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Preliminary communication

Synthesis of Cyclic Hydrocarbons via Intramolecular Coupling of bis-Pentadienyl Iron Tricarbonyl Cations

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Abstract. A general synthesis for the preparation of medium sized cycloalkanes having 1,2-butadienyl substituents is described. The reaction sequence involved acylation of butadiene-iron tricarbonyl with a diacid chloride, reduction of the resultant diketone to a diol derivative and conversion with HBF_4 to an acyclic bis-pentadienyl $Fe(CO)_3$ dicationic complex. Upon treatment with zinc the dication undergoes intramolecular ring closure to afford the bis-$Fe(CO)_3$ complex of the 1,2-dibutadienyl cycloalkane. Five-, six- and ten-membered cycloalkane derivatives have been prepared in this manner.

Due to the extreme difficulty involved in the isolation and handling of salts of purely organic carbonium ions, the formation of carbon-carbon bonds from such species, through intermediate conversion to radicals and subsequent coupling (eq. 1), has not proved to be a generally useful reaction sequence in organic synthesis.

$$2C^{+} \xrightarrow{2e} 2C^{\bullet} \longrightarrow C\text{–}C \qquad (1)$$

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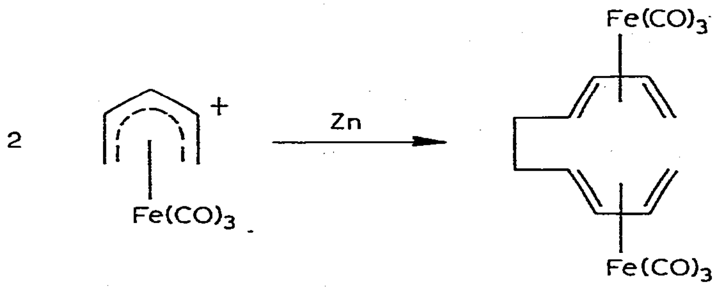
In the case of conjugated carbonium ions, *e.g.* allyl and pentadienyl systems, it is well established[1] that these afford thermodynamically stable salts when the organic moiety is coordinated to various transition metal systems and that these complexes retain properties of carbonium ions, for example nucleophilic attack will frequently occur on the hydrocarbon ligand. It has been previously shown in these laboratories[2] that treatment of the pentadienyl-iron tricarbonyl cation with zinc affords a mild method of formation of a new carbon-carbon bond (eq. 2), presumbaly via the mechanism implied in eq. 1, and we report now the general utility of this reaction for the formation of cyclic hydrocarbon systems.

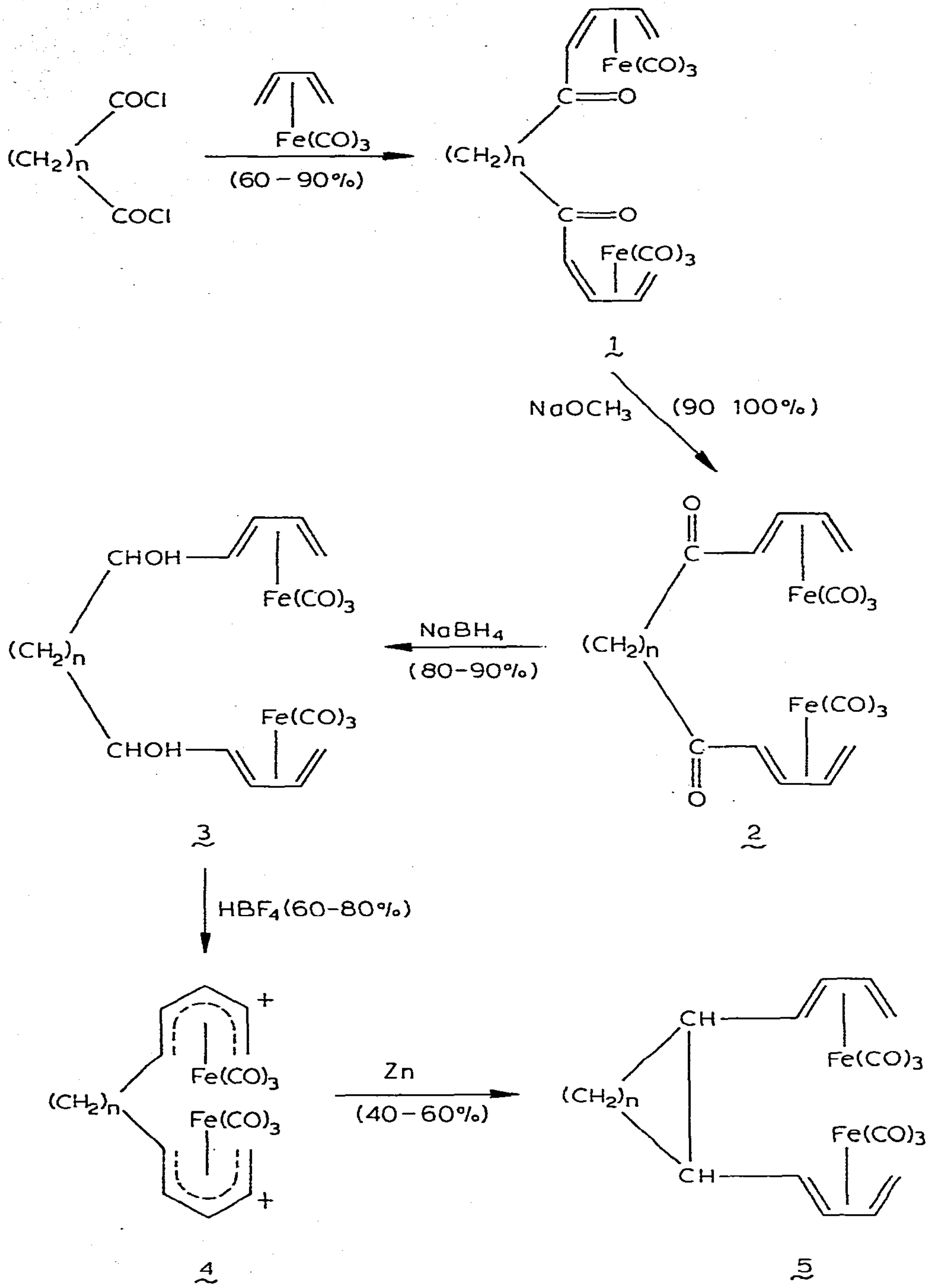


(2)

The general method of synthesis is outlined in Scheme 1.

The steps involve an acylation[3] of butadiene-iron tricarbonyl with a diacid chloride and isomerization[3] of the resultant bis-antiacyl complex (1) to the isomeric bis-syn complex (2). Reduction[4] of the diketone derivative (2) to the corresponding diol complex (3) followed by treatment with HBF$_4$ affords the salt[5] of the bis-pentadienyl Fe(CO)$_3$ cation (4). The salts (4) are yellow crystalline solids and are easily handled provided normal care is taken to exclude moisture.[6] Treatment of the salts with zinc dust in anhydrous acetone leads to intramolecular coupling with formation of the 1,2-bis-diene iron tricarbonyl derivatives of the cycloalkane (5).

Starting with the acid chlorides of glutaric, adipic, and sebacic acids we have prepared the corresponding 5,6 and 10 membered rings respectively of


COCl
(CH2)n
COCl
Fe(CO)3
(60 – 90%)
1
NaOCH3
(90 100%)
2
NaBH4
(80–90%)
CHOH
3
HBF4(60–80%)
4
Zn
(40–60%)
CH
5

Scheme 1

the complexes (5) (i.e. n=3,4 and 8). The range of yields for each step in these synthesis are indicated in the scheme. The free hydrocarbons can be liberated from the complexes through the standard technique of mild oxidative degradation.

Conceivably, the synthesis could have lead to a very complex mixture of isomeric products, however, in the cases mentioned, this was not realized; each step being highly selective. As was observed in the intermolecular coupling of 1-substituted pentadienyl-$Fe(CO)_3$ cations,[2] the intramolecular coupling in the cations (4) occurs between the terminal carbon atoms of the pentadienyl ligand which bear the alkyl substituent. Geometrical inversion also occurs during this coupling leading to syn substituted diene-$Fe(CO)_5$ complexes (5). A difference from the intermolecular coupling appears however, in the stereochemistry of the coupled products; whereas in the acyclic systems both meso- and racemic isomers were formed[2], in the cyclic system, where n=3, only one stereochemical isomer was obtained.

Especially to determine the stereochemistry involved at the ring closure step, the compound 5 (n=3) was studied by single crystal Xray analysis. The crystals obtained by vacuum sublimation were orthorhombic having a space group Pbcn, with a = 12.854, b = 13.248, c= 11,646 A and z = 4 molecules of $(C_{13}H_{18})Fe_2(CO)_6$ per unit cell. For z = 4 in space group Pbcn, the molecules must occupy sites of either C_i or C_2 symmetry with only the latter possibility being consistent with the expected molecular symmetry. Intensity data were gathered at ca. -35° C using a Syntex $P2_1$ diffractometer for the 2287 symmetry-independent Bragg reflections with $4 < 2\theta < 55$. Crystallographic experimental procedures are essentially as reported elsewhere.[7] The structure was solved by the heavy atom approach and refined isotropically by full-matrix least-squares methods to a conventional $F(=\Sigma||F_o| - |F_c||/\Sigma|F_o|)$ index of 0.16 using the 1151 reflections with intensities which were more than three times their corresponding standard deviations. The disposition of the atoms in the molecule is given in Fig. 1.

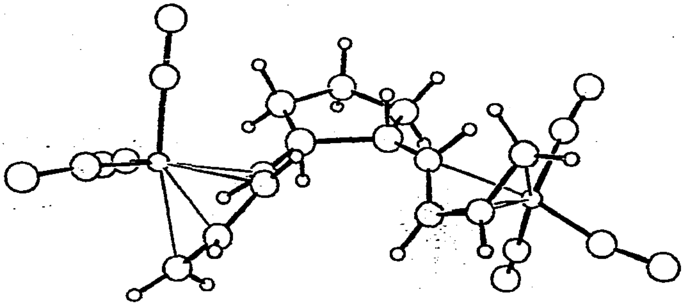


Fig. 1. The molecular structure of complex 5 (n=3).

The essential point which emerges from Fig. 1 is that the two diene-Fe$(CO)_3$ substituents on the five membered ring are disposed trans to each other. Presumably this reflects steric repulsion effects in the intermolecular coupling which are not present in intermolecular case. Less obvious is the reason for the formation of the particular compound given in Fig. 1, as compared to the isomeric material having the same structure but with one of the Fe$(CO)_3$ on the opposite face of the diene ligand. Apparently this latter stereo selectivity can be traced back to the formation of only one of two possible isomers of the ketone 1 in the initial substitution, but this remains to be established.

Further results pertaining to the utility of this synthetic scheme for the preparation of both smaller and larger ring systems and further study of the stereochemistry of the ring closure reactions will be reported later.

Acknowledgement

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References

1. G.E. Coates, M.L.H. Green and K. Wade, Organometallic Compounds, Vol. II, Methuen & Co., London, 1968.
2. J.E. Mahler, D.H. Gibson and R. Pettit, J. Am. Chem. Soc., 85, 3959 (1963).
3. P. Lillya and R.E. Graf, personal communication. The direct reduction of the ketones 1 proceeds in very low yields hence the extra step involving their isomerization.
4. J.E. Mahler and R. Pettit, J. Am. Chem. Soc., 84, 1511 (1962).
5. J.E. Mahler and R. Pettit, J. Am. Chem. Soc., 85, 3955 (1963).
6. Cyclic ethers are formed if water is not excluded.
7. P.E. Riley and R.E. Davis, Inorg. Chem., 14, 2507 (1975).