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## Eliminating Properties of Iron Carbonyls

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The most widespread method employed for the preparation of 1,3-cyclohexadienetricarbonyliron consists of reacting an iron carbonyl with cyclohexadiene. However, laboratory-scale syntheses leading to conjugate cyclic dienes have usually been based on elimination reactions [1].

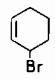
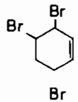
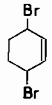
The object of this work was to study eliminating properties of iron carbonyls in reactions of splitting hydrogen halides off cyclohexene and cyclohexane derivatives. As an excess of iron carbonyl was used throughout, a transient diene should give 1,3-cyclohexadienetricarbonyliron or its derivatives.

In the literature, only one elimination reaction by means of iron carbonyl has been reported so far, which yielded a cyclohexadiene complex [2].

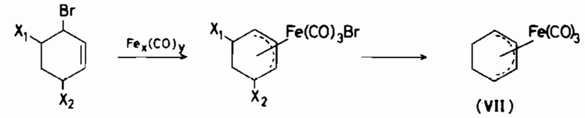
The possibility of splitting a hydrogen halide molecule has been studied using 1,2-dibromocyclohexane (I), 3-bromocyclohexene(II), 3,4-dibromocyclohexene (III), 3,6-dibromocyclohexene (IV), 2-chloro-3-bromocyclohexene (V) [4] and 2,3-dichlorocyclohexene (VI). Each of the compounds was reacted with $Fe(CO)_5$, $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$.

1,2-Dibromocyclohexane failed to react with any of the iron carbonyls studied. With II, III and IV, 1,3-cyclohexadienetricarbonyliron (VII) was the sole reaction product. The yields of this compound are shown in Table I.

TABLE I. Product Yields.

| | | $Fe(CO)_5$ | $Fe_2(CO)_9$ | $Fe_3(CO)_{12}$ |
|---|---|---|---|---|
| (II) |  | 29 | 36 | 42 |
| (III) |  | 14 | 18 | 25 |
| (IV) |  | 6.5 | 8 | 12.5 |

A high reactivity of bromocyclohexenes carrying a bromine atom at the allylic position is indicative of a reaction occurring as follows:



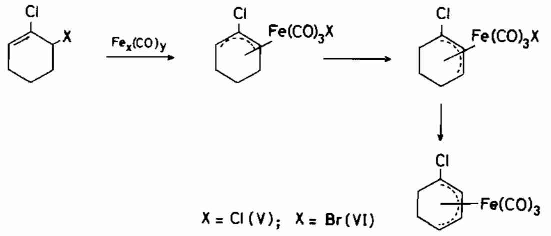
(VII)

$X_1 = X_2 = H$(II); $X_1 = Br$, $X_2 = H$ (III); $X_1 = H$, $X_2 = Br$ (IV)

Accordingly, elimination of one step of the synthesis of the diene complex results in an increased yield of the complex.

The sole complex isolated from reaction of 2-chloro-3-bromocyclohexene (V) and of 2,3-dichlorocyclohexene (VI) (prepared by racting $PCl_5$ with 2-chlorocyclohexanone) with tricarbonyliron was 1-chloro-1,3-cyclohexadienetricarbonyliron (VIII), obtained in both cases in 12% yield. Benzene was a side product in both reactions (GLC).

The formation of (VIII) is indicative of isomerization of a π-allyl complex formed in the first step according to the following scheme [5]:



X = Cl (V); X = Br (VI)

(VIII)

The structure of the complexes was determined based on elemental analyses as well as on the IR and $^1$H-NMR spectral evidence. Moreover, 1,3-cyclohexadienyltricarbonyliron tetrafluoroborates were synthesized from them [6].

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