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Phosgene-free synthesis of N-methyl-N′,N′-diphenylurea

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ABSTRACT

Akardite II (AK-II, N-methyl-N′,N′-diphenylurea) is a well-known stabilizer for nitrocellulose (NC) propellants as it scavenges NO_x. Currently, AK-II is produced using phosgene, a highly toxic gas. An alternative, two-step synthesis route is presented here that does not rely on phosgene. First, symmetrical organic carbonates (R_2CO_3, with R = Me, Et, or Ph) and diphenylamine react to form their corresponding carbamates in good yields for R = Me and Et (80% and 57%) and low yield for R = Ph (9%), catalyzed by 3-methyl-1-butylimidazolium chloride ([BMIM]Cl). The carbamate species are suggested to be formed in an equilibrium reaction. Evaporation of the alcohol side products pushes the equilibrium to the carbamate product. The second step converts the diphenyl carbamates into the targeted compound by treatment with (mono)methylamine (MMA), with reversed yield trend (4% for R = Me and Et, 81% for R = Ph). For the alkyl carbamates, the formation of AK-II appears to run in parallel with an MMA-alkylation reaction, which severely lowers the product yield. Overall, the synthesis of AK-II via the carbamate route is feasible, yet the carbonate side groups should be chosen carefully to obtain a high overall yield.

1. Introduction

Modern-day ammunition often uses a propellant based on the energetic material nitrocellulose (NC) [1]. Like most energetic materials, NC is thermodynamically unstable. It is subject to a chemical degradation process, during which a nitrate ester is removed, leaving an alcohol group at the cellulose scaffold. Ageing may lead to an enhanced instability of the energetic material, i.e. decreased functionality and safety, and imposes the risk of a (thermal) explosion [2,3]. During the degradation process, which may also be caused by UV light [4], species are formed that are catalytic to the O–NO_2 bond-breaking process, e.g. ·NO_2 radicals (involved in exothermic reactions with nitrate esters) and nitric acid (catalytic to the hydrolysis of the nitrate ester groups). Moreover, both the radical and acid products are catalysts for their own formation processes. Thus, ageing is autocatalytic as the reaction products accelerate the degradation of the energetic material, far beyond the speed of the natural, thermodynamically driven degradation [2]. To slow down NC degradation, the autocatalytic reaction products should be scavenged to prevent them from further accelerating the ageing process.

A number of substances have been identified as suitable NC stabilizers and have been used in mass-produced energetic formulations as such. These conventional stabilizers are divided into two classes: the aromatic amines and the aromatic urea derivatives. Examples of aromatic amines are pNMA (p-nitro-N-methylaniline), pNEA (p-nitro-N-ethylaniline), DPA (diphenylamine) and 2-NDPA (2-nitrodiphenylamine). Examples of aromatic urea are Centralite I (C–I, diethyl-N,N′-diphenylurea), Centralite II (C-II, dimethyl-N,N′-diphenylurea) and Akardite II (AK-II, N-methyl-N′,N′-diphenylurea) [5,6]. Among these compounds, DPA, pNEA, C–I and C-II are either toxic by themselves (DPA) or produce highly carcinogenic nitrosamines as they scavenge nitric oxide radicals (pNEA, C–I and C-II), and should preferably be avoided in commercial energetic compositions. On the other hand, AK-II is markedly less toxic than its competitors. Although nitrosamines are among the reaction products of AK-II [7], these nitrosamines are less carcinogenic and produced in lower amounts than the ones produced by the other NC stabilizing additives [6].

AK-II has a hidden drawback however: it is currently produced using phosgene gas (carbonyl dichloride) in stoichiometric amounts [8]. Exposure to phosgene can cause severe respiratory effects upon inhalation and may be fatal when inhaled. Furthermore, phosgene poisoning affects the brain, heart and blood indirectly, and contact with skin or eyes causes severe burns [9]. Phosgene should thus preferably be avoided in any production process. Phosgene-free routes have e.g. been studied for the synthesis of 1,3-diphenylurea [10], polyfunctional cyclic carbonates as intermediates for the formation of non-isocyanate polyurethane [11] and polyurethane precursors [12]. In view of the concerns regarding the

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use of phosgene in the AK-II production, the question rose whether an alternative, phosgene-free and less toxic production process can be identified. Several potential alternative synthetic pathways, based on literature, were evaluated, but all of these routes were not environmentally benign. Instead, a new environmentally benign route, free of phosgene, has been developed and experimentally verified. The feasibility of this new, phosgene-free synthesis pathway to produce AK II is demonstrated in this paper.

2. Experimental

All chemicals were purchased from Sigma Aldrich and used without further purification. Nitrogen gas (N50, 5.0 purity) was purchased from Air Liquide. Pure water was obtained by the purification of tap water using a Milli-Q Direct-Q 5. (Mono)methylamine (MMA) was purchased as a solution of 40 wt% MMA in H_2O and 33 wt% MMA in absolute ethanol. Ionic liquid 3-methyl-1-butylimidazolium chloride, [BMIM]Cl, was dried in a vacuum stove (Heraeus vacuum oven, Thermo Scientific) at 100 °C for 3 h and stored under a N_2 atmosphere before use. Ace pressure tubes were purchased from Sigma Aldrich and fitted with a Teflex® O-ring, purchased from Eriks. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Ascend 400 (400 MHz) (spectra in Supporting Information). Mass spectra were recorded on a Finnigan MAT900 using an electrospray ionization technique (ESI-MS), with methanol as the eluent. MS samples were prepared by dissolving a few milligrams of the compound in HPLC-grade acetone. IR spectra were recorded on a PerkinElmer Spectrum Two FT-IR spectrometer.

The general procedure for the synthesis of alkyl diphenyl carbamates is adapted from a literature procedure [13]. In a round-bottomed flask (3-neck, 50 ml, fitted with reflux equipment), 3-methyl-1-butylimidazolium chloride ([BMIM]Cl, 0.1 eq., 0.5 mmol, 88 mg; weighed directly in the flask by dropwise addition under an N_2 atmosphere), diphenyl amine (DPA, 1.0 eq., 5.0 mmol, 0.85 g) and anhydrous disubstituted carbonate (5 ml) were mixed under an N_2 atmosphere. The mixture was heated to 130 °C and stirred for 7 h. It was then cooled to room temperature, the solvent was evaporated and the crude was purified on a SiO_2 column (the eluent was a mixture of ethyl acetate (EtOAc) and petroleum ether (PetEt): EtOAc/PetEt 10:90). The pure product was obtained as a colorless liquid, which crystallized quickly into a white solid when pressurized air was passed over the liquid.

2.1. O-Methyl-N,N′-diphenyl carbamate (MdPC)

MdPC was synthesized following the general procedure for diphenyl carbamate synthesis described in the previous section. Dimethyl carbonate (DMC) was used to obtain the corresponding carbamate at a yield of 80%. ^{1}H NMR ($CDCl_3$): δ 7.40-7.35 (m, 4H, 2 or 3), 7.30-7.22 (m, 6H, 1 and 2 or 3), 3.78 (s, 3H, 6). ^{13}C NMR: δ 155.31 (5), 142.59 (4), 128.95 (1, 2, or 3), 126.95 (1, 2, or 3), 126.18 (1, 2, or 3), 53.14 (6). (ESI)-MS (calc.): 250.0 (250.3, $[M - Na]^+$) 282.1 (282.3, $[M\text{-}Na\text{-}MeOH]^+$, 308.0 (308.4, $[M\text{-}Na\text{-}Me_2CO]^+$, 475.2 (475.6, $[M_2\text{-}Na]^+$). IR (cm^{-1}): 3100-3000 (w, C–H stretch, Ph), 2900–3000 (w, C–H stretch, CH_3), 1708 (s, C═O stretch, NC(═O)N), 1588, 1492 and 1439 (m, C═C stretch, Ph).

2.2. O-Ethyl-N,N′-diphenyl carbamate (EdPC)

EdPC was synthesized following the general procedure for diphenyl carbamate synthesis described above. Diethyl carbonate (DEC) was used to obtain the corresponding carbamate EdPC at a yield of 57%. ^{1}H NMR ($CDCl_3$): δ 7.39-7.33 (m, 4H, 2 or 3), 7.28-7.20 (m, 6H, 1 and 2 or 3), 4.26 (q, 2H, 6), 1.27 (t, 3H, 7). ^{13}C NMR ($CDCl_3$): δ 154.86 (5), 142.70 (4), 128.87 (1, 2, or 3), 126.98 (1, 2, or 3), 126.01 (1, 2, or 3), 62.06 (6), 14.47 (7). (ESI)-MS (calc.): 242.1 (242.3, $[M - H]^+$), 264.1 (264.3, $[M - Na]^+$), 296.1 (296.3, $[M\text{-}Na\text{-}MeOH]^+$), 322.0 (322.4, $[M\text{-}Na\text{-}Me_2CO]^+$), 505.2 (505.6, $[M_2\text{-}Na]^+$). IR (cm^{-1}): 3100-3000 (w, C–H stretch, Ph), 3000-2900 (w, C–H stretch, CH_2, CH_3), 1715 (s, C═O stretch, NC(═O)O), 1590, 1491 and 1465 (m, C═C stretch, Ph).

2.3. O-Phenyl-N,N′-diphenyl carbamate (PdPC)

PdPC was synthesized following the general procedure for diphenyl carbamate synthesis described above. Diphenyl carbonate (DPC) was used to obtain the corresponding carbamate PdPC at a yield of 9%. ^{1}H NMR ($CDCl_3$): δ 7.439-7.34 (m, 9H), 7.31-7.15 (m, 6H). ^{13}C NMR ($CDCl_3$): δ 153.12 (5), 151.12 (6), 142.28 (4), 129.26 (2 or 8), 129.06 (2 or 8), 126.91 (1 or 9), 126.48 (1 or 9), 125.50 (3), 121.52 (7).

2.4. N-methyl-N′,N′-diphenylurea (Akardite II)

The synthesis of Akardite-II (AK-II) was performed with either MdPC, EdPC or PdPC as the starting material. A solution of MMA in EtOH/H_2O in a ratio of 3:1 was prepared by mixing 3.5 ml of 33 wt% MMA in EtOH and 10.5 ml of 40 wt% MMA in H_2O. The freshly prepared MMA solution was mixed with MdPC (1.0 eq., 2.0 mmol, 0.45 g), EdPC (1.0 eq., 2.0 mmol, 0.48 g) or PdPC (1.0 eq., 0.35 mmol, 100 mg) in a pressure tube (fitted with Teflex® O-ring). After sealing the tube, the reaction mixture was heated to 100 °C and stirred until the carbamate was completely consumed. Then the reaction mixture was cooled to room temperature, and the tube was left open to allow MMA to evaporate. Next, the solvent was evaporated, which turned the reaction mixture into an emulsion. Copious amounts of EtOAc were added and the two phases were separated. The water phase was washed with EtOAc. Both EtOAc solutions were combined and the solvent was evaporated. The contents of the resulting liquid were separated using a SiO_2 column (eluent: EtOAc/PetEt 25:75). The AK-II fractions were combined and the solvent was evaporated. The remaining solid was washed with PetEt and pure AK-II was obtained as a white solid. From MdPC: 17 mg = 4% (100 °C, overnight). From EdPC: 17 mg = 4% (100 °C, 12 days). From PdPC: 64 mg = 81% (20 °C, 5 days). ^{1}H NMR ($CDCl_3$): δ 7.36 – 7.32 (m, 4H, 2 or 3), 7. 30 – 7.20 (m, 6H, 1 and 2 or 3), 4.51 (s, 1H, 6), 2.84 (s, 3H, 7). ^{13}C NMR: δ 156.82 (5), 142.90 (4), 129.37 (1, 2, or 3), 127.42 (1, 2, or 3), 126.12 (1, 2, or 3), 27.48 (7). (ESI)-MS (calc.): 227.1 (227.3, $[M - H]^+$), 249.1 (249.3, $[M - Na]^+$), 281.1 (281.3, $[M\text{-}Na\text{-}MeOH]^+$), 307.1 (307.4, $[M\text{-}Na\text{-}Me_2CO]^+$), 475.2 (475.6, $[M_2\text{-}Na]^+$). IR (cm^{-1}): 3339 (m, N–H stretch, H–NMe), 3100-3000 (w, C–H stretch, Ph), 3000-2900 (w, C–H stretch, CH_3), 1653 (s, C═O stretch, NC(═O)N), 1587, 1486 and 1449 (m, C═C stretch, Ph), 1512 (N–H bend, H–NMe).

3. Results and discussion

Multiple synthetic routes towards AK-II [14–18] were identified in a literature search, summarized in Fig. 1. However, these routes trace back to phosgene, or its toxic derivatives like di-, tri- and thiophosgene (routes A, B, and E) or rely on other compounds that raise serious health and safety issues, like the highly toxic phosphorus oxychloride ($POCl_3$, route C), and the toxic gas methyl isocyanate (MeNCO, route D). Alternatively, a synthetic route to a compound structurally similar to AK-II was considered. Carbomethoxylation of carbazole, with dimethyl carbonate (DMC), occurs in high yields under mild reaction conditions (see Fig. 2), catalyzed by 3-methyl-1-butylimidazolium ($BMIM^+$) salts. Interestingly, these salts are ionic liquids, and can have a catalytic as well as a solvent function [19,20]. Appealing features of this synthetic procedure are its versatility (i.e. the ability to form carbamates from various N-heterocyclic structures or aromatic amines), the low toxicity of the compounds involved and the recyclability of the catalyst [21]. The advantage of using such organic carbonate, and more specifically DMC chemistry, is that it is versatile and well explored [21–25]. Moreover, these carbonates may even be sourced from CO_2, making it truly a green reagent [26,27].

Replacing carbazole with diphenylamine may yield O-methyl-N,N′-diphenyl carbamate (MdPC, see Fig. 3, step 1). MdPC is structurally very similar to AK-II and could be a useful intermediate in the synthesis of AK-II. Notably, the reaction is reported not to occur with aniline

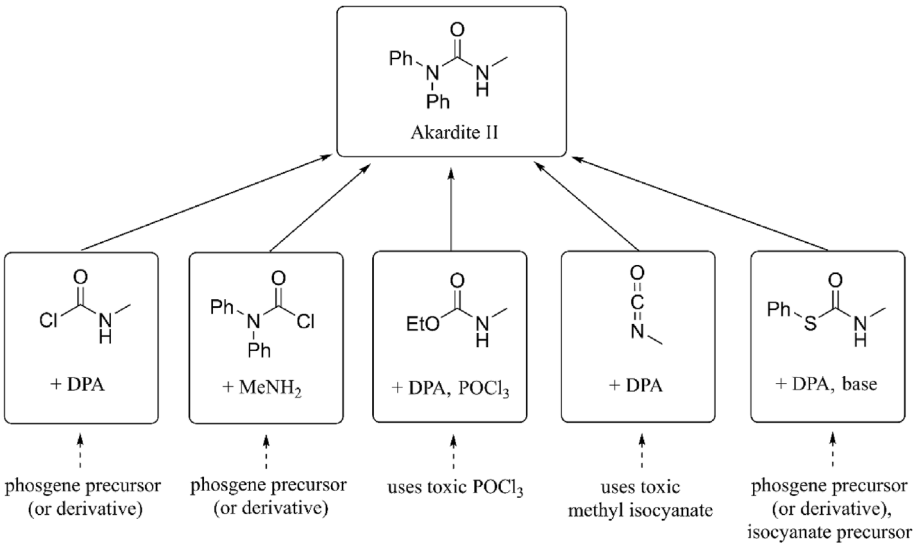

Fig. 1. Synthetic map towards AK-II, based on literature. AK-II can be synthesized using various precursors: (A) from N-methylcarbamoyl chloride and DPA [14], (B) from N,N-diphenylcarbamoyl chloride and methylamine [15], (C) from O-ethyl-N-methyl carbamate, DPA and $POCl_3$ [16], (D) from methyl isocyanate and DPA [17], and (E) from S-phenyl-N-methyl thiocarbamate, DPA and a base [18].

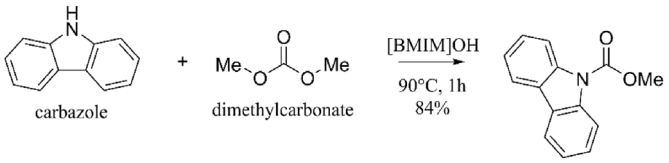

Fig. 2. Carbomethoxylation of carbazole with DMC under mild reaction conditions, catalyzed by a $BMIM^+$ salt [13].

(monophenylamine). However, the structural similarity between carbazole and DPA is of such extent that the likeliness of a successful carbomethoxylation of DPA is considered reasonably high. MdPC may be converted into AK-II, using (mono)methylamine (MMA) as a non-toxic reagent (see Fig. 3, step 2). The conversion of an O-methyl carbamate compound into its urea derivative using $MeNH_2$ has been reported before, with excellent yields (98%) [19]. This synthetic pathway should overcome the dependence of phosgene as a stoichiometric precursor, or other toxic compounds mentioned before (see Fig. 1). Phosgene is replaced here with dialkyl carbonate species like DMC, which are of little concern regarding their toxicity. The reagents, particularly the stoichiometric ones, are relatively cheap. The catalyst, although relatively expensive, may be recycled [13]. Moreover, all compounds are commercially available. Overall, the pathway proposed here relies on significantly less toxic reagents than the current production process, and uses relatively cheap chemicals. Therefore, this pathway was selected for further experimental investigation.

The synthesis of alkyl diphenyl carbamate was adapted from a literature procedure for the carbomethoxylation of carbazole [13]. Although the carbazole reaction was reported to be complete in 1 h at 90 °C, a similar conversion with diphenylamine and DMC, catalyzed by [BMIM]Cl, only resulted in the desired product in low yields, even after increasing the reaction time to 24 h (18%). O-methyl-N, N′-diphenylcarbamate (MdPC) was obtained, after purification on a SiO_2 column and evaporation of the product fractions, as a clear liquid which quickly crystallized when pressurized air was passed over the liquid. ^1H and ^{13}C NMR confirmed that MdPC was obtained as a pure compound (see supplementary material). Simply increasing the reaction time and temperature turned out to be a key step to improve reaction yields. Using excess DMC and 10 mol% [BMIM]Cl, significantly higher yields were obtained at 110 °C and 130 °C after 7 h (55% and 80%, respectively). At 130 °C, increasing the reaction time even further did not improve the yield (80% and 84% for 7 h and 16 h, respectively), suggesting that the reaction went to near completion within 7 h. Moreover, the amount of DMC with respect to DPA influences the carbomethoxylation reaction efficiency. Decreasing the DMC/DPA ratio from 10 to 5 resulted in a drop in MdPC yield from 18% to 13% at 90 °C for 24 h. The temperature and DMC/DPA dependence of the reaction suggest that this is an equilibrium reaction as described by Eq. I, pushed to the product side by the excess amount of DMC, and the evaporation of the reaction side product, methanol, from the reaction mixture. Notably, the reaction was less efficient when a closed vessel was used, as methanol could not escape.

$$k = \frac{[MdPC]\ x\ [MeOH]}{[DPA]\ x\ [DMC]} \qquad \text{I}$$

Replacing DMC for diethyl carbonate (DEC) allowed a successful conversion of DPA into O-ethyl-N,N′-diphenylcarbamate (EdPC), albeit

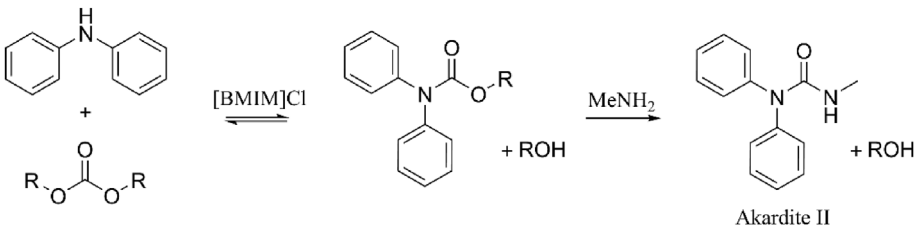

Fig. 3. An alternative two-step synthetic pathway towards AK-II. Step 1: carbomethoxylation of diphenylamine (DPA) with dimethyl carbonate, catalyzed by a $[BMIM]^+$ salt, yielding O-methyl-N,N′-diphenyl carbamate (MdPC). Step 2: the conversion of MdPC into the target molecule N-methyl-N′,N′-diphenylurea (AK-II) using $MeNH_2$.

in a lower yield (80% for MdPC versus 57% for EdPC at 10 mol% [BMIM]Cl, 130 °C, for 7 h). The chemical identity of the pure ethyl carbamate species was confirmed by ^{1}H and ^{13}C NMR (see supplementary material). Similarly, using diphenylcarbonate as a starting material instead of DMC or DEC, resulted in O-phenyl-N,N′-diphenylcarbamate (PdPC) at a yield of 9%.

The mechanism of the conversion of DPA to its carbamate equivalents is thought to be similar to the reported mechanism of the ionic liquid-catalyzed carbomethoxylation of carbazole and other N-heterocyclic compounds [13]. Coordination of the acidic proton from $[BMIM]^{+}$ to the carbonyl moiety on the dialkyl carbonate activates the carbonyl, which allows for the nucleophilic attack of DPA. Next, one of the alkyl groups is expelled as an alcohol when the C–N bond is formed. The catalytic cycle completes as the ionic liquid dissociates from the carbonyl that now belongs to the carbamate product (see Fig. 4).

The second and last step of the alternative synthesis of AK-II is the aminolysis of the remaining methoxy or ethoxy group with monomethylamine (MMA) (see Fig. 3). This reaction, the transformation of an O-methyl carbamate into its methylurea derivative was reported before, using pure liquid MMA at low temperatures [28]. For ease of the synthetic procedure, mixtures of saturated MMA solutions in water (40 wt% MMA) and EtOH (33 wt% MMA) were used instead. The rates of formation of AK-II and DPA significantly decreased when the ethanol content was increased at the expense of water. The optimal solvent system was chosen to be [ethanol (33 wt% MMA)]/[water (40 wt% MMA)] in a ratio of 1:3. Notably, the carbamate was not converted in the MMA solution in ethanol only.

At room temperature, the formation of AK-II from MdPC or EdPC was in trace amounts only, while the carbamates were consumed very slowly (weeks). The duration of the carbamate conversion reactions decreased drastically as the reaction temperature increased. In a closed vessel experiment at 100 °C, the reaction time decreased to 18 h for MdPC with complete consumption of the starting carbamate. The conversion of EdPC is slower: only after 12 days at 100 °C, EdPC was no longer present in the reaction mixture. However, poor yields of the targeted urea compound were obtained in these reactions. Both MdPC and EdPC yielded AK-II in only 4% while the carbamates were completely consumed at 100 °C. Remarkably, formation of AK-II in both reactions occurred only in the early stage of the reaction according to TLC; extending the reaction time resulted mainly in the degradation of the starting carbamate as observed by the increase of DPA. Remarkably, much higher yields of AK-II were obtained when using PdPC instead of MdPC or EdPC: even at room temperature a yield of 68% was obtained after 2 days, while after 5 days this increased to 81%. A possible explanation for the higher yield when using PdPC is that the OPh group appears to be a better leaving group compared to the OMe or OEt group, which allows to obtain good yields even at room temperature. The low AK-II yield for R = Me or Et at high temperatures, on the other hand, can be explained by competing reactions, i.e. carbamate hydrolysis, and/or the alkylation of MMA. DMC is known to react differently with hard or soft nucleophiles; hard nucleophiles can directly substitute the OMe group, while soft nucleophiles are more likely to be methylated when reacting with DMC: one of the methyl groups is transferred, and the carbonate is transformed in a carbonic acid [21]. Likewise, the alkyl carbamates carbamates could be involved in this side reaction as well. As $MeNH_2$ is a neutral and relatively bulky species, it can be considered a soft nucleophile indeed and hence this reaction is likely favoured over the direct substitution of the alcohol group. The formed carboxy-diphenylamine product during alkylation (or hydrolysis) can easily thermally decompose in DPA and CO_2 (see Fig. 5). The low yield for the conversion of both MdPC and EdPC seems to confirm this. For PdPC however, this side reaction with MMA is not expected to occur as there is no CH_2 group available for this reaction, and hence all of the carbamate is available for the formation of AK-II.

4. Conclusions and outlook

An alternative synthetic route towards AK-II was identified, which yielded the target compound in a two-step process. Most importantly, the newly found synthetic pathway avoids the use of the toxic gas phosgene. In the first step, the conversion of dimethyl-, diethylcarbonate or diphenylcarbonate and diphenylamine leads to their corresponding carbamates, using [BMIM]Cl in catalytic amounts. Next, these diphenyl carbamates were converted into AK-II by treatment with a methylamine solution. At this stage the alternative, phosgene-free synthesis has been demonstrated at small scale which would need further optimization before it can be scaled up with a continuous process. The origin of the dicarbonate species appears to play a crucial role, as it determines whether the first or second step of the presented route will be in high yield. Optimization should focus on finding a side group that gives a good yield for the conversion of the organic carbonate. The corresponding carbamate should not be prone to a degradation reaction as was found for MdPC and EdPC, which appears to be carbamate hydrolysis, and/or the alkylation of the soft nucleophile MMA.

In this synthesis route the only side-products are alcohols (ROH). Current research is focused on the direct synthesis of organic carbonates from such alcohols and CO_2 [27]. If the alcohol side-product of the

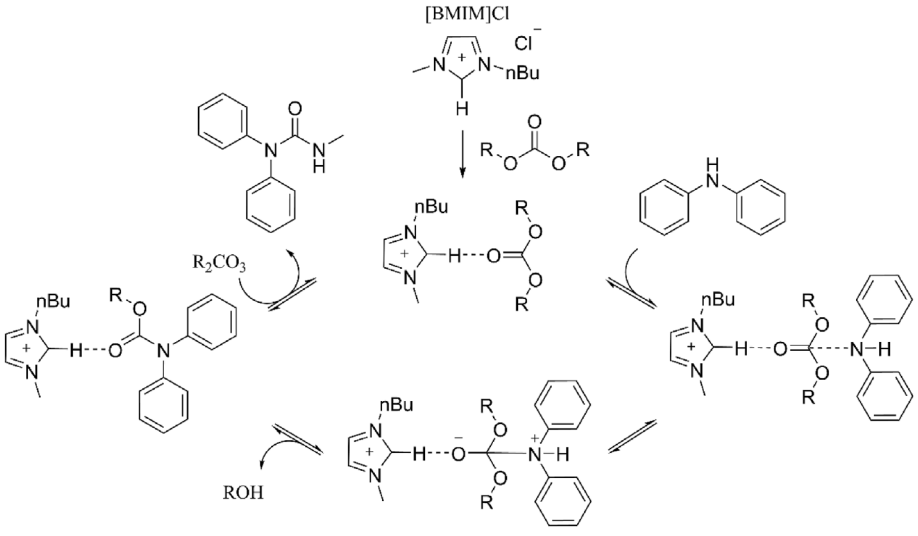

Fig. 4. Proposed reaction mechanism for the conversion of diphenylamine and dialkyl carbonates into O-alkyl-N,N′-diphenyl carbamates, catalyzed by a $BMIM^{+}$ salt. Adapted from Ref. [13].

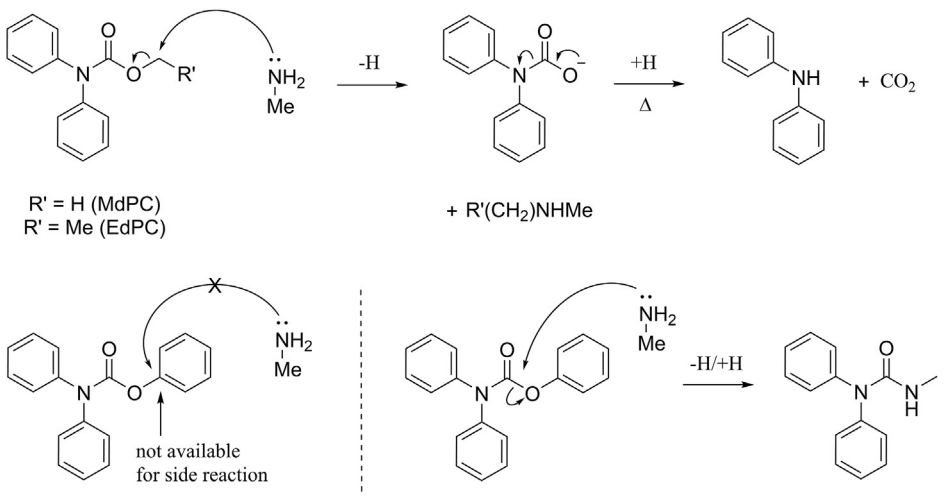

Fig. 5. Alkylation reaction as a side reaction for the conversion of MdPC and EdPC in AK- II, consuming the starting material, and thermal degradation into DPA and CO_2. For PdPC, this pathway is blocked and all starting material is available for the AK-II forming reaction.

proposed synthetic route are reused to form the organic carbonate starting material, AK-II may even be synthesized in the future using only CO_2, diphenyl amine and monomethylamine as precursors without the formation of side-products or the use of toxic reagents. In that way this synthesis procedure would have a negative overall carbon footprint.

Declaration of competing interest

The authors declare no conflict of interest.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.crgsc.2022.100336.

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