

# Electron Transfer Reactions in Organic Chemistry. XII.\* Reactions of 4-Substituted Triarylaminium Radical Cations with Nucleophiles; Polar vs. Electron Transfer Pathways

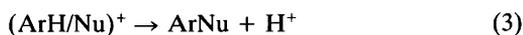
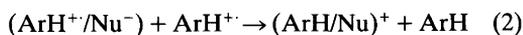
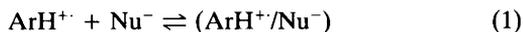
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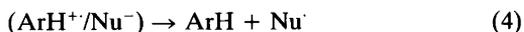
The reactions between tris(4-bromophenyl)aminium ion (TBPA<sup>+</sup>) and chloride, bromide, iodide and cyanide ion have been investigated. Chloride and cyanide ion reacted to give the product of substitution (in the 2-position), whereas bromide and iodide underwent ET oxidation with formation of tribromide and triiodide ion, respectively. A kinetic study gave results consistent with those obtained by other authors for reactions between (9,10-diphenylanthracene)<sup>+</sup> and the same nucleophiles, but not with those published for (perylene)<sup>+</sup>/nucleophile reactions.

The mechanisms by which nucleophiles react with aromatic radical cations have been extensively studied,<sup>1</sup> yet the statement “our knowledge of ion radical chemistry in homogeneous solution is far from complete”<sup>2</sup> is still valid in this particular area. The interaction between a nucleophile and a radical cation may proceed via a multiplicity of pathways designated the half-generation, complexation and disproportionation mechanisms.<sup>3</sup> Complicating factors are mechanism variation with concentration,<sup>4,5</sup> and complex formation between radical cation and parent molecule<sup>6,7</sup> or two radical cations.<sup>8</sup> For the reaction of an aromatic radical cation (ArH<sup>+</sup>) with a nucleophile (Nu<sup>-</sup>), the complexation mechanism [eqns. (1)–(3)] is often applicable.<sup>1a</sup>



Sometimes the radical cation may act as an oxidant toward the nucleophile, either in an outer-

sphere step<sup>9,10</sup> between ArH<sup>+</sup> and Nu<sup>-</sup> or in an inner-sphere step, e.g. via electron transfer within the complex of eqn. (1) [see eqn. (4)]. No



simple rules exist to predict the reaction mode and distinguish between the polar and electron transfer (ET) mechanisms. Attempts to apply the Dewar-Zimmerman rules,<sup>11</sup> thermochemical calculations,<sup>12,13</sup> nucleophilicity scales<sup>14</sup> and the configuration mixing (CM) model<sup>15</sup> for this purpose have been published, but so far these methods have had rather limited success and acceptance.<sup>1a</sup>

We have previously shown<sup>16</sup> that the tris(4-bromophenyl)aminium radical cation (TBPA<sup>+</sup>) reacts with acetate ion to give the 2-acetoxy derivative according to the polar mechanism, and not via an ET step as earlier suggested.<sup>17</sup> Depending on the reaction conditions, a competing debromodimerization process also took place, resulting in the formation of brominated derivatives of TBPA. These findings have led us to study further the properties of triarylaminium salts and their reactivity toward other nucleophiles such as

\*Part XI, see Ref. 45.

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chloride, bromide, iodide and cyanide ion. The proposed oxidation of cyanide ion by tris(4-methoxyphenyl)aminium ion ( $\text{TAA}^+$ )<sup>18</sup> is discussed, in view of the fact that the stronger oxidants  $\text{TBPA}^+$  ( $\Delta E_p > 0.5$  V) and tri(4-tolyl)aminium ion ( $\text{TTA}^+$ ,  $\Delta E_p = 0.3$  V) undergo substitution in the 2-position by cyanide ion.

## Results and discussion

*Triarylaminium salts – properties and stability.* Both the 4-substituent of the radical cation and the nature of the counter-ion influence the stability of these salts. With  $\text{TBPA}^+$  and tetrafluoroborate as the anion the salt changed during ageing and gave coupling products (via debromodimerization) from the radical cation. This was indicated by small but significant changes in the UV spectrum.<sup>16</sup> With hexafluorophosphate or hexachloroantimonate as the counter-ion these changes were not seen; only very slow reduction of the radical cation to the amine was detectable (Fig. 1). The hexachlorotungstate salt, prepared by oxidation of TBPA by tungsten hexachloride (a strong ET oxidant toward organic substrates),<sup>19</sup> was also stable over long periods in the solid state or in solution.

Addition of cyclohexene to a solution of  $\text{TBPA}^+$   $\text{SbCl}_6^-$  in acetonitrile led to the same changes in the UV spectrum as those attending the coupling process (Fig. 2). The same rate-accelerating effect of cyclohexene upon the dimerization reaction was seen with  $\text{BF}_4^-$  as the counter-ion,<sup>16</sup> with the difference that the

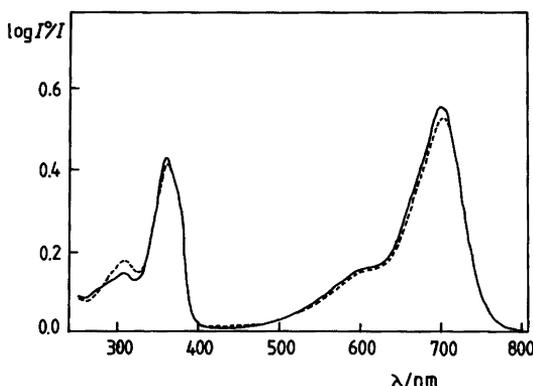


Fig. 1. UV/VIS spectra of solutions of  $\text{TBPA}^+$   $\text{PF}_6^-$  (0.20 mM) in acetonitrile. Solid curve, freshly prepared salt; broken curve, aged salt (1 month in the solid state).

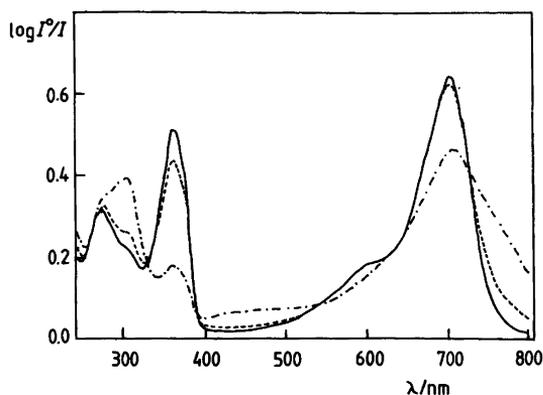


Fig. 2. UV/VIS spectra of solutions of  $\text{TBPA}^+$   $\text{SbCl}_6^-$  (5.0 mM) and cyclohexene (25 mM) in acetonitrile, diluted 25 times immediately before recording the spectrum. — Freshly prepared salt, ---- 1 h after the addition of cyclohexene, ..... 24 h after.

changes detected 24 h after the addition of cyclohexene to the  $\text{SbCl}_6^-$  salt were seen immediately after mixing in the case of tetrafluoroborate case.

The influence of the anion upon the stability of the radical cation salts is most likely dependent on the size and redox properties of the anion. Large anions, ion-paired with the radical cation, will prevent the two radical cations from coming close enough for coupling and they thereby increase the stability of the aminium salt. This was suggested on the basis of a study of the stability of  $\text{TTA}^+$ <sup>20</sup> as a function of the nature of the counter-ion ( $\text{ClO}_4^-$ ,  $\text{I}^-$  or  $\text{I}_3^-$ ). For  $\text{TBPA}^+$  it was shown that the perchlorate salt was far less stable than the hexachloroantimonate.<sup>21</sup> Thus, with the smaller anions  $\text{BF}_4^-$  and  $\text{ClO}_4^-$ ,  $\text{TBPA}^+$  couples to give dimers far more readily than with the larger ions  $\text{PF}_6^-$ ,  $\text{WCl}_6^-$  and  $\text{SbCl}_6^-$ . Another stabilizing factor for the latter two ions might be their oxidizing properties ( $E^\circ$  for both around 0.5 V vs NHE\*<sup>22</sup>).

With methoxy groups as 4-substituents ( $\text{TAA}^+$ ) the tetrafluoroborate salt was also stable. This is expected in view of the strongly stabilizing effect of methoxy groups upon radical cations, as reflected in a much lower  $E^\circ$  value (0.76 V)<sup>23</sup> for  $\text{TAA}^+/\text{TAA}$  than for  $\text{TBPA}^+/\text{TBPA}$  (1.30 V)<sup>23</sup> and a much higher chemical stability of  $\text{CH}_3(\text{Ph})(4\text{-MeOC}_6\text{H}_4)\text{N}^+$  than of

\*Normal hydrogen electrode; all potentials given in the following refer to this electrode unless otherwise stated.

Table 1. Products of the reaction between  $\text{TBPA}^+ \text{BF}_4^-$  and nucleophiles under different conditions of ageing and temperature (in acetonitrile, unless otherwise stated). Salt freshly prepared by the  $\text{Ag}^+/\text{I}_2$  method was used;  $[\text{TBPA}^+]/[\text{Bu}_4\text{N}^+\text{Nu}^-] = 0.5$ .

Reaction conditions		Nucleophile	Yield/% of recovered TBPA	Yield/% of TBPA derivative			
Ageing period/h	Temp./°C			2-Subst. <sup>a</sup>	<i>ipso</i> -Subst.	Brominated <sup>b</sup>	Dimer <sup>c</sup> (3a or 3b)
1	20	$\text{Cl}^-$ <sup>d</sup>	56	49 <sup>e</sup>	2		
1	20	$\text{Cl}^-$	45	43 <sup>e</sup>	2		
1	20	$\text{CN}^-$	49	54	Trace		
1	20	$\text{AcO}^-$	52	67 <sup>e</sup>			
1	20	$\text{Br}^-$	53				
1	20	$\text{I}^-$	56			1	
24	2-5	$\text{Cl}^-$	16			61	24
24	2-5	$\text{Cl}^-$	31			9	24
24	2-5	$\text{CN}^-$	48	21		7	
24	2-5	$\text{AcO}^-$ <sup>d</sup>	31	1		30	
24	2-5	$\text{Br}^-$	67				
24	2-5	$\text{I}^-$	26			7	31
24	2-5	$\text{I}^-$	46			11	25
1	2-5	$\text{Cl}^-$	48	42	1	6	
24	20	$\text{Cl}^-$	52	8	1	6	
1 (In $\text{CH}_2\text{Cl}_2$ )	2-5	$\text{Cl}^-$	43	28 <sup>e</sup>	2		
24 (In $\text{CH}_2\text{Cl}_2$ )	24	$\text{Cl}^-$	52	26 <sup>e</sup>	3		

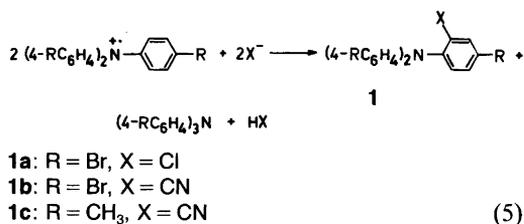
<sup>a</sup>Calculated for a two- and four-electron process for mono- and disubstituted TBPA, respectively. <sup>b</sup>Calculated with the assumption that 1 mol of bromine is required to substitute one position in TBPA. <sup>c</sup>Isolated yield. <sup>d</sup>Ref. 16. <sup>e</sup>Also disubstituted TBPA in 5-10% yield.

$\text{CH}_3(\text{Ph})_2\text{N}^+$ . The latter couples very rapidly to give a benzidine, whereas the former is stable as the radical cation.<sup>24</sup>

The tri(4-tolyl)aminium ion was reported to be unstable with  $\text{BF}_4^-$  as counter-ion but to give a stable salt with  $\text{SbCl}_6^-$ .<sup>25</sup> Interpreting this effect as being due to the size of the anion, we synthesized the corresponding  $\text{PF}_6^-$  salt, whose UV spectrum was in good agreement with published data.<sup>25,26</sup> This salt was relatively stable in the solid state; it underwent ageing at a rate that made the change from radical cation to amine detectable in the UV spectrum only after one week at room temperature.

**Product studies.** Having found that  $\text{TBPA}^+$  undergoes substitution by  $\text{RCOO}^-$  ( $\text{R} = \text{CH}_3, \text{C}_6\text{H}_{17}$ ),<sup>16</sup> i.e. reacts via a polar mechanism and not ET as earlier suggested,<sup>17</sup> we became interested in extending our studies to other nucleophiles and triarylaminium ions. We chose chloride, bromide, iodide and cyanide ion (with provisional<sup>27</sup>

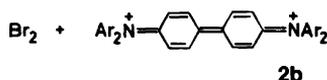
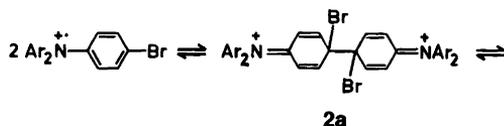
$E^\circ(\text{Nu}^+/\text{Nu}^-)$  of 2.1, 1.7, 1.2 and 1.6 V, respectively, in acetonitrile<sup>§</sup>)<sup>9,28</sup> for product and kinetic studies, with the intention of determining which factors influence the competition between the polar and ET pathways [summarized in eqns. (5) and (6)]. The results of product studies of the re-



<sup>§</sup>Pearson<sup>29</sup> recently reported a new method for estimating  $E^\circ(\text{Nu}^+/\text{Nu}^-)$ , and obtained slightly lower values for chloride (1.8 V), bromide (1.6) and iodide ion (1.1 V) and a considerably higher value for cyanide ion (2.2 V); the values given have been corrected for transfer of the redox system from water to acetonitrile.<sup>27</sup>

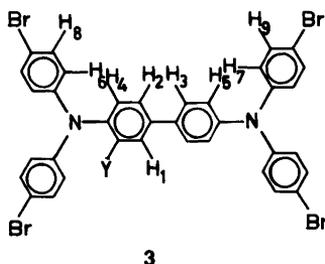


action between  $\text{TBPA}^+ \text{BF}_4^-$  and the above-mentioned nucleophiles are summarized in Table 1. As already demonstrated for the  $\text{TBPA}^+/\text{RCOO}^-$  reaction,<sup>16</sup> the ageing of this salt and the reaction conditions are essential for the outcome of the reaction. Using freshly prepared salt in acetonitrile at 20°C, the substitution product (**1a** or **1b**) was formed upon reaction with chloride or cyanide ion, whereas an aged sample (stored as solid for 24 h) at 2–5°C in acetonitrile gave brominated TBPA and, in the case of the chloride ion reaction, a dimer (**3b**). The latter precipitated from the initially homogeneous solution and was identified from its spectral (MS, NMR) characteristics. This type of product change upon ageing and/or temperature lowering was already observed in the  $\text{TBPA}^+/\text{RCOO}^-$  case,<sup>16</sup> and was ascribed to the operation of the dimerization process of eqn. (7), favoured as the temperature is decreased. The dication **2a** would then be responsible for the brominating properties of the system, either as such (source of positive halo-



(Ar = 4-BrC<sub>6</sub>H<sub>4</sub>)

(7)



**3** (a: Y = H; b: Y = Cl)

gen) or via formation of bromine or other brominating species. In this process, **2a** will eventually be converted to the biaryl (**3a**), a species that also is amenable to substitution under oxidizing conditions. With iodide ion as the nucleophile, the dimer precipitated at 2–5°C was isolated and showed to be biaryl **3a**. As for the  $\text{TBPA}^+/\text{AcO}^-$  reaction, the chloride ion reaction gave predominantly substitution products in dichloromethane. In this solvent, ion-pairing should be much more pronounced than in acetonitrile<sup>30</sup> and hence dimerization should be less favoured under otherwise similar conditions.

When tetrafluoroborate was exchanged for hexafluorophosphate or hexachloroantimonate, substitution into the aromatic ring prevailed even under those conditions which produced predominantly dimers from the tetrafluoroborate salt (Table 2).

With bromide or iodide ion, the reaction with  $\text{TBPA}^+$  followed exclusively an ET mechanism [eqn. (6)], as shown in the latter case by titration (thiosulfate) of the iodine formed ( $\approx 100\%$  yield). With bromide ion, the salt mixture isolated contained tetrabutylammonium tetrafluoroborate, bromide and perbromide in the proportions given by eqn. (8a) [note that an excess of tetrabutylammonium bromide over that required for the exclusive formation of the perbromide (**8b**) was used].

Table 3 shows that the elemental composition of the salt mixture was in good agreement with that expected for the stoichiometry of eqn. (8a). Moreover, an ESCA spectrum of the salt mixture showed Br  $3p_{3/2}$  peaks at  $E_b = 181.9$  and 183.1 eV, to be compared with those for  $\text{Bu}_4\text{NBr}$  (180.8),  $\text{Bu}_4\text{NBr}_3$  (182.3) and a mixture of the latter two salts (182.0 and 182.9). Finally, a control experiment with TBPA and  $\text{Bu}_4\text{NBr}_3$ , kept under the same conditions as in the  $\text{TBPA}^+/\text{Br}^-$  experiment, established that  $\text{Br}_3^-$  did not brominate TBPA.

Special attention was paid to the cyanide ion reaction, where  $\text{TBPA}^+$  gave 2-cyano-substituted TBPA (**1b**) in 54% yield, i.e. no ET reduction took place. This is unexpected in view of the proposal that the weaker oxidants  $\text{TAA}^+$  and  $\text{TTA}^+$  would undergo exclusive reduction by this ion.<sup>18,31</sup> Contradictory to the ET mechanism are also results for the anodic cyanation of many aromatic compounds with  $E_p$  in the region 0.5–2.2 V<sup>32</sup> and the fact that the perylene radical ca-

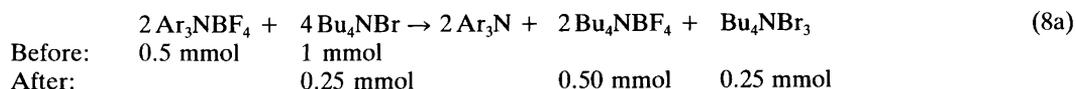
Table 2. Products of the reaction between  $\text{TBPA}^+ \text{PF}_6^-$  or  $\text{SbCl}_6^-$  and  $\text{Bu}_4\text{N}^+ \text{Cl}^-$  or  $[(\text{AcO})_2\text{H}]^-$  under different conditions in acetonitrile;  $[\text{TBPA}^+]/[\text{Bu}_4\text{N}^+ \text{Nu}^-] = 0.5$ .

Reaction conditions		Counter-ion	Nucleophile	Yield/% of recovered TBPA	Yield/% of TBPA derivative		
Ageing period/h	Temp./°C				2-Subst. <sup>a</sup> (di-)	<i>ipso</i> -Subst.	Brominated <sup>b</sup>
1	20	$\text{PF}_6^-$	$\text{Cl}^-$	54	43 (12)	7	
<sup>c</sup>	20	$\text{SbCl}_6^-$	$\text{Cl}^-$	47	19 (4)	8	
<sup>c</sup>	20	$\text{SbCl}_6^-$	$\text{AcO}^-$	51	44	Trace <sup>d</sup>	3
24	2-5	$\text{PF}_6^-$	$\text{Cl}^-$	57	41 (5)	7	2
<sup>c</sup>	2-5	$\text{SbCl}_6^-$	$\text{Cl}^-$	60	19 (4)	11	2
<sup>c</sup>	2-5	$\text{SbCl}_6^-$	$\text{AcO}^-$	46	49	Trace <sup>d</sup>	6

<sup>a</sup>Calculated for a two- and four-electron process for mono- and disubstituted TBPA, respectively. <sup>b</sup>Calculated with the assumption that 1 mol of bromine is required to substitute one position in TBPA. <sup>c</sup>Commercial sample. <sup>d</sup>This compound is chlorobrominated TBPA.

Table 3. Percentage composition of tetrabutylammonium salts.

Element	Calculated/% for			Mixture of tetrabutylammonium salt according to eqn. (8a)	
	$\text{Bu}_4\text{NBr}$	$\text{Bu}_4\text{NBr}_3$	$\text{Bu}_4\text{NBF}_4$	Calculated	Found
C	59.6	38.9	58.4	52.5	53.0
H	11.3	7.5	11.0	9.9	10.1
N	4.3	2.9	4.2	3.8	3.9
Br	24.8	49.7	0	21.8	22.1



tion ( $E^\circ = 1.30 \text{ V}$ )<sup>33</sup> undergoes substitution by cyanide ion.<sup>34</sup> Besides, both  $\text{TAA}^{+}$  and  $\text{TTA}^{+}$  undergo substitution upon treatment with bromide ion.<sup>35</sup> Why should the latter two species be capable of oxidizing cyanide ion, when the stronger oxidant  $\text{TBPA}^+$  undergoes substitution? In order to try to answer this question,  $\text{TAA}^+ \text{BF}_4^-$  was treated with cyanide ion (1:2 molar ratio) in acetonitrile. The reaction mixture turned dark brown and GLC/MS analysis revealed no volatile products other than recovered TAA (ca. 50%)

and traces of the cyano-substituted amine (both H and methoxy substitution). The same result was obtained on electrolyzing the amine in acetonitrile/tetrabutylammonium cyanide. The tarry, non-volatile portion of the product from both the homogeneous and anodic reaction presumably consisted of products of cascade oxidation; similar findings were reported for the anodic oxidation of 4,4'-dialkoxybiphenyls.<sup>36</sup>

Treatment of  $\text{TTA}^+ \text{BF}_4^-$  with cyanide ion in acetonitrile (1:2 molar ratio) gave, however, a

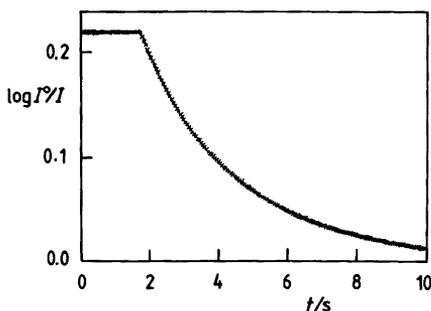


Fig. 3. Plot of absorbance at 705 nm vs. time for the reaction between  $\text{TBPA}^+$  (0.10 mM, prepared by the  $\text{NO}^+$  method) and  $\text{Cl}^-$  (1.0 mM) at 20°C.

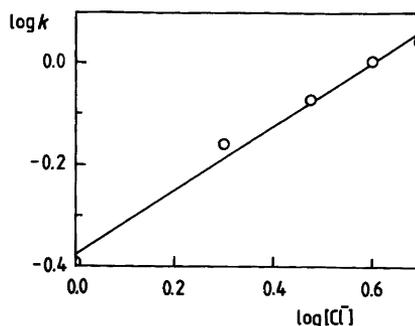


Fig. 5. Plot of  $\log(k_{\text{obs}}/\text{s}^{-1})$  vs.  $\log([\text{Cl}^-]/\text{mM})$  for the reaction between  $\text{TBPA}^+$  and chloride ion in acetonitrile at 20.0°C.

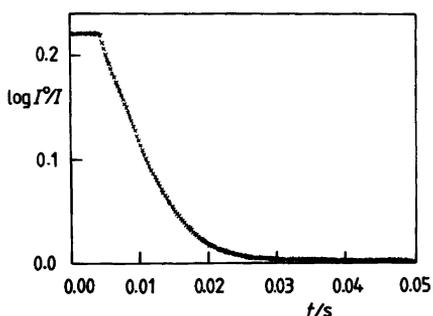


Fig. 4. Plot of absorbance at 720 nm vs. time for the reaction between  $\text{TAA}^+$  (0.10 mM, prepared by the  $\text{NO}^+$  method) and  $\text{CN}^-$  (1.0 mM) at 20°C.

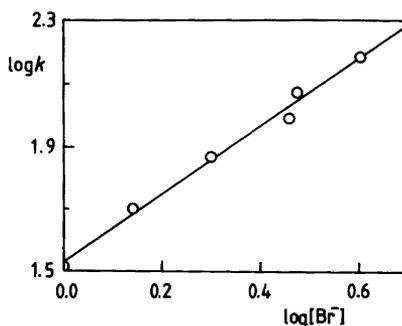


Fig. 6. Plot of  $\log(k_{\text{obs}}/\text{s}^{-1})$  vs.  $\log([\text{Br}^-]/\text{mM})$  for the reaction between  $\text{TBPA}^+$  and bromide ion in acetonitrile at 20.0°C.

low yield (20%) of the 2-cyano-substituted amine (**1c**) in addition to recovered TTA (ca. 20%). No other volatile products were formed. Anodic oxidation of TTA in acetonitrile/ $\text{Et}_4\text{NCN}$  gave **1c** in 23% yield (based on unrecovered amine), with no other volatile products.

*Kinetic studies.* The purpose of these studies was restricted to obtaining an approximate estimate of the reactivity of the nucleophiles used above in the reaction with  $\text{TBPA}^+$ ,  $\text{TAA}^+$ , and  $\text{TTA}^+$  and not to obtaining a detailed picture of the mechanism. For the latter goal to be fulfilled a

Table 4. Observed rate constants ( $k_{\text{obs}}$ ) for the reactions between  $\text{Ar}_3\text{N}^+$ , prepared by different methods, and  $\text{Bu}_4\text{N}^+\text{X}^-$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) in acetonitrile at 20.0°C;  $[\text{Ar}_3\text{N}^+]_0 = 0.1 \text{ mM}$ ,  $[\text{Bu}_4\text{NX}]_0 = 1.00 \text{ mM}$ .

$\text{Ar}_3\text{N}^+$	Method of preparation	Nucleophile	Number of runs	$k_{\text{obs}}/\text{s}^{-1}$ , mean value
$\text{TBPA}^+$	$\text{NOBF}_4$	$\text{Cl}^-$	4	0.43
	$\text{NOPF}_6$		2	0.40
	$\text{AgPF}_6/\text{I}_2$		2	0.46
$\text{TBPA}^+$	$\text{NOPF}_6$	$\text{Br}^-$	4	34
	$\text{AgPF}_6/\text{I}_2$		5	32
$\text{TAA}^+$	$\text{NOBF}_4$	$\text{I}^-$	5	5.2

much more detailed kinetic study would be necessary.

The kinetics of the disappearance of the radical cation were monitored at 20.0°C in acetonitrile under pseudo first-order conditions ( $[\text{Ar}_3\text{N}^+]/[\text{Nu}^-] \leq 0.1$ ) at 705 (TBPA<sup>+</sup>) or 720 (TAA<sup>+</sup>) nm. The initial absorbance was around 0.25 and the final reading was close to zero. The problems connected with the preparation of a kinetically well-behaved sample of TBPA<sup>+</sup>·BF<sub>4</sub><sup>-</sup> were described recently<sup>16</sup> and need not be repeated here; it suffices to note that the NO<sup>+</sup> method was used for the synthesis of the radical cation salt as long as tetrafluoroborate was employed as the counter-ion. With hexafluorophosphate as the counter-ion, the salt prepared by the Ag<sup>+</sup>/I<sub>2</sub> method could also be used. The initial concentration of the radical cation was determined spectrophotometrically and the solutions were then used directly for kinetic runs. TBPA<sup>+</sup> was employed to determine the reactivity of chloride and bromide ion, whereas the reactions with iodide or cyanide were too fast to be measurable by the stopped-flow technique under the conditions described above; TAA<sup>+</sup> was sufficiently unreactive to be used in the latter two cases.

Typical kinetic traces for halide ion reactions are shown in Fig. 3. From these, a suitable region was extracted in order to calculate  $k_{\text{obs}}$  by fitting the data to an exponential expression<sup>37</sup> via a non-linear regression treatment developed by Marquardt<sup>38</sup> (programme purchased from Hewlett-Packard Co.). However, with cyanide ion, first-order behaviour was not found (Fig. 4) and therefore cyanide ion reactions were not studied further. Observed rate constants,  $k_{\text{obs}}$ , for the other radical cation/nucleophile reactions are shown in Table 4. Figs. 5 and 6 show the linear dependence of  $\log k_{\text{obs}}$  upon  $\log [\text{Nu}^-]$ , the slopes and thus reaction orders with respect to halide ion concentration being 0.6(1) for chloride ion and 1.1(1) for bromide ion. For another nucleophile, hydrogendiacetate ion [(AcO)<sub>2</sub>H<sup>-</sup>], reacting via the polar pathway, the reaction order was 0.6(2).<sup>16</sup>

The latter reaction order is explicable if acetate ion, formed by dissociation of the hydrogendiacetate ion [eqn. (9)] is the kinetically active species and the hydrogendiacetate ion either is unreactive or much less reactive than acetate ion; the



Table 5. Observed rate constants ( $k_{\text{obs}}$ ) for the reaction between TBPA<sup>+</sup> and Bu<sub>4</sub>NCl in acetonitrile at 20.0°C in the presence of varying [TBPA]; [TBPA<sup>+</sup>]<sub>0</sub> = 0.1 mM, [Cl<sup>-</sup>]<sub>0</sub> = 1.00 mM.

[TBPA]/mM	$k_{\text{obs}}/\text{s}^{-1}$ <sup>a</sup>
0.10 <sup>b</sup>	0.46
1.10 <sup>c</sup>	0.40
2.30 <sup>c</sup>	0.35

<sup>a</sup>Average of two runs. <sup>b</sup>Residual [TBPA] after synthesis (NO<sup>+</sup> method). <sup>c</sup>TBPA added.

reaction order with respect to hydrogendiacetate would then be 0.5. For the chloride ion reaction, the non-integer reaction order cannot be explained similarly. It was reported<sup>3</sup> that the reaction between 9,10-diphenylanthracene radical cation (DPA<sup>+</sup>) and chloride ion was second order in [DPA<sup>+</sup>], and we therefore treated our data assuming second-order disappearance of TBPA<sup>+</sup>; however, the fit to the experimental data was much worse than in the first-order case, and thus it is not reasonable to attach any significance to the slightly increased order with respect to [Cl<sup>-</sup>], 0.8(1), obtained for the second-order assumption.

The influence of the concentration of the neutral amine would also be different for the two pathways. In the polar mechanism, [Ar<sub>3</sub>N] would have little or no influence on  $k_{\text{obs}}$  which was found previously for the acetate ion reaction<sup>16</sup> and in the present work for the chloride ion re-

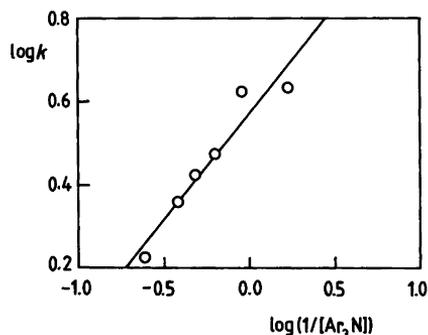


Fig. 7. Plot of  $\log(k_{\text{obs}}/\text{s}^{-1})$  vs.  $\log(1/[\text{TAA}]/\text{mM}^{-1})$  for the reaction between TAA<sup>+</sup> and iodide ion in acetonitrile at 20.0°C.

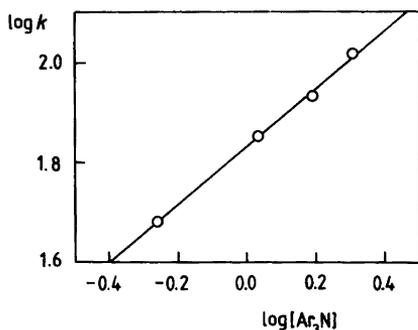


Fig. 8. Plot of  $\log(k_{\text{obs}}/\text{s}^{-1})$  vs.  $\log([\text{TBPA}]/\text{mM})$  for the reaction between  $\text{TBPA}^+$  and bromide ion in acetonitrile at  $20.0^\circ\text{C}$ .

action (Table 5); an increase in  $[\text{Ar}_3\text{N}]$  by more than 20-fold merely decreased  $k_{\text{obs}}$  by ca. 25%. On the other hand, an ET mechanism would be expected to be influenced strongly by  $[\text{Ar}_3\text{N}]$ , as was indeed also found. The rate of the  $\text{TAA}^+$ /iodide reaction was depressed by the addition of TAA, a plot of  $\log k_{\text{obs}}$  vs.  $1/[\text{TAA}]$  being linear with a slope of 0.5(2) (Fig. 7). Although it is impossible to express analytically the exact dependence of  $\log k_{\text{obs}}$  upon  $[\text{Ar}_3\text{N}]$ , the rate depression observed is generally in accordance with a mechanism involving a reversible ET step followed by fast coupling of iodine atoms to give iodine. More

Table 6. Effect of various inert salts or water upon the observed rate constant ( $k_{\text{obs}}$ ) in the reaction between  $\text{TBPA}^+$  and  $\text{Bu}_4\text{N}^+\text{X}^-$  ( $\text{X} = \text{Cl}, \text{Br}$ ) in acetonitrile at  $20.0^\circ\text{C}$ .  $[\text{TBPA}^+] = 0.10 \text{ mM}$ ,  $[\text{Bu}_4\text{NX}]_0 = 1.00 \text{ mM}$ . Without any additive,  $k_{\text{obs}} = 31 \text{ s}^{-1}$  for reaction with  $\text{Br}^-$  and  $0.46 \text{ s}^{-1}$  for reaction with  $\text{Cl}^-$ .

Additive	$k_{\text{obs}}/\text{s}^{-1}$ <sup>a</sup> for reaction with $\text{Br}^-$		$k_{\text{obs}}/\text{s}^{-1}$ <sup>a</sup> for reaction with $\text{Cl}^-$	
	<sup>b</sup>	<sup>c</sup>	<sup>b</sup>	<sup>c</sup>
$\text{Bu}_4\text{NBF}_4$	27	21	0.34	0.28
$\text{Bu}_4\text{NPF}_6$	28	21	0.34	0.27
$\text{Me}_4\text{NBF}_4$	23	17	0.26	0.22
$\text{LiClO}_4$	29	17	0.035	0.018
$\text{H}_2\text{O}$		35		0.39
$\text{Bu}_4\text{NClO}_4$			0.33	0.29
$\text{Me}_4\text{NClO}_4$			0.27	0.24

<sup>a</sup>Average of two runs. <sup>b</sup> $[\text{Additive}] = 5.0 \text{ mM}$ .

<sup>c</sup> $[\text{Additive}] = 10.0 \text{ mM}$ .

surprising was the dependence of  $\log k_{\text{obs}}$  upon  $\log [\text{Ar}_3\text{N}]$  for the  $\text{TBPA}^+$ /bromide ion reaction, a reaction order of +0.5(1) being observed (Fig. 8).

Finally, the effect of added inert salts or water upon  $k_{\text{obs}}$  for the  $\text{TBPA}^+$ /chloride and bromide ion reactions was investigated. As seen from Table 6, only weak effects of added tetramethyl- and tetrabutylammonium fluoroborate, hexafluorophosphate or perchlorate upon the rate constant of either reaction were observed, whereas lithium perchlorate decreased the rate constant for the chloride reaction by a factor of ca. 10 at the 5 mM level. This retarding effect was studied in more detail (Table 7 and Fig. 9). Assuming that it has its origin in the strong tendency of lithium and chloride ions to associate in acetonitrile ( $K_{\text{ass}} = \text{ca. } 4000 \text{ M}^{-1}$ )<sup>39</sup> and that both  $\text{Cl}^-$  and  $\text{LiCl}$  are kinetically active (eqn. 10), values of  $K_{\text{ass}}$ ,  $k_1$  and  $k_2$  could be determined by fitting  $k_{\text{obs}}$  to the theoretical expression relating these parameters. The curve of Fig. 9 represents the best fit to the

$$k_{\text{obs}} = k_1[\text{Cl}^-] + k_2[\text{LiCl}] \quad (10)$$

experimental points, giving  $K_{\text{ass}} = 2.9(2) \times 10^3 \text{ M}^{-1}$ ,  $k_1 = 450 \text{ M}^{-1} \text{ s}^{-1}$  and  $k_2 = (2-8) \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$ . The value of  $k_2$  was sensitive to the choice of seed values of the adjustable parameters, which is not surprising in view of the high  $k_1/k_2$  ratio which makes  $k_2$  subject to large errors. Considering the uncertainties inherent in fitting the experimental data to eqn. (10) using three adjustable parameters, the value of  $K_{\text{ass}}$  is in satisfactory agreement with the literature value determined by conductance measurements.<sup>39</sup>

**Concluding remarks.** It should first be noted that Pearson's new values<sup>29</sup> for  $E^\circ(\text{CN}^\cdot/\text{CN}^-)$  are considerably higher than those currently in use (2.2 vs. 1.6 V in acetonitrile, 2.52 vs. 1.9 V in water) and place cyanide in the class of difficultly oxidizable anions, even more difficult to oxidize than chloride or acetate ion. If we accept these values, many of the problems connected with the reactivity of cyanide ion toward radical cations become non-problems; cyanide ion should react like acetate and chloride, with bond formation. This is exactly what has been found above for the reaction between  $\text{TBPA}^+$  and these ions, and appears to be in line with most findings concerning anodic acetoxylation and cyanation at least (in

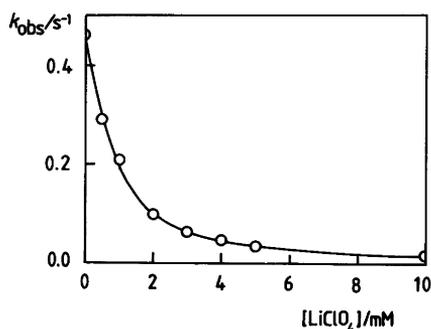


Fig. 9. Plot of  $k_{\text{obs}}/\text{s}^{-1}$  vs.  $[\text{LiClO}_4]/\text{mM}$  for the reaction between  $\text{TBPA}^{+\cdot}$  (0.10 mM) and  $\text{Cl}^-$  (1.0 mM) with added  $\text{LiClO}_4$  in acetonitrile at 20.0°C. The curve represents the best fit of eqn. (10) to the experimental points, using  $K_{\text{ass}}$ ,  $k_1$  and  $k_2$  as adjustable parameters (values, see text).

the case of anodic chlorination, relatively few studies have been performed under controlled potential conditions, so that the situation is not entirely clear; however, newer studies<sup>40</sup> favour the radical cation/nucleophile mechanism). This means that the claim<sup>18</sup> that cyanide ion undergoes ET oxidation by the weak oxidant  $\text{TAA}^+$ , and thus gives rise to anodic catalytic currents, in all probability cannot be correct. Instead, cascade oxidation involving reactions in which cyanide ion acts as a base in the chemical steps following initial electron transfer is a more likely mechanism.

For more easily oxidizable anions such as bromide and iodide ion, an ET mechanism seems to prevail for  $\text{TBPA}^{+\cdot}$  and 9,10-diphenylanthracene ( $\text{DPA}^{+\cdot}$ ).<sup>3</sup>

Table 7. Effect of the addition of  $\text{LiClO}_4$  upon the observed rate constant ( $k_{\text{obs}}$ ) for the reaction between  $\text{TBPA}^{+\cdot}$  and  $\text{Bu}_4\text{N}^+\text{Cl}^-$  in acetonitrile at 20.0°C.  $[\text{TBPA}^{+\cdot}]_0 = 0.10$  mM,  $[\text{Bu}_4\text{NCl}]_0 = 1.00$  mM.

$[\text{LiClO}_4]/\text{mM}$	$k_{\text{obs}}/\text{s}^{-1}$
0	0.46
0.50	0.290
1.00	0.208
2.00	0.0984
3.00	0.0630
4.00	0.0470
5.00	0.0345
10.0	0.0184

(Perylene)<sup>+</sup>, a widely studied<sup>34</sup> radical cation, has the same  $E^\circ$  value as  $\text{TBPA}^{+\cdot}$  and would be expected to display an analogous reactivity pattern. The literature data are, however, not internally consistent, nor are they consistent with those pertaining to  $\text{TBPA}^{+\cdot}$  and  $\text{DPA}^{+\cdot}$ . This can, for example, be seen in the kinetic data (Table 8) for the ET reactions of (perylene)<sup>+</sup> with bromide and iodide ion. These rate constants are larger than those for the significantly stronger oxidant,  $\text{DPA}^{+\cdot}$ , which is in disagreement with predictions based on the Marcus theory. A possible difficulty with this reasoning would be the operation of steric effects, which are known to be significant in radical cation/nucleophile interactions. However, electron transfer reactions are predicted<sup>41</sup> and shown<sup>42</sup> to be much less sensitive to steric hindrance than bond-forming processes, and we therefore deem this objection to be less important.

## Experimental

**General methods.** UV spectra were recorded on a Cary 219 spectrophotometer and <sup>1</sup>H NMR spectra on a Varian XL-300 instrument. Mass spectral analysis (at 70 eV) was carried out on a Finnigan 4021 instrument, using a heated inlet. ESCA spectra were measured on an AEI-100 spectrometer using Al  $K_\alpha$  (1486.6 eV) X-ray radiation.

Transmittance/time measurements were performed with a Hi-Tech SF-3L stopped-flow spectrophotometer (cell path 2 mm), equipped with a SF-3C control unit and DSF-3 data display system (from Hi-Tech Scientific Ltd., England). The system was connected to an HP-9835A microcomputer for control of the measurements and storage of the data. Calculations of rate constants were performed on this computer, using the NONLIN program purchased from Hewlett-Packard.<sup>38</sup>

GLC analysis was carried out as described previously.<sup>16</sup> Iodometric titration was performed on a Mettler DL-40 Memo Titrator. Elemental analyses were performed by the Microanalytical Laboratory of this department.

**Materials.** All chemicals except tris(4-methoxyphenyl)amine<sup>16</sup> and tris(4-methylphenyl)amine<sup>43</sup> were purchased as the highest commercial quality available; they were used without further purification except in the case of tris(4-bromophenyl)-

Table 8. Rate constants for the reaction between radical cations and charged nucleophiles in acetonitrile at 20.0°C.

Radical cation (A <sup>•+</sup> )	E <sup>o</sup> (A <sup>•+</sup> /A)/V	Log (rate constant/M <sup>-1</sup> s <sup>-1</sup> ) for reaction with				
		(AcO) <sub>2</sub> H <sup>-</sup>	Cl <sup>-</sup>	Br <sup>-</sup>	I <sup>-</sup>	CN <sup>-</sup>
TBPA <sup>•+</sup> <sup>a</sup>	1.30	4.76	2.65	4.54		
Perylene <sup>•+</sup> <sup>b</sup>	1.30		4.80	6.0	10.3	5.7 <sup>c</sup>
DPA <sup>•+</sup> <sup>d</sup>	1.44		(5.3) <sup>e</sup>	5.85	7.18	6.78
TAA <sup>•+</sup> <sup>f</sup>	0.72				3.72	

<sup>a</sup>This work and Ref. 16. <sup>b</sup>Ref. 34d. <sup>c</sup>Estimated from the value given for methanol, noting that rate constants in acetonitrile were approximately 10 times those measured in methanol.<sup>34d</sup> <sup>d</sup>Ref. 3. <sup>e</sup>Second-order rate constant estimated for the radical cation concentration employed. <sup>f</sup>This work.

amine (recrystallized from heptane) and tetrabutylammonium chloride and bromide (recrystallized from ethyl acetate/cyclohexane). Acetonitrile was of Baker HPLC quality and was stored in the dark. Dichloromethane (Merck zur Rückstandsanalyse) was dried and stored over 3 Å molecular sieves.

The radical cation salts were prepared in a manner similar to that used for radical cation tetrafluoroborates, i.e. by treating the triarylamine with either silver salt/iodine in diethyl ether<sup>25</sup> or nitrosonium salt in acetonitrile.<sup>44</sup> With AgPF<sub>6</sub>, the addition of iodine was made at ca. 0°C, since at lower temperature a complex precipitated from the ether solution. Yields and spectroscopic data for the TBPA<sup>•+</sup> and TAA<sup>•+</sup> tetrafluoroborates were reported previously;<sup>16</sup> for the hexafluorophosphates, the UV spectra were identical to those of the tetrafluoroborates and the yields were: TBPA<sup>•+</sup> PF<sub>6</sub><sup>-</sup>, 50% (96–98% purity) by the Ag<sup>+</sup>/I<sub>2</sub> method and 80% by the NO<sup>+</sup> method; TTA<sup>•+</sup> PF<sub>6</sub><sup>-</sup>, 50% by the Ag<sup>+</sup>/I<sub>2</sub> method and 70% by the NO<sup>+</sup> method [ $\lambda_{\max}(\epsilon)$ : 670 nm (2.4 × 10<sup>4</sup>)].

**Preparation of (2-chloro-4-bromophenyl)-bis(4-bromophenyl)amine (1a).** A solution of TBPA (3 mM) and Bu<sub>4</sub>NCl (9 mM) in acetonitrile containing Bu<sub>4</sub>NBF<sub>4</sub> (0.1 M) as the supporting electrolyte (total volume 75 ml) was electrolyzed as described for the analogous 2-acetoxy derivative.<sup>16</sup> Analysis (GLC) showed the monomeric fraction of the product mixture to contain **1a** (51%), dichlorinated TBPA (17%) and unreacted TBPA (13%). The products from five runs were combined and recrystallized from heptane, giving **1a** of 75% purity, m.p. 113–115°C (con-

taminated by 20% of TBPA and 5% of dichlorinated amine). MS [*m/z* (rel. intensity)]: 516 (*M*<sup>+</sup>), 519 (6.1), 517 (13.1), 515 (11.6), 513 (3.5), 403 (6.8), 401 (14.4), 399 (7.6), 241 (25), 139 (37), 138 (45), 129 (100), 119 (33), 76 (42), 75 (48). <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>): 6.93 and 7.45 (H2 and H3 in 4-BrC<sub>6</sub>H<sub>4</sub>), 7.29, 7.60 and 7.76 (H4, H5 and H6 in 2-Cl-4-BrC<sub>6</sub>H<sub>3</sub>; *J*<sub>45</sub> = 8.8 Hz, *J*<sub>56</sub> = 1.9 Hz).

**Preparation of (2-cyano-4-bromophenyl)-bis(4-bromophenyl)amine (1b).** An acetonitrile solution of TBPA (3 mM) and Bu<sub>4</sub>NCN (9 mM) was electrolyzed as above, except that Ar protection was employed and 2.2 F/mol of TBPA were passed before the solution was worked up. The product mixture contained 55% of **1b**, 6% of TBPA and 2% of 4-cyanophenyl-bis(4-bromophenylamine), besides oligomeric products. The product mixtures from five runs were combined and the yellow crystals of **1b** obtained, m.p. 62–65°C, were not further purified. MS [*m/z* (rel. intensity)]: 507 (*M*<sup>+</sup>), 510 (12), 508 (39), 506 (42), 504 (14), 426 (3), 348 (18), 347 (8), 346 (19), 267 (12), 266 (27), 191 (25), 166 (33), 165 (20), 164 (26), 134 (100), 133 (52), 129 (56), 76 (72), 75 (75). <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>): 7.03 and 7.51 (H2 and H3 in 4-BrC<sub>6</sub>H<sub>4</sub>), 7.26, 7.84 and 7.96 (H4, H5 and H6 in 2-cyano-4-bromophenyl; *J*<sub>45</sub> = 8.8 Hz, *J*<sub>56</sub> = 2.4 Hz).

**Preparation of (2-cyano-4-methyl)-bis(4-methylphenyl)amine (1c).** A solution of TTA<sup>•+</sup> PF<sub>6</sub><sup>-</sup> (0.5 mmol) in 20 ml of acetonitrile was added dropwise under Ar protection and with stirring to a solution of Bu<sub>4</sub>NCN (1 mmol) in 10 ml of aceto-

nitrile. The reaction mixture was freed from solvent and the residue extracted with diethyl ether. The extract was washed with water, dried and analyzed by GLC (33% yield, based on a  $2e^-$  reaction and unrecovered starting material). The 2-cyano derivative **1c** was isolated by flash chromatography on a silica gel column, using dichloromethane/light petroleum (20/80) as the eluent; yield 23% (based on unrecovered starting material). MS [ $m/z$  (rel. intensity)]: 312 ( $M^+$ ), 313 (23), 312 (100), 311 (21), 297 (5), 296 (5), 295 (4), 282 (2), 221 (6), 219 (6), 206 (9), 205 (10), 194 (19), 181 (12), 180 (22), 156 (22), 155 (26), 148 (72), 141 (16), 140 (17), 128 (9), 116 (11), 105 (9), 91 (72), 77 (48), 65 (61).  $^1\text{H NMR}$  (acetone- $d_6$ ): 2.28 (s,  $\text{CH}_3$  in 4- $\text{CH}_3\text{C}_6\text{H}_4$ ), 2.37 (s,  $\text{CH}_3$  in 2-cyano-4-methylphenyl), 6.85 and 7.10 (H2 and H3 in 4- $\text{CH}_3\text{C}_6\text{H}_4$ ), 7.09, 7.45 and 7.51 (H4, H5 and H6 in 2-cyano-4-methylphenyl).

*Reaction between radical cations and nucleophiles; product studies.* Solutions of tetrabutylammonium chloride, bromide, iodide and cyanide ion (1 mmol in 10 ml of solvent) were kept in a thermostat at the desired temperature. The radical cation salt solution (0.5 mmol in 20 ml of solvent) was added dropwise with stirring. The blue radical cation solution was instantaneously decolorized and became light yellow ( $\text{Cl}^-$ ), yellow ( $\text{Br}^-$ ) or red-brown ( $\text{I}^-$ ,  $\text{CN}^-$ ). The solution was decanted off in those cases in which a precipitate was formed (see text and below), evaporated and the residue extracted with ether. After washing, drying and addition of an internal standard, the product mixture was analyzed by GLC/MS. In the reaction with bromide ion, the insoluble residue of tetrabutylammonium salts was dried and analyzed by elemental analysis, iodometric titration and ESCA spectroscopy.

*Identification of the precipitates (dimers **3a** and **3b**).* The precipitate formed in the reaction between  $\text{TBPA}^+ \text{BF}_4^-$  (aged 24 h) and chloride or iodide in acetonitrile at 2–5 °C (see Table 1) was dried and analyzed by MS (direct inlet, only peaks with  $m/z$  above 300 were recorded) and  $^1\text{H NMR}$  spectrometry. In the case of the iodide reaction the dimer **3a** was identified; MS ( $m/z$ ): 804 ( $M^+$ ), 808, 807, 806, 805, 804, 802, 800, 725, 404, 402, 401, 400, 323, 322, 318, 317, 316;  $^1\text{H NMR}$  (acetone- $d_6$ ): 7.16 and 7.64 (protons in the biaryl

system), 7.05 and 7.48 (protons in 4-bromophenyl groups).

Dimer **3b** was identified in the chloride reaction; MS ( $m/z$ ): 838 ( $M^+$ ), 840, 838, 836, 724, 722, 437, 436, 421, 420, 419, 418, 380, 379, 363, 362, 361, 360.  $^1\text{H NMR}$  (acetone- $d_6$ ; for numbering of protons, see **3b**): 7.83 (H1), 7.72 (H2), 7.71 (H3), 7.40 (H4), 7.18 (H5), 6.96 (H6), 7.07 (H7), 7.45 (H8), 7.50 (H9);  $J_{24} = 8.3$  Hz,  $J_{12} = 2.3$  Hz.

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