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Direct Synthesis of Imines *via* Solid State Reactions of Carbamates with Aldehydes

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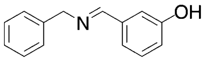
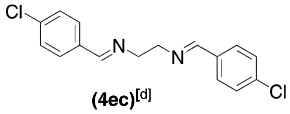
Abstract: Various solid carbamates were prepared from the reactions of liquid amines with carbon dioxide in an autoclave and these carbamates were used as stable, efficient alternatives for toxic liquid amines. Solid-state grinding of carbamates and aldehydes, using a mortar and pestle, produced imines as the sole products in greater than 97% yields. Complete conversions were generally accomplished within a day at 25 °C without using solvents or additives. Reaction rates were drastically enhanced upon increasing the reaction temperature. In contrast, reactions of aldehydes with liquid amines in the presence of solvent or in neat conditions afforded imines in moderate yields along with by-products.

Keywords: aldehydes; amines; grinding; imines; solid carbamates; solid state reaction

It has long been known that amines readily absorb carbon dioxide (CO_2) to yield liquid or solid adducts depending on the nature of the amine.[1–7] Usually, two equivalents of an amine (RNH_2) combine with a CO_2 molecule to form an alkyl ammonium carbamate salt ($RNHCO_2^-H_3N^+R$). Although it is stable, the carbamate can revert to the parent amine and CO_2 by external stimuli, such as heating or pressure.[3–7] This reversible interaction between amines and CO_2 is utilized in industry to capture and store CO_2 from flue gases.[6] A wide range of amines has been extensively investigated to develop new liquid absorbents for CO_2 capture.[4–9] In contrast, only a few studies on the reactivity of the carbamate salts have been performed,[1] due presumably to the lack of applications in organic syntheses. The majority of carbamates can generate amines by releasing CO_2 gas, which suggests they can be used as synthetic equivalents to liquid amines.[4–7] Compared to toxic and volatile amines, solid carbamates could prove to be better alternatives for the efficient synthesis of amine-derived chemicals largely because they are easy to store and handle in the lab. Moreover, solid carbamates would be appropriate precursors for the preparation of imines *via* the solid-state grinding method, which allows them to react readily with solid aldehydes.

The majority of organic synthetic methods proceeds in liquid media and involve multiple steps, which then require separation and purification processes. In contrast, organic solid-state reactions are able to synthesize useful chemicals in the absence of solvents. The solid-state grinding method can therefore minimize the synthetic steps and may thus allow the separation process to be skipped, which in turn could allow for an environmentally benign approach to synthesize various organic materials.[10,11] However, in order to apply this simple technique to a wide range of organic reactions, organic solids that can readily react with other substrates in the solid state are necessary. Within this context, we reported our studies of the solid state reactivity of hydrazinium carboxylate ($H_3N^+NHCO_2^-$), isolated from the reaction of liquid hydrazine (H_2NNH_2) with supercritical CO_2, towards carbonyl compounds.[12] The solid state reactions, performed by grinding a mixture of two reactants with a mortar and a pestle at ambient conditions, yielded azines as the sole products in yields greater than 97%.[12] This single-step process involves CO_2 evolution, which appears to trigger the close contact of hydrazine and the aldehyde at the molecular level and favours the forward reaction for azine formation.

Table 1. Reactions of aldehydes with solid carbamates (**2a**, **2e**) in the solid state and with amines (**1a**, **1e**) in solution.[a]

Entry	Carbamates/ Amine (mmol)	Aldehyde (mmol)	Solvent	Product	Time [h]	Conversion [%]	Selectivity [%]	Yield [%]	Remarks
1	**2a** (5)	**3a** (10)	none	 (4aa)	3	>98	~100	>98[b]	grinding
2	**1a** (10)	**3a** (10)	neat	**4aa**	3	>98	<77	75[c]	solution
3	**1a** (10)	**3a** (10)	MeOH[e]	**4aa**	3	~86	~90	~77[c]	solution
4	**2e** (5)	**3c** (10)[d]	none	 (4ec)[d]	<1	>98	~100	>98[b]	grinding
5	**1e** (5)	**3c** (10)[d]	neat	**4ec**[d]	3	<30	96	29[c]	solution[f]
6	**1e** (5)	**3c** (10)[d]	MeOH[e]	**4ec**[d]	1	>98	~90	~81[c]	solution

[a] *Reaction conditions:* 20-mL vial, 50 °C.

[b] Isolated yield based on **3**.

[c] Yield was determined by ^{1}H NMR.

[d] **3c**: 4-chlorobenzaldehyde, **4ec**: N^1,N^2-bis(4-chlorobenzylidene)ethane-1,2-diamine.

[e] MeOH: 10 mL.

[f] The volume of ethylenediamine (**1e**, 0.3 g, ~0.33 mL) seemed to be too small to react with the solid aldehyde (**3c**, 1.4 g) in the absence of a solvent.

As a continuing effort to understand the nature of organic reactions in the solid state, we synthesized solid carbamate salts by reacting liquid amines with CO_2 and investigated their solid-state reactivity towards aldehydes. Remarkably, the solid state grinding of carbamates and aldehydes produced various imine derivatives, which were isolated as sole products in over 97% yields. This is the first example to demonstrate that solid carbamates can be used as synthetic alternatives to toxic liquid amines.

In addition, the grinding method shows higher selectivity towards imine formation than the conventional solution-based synthesis.

A wide range of solid carbamates was prepared by the reactions of liquid amines with CO_2. All products were isolated as white solids, as shown in Table S1 in the Supporting Information. Their compositions and structures were initially identified by elemental analysis, melting point, ^{1}H NMR, and ^{13}C NMR. In addition, thermal gravimetric analysis, IR spectroscopy, UV-visible spectroscopy, and X-ray powder diffraction (XRD) were employed to characterize the compounds and confirm their structures. Generally two equivalents of monoamines (**1a–d**, see the Supporting Information) react with one CO_2 molecule to yield the corresponding carbamate salts (**2a–d**, see the Supporting Information). Meanwhile, the diamines (**1e**–**h**, see the Supporting Information) produced the corresponding carbamate salts (**2e–h**, see the Supporting Information) using a 1:1 ratio of amine and CO_2. All of the solid carbamates obtained from the reactions above are quite stable and do not show deterioration even after storing the solids for a long period (>6 months).

To explore the reactivity of the carbamate salt towards an aldehyde, the reaction between benzylamine carbamate (**2a**) and 3-hydroxybenzaldehyde (**3a**), both in the solid state, was initially investigated. Grinding **2a** with two molar equivalents of **3a**, using a mortar and pestle, and then storing the mixed powder at 50 °C produced the white crystalline powder 3-benzyliminomethylphenol (**4aa**) as the sole product. The solid-state reaction occurred rapidly (Table 1, entry 1) and complete conversion was achieved within 3 h without intermediate grinding of the mixture. Moreover, the selectivity was almost 100%. The reaction products were carefully analyzed by ^{1}H NMR and powder XRD. No by-product, besides the imine, was identified from the reaction mixture. In the course of the solid-state reaction, **2a** appears to dissociate gradually into benzylamine (**1a**) and CO_2. It is therefore conceivable that the solid carbamate (**2a**) could be useful for the preparation of imines and could also be used for other organic synthetic techniques as an alternative source to liquid amine (**1a**).[13–15] An additional advantage of the grinding method is that it allows the solid reactants to react efficiently at ambient conditions and leads to the formation of the product without producing any waste.

To confirm the solid state structure of **4aa**, we grew single crystals of **4aa** from a chloroform/ether (1:1) solution. The crystal structure of **4aa** was determined by single crystal X-ray diffraction, and it indicated that the structure was composed of two crystalographically independent imine molecules. The two molecules are virtually identical although they have subtle differences in their bond distances and angles.

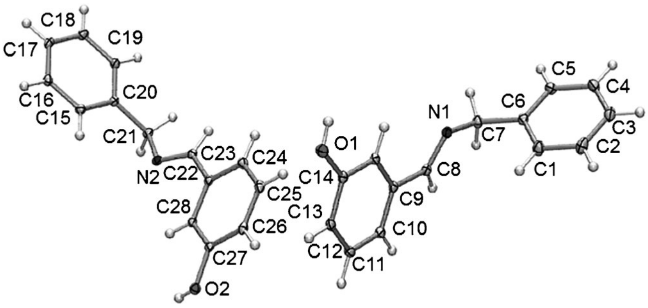


Figure 1. ORTEP plot of the asymmetric unit of 3-benzyliminomethylphenol (**4aa**), at 30% probability level of the thermal ellipsoids. Hydrogen atoms are not labelled for clarity. CCDC 882727 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Figure 1 shows the ORTEP diagram of **4aa**, which is based on the amine and aldehyde units linked by an imine (−N=C−) group. The bond distance of N1−C8 in the imine group is 1.266 Å, and it is similar to those of typical N=C double bonds.[15,16] The bond angles of C8−N1−C7 and N1−C8−C9 are 116.50° and 124.00°, respectively (see Table S1, Table S2 and Table S3, in the Supporting Information). Detailed data are presented in Table S2 in the Supporting Information.

Liquid benzylamine (**1a**) was reacted with **3a** to determine whether the solution-based reaction also yields the imine (**4aa**) selectively. The reaction was performed in CH_3OH as well as in neat conditions using benzylamine as the solvent. Both reactions produced the imine (**4aa**) along with unknown by-products in yields of less than 75% (Table 1, entries 2 and 3). The selectivities towards **4aa** in CH_3OH and neat conditions are lower by 10% and 23% than that of **2a**, respectively. These values are significantly lower than those corresponding to the solid-state reaction. Excellent reactivity towards the aldehyde was also observed in the 2-ammonio ethyl carbamate (**2e**), provided in Table 1 (entry 4). As anticipated, the solution-state yield from the reaction between ethylenediamine and aldehyde (**3c**) is lower compared to that from the solid-state reaction (Table 1, entries 5 and 6).

Based on the results described above, the solid-state grinding approach provided better yields and higher selectivities for the imine formation than the solution-based method. The solid-state reaction between ionic or covalent solids is generally poorly able to produce new phases at ambient conditions although solid-state transformations of metal oxides into metal-organic materials can be accomplished by mechano-chemical milling near room temperature.[17] This is because a conventional solid-state reaction typically requires reaction temperatures over 1,000 °C. This difficulty is largely due to the presence of strong ionic or covalent bonds in the solids. In molecular solids like ice and **2a**, however, the molecules are held together by van der Waals forces, which are weak intermolecular bonds. Accordingly, freestanding molecules can be released from the solid matrix simply by imposing external forces, and can therefore react with other molecular solids at the molecular level. The carbamate (**2a**) has important characteristics as a solid reagent because of the orderly packing of the molecules of benzylamine carbamate; this allows **2a** to be as reactive as benzylamine, even in the solid state. Moreover, **2a** has the ability to sublime at elevated temperatures and can easily produce pure amines by releasing CO_2 gas.

Thus, these characteristics may exert advantageous effects on the reactivity of **2a**, which could in turn contribute to the high selectivity of **2a** in the solid state reaction.

To understand how the solid-state reaction occurs at the interface to yield the product selectively, the simple grinding method was further explored. We chose the reaction between **2a** and **3a** as a model system mainly because the product (**4aa**) is well characterized by single crystal X-ray diffraction, which allows for easy monitoring of the reaction products by XRD. Solid state reactions between the two reactants were performed at room temperature. Ground powders were stored in a vial, without any additional agitation, at 50 °C. The products were carefully analyzed by powder XRD and ^1H NMR as a function of reaction time. New peaks corresponding to **4aa** appeared in the XRD patterns after only 30 min, as illustrated in Figure 2. Over 98% conversion of the reactants to **4aa** was accomplished in the solid state within 3 h in the absence of intermediate grinding. These results suggest that free benzylamine molecules, produced *via* the dissociation of **2a**, react directly with the surface molecules of **3a** to yield the imine as the sole product. It is worth mentioning that the CO_2 gas that evolved upon grinding accelerated the forward reaction. This could be the reason why solid carbamates are as reactive as liquid amines. The ease of product formation *via* grinding also suggests that the highly pure amines produced by the release of CO_2 gas play a major role in determining the reactivity.

To extend the scope of the solid-state reaction, we reacted **2a** with other benzaldehydes (**3b–3e**, Table 2, entries 1–4). By grinding a mixture of two reactants alone, complete conversion was typically accomplished in a 24 h period at room temperature. To reduce the reaction time, ground powders stored in vials were allowed to react at elevated temperatures. Reaction rates were drastically enhanced and conversions were complete within 3 h. Imines were obtained as sole products in high yields and excellent selectivi-

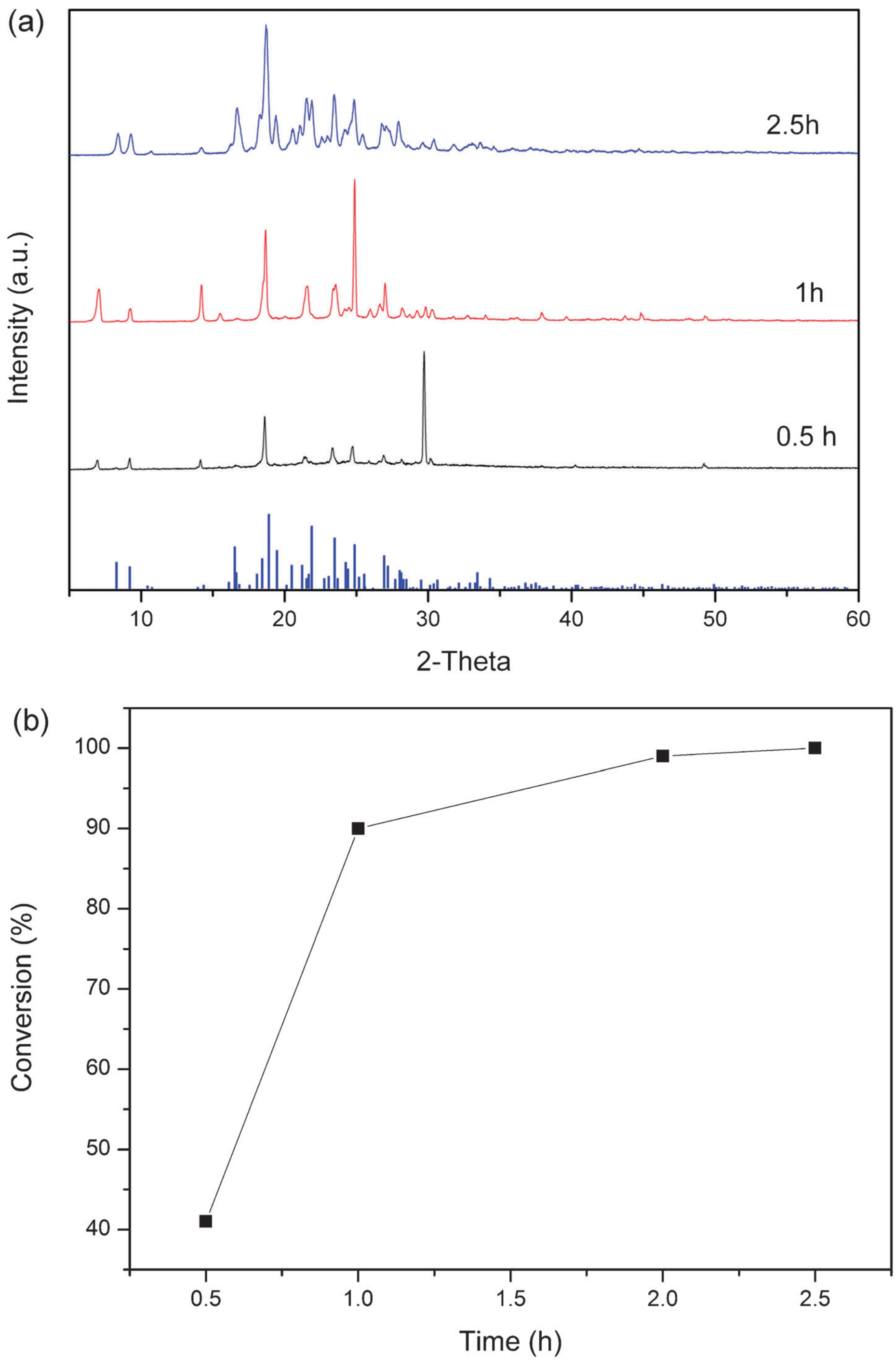
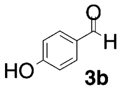
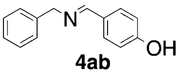
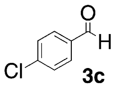
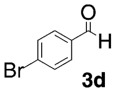
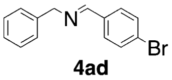
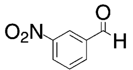
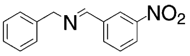


Figure 2. (a) Powder XRD patterns of the products obtained by grinding a mixture of **2a** and the aromatic aldehyde (**3a**, Table 1, entry 1) at intervals of 30 min, 1 h, and 2.5 h at 25 °C. The vertical bars at the bottom of the spectrum correspond to the theoretical diffraction peaks of **4aa. (b)** Yields of **4aa** as a function of reaction time were determined by ^{1}H NMR spectroscopy.

ties (~100%), regardless of the substituents on the aldehydes. We also evaluated the scope of this remarkable grinding method with diamine carbamates, prepared by the reaction of diamines with CO_2. The diamine carbamates, listed in Table S1 in the Supporting Information, were used as solid reagents, and found to be excellent precursors for the substitution of liquid amines.

As shown in Table 3, various imines were isolated as sole products, in which a 1:2 mixture of a diamine carbamate and an aldehyde were ground at room temperature and stored in a vial at 50 °C. Complete

Table 2. Solid-state reactions of four aldehydes with the solid carbamate (**2a**).[a]

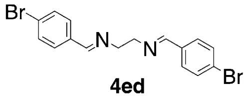
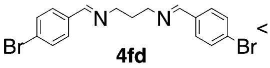
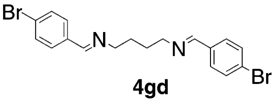
Entry	Reactants	Product	Time [h]	Temp. [°C]	Yield [%][b]	Remarks[c]
1	 **3b**	 **4ab**	<3	80	>98	grinding
2	 **3c**	 **4ac**	<2	50	>98	mixing
3	 **3d**	 **4ad**	<2	25	>98	mixing
4	 **3e**	 **4ae**	1	25	>97	mixing

[a] *Reaction conditions:* **3** (10 mmol), carbamate (**2**, 5 mmol) in a 10-mL vial.

[b] Isolated yield based on **3**.

[c] Mixing: powders in the same vial are shaken, grinding: powders are ground with a mortar and pestle.

Table 3. Solid state reactions of the aldehyde (**3d**) with three solid carbamates obtained from the corresponding diamines.[a]

Entry	Reactants	Product	Time [h]	Temp. [°C]	Yield [%][b]	Remarks[c]
1	**2e**	 **4ed**	3	50	>98	mixing
2	**2f**	 **4fd**	<1	50	>98	mixing
3	**2g**	 **4gd**	3	50	>98	mixing

[a] *Reaction conditions:* **3d** (10 mmol), carbamate (**2**, 5 mmol) in a 10-mL vial.

[b] Isolated yield based on **3d**.

[c] Mixing: powders in the same vial are shaken.

conversion to the corresponding imines was achieved within 3 h at 50 °C. The solid-state reactions yield highly selective products without producing waste; these are distinct advantages over conventional organic reactions performed in solvent. Accordingly, this simple grinding method is in accordance with a green reaction that proceeds at ambient conditions, requires no solvent, produces no waste, is very selective, and shows high atom efficiency.

In summary, we have demonstrated that a wide range of solid carbamates, prepared by the reactions of liquid amines with CO_2, could be used as stable, solid alternatives for toxic liquid amines. A remarkable feature is that they readily react with aldehydes, even in the solid state, to generate imines as the sole products, besides the CO_2 and H_2O generated from the reaction. The solid-state grinding method also has the potential to synthesize organic solids that are unavailable by conventional solvent-assisted methods. Moreover, this method exhibits the possibility of large-scale production with a very small vessel: for example, we could produce more than 20 g of imine in a 50-mL vial. This grinding methodology could thus be exploited for industrial applications. It is worth noting that similar methods such as accelerated aging and vapour digestion have been developed for the large-scale synthesis of metal-organic materials and co-crystals.[18]

Experimental Section

Synthesis of Solid Carbamates

The glass liner of an autoclave (Parr 4760, 300 mL) was charged with an amine (**1**, 200.0 mmol, see Table S1 in the Supporting Information) and dry ice (100 g), and the gauge and gauge block assembly were attached. Subsequently, the autoclave was placed in an oil bath on a hot plate. The reaction temperature was about 130 °C and the CO_2 pressure was in the range of *ca.* 90–110 bar. After the appropriate time, the autoclave was removed from the oil bath and cooled to ambient temperature very slowly. The excess gas was discharged and the system was disassembled. The white crystalline powders (**2**) in the glass liner were filtered in air, followed by washing with cold methanol (3 × 100 mL), cold diethyl ether (3 × 100 mL), and pentane (3 × 100 mL). The resulting solid was then dried under vacuum. The typical yields of solid carbamates (**2**) based on the used amines were over 95%. The solid carbamates were fully characterized by various analytical techniques, which are given in Supporting Information.

General Procedure for the Preparation of Imines from the Solid-State Reactions between Carbamates and Solid Aldehydes

About 1:2 mixtures of carbamate (5.03 mmol, **2**) and aldehyde (10.0 mmol, **3**) were ground at room temperature using a pestle and mortar for 5 min. The ground mixture was placed in a vial and warmed to the desired temperature in an oven. CO_2 and water were gradually released from the reaction mixture. Complete conversion to imine was strongly dependent upon the nature of aldehydes. Both yield and selectivity are typically over 97%. The resulting products were identified by ^1H NMR, ^{13}C NMR, IR, and GC/MS. To measure UV-visible, melting point, and elemental analysis, a small portion of the product (*ca.* 0.2 g) was purified by washing with cold ether (3 × 5 mL) and pentane (3 × 5 mL), followed by drying under vacuum. Analytical data for the products are given in Supporting Information.

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