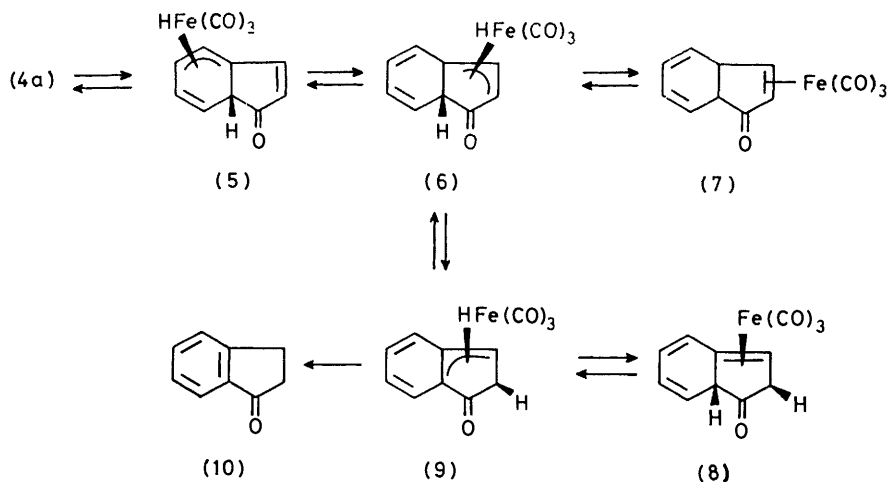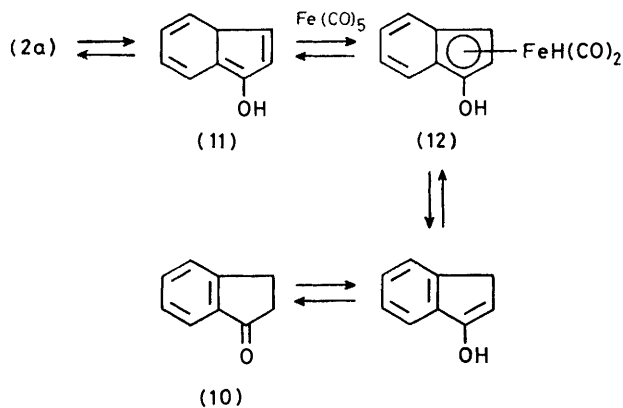
SCHEME 1

assigned on the basis of n.m.r. and mass spectrometric data; no deuterium scrambling was observed in (14) under the reaction conditions. This result favours the rearrangement mode involving two successive 1,3-hydrogen shifts as outlined in Scheme 1. The fact that

SCHEME 2

(14) was obtained as the sole product suggests that the hydrogen (or double-bond) migration is regiospecific. The mechanistic pathway shown in Scheme 2, however, would lead to more random deuterium distribution and, therefore, is ruled out, even though a more stable intermediate (12), which is aromatic, may be involved. Furthermore, it is well known that (2a) is very susceptible to Lewis acids, which can catalyse similar isomerization reactions.[6,7] The latter species could be generated under our reaction conditions. However, the results of the
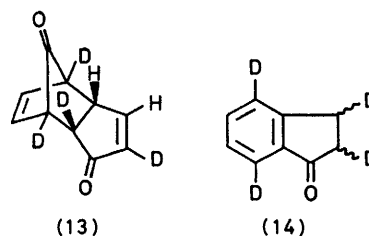
detected. Similarly, treatment of (3b) with pentacarbonyliron in xylene gave (15a) in 33% yield. Moreover, the isolation of the adduct (5b) from the reaction in the presence of maleic anhydride indicated that the transformation of (3b) to (15a) occurred via (2b) as intermediate, which underwent double-bond migration and subsequent debromination. The latter reaction is particularly noteworthy. Related reductive debromination promoted by pentacarbonyliron has been reported.[14] We have also established that (15b) can be smoothly transformed into (15a) by treatment with pentacarbonyliron in refluxing xylene.[15] A free-radical mechanism has been established for these reactions.[15]

Thermolysis of the Diels–Alder adducts with tetraphenylcyclopentadienone to extrude the CO moiety has

been known and used in various organic syntheses.[16] This reaction has indeed been observed in the thermal decomposition of 4,5,6,7-tetraphenyl-3a,4,7,7a-tetrahydro-4,7-methanoinden-8-one (16) to give 4,5,6,7-tetraphenyl-3a,7a-dihydroindene.[17] Thus, treatment of (16) with pentacarbonyliron in refluxing xylene afforded neither the desired 4,5,6,7-tetraphenylindane nor diene–

metal complexes, but a mixture of dicyclopentadienyl-tetracarbonyldi-iron, tetraphenylcyclopentadienone-tricarbonyliron, and the corresponding uncomplexed organic ligands. This result apparently suggests that retro-Diels–Alder reaction may be overwhelmingly more favourable than the decarbonylation process under the *reaction* conditions. The function of pentacarbonyliron
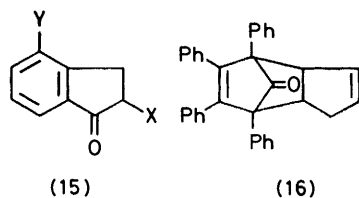
(15)   (16)

a; X = H, Y = Br

b; X = Y = Br

in this reaction is not clear. However, some complex-ation between iron and (16) may occur so as to promote the decomposition in the manner described above.
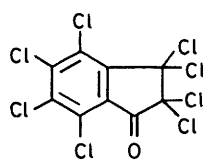
Along with the work on double-bond migration, it was of interest to know whether pentacarbonyliron would catalyse chlorine shifts in the corresponding system in the same manner as the hydrogen shifts. Thus, 2,3,3a,4,5,6,-7,7a-octachloro-3a,7a-dihydroindenone (17) was pre-
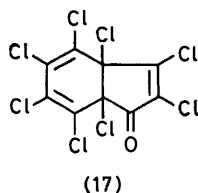
(17)
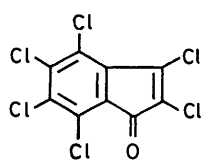
(18)   (19)

pared according to the literature method.[18] Treatment of (17) with a solution of pentacarbonyliron in refluxing xylene yielded hexachloroindenone (18) in 62% yield. The corresponding organometallic compound and/or the rearranged product (19) were not detected. It is important to note that (18) can be obtained when (17) is treated with boiling water.[19] However, we have established that (17) is surprisingly stable in refluxing xylene. Therefore, pentacarbonyliron does play an important role here and a related reaction has been reported,[20] although the detailed mechanism is not clear.

Conclusions.—We have demonstrated the first instance of a pentacarbonyliron-promoted rearrangement of the 5-alkenylcyclohexadiene system to benzenoid deriva-tives, rather than affording the corresponding iron carbonyl complex as found in other systems.[3-5] The driving force for this rearrangement may arise from the fact that the C–H bond is activated by the neighbouring

carbonyl group and is thus ready to undergo oxidative addition as described. Such an effect may also activate the C–Cl bond to yield the oxidative addition inter-mediate, which would then decompose to give the elimination product.

EXPERIMENTAL

I.r. spectra were recorded on a Beckman IR-10 or Perkin-Elmer 283 spectrophotometer, [1]H n.m.r. spectra on a JOEL 60 HL spectrometer (tetramethylsilane as the internal standard), and mass spectra on a Hitachi RMS-4 spectro-meter. Microanalyses were performed by the Australian Microanalytical Service, Melbourne. Pentacarbonyliron (Merck) was used without further purification.

2,4-*Dibromo*-3a,7a-*dihydroindenone* (2b).—Compound (3) (4.5 g, 4.2 mmol) in xylene (200 ml) was refluxed under nitro-gen for *ca.* 7 h. The mixture was cooled, the solvent re-moved *in vacuo*, and the oily residue then placed in a refrigerator for one week to give a yellow solid. Re-crystallization from benzene–pentane afforded 2,4-dibromo-3a,7a-dihydroindenone (2b) (3.2 g, 78%), m.p. 43—45 °C (Found: C, 37.65; H, 2.3. $C_9H_6Br_2O$ requires C, 37.28; H, 2.09%); $\nu_{max.}$ (KBr) 1 720 (C=O) and 1 598 cm^{-1} (C=C): δ (CCl$_4$) 3.54 (1 H, m), 3.94 (1 H, m), 5.62 (2 H, m), 6.18 (1 H, m), and 7.82 (1 H, d, *J* 3 Hz); *m/e* 288 (M^+), 290 (M^+ + 2), and 292 (M^+ + 4).

Adduct of 2,4-*Dibromo*-3a,7a-*dihydroindenone* (2b) *with Maleic Anhydride.*—A mixture of compound (2b) (0.5 g, 1.7 mmol) and maleic anhydride (0.17 g, 1.7 mmol) in xylene (30 ml) was stirred at room temperature for 4 h. The solid was filtered off and recrystallized from ethanol to afford the 2,4-*dibromo*-3a,7a-*dihydroindenone–maleic anhydride adduct* (5b) (0.59 g, 88%), m.p. 292—294 °C (Found: C, 40.45; H, 2.25; Br, 41.00. $C_{13}H_8Br_2O_4$ requires C, 40.24; H, 2.08; Br, 41.19%); $\nu_{max.}$ (KBr) 1 858 and 1 781 (C=O, anhydride), 1 710 (C=O), and 1 587 cm^{-1} (C=C); δ (CD$_3$CO-CD$_3$) 3.12—3.46 (1 H, m), 3.40—3.80 (2 H, m), 3.88—3.98 (2 H, m), 6.06—6.20 (2 H, m), and 7.95 (1 H, d, *J* 4 Hz); *m/e* 386 (M^+), 388 (M^+ + 2), and 390 (M^+ + 4).

Reaction of 3a,7a-*Dihydroindenone* (2a) *with Pentacar-bonyliron.*—A mixture of (2a) (1.5 g, 11.4 mmol) and penta-carbonyliron (4.5 g, 23 mmol) in xylene (100 ml) was re-fluxed under nitrogen for *ca.* 12 h. The reaction mixture was then cooled, filtered, and the solvent removed *in vacuo*. The solid residue was recrystallized from ethanol to give in-dan-1-one (10) (1.0 g, 67%), identical in every respect with an authentic sample.

Reaction of 3a,4,7,7a-*Tetrahydro*-4,7-*methanoindene*-1,8-*dione* (3a) *with Pentacarbonyliron.*—A mixture of (3a) (4.2 g, 6.3 mmol) and pentacarbonyliron (10.3 g, 2.6 mmol) in xylene (200 ml) was refluxed under nitrogen for 16 h. The reaction mixture was then cooled, filtered, and the solvent evaporated *in vacuo*. The solid residue was recrystallized from ethanol to afford indan-1-one (1.85 g, 53%).

Reaction of 3a,4,7,7a-*Tetrahydro*-4,7-*methanoinden*-1,8-*dione* (3a) *with Pentacarbonyliron in the Presence of Maleic Anhydride.*—A mixture of (3a) (0.8 g, 5 mmol), penta-carbonyliron (2.0 g, 10 mmol), and maleic anhydride (0.5 g, 5 mmol) in xylene (75 ml) was allowed to reflux under nitro-gen for 16 h. The reaction mixture was then cooled, filtered, and the residue washed with hot acetone. The combined filtrates were evaporated *in vacuo*, and the residue re-crystallized from acetone to give the adduct (5a) (0.82 g, 71%), m.p. 244—245 °C (lit.,[21] 243—244 °C).

Reaction of 2,4-*Dibromo*-3a,7a-*dihydroindenone* (2b) *with Pentacarbonyliron.*—Compound (2b) (0.7 g, 2.4 mmol) was mixed with pentacarbonyliron (1.0 g, 5.1 mmol) and refluxed in xylene (75 ml) under nitrogen for 8 h. The reaction mixture was cooled, filtered, and the solvent removed *in vacuo.* The solid residue was recrystallized from cyclohexane to give 4-bromoindan-1-one (15a) (0.19 g, 38%), m.p. 93—94 °C (lit.,[15] 93—94 °C).

Reaction of 2,4-*Dibromo*-3a,4,7,7a-*tetrahydro*-4,7-*methanoindene*-1,8-*dione* (3b) *with Pentacarbonyliron.*—A mixture of (3b) (0.52 g, 1.6 mmol) and pentacarbonyliron (0.64 g, 3.3 mmol) in xylene (75 ml) was refluxed under nitrogen for 12 h. The reaction mixture was cooled, filtered, and the solvent removed *in vacuo.* The residue was recrystallized from cyclohexane to give 4-bromoindan-1-one (15a) (0.11 g, 33%).

Reaction of 2,4-*Dibromo*-3a,4,7,7a-*tetrahydro*-4,7-*methanoindene*-1,8-*dione* (3b) *with Pentacarbonyliron in the Presence of Maleic Anhydride.*—A mixture of (3b) (0.3 g, 0.94 mmol), pentacarbonyliron (0.36 g, 1.9 mmol), and maleic anhydride (0.1 g, 1.0 mmol) in xylene (50 ml) was refluxed under nitrogen for 12 h. The reaction mixture was cooled, filtered, and the residue washed with hot ethanol. The combined filtrates were evaporated *in vacuo* to afford a solid residue. Recrystallization from ethanol gave the adduct (5b) (0.25 g, 70%), identical in all respects with an authentic sample.

Reaction of 3a,4,7,7a-*Tetrahydro*-4,7-*methano*[2,4,7,7a-$^2H_4$]-*indene*-1,8-*dione* (13) *with Pentacarbonyliron.*—Compound (13) (0.16 g, 1 mmol) was treated with pentacarbonyliron (0.40 g, 2 mmol) in a similar manner to that described above to yield [2,3,4,7-$^2H_4$]indan-1-one (0.064 g, 47%); m/e 136 (M^+); δ (CDCl$_3$) 2.65 (1 H, m), 3.15 (1 H, m), and 7.10—7.90 (m, 2 H).

Reaction of 4,5,6,7-*Tetraphenyl*-3a,4,7,7a-*tetrahydro*-4,7-*methanoinden*-8-*one* (16) *with Pentacarbonyliron.*—A mixture of compound (16) (0.31 g, 0.7 mmol) and pentacarbonyliron (0.27 g, 1.4 mmol) in xylene (50 ml) was refluxed under nitrogen for 5 h. The mixture was cooled, filtered, and the residue washed with acetone. The combined filtrates were evaporated *in vacuo* and the residue was chromatographed on neutral alumina. Dicyclopentadiene (0.01 g, 22%), tetraphenylcyclopentadienone (0.05 g, 18%), and dicyclopentadienyltetracarbonyldi-iron (0.06 g, 27%), m.p. 188—190 °C (lit.,[22] 192 °C), were eluted successively by benzene. Tetraphenylcyclopentadienonetricarbonyliron (0.05 g, 12%), m.p. 178—180 °C (lit.,[23] 180 °C), was obtained by flushing the column with acetone.

Reaction of Octachloro-3a,7a-*dihydroindenone* (17) *with Pentacarbonyliron.*—A mixture of compound (17) (0.5 g, 1.2 mmol) and pentacarbonyliron (0.5 g, 2.5 mmol) in xylene (50 ml) was refluxed under nitrogen for 12 h. The

reaction mixture was cooled, filtered, and the residue washed with acetone. The combined filtrates were evaporated *in vacuo.* The residue was recrystallized from acetone to afford hexachloroindenone (18) (0.25, 62%), m.p. 147—149 °C (lit.,[19] 149 °C).

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