

AROMATIC $S_{RN}1$ REACTIONS IN AQUEOUS TERTIARY BUTYL ALCOHOL

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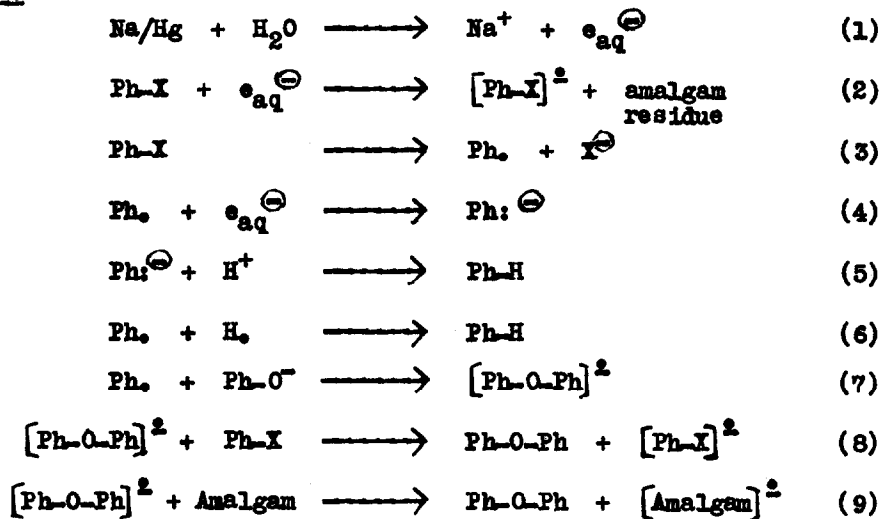
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Simple halobenzenes do not undergo aromatic nucleophilic substitution reactions, except under benzyne conditions². However, recently Bunnett and his coworkers³ have successfully carried out many nucleophilic substitution reactions on simple halobenzenes, under stimulation either by ammoniated electrons or light. These reactions, according to them, proceed via $S_{RN}1$ mechanism^{3a}. The present paper deals with nucleophilic substitution reactions on halobenzenes in aqueous solvents stimulated by hydrated electrons.

Bunnett³ and his coworkers used ammoniated electrons for nucleophilic substitution reactions in liquid ammonia solvent. Because of the inherent drawbacks in using liquid ammonia, such as its high volatility and unpleasant smell, it would be attractive to use solvents different from liquid ammonia. We report here that 50% v/v aqueous tertiary butyl alcohol is a good solvent for $S_{RN}1$ reactions, phenoxide ion is a suitable anion and that sodium amalgam is a suitable source of electrons. Sodium amalgam dissolves in water to produce hydrated electrons⁴, and these electrons provoke the formation of aryl radicals from the halobenzenes.

Details on a number of reactions are given in Table 1. The products obtained are benzene and diphenyl ether along with unreacted phenol, which is always present in excess. The yields are by glpc and the products are characterized by mp, ir and glpc retention times with known samples. In spite of assiduous search no hydroxy biphenyls were observed.

We sketch scheme 1 to explain the formation of the products. This in its general sense is a $S_{RN}1$ pathway.

SCHEME 1 :

Sodium amalgam is necessary for provoking the reaction as is suggested by run 6. Halide ions are released, according to this scheme, which are identified qualitatively and also quantified by potentiometric titrations (Run 8). Oxygen inhibits the reaction, as is shown in run 7. For the formation of benzene, equations 4 and 5 are more likely than 6 in the solvent under investigation. The order of reactivity qualitatively follows $\text{I} > \text{Br} > \text{Cl}$, as indicated by the deposition of mercury at the bottom of the flask (see table 1). Similar reactivity order was earlier reported by Bunnett³.

With chlorobenzene as the substrate, benzene is formed predominantly whereas with iodobenzene, diphenylether is the major product. This is explained as follows: In the case of the least reactive chlorobenzene, once the aryl radicals are formed, there is enough time left out for them to react on the sodium amalgam surface wherein there will be a higher concentration of electrons (equation 4). In the case of iodobenzene, the reaction is fast and therefore the aryl radicals, once formed, escape in to the open solution wherein there is excess concentration of phenoxide ion (equation 7). So with chlorobenzene, equation 4 predominates over equation 7 and with iodobenzene the reverse is true.

TABLE 1 : Reactions of halobenzenes with phenoxide ion in 50/50 v/v water-t-butyl alcohol stimulated by sodium amalgam

Run	Substrate	Substrate concn.(M)	Phenoxide concn.(M)	NaOH ^{a,b} (M)	Time (minutes)	Results product, yields ^c
1.	Ph - Br	0.0950	0.2860	0.0933	90	Ph-O-Ph (67); Ph-H ^d
2.	Ph - I	0.1346	0.4027	0.1343	70	Ph-O-Ph; Ph-H ^d
3.	Ph - I	0.0898	0.2691	0.1789	30	Ph-O-Ph (55.7); Ph-H (44.3)
4.	Ph - Br	0.0950	0.2860	0.0933	45	Ph-O-Ph (51.6); Ph-H (48.4)
5.	Ph - Cl	0.0976	0.2919	0.1853	90	Ph-O-Ph (19.8); Ph-H (80.2)
6.	Ph - Cl ^e	0.0976	0.2919	0.1853	120	Ph-Cl
7.	Ph - Cl ^f	0.1169	0.3508	0.2340	120	Ph-Cl
8.	Ph - Cl ^g	0.1169	0.3508	0.2340	100	...

a - sodium hydroxide remaining after neutralisation.

b - solvent is 100 ml of 50/50 v/v water-t-butyl alcohol unless otherwise mentioned.

c - the products are identified by glpc and the percentage are by glpc unless otherwise stated.

d - biphenyl is used as an internal standard.

e - percentage is not determined. products are identified in glpc. yields in run 1 are by isolation.

f - reaction is carried out in the absence of Na/Hg and the substrate is recovered back quantitatively.

g - reaction is carried out in the presence of oxygen and the substrate is recovered back.

h - the liberated chloride ion is estimated potentiometrically.

This is the first paper, to our knowledge, which describe hydrated electrons being employed in aromatic nucleophilic substitution reactions and also wherein transient radical anions are proposed as intermediates in aqueous tertiary butyl alcohol solvent system. Further research is in progress with other phenoxide and naphthoxide ions.

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