

Homolytic Arylation By Polyhalogenoaromatic Radicals The 2,3,4,5,6-Pentabromophenyl Radical

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Summary: 2,3,4,5,6-Pentabromobiphenyl has been prepared by the decomposition of pentabromoaniline by pentyl nitrite in benzene at 80°, and by the Ullmann reaction between iodobenzene, pentabromiodobenzene and copper powder. The yield of the biaryl formed from the homolytic arylation of benzene decreases as *o*-bromoaniline, 2,4,5-tribromoaniline, or pentabromoaniline is the source of the attacking radical. This decrease is paralleled by an increase in the yield of the benzene derivative arising from the formal protodeamination of the parent aniline derivative.

Pentabromophenylation by homolytic aromatic substitution has not been reported. The ready formation of pentafluorophenyl radical by the reaction of pentafluoroaniline and pentyl nitrite², by the thermolysis of bis(pentafluorobenzoyl) peroxide³⁻⁵, 2,3,4,5,6-pentafluorophenylazotriphenylmethane⁶, or of pentafluorobenzenesulphonyl chloride⁷, as well as by the photolysis of iodopentafluorobenzene⁸, allowed a considerable extension of fluorocarbon chemistry, and particularly contributed an understanding of the effect of five fluorine substituents upon the rate and orientation of homolytic phenylation⁹. The extension of this field to pentachlorophenylation considerably complicated the experimental aspects of the work and introduced two new factors¹. The first was protodiazotiation, in which the formation of pentachlorobenzene accompanied that of 2,3,4,5,6-pentachlorobiphenyl in the decomposition of pentachloroaniline by pentyl nitrite in benzene. This appeared to result from a competition between two processes in which the ease of formation of the biaryl is rather more sensitive to increased extent of chlorine substitution than is the formation of pentachlorobenzene.

The second novelty was the identification of hexachlorobenzene. This was held to arise from heterolytic attack by chloride ion upon pentachlorophenyldiazonium ions or their mechanistic equivalent.

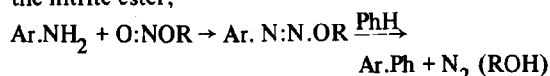
In view of the sensitivity of these competing processes to the degree of halogen substitution, and the steric and electronic consequences of replacing chlorine by bromine, we have studied the pentabromophenylation of benzene, using pentabromoaniline and pentyl nitrite, and have compared our findings with the results of pentachlorophenylation,

as well as with the corresponding arylation by 2,4,5-tribromoaniline and by *o*-bromoaniline.

Discussion

Table 1 summarises the yields of identified organic products from the reactions of pentyl nitrite (0.01 mole) and three aromatic primary amines (0.01 mole each) in benzene (100 cm³) at 80° for two hours.

The mechanism of the formation of aryl radicals under these conditions is generally^{9,10} held to involve the homolysis of a diazo ester, such as (I), obtained by the condensation of the amine with the nitrite ester;



Under these reaction conditions, none of the aromatic amines underwent quantitative conversion to (I). This suggested that thermolysis of pentyl nitrite was an important and competing side reaction in the preparation of (I); and, because both 2,4,6-tribromoaniline and pentabromoaniline were less readily attacked than *o*-bromoaniline, the relative reactivities of the primary amines may arise from steric effects around nucleophilic nitrogen.

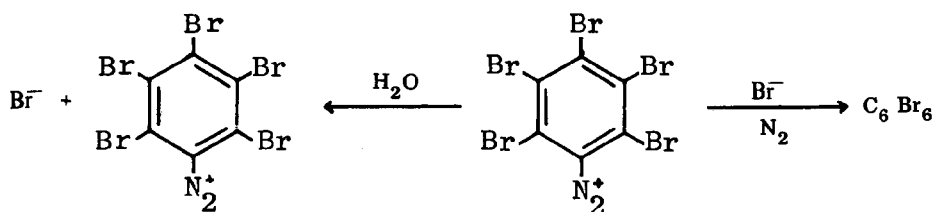
Of the amines which was attacked, about 80% was converted into identifiable reaction product; azo dyes and phenolic materials were also evident and suggested the formation of a diazonium ionic species, ArN₂⁺. This ionic compound also allowed an explanation of the formation of hexabromobenzene from pentabromoaniline. This type of reaction (Ar.NH₂ → Ar.Br) only occurred when pentabromoaniline, and not the less fully brominated amines,

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Table 1. Organic products from homoytic arylation of benzene.

Aromatic amine	Moles amine (ArNH ₂) consumed	Moles biaryls (ArPH) formed	Moles arene (ArH) formed
<i>o</i> -Bromoaniline	0.0076	0.0042 (55%)	0.0016 (21%)
2,4,6-Tribromoaniline	0.0054	0.0026 (48%)	0.0016 (30%)
Pentabromoaniline	0.0058	0.0009 (16%)	0.0017 (29%)

In addition, pentabromoaniline gave hexabromobenzene (0.0021 moles, 36%)



was used; its analogue (Ar.NH₂ → Ar.Cl) has also been identified in the corresponding reactions of pentachloroaniline. Bromide ion was detected among the inorganic products of the pentabromophenylation process, and we suggest an origin and reaction of this ion entirely similar to that of chloride ion in the earlier work:

It should also be noted that, in both cases, the nucleophilic attack to form bromide ion need not necessarily involve a diazonium ionic species. The azo-linkage itself (-N:N-), like the nitroso group (-N:O), is an effective activating substituent to heterolytic nucleophilic displacement of halogen at sites *ortho*- and *para*- to it in the benzene ring¹¹; although not as potent as the diazonium group (-N₂⁺) in this respect, it is still necessary allow that activation from the azo group in (I) may be sufficient to cause the nucleophilic displacement of bromine in a pentabromophenyl fragment.

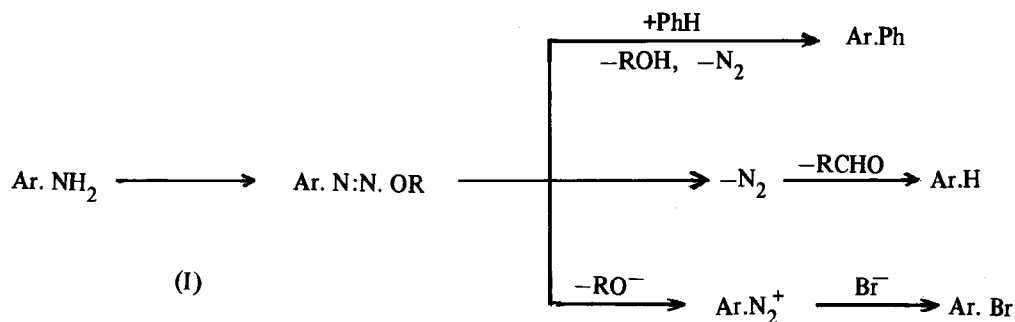
The greater susceptibility of the pentabromophenyl system towards such displacement strengthens our suggestion of a heterolytic mechanism. Homolytic processes, such as the abstraction of bromine by aryl radicals, appear to be less likely because of the absence of detectable amounts (<<1%) of the analogous bromo-compounds (1, 2, 3, 5-tetrabromobenzene and

o-dibromobenzene) in the reactions of 2, 4, 6-tribromoaniline or of *o*-bromoaniline.

The relative amounts of the products of protodiazonation (Ar.NH₂ → Ar.H) are similar, but the extent of biaryl formation (Ar.NH₂ → Ar.Ph) falls sharply in the case of pentabromophenylation, where the competing halide ion attack is well marked. It therefore seems that both heterolytic and homolytic pathways are fast processes, the rate-determining stage being the formation of the diazo-ether (I) or its equivalent. Whether homolysis or heterolysis of the ether is preferred energetically is decided by a number of factors, not the least of which is the degree of polarisation of (I) brought about by the halogen substituent:

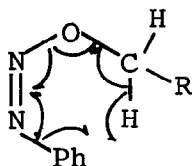
Any or all of these alternatives may be far more complex mechanistically than is implied in Scheme 1, and the incidence of side reactions such as the thermalolysis of pentyl nitrogen, may selectively assist some processes. However, we deduce that, if the internal hydrogen-abstraction shown in (II) is indeed the source of the arene, ArH, all processes in competition with it to give biaryl and bromoarene must proceed with similar velocities.

This rearrangement implies also the formation of the aldehyde formally derived from oxidation of



Scheme 1. Possible routes to the organic products from the reaction of aromatic amine and pentyl nitrite in benzene.

the pentyl alcohol system associated with the nitrite ester. However, thermolysis of pentyl nitrite gives the aldehyde; positive tests were obtained whether aniline derivatives were present or not, and we could find no conclusive evidence to support the suggestion.



II

Experimental

p-Nitroaniline gave 2,6-dibromo-4-nitroaniline which by reported methods gave 2,3,4,5,6-pentabromoaniline, m.p. 261-2° from toluene (lit., 262°)¹² Iodopentabromobenzene., m.p. 312-4° from chloroform (lit., 315-6°)¹³ was obtained through the diazotisation of pentabromoaniline in acetic acid by treatment with nitrosylsulphuric acid and the subsequent and slow addition of saturated aqueous potassium iodide.

In a typical reaction, pentabromoaniline (2.44 g; 0.005 mole) in benzene (200 cm³) was boiled under reflux while pentyl nitrite (2 cm³; excess) was added, for 2.5 hours. The cooled reaction mixture was first extracted with sulphuric acid (18M) to remove unreacted amine, which was recovered by dilution with water; the organic layer was washed with water, sodium hydroxide (10%) and again with water before drying (CaCl₂) and evaporation under reduced pressure. Three components were obtained upon chromatography on alumina. The two major

fractions were hexabromobenzene and pentabromobenzene, but a more soluble fraction which eluted close to pentabromobenzene yields a small amount of a material, m.p. 138° from ethanol. This species analysed as pentabromobiphenyl (Found; C, 26.4; H, 0.9%. C₁₂H₅Br₅ requires C, 26.2; H, 0.9%). The mass spectrum (VG Micromass 12B instrument) of this material showed peaks consistent with this structure (M/e, 544, 546, 548, 550, 552, 554; expected relative intensities 1:5:10:10:5:1), but the presence of hexabromobenzene impurity (M/e, 546, 548, 550, 552, 554, 556, 558; relative intensities 1:6:15:20:15:6:1), complicated and obscured the pentabromobiphenyl spectrum and limited its diagnostic use. Gas chromatography (Pye 104 instrument; OV-1 column) showed by the presence of small amounts of both penta- and hexa-bromobenzene in this material, together with a third and much larger peak which was ascribed to pentabromobiphenyl. The machine response, found to be the same for the two poly-bromobenzenes, was taken to be the same also for the biaryl; on this basis our sample was ca. 90% pure.

Authentic 2,3,4,5,6-pentabromobiphenyl was prepared by heating together iodobenzene (0.05 mole), pentabromoiodobenzene (0.05 mole) and activated copper bronze (0.25 mole) at 225° for thirty minutes. The crude material was shown by t.l.c. and by mass spectrometry to be mixture of pentabromobenzene and pentabromobiphenyl. Column chromatography gave a material, m.p. 128-131°, which still contained pentabromobenzene (Found: C, 25.4; H, 0.9%. C₁₂H₅Br₅ requires C, 26.2; H, 0.9%). The gas chromatogram confirmed the presence of pentabromobiphenyl as the major reaction product.

The corresponding reaction with 2,4,6-tribromoaniline gave a dark red oil which contained a number of components. Two of these showed identical retention times, upon gas chromatography, to those of 1,3,5-tribromobenzene and 2,4,6-tribromobiphenyl. An authentic sample of tribromobiphenyl was prepared¹⁴ by the Ullmann reaction between iodobenzene and 2,4,6-tribromobenzene (*M/e*, 338, 390, 392, 394; relative intensities 1:3:3:1).

Similarly, 2-bromobiphenyl was recognized as major product from *o*-bromoaniline, pentyl nitrite and benzene, and gas chromatography was used to estimate its relative amount using a pure sample as calibrant.

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