The Reaction of Acetylenes with Compounds containing Fe–Aryl Bonds. A Convenient and Novel Synthesis of Indenones

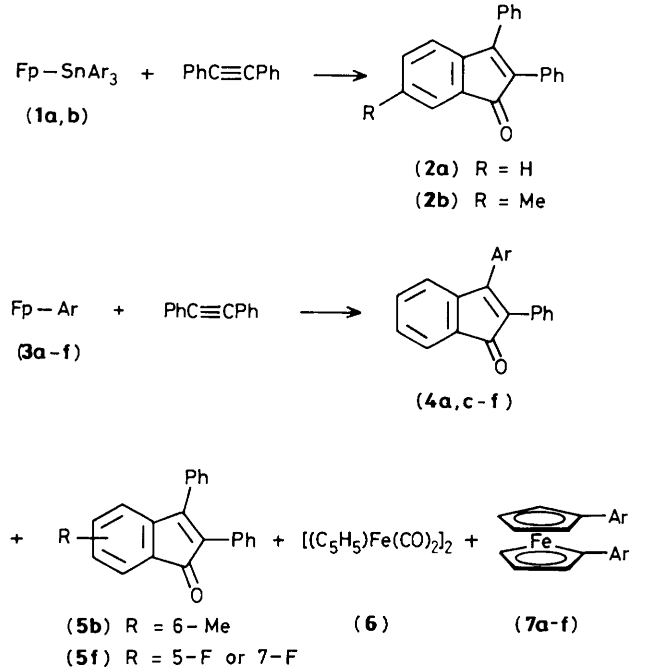
Ian R. Butler,[a] William R. Cullen,*[a] W. Edward Lindsell,[b] Peter N. Preston,[b] and Steven J. Rettig[a]

[a] *Chemistry Department, University of British Columbia, Vancouver, B.C., Canada V6T 1Y6*
[b] *Chemistry Department, Heriot Watt University, Edinburgh, Scotland EH14 4AS*

The reaction of diphenylacetylene with (η^5-C_5H_5)Fe(CO)$_2$Ar (**3**) affords the indenones (**4**) and/or (**5**); a cyclohexadienyliron derivative (**10**) is obtained when the acetylene is 2-ethynylpyridine, the structure of which was determined by *X*-ray crystallography.

In 1971 Nesmeyanov and coworkers[1] found that indenones (**2**) are produced when the organometallic derivatives (**1**), Fp = (η^5-C_5H_5)Fe(CO)$_2$, are heated or irradiated in the presence of diphenylacetylene, Scheme 1. These authors postulated that benzyne complexes are intermediates in this unusual reaction. We now report that the same and related indenones (**4**) and/or (**5**) are major products when the more accessible aryl- or ferrocenyl-iron derivatives (**3**) are treated in the same way, Scheme 1.

Typically Fp–Ar (0.5 g) and a 2.5 molar excess of PhC≡CPh are weighed into a Schlenk tube and dissolved in 10 ml of carefully degassed decalin under an argon atmosphere. The solution on refluxing for 5 min darkens considerably in colour. After cooling the tube to 20 °C, t.l.c. examination of the contents reveals the presence of the highly coloured indenones as orange (Ar = aryl) or purple (Ar = ferrocenyl) spots. Column chromatography on neutral alumina, activity I, affords the following fractions: decalin, eluted with hexanes;

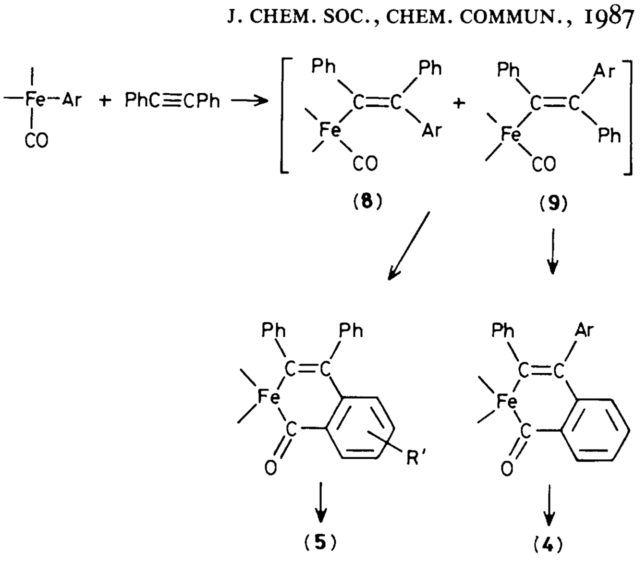


a; Ar = phenyl
b; Ar = *p*-tolyl
c; Ar = 2-chlorophenyl
d; Ar = 2-fluorophenyl
e; Ar = ferrocenyl
f; Ar = 3-fluorophenyl

Scheme 1

organometallic species, eluted with hexanes–diethyl ether; indenones, eluted with diethyl ether–CH_2Cl_2. When Ar = ferrocenyl the reaction proceeds slowly in diethyl ether (2 weeks) at 20 °C. The yield of (**4e**) is almost quantitative.

The usual indenone product has the structure (**4**)† where the Ar group of Fp–Ar ends up in the 3-position;‡ the diphenylacetylene supplies the phenyl substitutent at the 2-position and the six-membered ring of the indenone unit. In one case, Ar = *p*-tolyl, compound (**5b**)‡ is the only indenone isolated. This is the same compound isolated earlier from (**1b**).[1] Here the diphenylacetylene provides the phenyl group in the 2- and 3-positions. Only one example has been found to date, compound (**3f**), from which a mixture of indenones is produced. Three products can be isolated which have the expected properties; presumably these are (**4f**) and the two isomers of (**5f**). These structures have not yet been established unequivocally.



Scheme 2

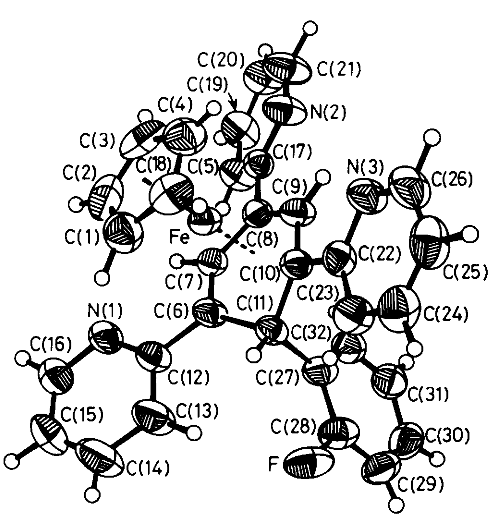


Figure 1. Molecular structure of compound (**10**). Selected bond lengths and angles: Fe–(C_5H_5) 1.681(3); Fe–Ch 1.545(2); C(6)–C(7) 1.418(6); C(6)–C(11) 1.523(6); C(11)–C(27) 1.521(6); C(6)–C(12) 1.475(6) Å; (C_5H_5)–Fe–Ch 176.67(14), C(7)–C(6)–C(11) 118.8(4); C(6)–C(7)–C(8) 120.7(4); C(7)–C(8)–C(9) 117.1(4); C(8)–C(9)–C(10) 121.0(4); C(9)–C(10)–C(11) 118.8(4); C(6)–C(11)–C(10) 102.8(3); C(6)–C(11)–C(27) 115.9(4)°. Ch = centroid of the five iron-bound atoms of the cyclohexadienyl ring.

The simplest mechanism to account for the organic products involves insertion of the acetylene into the Fe–Ar bond followed by ortho-metallation, CO migration, and metal fragment elimination, Scheme 2. Under the reaction conditions easy interchange between (**8**) and (**9**) should be possible so that (**4**) could be the final product even if the geometry of the initial adduct is the more likely *cis*-arrangement of (**8**).[2] Labelling studies are needed to establish which ring is metallated in the case of (**4a**). The other products (**6**) and (**7**) are formed in appreciable amounts indicating that homolytic

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‡ Satisfactory microanalytical data, mass spectra, and ^1H n.m.r. spectra have been obtained for these compounds.

† *Crystal data:* (**4d**) $C_{21}H_{13}FO$, monoclinic, space group $P2_1/n$, a = 9.529(1), b = 17.299(1), c = 9.9191(5) Å, β = 110.547(5)°, Z = 4, D_x = 1.303 g cm^{-3}.

(**5b**) $C_{22}H_{16}O$, monoclinic, space group $P2_1/c$, a = 6.4539(7), b = 12.967(2), c = 19.040(2) Å, β = 96.549(8)°, Z = 4, D_x = 1.244 g cm^{-3}.

(**10**) $C_{32}H_{24}FFeN_3$, triclinic, space group $P\bar{1}$, a = 9.6809(9), b = 9.7815(9), c = 13.465(2) Å, α = 82.60(1), β = 77.923(8), γ = 78.850(8)°, Z = 2, D_x = 1.432 g cm^{-3}.

In each case data were collected at 22 °C with nickel-filtered Cu-K_α radiation ($2\theta < 150°$) on an Enraf-Nonius CAD4-F diffractometer. The structures of (**4d**) and (**5b**) were solved by direct methods and that of (**10**) by the heavy atom method. The structures were refined by full-matrix least-squares procedures to final R values of 0.041, 0.045, and 0.053 for 1493, 1538, and 3012 absorption-corrected reflexions with $I > 3\sigma(I)$.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

cleavage of the Fe–Ar bond is taking place. The ferrocene derivatives, isolated in *ca.* 10% yield, are particularly interesting and all compounds (**7a—f**) have been characterized.‡

The procedure outlined above is a convenient one for the synthesis of indenones in reasonable yields, 20—40%, which would not be readily available by more conventional methods.[3] When Ar = ferrocenyl, the yield is 70% or greater. The Fp–Ar compounds are usually easily prepared in high yield from FpI and LiAr;[4] alternatively FpCOAr (from FpNa and ArCOCl) can be used as the initial reagent. This is especially useful if Fp–Ar is difficult to isolate in good yield, as is the case for Ar = *p*-tolyl. In this connection, some heterocyclic isosteres of indenone have been isolated following u.v. irradiation of solutions of FpCOAr′ and diphenylacetylene.[5]

Some initial work on varying the metal derivative, aryl groups, and acetylenes, has been carried out. As an example, heating compound (**3d**) with PhC≡CMe in decalin as described above, affords 4-fluoro-3-methyl-2-phenylindenone.‡ The cyclohexadienyl derivative (**10**) shown in Figure 1† is obtained when the acetylene is changed to 2-$C_5H_4NC{\equiv}CH$. The acetylene has trimerized and the aryl group is found in the 1-*exo*-position. Similar derivatives have been obtained following u.v. irradiation of solutions containing Fp–R (R = Me or CH_2Ph) and $CF_3C{\equiv}CH$ although the group in the 1-*exo*-position proved to be the acyl group, –C(O)R.[6] This reaction does not occur on heating.[6]

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