Chemistry

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

1960

SovietRxiv

Abstract

Full Text

Chemistry

Corresponding Member of the Academy of Sciences of the USSR N. N. Vorozhtsov, Jr., G. G. Yakobson,
and T. D. Rubina

AMINATION OF POLYHALOGEN DERIVATIVES OF BENZENE

For reactions of aromatic halogen derivatives with nucleophilic agents that proceed by a bimolecular mechanism, the following order of mobility of the halogens has been established: F $>$ Cl Br (1). In the case of reactions of haloaryls with alkali-metal amides in liquid ammonia, proceeding with intermediate formation of dehydrobenzenes, the ease of exchange of halogens for an amino group is the opposite: F Cl $<$ Br (2). The same order of halogen mobility is also observed in the amination of aromatic halogen derivatives with aqueous ammonia in the presence of copper salts (3).

We believed that the interaction of halogenated aromatic compounds with aqueous ammonia and with alkali-metal amides in liquid ammonia may also proceed by a bimolecular mechanism. Under the action of metal amides this is possible in cases where dehydrobenzene derivatives cannot be formed. However, there is no direct evidence for such an assumption. Benkeser and Batting explain the absence of reaction between 2-bromo-3-methoxytoluene and sodium amide in liquid ammonia by the impossibility of forming the corresponding dehydrobenzene derivative (4). It seems to us that this result is due to the low mobility of bromine in nucleophilic-substitution reactions proceeding by a bimolecular mechanism, as well as to steric hindrance.

The exchange of halogens for an amino group under the action of aqueous ammonia on haloaryls with an unactivated halogen atom will proceed by the usual bimolecular mechanism in the absence of copper salts. Previously such a mechanism of exchange of a halogen atom for an amino group had been noted only for nitrohalobenzenes.

If these assumptions are correct, then under the action of both aminating agents the ease of exchange for an amino group of fluorine atoms will be greater than that of atoms of the other halogens. To test this assumption we studied

Table 1

Amination of hexahalobenzenes with potassium amide in liquid ammonia (10 min.)

No.	Starting compound	Split-off halogen atoms	Split-off halogen atoms	Split-off halogen atoms	Isolated from the reaction, % of charged product	Isolated from the reaction, % of charged product
No.	Starting compound	F	Cl	Br	amine	starting compound
1	C_6Cl_6	–	0.1	–	$C_6Cl_5NH_2$ 5	87
2	C_6Cl_5F	0.62	0.02	–	$C_6Cl_5NH_2$ 57	33
3	C_6Br_6	–	–	0.91	–	76
4	C_6Br_5F	0.16	–	0.82	–	65

the interaction of hexahalobenzenes with potassium amide in liquid ammonia and of a series of polyhalogen derivatives of benzene with aqueous ammonia in the absence of copper salts. The results of the experiments are given in Tables 1 and 2.

Table 2

Amination of polyhalobenzenes with aqueous ammonia

Starting compound	Reaction conditions, temp., °C	Reaction conditions, holding time, h	Halogen atoms split off, F	Halogen atoms split off, Cl	Halogen atoms split off, Br	Isolated from the reaction, based on charged product: amine	Isolated from the reaction, based on charged product: amount, %	Isolated from the reaction, based on charged product: starting compound, %
C_6Cl_6	200	1	–	0.13	–	$C_6Cl_5NH_2$	5	80
C_6Cl_5F	200	0.5	0.89	0.01	–	$C_6Cl_5NH_2$	79	3
C_6Cl_5F	200	1	1	0.03	–	$C_6Cl_5NH_2$	85	–
C_6Br_6	200	1	–	–	0.15	$C_6Br_5NH_2$	8	83

Starting compound	Reaction conditions, temp., °C	Reaction conditions, holding time, h	Halogen atoms split off, F	Halogen atoms split off, Cl	Halogen atoms split off, Br	Isolated from the reaction, based on charged product: amine	Isolated from the reaction, based on charged product: amount, %	Isolated from the reaction, based on charged product: starting compound, %
C_6Br_5F	200	1	0.79	–	0.09	$C_6Br_5NH_2$	65	15
m-C_6H_4ClF	250	6	0.41	0.06	–	m-$C_6H_4ClNH_2$	20	32

It is known that, on treating hexafluorobenzene with sodium amide in liquid ammonia at −70°, pentafluoroaniline is readily obtained (^{5}). The formation of pentachloroaniline has been observed upon heating hexachlorobenzene (1 h, 250°) with aqueous ammonia (^{6}).

When potassium amide was allowed to act on hexabromobenzene and fluoropentabromobenzene, it was not possible to isolate reaction products. Comparison of the amounts of bromine split off and of the returned unreacted bromo derivative indicates that, in the reaction, 3–4 bromine atoms are split off simultaneously.

The data obtained by us show that the fluorine atom is replaced by an amino group at a higher rate than chlorine and bromine atoms. This to some extent substantiates our assumption that the reactions we have studied proceed by the usual bimolecular mechanism.

Experimental Part

1. To a solution of potassium amide, prepared in the usual manner (^{2}) from 20 mmoles of metallic potassium and 100 ml of anhydrous liquid ammonia, 10 mmoles of finely powdered hexahalobenzene is added. The mixture is stirred for 10 min, 1.7 g of NH_4NO_3 is added, and the ammonia is evaporated. The residue is treated with ether and filtered. The residue insoluble in ether is dissolved in water and the amount of halides split off is determined. From the ethereal solution the solvent is distilled off; the residue is treated at 50–60° with conc. H_2SO_4, filtered from undissolved hexahalobenzene, and the amine is isolated by pouring the filtrate into water.

Table 3

Name	Formula	M.p., °C*	Results of analysis, %, found: nitrogen	Results of analysis, %, found: halogen	Results of analysis, %, calculated: nitrogen	Results of analysis, %, calculated: halogen
Pentachloroaniline	$C_6Cl_5NH_2$	232 (232)	5.195.20	67.267.2	5.29	66.8
Diacetyl derivative	$C_{10}H_6Cl_5NO_2$	143.5	4.044.08		4.01	
Pentabromoaniline	$C_6Br_5NH_2$	262 (262)	2.802.72	81.981.6	2.87	81.9
Diacetyl derivative	$C_{10}H_6Br_5NO_2$	192.5	2.492.58		2.45	

* The melting point according to (^{7}) is given in parentheses.

2. a) Into a rotating autoclave of 200 ml capacity are charged 20 mmoles of hexahalobenzene and 150 ml of 30% aqueous ammonia. After the holding period is completed, the mixture is filtered, and the amount of halides split off is determined in the filtrate. The precipitate is treated with H_2SO_4. Further treatment is as described above. b) 2.93 g of *m*-fluorochlorobenzene and 150 ml of 30% aqueous ammonia are heated for 6 hr at 250°. By the method described previously (^{3}), 0.82 g (29%) of *m*-chloroaniline is isolated, b.p. 142°/68 mm, $n_D^{16.5}$ 1.5945. A mixed sample of the acetyl derivative (m.p. 77.5°) gives no depression with the authentic product.

The diacetyl derivatives of polyhaloanilines are obtained by boiling 0.4 g of the amine for several minutes with 5 ml of acetic anhydride in the presence of 2–3 drops of H_2SO_4 (1.84). The mixture is poured into water and filtered. The products are recrystallized from alcohol. The properties of the products are given in Table 3.

Moscow Chemical-Technological Institute
named after D. I. Mendeleev

Received
25 VI 1960

REFERENCES

[1] J. Bunnet, R. Zahler, Chem. Rev., **49**, 273 (1951); L. van de Lande, Rec. trav. Chim., **51**, 98 (1932); M. Liveris, J. Miller, Chem. and Ind., **1957**, 954.

[2] F. Bergstrom, R. Wright, C. Chandler, W. Gilkey, J. Org. Chem., **1**, 170 (1936).

[3] N. N. Vorozhtsov, G. G. Yakobson, T. D. Rubina, DAN, **127**, 1225 (1959).
[4] R. Benkeser, W. Butting, J. Am. Chem. Soc., **74**, 3011 (1952).
[5] E. Forbes, R. Richardson, J. Tatlow, Chem. and Ind., **1958**, 630.
[6] A. Rocklin, J. Org. Chem., **21**, 1478 (1956).
[7] F. K. Beilstein, Handb. d. org. Chem., **12**, Berlin, 1930, pp. 631, 669.