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THE ISOMERISATION OF SOME 2,4–DIHALOGENOBENZENE-DIAZONIUM COMPOUNDS

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ABSTRACT

In this study the isomerisation of some 2,4–dihalogeno benzenediazonium compounds was investigated and the isomerisation products were obtained. The halogenoanilines containing chlorine, bromine and iodine in their 2– and 4– positions were used as substrates. The diazotisation reactions were carried out in concentrated sulphuric acid. The nucleophiles used in Sandmeyer reaction were chloride, bromide and iodide. During the isomerisation reactions the chlorine and bromine in 4– position were found to give 1—2 and 1—3 shifts respectively. The structures of the products obtained were elucidate with their physical constants and with spectroscopic methods.

INTRODUCTION

The aromatic rearrengement reactions do not cover a large area, but they constitute an interesting place among the reactions of aromatic compounds. The rearrengement reactions take place in several ways. These follow acid catalysed, base catalysed, photochemical and radical mechanisms. The most common one among these is acid catalysed rearrengement reactions. In recent years there have been extensive studies upon the many new rearrengement reactions and mechanisms of known rearrengements.

The first example of acid catalysed isomerisation was Reverdin isomerisation.[1] The mechanism of this reaction first found in 1860 was englightened by Butler and Sanderson in 1972[3]. The Jacobsen reaction are the isomerisation of the ployalkyl, halogenated polyalkyl and polyhalogenobenzene sulphonic acids. The halogen shift at this reaction

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conditions was extensively investigated 3,4,5. The Friedel Crafts isomerisations of some halogenobenzenes and halogenotoluenes were investigated by G.A. Olah et al[3].

There were no isomerisation reactions of 2,4–dihalogenoanilines and anilines in general seen in the literature. The diazonium compounds also do not give aromatic rearrengement reactions.

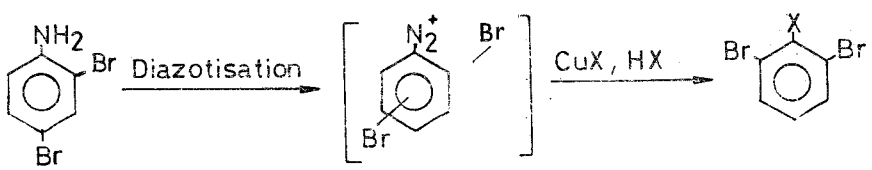
In the diazotisation reactions to obtain 1,2,4–trihalogeno benzenes from 2,4–dihalonego anilines with high yields, there observed isomerisation products as well. In the first experiments there was 1,2,3–tribromobenzene instead of 1,2,4–tribromo benzene obtained from 2,4–dibromoaniline.

In this study the isomerisation of all 2,4–dihalogenoanilines containing chlorine, bromine and iodine, through diazonium compounds was investigated and a number of unexpected products were obtained.

RESULTS AND DISCUSSION

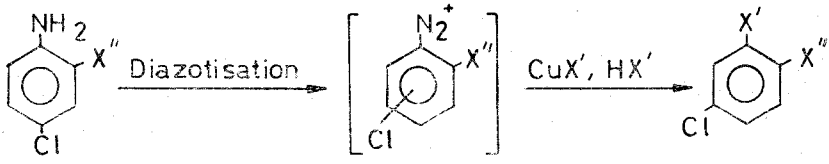
In this study 2,4–dichloroaniline, 2–bromo–4–chloroaniline, 2–iodo–4–chloroaniline and 2,4–dibromoaniline were used as substrates and isomerisation products were obtained. The products are tabulated in Table I. There were no single products isolated from the other substrates employed. These substrates gave isomer mixtures.

The diazotiazation and Sandmeyer reactions of three 2,4–dihalogenoanilines containing chlorine in 4–position gave products formed by the 1–2 shift of chlorine atom.



There is no record in the literature of 1–bromo–4–chloro–2–iodo benzen among the products listed in the table.

Only 2,4–dibromo aniline gave three izomerisation products among the 2,4–dihalogenoanilines containing bromine in 4– position. The products were formed by 1–3 shift of the bromine in 4– position.



The products formed by the reactions of the other dihalogeno anilines containing bromine in 4–position were obtained as mixtures. These mixtures were tried be chromatographically seperated. The NMR spectrums of the fractions obtained showed that these contained varying amounts 1,2,4–and 1,2,3–tribusstituted products.

The substrates containing iodine in 4–position gave the similar results. Finally the NMR spectra of the three fractions of the mixtiure, formed by the diazotisation and Sandmeyer reaction of 2,4–diiodo aniline, obtained by column chromatography indicated that the first fraction consisted 1,2,4–triiodo benzene, while the second one was a mixture and the third one had a symmtrical structure.

In general the 1,2,4–structures of the substates is understood to change significantly in these reactions.

The solutions of dihalogeno anilines in acetic acid was mixed with concontrated sulphuric acid. These solutions were first kept cold for two hours than left at room temperature for a few weeks. Finally the anilines were recovered and controlled by NMR spectra. They were seen to be unchanged.

The isomerisation takes place by the conversion of amino group into diazonium group. Diazonium group is a strong electron withdrowing group. Similar to Jacobsen reaction form by the attachment of a sulfonium group to the ring.

During the isomerisation of the substrates used, chlorine and bromine were seen to make 1–2 and 1–3 shifts respectively. This is due to the difference in the electronegativities and the bulkiness of these two halogene atoms.

The fact that the reactions outlined in Table I give only one product show that these are of synthetic value. It is also possible to obtain two different products by starting from the same substrate but changing the diazotisation conditions. Another important point which must be taken into account is that in diazotisation of the com-

pounds which can give isomerisation reactions in sulphuric acid, there is a possibility that the yield will decrease by the increase in the side products. As the study to synthesise o-iodo nitrobenzene from o-nitroanilie was not succesful in a medium of concentrated sulphiric acid. But if the diazotisation is carried out in dilute acidic medium, o-idonitrobenzene is obtained with a good yield.

Table I

Substrate	Product	Yield %
2,4–Dichloroaniline	1,2,4–Trichlorobenzene	52
2,4–Dichloroaniline	1–Bromo–2,5–dichlorobenzene	56
2,4–Dichloroaniline	1,4–Dichloro–2–iodobenzene	49
2–Bromo–4–chloroaniline	1–Bromo–2,4–dichlorobenzene	59
2–Bromo–4–chloroaniline	1,2,–Dibromo–4–chlorobenzene	61
2–Bromo–4–chloroaniline	1–Bromo–4–chloro–2–iodobenzene	52
2–iodo–4–chloroaniline	1,5–Dichloro–2–iodobenzene	57
2–iodo–4–chloroaniline	2–Bromo–4–chloro–1–iodobenzene	54
2–iodo–4–chloroaniline	1–Chloro–3,4–diodobenzene	65
2,4–Dibromoaniline	1,3–Dibromo–2–chlorobenzene	53
2,4–Dibromoaniline	1,2,3–triboromobenzene	66
2,4–Dibromoaniline	1,3–Dibromo–2–iodobenzene	63

EXPERIMENTAL

All the substrates used in this study were obtained by the methods or the modification of the methods given in the literature starting from aniline or acetanilide. The structures of the products obtained were investigated by NMR spectra. The NMR spectra were recorded with a Varian CFT–20 spectrometer at 20 MHz for ^{13}C and 80 MHz for ^{1}H. The melting points were determined by using Electrothermal capillary melting point apparatus without being subjected to further correction.

The substrates used in this study were; 2,4–dichloroaniline, 2–bromo–4–chloroaniline, 2–iodo–4–chloroaniline, 2–Chloro–4–bromo- aniline 2,4–dibromoaniline, 2–iodo–4–bromoaniline, 2–choro–4–iodoaniline, 2–bromo–4–iodoaniline and 2,4–diiodoaniline.

General Procedure: A 250 ml flask is immersed upto its half into a bath cooled down 0 °C. Then 50 ml of concentrated sulphuric acid (d: 1,84) is put in it and cooled stirring with a mechanical stirrer. 4 g (0,058 mole) finely powdered sodium nitrite is added to the acid in small portions Durîng this addition there should be no nitrogen dioxide evolution.

After this addition a clear solution is obtained. The solution is then cooled down to —10 °C. On the side 0,05 mole 2,4–dihalogenoaniline is dissolved in 40–60 ml acetic acid. This solution is slowly added to the diazotisation solution. The temperature should never exceed 0 °C during this addition. The addition is completed in thirty minutes and continued for twenty minutes.

For Sandmeyer reaction 40 ml concentrated hydrochloric acid (d: 1.19) and 5 g (0,05 mole) copper (I) chloride were put in a 400 ml beaker and heated tiil it gives a clear solution. If the solution is coloured, it is removed by adding a small quantily of copper bronze and cooled down to room temperature. The diazonium solution is rapidly poured into this solution by vigorous stirring. It is kept for two hours until the nitrogen evolution have been ceased. It is then heated for 15–20 minutes over a water bath at 80 °C. This homogenous mixture is finally poured in a 250–300 ml iced water by vigorous stirring. The precipitate is filtered off, washed with 50 ml staturated sodium carbonate sloution and cold water and thoroughly sucket off. The raw product is dissolved in 40–50 ml ethyl alcohol, filtered and left for crystalisation. Crystals are filtered of and dried in air.

For replacing diazonium group with bromine and iodine, the cold solutions of 14,2 g (0,005 mole) coopper (I) bromide and 80 ml hydrobromic acid (d:1.49) and 10 g (0.06 molde) potassium iodite in 30 ml water were used respectively.

Products obtained with above procedure: 1,2,4–trichlorobenzene; 4,72 g, bp. 208–211 °C (lit. 213,5 °C), 1–bromo–2,5–dichlorobenzene; needles from ethanol, 639, g mp. 35 °C (lit. 35 °C), 1,4–dichloro–2–iodobenzene; needles from ethanol, 6,69 g, mp. 20–21 °C (lit 21 °C), 1–bromo–2,4–dichlorobenzene; needles from from ethanol, 6,67, mp. 25 °C (lit. 25 °C), 1,2–dibromo–4–chlorobenzene; needles from ethanol, 8,250, mp. 35 °C (lit. 35 °C), 1–bromo–4–chloro–2–idobenzene; prisms from ethanol, 8,26 g, mp. 36–37 °C, 1, 4–dichloro–2–iodobenzene: 7,7 g, bp. 258–60 °C (lit. 262 °C), 2–bromo–4–chloro–1–iodobenzene; needles from ethanol, 8,58 g, mp. 33–34 (lit. 33 °C), 1–chloro–3,4–diodobenzene; needles from ethanol, 11,8 g. mp. 490 °C (lit. 39,5 °C), 1,3–dibromo–2–chlorobenzene; plates from ethanol, 7,46 g, mp. 69–70 °C (lit. 70 °C), 1,2,3–tribromobenzene; plates from ethanol, 10,58 g, mp. 89 °C (87,9 °C) and 1,3–dibromo–2–iodo benzene; plates from ethanol, 11,42 g, mp. 98–99 °C (lit. 99,8 °C).

REFERENCES

F. REVERDIN, Ber., 29 (1896) 997, 2595.

A.R. BUTLER and A.P. SANDERSON, J. Chem. Soc., Perkin Trans. II, 989 (1972)

L.I. SMITH, Org. Reactions, Vol. I (1942) p. 370.

H. SUZUKI, Bull. Chem. Soc. Japan, 36 (1968) 1642.

H. SUZUKI, T. SUGIYAMA and R. GOTO, Bull. Chem. Soc. Japan, 37 (1964) 1858.

G.A. OLAH, W.S. TOLGYESI and R.E.A. DREAR, J. Org. Chem., 27 3455 (1962).