Rearrangement of Bicyclo[4,2,0]oct-7-ene Catalysed by Di-iron Nonacarbonyl

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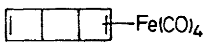
Summary Bicyclo[4.2.0]oct-7-ene rearranges to bicyclo-[4.2.0]oct-2-ene in high yield on treatment with $Fe_2(CO)_9$ in refluxing hexane.

THE thermally-induced rearrangement of tricyclo[4.2.0.0^{2,5}]-octadieneiron tetracarbonyl (I) to bicyclo[4.2.0]octatrieneiron tricarbonyl (II) shows that iron in certain systems allows a disrotatory cyclobutene-butadiene ring opening to take place.[1] The corresponding conrotatory process is precluded because the product of such a ring opening, in which one of the double bonds of the six-membered ring is *trans*, possesses very large ring strain. We have now applied this reaction to bicyclo[4.2.0]oct-7-ene (III), from which the conrotatory product, *cis,trans*-1,3-cyclo-octadiene, is energetically attainable. In fact, neither of the expected ring-opening pathways was followed when (III) was treated with $Fe_2(CO)_9$, instead another rearrangement process was observed.

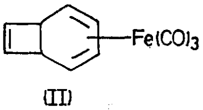
When *cis*-bicyclo[4.2.0]oct-7-ene (III)[2] was treated with $Fe_2(CO)_9$ in refluxing hexane, a mixture of hydrocarbons was obtained, which consisted of one major product (*ca.* 95% by gas chromatography) and one minor product, in addition to small amounts of starting material. The minor product could not be isolated in sufficiently large quantities to make identification possible, but gas chromatography indicated that it was not *cis,cis*-1,3-cyclo-octadiene and it could not have been the *cis,trans*- isomer[3] since it has been shown that under these reaction conditions *cis,trans*-1,3-cyclo-octadiene rearranged quantitatively to *cis,cis*-1,3-cyclo-octadiene. The major product was identified as *cis*-bicyclo[4.2.0]oct-2-ene† from spectroscopic data, its catalytic hydrogenation to bicyclo[4.2.0]octane, and comparison with the major product obtained from pyrolysis of the tosylhydrazone obtained from bicyclo[4.2.0]octan-2-one[4] in basic medium.[5] An unstable red oil, presumably the olefiniron tetracarbonyl complex (IV), could be isolated when the reaction was stopped in its early stages; its identification was based on the observation that oxidative decomposition of the complex with $Ce(NH_4)_2(NO_3)_6$ yielded (III) as the sole product.

The rearrangement apparently involves hydrogen transfer from the six-membered ring to the cyclobutene *via* the iron centre without involving opening of the four-membered ring. Under these conditions, neither *cis,cis*- nor *cis,trans*-1,3-cyclo-octadienes yielded bicyclic products. Our results cannot distinguish between direct formation of bicyclo[4.2.0]oct-2-ene and prior formation of the more symmetrical bicyclo[4.2.0]oct-3-ene with subsequent rearrangement. The latter pathway was shown to be a possibility when independently synthesized bicyclo[4.2.0]oct-3-ene[6] under the reaction conditions used for the transformation of (III) yielded only bicyclo[4.2.0]oct-2-ene.

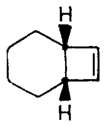
Rearrangements involving hydrogen migration in the presence of iron carbonyl compounds are not uncommon. For example, 1,3-cyclo-octadiene is the product of treatment of 1,5-cyclo-octadiene with $Fe(CO)_5$,[7] while tricyclo[5.2.1.0^{2,6}]decan-3-one is produced when the allylic alcohol (V) is treated with the same reagent.[8] Rearrangement, at least in (V), appears to involve suprafacial hydrogen transfer through a complexing iron group on the same face of the allylic system as bears the iron group. Assuming that the $Fe(CO)_4$ group is in an *exo*-configuration as indicated in structure (IV), another mechanism is apparently operative in the present case. While we have no conclusive evidence to support it, we favour hydrogen transfer through a second iron group on the opposite face of the molecule.



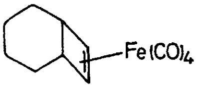
(I)



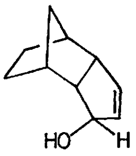
(II)



(III)



(IV)



(V)

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† We believe that the approach to bicyclo[4.2.0]oct-2-ene reported here represents the best, most direct synthesis of the hydrocarbon.

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