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THE REACTIONS OF TRICHLORO-AND TRIBROMOBENZENES WITH HYDROXIDE ION AND PREPARATION OF DIHALOPHENOLS

A. ÖKTEMER and M. GÜLLÜ

Chemistry Department, Faculty of Science, University of Ankara, Turkey

ABSTRACT

Trichloro and tribromobenzenes form dichloro-and dibromophenols with excess KOH in DMSO and water. The reactions are of bimolecular addition-elimination S_N Ar type where a hydroxide ion displaces a halogen atom. Due to the deactivation effect of hydroxide group, bound to the ring, no other hydroxide displacement was observed.

INTRODUCTION

There are many studies on the reactions of aryl halides with various nucleophiles. The general conclusion drawn in these studies is that trichlorobenzenes easily give S_NAr reactions with strong nucleophiles, in activating solvents (especially in HMPA). Testaferri et al. (1983) Observed that di-, tri-, and tetrachlorobenzenes give anisols in HMPA with methoxide with very good yields and at excess methoxide concentrations, anisols are converted into phenols, in addition to another type of substitution similar to studies of Shaw et al, (1976) upon the reactions of dichlorobenzenes with methoxide in HMPA. Furthermore polychlorobenzenes were found to give polyalkylthiobenzenes with excess thiolate ions in HMPA (Testaferri et al., 1980), Since alkyl thio group facilitates further substitution, all the chloro atoms are displaced with thiolat anion, Huismann and Smith (1955) found that 1,2,4-trichlorobenzene can only form 2,5-dichlorophenol with hydroxide in methanol at high temperature and pressures and in poor yields, 1,3,5-Tribromobenzenes were found to give aromatic nucleophilic substitution reaction with methoxide (McKillop, 1974). There are no studies in the literature about the reactions of tribromobenzenes with hydroxide ion.

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RESULTS AND DISCUSSION

We observed that trichloro-and tribromobenzenes gave dichloro, and dibromophenols with hydroxide ion in DMSO and water mixture (Figure–1). The reactions were carried out in pure DMSO initially. Product yields however were very poor due to the insolubility of KOH in DMSO. A heterogenous phase formed by the rKOH solution in veyr little water and DMSO in which the organic substrate had been solved, was found to give the most satisfactory results. The yields tend to decrease when the amount of water in the mixture is increased. The possibility of a further substitution in presence of excess KOH is eliminated due to deactivating effect of phenolete. In this study, we observed that although the yields are poor tribromobenzenes react with hydroxide anion.

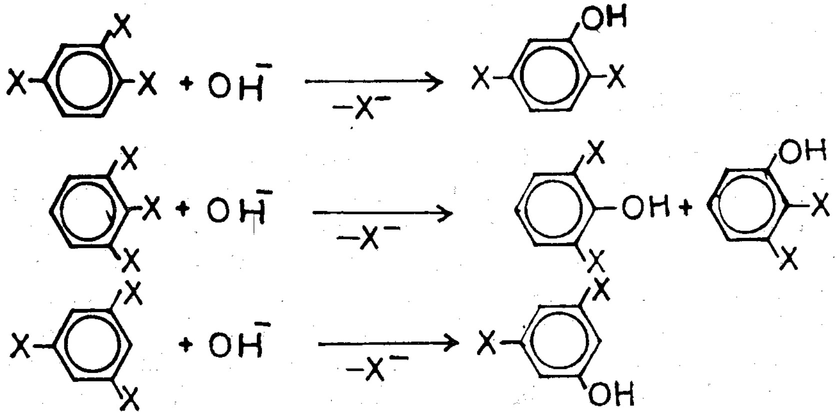

Figure 1. The reactions of trihalobenzenes with hydroxide ion.

Table, 1 shows the yields for the reaction of trichlorobenzenes. 1,2,4-Trichlorobenzene gave 2,5-dichlorophenol with highest yield. 1,2,3-Trichlorobenze was found to give two different isomers by the displacement of two different chloro atoms. All the experiments were carried out with excess KOH. No further reaction with hydroxide ion was observed even at high temperatures and prolonged reaction periods. The reaction of tribromobenzenes with hydroxide ion gave dibromophenols except 1,2,3-tribromobenzene. Table–2 shows the results obtained for tribomobenzenes.

Table 1. The products and the yields obtaine by refluxing trichlorobenzenes (0,01 mol) with excess KOH (0,05 mol) amixture of DMSO and water (25:5 v/v) at 110 °C for 24 hours

Substrate	Products	Yields
1,2,4-Trichloro	2,5-Dichlorophenol	% 61.0
1,3,5-Trichloro	3,5-Dichlorophenol	% 56,0
1,2,3-Trichloro	2,3-Dichlorophenol	% 30.7.
	2,6-Dichlorophenol	% 24.5

Table 2. The products and yields obtained by refluxing tribromo benzenes (0,01 mol) with excess KOH (0,05 mol) in amixture of DMSO and water (35:5 v/v) at 140 °C for 28 hours

Substrate	Products	Yields
1,2,4-Tribromo	2,5-Dibromophenol	% 30.0
1,3,5-Triblromo	3,5-Dibromophenol	% 24.0
1,2,3-Triblromo	None	

Aromatic S_N mechanism has been the subject of many investigations (Bunnet, 1951 and Miller, 1968) In our study dichloro- and dibromophenols were obtained by the displacement reaction of one halogen with hydroxide group. There is no specific preference of the location of the halogenes to be displaced. In 1,2,4-isomer the halogen in 2-position is displaced due to the inductive and conjugative effects of other halogen atoms. Therese results clearly show that reactions occurs through addition-elemination mechanism.

EXPERIMENTAL

The experiments were carried out by using commercial DMSO and tricholorobenzenes without being subjected to any further purification. Tribromobenzenes were synthesised by various ways. 1,3,5-Tribromobenzene was prepared by the deamination reaction of 2,4,6-tribromoaniline 1,2,4-Tribromobenzene was synthesised by the diazotization and Sandmeyer reaction of 2,4-dibromoaniline (Moodine, 1976) and 1,2,3-tribromobenzene was obtained by the isomerisation reaction during diazotization of 2,4-dibromoaniline (A.Öktemer, 1980). Dichloro- and dibromo phenols were recrystalised with petroleum ether and cyclohexane respectively. The products of 1,2,3-trichlorobenzene, 2,3- and 2,6-dichloro phenols were seperated and purified by column chromatography on silica gel using a mixture of petroleum and ethyl ether

(85:15) as eluent. The products had been previously identified by comparing their phsical properties with those in the literature.

General Procedure: KOH (0,05 mol) was dissolved in 5 ml of water in a two necked flask. Then one of the the trichloro- or tribromobenzene (0,01 mol) and DMSO (25 ml for trichlorobenzenes and 35 ml for tribromobenzenes) were added in it. The mixture was refluxed by vigorous stirring at 110 °C for 24 hours for trichlorobenzenes and at 140 °C for 28 hours for tribromobenzenes. The mixture was cooled down and at the end of the reaction content of the flask was poured into the water. The organic phase was extracted with ether. The aqueous phase was acidified with HCl and the phenols were extracted with ether. The ether phase was washed with water in order to remove DMSO. Ether was dried over Na_2SO_4. When the ether was evcporated, the phenols had seperated as an oily mass.

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