

OPTICAL RESOLUTION OF TRICARBONYL(1-CARBOXYCYCLOHEXA-1,3-DIENE) IRON
AND THE ABSOLUTE CONFIGURATION OF THE PRODUCTS

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Summary: Resolution of the acid (1) (shown as the (+)-isomer) into its optically pure (+) and (-) isomers and reduction of the CO₂H yields the 2-Me derivative (2) (shown as the (-)-isomer). The absolute configuration of (2) is defined by conversion of the salt (3) of known configuration into (2) and (4). This is the first resolution leading to preparation of pure complexes of known absolute configuration.

Some uses for organic synthesis of chiral tricarbonylcyclohexadienylium-iron salts are based on the production of a new resolved chiral centre, by stereospecific nucleophilic attack followed by removal of the initial chirality on removal of the Fe(CO)₃. To make full use of this capability involves a knowledge of the absolute configurations of the chiral cations, and an ability to produce them in fully resolved form. Although chiral transfer of Fe(CO)₃ to cyclohexadienes has been accomplished¹ and the absolute configurations of some of the substituted cations (2-OMe, 2-Me) which can be derived from the initial products are known,² they are only partially resolved.

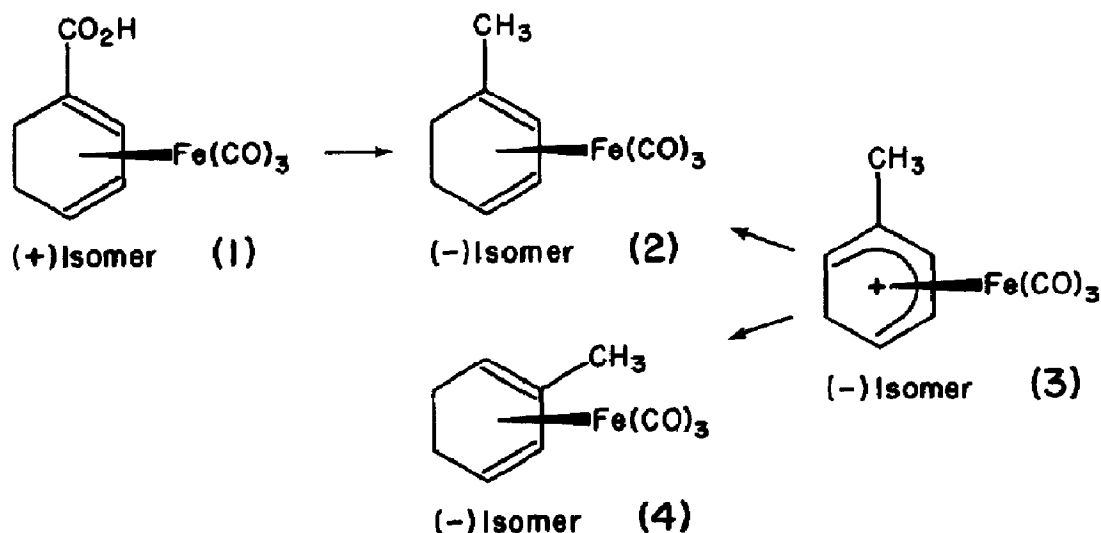
The first step to preparations of the cations is the production of related neutral complexes.³ The title acid belongs to a particularly important series since not only does CO₂H provide a basis for classical resolutions, but it is a functional group which can be used to form other substituents. In particular, conversion into CH₂OH or CMe₂OH is known⁴ to permit direct conversion by acid into the 1-Me or 1-CHMe₂ cation, providing a model for a number of synthetic processes.

We now report a classical resolution of the title acid through the salts of (-)-1-phenylethylamine. Recrystallised from CHCl₃-acetone, the salt was separated into more and less soluble fractions which were recrystallised to constant rotation from acetone. The former, after treatment with dilute HCl, gave (+)-tricarbonyl(1-carboxycyclohexadiene)iron m.p. 147-149°C [α]_D²⁵+136° (acetone, c = 3) and the (-)-isomer m.p. 147-149°C [α]_D²⁵-136°. The total yield of resolved acid was 34%. The ORD curves are not simple ones, but show maxima at 484-490 nm [α] _{λ} ²⁵(+) or (-) 214°; they do not cross the zero line and [α]_D is sufficient to indicate the configuration.

To find the absolute configuration, the (+) acid (1) was reduced by BH₃-Me₂S with BF₃-Et₂O in refluxing THF, resulting in conversion of the

1-CO₂H into a 1-Me to yield the (-)-1-methyl complex (2). This same complex has been produced by borohydride reduction² from the (-)-tricarbonyl(2-methylcyclohexadienyl)iron PF₆ [α]_D²⁵ = -2.5° (c = 9, CH₃CH) of the known absolute configuration (3) shown. Some (-)-2-tricarbonyl(2-methylcyclohexadiene)iron (4) formed simultaneously in the reduction was separated² by chromatography on silica impregnated with silver nitrate. The relations between absolute configurations and the directions of rotation are those shown.

There is no obvious mechanism for, or expectation of, racemisation in these processes so that [α]_D²⁵ -18° (c = 1, CHCl₃) is believed to be that of the optically pure isomer (2). This contrasts with [α]_D²⁵ -1.7° (c = 3, CHCl₃) for (2) obtained via the transfer method² and reduction of (3), which leads to an enantiomeric excess of only about 10%. The observed value of [α]_D²⁵ -1.5° (c = 7, CHCl₃) for (4) produced in the same reduction process with presumably the same e.e. leads to about [α]_D²⁵ -15° as the calculated value for pure (4).



REFERENCES

1. A.J. Birch, W.D. Raverty and G.R. Stephenson, Tet. Lett., 21, 197 (1980).
2. A.J. Birch, W.D. Raverty and G.R. Stephenson, J.C.S. Chem. Comm., in preparation.
3. A.J. Birch and I.D. Jenkins, Transition Metal Organometallics in Org. Syn., Vol. 1, ed. H. Alper, 1 (1976).
4. C.R. Jablonski and T.S. Sorensen, Can. J. Chem., 52, 2085 (1974); B.M.R. Bandara and A.J. Birch, unpublished work.

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