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THE RESOLUTION OF THE FUMARIC ACID-IRON-TETRACARBONYL COMPLEX.

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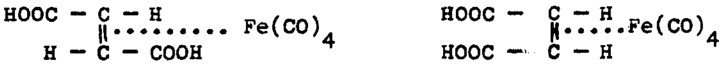
It has already been pointed out, from the study of Pt(II) square complexes, that olefinic compounds with a symmetry grade lower than $2\ \underline{m\ m}$, which are bonded in metal-complexes, give rise to a racemic mixture (1).

Both carbon atoms of the double bond, when linked to two different groups, ${}^{R\searrow}_{R\nearrow}C =$, become asymmetric. This type of molecular asymmetry is related to the complexing step of a vinylic monomeric unit in the stereospecific polymerization (2,3).

In this field of studies we also considered metal-olefin complexes having molecular geometry differing from the square one.

Examples of resolution of asymmetric carbonyl derivatives of Cr, Fe and Mn with arene and cyclopentadienyl substituent groups were recently described (4).

A survey of different stable olefinic complexes has brought to our attention some π-olefin complexes between $Fe(CO)_4$ and unsaturated carboxylic acids (5). The complex with fumaric acid (Fig.1,a) is clearly asymmetric and should be resolvable in enantiomers, while the corresponding compound with maleic acid (Fig.1,b) should not be resolvable.



$$\begin{array}{l} HOOC - C - H \\ \quad\quad\quad\; \| \cdots\cdots\; Fe(CO)_4 \\ \;\; H - C - COOH \end{array} \qquad \begin{array}{l} HOOC - C - H \\ \quad\quad\quad\; \| \cdots\; Fe(CO)_4 \\ HOOC - C - H \end{array}$$

a b

Fig.1

Actually, the last compound has a symmetry plane perpendicular to the plane of the double bond.

The resolution of enantiomers of the compound containing fumaric acid, $C_4H_4O_4\,Fe(CO)_4$, was achieved by fractional crystallization of monobrucine salts.

The best way to achieve the separation is as follows:-
Fumaric acid-iron-tetracarbonyl (2.30 g, $8.1 \cdot 10^{-3}$ moles) was added to a solution of brucine (3.18 g, $8.1 \cdot 10^{-3}$ moles) in 200 ml of acetone with 2% water, at 60°C and the mixture was left ohe hour.

After this time the yellow microcrystalline precipitate was collected by filtration and dried (2.30 g, yield 42%). It was recrystallized from ethanol-acetone 1/10 to give the diastereoisomeric salt (I), $[\alpha]_D^{25}$ - 203 (ethanol; c, 1.26).

This salt was decomposed in acetone solution by the addition of 6 N HCl. The solvent was removed under vacuum; the solid residue was carefully washed with water and then crystallized from acetone (A).

Optical activity of (A), $[\alpha]_D^{25}$ - 593 (acetone; c, 0.848).
A second crop of crystals separated at 0°C; this crop (1.15 g, yield 21%)

was filtered off and discarded. The solution was evaporated to dryness, and a yellow powder obtained. Without further purification the diastereoisomeric salt (II) was decomposed, in the same manner as diastereoisomer (I), and the enantiomeric fumaric acid complex (A'), $[\alpha]_D^{25}$ + 587; (c,0.921, acetone) was obtained. Analyses and IR spectra of two enantiomers (A) and (A') are identical with those of the racemic mixture.

A similar procedure was used for the complex compound with maleic acid.

In this case we collected four crops of monobrucine salt from the acetone solution.

All these fractions showed very low rotations and, when decomposed with hydrochloric acid gave an optically inactive complex.

Other complexes of this type (for example, with acrylic and citraconic acid) are resolvable and are under study in our laboratory.

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