

The substitution and the nucleophilic substitution of ferrocene and derivative

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Abstract. Ferrocene, as a significant part of the organic synthesis, who can derivatives a large amount of compounds. This research expresses the progress from the preparation of η^6 - dichlorobenzene - η^5 - cyclopentadienyliron to the formation of η^6 - Bis (phenoxy) - η^5 -cyclopentadienyliron. Nesmeyanov's theory, throughout the thin layer chromatography, is observed to be applied in this program. This experiment attest that not only the substitution of ferrocene, but also the nucleophilic substitution of η^6 -dichlorobenzene- η^5 -cyclopentadienyliron.

Introduction

Organometallic complex is an extensive field which connects both organic chemistry and inorganic chemistry. Ferrocene, as one of the core researching compounds in this field, exhibits some special properties differ from both organic and inorganic materials. η^6 -arene- η^5 -cy-clopentadienyliron is an analogue of ferrocene, as a successful preparation, was reported by Nesmeyanov, in 1963, at the same time, broaden the range of the coordination chemistry research. After which, a large amount of compounds with similar foundational conformation is able to be obtained, throughout the reaction of ferrocene, who is the main reactant to prepare the η^6 -arene- η^5 -cyclopentadienyliron accompanying with AlCl_3 , KMnO_x and H_2O . Then η^6 -arene- η^5 -cyclopentadienyliron is an instability compound under the light, which will lead it to polymerization, so reacts in a dark place is required in all of the progress relates to η^6 -arene- η^5 -cyclopentadienyliron. For this reason, this kind of compounds act as photoinitiator is possible. Nucleophiles can activate the aromatic ring. For example, η^6 - dichlorobenzene - η^5 -cyclopentadienyliron has the capability to react with phenol, whose product is that the chlorine atoms are substituted by the oxygen atoms, coming from the phenols. Usually, nucleophilic substitution is hardly reacting on aryl halides. While under the effect of electron-withdrawing groups, the nucleophilic substitution is able to bear isen. Overall, the η^6 -dichlorobenzene- η^5 -cyclopentadienyliron can be used as an active photoinitiator due to the electro-withdraw effecting of chlorine atoms.

Experimental

The preparation of η^6 -dichlorobenzene- η^5 -cyclopentadienyliron.

Apparatus: Round bottom flask (250ml), reflux condenser, dry pipe, chemi-stirrer, separating funnel, beaker, thermometer, IR spectra, H-NMR spectra and silver paper.

Compound: ferrocene (4.7g), aluminum chloride (10g), powdered aluminum (2g), paradichlorobenzene (40g), cyclohexane (50ml), light petroleum, potassium hexafluorophosphate saturated solution (100ml).

Progress: Add the ferrocene, aluminum chloride, powdered aluminum, paradichlorobenzene into round bottom flask and heat steadily after well-stir. Approximately 2 minutes later, accompanying the appearance of a little white needle crystal on the inside, the mixture became invisible green. It took about 10 minutes that the solid melted, while some brown liquid was discovered in the inside. When the temperature in the inside reached to 90°C , the liquid turned to become dark green, with

the appearance of white mist. 27 minutes passed, the temperature climbed to 120°C and stable. Withdraw the heater, natural cooling to about 70°C. The solution changed to black, after adding the cyclohexane. Next, poured the liquid into a beaker filled with ice, with large amount of white mist (aqueous phase was dark green and the organic phase was dark brown). Before skimming with light petroleum, suction filtration was required. Skimming until the organic phase was achromatous. And then suction filtrate again, after the stirred (avoid light) for 20 minutes. Finally, stoved the greenyellow solid.

The nucleophilic substitution of η^6 - dichlorobenzene- η^5 -cyclopentadienyliron.

Apparatus: three-neck round-bottom flask (100ml), reflux condenser, chemi-stirrer, Buchner funnel, suction flask, beaker, thermometer, silver paper, chromatographic column, conical flask, silica gel plate.

Compound: anhydrous potassium carbonate (0.27g), η^6 - dichlorobenzene - η^5 - cyclopentadienyliron (0.2g), phenol (0.1g), DMF (20ml), acetone (10ml), methyl alcohol, light petroleum (80ml), aluminium oxide, potassium hexafluorophosphate saturated solution (100ml).

Progress: Mixed the phenol, η^6 - dichlorobenzene- η^5 -cyclopentadienyliron, DMF, anhydrous potassium carbonate together, using TLC (thin—layer chromatography) to monitor the extent of reaction and heating slow to 60°C. The heating should be stopped after the disappearing of the point of η^6 - dichlorobenzene- η^5 -cyclopentadienyliron in TLC plate, and filtrated before poured the filter liquor into a beaker filled with KPF₆ solution. The product, greenyellow sediment, can demonstrate the substitution of η^6 - dichlorobenzene- η^5 -cyclopentadienyliron. Dissolving the product into acetone, adding light petroleum meanwhile. Greenyellow crystal was found in the aqueous phase. Finally, use the column chromatography to purification.

Theory

As for the principle of the preparation of η^6 - dichlorobenzene- η^5 -cyclopentadienyliron, is that one of the cyclopentadiene rings in the ferrocene is substituted by a paradichlorobenzene, which is just a kind of the ferrocene's substitutions in all varieties (figure 1.).

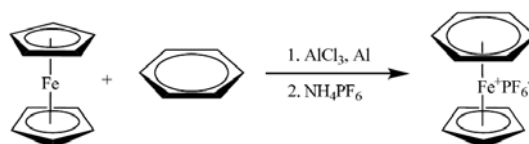


Figure. 1 The substitution of ferrocene

The reason why the powdered aluminum is necessary to be put into the system in advance of the aluminum chloride is that prevent the ferrocene from being oxidation. Two aspects are discovered to impact the arene-substitution of ferrocene. One is the electrical properties of substituted groups. As for the electron donating group, increasing the electron cloud density of arene, has the ability to force the ferri ion and the arene combining together, improve the productivity, while the electron withdraw group plays a reverse role. The electron withdraw group, moreover, is unable to react with ferrocene, because it's strong electric absorption. Another is the steric effect. The substituent group belongs to the arene will affect the reaction of ferrocene. The more or the bigger, this substituent group is, the more difficult this reaction displays. In regard to the nucleophilic substitution of η^6 -dichlorobenzene- η^5 -cyclopentadienyliron, in fact this reaction can be divided into 2 stages. Stage 1 is one of the chlorine is substituted by a phenol, which is easy to occur. Nevertheless, stage 2, another one phenol substitutes the chlorine, is relatively hard, due to the both electric absorption effect and steric effect. Therefore the phenol is required to be excessive.

Result

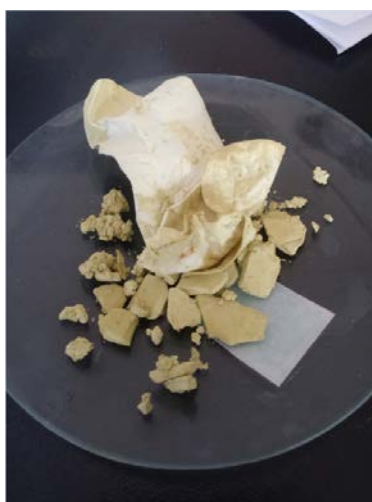


Figure. 2 η^6 -dichlorobenzene- η^5 -cyclopentadienyliron

As the figure 2 demonstrates is the η^6 -dichlorobenzene- η^5 -cyclopentadienyliron. While being reacted with phenol, η^6 -Bis(phenoxy)- η^5 -cyclopentadienyliron is produced, which presents a bronzing floc.

Discussion

Some related research shows that η^6 -haloarene- η^5 -cyclopentadienyliron tends to be nucleophilic substituted. Because the nucleophile has the electron donate effect, while the force between chlorine and benzene is weak, due to both chlorine and benzene are electron withdraw group, so the benzene prongs to combine with nucleophile. For some organic synthesis, η^6 -(arene)- η^5 -cyclopentadienyliron(II) moiety is useful. However, the separation of it is tough. Pyrolysis, electrolysis and photolysis are the mainly used approaches to solve this task. The pyrolysis has the short reacting time while strict high temperature. Electrolysis is effective, but the certain potentials is demanded. Photolysis is the primary mean, which can be used with heat-sensitive arenes and reducible substituents.

In this research, the reaction of η^6 -dichlorobenzene- η^5 -cyclopentadienyliron is concentrated, while there are also a large amount of derivatives of ferrocene, produced by differ ways.

Conventional ways (Nesmeyanov mainly) tends to be applied extensively, on account of the simple theory, in another words, ligands can be exchanged with ferrocene, to acquire the complex structure. Some disadvantages are also likely to be found, for example, some solid arenes or inert liquid should be pretreated.

In contrast, microwave method can induce the reactions within minutes, and generally higher yields than the conventional way.

Concentrate on the nucleophilic substitution of η^6 -dichlorobenzene- η^5 -cyclopentadienyliron, the difficulty of this experiment is the substitution of the second phenol. The electron density on the paradichlorobenzene increases result of the substitution of the first phenol.

Conclusion

In summary, this experiment concentrates on, η^6 -Bis(phenoxy)- η^5 -cyclopentadienyliron, a product of the nucleophilic substitution of η^6 -dichlorobenzene- η^5 -cyclopentadienyliron. What is the key of this experiment is that the control of the reaction time. The main ways to monitor the process is the TLC, which should be done during a certain period of time. The purpose of this research is to prove the Nesmeyanov's report, meanwhile explore the nucleophilic substitution of η^6 -dichlorobenzene- η^5 -cyclopentadienyliron. In fact, the important achievement is not the product itself, but the theory, which can be used more comprehensively to prepare the material with the

ferrocene similar structure, throughout the substitution of different ligand.

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