Benzenediazonium Ions: Structure, Complexation, and Reactivity

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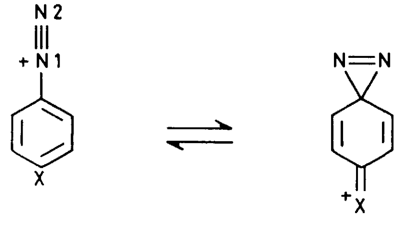
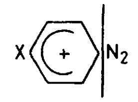
No evidence was obtained from ^{15}N n.m.r. spectroscopy for the scrambling of the nitrogens of benzenediazonium ions in solution or during coupling. The ^{15}N chemical shifts in acetonitrile solution are modified on complexation with a crown ether. The scope of crowns as phase-transfer catalysts for azo-coupling reactions has been examined.

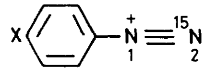
The possibility that valence tautomerism of a benzenediazonium ion (**1**) could give the spiro structure (**2**) is an attractive idea. Such a structure should be favoured most by X = MeO and least by X = NO_2. It should also result in the scrambling of the nitrogens at positions 1 and 2. There is good evidence in the literature from labelling experiments that such scrambling does occur, although the early analytical techniques used for the location of ^{15}N were, by necessity, rather elaborate. Insole and Lewis,[1] by use of mass spectroscopic analysis of the nitrogen evolved after reaction with azide, found evidence for nitrogen scrambling accompanying decomposition of benzenediazonium ions. Bose and Kugajevsky[2] used the nuclear spin–spin interaction between ^{15}N–^{1}H after coupling with ethyl acetoacetate and could not confirm the conclusions of Insole and Lewis.[1] However, Lewis and Kotcher[3] used the same n.m.r. technique and reaffirmed the previous conclusion. Swain *et al.*,[4] by use of mass spectroscopy after coupling to R salt, showed that, after 79% hydrolysis of a benzenediazonium ion in 1% sulphuric acid, the unchanged material had undergone 1.6% nitrogen rearrangement. They proposed a phenyl cation–dinitrogen pair (**3**), rather than (**2**), as the intermediate. Further evidence for nitrogen rearrangement during dediazoniation has come from a series of studies by Zollinger and his co-workers.[5–8] The use of solvents of low nucleophilicity, such as trifluoroethanol, increases the extent of rearrangement and values as high as 37% have been detected.[7] There is also evidence for incorporation of isotopically different dinitrogen, confirming the intermediacy of (**3**). There seems little doubt, in spite of the work of Bose and Kugajevsky,[2] that dediazoniation of a benzenediazonium ion is accompanied by nitrogen rearrangement. Now that ^{15}N n.m.r. spectroscopy is a routine analytical tool it seemed to be worth confirming directly the view expressed by Hegarty[9] that benzenediazonium ions, in the absence of a reactant, do not undergo nitrogen rearrangement and to offer an explanation for this situation.



(**1**) (**2**)



(**3**)

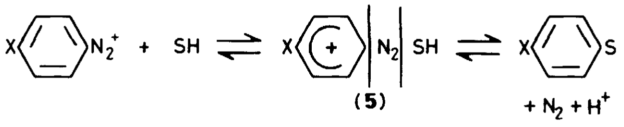


(**4**)

a; X = MeO
b; X = NO_2
c; X = SO_2OH

Results and Discussion

By the use of 98% ^{15}N-labelled sodium nitrite we prepared three labelled benzenediazonium tetrafluoroborates (**4a**—**c**). The classical shifts are displayed in Table 1. They are slightly different from those reported earlier,[10] which were taken at higher concentrations because of the use of natural-abundance ^{15}N n.m.r. spectroscopy. The acetonitrile solutions of (**4a** and **b**) were allowed to stand overnight at room temperature but this resulted in no change in the spectra. The chemical shifts of N(1) of both ions are *ca.* 25 p.p.m. but no peak in this region was observed with an accumulation time of 1 h. The use of isotopic labelling gave a sensitivity such that 1% rearrangement could have been detected. An aqueous solution of (**4a**) was allowed to stand for 4 days at 0 °C with no change in the ^{15}N spectrum. U.v. spectroscopy showed that, during that time, there had been little decomposition of the benzenediazonium ion. These experiments show that (**2**) makes no substantial contribution to the structure of a benzenediazonium ion. From *X*-ray crystallography[11] we know that, in the solid state, a benzenediazonium ion is essentially linear as in (**1**) and MO calculations[12] do suggest that (**2**) is a relatively high energy state. The absence of scrambling is, therefore, consistent with other data. We suggest that during dediazoniation nitrogen scrambling occurs within an addition complex (**5**) in equilibrium with reactants which may, or may not, go on to lose dinitrogen. The work of Zollinger[5–8] suggests that the second step is also an equilibrium.



SH = solvent (H_2O or CF_3CH_2OH)

Scheme.

When the pH of an acid solution of a benzenediazonium tetrafluoroborate is raised to 7.3 some triazene (**6**) (ArNH–N=N–Ar) is formed.[13] This could be the result of reaction of the diazonium ion with amine contaminating the sample from its preparation which becomes deprotonated, and therefore reactive, at the higher pH. Equally, the free amine could be the result of the reversal of diazotisation, see equation (1). Starting

$$ArN_2^+ + 2H_2O \rightleftharpoons ArNH_2 + HNO_2 + H^+ \quad (1)$$

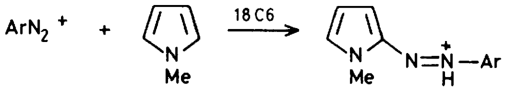
with N(2)-labelled (**4c**) in dilute acid, the spectrum resulting from an increase of pH to 7.3 by addition to a buffer contained a single peak corresponding to N(2) of unchanged (**4c**) and a new peak at +61.43 p.p.m., which is that expected for the central nitrogen of (**6**; Ar = $C_6H_4SO_3^-$).[14] From this it may be concluded first that, under the conditions of this experiment, diazotisation is not reversible (if it were, the peak at −66.86 p.p.m. would have disappeared completely) and the amine necessary for triazene formation must be a contaminant and, secondly, that no scrambling of N(1) and N(2) occurs on coupling. This is consistent with the recent work of Mitsuhashi *et al.*[15] The observation of triazene formation at pH values as low as 7 is significant in relation to any colorimetric procedure using benzenediazonium ions at high pH, *e.g.* the modified van den Bergh assay of bilirubin.[16] Unless the pH is kept low, or the absence of unchanged amine is certain, spurious results will be obtained.

Benzenediazonium ions may be solubilised in hydrophobic solvents by alkylammonium ions,[17] polyethylene glycol (PEG),[18] and 18-crown-6 (18C6).[19] In the latter the crown forms a collar around the diazo group and this complexation is known to retard the rate of reaction.[20,21] Complexation may also be detected by its effect on the chemical shifts of the nitrogens of benzenediazonium ions in organic solvents such as chloroform and dimethylformamide.[10,22] Similar changes were observed when 18C6 was added to an acetonitrile solution of (**4b**) (see Table 1). This suggests that the formation constant of the crown–diazo complex is much greater than that of the crown–acetonitrile complex, recently determined as *ca.* unity.[23] If this were not the case, then owing to the large excess of acetonitrile no crown–diazo complex would have formed. It seems probable that, in the case where the crown: diazonium ion concentration ratio is 20:1, complexation is complete and the change in chemical shift of N(2) of 3.3 p.p.m. is a maximum. With a deficit of 18C6 (see Table 1) the change in chemical shift was smaller, but there was still only one peak, indicating rapid exchange between free and complexed diazonium ion. On cooling to −35 °C a simple peak remained with no sign of broadening. Exchange is fast on the n.m.r. time scale even at this temperature.

Table 1. ^{15}N Chemical shifts of N(2) in substituted benzenediazonium ions in p.p.m. relative to nitromethane

0.05M (**4a**) in acetonitrile	−57.2
0.05M (**4b**) in acetonitrile	−65.2
0.05M (**4a**) in 0.10M-HCl	−57.9
0.11M (**4c**) in 0.10M-HCl	−66.9
0.05M (**4b**) and 1M 18C6 in acetonitrile	−62.9
0.10M (**4b**) and 0.05M 18C6 in acetonitrile	−64.5

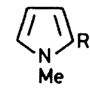
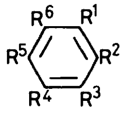
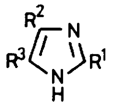
In a previous study[24] it was shown that dicyclohexyl-18-crown-6 is an excellent phase-transfer catalyst for the reaction of benzenediazonium ions with aromatic compounds. When a solution of, say, 1-methylpyrrole is added to a benzenediazonium salt, which remains as a suspension, no substantial reaction occurs. Addition of a catalytic amount of the crown, followed by stirring, resulted in coupling and precipitation of the product as its tetrafluoroborate in high yield (>90%) and analytically pure form, see equation (2). We explored the extent of this preparative procedure by examining a number of substrates with the results displayed in Table 2. The products were characterised by mass spectroscopy ($M^+ - BF_4$ in all cases) and the position of substitution taken from previous studies of electrophilic attack.



(2)

Reaction with 1-methylpyrrole occurs readily because of the ease of electrophilic attack and because the positive charge on the product can be delocalised onto the pyrrole ring. With thiophene, although electrophilic attack occurs readily,[25] no reaction under these experimental conditions was observed because the sulphur of the heterocyclic ring cannot readily

Table 2. Reaction of $XC_6H_4N_2BF_4$ with various substrates

Substrate	X	Reaction *t*/h	Product as BF_4^- salt
			
$R^1 = H$	NO_2	0.25	$R^1 = N{=}\overset{+}{N}HC_6H_4NO_2$
$R^1 = H$	MeO	0.25	$R^1 = N{=}\overset{+}{N}HC_6H_4OMe$
			
$R^1 = R^3 = R^5 = OMe, R^2 = R^4 = R^6 = H$	NO_2	1.0	$R^1 = R^3 = R^5 = OMe, R^2 = N{=}\overset{+}{N}HC_6H_4NO_2, R^4 = R_6 = H$
$R^1 = R^2 = R^3 = R^4 = R^6 = H, R^5 = Me_2N$	NO_2	0.25	$R^1 = R^3 = R^4 = R^6 = H, R^2 = N{=}\overset{+}{N}HC_6H_4NO_2, R^5 = Me_2N$
	MeO	1.0	$R^1 = R^3 = R^4 = R^6 = H, R^2 = N{=}\overset{+}{N}HC_6H_4OMe, R^5 = Me_2N$
$R^1 = R^2 = R^3 = R^4 = R^6 = H, R^5 = MeHN$	NO_2	0.25	$R^1 = R^3 = R^4 = R^5 = R^6 = H, R^2 = N(Me)N{=}\overset{+}{N}HC_6H_4NO_2$
	MeO	1.0	$R^1 = R^3 = R^4 = R^5 = R^6 = H, R^2 = N(Me)N{=}\overset{+}{N}HC_6H_4OMe$
$R^1 = R^2 = R^3 = R^4 = R^6 = H, R^5 = H_2N$	NO_2	0.25	$R^1 = R^3 = R^4 = R^5 = R^6 = H, R^2 = NH{-}N{=}\overset{+}{N}HC_6H_4NO_2$
			
$R^1 = R^2 = R^3 = H$	NO_2	1.0	$R^1 = N{=}\overset{+}{N}HC_6H_4NO_2, R^2 = R^3 = H$
$R^1 = H, R^2 = R^3 = Me$	NO_2	1.0	$R^1 = N{=}\overset{+}{N}HC_6H_4NO_2, R^2 = R^3 = Me$

accommodate the charge on the product. In contrast, 1,3,5-trimethoxybenzene does provide delocalisation and the reaction proceeds readily with 4-nitrobenzenediazonium tetrafluoroborate, but not with the 4-methoxy compound. Couplings to the nitrogens of aniline and *N*-methylaniline occur as readily as does coupling to carbon of *N*,*N*-dimethylaniline.[20] The use of a crown as a phase-transfer catalyst provides a method of preparing azoimidazoles[26] under non-acidic conditions, thus avoiding the problem of inactivation of the substrate by protonation. Further use of crowns in target syntheses will be described in subsequent publications.

Experimental

Benzenediazonium salts were prepared by the method of Starky.[27] For the labelled salts 98% [^{15}N]sodium nitrite (Cambrian Gases) was used. The phase-transfer procedure was that described previously except that the solvent was dichloromethane. The yield was essentially quantitative but the rate of reaction was found to depend upon the particle size of the benzenediazonium salt. Too short a reaction time resulted in contamination of the product with unreacted benzenediazonium tetrafluoroborate.

The n.m.r. spectra were run by Drs. Ian Sadler and David Reed of the S.E.R.C. high-field n.m.r. unit at the University of Edinburgh.

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