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Novel, CO_2-promoted synthesis of anhydrous alkylammonium tetraphenylborates: a study on their reactivity as intra- and inter-molecular proton-transfer agents ☆

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Abstract

Anhydrous alkylammonium tetraphenylborates $(RR'R''NH)BPh_4$ [R′ = R″ = H, R = allyl (**1**), cyclohexyl (**2**), or benzyl (**3**); R″ = H, R = R′ = ethyl (**4**); R″ = H, RR′ = $-CH_2CH_2OCH_2CH_2-$ (**5**); R = R′ = R″ = Bu (**6**)] have been prepared with high yield in mild conditions from the corresponding amines and $NaBPh_4$ in the presence of carbon dioxide. The synthesis of trialkylammonium salts, $(R_3NH)BPh_4$, also requires a suitable reagent that can act as a proton source. The method has been extended to the direct synthesis of $[RNH_3 \cdot (18\text{-crown-6})]BPh_4$ salts [R = allyl (**1a**), cyclohexyl (**2a**), or benzyl (**3a**)]. The behaviour of **1–6** in several solvents has been investigated. In CH_2Cl_2 or THF, **1–6** salts can undergo intramolecular protolytic cleavage of a B–C bond to form benzene and $RR'R''N{-}BPh_3$ adducts. In acetone, both mono- and di-alkylammonium tetraphenylborates easily convert in high yield into the corresponding iminium–BPh_4 salts, $(RR'N{=}CMe_2)BPh_4$ (R = alkyl; R′ = H, or alkyl) through intermolecular transfer of a proton to a solvent molecule.

The reactivity of alkylammonium tetraphenylborates can be modified markedly by a complexing agent that firmly coordinates the cation and acts as a proton-transfer inhibitor.

Keywords: Group 1; Tetraphenylborate; Carbon monoxide; Boron; Hydrogen bond; Anhydrous alkylammonium salts

1. Introduction

Alkylammonium tetraphenylborate salts, $(RR'R''NH)BPh_4$, represent a class of compounds that have attracted growing attention in the last few years, both for their structural features, which allow peculiar dynamic properties in the solid state [1], and for their potential as reagents in pure and applied chemistry. These compounds have interesting properties as accelerators in epoxy resin-nitrile rubber adhesives [2], charge-controlling agents contained in electrophotographic developer toner [3], and agrochemical industrial microbicides [4]. Moreover, they are good precursors of new products or materials. Pyrolysis of $(RR'R''NH)BPh_4$ (R = alkyl; R′, R″ = H, or alkyl) has been claimed to afford *B*-triphenyl-*N*-trialkylborazines, $(RNBPh)_3$, or, depending on the experimental conditions, polymeric materials involving catenation of borazine rings [5].

Alkylammonium tetraphenylborate salts have found recently wide utilization in organometallic chemistry as protonating agents. These compounds are effective in promoting the protolytic cleavage of several M–C bonds (M = Th [6], Ti [7], Zr [7b–e,8], Hf [7c], Cr [9], Pd [10], Ce [11]), facilitating the synthesis of a large variety of otherwise difficult to obtain cationic or zwitterionic-η^n-$PhBPh_3$ metal complexes, most of which are good catalysts in alkene polymerization or olefin amination.

As far as the synthesis is concerned, $(RR'R''NH)BPh_4$ salts are usually precipitated from an aqueous medium by reaction of the corresponding alkylammonium halide with $NaBPh_4$ (Eq. (1)) [1,5,7e,10–12]. Reaction (1) has been known for a long time [12]

$$(RR'R''NH)Cl + NaBPh_4 \xrightarrow{H_2O} (RR'R''NH)BPh_4 + NaCl \quad (1)$$

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☆ Dedicated to Prof. F. Calderazzo on the occasion of his 65th birthday.

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and has found useful analytical application for the detection, identification and quantitative determination of basic organic nitrogen compounds in aqueous solutions [12c,13].

A major drawback related to Eq. (1) is, however, that the salts precipitate as hydrates. The isolation of the anhydrous form, that is usually required in most applications, needs further work-up and drying in vacuo for several days under strictly controlled conditions in order to avoid decomposition [7e,12c–e,13].

As a part of our studies on CO_2 fixation by amines to obtain metal or organic carbamates [14] and on tetraphenylborate anion reactivity [15], we have investigated the reaction of ammonium carbamates with alkali metal tetraphenylborates. In this paper we focus on a few aspects of this reaction, a new straightforward CO_2-promoted method of synthesis of anhydrous alkylammonium tetraphenylborate salts. Moreover, we show that both the stability and reactivity of the salts in solution are remarkably influenced by solvent or suitable complexing agents, that can selectively modulate, or, even, completely inhibit, the ability of these compounds to act as intra- or inter-molecular proton-transfer agents.

2. Results and discussion

2.1. Synthesis of alkylammonium tetraphenylborates

Mono- and di-alkylammonium tetraphenylborates, $(RNH_3)BPh_4$ and $(RR'NH_2)BPh_4$, have been prepared anhydrously in high-yield by direct reaction of $NaBPh_4$ with the corresponding primary or secondary amine in the presence of carbon dioxide (Eq. (2)).

$$2\ RR'NH + MBPh_4 + CO_2 \longrightarrow (RR'NH_2)BPh_4 + RR'NC(O)OM \quad (2)$$

(M = Na; R' = H or alkyl)

Reaction (2) is usually carried out in anhydrous THF, under very mild conditions (273–293 K; 0.103 MPa CO_2 pressure). The formation of tetraphenylborate salt is accompanied by production of the starting amine carbamic acid sodium salt, which usually separates rapidly as a microcrystalline solid from the reaction solution after mixing. The process summarized by Eq. (2) can also represent a new facile synthetic route to sodium carbamate salts, which are usually obtained by direct interaction of the metal with amines in the presence of CO_2 [16], by reaction of organic isocyanates with sodium hydroxide in organic solvents [17] or by reaction of phosphocarbamates with alkali halides [14e]. The full significance of Eq. (2) as a new general synthetic route to alkali (M = Li, Na, or K) *N*-alkylcarbamate salts will be extensively highlighted in a forthcoming paper [18].

Primary and secondary aromatic amines do not react according to Eq. (2) to afford arylammonium tetraphenylborate salts. Whatever reaction mechanism we consider for reaction (2) [18], the formation of the carbamate and tetraphenylborate salts requires that the amine simultaneously acts as a nucleophile towards CO_2 and as a base, extracting a proton from an acid species present in the reaction medium. Both the weaker nucleophilic and basic properties displayed by aromatic amines compared to aliphatic amines can account for the low reactivity of aromatic amines towards $NaBPh_4$ in the presence of CO_2.

Tertiary aliphatic amines, however, are unable to react according to Eq. (2) because of structural features. The preparation of trialkylammonium tetraphenylborates requires the presence or formation in the reaction medium of a suitable proton source. The attempt to use an aliphatic amine such as diethylamine failed. The reaction of tributylamine (1 mol) with $NaBPh_4$ (1 mol) in the presence of CO_2 and diethylamine (1 mol) did not yield $(Bu_3NH)BPh_4$, but $(Et_2NH_2)BPh_4$ was isolated from the reaction mixture [19,20]. However, the synthesis of $(Bu_3NH)BPh_4$ was successfully accomplished when tributylamine (1 mol) reacted with $NaBPh_4$ (1 mol) in the presence of CO_2 and an aromatic amine, such as aniline (1 mol), according to Eq. (3).

$$RR'R''N + MBPh_4 + CO_2 + ArNH_2 \longrightarrow (RR'R''NH)BPh_4 + ArNHCO_2M \quad (3)$$

(M = Na; R, R', and R'' = alkyl; Ar = aryl)

In this reaction, the sodium salt of a *N*-aryl substituted carbamic acid is formed, and is easily isolated as a pure compound. From a synthetic point of view, therefore, Eq. (3) holds a two-fold potential because it allows the synthesis of anhydrous trialkylammonium tetraphenylborates and re[illegible] sents a general way to the synthesis of sodium and, more generally, alkali *N*-aryl carbamate salts [18].

A few compounds could be isolated only as solvated species because of their tendency to bind THF molecules through hydrogen bonds. Tetraphenylborates **1–6** are all stable in the solid state at room temperature (293 K) and under an inert gas. Upon exposure to air some display hygroscopic properties, as revealed by the change of their spectra (see Experimental details).

2.2. Synthesis of $[RNH_3 \cdot (18\text{-crown-}6)]BPH_4$ salts

In order to better understand the factors governing the stability and aspects of the reactivity of alkylammonium tetraphenylborates in solution, we have prepared

a few adducts with a complexing agent able to engage the cation in an "host-guest" interaction. 1, 4, 7, 10, 13, 16-Hexaoxacyclooctadecane (18-crown-6) was choosen as the "host" receptor, and our investigations were restricted to compounds of the type $[RNH_3 \cdot (18\text{-crown-6})]BPh_4$ because of the higher stability of $[RNH_3 \cdot (18\text{-crown-6})]^+$ complexes towards dissociation compared to similar adducts involving di- or tri-alkylammonium cations [21].

Although in principle, compounds $[RNH_3 \cdot (18\text{-crown-6})]BPh_4$ can be prepared by treating $(RNH_3)BPh_4$ with a stoichiometric amount of the macrocyclic polyether, we have used a "one-pot" route summarized by Eq. (4).

$$2\ RNH_2 + NaBPh_4 + CO_2 + 18\text{-crown-6} \longrightarrow [RNH_3 \cdot (18\text{-crown-6})]BPh_4 + RNHCO_2Na \quad (4)$$

The $[RNH_3]O_2CNHR$ carbamate [14c,d], that rapidly precipitates upon reaction of CO_2 with the amine, redissolves quickly in the presence of the crown-ether to give $[RNH_3 \cdot (18\text{-crown-6})]O_2CNHR$ [14d], which, in turn, is converted into the tetraphenylborate salt by $NaBPh_4$ (Eqs. (5) and (6)).

$$2\ RR'NH + CO_2 + 18\text{-crown-6} \rightleftharpoons [RNH_3 \cdot (18\text{-crown-6})]O_2CNHR \quad (5)$$

$$[RNH_3 \cdot (18\text{-crown-6})]O_2CNHR + NaBPh_4 \longrightarrow [RNH_3 \cdot (18\text{-crown-6})]BPh_4 + RNHCO_2Na \quad (6)$$

Tetraphenylborates **1–6** and **1a–3a** have been characterized by IR, ^1H and, when required, ^{13}C NMR spectroscopy. Table 1 summarizes some selected IR data for compounds **1–6** and **1a–3a**. All the compounds show characteristic aromatic resonances as-

Table 1
Selected IR data (Nujol, NaCl disks, cm^{-1}) for **1–6** and **1a–3a** tetraphenylborate salts

BPh_4^- salt	ν(NH)	δ(NH)	$[BPh_4]^-$ ring skeletal stretching	$[BPh_4]^-$ ring out-of plane C–H deformation	
$NaBPh_4$	–	–	1578(m), 1475(m-s), 1426(m)	744(s),	713(s)
$KBPh_4$	–	–	1575(m), 1476(m-s), 1425(m)	743(s),	712(s)
1	3215(m-w,br) 3173(m,br) 3130(m,br) 3100(m,br)	1565(m,br) [a]	1578(m), 1475(m-s), 1425(m)	740(s),	710(s)
2	3207(m) 3180(m-s) 3150(m)	[b] 1485(m)	1575(m), 1475(m-s), 1425(m)	745(m-s) 739(s) 728(s) 720(m-s)	708(vs) 700(s)
3	3171(m,br) 3130(m,br) 3105(m)	[c] 1495(m)	1575(m), 1478(m-s), 1427(m)	740(vs) [d]	710(vs) [d]
4 [e]	3161(m-s) 3145(m-s) 3099(m)	1564(m,br)	1578(m), 1479(m-s), 1427(m-s)	741(vs)	710(vs)
5 [f]	3160(m-s) 3130(m-s)	1595(m-w) 1555(m-w)	1582(m), 1480(s), 1430(m-s)	738(vs)	712(vs)
6	3115(m,br)	1560(vw)?	1580(m), 1477(m-s), 1428(m-s)	736(vs)	708(vs)
1a [g]	3145(m,br) 3115(m) 3078(m-s,br)	1606(m,br) 1535(m-w,br)	1581(m), 1475(m), 1430(m)	750(m-s) 733(s)	707(s)
2a [h]	3150(m,br) 3103(m,br)	1604(m,br) 1535(m,br)	1579(m), 1475(m), 1427(m)	747(m-s) 733(s)	707(s)
3a [i]	3137(m) 3092(m-s,br)	1598(m-s,br) 1529(m,br)	1578(m), 1475(m), 1430(m)	750(m-s) [j] 731(s) [j]	716(m-s) [j] 707(s) [j] 691(m-s) [j]

[a] A shoulder centred at 1555 cm^{-1} is also observed. [b] Shoulder centred at about 1565 cm^{-1}. [c] Shoulder at about 1560 cm^{-1}. [d] A strong absorption is found at 698 cm^{-1} because of the phenyl ring of the benzyl cation. [e] Other bands of variable intensity (m → m-s) are found at 1358 (m), 1268 (m), 1184 (m-s), 1154 (m-s), 1147 (m-s), 1067 (m), 1044 (m), 1030 (m), 863 (m), 849 (m), 726 (m-s) cm^{-1}. [f] Other absorptions of medium intensity are found at 1405 (m), 1218 (m), 1185 (m), 1150 (m), 1107 (s), 1068 (m-w), 1045 (m), 1030 (m), 905 (m), 895 (m-w), 872 (m-s), 850 (m), 725 (m) cm^{-1}. [g] Other characteristic absorptions are found at 3062 (s), 3040 (m-s), 3002 (m-s), 1450 (m-s), 1350 (s, sh), 1283 (m), 1250 (m), 1130 (m-s), 1098 (vs), 1032 (m), 958 (s), 835 (m-s) cm^{-1}. [h] Other bands are observed at 3037 (m) 1452 (s), 1350 (s, sh), 1284 (m), 1267 (m), 1248 (m), 1125 (m-s), 1100 (vs), 1032 (m), 959 (s), 837 (m-s) cm^{-1}. [i] Other bands are found at 3068 (s), 3045 (m-s), 1450 (m-s), 1422 (m), 1350 (s, sh), 1284 (m), 1248 (m-s), 1133 (m = s), 1097 (vs), 1031 (m), 961 (s), 836 (s) cm^{-1}. [j] Accurate assignment of these absorptions is made difficult because of signals from the benzyl cation.

signed to the tetraphenylborate, multiplets at δ ca. 7.3 for *o*-protons, pseudo-triplets at δ ca. 6.9 for *m*-protons, and pseudo-triplets of triplets at δ ca. 6.8 for *p*-protons. These resonances are slightly solvent-dependent.

2.3. Stability and reactivity of alkylammonium BPh_4^- salts in solution

Although long known, the stability of alkylammonium tetraphenylborates has been studied in detail only in the solid state [5,12e]. Upon pyrolysis above 383 K solid alkylammonium tetraphenylborates decompose, generating benzene and amine-triphenylborane adducts, RR'R''N-BPh_3, and they also form, depending on the experimental conditions (temperature, number and size of the alkyl groups) other products, such as aminodiphenylboranes, borazine derivatives, and polymeric materials.

As far as the stability of this class of compound in solution is concerned, scanty information is available. Mordenti et al. [22] have reported the formation of $[Fe(NO)_2\{PhP(OCH_2CH_2)_2N(H)\cdot BPh_3\}_2]$ from $[Fe(NO)_2\{PhP(OCH_2CH_2)_2NH_2\}_2][BPh_4]_2$ in CH_3CN/diethyl ether, a transformation reminiscent of the conversion of cationic cyclopentadienyl iron complexes, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(LH)]BPh_4$, containing protonated imidazole or triazole (LH), into benzene and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(L\text{-}BPh_3)]$ upon heating in reflux THF [23]. These reactions involve the cleavage of a $[BAr_4]^-$ B–C bond, a process which is reported to be promoted both by transition metal [15a,c,e] and strong (on the aqueous scale) Brønsted acids [24].

We have decided to investigate more extensively the chemical behaviour of alkylammonium tetraphenylborates in solution.

2.3.1. Conversion of alkylammonium BPh_4^- salts into amine · BPh_3 via intramolecular protolytic cleavage of B–C bond

Although stable in the solid state, these salts exhibit only modest stability in solution.

The ^1H NMR spectra (293 K) of both CD_2Cl_2 and THF-d_8 solution of **1–6** salts can show significant changes with time. The appearance of a singlet at 7.36 ppm in CD_2Cl_2 solution, or 7.30 ppm in THF-d_8, reveals the formation of benzene and suggests the following transformation.

$$(RR'R''NH)BPh_4 \xrightarrow{THF \text{ or } CH_2Cl_2} PhH + RR'R''N\text{-}BPh_3 \quad (7)$$

(R = alkyl; R' or R'' = H or alkyl)

The formation of RR'R''N · BPh_3 has been confirmed by comparison of the spectra with those of authentical samples of the compounds prepared in situ by direct interaction of BPh_3 with RR'R''N.

We can exclude the solvent acting as a hydrogen-atom source in the process summarized by Eq. (7). No benzene-d_1 was detected (by GC-MS) in the reaction mixture when reaction (7) was carried out in deuterated solvents in CD_2Cl_2 or THF-d_8. The decomposition of the alkylammonium salts (Eq. (7)) must be strictly related to the acid character of the hydrogen atoms N-bonded in the cation. This is supported by the results obtained in the presence of suitable complexing agents (see below). These findings unequivocally show that alkylammonium cations, weak Brønsted acids on the aqueous scale, can promote the protolytic cleavage a B–C bond of $[BPh_4]^-$ and demonstrate that homogeneous conversion of alkylammonium tetraphenylborates into RR'R''N · BPh_3 is a general feature of the reactivity of alkylammonium tetraphenylborate.

In both azole complexes $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(LH)]BPh_4$ [23] and $[Fe(NO)_2\{PhP(OCH_2CH_2)_2NH_2\}_2][BPh_4]_2$ [22], decomposition has been postulated to be related, from a mechanistic point of view, to the presence of suitably arranged crystallization solvent molecules (acetone, water, ethanol) interacting through hydrogen bonds with the protonated nitrogen sites and acting as proton relay between the protonated nitrogen atoms and $[BPh_4]^-$. However, **1**, which has been obtained free of solvent of crystallization (THF), smoothly changes to the corresponding BPh_3 adduct in dichloromethane. Small amounts of water in a THF-d_8 solution of **6** have practically no effect on the decomposition rate of the $[BPh_4]^-$ salt. This suggests that proton-transfer from an alkylammonium ion to $[BPh_4]^-$ can occur directly, and not as reported for azole bound to iron.

At room temperature the complete conversion of the $[BPh_4]^-$ salts requires reaction times ranging from a few hours to several days. For example, in CH_2Cl_2 (or CD_2Cl_2), **1** almost completely converts into the

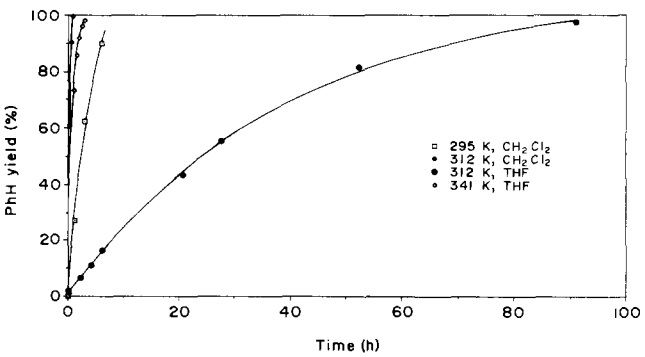


Fig. 1. Kinetics of decomposition of **1** (Eq. (7), R = allyl) in different solvents (CH_2Cl_2, THF) and at different temperatures. Molar concentration of **1** in the different runs: 9.6 mM (295 K, CH_2Cl_2); 8.2 mM (312 K, CH_2Cl_2); 7.9 mM (312 K, THF); 8.0 mM (341 K, THF).

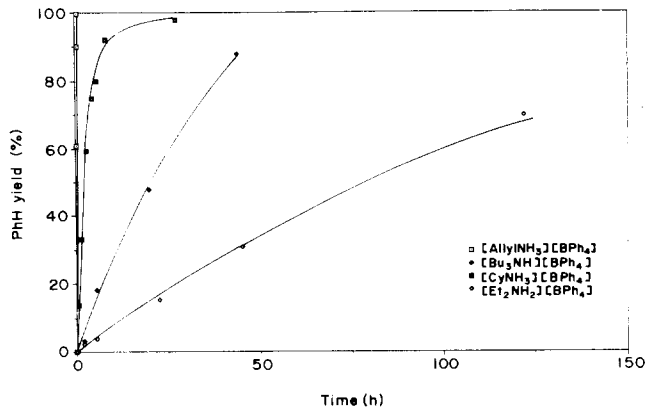


Fig. 2. Kinetics of decomposition of **1**, **2**, **4** and **6** salts (Eq. (7)) in CH_2Cl_2 at 312 K. Molar concentrations: **1**, 8.2 mM; **2**, 6.3 mM; **4**, 7.3 mM; **6**, 10.5 mM.

corresponding adduct within 6 h at 293 K (see Fig. 1). Conversely, only small amounts of benzene could be detected by ^1H NMR in a CD_2Cl_2 solution of **4** or **6** held at room temperature for a few days. In general, the decomposition rate varies with alkylammonium cation and solvent [25].

The dependence on the cation is demonstrated in Fig. 2, in which the kinetics of decomposition of **1**, **2**, **4**, **6**, at 312 K, in CH_2Cl_2, are reported. These data unequivocally show that the reactivity of primary alkylammonium tetraphenylborates is higher than that of di- and tri-alkylammonium tetraphenylborates and underline the influence of steric factors on the rate of reaction (7).

Fig. 1 also illustrates the influence of the solvent on **1**. At 312 K in THF, the decomposition of **1** is much slower than in CH_2Cl_2. Such behaviour has also been observed for **2** and **6**, and may be a result of the different abilities of the solvents to interact through hydrogen bonds with the alkylammonium ions, which can influence the reactivity of the cation as proton transfer agent. The influence of the temperature is

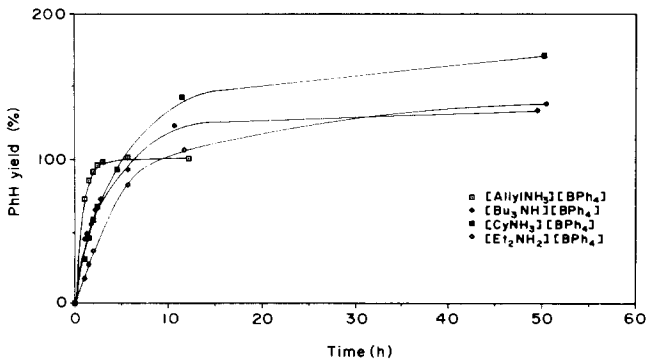


Fig. 3. Kinetics of decomposition of **1**, **2**, **4** and **6** salts (Eq. (9)) in THF at 341 K. Molar concentrations: **1**, 8.0 mM; **2**, 7.5 mM; **4**, 7.3 mM; **6**, 7.9 mM.

Table 2
Conductivity data for some alkylammonium tetraphenylborate [a]

BPh_4^- salt	Solvent	Concentration	Λ [b]
1	CH_2Cl_2	0.011 M [c]	2.6
1	CH_2Cl_2	0.0020 M	1.5
1	THF	0.10 M	12.0
1	THF	0.0021 M	16.3
1a [d]	CH_2Cl_2	0.047 M	14.1
1a	CH_2Cl_2	0.00046 M [c]	68.6

[a] All samples were prepared under dinitrogen and the measurements were carried out at 293 K. [b] In ohm^{-1} cm^2 mol^{-1}. [c] The poor solubility of **1** in CH_2Cl_2 prevented us from obtaining conductance data at higher concentrations. [d] Prepared in situ by dissolving **1** and an excess of 18-crown-6 (BPh_4^-: crown-ether molar ratio-1:2.5) in CH_2Cl_2. [e] Prepared by diluting the 0.047 M solution (see footnote [d] in this table).

shown in Fig. 3. At 341 K, compounds **1**, **2**, **4** and **6** decompose quite fast even in THF. However, for **2**, **4** and **6**, benzene yields exceed 100% (Fig. 3). This suggests that at 341 K in THF, more than one phenyl group per $[BPh_4]^-$ can be eliminated.

These preliminary kinetic data fit a first-order rate law, consistent with the intramolecular character of the proton transfer, and suggest that alkylammonium tetraphenylborates may exist as ion-pairs in CH_2Cl_2 and THF. The occurrence of an ion pairing phenomenon seems to be supported by conductivity data (Table 2) [26–28].

2.3.2. Intermolecular proton transfer from alkylammonium salts to acetone: easy synthesis of iminium tetraphenylborates

A further type of reaction takes place in acetone.

The ^1H NMR (200 MHz, 293 K) spectrum of a solution obtained by treating **4** with acetone-d_6 shows, two quadruplets at 4.00 ppm and 3.33 ppm, (4H) and a triplet (6H) at 1.38 ppm besides the usual signals of $[BPh_4]^-$ anion [29]. Both decoupling and D_2O addition [29] experiments reveal that the signal at 1.38 ppm is a result of accidentally isochronous, but non-equivalent, methyl protons and, more generally, confirm the presence of two sets of non-equivalent ethyl protons. Further evidence comes from the $^{13}C\{^1H\}$ NMR (125.7 MHz, 293 K) spectrum of the same sample which shows two singlets at 12.44 ppm and 12.29 ppm (CH_3) and two other signals at 51.13 ppm and 44.02 ppm (CH_2) [30]. These findings suggest that $[Et_2NH_2]^+$ in acetone is involved in a reaction, most probably with the solvent.

When **4** was treated in a bulk experiment with acetone under dinitrogen at 295 K, a new colourless solid, slightly soluble in acetone, was isolated and identified as $[Et_2N{=}CMe_2][BPh_4]$. The IR spectrum (Nujol) of $[Et_2N{=}CMe_2][BPh_4]$ shows a medium-strong band at 1655 cm^{-1}, assigned to ν(C=N). The high-field region of the ^1H NMR spectrum (200 MHz, 293 K) of

$[Et_2N{=}CMe_2][BPh_4]$ in acetone-d_6 shows signals at 4.05 (q, 4H), 2.64 (s, slightly broad, ≅ 6H) and 1.41 ppm (t, 6H) resulting from the $[Et_2N{=}CMe_2]^+$ cation [31]. Therefore, in acetone, **4** is easily (293 K) converted in good yield into a tertiary iminium tetraphenylborate salt according to Eq. (8).

$$[Et_2NH_2][BPh_4] + Me_2C{=}O \rightleftharpoons [Et_2N{=}CMe_2][BPh_4] + H_2O \quad (8)$$

This behaviour is not confined to secondary amine tetraphenylborates. In fact, **1** easily reacts with acetone to give $[CH_2{=}CHCH_2NH{=}CMe_2][BPh_4]$, which can be isolated as a pure salt in practically quantitative yield. Similarly, the ^1H spectrum (200 MHz, 293 K) of **2** in acetone-d_6 shows two multiplets at 4.09 ppm and 3.37 ppm, (1H) (compared to the signals of $[BPh_4]^-$) and assigned to the methine protons of $CyNH{=}C(CD_3)_2^+$ and $CyNH_3^+$ respectively. No reaction seems to take place when a tertiary amine derivative, such as **6**, is dissolved in acetone. The ^{13}C NMR spectrum of such a solution (125.76 MHz, 293 K, CD_3CN ext. ref.) shows that only **6** is present, and it can be recovered by evaporating the solvent in vacuo.

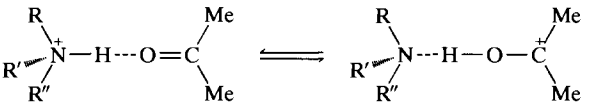
Therefore, mono- and di-alkylammonium tetraphenylborates easily convert in acetone into the corresponding iminium salts (Eq. (9)). The importance of the iminium group in

$$[RR'NH_2][BPh_4] + Me_2C{=}O \rightleftharpoons [RR'N{=}CMe_2][BPh_4] + H_2O \quad (9)$$

R′ = H, alkyl

preparative chemistry is well-documented [32]. The reaction of anilinium or secondary amine salts with carbonyl compounds can afford iminium salts [33], but the usefulness of this reaction as a synthetic route to iminium derivatives is limited by the use of unsafe amine perchlorate salts, because unsatisfactory results were found with other anions (fluoroborates, chlorides, bromides, nitrates, sulphates) [33a]. Indeed, reaction (9) offers a few advantages from a synthetic point of view, as iminium tetraphenylborates can be obtained in good-to-excellent yields and under safer conditions than with the perchlorates.

The reactivity of alkylammonium tetraphenylborates in acetone clearly indicates that, in this solvent, the intermolecular transfer of a proton to a solvent molecule is much more kinetically favoured than the intramolecular proton transfer to one of the $[BPh_4]^-$ phenyl rings, which is completely inhibited. The change of reactivity can be explained assuming that alkylammonium tetraphenylborates are strong electrolytes in acetone [34*]. The alkylammonium cations hydrogen-bond with the carbonyl oxygen of solvent molecules, so that proton transfer to carbonyl can once more be considered as an "intramolecular" process rather than an "intermolecular" process (Scheme 1).



Scheme 1.

2.3.3. Proton transfer inhibition: the effect of a complexing agent

The engagement of the alkylammonium cation in a "host-guest" interaction with a suitable complexing agent further modifies the reactivity of the salts. This clearly emerges from the reactivity of **1a–3a** salts in both CD_2Cl_2 and acetone-d_6. The low solubility of **1a–3a** in THF prevented us from studying the behaviour of the compounds in this solvent.

The ^1H spectrum of a CD_2Cl_2 solution of **3a** does not show signals resulting from the formation of benzene, even after one day at room temperature. Analogous stability is shown in CD_2Cl_2 on **1a** prepared in situ by treating **1** with an excess of 18-crown-6. The change of reactivity can be ascribed to thermodynamic factors, such as the lower acidity of complexed alkylammonium cation [35] and the stability of the "host-guest" adduct towards dissociation (Eq. (10)).

$$[RNH_3 \cdot (18\text{-crown-6})]^+ \rightleftharpoons 18\text{-crown-6} + RNH_3^+ \quad (10)$$

No iminium salts have been observed (by ^1H NMR spectroscopy) when **1a–3a** salts were dissolved in acetone-d_6. The higher coordinating power of acetone-d_6 with respect to CD_2Cl_2 is still not sufficient to shift equilibrium (11) to the right.

$$[RNH_3 \cdot (18\text{-crown-6})]^+ + Me_2C{=}O \rightleftharpoons [RNH{=}CMe_2]^+ + 18\text{-crown-6} + H_2O \quad (11)$$

These findings clearly demonstrates that proton transfer from alkylammonium ion to $[BPh_4]^-$ or acetone (Eqs. (7) and (9), respectively) can be effectively blocked by a suitable complexing agent able to bind the cation firmly.

3. Conclusions

We have shown that anhydrous alkylammonium tetraphenylborate salts can be easily prepared in mild conditions and high yield from amines and $NaBPh_4$ in the presence of CO_2. The marked tendency of these systems to act as proton transfer agents considerably affects their stability in solution.

In both CH_2Cl_2 and THF solution, alkylammonium tetraphenylborate salts can generate benzene through

intramolecular protolytic cleavage of a B–C bond, also forming amine · BPh_3 adducts.

In acetone, proton transfer from the ammonium cation to a solvent molecule takes place, that results in a high yield of secondary or tertiary iminium tetraphenylborate. Indeed, this conversion must be considered an intramolecular transfer to acetone bound via H-bonds to the ammonium cation.

We have also found that the proton transfer from alkylammonium cations can be inhibited by complexing the cation with a crown ether.

4. Experimental details

Unless otherwise stated, all reactions and manipulations were carried out under dinitrogen or carbon dioxide (as specified in the text) with rigorous exclusion of both air and atmospheric moisture, by using vacuum line techniques. All solvents were dried as described in the literature [36] and stored under dinitrogen. The amines used (from Fluka, Aldrich, Farmitalia Carlo Erba) were dried according to conventional methods [36] and, then, distilled before use. $Na[BPh_4]$ and 18-crown-6 were Aldrich products. CO_2 (99.99% pure) was from SIO S.p.A.

IR spectra were obtained with a Perkin Elmer 883 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded with a Varian XL 200 or a Bruker AM 500 machine. Proton and carbon chemical shifts are in ppm vs. TMS and have been referenced to the solvent peak. GC-MS analyses were carried out with a HP 5890 gas-chromatograph linked to a HP 5970 selective mass detector (capillary column: 30 m SE-30, 0.25 mm film thickness). HPLC analyses were performed with a Perkin Elmer Series 4 LC (column: Erbasil C18/M, 10 μm, 250 × 4,6 mm) connected with a LC 290 UV/Vis spectrophotometer detector. Electrolytic conductivity measurements were made on a WTW conductivity meter apparatus.

4.1. Synthesis of $[CH_2{=}CHCH_2NH_3][BPh_4]$ (1)

A THF (50 ml) solution of $NaBPh_4$ (4.558 g, 13.3 mmol) and $CH_2{=}CHCH_2NH_2$ (2.0 ml, 26.6 mmol), prepared under dinitrogen, was saturated with CO_2 at 273 K. The white precipitate was filtered under CO_2, washed with dichloromethane (2 × 15 ml) and dried in vacuo. The mother liquor and washing solutions were collected and concentrated in vacuo. Addition, under a dinitrogen stream, of petroleum ether (60 ml) and cooling to 253 K yielded a white precipitate of $[CH_2{=}CHCH_2NH_3][BPh_4]$, which was filtered off, washed with more petroleum ether (2 × 20 ml) and dried in vacuo (yield: 4.266 g, 85%).

Anal. Calc. for $C_{27}H_{28}BN$: C, 85.94; H, 7.48; N, 3.71. Found: C, 85.79; H, 7.41; N, 3.65%. IR (Nujol, NaCl disks, cm^{-1}): see Table 1. ^1H NMR (THF-d_8, 200 MHz, 293 K): δ 2.88 (dt, CH_2^3, J_{H-H} = 6.10 Hz, $^4J_{H-H}$ = 1.2 Hz), 5.15 (dq, C=C(H)H, $^3J_{trans}$ = 17.04 Hz, $^2J_{H-H} \cong {}^4J_{H-H}$), 5.24 (dq, C=C(H)$H$, $^3J_{cis}$ = 10.37 Hz), 5.54 (m, CH=CH_2), 5.9 (broad, NH_3). ^1H NMR (CD_2Cl_2, 200 MHz, 293 K): δ 2.14 (d, CH_2, $^3J_{H-H}$ = 5.56 Hz), 4.92 (dd, C=C(H)H, $^3J_{trans}$ = 16.58 Hz, $^2J_{H-H}$ = 2.04 Hz), 5.06 (m, CH=CH_2), 5.19 (dd, C=C(H)H, $^3J_{cis}$ = 9.44 Hz).

4.2. Synthesis of $[CyNH_3][BPh_4]$ · THF (2)

To a THF (60 ml) solution of $NaBPh_4$ (2.988 g, 8.73 mmol) and $CyNH_2$ (2.0 ml, 17.5 mmol), prepared under dinitrogen and then saturated with CO_2 at 273 K, 30 ml of petroleum ether were added. The white precipitate formed was filtered off under CO_2, washed with dichloromethane (2 × 15 ml) and dried in vacuo. The mother liquor and washing solutions were collected and concentrated in vacuo. Addition under dinitrogen of petroleum ether (40 ml) and cooling to 253 K yielded a white precipitate of $[CyNH_3][BPh_4]$ · THF, which was filtered off, washed with more petroleum ether (2 × 15 ml) and dried in vacuo (yield: 3.818 g, 89%).

Anal. Calc. for $C_{34}H_{42}BNO$: C, 83.08; H, 8.61; N, 2.85. Found: C, 82.86; H, 8.64; N, 2.79%. IR (Nujol, NaCl disks, cm^{-1}): see Table 1. Upon exposure of the sample to the air (15 min), two slightly broadened bands appear at 3580 cm^{-1} and 3515 cm^{-1}, while a lower resolution is observed in the region 3200–3100 cm^{-1}, and the absorptions between 700 cm^{-1} and 750 cm^{-1} convert into two bands at 740 cm^{-1} and 710 cm^{-1}. ^1H NMR (THF-d_8, 200 MHz, 293 K): δ 0.87–1.28 (m, slightly broad, 5H, CH_2), 1.50–1.84 (m, remaining CH_2 protons), 1.77 (m, THF-protons), 2.44 (m, slightly broad, H_3NCH), 3.62 (m, THF protons), 5.8 (broad, NH_3). ^1H NMR (CD_2Cl_2, 200 MHz, 293 K): δ 0.46–0.58 (m, broad, 2H, CH_2), 0.85–1.15 (m, broad, 3H, CH_2), 1.22–1.29 (d, broad, 2H, CH_2), 1.45–1.70 (m, broad, 3H, CH_2), 1.75 (m, H_3NCH), 1.83 and 3.63 (m, THF protons). ^1H NMR (acetone-d_6, 200 MHz, 293 K): δ 1.78 and 3.62 (m, THF protons); the region 1.1–2.2 ppm shows signals assigned to the methylene protons of both $CyNH_3^+$ and $CyNH{=}C(CD_3)_2^+$ cations; the methine protons of both $CyNH_3^+$ and $CyNH{=}C(CD_3)_2^+$ cations resonate, respectively, at 3.37 (m) and 4.09 ppm (m), the sum of their integrals being equal to 1H.

4.3. Synthesis of $[PhCH_2NH_3][BPh_4]$ · 0.5 THF (3)

This salt was obtained using the same procedure followed for **1** [THF: 45 ml; $NaBPh_4$: 3.136 g, 9.16 mmol; $PhCH_2NH_2$: 2.0 ml, 18.3 mmol] (yield: 3.608 g, 85%).

Anal. Calc. for $C_{33}H_{34}BNO_{0.5}$: C, 85.52; H, 7.39; N, 3.02. Found: C, 85.18; H, 7.28; N, 3.09%. IR (Nujol, NaCl disks, cm^{-1}): see Table 1. ^1H NMR (THF-d_8, 200 MHz, 293 K): δ 1.77 and 3.62 (m, THF protons), 3.51 (s, slightly broad, CH_2), 5.65 (broad, NH_3), 7.15 (m, 2H, $PhCH_2$ protons), 7.35 (m, 11H, H_{o,BPh_4} and remaining $PhCH_2$ protons). ^1H NMR (CD_2Cl_2, 200 MHz, 293 K): δ 1.84 and 3.63 (m, THF protons), 2.93 (s, slightly broad, CH_2), 6.94 (m, 2H, $PhCH_2$ protons), 7.35 (m, 3H, $PhCH_2$ protons).

4.4. Synthesis of $[Et_2NH_2][BPh_4]$ (4)

A THF (30 ml) solution of $NaBPh_4$ (3.319 g, 9.70 mmol) and Et_2NH (2.0 ml, 19.3 mmol), prepared under dinitrogen, was saturated with CO_2 at 273 K. The solution remained limpid and was stirred vigorously for 0.5 h. Upon addition of pentane (60 ml) a colourless solid precipitated, that was filtered off, washed with pentane (2 × 10 ml) and dried in vacuo. Upon recrystallization from THF: diethyl ether (1 : 1 v/v) 2.926 g of pure **4** were recovered. By adding diethyl ether to the recrystallization liquor more tetraphenylborate was obtained (overall yield = 3.320 g, 87%).

Anal. Calc. for $C_{28}H_{32}BN$: C, 85.49; H, 8.20; N, 3.56. Found: C, 85.15; H, 8.38; N, 3.45%. IR (Nujol, NaCl disks, cm^{-1}): see Table 1. ^1H NMR (THF-d_8, 200 MHz, 293 K): δ 0.99 (t, CH_3, $^3J_{H-H}$ = 7.30 Hz), 2.53 (q, CH_2), 4.74 (broad, NH_2). ^1H NMR (CD_2Cl_2, 200 MHz, 293 K): δ 0.75 (t, CH_3, $^3J_{H-H}$ = 7.30 Hz), 2.03 (q, CH_2). $^{13}C\{^1H\}$ NMR (THF-d_8, 125.76 MHz, 293 K): δ 10.61 (s, CH_3), 42.25 (s, CH_2), 120.68 (s, C_{para}), 124.55 (q, C_{meta}, $^3J_{C-B}$ = 2.66 Hz), 135.76 (s, C_{ortho}), 163.84 (q, C_{ipso}, $^1J_{C-B}$ = 49.26 Hz).

4.5. Synthesis of $[C_4H_{10}NO][BPh_4] \cdot 0.5$ THF (5)

To a THF (100 ml) solution of $NaBPh_4$ (3.936 g, 11.5 mmol), saturated with CO_2 at 273 K, morpholine (2.0 ml, 22.9 mmol) was added. The resulting suspension was treated with pentane (170 ml) and, after cooling to 253 K, filtered under CO_2. The filtered solid was extracted with THF (3 × 30 ml), and the resulting THF solution concentrated in vacuo. By addition of pentane and cooling to 253 K a white solid was obtained, which was isolated by filtration under dinitrogen and recrystallized from THF: diethyl ether to give, after drying in vacuo, pure **5** (yield: 3.977, 78%).

Anal. Calc. for $C_{30}H_{34}BNO_{0.5}$: C, 81.26; H, 7.73; N, 3.16. Found: C, 81.53; H, 7.85; N, 3.06%. IR (Nujol, NaCl disks, cm^{-1}): see Table 1. ^1H NMR (THF – d_8, 200 MHz, 293 K): δ 1.77 and 3.61 (m, THF protons), 2.58 (m, NCH_2), 3.49 (m, OCH_2), 4.62 (broad, NH_2). ^1H NMR (CD_2Cl_2, 200 MHz, 293 K): δ 1.82 and 3.68 (m, THF protons), 2.04 (pseudo-t, broad, NCH_2, $J \cong 5$ Hz), 3.32 (pseudo-t, OCH_2, $J \cong 5$ Hz).

4.6. Synthesis of $[Bu_3NH][BPh_4] \cdot 0.25$ THF (6)

To a THF (30 ml) solution of $NaBPh_4$ (3.754 g, 11.0 mmol), saturated with CO_2 at 273 K, aniline (1.0 ml, 11.0 mmol) and tri-butylamine (2.6 ml, 11.0 ml) were added. The resulting suspension was treated with 80 ml of pentane, cooled to 253 K, and filtered under CO_2. The solid on the filter was extracted with dichloromethane (3 × 20 ml), the CH_2Cl_2 solution was evaporated in vacuo, and the residue recrystallized under dinitrogen from THF (10 ml)/diethyl ether (70 ml) at 253 K. The white solid precipitated was isolated by filtration, washed with diethyl ether (3 × 15 ml) and dried in vacuo (yield: 4.453 g, 77%).

Anal. Calc. for $C_{37}H_{40}BNO_{0.25}$: C, 84.87; H, 9.63; N, 2.67. Found: C, 84.60; H, 9.78; N, 2.62%. IR (Nujol, NaCl disks, cm^{-1}): see Table 1. Upon exposure of a sample to the air, new absorptions appear at 3585 (m), 3510 (m), 1595 (m-w) cm^{-1} in the IR spectrum; minor changes are also observed in the regions 1020–1050 cm^{-1}, and 700–750 cm^{-1}. ^1H NMR (THF-d_8, 200 MHz, 293 K): δ 1.78 and 3.62 (m, THF protons), 0.93 (t, CH_3, $^3J_{H-H}$ = 7.13 Hz), 1.28 (m, CH_2CH_3), 1.46 (m, CH_2CH_2), 2.77 (m, slightly broad, NCH_2; this signal lies on a broad resonance assigned to the NH proton). The assignment was supported by decoupling experiments. ^1H NMR (CD_2Cl_2, 200 MHz, 293 K): δ 1.82 and 3.68 (THF protons), 0.91 (t, CH_3, $^3J_{H-H} \cong 7$ Hz), 1.18 (m, CH_2CH_2), 2.22 (m, slightly broadened, (NCH_2). ^1H NMR (acetone-d_6, 200 MHz, 293 K): δ 3.62 (m, THF protons; the remaining THF protons are masked by the multiplet at 1.79 ppm), 0.94 (t, CH_3, $^3J_{H-H}$ = 7.37 Hz), 1.40 (m, CH_2CH_3), 1.79 (m, CH_2CH_2), 3.33 (m, slightly broad, NCH_2). The assignment was established by decoupling experiments. A slightly different assignment was reported by Petersen [7e]. $^{13}C\{^1H\}$ NMR (acetone-d_0, 125.76 MHz, 293 K, CD_3CN ext. ref.): δ 13.01 (s, CH_3), 19.64 (s, NCH_2CH_2), 25.78 (s, CH_2CH_3), 53.43 (s, NCH_2), 121.45 (s, C_{para}, 125.20 (q, C_{meta}, $^3J_{C-B}$ = 2.8 Hz), 136.28 (s, C_{ortho}), 164.41 (q, C_{ipso}, $^1J_{C-B}$ = 49.0 Hz).

4.7. Synthesis of $[PhCH_2NH_3 \cdot (18\text{-crown-}6)][BPh_4]$ (3a)

A THF suspension of $[PhCH_2NH_3][O_2CNH(CH_2Ph)]$, obtained by saturating a THF (40 ml) solution of $PhCH_2NH_2$ (3.0 ml, 27.5 mmol) with CO_2 at 293 K, was treated with 18-crown-6 (3.69 g, 14.0 mmol). After dissolution of the carbamate, a THF (25 ml) solution of $NaBPh_4$ (4.680 g, 13.7 mmol) was added to the reaction mixture. The white precipitate formed was filtered off under CO_2, washed with THF (2 × 20 ml), and then extracted with dichloromethane (4 × 20 ml). The CH_2Cl_2 fractions were collected together and the resulting solution concentrated in vacuo and then treated with THF (100 ml). By cooling to 253 K a white

precipitate was obtained, which was filtered off, washed with THF (2 × 15 ml) and dried in vacuo (yield: 8.055 g, 85%).

Anal. Calc. for $C_{43}H_{54}BNO_6$: C, 74.67; H, 7.87; N, 2.02. Found: C, 74.95; H, 8.00; N, 2.00%. IR (Nujol, NaCl disks, cm^{-1}): see Table 1. ^1H NMR (acetone-d_6, 200 MHz, 293 K): δ 3.60 (s, OCH_2CH_2O), 4.09 (s, broad, $PhCH_2$), 7.4–7.6 (m, $PhCH_2$ protons). The multiplet at 7.5 ppm lies on a very broad signal assigned to the NH_3 group protons [37]. ^1H NMR (CD_2Cl_2, 200 MHz, 293 K): δ 3.50 (m, OCH_2CH_2O), 3.83 (s, broad, $PhCH_2$), 7.49 and 7.4 (m, $PhCH_2$ protons). The NH_3 protons give a broad resonance between 7.0 ppm and 7.7 ppm [38]. The spectrum was also measured at 308 K, and the multiplet at 3.50 ppm almost completely collapsed into a broad singlet, most probably, as a result of the higher face-to-face exchange rate of the alkylammonium guest [38].

4.8. Synthesis of $[CH_2=CHCH_2NH_3 \cdot (18\text{-crown-}6)][BPh_4]$ (1a)

2.282 g of $NaBPh_4$ (6.67 mmol), dissolved in THF (25 ml), were added under a CO_2 stream to a THF (20 ml) solution of $[CH_2=CHCH_2NH_3 \cdot (18\text{-crown-}6)][O_2CNH(CH_2CH=CH_2)]$, prepared as described for (**3a**) [$CH_2=CHCH_2NH_2$: 1.0 ml, 13.3 mmol; 18-crown-6: 1.763 g, 6.66 mmol]. The white precipitate formed was filtered under CO_2, washed with THF (2 × 5 ml) and dried in vacuo. More solid could be isolated from the mother liquor and washing solutions upon addition of petroleum ether (40 ml) and cooling to 253 K. The collected solids were extracted with dichloromethane (4 × 20 ml) under a CO_2 atmosphere and the resulting solution was concentrated in vacuo. By adding petroleum ether (40 ml) and cooling to 253 K, a white precipitate of pure $[CH_2=CHCH_2NH_3 \cdot (18\text{-crown-}6)][BPh_4]$ was obtained, which was isolated by filtration under dinitrogen, washed with petroleum ether and dried in vacuo (yield: 3.681 g, 86%).

Anal. Calc. for $C_{39}H_{52}BNO_6$: C, 73.00; H, 8.17; N, 2.18. Found: C, 72.71; H, 8.18; N, 2.11%. IR (Nujol, NaCl disks, cm^{-1}): see Table 1. ^1H NMR (acetone-d_6, 200 MHz, 293 K): δ 3.56 (d, broad, CH_2), 3.67 (s, OCH_2CH_2O), 5.43 (dm, C=C(H)*H*, $^3J_{cis}$ = 10.12 Hz), 5.51 (dq, C=C(*H*)H, $^3J_{trans}$ = 17.07 Hz, $^2J_{H-H} \cong {}^4J_{H-H}$ = 1.36), 6.00 (m, $CH=CH_2$, $^3J_{H-H}$ = 6.95 Hz). A very broad signal, from the NH_3 protons [37], is evident in the aromatic region, but is partially covered by the signals of the $[BPh_4]^-$ *ortho* protons. ^1H NMR (CD_2Cl_2, 200 MHz, 293 K): δ 3.37 (d, slightly broad, CH_2, $^3J_{H-H}$ = 6.95 Hz), 3.60 (s, OCH_2CH_2O), 5.45 (dm, C=C(H)*H*, $^3J_{cis}$ = 9.91 Hz, $^2J_{H-H} \cong {}^4J_{H-H}$ = 0.99 Hz), 5.46 (dm, C=C(*H*)H, $^3J_{trans}$ = 17.23 Hz, $^2J_{H-H} \cong {}^4J_{H-H}$ = 1.23), 5.90 (m, $CH=CH_2$). The spectrum also shows a very broad signal at approximately 7.4 ppm and assigned to the cation NH protons [38].

4.9. Synthesis of $[CyNH_3 \cdot (18\text{-crown-}6)][BPh_4]$ (2a)

This compound was prepared using the procedure described for (**1a**) [$CyNH_2$: 1.0 ml, 8.74 mmol; 18-crown-6: 1.159 g, 4.38 mmol; $NaBPh_4$: 1.501 g, 4.38 mmol] (yield: 2.545 g, 85%).

Anal. Calc. for $C_{42}H_{58}BNO_6$: C, 73.78; H, 8.55; N, 2.05. Found: C, 74.00; H, 8.64; N, 1.98%. IR (Nujol, NaCl disks, cm^{-1}): see Table 1. ^1H NMR (acetone-d_6, 200 MHz, 293 K): δ 1.1–1.5 (m, broad, 5H, cyclohexyl CH_2 protons), 1.6–1.9 (m, broad, 3H, cyclohexyl CH_2 protons), 2.13 (m, broad, 2H, cyclohexyl CH_2 protons), 3.1 (m, broad, $CyNH_3^+$ methine proton), 3.67 (s, OCH_2CH_2O). The $CyNH_3^+$ protons give a very broad signal centred between 7.2 ppm and 7.1 ppm [37].

4.10. Conversion of $[RR'R''NH][BPh_4]$ (1–6) into benzene and $RR'R''N \cdot BPh_3$ adducts (293 K, CD_2Cl_2 or THF-d_8 solution)

The CD_2Cl_2 or THF-d_8 solution of the $[BPh_4]^-$ salt (**1–6**) was prepared under dinitrogen, transferred to an NMR tube and sealed under an inert gas. The ^1H spectra were measured at 200 MHz and 293 K. In all runs the benzene was found as a singlet at 7.36 ppm in CD_2Cl_2 and at 7.30 ppm in THF-d_8 solution.

4.10.1. $[CH_2=CHCH_2NH_3][BPh_4]$ in CD_2Cl_2

The ^1H NMR spectrum of the solution, after the complete conversion (6.5 h) of **1**, showed the presence of benzene and $CH_2=CHCH_2NH_2 \cdot BPh_3$: δ 3.31 (m, broad, CH_2), 4.37 (broad, NH_2), 5.2–5.4 (m, broad, C=CH_2), 5.91 (m, slightly broad, $CH=CH_2$, $^3J_{H-H}$ = 6.2 Hz, $^3J_{trans}$ = 17.6 Hz, $^3J_{cis}$ = 9.8 Hz), 7.12–7.29 (m, BPh_3 protons).

4.10.2. $[CH_2=CHCH_2NH_3][BPh_4]$ in THF-d_8

After 36 h the conversion was estimated to be more than 90%. The ^1H NMR spectrum of the solution showed signals resulting from $CH_2=CHCH_2NH_2 \cdot BPh_3$ at: δ 3.26 (m, broad, CH_2), 5.16 (dq, C=C(H)*H*, $^3J_{cis}$ = 10.23 Hz), 5.22 (dq, C=C(*H*)H, $^3J_{trans}$ = 17.20 Hz, $^2J_{H-H} \cong {}^4J_{H-H}$ 1.47 Hz), 5.78 (broad, NH_2), 5.95 (m, $CH=CH_2$), 6.98–7.28 (m, BPh_3 protons).

4.10.3. $[CyNH_3][BPh_4] \cdot THF$ in CD_2Cl_2

Almost complete conversion (almost 90%) was observed after 2.5 days. The ^1H signals from $CyNH_2 \cdot BPh_3$ appeared at: δ 1.1 (broad, 5H, CH_2), 1.6 (broad, 5H, CH_2), 1.9 (very broad, H_2NCH), 4.1 (very broad, NH_2), 7.11–7.37 (m, BPh_3 protons).

4.10.4. $[CyNH_3][BPh_4] \cdot THF$ in THF-d_8

The conversion was more than 90% after 36 h. The signals from $CyNH_2 \cdot BPh_3$ were found at: δ 0.9–1.3 (broad, 5H, CH_2), 1.3–1.7 (broad, 5H, CH_2), 2.82 (very broad, H_2NCH), 5.13 (very broad, NH_2), 6.96–7.15 and 7.32–7.39 (m, BPh_3 protons).

4.10.5. $[PhCH_2NH_3][BPh_4] \cdot 0.5\ THF$ in CD_2Cl_2

The conversion was complete within 4 h. The signals from $PhCH_2NH_2 \cdot BPh_3$ appeared at: δ 3.85 (m, broad, CH_2), 4.65 (broad, NH_2), 7.13–7.44 (BPh_3 and $PhCH_2$ protons).

4.10.6. $[PhCH_2NH_3][BPh_4] \cdot 0.5\ THF$ in THF-d_8

The conversion was approximately equal to 60–70% after 3 days. The signals from $PhCH_2NH_2 \cdot BPh_3$ were observed at: δ 3.75 (broad, CH_2), 5.96 (br, NH_2), 6.95–7.40 (BPh_3 and $PhCH_3$ protons).

4.10.7. $[Et_2NH_3][BPh_4]$ in CD_2Cl_2

The spectrum measured after 15 h showed the presence of small amounts of benzene. However, the conversion still was very low after 2 days.

4.10.8. $[Et_2NH_2][BPh_4]$ in THF-d_8

The system showed no signs of reaction after 15 h.

4.10.9. $[C_4H_{10}NO][BPh_4] \cdot 0.5\ THF$ in CD_2Cl_2

A complete conversion was observed within 15 h. The ^1H signals of the adduct $O(CH_2CH_2)_2NH \cdot BPh_3$ were found at δ 2.65 (broad, 2H, NCH_2), 3.31 (broad, 2H, NCH_2), 3.85 (broad, OCH_2), 4.4 (very broad, NH), 7.09–7.39 (m, BPh_3 protons).

4.10.10. $[C_4H_{10}NO][BPh_4] \cdot 0.5\ THF$ in THF-d_8

The signals from the decomposition of the salt were evident within 14 h. However, the conversion was approximately 40–50% after 3.5 days. The ^1H NMR spectrum of the solution showed new signals at 2.47 (m, slightly broad), 2.65 (m, slightly broad), 3–4 (very broad), 6.95–7.20 and 7.25–7.45 ppm.

4.10.11. $[Bu_3NH][BPh_4] \cdot 0.25\ THF$ in CD_2Cl_2

The signal of benzene was already evident in the spectrum after 24 h. However, the conversion was very slow (approximately 10% after 2 days).

4.10.12. $[Bu_3NH][BPh_4] \cdot 0.25\ THF$ in THF-d_8

The system showed no sign of decomposition after 1 d, even when traces of water were added.

4.11. Kinetic measurements

In a typical experiment, a CH_2Cl_2 or THF solution of the tetraphenylborate salt containing toluene as internal standard was heated at a given temperature (± 1 K). At measured times the solution was cooled in an ice bath and analyzed by HPLC.

4.12. Synthesis of $[Et_2N{=}CMe_2][BPh_4]$

0.971 g (2.47 mmol) of **4** were treated under dinitrogen with 30 ml of acetone and an excess (1 ml, 8.13 mmol) of 2,2-dimethoxypropane. The reaction mixture was stirred at room temperature (295 K) for 3 h, concentrated in vacuo to a smaller volume and filtered. The solid on the filter was washed with THF (2×10 ml) and dried in vacuo (yield: 0.749 g, 70%). Anal. Calc. for $C_{31}H_{36}BN$: C, 85.90; H, 8.37; N, 3.23. Found: C, 86.26; H, 8.62; N, 3.13%. IR (Nujol, NaCl disks, cm^{-1}): 3060 (m, broad), 1660 (m-s), 1580 (m), 1480 (m-s, slightly broad), 1428 (m), 1150 (m), 1030 (m), 745 (m-s), 735 (s), 711 (s). ^1H NMR (acetone-d_6, 200 MHz, 293 K): δ 1.41 (t, CH_3, $^3J_{H-H} = 7.30$ Hz), 2.64 (s, $=CMe_2$), 4.05 (q, CH_2), 6.76 ("t", H_{p,BPh_4}), 6.92 ("t", H_{m,BPh_4}), 7.32 (m, H_{o,BPh_4}).

4.13. Synthesis of $[CH_2{=}CHCH_2NH{=}CMe_2][BPh_4]$

To an acetone (15 ml) solution of **1** (0.462 g, 1.22 mmol), prepared under dinitrogen, 4 Å molecular sieves were added. The mixture was stirred for 1 h at room temperature (293 K) and then filtered. After washing the residue on the filter with acetone (2×7 ml), the mother liquor and collected washing solutions were concentrated in vacuo to a small volume. By adding of pentane (70 ml) and cooling to 253 K, pure $[CH_2{=}CHCH_2NH{=}CMe_2][BPh_4]$ precipitated, was filtered off, washed with pentane (2×30 ml) and dried in vacuo. More pure compound could be obtained from the mother liquor by further addition of pentane (overall yield: 0.480 g, 94%). Anal. Calc. for $C_{30}H_{32}BN$: C, 86.32; H, 7.73; N, 3.35. Found: C, 86.19; H, 7.81; N, 3.22%. IR (Nujol, NaCl disks, cm^{-1}): 3238 (m-s, broad), 3150 (m, broad), 3058 (m), 3040 (m), 1677 (m-s), 1578 (m), 1480 (m-s), 1427 (m), 1150 (m), 1145 (m), 1030 (m), 745 (m-s), 737 (s), 710 (s). ^1H NMR (THF-d_8, 500 MHz, 293 K): δ 1.61 (s, CH_3), 1.78 (s, CH_3), 3.57 (d, broad, CH_2, $^3J_{H-H} = 6.10$ Hz), 5.11 (dm, C=C(H)H, $^3J_{trans} = 17.12$ Hz), 5.24 (dm, C=C(H)H, $^3J_{cis} = 10.35$ Hz), 5.57 (m, $CH{=}CH_2$), 6.76 ("t", H_{p,BPh_4}), 6.90 ("t", H_{m,BPh_4}), 7.33 (m, H_{o,BPh_4}).

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[25] The replacement of undeuterated THF with the *per*-deuterated solvent can affect the decomposition rate of a few of the salts investigated. As an example, at 293 K in THF-d_8, the conversion of **1** and **2** into the corresponding adducts was more than 90% after 36 h. The data obtained in THF at 312 K (Fig. 1) suggest that the decomposition of **1** takes place faster in the deuterated solvent. An analogous deceleration has been found for the decomposition of **2**: in fact, the benzene yield obtained upon heating a THF solution of **2** at 312 K for 2.5 d was equal to 42%. This effect is currently under investigation.

[26] The molar conductivity of **1** in CH_2Cl_2 solution at concentrations ranging from 0.011 M to 0.0020 M is very low. Comparison of these data with those found for **1a** in the same solvent and within a larger concentration range clearly indicates that in CH_2Cl_2 complexation of allylammonium cation with 18-crown-6 can promote ionic dissociation phenomena. Ion pairing seems to be important also in THF, as suggested by the molar conductance values of THF solutions of **1** in the range 0.10–0.0021 M compared with those reported for THF solutions of $NaBPh_4$ [Λ(0.1000 M, 298 K) = 26.64 ohm^{-1} cm^2 mol^{-1}] [27] or Na(18-crown-6)BPh_4[Λ(0.1001 M, 298 K) = 14.83 ohm^{-1} cm^2 mol^{-1}] [27]. In THF, $NaBPh_4$ and Na(18-crown-6)[BPh_4] exist primarily as solvent-separated [28] and crown-separated ion pairs [27], respectively.

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[29] A very broad signal is observed in the range 3.5–5 ppm, while a slightly broadened singlet and an unresolved partially masked multiplet are found at 2.58 ppm that disappeared slowly upon addition of D_2O. The location and relative intensity of the higher field signals (below 5 ppm) may change with time and seem to be affected by traces of water. Addition of a small amount of D_2O, besides shifting the signals of $[BPh_4]^-$ protons [δ 7.29 (m, H_{o,BPh_4}), 6.89 ("t", H_{m,BPh_4}), 6.75 ("t", H_{p,BPh_4})], also moves the two quartets [3.94 ppm and 3.10 ppm] upfield, and separates the triplet at 1.38 ppm into two triplets at 1.35 ppm (less intense) and 1.28 ppm (more intense), totally integrating to 6H. New lines appear with time in the spectrum at 2.08 (s) ppm and 2.06 ppm (line separation = 2.17 Hz), probably assignable to acetone-d_n (n = 0–4).

[30] Other signals, from $[BPh_4]^-$ appear at δ 122.22 (s, C_{para}), 125.98 (q, C_{meta}, $^3J_{C-B}$ = 2.35 Hz), 137.07 (s, C_{ortho}), 165.04 (q, C_{ipso}, $^1J_{C-B}$ = 49.43 Hz).

[31] Traces of water in the deuterated solvent cause partial hydroly-

sis of the iminium salt, as confirmed by the appearance in the spectrum of the signals from $[Et_2NH_2]^+$ and acetone (2.07 ppm). Other signals, assigned to acetone-d_n ($n = 1$–4) are evident near 2.05 ppm.

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