Fulvalen
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I) **Introduction**

With fulvalen is mostly associated the pentafulvalen, but the fulvalens describe the group of organic compounds. Characteristics of fulvalens are two conjugated rings which are connected with a double bond. Because of its special π-electron situation the molecules can be used as a ligand in the coordination chemistry. For example, transition metals like iron, manganese or molybdenum can be coordinated. Therefore, not interacting metal ions are parallel bonded. The distance between the metal centers is a few 4·10^{-10} m. This is possible because the double bond creates a rotation-barrier and makes the structure of the ligand planar. Furthermore, electronic interactions can be exchanged over the aromatic system and this skill is the basis for organic conductors. But instability of the Fulvalen is a problem in its use as an organic ligand, also it dimerizes in a Diels-Alder-Reaction.

II) **Historical background**

1951 Kealy and Pauson aimed for the synthesis of pentafulvalen C_{10}H_{8}. They choose the method that Cyclopentadienylmagnesiumbromide should reductively be bonded with FeC_{13}. However, the aimed product could not be created with this way of reaction, but they synthesized the Ferrocene C_{10}H_{10}Fe, which has amazing skills for an organometallic compound. The product is easy to sublimate and very stable.

III) **Overview of unsymmetrical fulvalens**

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This picture shows examples of the combination from conjugated rings which can be synthesized.
IV) **First Synthesis**

Oxidative coupling of cyclopentadiene-salt with Ferrum(III)-chloride. This did not lead to the aimed fulvalene, but to the invention of ferrocene.

**a. Synthesis of Pentafulvalen**

Fulvalene could be synthesized by treating cyclopentadiene with butyllithium.

**Step 1** Formation of an intermediate cyclopentadienylradical which is able to make a dimerisation.

**Step 2** Oxidation with oxygen to fulvalene

The first step of this synthesis was done by Doering in 1959. He generated the dimere 9,10-dihydropentafulvalene. Doering formed it by the reaction of cyclopentadienide with iodine. The following deprotonation led to the bisanion which could be transferred to the product with oxygen. But this path didn’t led to great amounts of the product.

![Synthesis Diagram](image)

**Synthesis „Neuenschwander“**

A better way of formation was found by Neuenschwander. He made a reductive coupling of cyclopentadienyllithium with anhydrous cupric-chloride or iodine.

As a solvent he used THF at -30°C. The path of reaction led to 9,10-dihydropentafulvalene. This way also has the anion as an intermediate and cupric-chloride is also used for the last oxidation step.

Furthermore, fulvalene could be formed with diazo-2,4-cyclopentadiene. The monomere could be made by removing the azogroup. The following dimerisation took place at low temperature, inert gas and irradiation of that molecule, which carries the azogroup.

**b. Unsymmetrical fulvalens**

Unsymmetrical fulvalens are especially interesting because they can develop a dipole moment. From the reduction of the double bond both halves of the molecule profit, because both parts acquire aromatic character. The barrier to rotation around this central double bond is lower than the barrier to isomerization.
Example for synthesis of unsymmetrical fulvalens:

The first attempts to prepare heptafulvalene were done at the beginning of the 1960s by Prinzbach. He obtained a red solution in which he found a fulvalene - similar structure by analyzing the UV spectrum. Neunschwander and co-workers managed the actual chemical characterization ten years later. The reaction of acetoxy tropylium tetrafluoroborate with sodium cyclopentadienide results in acetoxy cyclopentadienylcycloheptatriene. When these acetates were transferred by flash vacuum pyrolysis in presence of triethylamine they are converted into esters, which can be transposed into the intended heptafulvalene. All in all the synthesis runs with a good yield of 53%.

V) Application of fulvalene

Organic conductors:

The electrical conductivity of an organic compound results of the sp2- hybridization of the carbon atoms. The 2s, 2px and 2py make solid $\sigma$- bounds with the angle of 120° and the 2pz make $\pi$- bounds. If this pi bounds are conjugated (“delocalized $\pi$- System”), then you can speak of intramolecular conductivity.

The fulvalens have such a conjugated $\pi$- System. This and the property to connect mononuclear complex fragments make the fulvalens very interesting in the transition metal chemistry.

The following structures can be realized by rotation around the C-C bond of the bridge:

Electronical interaction can be found in both configurations on the $\pi$-electronic systems between the metals.

Compounds with configuration IV can be used in catalytically active metal surfaces.
VI) Sources


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