Synthesis of Bicyclic Cyclo-octadienones: Photolysis of Divinylcyclopropanes Induced by Pentacarbonyliron

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Summary A novel 1,7-cycloaddition involving a divinylcyclopropane system and $Fe(CO)_5$ to form an eight-membered ring system is described.

The divinylcyclopropane unit in the spiro[2.*x*]alkanes (**1**) was shown to undergo a ready 1,7-cycloaddition with tetracyanoethylene (TCNE) to yield the bicyclic system (**2**) containing a cyclononadiene unit.[1] We demonstrate another type of 1,7-cycloaddition of carbon monoxide across the divinylcyclopropane system in (**1**), mediated by iron carbonyl and induced by light with ring expansion, providing novel examples of bicyclic systems (**4**) and (**5**) which contain cyclo-octadiene units.

An ice cooled solution of (**1b**)† (5 mmol) and $Fe(CO)_5$ (15 mmol) in light petroleum (b.p. 40–60 °C, 100 ml) placed in a Dema apparatus, was irradiated under N_2 by a Philips HPK 125 W lamp for 4 h. Monitoring the reaction both by t.l.c. and i.r. spectrophotometry indicated the formation of an iron tricarbonyl complex (**6**) at early stages of the reaction, which was subsequently transformed into other iron carbonyl complexes with, much later, a build-up of a new metal-free species. Column chromatography with light petroleum separated the yellow organometallic complexes (**6**) and (**7**) from the colourless metal-free oily products (**4**) and (**5**) which were further separated by g.l.c. [6 ft × $\frac{1}{4}$ in, 20% Carbowax 20M, GCQ, 160 °C,

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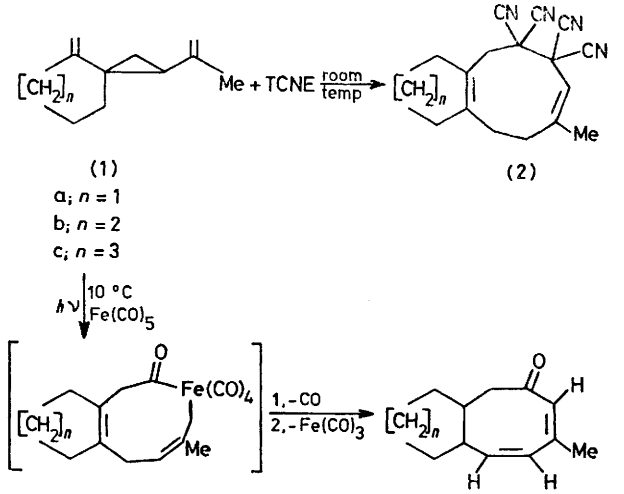
† Reactions with (**1a**) and (**1c**) were carried out similarly.

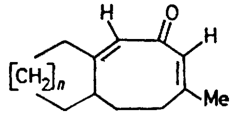


(1)
a; $n = 1$
b; $n = 2$
c; $n = 3$

(2)

(3)

(4)
a; $n = 1$
b; $n = 2$
c; $n = 3$



(5)
a; $n = 1$
b; $n = 2$
c; $n = 3$

$[C_{n+10}H_{2n+14}\cdot Fe(CO)_3]$
(6)

$[C_{n+10}H_{2n+14}Fe_2(CO)_6]$
(7)

40 ml He min^{-1}; retention time (**4b**) : 9 min and 20 s, (**5b**) : 9 min and 55 s]. The structure of (**4b**) was inferred from its analytical and spectral data [ν (NaCl) : 2920s, 2845m, 1665s, 1430m, 1365m, and 880 cm^{-1}; λ_{max} (C_5H_{12}) 239 nm (ε 13,600); *m/e* 190 (M^+, $C_{13}H_{18}O$, 9%), 148 (72%, $M-C_3H_6$), 133 (32%, C_9H_9O) 119 (32%, C_8H_7O), 105 (C_7H_5O, 42%), 91 (62%, C_7H_7), and 82 (100%, C_6H_{10})]. Its n.m.r. spectrum ($CDCl_3$) indicated the disappearance of the cyclopropane proton and of the terminal vinylic resonances and instead showed resonances at τ 4·22 (1H, finely split s, *J* 1 and 2 Hz), 5·45 (2H, dd, *J* 13 and 1 Hz, CH=CH), and 8·11 (3H, dd, *J* 1 and 2Hz, Me).

The structure of (**5b**) was deduced from its n.m.r. ($CDCl_3$) spectrum, exhibiting absorptions at τ 4·25 (1H, finely split s, CH=CH), 5·31 (1H, br s, CH=CH), and 8·17 (3H, s, Me). However, the relative abundances, and the pattern, of the mass spectral fragmentation of (**5b**) differ remarkably from those of (**4b**). The base peak occurs at *m/e* 88 (100%) and the next prevalent ion in its spectrum is of *m/e* 93 (89%), corresponding to C_6H_5O.

The cyclo-octadienones (**4**) and (**5**) are assumed to be formed by attachment of an acyl–metal bond to the terminal vinylic carbons to give a ferra-cyclononadiene species of structure (**3**) which upon subsequent losses of carbon monoxide and $Fe(CO)_3$, coupled with $Fe(CO)_5$-induced double-bond migration, affords the isomeric dienones, (**4**) and (**5**) which were isolated.[2] The structures of (**6**) and (**7**), characterized as the irontricarbonyl and the di-iron-hexacarbonyl π-complexes will be published elsewhere.

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[1] S. Sarel and M. Langbeheim, *J.C.S. Chem. Comm.*, 1977, 593.

[2] For a more detailed discussion of the mechanism of metal-induced 1,5-carbonyl insertion across the homodienic system in vinylcyclopropane, see S. Sarel, *Accounts Chem. Res.*, in the press.

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