

Reaction of 1,1-Dicyclopropylethylene with Pentacarbonyliron: a Novel Carbon Monoxide Insertion Coupled with a Double Cyclopropane Ring-opening

By RAPHAEL BEN-SHOSHAN and SHALOM SAREL*

(Department of Pharmaceutical Chemistry, The Hebrew University, Jerusalem, Israel)

Summary 1,1-Dicyclopropylethylene reacts with pentacarbonyliron to give 2-cyclopropylpenta-1,3-dienetricarbonyliron (V) and, after a longer reaction time, a mixture of (V) and 3-(1'-propenyl)-cyclohex-2-enonetri-carbonyliron—a carbon monoxide insertion reaction.

EARLIER work¹ has shown that 1-aryl-1-cyclopropylethylene (I) reacts with pentacarbonyliron (II) to yield stable diene complexes of structure (III). More recently, the rearrangements of vinylcyclopropane systems to π -allyl complexes on reaction with palladium (II) salts,^{2,3} and to a fulvene-type hexacarbonyl-di-iron π -complex on reaction with $\text{Fe}_2(\text{CO})_9$,⁴ have been reported.

We report the reactions of 1,1-dicyclopropylethylene⁵ (IV) with (II). This study was aimed at establishing whether the reaction of (IV) with (II) generates the 2-cyclopropylpenta-1,3-diene π -complex (V) in parallel to (I) \rightarrow (III) conversion, or possibly lends itself to a double cyclopropane ring-opening to provide a di-iron π -complex.

When a mixture of equimolar quantities of (IV) and (II) in ethylcyclohexane was heated at 140° for 6 hr. and then

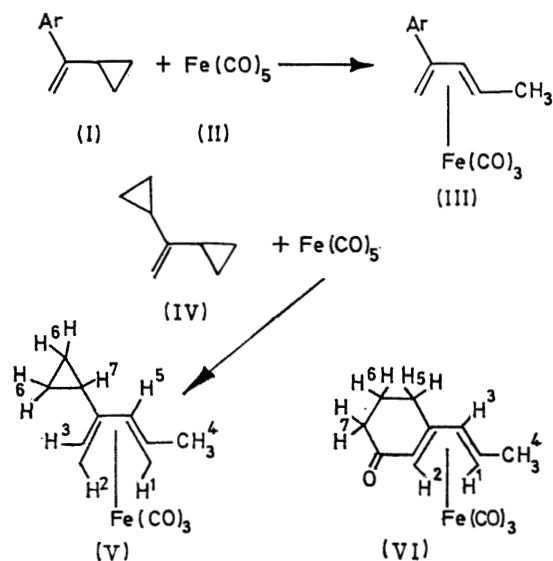
chromatographed on Florisil, a yellow oil, an iron π -complex of structure (V), was obtained.

The assignment of 2-cyclopropylpenta-1,3-dienetricarbonyliron structure (V) for the product is inferred from: (i) its elemental analysis; (ii) the absorption bands at 1975, 1985, and 2052 cm^{-1} in the i.r. spectrum (cyclohexane); (iii) the mass spectrum of (V) exhibiting the parent molecular ion at m/e 248 and peaks at 220, 192, and 164 corresponding to the successive loss of three CO ligands, and (iv) the 100 MHz. n.m.r. spectrum in CDCl_3 (lock signal benzene)[†] showing high-field resonances ranging from τ 9.20—9.58 (4H, m, 6-H) attributable to cyclopropane protons, a quintet centred at τ 8.57 (1H, 7-H), a doublet at τ 8.75 (3H, 4-H; J 6Hz.) attributable to methyl group protons, and four additional signals assigned to four diene protons: τ 8.4 (1H, m, 1-H), 9.08 (1H, d, 2-H), 8.08 (1H, double d, 3-H), 5.18 (1H, d, 5-H; J 8Hz.). The chemical shifts of the cyclopropane protons in the substrate (IV) and in the iron π -complex (V) are very similar, suggesting little, if any, interaction between the metal and the small ring.

When (IV) was similarly exposed to the action of (II) for

[†] N.m.r. spectra were measured on a Varian HA-100 spectrometer. Chemical shifts are reported in τ units relative to internal Me_4Si .

a much longer period (16 hr.) and then processed as described above, two metal carbonyl π -complexes: a yellow oil (A) and a yellow crystalline product melting at 76–78° (B), in 1:1 ratio, were obtained. Compound A is identical in all respects with (V). Product B is assigned the 3-(1'-propenyl)-cyclohex-2-enetricarbonyl iron formulation (VI)



on the basis of: (i) its elemental analysis; (ii) its i.r. spectrum in cyclohexane, displaying intense peaks at 1980, 2000, and 2060 (Fe–CO) cm^{-1} , and an additional band at 1685 cm^{-1} corresponding to a conjugated ketone absorption;⁶ (iii) its 100 MHz. n.m.r. spectrum in CDCl_3 (lock signal benzene), indicating the disappearance of cyclopropane resonances and consequently the appearance of new signals assigned to structure (VI) as follows: τ 8.75 (3H, d, 4-H; J 5Hz.), 8.88 (1H, double quartet, collapsing to q on irradiation at τ 5.10), 8.48 (1H, s, 2-H), 5.10 (1H, d, 3-H; J 8Hz., collapsing to s on irradiation at τ 8.88), 7.25–7.93 (4H, m, 5-H + 7-H), 8.0–8.35 (2H, m, 6-H). A *trans*-relation between 1-H and 3-H is inferred from the coupling constant J_{13} .[†]

The mass spectrum of (VI) exhibits the parent molecular ion at m/e 276 and peaks at m/e 248, 220, and 192, corresponding to the successive loss of three CO ligands, after which the cracking pattern arising from fragmentation of the cyclohexenoneiron becomes complex.

The data presented here provide a new type of carbon monoxide insertion reaction coupled with a double cyclopropane ring-opening on reaction with pentacarbonyliron. Formation of the diene complex (V) provides the first known example of a metal carbonyl π -complex bearing a cyclopropane ring which is not a part of a bicyclic system.

We thank Badische Anilin und Soda Fabrik, A.G., Germany, for a gift of pentacarbonyliron.

(Received, June 11th, 1969; Com. 837.)

[†] The *trans*-1,3 coupling constant for compounds of structure (III) has been found to be 9 Hz. (ref. 1).

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