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Synthesis of dialkyl hexamethylene-1,6-dicarbamate from 1,6-hexamethylenediamine and alkyl carbamate over $FeCl_3$ as catalyst

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ABSTRACT

A series of catalysts (e.g. $FeCl_3$, $Zn(OAc)_2$, $Pb(NO_3)_2$, etc.) were tested for the trans-esterification reaction of 1,6-hexamethylenediamine (HDA) with methyl carbamate (MC), ethyl carbamate (EC), and butyl carbamate (BC) to afford dialkyl hexamethylene-1,6-dicarbamate (AHDC). By applying the optimized condition, 100% conversion of HDA and 93% yield to diethyl hexamethylene-1,6-dicarbamate (EHDC) could be obtained using $FeCl_3$ as catalyst. The desired products could be precipitated by adding water into the resulting mixture, and the activity of recovered catalyst could be maintained.

1. Introduction

As the key intermediates for the non-phosgene synthesis of isocyanates, the development of eco-friendly processes for carbamate synthesis have been extensively studied [1–4]. Typical protocols for the synthesis of carbamates include oxidative carbonylation of amines [5,6], reductive carbonylation of nitro derivatives [7–10] and methoxycarbonylation of amines [11–14]. The intrinsic problems, i.e. the usage of poisonous CO/explosive $CO + O_2$, the deactivation of noble metal catalyst and the higher cost of dimethyl carbonate (DMC) [15], make their practical application difficult. On the other hand, recently, the utilization of alkyl carbamates (AC) (e.g., MC, EC and BC) as eco-friendly carbonyl source for non-phosgene carbonylation also attracted much attention [16,17]. In the meantime, MC, EC and BC can be produced from the alcoholysis of urea and the usage of phosgene and carbon monoxide is avoided. However, the reports for producing carbamates, in particular dialkyl hexamethylene-1,6-dicarbamate (AHDC), which is the precursor for non-phosgene synthesis of hexamethylene-1,6-diisocyanate, are still limited [18,19]. At the same time, rigorous reaction conditions such as high temperature (>473 K) or long reaction time (>10 h) are normally concerned.

With our continuous efforts to develop novel non-phosgene carbonylation process [20,21], the synthesis of AHDC via the trans-esterification reaction of HDA and AC using $FeCl_3$ as catalyst will be presented here, Scheme 1.

2. Experimental

2.1. Compounds and materials

All chemicals used in the experiments were of analytical grade, and used without further purification. Catalysts were dried at 333 K prior to use. MC, EC, and BC with 98–99% purity (GC purity) were synthesized in our laboratory. The methanol, ethanol and *n*-butanol used as solvents were dehydrated and purified with distillation before use.

2.2. Reaction procedure

All reactions were carried out in a 120 mL autoclave equipped with magnetic stirring. HDA (10 mmol), AC (0–40 mmol), corresponding alcohol (methanol, ethanol and *n*-butanol) (0–250 mmol) and the catalysts (0–0.7 mmol) were charged successively into the reactor flushed with N_2 gas. After reaction the reactor was cooled to room temperature, ~20 mL alcohol was added to dissolve the soluble product and iron salts. Then it was filtrated to separate the polyurea. The yield to polyurea was based on the monomer

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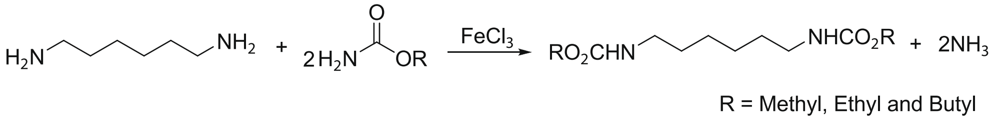


Scheme 1. The synthesis of AHDC from HDA and AC.

(–$HNCH_2CH_2CH_2CH_2CH_2CH_2NHCO$–). The filtrate was concentrated till ~5 mL solution was left and the precipitation of iron salts formed. The iron catalyst therefore could be recovered by filtration. After vacuum drying, ~92 mg iron salts could be obtained (~95% in comparison with $FeCl_3$ by weight). XPS analysis of the iron salts suggested it is a mixture of iron chloride, iron hydroxide and iron oxide. The liquid mixture was further evaporated at 353 K and a white mixture including AHDC and AC were obtained. Then, 50 mL water was charged to dissolve AC and residual catalyst. The desired AHDC product could be obtained after filtering and vacuum drying. Qualitative and quantitative analysis were carried with HP 6890/5973 GC–MS and Agilent 1790 GC–FID.

3. Results and discussions

3.1. Effects of the catalysts and solvents

Firstly, the reactions of HDA (10 mmol), EC (30 mmol) (entries 1–11) and ethanol (200 mmol) were carried out over $H_3PO_4{\cdot}12WO_3$, $Zn(OAc)_2$ [22], $ZnCl_2$ [17,23], $Pb(NO_3)_2$ [13], $NaOCH_3$ [24], $Zn(NO_3)_2$, or $FeCl_3$ (0.6 mmol), Table 1. In the absence of catalyst, entry 1, the yield to EHDC was only 10% with 100% conversion, which means that this reaction could proceed without catalyst but with low yield. Better results were obtained with the addition of different metal salts, entries 2–8. Similar as the control reaction, 85–100% conversion exhibited under all cases. Up to 96% selectivity was achieved when $FeCl_3$ as catalyst was employed. The isolated yield to EHDC reached to 93%, entry 8.

The effect of the catalyst loading on the reaction was further screened. Less $FeCl_3$ catalyst addition caused lower selectivity and yield to the desired product and more polyurea [25,26] byproduct was isolated, entry 9. Further increasing of the amount of catalyst to 0.7 mmol presented similar result as 0.6 mmol, entry 10. Therefore, 6 mol% of $FeCl_3$ should be the suitable catalyst loading with the conditions employed in this work.

Noteworthy, the iron catalyst could be isolated after reaction. By the analysis of XPS, although it was not shown here, the recovered iron salt was a mixture of iron hydroxide, iron oxide and iron chloride. The weight is ~95% in comparison with the $FeCl_3$ added at the initial stage. To our delight, similar catalytic activity exhibited if 0.03 mmol (5%) fresh $FeCl_3$ was re-supplied and 92% EHDC yield maintained at the 4th run, entry 11. Thus the recovered catalyst mixture was active enough although its real component was still unclear at this stage.

Further applying of MC and BC as carbonyl source gave 84% yield to dimethyl hexamethylene-1,6-dicarbamate (MHDC) and 91% yield to dibutyl hexamethylene-1,6-dicarbamate (BHDC), entries 12–13. Moreover, good results were also obtained if using aniline and cyclohexylamine used as substrates under the same reaction conditions, entries 14–15. The yields to ethyl *N*-phenyl carbamate and *N*-cyclohexyl carbamate were 85% and 94%, respectively. These results suggested our iron catalyst has good generality in the trans-esterification of amines and AC.

By GC–MS and GC–FID analysis, the detectable byproducts were 1–10% of alkyl hexamethylene-1-carbamate-6-isocyanate (AHCI) and 5–20 % of dialkyl carbonate (DAC). AHCI may be produced via the thermal decomposition of AHDC, Scheme 2-I. Among all the reactions, much more DEC was observed when $NaOCH_3$ was used as catalyst, which was resulted from the alcoholysis of EC, Scheme 2-II.

Table 1
Optimization of the reaction conditions for the synthesis of AHDC[a].

Entry	Catalyst/mmol	Con. (%)[b]	Sel. (%)[c]	Byproduct (%)		Yield (%)[f]
				AHCI[d]	Polyurea[e]	
1	––	100	14	10	76	10
2	$H_3PO_4{\cdot}12WO_3$/0.6	85	36	4	60	27
3	$Zn(OAc)_2$/0.6	100	59	2	39	56
4	$ZnCl_2$/0.6	92	64	4	33	55
5	$Pb(NO_3)_2$/0.6	100	80	3	17	76
6	$NaOCH_3$/0.6	100	83	7	10	80
7	$Zn(NO_3)_2$/0.6	100	86	6	9	83
8	$FeCl_3$/0.6	100	96	1	3	93
9	$FeCl_3$/0.5	100	91	2	8	88
10	$FeCl_3$/0.7	100	96	2	3	93
11[g]	$FeCl_3$/0.6	100	94	2	4	92
12[h]	$FeCl_3$/0.6	100	90	1	10	84
13[i]	$FeCl_3$/0.6	100	95	4	2	91
14[j]	$FeCl_3$/0.6	92	99	1 (Diphenyl urea)		85
15[k]	$FeCl_3$/0.6	>99	98	2 (Dicyclohexyl urea)		94

[a] Reaction conditions: HDA, 10 mmol; EC, 30 mmol; ethanol (solvent), 200 mmol (11.5 mL); $FeCl_3$, 0.6 mmol; 453 K, 5 h.

[b] Conversion of HDA.

[c] Selectivity to EHDA.

[d] The number was estimated with GC–FID by comparing the peak area of EHDA.

[e] Isolated yield of polyurea. It was based on the monomer (–$HNCH_2CH_2CH_2CH_2CH_2CH_2NHCO$–).

[f] Isolated yield.

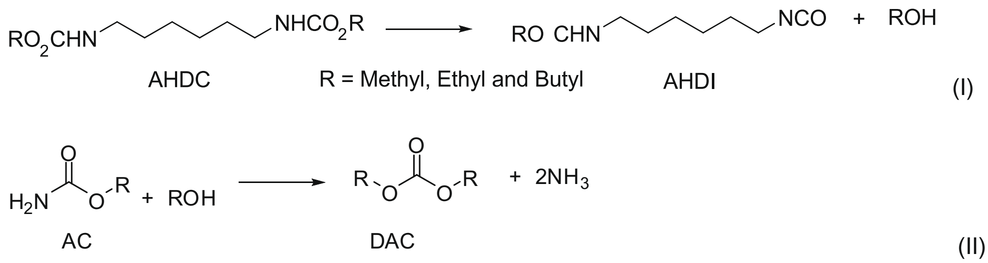
[g] Recovered catalyst added with fresh $FeCl_3$ in ca. 5% total amount charged was used at the fourth run.

[h] MHDC was synthesized from HDA and MC using methanol as solvent.

[i] BHDC was synthesized from HDA and BC using *n*-butanol as solvent.

[j] Ethyl *N*-phenyl carbamate was obtained from aniline and EC.

[k] Ethyl *N*-cyclohexyl carbamate was produced from cyclohexylamine and EC.



Scheme 2. Possible side reactions.

3.2. Effects of the molar ratio of ethanol/HDA and EC/HDA

The effects of the molar ratios of ethanol and HDA on the EHDC synthesis were further investigated using $FeCl_3$ (0.6 mmol) as catalyst, Fig. 1. The molar ratios of ethanol and HDA increased from 0:1 to 25:1 step by step. In the absence of ethanol, 60% of polyurea and 6% of ethyl hexamethylene-1-carbamate-6-isocyanate (EHCI) formed and the yield to EHDC was only ~5%. The yield of EHDC could be improved with the addition of ethanol and it reached to the maximum when ethanol: HDA = 20. The corresponding yield was 93%. The introduction of more ethanol caused lower yield. Possibly it is because of the low concentration of catalyst and reactants.

Using $FeCl_3$ (0.6 mmol) as catalyst and with a fixed molar ratio of ethanol/HDA = 20, the impact of ratio between EC and HDA on EHDC synthesis was investigated, Fig. 2. The ratio of EC and HDA varied from 2:1 to 9:1. The yield to EHDC firstly increased and kept unchanged when the ratio of EC to HDA reached to 3. The presence of more EC would promote it further alcoholysis to diethyl carbonate. If too less EC was used, much more polyurea would form. For example, when EC/HAD = 2, the EHDC yield was only 21% and 70% polyurea formed.

3.3. Effects of reaction temperature and time

The effect of reaction temperature on the synthesis of EHDC was further tested, Fig. 3. With temperatures being increased from 393 to 473 K, HDA conversion and EHDC yield increased correspondingly. The highest yield to EHDC, i.e. 93%, was obtained at 453 K. At 393 K, the EHDC yield was 3% and the main product was polyurea. If the reaction was carried out at higher temperature (>453 K), the thermal decomposition of EHDC occurred and 9% EHCI was observed at 493 K, Scheme 2-I.

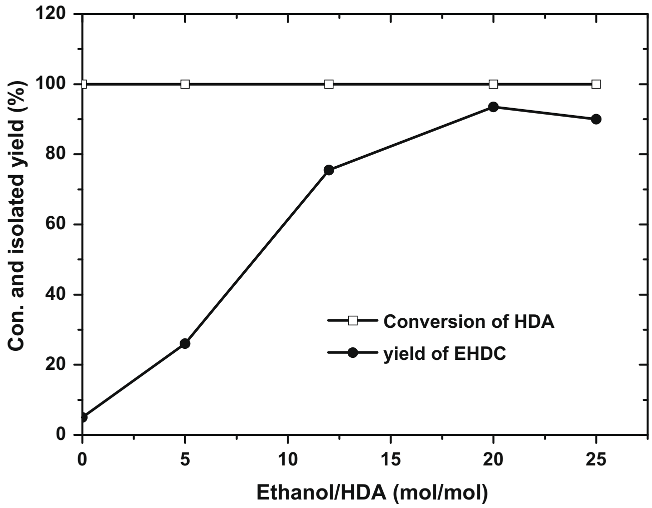


Fig. 1. Effects of molar ratio of ethanol to HDA on the synthesis of EHDC. Reaction condition: HDA, 10 mmol; EC, 30 mmol; FeCl3, 0.6 mmol; 453 K, 5 h.

The effect of reaction time on the synthesis of EHDC was also examined, Fig. 4. At the initial stage, the main product observable was polyurea and it decreased with longer reaction time. At 3 h, the yield to EHDC was 81% and 10% of polyurea was detected. If the reaction progressed for 5 h, the selectivity to EHDC reached to 96% and the corresponding isolated yield was 93%. These results

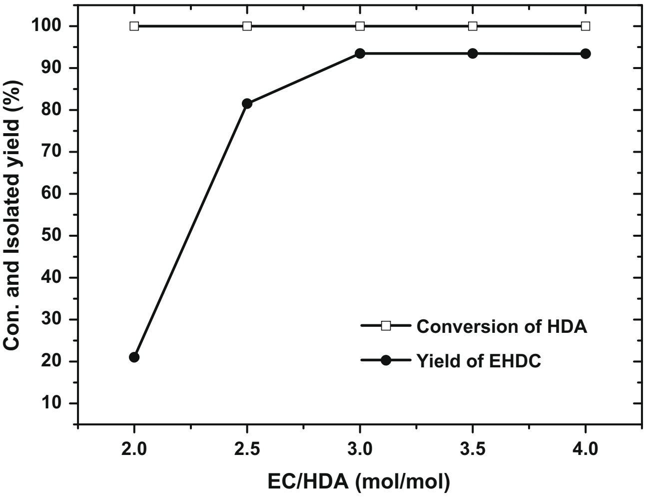


Fig. 2. Effects of molar ratio of EC to HDA on the synthesis of EHDC. Reaction condition: HDA, 10 mmol; ethanol, 200 mmol (11.5 mL); FeCl3, 0.6 mmol; 453 K, 5 h.

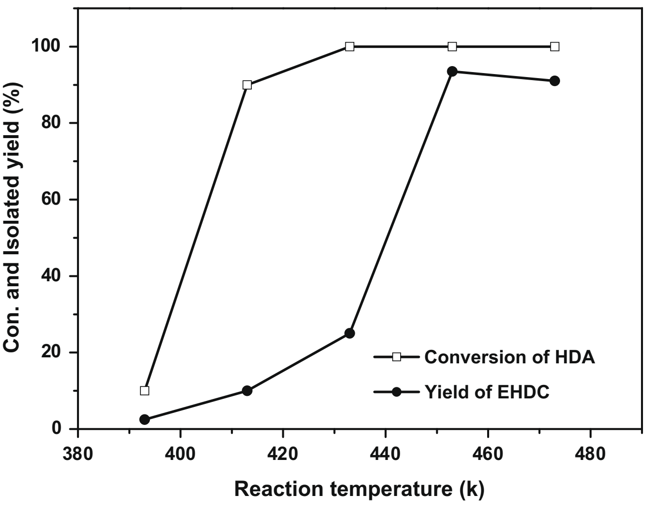


Fig. 3. Effects of reaction temperature on the synthesis of EHDC. Reaction condition: HDA, 10 mmol; EC, 30 mmol; ethanol, 200 mmol (11.5 mL); FeCl3, 0.6 mmol; 5 h.

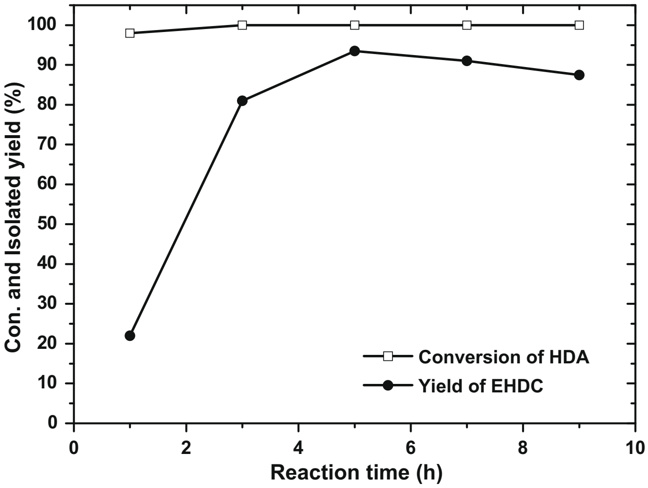


Fig. 4. Effects of reaction time on the synthesis of EHDC. Reaction condition: HDA, 10 mmol; EC, 30 mmol; ethanol, 200 mmol (11.5 mL); FeCl3, 0.6 mmol; 453 K.

indicated that polyurea is the possible intermediate for the formation of EHDC and EHDC might be produced via the alcoholysis of polyurea. Similar as we discussed above with higher reaction temperature, longer reaction time also caused the thermal decomposition of EHDC and therefore the corresponding yield would decrease.

4. Conclusions

In summary, non-phosgene synthesis of EHDC from HDA and EC was realized using FeCl$_3$ as catalyst. This method was simple, environmentally benign and easily manageable. More importantly, the application of alkyl carbamate as carbonyl source makes the usage of carbon dioxide as carbonyl source possible. Further improving of the catalyst system is now under going.

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