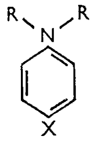
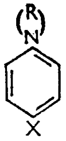
1151. *A New Preparation of Aryldiazonium Tetrafluoroborates*

By C. Sellers and H. Suschitzky

The preparation of some aryldiazonium tetrafluoroborates with tertiary-amine substituents by direct introduction of the diazonium group and by the Schiemann reaction is described. Thermal decomposition of the tetrafluoroborates yields *para*-derivatives of fluorobenzene.

Recent work by Tedder on the direct introduction of the diazonium group into aryl structures [1] prompted us to apply this method to the preparation of aryldiazonium tetrafluoroborates. As we required the *p*-fluoro-compounds of the aromatic amines (I; R = Me or Et, X = F) and (II; R = $[CH_2]_4$, $[CH_2]_5$, $[CH_2]_6$, $[CH_2]_2{\cdot}O{\cdot}[CH_2]_2$, X = F) for another research we made the intermediate diazonium tetrafluoroborates (I and II; R as above, X = $N_2^+BF_4^-$) by the conventional Schiemann reaction from the primary amine (I and II; R as above, X = NH_2) as well as by direct introduction of the diazonium group into the tertiary amines (I and II; R as above, X = H). The latter route appeared to be advantageous because it involves fewer steps and tertiary amines are reported [2] to respond in good yield to this procedure. Thus, we modified the diazotisation method by treating the requisite tertiary amine (I and II; R as above, X = H) with an aqueous solution of sodium nitrite, ethyl acetate, and tetrafluoroboric acid followed by addition of ether to precipitate the diazonium tetrafluoroborate. The results of the two preparations are set out in Table 1.


(I)


(II)

$p\text{-}Et_2N{\cdot}C_6H_4\text{-}C_6H_4{\cdot}Cl\text{-}p$

(III)

The authenticity of the diazonium tetrafluoroborates followed from their thermal decomposition which gave the corresponding fluoro-compounds (cf. Table 2). When the diethyldiazonium tetrafluoroborate (I; R = Et, X = $N_2^+BF_4^-$) was decomposed in chlorobenzene not only the expected fluoro-compound (I; R = Et, X = F) but also the diethylaminobiphenyl (III) was formed, undoubtedly by attack of the radical $Et_2N{\cdot}C_6H_4{\cdot}$ on the solvent.

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[1] J. M. Tedder, *J.*, **1957**, 4003, and subsequent Papers.
[2] H. P. Patel and J. M. Tedder, *J.*, **1963**, 4889.

TABLE 1

Yields of aryldiazonium tetrafluoroborates (p-$X{\cdot}C_6H_4N_2^+BF_4^-$) by direct introduction of the diazonium group (A) and by the Schiemann reaction (B)

p-$X{\cdot}C_6H_4{\cdot}N_2^+BF_4^-$ X	Method A Yield (%)	Method B Yield (%)
Me_2N	16	52
Et_2N	52	72
C_4H_8N	14	49
$C_5H_{10}N$	20	72
$C_6H_{12}N$	26	61
$\overline{CH_2{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}N}$	25	63

Although the Schiemann route involves more stages than the direct introduction of the diazonium group it is still preferable for the preparation of the p-substituted anilines (I and II; X = F) because of higher overall yields. The low yields in the latter procedure were found to be due to solubility of the diazonium compounds in the reaction medium. Yields could not, however, be improved by reducing the quantity of water as this was incompatible with maintaining the optimal pH for the reaction.

Attempts to introduce the diazonium group into the tertiary aromatic amines (I and II; X = H) with nitrosyl tetrafluoroborate ($NOBF_4$) failed, yielding only the tertiary amine tetrafluoroborates. Nor was a diazonium tetrafluoroborate produced by the action of this reagent on an ethereal solution of benzylideneaniline which was recently reported to give a diazonium salt with nitrogen tetroxide.[3] On working up the reaction mixture, aniline tetrafluoroborate and benzaldehyde were obtained.

EXPERIMENTAL

Diazonium Tetrafluoroborates.—(*a*) *By the Schiemann reaction.* The required amines were made by condensing p-chloronitrobenzene with piperidine, morpholine, pyrrolidine, or perhydroazepine followed by reduction of the nitro-compounds as previously described for the *ortho*-isomers.[4] p-*NN*-Diethyl- and -dimethyl-aniline were redistilled, commercial samples. The requisite amine was dissolved in the minimum amount of concentrated hyrochloric acid and diazotised at −5° with solid sodium nitrite with stirring and then treated with a saturated aqueous solution of sodium tetrafluoroborate. The reaction mixture was kept for 1 hr. at −5°, the diazonium tetrafluoroborate was filtered off, washed with ice-cold ether and dried *in vacuo*. For yields, see Table 1, method B.

(*b*) *By direct introduction of the diazonium group.* The required tertiary amines were made by adaptation of a literature method.[5] Dimethyl- and diethyl-aniline were redistilled, commercial samples.

In a typical experiment phenylpiperidine (4·2 g.) in ethyl acetate (200 ml.) was diazotised with sodium nitrite (27 g.) in water (80 ml.) at 0°. Then tetrafluoroboric acid (40%, 41 ml.) was added over 1 hr. and the mixture kept for 48 hr. at 5°. The ethyl acetate layer was separated from the aqueous layer and treated with ether to precipitate the diazonium borofluoride. Yields were slightly improved by extracting the aqueous layer with nitrobenzene which on addition of ether deposited a small, additional quantity of diazonium borofluoride. For yields see Table 1, method A.

Decomposition of Diazonium Tetrafluoroborates.—This was done by heating a mixture of the diazonium compound and dry sand.[6] The reaction mixture was made alkaline (aqueous solution of sodium hydroxide) and then steam-distilled and the product extracted from the distillate with chloroform. Purification of the fluoro-compounds obtained by driving off the solvent was by distillation or chromatography over silica with a mixture of ethanol in benzene (5% ethanol). p-Diethylaminobenzenediazonium tetrafluoroborate was also decomposed in boiling chlorobenzene and the steam distillate of the reaction mixture contained, apart from the fluorine compound, 4-*chloro*-4′-*diethylaminobiphenyl* (III) (14·3%), m. p. 116° (Found: C, 74·1; H, 7·1; N, 5·4. $C_{16}H_{18}ClN$ requires C, 73·9; H, 7·0; N, 5·4%). Its n.m.r. spectrum shows the aliphatic protons of the ethyl groups as a quartet at 6·41 τ (4 protons) and a triplet at 8·74 τ (6 protons).

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[3] R. M. Scribner, *J. Org. Chem.*, 1964, **29**, 3429.

[4] O. Meth-Cohn, R. K. Smalley, and H. Suschitzky, *J.*, 1963, 1666.

[5] J. F. Bunnett, T. K. Brotherton, and S. M. Williamson, *Org. Synth.*, 1960, **40**, 74.

[6] H. Suschitzky, *J.*, 1953, 3042.

The four aromatic protons of the Et_2N-substituted ring form an A_2X_2 system centred at 2·94 τ (two protons *ortho* to Et_2N) and 2·26 τ. The four protons in the chlorine-substituted ring form an A_2B_2 system at 2·21 τ.

Decomposition of the pyrrolidinediazonium tetrafluoroborate (II; R = $[CH_2]_4$, X = N_2BF_4) gave not only the fluoro-compound but also a small quantity of *p*-chlorophenylpyrrolidine, m. p. 83° (lit.,[7] 85°) (Found: C, 66·1; H, 6·7. Calc. for $C_{10}H_{12}ClN$: C, 66·1; H, 6·6%).

Details of the *fluorine compounds* are given in Table 2.

TABLE 2

Fluorine compounds *p*-X·C_6H_4F and their picrates

p-X·C_6H_4F X	M. p. (b. p./mm.)	Yield * (%)	Found (%) C	Found (%) H	Formula	Reqd. (%) C	Reqd. (%) H
Me_2N	33° †	15	—	—	—	—	—
picrate	151 ‡		—	—	—	—	—
Et_2N	42/0·2	17	—	—	—	—	—
picrate	149 §		—	—	—	—	—
C_4H_8N	122/13	22	73·0	7·2	$C_{10}H_{12}FN$	72·7	7·3
picrate	113		48·6	3·9	$C_{16}H_{15}FN_4O_7$	48·7	3·8
$C_5H_{10}N$	70/3	25	74·3	8·3	$C_{11}H_{14}FN$	73·8	7·9
picrate	149		50·2	4·0	$C_{16}H_{17}FN_4O_7$	50·2	4·2
$C_6H_{12}N$	126/3·7	15	75·0	8·0	$C_{12}H_{16}FN$	74·5	8·3
picrate	141		51·4	4·5	$C_{18}H_{19}FN_4O_7$	51·2	4·5
$CH_2{\cdot}CH_2{\cdot}O{\cdot}(CH_2)_2{\cdot}N$	53	16	66·7	6·7	$C_{10}H_{12}FNO$	66·35	6·7
picrate	175		47·1	3·5	$C_{16}H_{15}FN_4O_8$	46·8	3·7

* Based on parent amine. † Lit.,[8] m. p. 25°. ‡ Lit.,[8] m. p. 151·5°. § Lit.,[8] m. p. 150·5°.

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[7] G.P. 812,552/1951.

[8] G. Schiemann, *Ber.*, 1933, **66**, 727.