Reaction of Alkali-metal Tetraphenylborates with Amines in the Presence of CO_2: a New Easy Way to Aliphatic and Aromatic Alkali-metal Carbamates

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A new method of synthesis of both aliphatic and aromatic alkali-metal carbamates and anhydrous alkylammonium tetraphenylborates by reaction, at room temperature, of amines with alkali-metal tetraphenylborates in the presence of CO_2 (0.1 MPa) has been determined. This reaction represents the first step of a new very selective synthetic route to alkali-metal carbamates from amines, carbon dioxide and alkali-metal hydroxides at room temperature and pressure. It is also the first example of the isolation of aromatic amine alkali-metal carbamates through a non-isocyanate route.

As part of our studies of new mild syntheses and clean processes based on the use of carbon dioxide as a source of carbon[1] we have developed new CO_2-based synthetic routes to carbamate esters, a class of compounds with a large utilization in pharmacology, agriculture and industry.[2] The new methods[3] are alternative to the traditional use of phosgene ($COCl_2$) or isocyanates.[4] In particular, we have demonstrated that alkali-metal carbamates, under suitable conditions, can transfer the carbamic group to alkylating[3a,b,d,e,g] or acylating[3c,f] organic substrates to afford carbamic esters in excellent yield.

Alkali-metal carbamates of formula $M(O_2CNH_2)$ (M = Li, Na, K, Rb or Cs) are usually synthesized from carbon dioxide and an alkali-metal salt (nitrate or perchlorate) soluble in liquid ammonia.[5] Alternatively, the reaction of primary or secondary amines with carbon dioxide in the presence of the metal can afford, under harsh conditions, alkali-metal carbamates.[6] To the best of our knowledge, these methods are not applicable to *N*-arylcarbamates, $M(O_2CNHR)$ (M = alkali metal, R = aryl) that are prepared by reaction of the corresponding aromatic isocyanate with sodium hydroxide in organic solvents.†,[7] We have reported that phosphocarbamates $P(NR_2)_{3-x}(O_2CNR_2)_x$ ($x = 1$ or 2, R = alkyl) are an excellent source of carbamate groups which can be transferred to a Group 1 metal halide, MX, at room temperature and pressure.[3a,b,e] This method was shown to be very effective for the synthesis of metal carbamates of aliphatic amines (yield >98%, selectivity 100%) when the Group 1 metal was potassium and the halide was fluorine, however, it failed with aromatic amines as it is impossible to synthesize monomeric phosphorus amides of formula $P(NHR)_3$ (R = aryl).[3d]

In this paper we report a new reaction involving carbon dioxide fixation by amines in the presence of alkali-metal tetraphenylborate salts. This reaction permits a new versatile synthesis of both aliphatic and aromatic amine (primary and secondary) alkali-metal carbamates [equation (1): R = alkyl,

$$NHRR' + L + MBPh_4 + CO_2 \longrightarrow M(O_2CNRR') + [HL]BPh_4 \quad (1)$$

$R' = H$ or alkyl, $L = NHRR'$; R = aryl, $R' = H$, $L = NR''_3$ (R'' = alkyl); M = Na, Li or (K)]. It also represents the first step of a new selective process for the synthesis of alkali-metal carbamates from amines, carbon dioxide and alkali-metal hydroxides.

Reaction (1) affords an alkylammonium tetraphenylborate salt, $[NH_2RR']BPh_4$ or $[NHR''_3]BPh_4$, as co-product. Alkylammonium tetraphenylborates are compounds of growing interest as reagents in several technological fields[8] and in pure and applied chemistry. They are synthons for new products or materials such as *N*-alkyl-*B*-phenylborazines, $(RNBPh)_3$, or polymers involving borazine-ring catenation.[9] Recently, alkylammonium tetraphenylborates have found a wide utilization in organometallic chemistry as protonating agents for several M–C bonds (M = Th,[10a] Ti,[10b] Zr,[10b] Hf,[10b] Cr,[10c] Pd[10d] or Ce[10e]), allowing the synthesis of a large variety of cationic- or zwitterionic-η^n-$PhBPh_3$ metal complexes that are otherwise difficult to obtain.

The synthesis of alkylammonium tetraphenylborates involves the reaction of the corresponding alkylammonium halide with $NaBPh_4$ [equation (2)] in an aqueous medium.[11] The isolation

$$[NHRR'R'']Cl + NaBPh_4 \xrightarrow{H_2O} [NHRR'R'']BPh_4 + NaCl \quad (2)$$

of the anhydrous form, which 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.[11] Reaction (1), therefore, also represents a new straightforward CO_2-promoted synthesis of anhydrous alkylammonium tetraphenylborate salts. The latter aspect, as well as the reactivity of alkylammonium tetraphenylborates in solution, has been discussed elsewhere.[12]

Results and Discussion

General Method of Preparation of Group 1 Metal Carbamates.—Recently, we have shown that alkylammonium carbamates of formula $[NH_3R(18\text{-crown-}6)][O_2CNHR]$ (R = alkyl, 18-crown-6 = 1,4,7,10,13,16-hexaoxacyclooctadecane), easily prepared by reaction of the corresponding amine with carbon dioxide in the presence of a stoichiometric amount of crown ether [equations (3) and (4)], are able to transfer, under controlled reaction conditions, the carbamate group to organic electrophiles such as alkyl halides ($R'''X$), affording organic carbamates $RHNCO_2R'''$ [equation (5)] in satisfactory yield.[3d]

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† This method has been used for the synthesis of several sodium *N*-arylcarbamates, but no data are available on its selectivity. The materials obtained have been characterized on the basis of the spectral changes in the UV region upon hydrolysis.

$$2NH_2R + CO_2 \rightleftharpoons [NH_3R][O_2CNHR] \qquad (3)$$

$$[NH_3R][O_2CNHR] + 18\text{-crown-6} \rightleftharpoons [NH_3R(18\text{-crown-6})][O_2CNHR] \qquad (4)$$

$$[NH_3R(18\text{-crown-6})][O_2CNHR] + R'''X \longrightarrow RHNCO_2R''' + [NH_3R(18\text{-crown-6})]X \qquad (5)$$

We have now found that the reaction of $[NH_3R(18\text{-crown-6})][O_2CNHR]$ with $NaBPh_4$ under mild conditions (273–293 K, 0.1 MPa CO_2 pressure) affords sodium carbamates NaO_2CNHR (R = allyl **1a**, cyclohexyl **2** or benzyl **3a**) in very high yield according to reaction (6). The salts $[NH_3R(18\text{-crown-6})]BPh_4$ and $Na(O_2CNHR)$ separate from the reaction medium after the reagents are mixed and are easily isolated by selective extraction with CH_2Cl_2. Reaction (6) requires the use of expensive reagents such as 18-crown-6 and the tetraphenylborate anion. Therefore, we have developed a procedure for their recovery (see below). However, the use of crown ether is not essential in many cases.

$$[NH_3R(18\text{-crown-6})][O_2CNHR] + NaBPh_4 \xrightarrow{\text{thf}} [NH_3R(18\text{-crown-6})]BPh_4 + Na(O_2CNHR) \qquad (6)$$

Alkali-metal tetraphenylborates $MBPh_4$ (commercial $NaBPh_4$ or $LiBPh_4 \cdot 3MeOCH_2CH_2OMe$, 1 mol) and a primary or secondary aliphatic amine NHRR′ (2 mol), in the presence of CO_2 (0.1 MPa) at room temperature (273–293 K), afford the corresponding alkali-metal carbamate in good to excellent yield [equation (1)]. The alkali-metal carbamate separates as a white microcrystalline solid and can be isolated by filtration under a CO_2 atmosphere. The alkylammonium tetraphenylborate is recovered in high yield from the mother-liquor by crystallization.[12]

By interacting with the cation and anion formed [equation (7)] the tetraphenylborate salts push equilibrium (3) to the right.[13]

$$[NH_2RR'][O_2CNRR'] + MBPh_4 \longrightarrow [NH_2RR']BPh_4 + M(O_2CNRR') \qquad (7)$$

It is worth noting that, when aniline is used, equilibrium (3) (R = Ph) is shifted to the left as a result of the low basicity and nucleophilicity of the aromatic amine, and the anilinium carbamate is not formed. Consequently, the direct reaction of aniline with CO_2 and an alkylating agent does not produce the carbamate ester, but only alkylated aniline. The addition of a $MBPh_4$ salt (M = Na or Li, 1 mol) to a CO_2-saturated (0.1 MPa) thf (Na) [equation (8)] or CH_2Cl_2 (Li) [equation (9)] solution of aniline (1 mol) at 273–293 K in the presence of a tertiary amine, such as tributylamine (1 mol), affords $M(O_2CNHPh)$ and $[NHBu_3]BPh_4$ almost quantitatively. This reaction represents the first example of the synthesis of alkali-metal *N*-arylcarbamate salts using carbon dioxide.

$$NH_2Ph + NBu_3 + NaBPh_4 + CO_2 \longrightarrow Na(O_2CNHPh) + [NHBu_3]BPh_4 \qquad (8)$$

$$NH_2Ph + NBu_3 + LiBPh_4 \cdot 3MeOCH_2CH_2OMe + CO_2 \longrightarrow Li(O_2CNHPh) + [NHBu_3]BPh_4 + 3MeOCH_2CH_2OMe \qquad (9)$$

The extension of the procedure shown in equation (1), which is very efficient with Li and Na, to the synthesis of potassium carbamate salts, $K(O_2CNRR')$, is difficult as $KBPh_4$ is only sparingly soluble in most organic solvents. The choice of solvent is of crucial importance in this reaction as protic solvents, which would dissolve $KBPh_4$, cause decomposition of alkali-metal carbamates (see below). The solubility of $KBPh_4$ in both thf and CH_2Cl_2 is markedly enhanced upon addition of 18-crown-6 (K–polyether molar ratio 1 : 1) giving $[K(18\text{-crown-6})]BPh_4$ which is unable to react with alkylammonium carbamate.[*] Conversely, when enough crown ether is used to complex both the potassium and the ammonium cations, potassium carbamate is formed, but the isolation of the pure compound is difficult because of its similar solubility to that of the ammonium salt.[†] The extension of this synthetic route to other metal systems is currently under investigation.

Spectroscopic and Chemical Properties of Alkali-metal Carbamates.—Reaction (1) has been used for synthesizing a variety of both $M(O_2CNRR')$ alkali-metal carbamates and alkylammonium tetraphenylborate salts $[HL]BPh_4$. The yields of isolated carbamates, $M(O_2CNRR')$, are reported in Table 1. The compounds have been characterized by means of elemental analyses, spectroscopic techniques and chemical reactivity. In the solid state these compounds are stable at room temperature under CO_2 or an inert-gas atmosphere; however, upon exposure to atmospheric moisture some exhibit hygroscopic properties, as confirmed by the modification of their IR spectra.

All the carbamates prepared show strong IR absorptions (Table 1) due to the carbamic group in the ranges 1611–1570 [$\nu(NCO_2)$], 1503–1210 ('NCO_2' skeletal vibrations) and 800–820 cm^{-1} [$\omega(OCN)$].[3d] The N-monosubstituted salts also exhibit a medium to strong band between 3439 and 3354 cm^{-1} assigned to $\nu(NH)$. The very low solubility in organic solvents prevented the characterization of the compounds by solution NMR spectroscopy.

Addition of dilute HCl to a solid sample of these salts causes the stoichiometric evolution of CO_2 as confirmed by gas chromatography (GC) analysis.

The sodium salts **1**–**5** react with alkyl halides, R‴X (MeI, $PhCH_2Cl$ or $CH_2{=}CHCH_2Br$), in the presence of a suitable complexing agent [18-crown-6 or 15-crown-5 (1,4,7,10,13-pentaoxacyclopentadecane)], in thf at 293 K, to afford the corresponding carbamic esters, RR′NC(O)OR‴ [equation (10)] which have been isolated in moderate yield (50–70%) according to previously reported procedures.[3b–e,h] In particular, the reaction of $Na(O_2CNHPh)$ with MeI and 18-crown-6 in thf (293 K, 15 h) produces methyl *N*-phenylcarbamate (> 95% as crude product) which can be isolated as a pure compound by column chromatography in 65% yield.[3h]

$$Na(O_2CNRR') + \text{crown ether} + R'''X \longrightarrow R'RNCO_2R''' + [Na(\text{crown ether})]X \qquad (10)$$

The lithium carbamate $Li(O_2CNHPh)$ shows quite different reactivity. Reaction with MeI in the presence of 12-crown-4 ether (1,4,7,10-tetraoxacyclododecane) promotes decarboxylation of the alkali-metal carbamate and generates CO_2 [confirmed by GC and the IR spectrum of the reaction mixture

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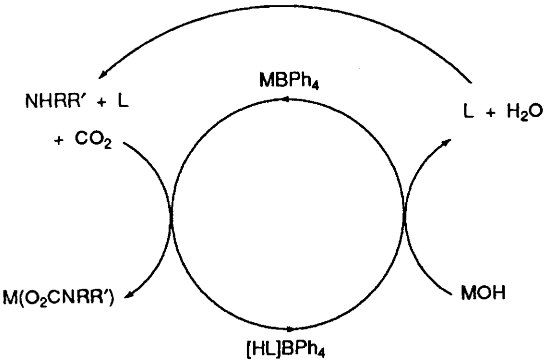
[*] Only the alkylammonium carbamate, $[NH_3R][O_2CNHR]$ (R = benzyl), and the starting tetraphenylborate salt were isolated from the reaction of $[K(18\text{-crown-6})]BPh_4$ (1 mol) with NH_2R (2 mol) and CO_2, in thf or CH_2Cl_2 at 293 K.

[†] As an example, the reaction of $[K(18\text{-crown-6})]BPh_4$ (1 mol) with $[NH_3R(18\text{-crown-6})][O_2CNHR]$ (R = benzyl, 1 mol) (thf or CH_2Cl_2, 293 K) affords $[K(18\text{-crown-6})][O_2CNHR]$ and $[NH_3R(18\text{-crown-6})]BPh_4$. However, only $[NH_3R(18\text{-crown-6})]BPh_4$[12] was isolated as a pure compound in yield >60%. The compound $[K(18\text{-crown-6})][O_2CNHR]$ was obtained as a colourless microcrystalline solid contaminated by the alkylammonium salt. This material showed the typical bands of the carbamate anion (3250, 1560 cm^{-1}) in the IR spectrum and gave a signal at δ 162.05, assignable to the carbonylic carbon of the carbamate anion, in the ^{13}C attached proton text NMR ($CDCl_3$, 293 K) spectrum.

Table 1 Relative yields and selected IR data (cm^{-1}, Nujol) for the alkali-metal carbamates **1**–**5**

Compound	Yield (%)[a]	ν(NH)	ν(NCO$_2$)	Skeletal vibrations (NCO$_2$)	ω(OCN)	δ(NCO$_2$)
1a Na[$O_2CNH(CH_2CH{=}CH_2)$]	86	3439ms	1595vs	1484s, 1448ms, 1391ms, 1313s	809s	*b*
1b Li[$O_2CNH(CH_2CH{=}CH_2)$]	80	3390s	1605s 1580vs	1495vs, 1450vs, 1380s, 1320s	820ms	*b*
2 Na[$O_2CNH(C_6H_{11})$]	92	3354s	1585vs	1480s, 1445ms, 1392ms, 1348ms	815s	643m
3a Na[$O_2CNH(CH_2Ph)$]	80	3392s	1611vs	1484s, 1452s, 1412s, 1344s	821ms	637ms
3b Li[$O_2CNH(CH_2Ph)$]	80	3390s	1575s	1500vs, 1452s, 1442s, 1380ms, 1335s	810ms	*b*
4 Na[O_2C(morph)]	86	—	1570vs	1432vs, 1280s	810ms	*b*
5a Na(O_2CNHPh)	74	3435s	1605vs 1585s	1503s, 1433s, 1360s, 1240s	803ms	640ms
5b Li(O_2CNHPh)	70	3370m (br)	1610s	1500s (br), 1440s (br), 1320s (br)	805ms	*b*

[a] Isolated pure salt. The crude product yield is > 95% in all cases. [b] Not assigned.



Scheme 1 M = Li or Na; R = alkyl, R′ = H or alkyl, L = NHRR′; R = aryl, R′ = H, L = NR″$_3$ (R″ = alkyl)

(2340 cm^{-1})] and a mixture of methylated amines [equation (11)].[3b,d,e,6b] It is known that N-alkylation products are formed

$$\mathrm{Li(O_2CNHPh) + MeI \xrightarrow{\text{crown ether}} CO_2 + NHMePh + NMe_2Ph + (NMe_3Ph)I} \quad (11)$$

when both carbamates **1**–**5** of Li and Na are treated with an alkyl halide in the absence of any complexing agent. Elsewhere[3b,d,e] the role of complexing agents, such as macrocyclic polyethers, in increasing the reactivity of both alkali-metal and alkylammonium carbamates towards alkyl halides, in terms of the increase of O-nucleophilicity of the carbamate anion, has been described. In the case of lithium, the use of the crown ether does not increase the O-nucleophilicity enough and the carbamic nitrogen is more reactive towards the incoming methyl group.

Acetone or protic solvents, such as alcohols, decompose alkali-metal carbamates. Upon treating Na[$O_2CNH(CH_2Ph)$] with methanol under a carbon dioxide atmosphere a new material was isolated and identified as sodium methyl carbonate, Na(O_2COMe) [equation (12)], on the basis of the

$$\mathrm{Na[O_2CNH(CH_2Ph)] + MeOH \longrightarrow Na(O_2COMe) + NH_2(CH_2Ph)} \quad (12)$$

elemental analysis and the comparison of its IR spectrum with that of an authentic sample prepared from methanol, sodium metal and carbon dioxide. This reaction puts a serious limitation on the use of protic solvents.

Recovery of the Crown Ether and the Tetraphenylborate Anion.—The synthetic methodology reported in this paper affords anhydrous alkylammonium tetraphenylborate salts[8–10] in addition to the metal carbamates. If a crown ether is used [equation (6)] for enhancing the solubility of the ammonium carbamate, it remains co-ordinated to the alkylammonium cation in the tetraphenylborate salt.

We report on a very simple method for recovering the tetraphenylborate anion, which, thus, can be recycled (Scheme 1). The reaction of isolated [HL]BPh$_4$ (L = NHRR′ or NR″$_3$) with MOH in methanol, at room temperature under dinitrogen, regenerates the starting alkali-metal tetraphenylborate, MBPh$_4$, and the amine [equation (13)]. This procedure can also be

$$\mathrm{[HL]BPh_4 + MOH \longrightarrow MBPh_4 + L + H_2O} \quad (13)$$

applied to alkylammonium tetraphenylborates complexed with crown ethers [equation (14)]. Both MBPh$_4$ and [Na(18-crown-6)]BPh$_4$ can easily be recovered in quantitative yield. Distillation or evaporation of the mother-liquor allows the recovery of the amine not fixed by CO$_2$. Therefore, the overall process derived from reactions (1) and (13) describes the selective synthesis of a metal carbamate from amine, alkali-metal hydroxide and carbon dioxide according to equation (15).

$$\mathrm{[NH_3R(18\text{-}crown\text{-}6)]BPh_4 + NaOH \longrightarrow [Na(18\text{-}crown\text{-}6)]BPh_4 + NH_2R + H_2O} \quad (14)$$

$$\mathrm{NHRR' + CO_2 + MOH \longrightarrow M(O_2CNRR') + H_2O} \quad (15)$$

It is worth noting that the direct reaction of primary or secondary amines with an alkali-metal hydroxide in the presence of CO$_2$ leads to carbamate–carbonate mixtures.[14]

Conclusion

The reaction of Group 1 metal tetraphenylborates with either aliphatic or aromatic amines in the presence of CO$_2$, under very mild conditions (0.1 MPa CO$_2$ pressure, 273–293 K) affords, selectively and in high yield, alkali-metal carbamates and anhydrous alkylammonium tetraphenylborates. The two species can easily be separated (M = Li or Na) owing to their different solubilities in the reaction medium.

Alkylammonium tetraphenylborates can be used for several specific purposes. Alternatively, by reaction with MOH, they can regenerate the corresponding metal tetraphenylborate salts which can be recycled. The latter feature makes this method of potential use in synthetic chemistry.

Experimental

General Methods.—All reactions and manipulations were performed under a dinitrogen or carbon dioxide atmosphere with rigorous exclusion of both air and atmospheric moisture using vacuum-line techniques. Solvents were dried according to conventional procedures[15] and stored under dinitrogen. The amines used (Fluka, Aldrich or Farmitalia Carlo Erba) were dried[15] and distilled before use. The salts NaBPh$_4$ (Aldrich or

Baker) and $LiBPh_4{\cdot}3MeOCH_2CH_2OMe$ (Strem or Aldrich) were used as received, $KBPh_4$ was prepared as described in the literature[16] and [K(18-crown-6)]BPh_4[16] was prepared *in situ* (thf or CH_2Cl_2) from $KBPh_4$ and 18-crown-6 (molar ratio 1 : 1). Commercial 18-crown-6 (Aldrich or Janssen) was purified before use by treatment with anhydrous acetonitrile[17] and CO_2 (99.99% pure) was from SIO.

Infrared spectra were obtained with a Perkin-Elmer 883 spectrophotometer, ^1H and ^{13}C NMR spectra on a Varian XL 200 or Bruker AM 500 spectrometer with chemical shifts in ppm *vs.* $SiMe_4$ and referenced to the solvent peak. The 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, film thickness 0.25 μm). The GC analysis of the gas phase was performed with a DANI 8610 gas chromatograph equipped with a TCD 866 detector using a Carbosieve S II column.

Syntheses.—$Na[O_2CNH(CH_2CH{=}CH_2)]$ **1a**. (*a*) *From* $CH_2{=}CHCH_2NH_2$, $NaBPh_4$ *and* CO_2. A thf (50 cm^3) solution of $NaBPh_4$ (4.558 g, 13.3 mmol) and $CH_2{=}CHCH_2NH_2$ (2.0 cm^3, 26.6 mmol), prepared under dinitrogen, was saturated with CO_2 at 273 K. The white precipitate thus formed was filtered off under a CO_2 atmosphere, washed with thf (20 cm^3), dichloromethane (2 × 15 cm^3) and dried *in vacuo* (1.400 g, 86%) (Found: C, 39.10; H, 5.05; N, 11.30. $C_4H_6NNaO_2$ requires C, 39.05; H, 4.90; N, 11.35%). Upon exposure of the sample to the atmosphere (15 min) a broad band appeared at about 3400 cm^{-1} in the IR spectrum.

(*b*) *From* $[NH_3(CH_2{=}CHCH_2)(18\text{-crown-}6)][O_2CNH(CH_2CH{=}CH_2)]$ *and* $NaBPh_4$. A thf suspension of $[NH_3(CH_2{=}CHCH_2)][O_2CNH(CH_2CH{=}CH_2)]$, obtained by saturating a thf (20 cm^3) solution of $NH_2(CH_2CH{=}CH_2)$ (1.0 cm^3, 13.3 mmol) with CO_2 at 293 K, was treated with 18-crown-6 (1.763 g, 6.66 mmol). After dissolution of the solid due to the formation of $[NH_3(CH_2CH{=}CH_2)(18\text{-crown-}6)][O_2CNH(CH_2CH{=}CH_2)]$,[3d] a thf (25 cm^3) solution of $NaBPh_4$ (2.282 g, 6.67 mmol) was added. The white precipitate thus formed was filtered off under CO_2, washed with thf (2 × 5 cm^3) and dried *in vacuo*. More solid was isolated from the mother-liquor and washing solutions upon addition of pentane (40 cm^3) and cooling to 253 K. The solids were washed with dichloromethane (4 × 20 cm^3) under CO_2 and the residual solid dried *in vacuo* (0.62 g, 78%) (Found: C, 39.00; H, 5.00; N, 11.25. $C_4H_6NNaO_2$ requires C, 39.05; H, 4.90; N, 11.35%).

$Li[O_2CNH(CH_2CH{=}CH_2)]$ **1b**. A thf (35 cm^3) solution of $LiBPh_4{\cdot}3MeOCH_2CH_2OMe$ (0.964 g, 1.62 mmol) and $NH_2(CH_2CH{=}CH_2)$ (0.25 cm^3, 3.32 mmol), prepared under dinitrogen, was saturated with CO_2 at 273 K. The resulting white suspension was treated with pentane (25 cm^3), cooled to 253 K and filtered. The solid was washed with dichloromethane (2 × 5 cm^3), thf (2 × 5 cm^3) and dried *in vacuo* (0.139 g, 80%) (Found: C, 44.25; H, 5.60; N, 12.90. $C_4H_6LiNO_2$ requires C, 44.75; H, 5.65; N, 13.05%).

$Na[O_2CNH(C_6H_{11})]$ **2**. (*a*) *From* $NH_2(C_6H_{11})$, $NaBPh_4$ *and* CO_2. To a thf (60 cm^3) solution of $NaBPh_4$ (2.988 g, 8.73 mmol) and $NH_2(C_6H_{11})$ (2.0 cm^3, 17.5 mmol), prepared under dinitrogen and saturated with CO_2 at 273 K, pentane (30 cm^3) was added. The white precipitate thus formed was filtered off under CO_2, washed with dichloromethane (2 × 15 cm^3) and dried *in vacuo* (1.330 g, 92%) (Found: C, 50.50; H, 7.20; N, 8.35. $C_7H_{12}NNaO_2$ requires C, 50.90; H, 7.30; N, 8.50%). Upon exposure of the sample to air (15 min) broad bands appeared at 3400 and 1660 cm^{-1} in the IR spectrum.

(*b*) *From* $[NH_3(C_6H_{11})(18\text{-crown-}6)][O_2CNH(C_6H_{11})]$ *and* $NaBPh_4$. The compound $Na[O_2CNH(C_6H_{11})]$ was prepared using the crown ether method as described for **1a** [$NH_2(C_6H_{11})$ 1.0 cm^3, 8.74 mmol; 18-crown-6 1.159 g, 4.38 mmol; $NaBPh_4$ 1.501 g, 4.38 mmol] yield 0.487 g, 80% (Found: C, 50.60; H, 7.25; N, 8.35. $C_7H_{12}NNaO_2$ requires C, 50.90; H, 7.30; N, 8.50%).

$Na[O_2CNH(CH_2Ph)]$ **3a**. (*a*) *From* $NH_2(CH_2Ph)$, $NaBPh_4$ *and* CO_2. To a thf (45 cm^3) solution of $NaBPh_4$ (3.136 g, 9.16 mmol) and $NH_2(CH_2Ph)$ (2.0 cm^3, 18.3 mmol), prepared under dinitrogen and saturated with CO_2 at 273 K, pentane (11 cm^3) was added. The white precipitate thus formed was filtered off under CO_2, washed with thf (2 × 15 cm^3) and dried *in vacuo* (1.265 g, 80%) (Found: C, 55.50; H, 4.75; N, 7.90. $C_8H_8NNaO_2$ requires C, 55.50; H, 4.65; N, 8.10%).

(*b*) *From* $[NH_3(CH_2Ph)(18\text{-crown-}6)][O_2CNH(Ph)]$ *and* $NaBPh_4$. A thf suspension of $[NH_3(CH_2Ph)][O_2CNH(CH_2Ph)]$, obtained by saturating a thf (40 cm^3) solution of $NH_2(CH_2Ph)$ (3.0 cm^3, 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 cm^3) solution of $NaBPh_4$ (4.680 g, 13.7 mmol) was added. The white precipitate thus formed was filtered off under CO_2, washed with thf (2 × 20 cm^3), dichloromethane (4 × 20 cm^3) and dried *in vacuo* (1.010 g, 78%) (Found: C, 55.50; H, 4.70; N, 7.95. $C_8H_8NNaO_2$ requires C, 55.50; H, 4.65; N, 8.10%).

$Li[O_2CNH(CH_2Ph)]$ **3b**. A thf (85 cm^3) solution of $LiBPh_4{\cdot}3MeOCH_2CH_2OMe$ (2.601 g, 4.36 mmol) and $NH_2(CH_2Ph)$ (0.95 cm^3, 8.72 mmol), prepared under dinitrogen, was saturated with CO_2 at 273 K. The resulting white suspension was treated with pentane (20 cm^3), cooled to 253 K and filtered. The solid was washed with thf (3 × 10 cm^3), and dried *in vacuo* (0.547 g, 80%) (Found: C, 61.35; H, 5.20; N, 8.75. $C_8H_8LiNO_2$ requires C, 61.15; H, 5.15; N, 8.90%).

$Na[O_2C(morph)]$ (morph = morpholino) **4**. To a thf (100 cm^3) solution of $NaBPh_4$ (3.936 g, 11.5 mmol), saturated with CO_2 at 273 K, morpholine (2.0 cm^3, 22.9 mmol) was added. The resulting suspension was treated with pentane (70 cm^3) and, after cooling to 253 K, filtered under CO_2. The solid was washed with thf (3 × 30 cm^3) and dried *in vacuo* (1.514 g, 86%) (Found: C, 38.85; H, 5.15; N, 9.05. $C_5H_8NNaO_3$ requires C, 39.20; H, 5.25; N, 9.15%). New broad bands (3400 and 1700 cm^{-1}) appear in the IR spectrum upon exposure of the sample to air for < 5 min.

$Na(O_2CNHPh)$ **5a**. To a thf (30 cm^3) solution of $NaBPh_4$ (3.754 g, 11.0 mmol), saturated with CO_2 at 273 K, aniline (1.0 cm^3, 11.0 mmol) and tributylamine (2.6 cm^3, 11.0 mmol) were added. The resulting suspension was treated with pentane (80 cm^3), cooled to 253 K, and filtered under CO_2. The solid was washed with dichloromethane (4 × 20 cm^3) and dried *in vacuo* (1.290 g, 74%) (Found: C, 52.60; H, 4.15; N, 8.65. $C_7H_6NNaO_2$ requires C, 52.85; H, 3.80; N, 8.80%).

$Li(O_2CNHPh)$ **5b**. To a CH_2Cl_2 (60 cm^3) solution of $LiBPh_4{\cdot}3MeOCH_2CH_2OMe$ (2.142 g, 3.59 mmol), saturated with CO_2 at 273 K, aniline (0.33 cm^3, 3.60 mmol) and tributylamine (0.85 cm^3, 3.59 mmol) were added. The resulting suspension was filtered under CO_2 and the solid washed with dichloromethane and dried *in vacuo* (0.466 g, 70%) (Found: C, 48.30; H, 3.80; N, 7.50. $C_7H_6LiNO_2{\cdot}0.5CH_2Cl_2$ requires C, 48.55; H, 3.80; N, 7.55%).

Recovery of Tetraphenylborate.—The following procedure was adopted for recovering the tetraphenylborate anion as its sodium salt. As examples we describe the recovery from $[NH_3(CH_2CH{=}CH_2)]BPh_4$ and $[NH_3(CH_2Ph)(18\text{-crown-}6)]BPh_4$.

(*a*) *From* $[NH_3(CH_2CH{=}CH_2)]BPh_4$. The salt $[NH_3(CH_2CH{=}CH_2)]BPh_4$ (0.961 g, 2.54 mmol) dissolved in thf (20 cm^3) under dinitrogen was treated with NaOH (0.102 g, 2.54 mmol) in MeOH (5 cm^3). The reaction mixture was stirred at 293 K for 2 h in the presence of molecular sieves (5 A) and then filtered. After washing the residue with thf (2 × 15 cm^3), the mother-liquor and washing solutions were combined and evaporated *in vacuo* to give pure $NaBPh_4$ (0.852 g, 98%).

(*b*) *From* $[NH_3(CH_2Ph)(18\text{-crown-}6)]BPh_4$. The salt $[NH_3(CH_2Ph)(18\text{-crown-}6)]BPh_4$ (1.010 g, 1.46 mmol) was dissolved in a MeOH (20 cm^3) solution of NaOH (0.180 g, 4.50 mmol) under N_2 and stirred at 293 K for 1 h. After filtration the mother-liquor was concentrated *in vacuo* and cooled to 253 K. The white solid precipitate was filtered off and identified as [Na(18-crown-6)]BPh$_4$ (0.868 g, 98%) (Found: C, 71.05; H, 7.30. Calc. for $C_{36}H_{44}BNaO_6$: C, 71.30; H, 7.30%). IR (Nujol, NaCl disc): 3059m, 3043mw, 1579m, 1426m, 1352m, 1295m, 1246m, 1099vs, 1031m, 961m, 839m, 749mw, 732ms, 708ms and 611ms cm^{-1}. δ_H[(CD$_3$)$_2$CO, 200 MHz, 293 K] 7.32 (8 H, m, H$_o$), 6.92 (8 H, t, H$_m$), 6.77 (4 H, m, H$_p$) and 3.61 (24 H, s, CH$_2$).

Acknowledgements

We thank the Ministero dell' Universitá e della Ricerca Scientifica e Tecnologica (40 and 60% Funds) and the Consiglio Nazionale della Ricerce (Progetto Finalizzato 'Chimica Fine II') for financial support, and Dr. Daniela Balzano and Miss Antonella Fiorino for experimental assistance.

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Received 6*th April* 1995; *Paper* 5/02223A