PREPARATION OF FLUOROPHENOLS BY HYDROLYSIS OF FLUOROHALOBENZENES

1961

SovietRxiv

Abstract

Full Text

CHEMISTRY

G. G. Yakobson, T. D. Rubina

and Corresponding Member of the Academy of Sciences of the USSR N. N. Vorozhtsov, Jr.

PREPARATION OF FLUOROPHENOLS BY HYDROLYSIS OF FLUOROHALOBENZENES

It was previously shown by us that, when fluorochlorobenzenes are treated with aqueous ammonia in the presence of copper compounds, only chlorine atoms are replaced by an amino group, with formation of the corresponding fluoroanilines, and an explanation was given for this direction of the reaction ([1]). We considered that an analogous dependence would also occur in the exchange of halogen atoms for a hydroxy group, i.e., in the hydrolysis of halobenzenes in the presence of copper compounds the ease of halogen exchange should increase with increasing atomic weight. Accordingly, it was to be expected that, in the catalytic hydrolysis of fluorohalobenzenes, the main reaction products would be fluorophenols, which would open a new route to the preparation of interesting compounds.

Weak bases were taken as hydrolyzing agents—aqueous solutions of alkali-metal fluorides and potassium acetate—since it is known that hydrolysis with caustic alkalis may be accompanied by isomerization of the reaction products ([2]). Hydrolysis of halogen derivatives with solutions of metal fluorides had not been described previously.

Experiments on the hydrolysis of fluoro-, chloro-, bromo-, and iodobenzenes with an aqueous solution of potassium fluoride in the presence of cuprous oxide showed that at 250° in 4 hours bromo- and iodobenzene are almost quantitatively converted into phenol. The degree of conversion of chlorobenzene under these conditions is low, while fluorobenzene practically does not enter into the reaction. Chlorobenzene is converted into phenol at an appreciable rate only at 300°. Hydrolysis of fluorobromobenzenes gave the corresponding fluorophenols. The results of the experiments are given in Table 1.

Replacement of potassium fluoride by an equivalent amount of sodium or cesium fluorides, potassium bifluoride, or potassium acetate has practically no effect on the yield and composition of the reaction products.

In the hydrolysis of *m*- and *p*-fluorobromobenzenes, 1–3% of the corresponding fluorodiphenyl ethers are formed as by-products. From *o*-fluorobromobenzene, 2–3% of diphenylenedioxide is obtained. The formation of these compounds was proved by the identity of their IR spectra and gas-liquid chromatograms with those of authentic substances. The acceleration of the reaction with increasing atomic weight of the halogen in catalytic hydrolysis makes it possible to assert that exchange of halogen for a hydroxy group in the presence of copper compounds, like the reaction of exchange of halogen for an amino group, proceeds through the intermediate formation of a complex of the type Ar—Hal · Cu^+, in which the copper cation is directly bonded to the halogen atom (^{1}).

By analogy with noncatalytic amination of fluorochlorobenzenes (^{3}), we expected that, in the hydrolysis of fluorohalobenzenes in the absence of copper compounds, the fluorine atom would prove to be the more labile. Indeed, upon heating *m*-fluorochlorobenzene with an aqueous solution of potassium acetate (300°, 6 hr), *m*-chlorophenol is formed. The change in the order of halogen lability during hydrolysis in the absence of catalysts is explained by the fact that the reaction proceeds by the usual bimolecular mechanism of nucleophilic substitution.

Table 1

No.	Starting compound	Reaction products: name	Yield, %	B.p., °C	M.p., °C	n_D ($t°$)	M.p. of phenoxyacetic acid
1	*o*-Fluorobromobenzene	*o*-Fluorophenol	73	73/50 mm	—	1.5118 (22°)	139°
2	*m*-Fluorobromobenzene	*m*-Fluorophenol	78	177	—	1.5075 (21°)	115°
3	*p*-Fluorobromobenzene	*p*-Fluorophenol	73	179	47	—	104.5°
4	2,4-Difluorobromobenzene	2,4-Difluorophenol	53	150	20	—	126°

Experimental Part

Into a rotating autoclave with a capacity of 200 ml are charged 0.04 g-mole of the halo derivative, 0.16 g-mole of sodium, potassium, or cesium fluoride, potassium bifluoride or potassium acetate, 100 ml of water, and 0.5 g of cupric oxide. After the holding period is completed, 10 g of caustic potash are added to the reaction mixture, and the unreacted starting material and diphenyl ethers are removed by steam distillation. The residue after steam distillation is acidified, the organic substances are extracted with ether (8–10 portions of 50 ml each) and dried over sodium sulfate. After removal of the ether, the phenol is isolated from the residue by distillation. The properties of the phenols and of the phenoxyacetic acids obtained from them correspond to the literature data (^{4}).

5.22 g (0.04 g-mole) of *m*-fluorochlorobenzene, 15.7 g (0.16 g-mole) of potassium acetate, and 120 ml of water are heated for 6 hours at 300°. By the method described above, 0.72 g of *m*-chlorophenol with b.p. 205–208° is isolated. A mixed melting-point test of the 2,4-dinitrophenyl derivative (m.p. 72°), obtained according to (5), gives no depression with the 2,4-dinitrophenyl derivative of authentic *m*-chlorophenol.

Novosibirsk Institute of Organic Chemistry
Siberian Branch
Academy of Sciences of the USSR

Received
22 IX 1961

References Cited

1. N. N. Vorozhtsov, Jr., G. G. Yakobson, T. D. Rubina, DAN, **127**, 1225 (1959).
2. A. Bottini, J. Roberts, *J. Am. Chem. Soc.*, **79**, 1458 (1957).
3. N. N. Vorozhtsov, Jr., G. G. Yakobson, T. D. Rubina, DAN, **134**, 821 (1960).
4. G. Finger, M. Gortatowski et al., *J. Am. Chem. Soc.*, **81**, 94 (1959).
5. N. N. Vorozhtsov, Jr., G. G. Yakobson, ZhOKh, **28**, 40 (1958).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.