Reaction Between an Azabullvalene and Nonacarbonyldi-iron

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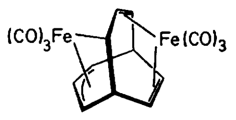
Summary The reaction between 3-methoxy-4-azatricyclo-[3,3,2,$0^{2,8}$]deca-3,6,9-triene and $Fe_2(CO)_9$ gives a novel σ–π-allyl heterocyclic tricarbonyliron complex (III) and methoxycarbonylcyclo-octatetraenetricarbonyliron complex (IV).

It has been recently reported that several polycyclic olefins, which include a cyclopropane ring, react with $Fe_2(CO)_9$ to give rearranged complexes. It was suggested that the bonding between the $Fe(CO)_3$ fragment and the modified unsaturated hydrocarbon involved σ- and π-allyl type bonds.[1,2] Structure (I), which was assigned to the major product of the reaction between bullvalene and $Fe_2(CO)_9$,[1] is an example of this type of bonding.

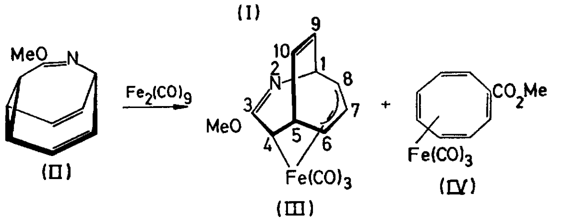
We have studied the reaction between the azabullvalene[3] (II),† which is homomorphic with bullvalene, and $Fe_2(CO)_9$. The two components were heated at 40° in dry benzene under nitrogen for 1 h and the reaction mixture was chromatographed on basic alumina. Structure (III) and (IV) are suggested for the two products which were obtained in 40 and 21% yield respectively. Compound (III)‡ is a yellow-brown oil, ν (hexane) 1942, 2000, and 2016 cm^{-1} (co-ordinated CO); ν ($CHCl_3$) 1625 cm^{-1} [–C(OMe)=N–]. N.m.r. results (100 MHz), including extensive spin-decoupling experiments, support assignment of structure (III). The detailed n.m.r. analysis will be reported elsewhere. The most instructive feature of the n.m.r. spectrum of (III) is the high-field shift of 4-H [δ 1·32 (d) p.p.m.]. Similar shifts for this type of protons have been reported.[1,2]

Compound (IV)‡ forms red crystals, m.p. 44 °C, ν (hexane) 2056, 2000, and 1974 cm^{-1} (co-ordinated CO), 1720 cm^{-1} (unco-ordinated CO); δ (100 MHz; $CDCl_3$): 6·85 (d), 5·35 (dd) 4·72 (m). Assignment of structure (IV) was confirmed by comparison (i.r., n.m.r., m.p.) with an authentic sample prepared from methoxycarbonylcyclo-octatetraene.[4]

According to Paquette[5] (n.m.r. analysis) the ground-state structures of an azabullvalene are those in which nitrogen is bonded to a bridgehead carbon atom. There are possibly four such interconverting isomers, in equilibrium. In principle each isomer can react with $Fe_2(CO)_9$ by two different routes, depending on the mode of scission of the cyclopropane ring. Structural analysis of all the eight possible isomeric complexes shows that structure (III), which results from a symmetric scission of the cyclopropane ring of (II), is in best agreement with the n.m.r. results. This is in agreement with the fact that (II) was described by Paquette[5] as the most stable structure of the azabullvalene under consideration. It is also noteworthy that unlike the complex (I) resulting from bullvalene, the imino double bond of (III) does not enter into a second complexation.



(I)



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† Compound (II) was obtained in a quantitative yield by methylation of 7-azabicyclo[4,2,2]deca-2,4,9-trien-8-one with methyl fluorosulphonate.

‡ Mass spectral data were consistent with this formulation.

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