Catalytic methoxycarbonylation of aromatic diamines with dimethyl carbonate to their dicarbamates using zinc acetate

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The methoxycarbonylation of 2,4-toluene diamine and 4,4′-diphenylmethane diamine with dimethyl carbonate to the corresponding dicarbamates using zinc acetate was carried out at 453 K. Zn(OAc)$_2$, prepared by evacuating Zn(OAc)$_2$·2H$_2$O at 383 K for 2 h, yields dimethyltoluene-2,4-dicarbamate in 96% yield in 2 h, while Zn(OAc)$_2$·2H$_2$O yields dimethyl-4,4′-methylenediphenyldicarbamate in 98% yield at 453 K in 2 h.

The structure of methyl 3-amino-4-methyl phenyl carbamate, which is one of the intermediates for the reaction of 2,4-toluene diamine with dimethyl carbonate into dimethyltoluene-2,4-dicarbamate, has been determined by measuring the NOE spectrum of ^{1}H NMR.

KEY WORDS: methoxycarbonylation; dimethyl carbonate; dimethyltoluene-2,4-dicarbamate; dimethyl-4,4′-methylenediphenyldicarbamate; zinc acetate.

1. Introduction

Dimethyltoluene-2,4-dicarbamate, **2**, and dimethyl-4,4′-methylenediphenyldicarbamate, **4**, are precursors to 2,4-toluene diisocyanate and 4,4′-diphenylmethane diisocyanate, respectively, which are useful for the production of polyurethane and in various other expanding fields of applications. For instance, 4,4′-diphenylmethane diisocyanate is used as a monomer in the production of polyurethane elastomer and spandex, and in the coating process of artificial leather.

These aromatic diisocyanates are commercially synthesized by the reaction of phosgene with the corresponding diamines. The reaction, however, has several serious drawbacks. Phosgene is an extremely toxic reagent and a stoichiometric amount of HCl is produced as a byproduct. Furthermore, HCl causes serious corrosion.
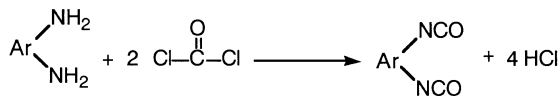
Since carbamates are convertible to isocyanates, *e.g.*, under the influence of heat [1], the methoxycarbonylation of 2,4-toluene diamine (TDA) and 4,4′-diphenylmethane diamine (MDA) with dimethyl carbamate (DMC) to produce the corresponding aromatic dicarbamates are

one of the attractive synthetic routes to isocyanates without using phosgene. DMC is currently produced on a large scale by the oxidative carbonylation of methanol with CO.

It was reported that Ti, Zr and Zn compounds [2–5] and Pb compounds [6,7] catalyzed the methoxycarbonylation of aromatic amines with DMC to carbamates. We also reported that Pb(NO$_3$)$_2$ showed a high catalytic activity for the reaction of aliphatic mono-amines such as hexyl amine with DMC into mono-carbamates [8]. Furthermore, we reported the methoxycarbonylation of diamine, *i.e.,* 1,6-hexanediamine with DMC to dimethyl-hexane-1,6-dicarbamates using Bi compounds [9], and the carbonylation of *o*-phenylenediamine with DMC to 2-benzimidazolone using Pb compounds such as Pb(NO$_3$)$_2$ [10].
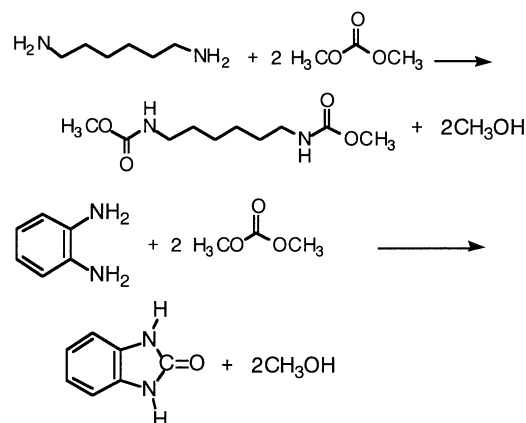
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In this work, we expand the catalytic methoxycarbonylation into the reaction of TDA or MDA with DMC to selectively produce **2** or **4**. We report that zinc acetate is a highly effective catalyst for the methoxycarbonylation of TDA and MDA with DMC.
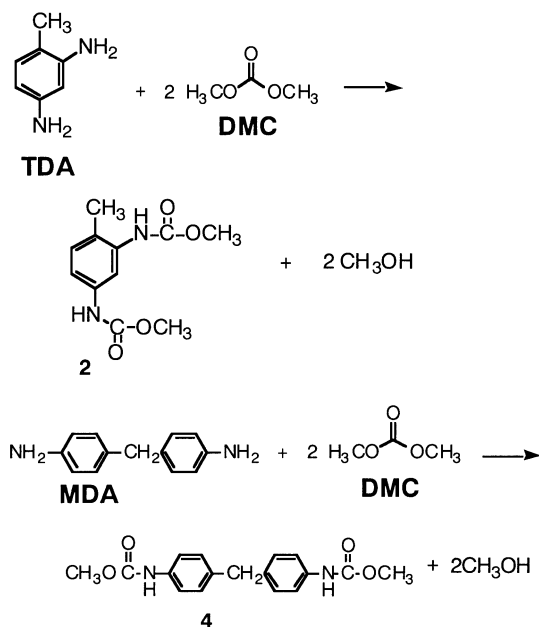
2. Experimental

2.1 Catalysts and reaction procedures

Metal salts such as $Zn(OAc)_2 \cdot 2H_2O$ were used as received, unless otherwise noted. $Zn(OAc)_2$ was obtained by evacuating $Zn(OAc)_2 \cdot 2H_2O$ at 383 K for 2 h, since dehydration of $Zn(OAc)_2 \cdot 2H_2O$ was observed around 383 K by TG/DTA analysis. DMC of guaranteed grade was purified by distillation before use, while TDA and MDA of guaranteed grade were used without further purification.

The reaction was carried out in a Teflon vessel placed in a $50 \, cm^3$ stainless-steel autoclave with a magnetic stirrer. The reaction and the manipulation of the reaction mixture were carried out under a nitrogen atmosphere.

2.2 Identification and quantitative analysis of reaction products

The reaction products (**2–4**) were identified by ^{1}H and ^{13}C NMR, and GC-MS. ^{1}H and ^{13}C NMR spectra were recorded on a JOEL ECP 400 spectrometer, while GC-MS analyses of the reaction products were performed on a Shimadzu GCMS-OP 5000 spectrometer. The NMR data of **2**, **3** and **4** obtained in this work were in good agreement with those reported in Ref. [11]. Mono-carbamates of TDA were further identified by measuring NEO spectra of ^{1}H NMR.

The conversions of diamines and the yields of reaction products were determined with HPLC, while the conversion of DMC was done by gas chromatography. Propyl benzene was used as an internal standard to determine both the conversions of diamines and the yields of reaction products. Unless otherwise noted, the yields of reaction products were expressed based on the amount of diamine charged.

3. Results and discussion

3.1 Methoxycarbonylation of 2,4-toluene diamine

To examine the catalytic activities of various metal salts, the reaction of TDA with DMC was carried out at 453 K. The amount of catalyst was 0.04 mmol, while those of DMC and TDA were 100 mmol and 4 mmol, respectively. A quantity of DMC in excess with respect to TDA is preferably used as it also acts as a solvent. Metal salts easily dissolved in DMC, and the reaction proceeded in a homogenous reaction system.

Without a catalyst, methoxycarbonylation of MDA with DMC did not proceed, while N-methylation of MDA proceeded, and the yields of N-methylated compounds were 1.2%. A small amount of urea was also formed in 0.2% yield.

The selection of metal salt is crucial for the formation of mono-carbamate and **2**. The structure of mono-carbamate was identified by measuring the NOE spectrum of ^{1}H NMR (figure 1). The data of ^{1}H and ^{13}C NMR spectra are summarized in table 1. According to the results of NMR measurements, the mono-carbamate has been assigned as methyl 3-amino-4-methyl phenyl carbamate, **1**. Thus, the methoxycarbonylation of TDA with DMC predominantly proceeds as expressed by following reaction at the initial stage, since the steric hindrance between the NH_2 group at the position of **2** and the CH_3 group may contribute to the selective formation of **1**.
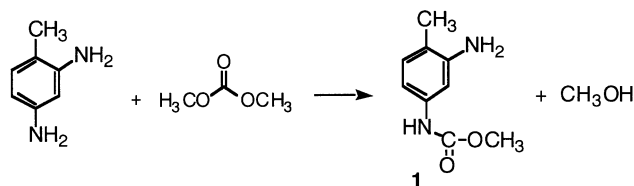
Among the catalysts, zinc carboxylates showed a high catalytic activity, as shown in table 2. For example, using $Zn(OAc)_2 \cdot 2H_2O$, the yield of **2** was 92% in 2 h at 100% conversion of TDA. The conversion of DMC was 14%, while the selectivity for **2** was 52% based on DMC converted.

The yield and selectivity of **2** increased when $Zn(OAc)_2$ was used as a catalyst, prepared by dehydration of $Zn(OAc)_2 \cdot 2H_2O$ at 383 K for 2 h under reduced
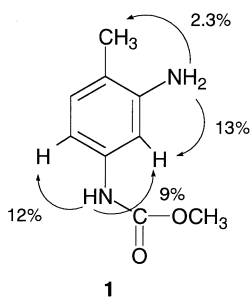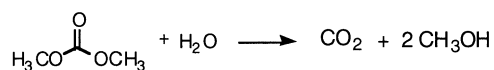
Figure 1. NOE spectrum of ^{1}H NMR of methyl 3-amino-4-methyl phenyl carbamate **1**.

pressure. Thus, the yield of **2** was 95%, while the selectivity based on DMC converted was 61%. In the presence of H_2O, DMC was presumably hydrolyzed to CO_2 and CH_3OH. The yield of **2** further increased by prolonging reaction time, and was 98% in 4 h.

$$H_3CO \overset{O}{\underset{}{C}} OCH_3 + H_2O \longrightarrow CO_2 + 2\,CH_3OH$$

Pb, Sm, Bi and Sn compounds, which were effective for the methoxycarbonylation of 1,6-hexanediamine

Table 1

(a) ^{1}H Chemical shift for methyl 3-amino-4-methyl phenyl carbamate, **1**, in DMSO-d$_6$ solvent

		Chemical shift (ppm)
1	$-NH$	9.13
2		6.76 d (2.0 Hz)
3	$-NH_2$	4.71
4	$-CH_3$	1.97
5		6.76 d (8.0 Hz)
6		6.53 dd (2.0 Hz, 8.0 Hz)
$O-CH_3$		3.61

(b) ^{13}C chemical shift for methyl 3-amino-4-methyl phenyl carbamate, **1**, in DMSO-d$_6$ solvent

	Chemical shift (ppm)
1	137.4
2	104.4
3	146.4
4	115.4
5	129.6
6	106.8
4 $-CH_3$	16.6
$O-CH_3$	51.1
$C=O$	153.8

Table 2

Catalytic activities of various metal salts for the methoxycarbonylation of TDA with DMC at 453 K

Catalyst	Conversion (%)		Yield ^{a} (%)		Selectivity ^{b} (%)	
	TDA	DMC	**2**	**1**	**2**	**1 + 2**
$Zn(CH_3COO)_2 \cdot 2H_2O$	100	13	77	14	44	48
$Zn(CH_3COO)_2 \cdot 2H_2O$ ^{c}	100	14	92	3	52	53
$Zn(CH_3COO)_2$ ^{c}	100	12	96	3	61	65
$Zn(CH_3COO)_2$ ^{d}	100	16	98	–	50	50
$Zn(CH_3COO)_2$ ^{e}	100	20	98	–	42	42
$Zn(C_2H_5COO)_2$	86	9	20	44	18	37
$Zn(C_{11}H_{23}COO)_2$	31	12	0	17	0	6
$Zn(C_{17}H_{35}COO)_2$	43	8	8	21	8	18
$Zn(HCOO)_2 \cdot 2H_2O$	0	18	0	0	0	0
$Zn(Et_2NCSS)_2$	85	28	12	25	4	7
ZnO	48	12	0	3	0	1
$Zn(HCOO)_2$	0	18	0	0	0	0
$Ti(O\text{-}iso\text{-}C_3H_7)_4$	93	20	8	41	5	19
$Sn(C_8H_{15}O_2)_2$	91	14	22	53	13	28
$Zr(O\text{-}n\text{-}C_4H_9)_4$	56	23	12	11	7	10
$Bi(NO_3)_3 \cdot 5H_2O$	54	11	0	3	0	1
$Sm(CH_3COO)_3 \cdot 4H_2O$	26	10	0	0	0	0
$Pb(NO_3)_2$	4	18	0	0	0	0
PbO	4	11	0	3	0	1
Without catalyst	15	16	0	0	0	0

^{a} Based on TDA.
^{b} Based on DMC.
^{c} Reaction time 2 h.
^{d} Reaction time 4 h.
^{e} Reaction time 8 h.
TDA 4 mmol, DMC 100 mmol, catalyst 0.1 mmol, reaction time 1.5 h.
$Zn(CH_3COO)_2$ was prepared by evacuating $Zn(CH_3COO)_2 \cdot 2H_2O$ at 483 K for 2 h.
$Zn(C_{11}H_{23}COO)_2$: zinc laureate; $Zn(C_{17}H_{35}COO)_2$: zinc stearate; $Ti(O\text{-}iso\text{-}C_3H_7)_4$: titanium tetra-iso-propoxide; $Sn(C_8H_{15}O_2)_2$: tin-2-ethylhexanoate; $Zr(O\text{-}n\text{-}C_4H_9)_4$: zirconium-$n$-butoxide.

Table 3
Catalytic activities of various metal salts for the methoxycarbonylation of MDA with DMC at 453 K

| Catalyst	Conversion (%)		Yield [a] (%)		Selectivity [b] (%)	
	MDA	DMC	4	3	4	4 + 3
$Zn(CH_3COO)_2 \cdot 2H_2O$	100	9	98	1	91	92
$Zn(C_2H_5COO)_2$	100	14	87	3	49	50
$Pb(CH_3COO)_2 \cdot 3H_2O$	100	11	90	2	62	63
$PbCO_3$	10	5	0	0	0	0
$Sn(C_8H_{15}O_2)_2$	56	18	25	5	11	12
$Sm(CH_3COO)_3 \cdot 4H_2O$ [c]	26	10	0	0	0	0
$Bi(NO_3)_3 \cdot 5H_2O$ [c]	54	11	0	3	0	1
$Pb(NO_3)_2$	4	18	0	0	0	0
PbO [c]	4	11	0	3	0	1
Without catalysts	7	6	0	0	0	0

[a] Based on MDA.
[a] Based on DMC.
MDA 4 mmol, catalyst 0.04 mmol, DMC 100 mmol, reaction time 2 h.
$Sn(C_8H_{15}O_2)_2$: tin-2-ethylhexanoate.

with DMC around 350 K [9], showed lower catalytic activities than $Zn(OAc)_2$.

3.2 Methoxycarbonylation of 4,4'-diphenylmethane diamine

Zn, Pb and Sn carboxylates also catalyzed the methoxycarbonylation of MDA with DMC at 453 K, as shown in table 3. Among the catalysts, $Zn(OAc)_2 \cdot 2H_2O$ showed the highest catalytic activity. The yield of **4** was 98% at 453 K in 2 h, when the conversion of MDA and DMC were 100% and 9%, respectively. A small amount of methyl 4[(4-aminophenyl)methyl] phenyl carbamate **3** was also observed, the yield of **3** being 2%. The selectivity for **4** based on DMC was 91%.
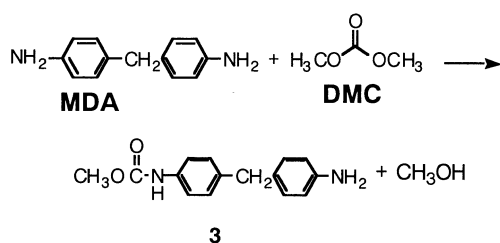
In the presence of $Zn(C_2H_5COO)_2$ and $Pb(OAc)_2 \cdot 3H_2O$, **4** was formed in a yield of 87% and 90%, respectively, by methoxycarbonylation of MDA with DMC in 2 h at 453 K, while tin(II)-2-ethylhexanoate showed a low catalytic activity. $PbCO_3$ did not show a catalytic activity, since it slightly dissolved in the solution of the DMC-MDA mixture.

Without a catalyst, the methoxycarbonylation of MDA with DMC did not proceed (table 3), similarly to that of TDA. In the case of methoxycarbonylation of 1,6-hexanediamine, dimethylhexane-1,6-dicarbamate and methyl-6-aminohexane-1-carbamate were formed

without a catalyst around 350 K [9]. These results suggest that the reactivities of TDA and MDA are much lower than that of 1,6-hexanediamine, since the basicity of aromatic amines is generally much lower than that of aliphatic amines. For example, the pK_a value of aniline is about 10^6 times smaller than that of aliphatic amine [12]. In the case of aliphatic amines, they possibly act as a base catalyst for the methoxycarbonylation with DMC, suggesting that the reaction mechanism for the formation of aromatic carbamates such as **2** is presumably different from that for the formation of dimethylhexane-1,6-dicarbamate. The study of the reaction mechanism is in progress.

4. Conclusions

Zinc acetate is an efficient catalyst for the methoxycarbonylation of 2,4-toluene diamine (TDA) and 4,4'-diphenylmethane diamine (MDA) with dimethyl carbamate to dimethyltoluene-2,4-dicarbamate and dimethyl-4,4'-methylenediphenyldicarbamate, respectively. The highly efficient conversion of aromatic diamines into the corresponding dicarbamates may offer a convenient route to the synthesis of diisocyanates for the production of polyurethane and in various other expanding fields of application.

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