Erc.Üni.Fen.Bil.Derg., 5, 1-2 (1989), 810-815

CHLORINATION OF SOME NAPHTHALENE COMPOUNDS BY CUPRIC CHLORIDE

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CHLORINATION OF AROMATIC COMPOUNDS

SUMMARY

In this study, the chlorinations of naphthalene and 1 chloro-naphthalene by cupric chloride were investigated.

Naphthalene and 1-chloro naphthalene, in an non-solvent medium, were heated up to boiling points and stirred for 6-8 hours. 1-chloro naphthalene and 1,4-dichloro naphthalene were obtained.

BAZI NAFTALİN BİLEŞİKLERİNİN BAKIR (II) KLORÜR İLE KLORLANMASI

ÖZET

Bu çalışmada, naftalin ve 1-klor naftalinin $CuCl_2$ ile klorlanması incelenmiştir. Naftalin ve 1-klor naftalin, çözücüsüz ortamda, kaynama noktaları civarında, 6-8 saat $CuCl_2$ ile karıştırılarak ısıtılmış, yüksek verimlerle 1-klor naftalin ve 1,4-diklor naftalin elde edilmiştir.

1. INTRODUCTION

Aromatic compounds can be chlorinated by various methods. For example, chlorine can be passed through a proper solution of a compound to be chlorinated by a catalyst [1]. As a chlorinating agent PCl_3, PCl_5, $SOCl_2$, HOCl, SO_2Cl_2, $FeCl_3$, $CuCl_2$, or $SbCl_5$ can be used in the chlorination of aromatic compounds [2].

1,4-dichloro naphthalene is used in the synthesis of 5,8-dichloro-1-naphthalene acetic acid. It is thought that this acid has a special effect as a plant-growth substance. A plant-growth substance has a unsaturated ring system with a carboxyl group. When naphthalene is chlorinated in CCl_4 with Fe catalyst, over 50 % 1,4-dichloro naphthalene is obtained [3]. Purification of the product is difficult. The product is separated from mono-chloro naphthalenes and other dichloro naphthalenes (expect 1,5-dichloro naphthalene) by mild sulphonation. Through repeated crystallization, 1,4-dichloro naphthalene can be seperated from 1,5 dichloro naphthalene.

The chlorination of naphthalene $CuCl_2$ without solvent at 100° for 0,5 hour, no product was obtained (2c). In this study, $CuCl_2$ (moles) : hydrocarbon ratio was chosen as seven. In the so-far known literature no chlorination of 1-chloro naphthalene by $CuCl_2$ has been encountered. We investigated the chlorination of naphthalene and 1-chloro naphthalene by $CuCl_2$.

2. MATERIAL AND METHOD

In this study, naphthalene (re-crystallized from ethanol) and 1-chloro naphthalene (Merck) were used. Anhydrous cupric chloride was dried in an oven at 110-120° for several hours and stored in a desiccator of over phosphorus pentoxide before use. In this study, two-necked flask, equipped with a mechanical stirrer and a reflux condenser was used.

In the analyses of the results obtained, were used a melting point apparatus (Büchi), IR spectrophotometer (Perkin-Elmer) and NMR spectrophotometer (Shimadzu).

3. EXPERIMENTAL

3.1. 1-CHLORO NAPHTHALENE

In a dry, 500 ml.,two-necked flask, equipped with a mechanical stirrer and a reflux condenser fitted with a drying tube, are placed 12.8 g.

(0.100 mole) of naphthalene, 27.2 g. (0.202 mole) of anhydrous cupric chloride. The reaction mixture is stirred and heated under reflux for 6-8 hours. The brown cupric chloride is gradually converted to white cuprous chloride, and hydrogen chloride is gradually evolved. At the end of reaction the mixture is cooled to room temperature.The reaction mixture is treated with 150 ml. of dil. H_2SO_4. The cuprous salts are solved and removed by decantation. After drying, the mixture of naphthalene and 1-chloro naphthalene sublimate in vacuo. Naphthalene is separated. The residue is distilled under reduced pressure. 1-chloro naphthalene is collected at 130°/20 mm. Hg, yield: 80 %

3.2. 1,4-DICHLORO NAPHTHALENE

In a dry, 500 ml., two-necked flask, equipped with a mechanical stirrer and a reflux condenser (air-cooled) fitted with a drying tube, are placed 17.82 g (14.85 ml, 0.11 mole) of 1-chloro naphthalene, 27.2 g (0.202 mole) of anhydrous cupric chloride. The reaction mixture is stirred and heated (appr. 230) under reflux for 6 hours. The brown cupric chloride is gradually converted to white cuprous chloride, and hydrogen chloride is gradually evolved. At the end of the reaction, the mixture is cooled to room temperature and treated with dil. H_2SO_4. The aqueous phase is separated by decantation from organic phase. The crude product is washed with 500 ml of cold water, and than the crude product is treated with 250 ml of conc. H_2SO_4. The mixture is stirred in room temperature for two days. After the sulphonations of naphthalene, mono- and dichloro naphthalenes (except 1,4- and 1,5-dichloro naphthalenes), the mixture poured on ice. The product (the mixture of 1,4- and 1,5-dichloro naphthalenes) is not solved in water, and separated from the solution of sulphonated compounds by filtration. The product is recrystallized from ethanol, m.p. 68°, 90 %.

4. RESULT AND DISCUSSION

The first aim of this study is to try $CuCl_2$'s effect over new substances. The secondary aim is that 1,4-dichloro naphthalene is synthesized with high yield. The chlorination of aromatic hydrocarbons (benzene, naphthalene, phenanthrene, anthracene, tetracene, and pyrene) by $CuCl_2$ was investigated by Ware and Borchert (2c). According to the authors, reaction of solids seldom produced much product and so, usually, the hydroocarbon to be investigated was dissolved in nitrobenzene and treated with an excess of cupric chloride. The results of authors' studies are presented in Table 1.

TABLE - 1

Hydrocar.	$CuCl_2$: Hyrdoc,	Solvent.	Temp.	Time (h)	Nature of Product
Naphth.	7	None	100°	0.5	None
"	6.4	Nitroben.	210°	72	1-chloro naphtalene 1,4-dichluoro naphthalene[a]
"	12	None-sea	210°	72	Unidentified yellow cyrstals, analysis approximated that for a tetra chloro naphthalene[b]

[a]Separation from solvent was incomplete.

[b]The tip of the tube broke and the crystals remaining within the tube were examined.

It has been determined that, as a result of the studies given above, naphthalene did not give reaction by cupric chloride (moles ratio naphthalene : $CuCl_2$, 1 : 7). Naphthalene reacted with difficulty in a

solvent (nitrobenzene) and in a sealed-tube at high temperature. In this study, the chlorination of 1-chloro naphthalene by $CuCl_2$ does not exist. In our study:

1. 1-chloro naphthalene is synthezed in non-solvent medium with high yield. The experiment temperature is chosen in the boiling point of naphthalene and 6 hours instead of 100° and 0.5 hour.

2. In the so-far known literature no chlorination of 1-chloro naphthalene by $CuCl_2$ has been encountered. In this study, 1,4-dichloro naphthalene is obtained with very high yield. This reaction is easier to do than the chlorination of 1-chloro naphthalene by chlorine.

As a result, the method of chlorination of aromatic compounds has been developed. 1,4-dichloro naphthalene is synthezed by the new method. In additon, the reaction of chlorination of naphthalene by $CuCl_2$ that was not realized by Ware and Borchert is realized.

Results of analyses:

For the product of first experiment,

m.p.	Lit. -2,3°C	Found. -2,4°C
d_4^{20}	Lit. -1,1938	Found. 1,1931
n_D	Lit. -1,6326	Found. 1,6327

For the product of second experiment,

m.p.	Lit. 68°C	Found. 68°C

Enclosed find IR spectrum.

5. REFERENCES

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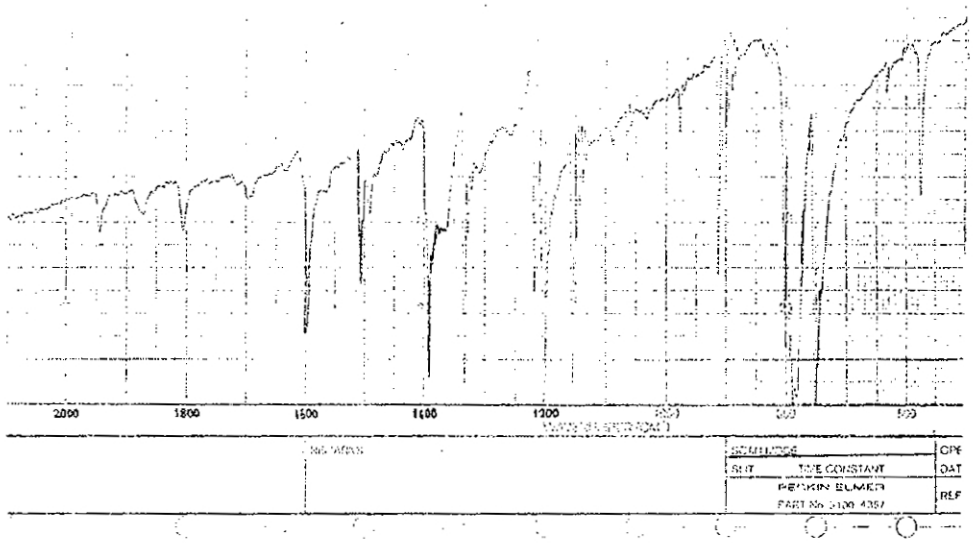

IR spectrum of the product of second experiment.