

# Carbonylation of *o*-Phenylenediamine and *o*-Aminophenol with Dimethyl Carbonate Using Lead Compounds as Catalysts

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Lead compounds are active catalysts for carbonylation and carbonylation/methylation of *o*-phenylenediamine and *o*-aminophenol with dimethyl carbonate (DMC). 2-Benzimidazolone was obtained in 84% yield by the reaction of *o*-phenylenediamine with DMC for 1 h at 443 K in the presence of Pb(NO<sub>3</sub>)<sub>2</sub>. In the presence of Pb(OAc)<sub>2</sub>, the reaction quantitatively gave 1,3-dimethyl-2-benzimidazolone, which was formed by methylation of the primary product, 2-benzimidazolone, at 473 K. The effects of reaction variables on the yields of 2-benzimidazolone and 1,3-dimethyl-2-benzimidazolone were examined. The reaction of *o*-aminophenol with DMC selectively gave a carbonylation product, 2-benzoxazolone, or a carbonylation/methylation product, 3-methyl-2-benzoxazolone, depending on the reaction conditions in the presence of Pb(OAc)<sub>2</sub>. © 2001 Academic Press

**Key Words:** *o*-phenylenediamine; *o*-aminophenol; dimethyl carbonate; lead compounds; 2-benzimidazolone; 2-benzoxazolone.

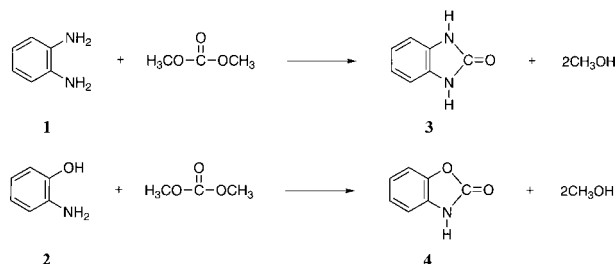
## INTRODUCTION

2-Benzimidazolone **3** and 2-benzoxazolone **4** and their derivatives are useful chemicals mainly as the intermediates in production of pharmaceuticals, pesticides, and herbicides. In practice, these compounds are produced by the reactions of phosgene with *o*-phenylenediamine **1** and *o*-aminophenol **2** and their derivatives (1–3). Because phosgene is a very toxic substance, it is important to develop a nonphosgene reaction.

Several other synthetic methods have also been reported. The direct carbonylation of **1** and **2** with carbon monoxide catalytically affords **3** and **4**, respectively, in the presence of selenium and a base (4, 5). High yields of **3** (99%) and of **4** (84%) were attained at 373 K. **3** and **4** can be also prepared in high yields by reductive carbonylation of *o*-nitroaniline and *o*-nitrophenol, respectively, with carbon monoxide, sulfur, and water in the presence of Et<sub>3</sub>N (6, 7). **3** and **4** are also synthesized by the reaction of urea with **1** and **2**, respectively, in the presence of H<sub>2</sub>SO<sub>4</sub> or HCl (1–3).

Dimethyl carbonate (DMC) has been used as a substitute of phosgene for a variety of carbonylation reactions (8, 9). For example, aniline undergoes methoxycarbonylation to afford methyl phenylcarbamate in the presence of lead compounds (10). Since DMC can be industrially produced by the reaction of methanol and carbon monoxide, carbonylation reactions with DMC are becoming more attractive in many cases.

In this work, we attempted the carbonylation of **1** and **2** with DMC to synthesize **3** and **4**, respectively. We found that lead compounds were very good catalysts for these carbonylations.



1,3-Dimethylbenzimidazolone **5** and 3-methyl-2-benzoxazolone **6**, respectively, are also important intermediates for various synthetic purposes. These compounds are prepared by methylation of **3** and **4**, respectively, with use of methyl iodide or dimethyl sulfate as a methylating agent. We found that **5** and **6** were easily obtained directly from **1** and **2** by their reactions with DMC in the presence of lead compounds. Here, these reactions give rare examples in which DMC serves as both carbonylation and methylating agents at the same time.

## EXPERIMENTAL

Metal salts of Pb, Sn, and Zn and metal oxides of Pb, Sn, and Ti obtained from Wako Pure Chemicals Ind., were used without treatment, unless otherwise note. Pb(OAc)<sub>2</sub> was obtained by heating Pb(OAc)<sub>2</sub> · 3H<sub>2</sub>O at 353 K for 2 h. DMC of guaranteed grade was dehydrated with molecular sieve 3A. Other reagents were of guaranteed grade and used without further purification.

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The reactions were carried out in a 50 cm<sup>3</sup> autoclave without using a solvent. DMC, **1** (or **2**), and a catalyst were charged in the autoclave under a nitrogen atmosphere. The autoclave was then set in an oil bath heated at the reaction temperature. At the end of the reaction time, the autoclave was cooled to room temperature and the catalyst was separated by a centrifuge. The products in the reaction of **1** with DMC were analyzed by HPLC equipped with a column of Crest Pak C-185 (4.6 mm i.d. × 150 mm) and an UV detector. The mobile phase was a 35 : 65 (v/v) methanol-water solution of NaH<sub>2</sub>PO<sub>4</sub>. The products **3** and **5** in the reaction of **1** with DMC were identified with GC-MS and <sup>1</sup>H NMR. The authentic sample of **5** was prepared by the reaction of **3** with dimethyl sulfate. The products in the reaction of **2** with DMC were identified with GC-MS and <sup>1</sup>H NMR and determined with a gas chromatograph with a capillary column of CT-1.

## RESULTS AND DISCUSSION

### Carbonylation of Phenylenediamine with DMC

(a) *Catalytic activities of metal compounds.* The reaction of **1** with DMC was carried out without using a solvent. Without a catalyst, the conversion of **1** was 30% at 433 K for 20 h and the product mainly consisted of *N*-methylphenylenediamine **7** (selectivity, 75%) and *N,N*-dimethylphenylenediamine (selectivity, 20%). The selectivity for **3** was 5%. The predominant reaction is therefore *N*-methylation of **1** rather than carbonylation.

Table 1 shows the results of the reactions of **1** with DMC in the presence of lead, zinc, tin(II), and titanium(IV) compounds at 433 K or 443 K for 1 h. In the presence of these compounds as catalysts, **3** (carbonylation prod-

uct), 1-methyl-2-benzimidazolone **8**, and **5** (carbonylation/methylation products) were the predominant products, though *N*-methyl-*o*-phenylenediamine was also produced. This indicates that carbonylation was promoted selectively over these catalysts.

The product distribution strongly depended on the catalyst. Pb(NO<sub>3</sub>)<sub>2</sub> and PbI<sub>2</sub> catalysts selectively gave **3**, the highest selectivity of 77% for **3** being obtained with Pb(NO<sub>3</sub>)<sub>2</sub>. The selectivities for **3** in the presence of PbO and Ti(OCH<sub>3</sub>)<sub>4</sub> were 65 and 66%, respectively. Pb(OAc)<sub>2</sub> · 3H<sub>2</sub>O and Pb(OAc)<sub>2</sub> · Pb(OH)<sub>2</sub> were selective for the production of **5**. Zn(OAc)<sub>2</sub> · 2H<sub>2</sub>O and Zn(OAc)<sub>2</sub> also showed high activities and selectivities for **5**. Sn(OAc)<sub>2</sub> showed a high activity with a moderate selectivity for **5**. PbCO<sub>3</sub> and 2PbCO<sub>3</sub> · Pb(OH)<sub>2</sub> showed very low activities, probably because these compounds hardly dissolved in the reaction medium. The other compounds dissolved in the reaction medium. However, solids came out of the reaction medium while the reaction proceeded. For example, the formation of PbCO<sub>3</sub> was observed by XRD measurements after the reaction was carried out by using Pb(NO<sub>3</sub>)<sub>2</sub>.

In the presence of TiO<sub>2</sub>, SnO<sub>2</sub>, and MgO, the conversion of **1** was improved, but the yields of **3** were 4, 1, and 7%, respectively.

The results in Table 1 show that the selectivities for carbonylation and methylation strongly depend on the nature of catalysts. An effort was made to maximize the yield of **3** or **5** with use of lead compounds as catalysts.

(b) *Change in the yield of 2-benzimidazolone 3 with reaction time.* As shown in Table 1, Pb(NO<sub>3</sub>)<sub>2</sub> is the most active and selective catalyst for the production of **3** in the reaction of **1** and DMC. Figure 1 shows the effect of reaction time on the conversion of **1** and the yields of the products in the

TABLE 1  
Catalytic Activities of Various Compounds for the Reaction of **1** with DMC

Catalyst	Conversion of <b>1</b> /%	Selectivity/%			
		<b>3</b>	<b>8</b>	<b>5</b>	<b>7</b>
Pb(NO <sub>3</sub> ) <sub>2</sub>	89	77	10	2	13
PbO yellow	60	65	3	4	28
PbI <sub>2</sub>	53	72	3	1	24
Pb(OAc) <sub>2</sub> · 3H <sub>2</sub> O	51	29	2	54	15
Pb(OAc) <sub>2</sub> · Pb(OH) <sub>2</sub>	48	31	2	56	12
Zn(OAc) <sub>2</sub> · 2H <sub>2</sub> O	35	11	5	63	23
Zn(OAc) <sub>2</sub>	38	19	3	59	20
PbCO <sub>3</sub>	13	69	2	5	24
Ti(OCH <sub>3</sub> ) <sub>4</sub> <sup>a</sup>	79	66	3	1	30
Sn(OAc) <sub>2</sub> <sup>a</sup>	63	4	13	39	44
None <sup>a</sup>	30	5	0	0	75

Conditions: reaction temperature = 433 K (\*443 K); reaction time = 1 h; **1** = 3 mmol; DMC/**1** = 2; catalyst = 0.3 mmol.

<sup>a</sup>Other product was *N,N*-dimethyl-*o*-phenylenediamine.

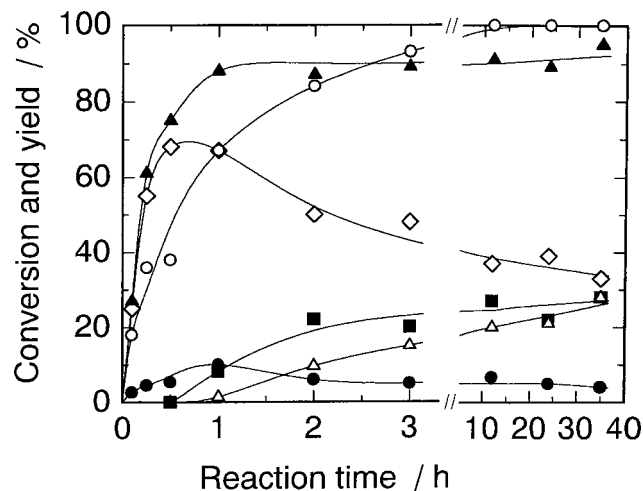
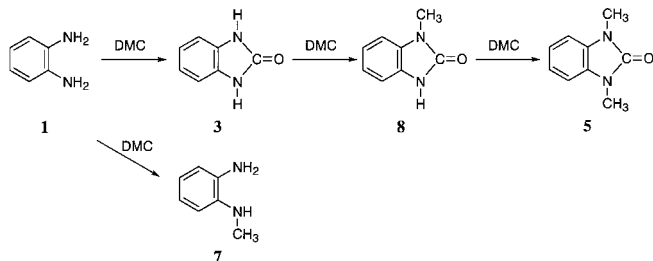


FIG. 1. Effect of reaction time on the product distribution in the reaction of **1** with DMC at 433 K; **1** = 3 mmol, DMC = 6 mmol, Pb(NO<sub>3</sub>)<sub>2</sub> = 0.3 mmol. Conversions of **1** (▲) and DMC (○); yields of **3** (◇), **8** (■), **5** (△), and **7** (●).

presence of  $\text{Pb}(\text{NO}_3)_2$  at 433 K. The conversion of **1** rapidly increased to 90% in 1 h and then stayed constant at longer reaction times. The yield of **3** went through a maximum at a reaction time of 30 min, the maximum yield being 67%. The yields of **8** and **5** increased concomitantly with a decrease in the yield of **3**. The yield of *N*-methylphenylenediamine **7** reached 6% in 1 h and stayed constant. The yields of **8** and **5** were not increased by increasing the reaction time from 14 h to 35 h. This was simply due to almost complete consumption of DMC in the first 3 h.

These results clearly indicate that **8** and **5** were formed by the methylation of **3**, not by the carbonylation of **7**. This does not mean that the carbonylation of **7** with DMC does not proceed. By raising the reaction temperature from 433 to 473 K, the carbonylation of **7**, however, proceeded. Thus, **8** was obtained with 100% selectivity at a complete conversion of **7** in 20 h, when the reaction of **7** (3 mmol) with DMC (9 mmol) was carried out in the presence of  $\text{Pb}(\text{NO}_3)_2$  (0.3 mmol). This result shows that the formation of **3** by the reaction of **1** with DMC proceeds more easily than that of **7**. The carbonylation of **7** with DMC for the formation of **8** proceeded at 473 K but did not proceed at 433 K, since **7** is presumably more sterically hindered than **1** though the basicity of **3** is lower than that of **7**.



(c) *Effect of reaction temperature on the yield of 2-benzimidazolone 3.* The reaction of **1** with DMC in the presence of  $\text{Pb}(\text{NO}_3)_2$  was carried out at various temperatures. The reaction time was shortened, being 30 min. The changes in the conversion of the reactants and the yields of the products are shown in Fig. 2. The conversions of both **1** and DMC increased with reaction temperature. The yield of **3** monotonically increased from 21% to 80% by increasing the reaction temperature from 413 to 443 K and stayed constant in the range from 443 to 473 K. **8** and **5** were not formed below 443 K, since the reaction time was not enough long. These compounds were formed at 473 K, the yields of **8** and **5** being 10% and 5%, respectively. **7** was formed in about 4% yield in the temperature range studied.

At 443 K, **3** was obtained in about 80% yield with a 95% selectivity based on **1**. The selectivity for **3** based on DMC was about 80% in the temperature range of 413–443 K, but decreased to 42% at 473 K.

(d) *Effect of the ratio of DMC/1 on the product distribution.* Figure 3 shows the effect of the ratio of DMC/1 on

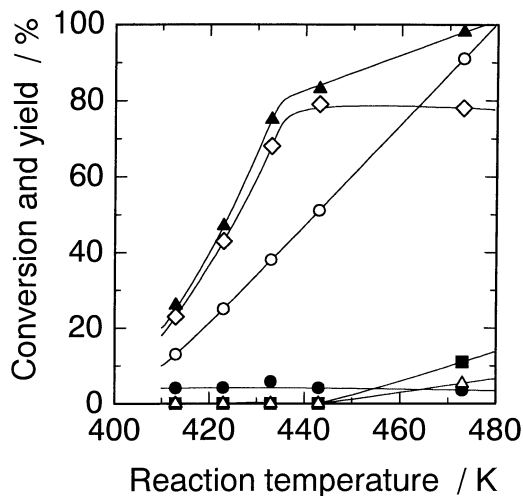


FIG. 2. Effect of reaction temperature on the product distribution in the reaction of **1** with DMC. Reaction time = 0.5 h; **1** = 3 mmol, DMC = 6 mmol,  $\text{Pb}(\text{NO}_3)_2$  = 0.3 mmol. Conversions of **1** ( $\blacktriangle$ ) and DMC ( $\circ$ ); yields of **3** ( $\diamond$ ), **8** ( $\blacksquare$ ), **5** ( $\triangle$ ), and **7** ( $\bullet$ ).

the conversion of **1** and the yields of products at 443 K in the reaction of **1** with DMC in the presence of  $\text{Pb}(\text{NO}_3)_2$ . At a DMC/**1** ratio of 1.0, the yield of **3** was 55%. With increasing the DMC/**1** ratio, both the conversion of **1** and the yield of **3** increased. The yield of **3** attained the highest value of 88% with a 92% conversion of **1** at the ratio of 2.5. Increasing the ratio to 3 was not favorable for selective production of **3** because of the methylation of **3** to **5**.

(e) *Effect of the ratio of  $\text{Pb}(\text{NO}_3)_2$ /1.* The effect of the molar ratio of  $\text{Pb}(\text{NO}_3)_2$ /**1** on the yield of **3** at 443 K is shown in Fig. 4. Both the conversion of **1** and the yield of **3** at 30 min increased with the ratio up to 0.1 and were unchanged with

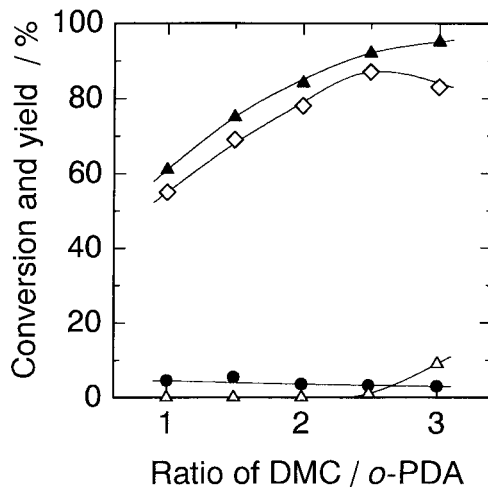


FIG. 3. Effect of the ratio of DMC/1 on the product distribution in the reaction of **1** with DMC at 443 K. Reaction time = 0.5 h; **1** = 3 mmol,  $\text{Pb}(\text{NO}_3)_2$  = 0.3 mmol. Conversions of **1** ( $\blacktriangle$ ); yields of **3** ( $\diamond$ ), **5** ( $\triangle$ ), and **7** ( $\bullet$ ).

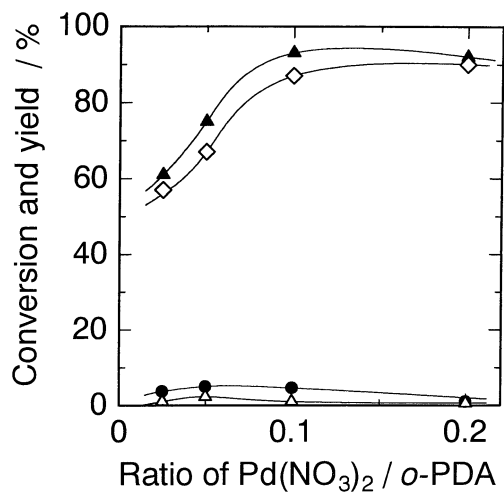


FIG. 4. Effect of the ratio of  $\text{Pb}(\text{NO}_3)_2/1$  on the product distribution in the reaction of **1** with DMC at 443 K. Reaction time = 0.5 h; **1** = 3 mmol, DMC = 7.5 mmol. Conversions of **1** (▲); yields of **3** (◇), **5** (△), and **7** (●).

further increasing the ratio of  $\text{Pb}(\text{NO}_3)_2/1$ . The selectivity for **3** was always high at this temperature.

(f) *Synthesis of 1,3-dimethylbenzimidazolone 5*. The general synthesis method for **5** is *N*-methylation of **3** with methyl iodide in the presence of sodium hydroxide. As described earlier, an appreciable amount of **5** was formed in the reaction of **1** with DMC depending on the catalyst used. Here, we attempted the direct synthesis of **5** from **1** by its reaction with DMC.

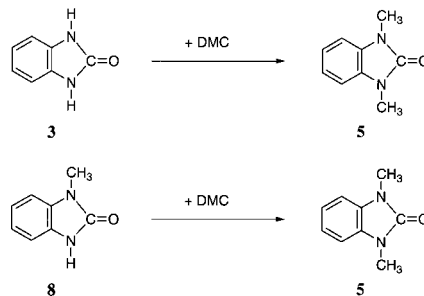
To enhance the selectivity for **5** the higher DMC/**1** ratio of 5 and longer reaction time of 20 h were employed. The catalysts used were acetates of Pb, Sn, and Zn and  $\text{Pb}(\text{NO}_3)_2$ . The results are shown in Table 2. Under these conditions, the conversion of **1** was 100% in every case. The reaction was very selective in the presence of  $\text{Pb}(\text{OAc})_2$  and  $\text{Sn}(\text{OAc})_2$ , the selectivities for **5** being 100% and 98%, respectively. The selectivity was moderate in the case of  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ . However,  $\text{Pb}(\text{NO}_3)_2$  was not an effective catalyst for selective production of **5**, this catalyst being more suitable for selective production of **3**.

TABLE 2  
Synthesis of **6** by the Reaction of **1** with DMC

Catalyst	Conversion of <b>1</b> /%	Yield/%			
		<b>3</b>	<b>8</b>	<b>5</b>	<b>7</b>
$\text{Pb}(\text{OAc})_2$	100	0	0	100	0
$\text{Sn}(\text{OAc})_2$	100	0	0	98	2
$\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$	100	0	13	83	4
$\text{Pb}(\text{NO}_3)_2$	100	23	39	29	9

Conditions: reaction temperature = 473 K; reaction time = 20 h; **1** = 3 mmol; DMC/**1** = 5; catalyst = 0.6 mmol.

(g) *Methylation of 2-benzimidazolone 3 and 1-methyl-2-benzimidazolone 8*. In order to show that DMC serves as a methylating agent, the reaction of **3** and **8** with DMC was carried out at 473 K in the presence of  $\text{Pb}(\text{NO}_3)_2$ . The reaction conditions were as follows: reactant, 3 mmol; DMC, 15 mmol;  $\text{Pb}(\text{NO}_3)_2$ , 0.3 mmol; reaction time, 20 h. In both cases, **5** was obtained in a 100% yield.



The reactions of **3** and **8** with methanol, one of the products, was also carried out under the same reaction conditions. The conversions were low (4–6%) in both cases. Therefore, methanol was not reactive for the methylation involved. This indicates that the active reagent for methylating the intermediates **3** and **8** is almost exclusively DMC, but not methanol.

#### Carbonylation of *o*-Aminophenol with DMC

(a) *Effect of reaction temperature*. The reaction of **2** with DMC (DMC/**2** = 2) was carried out in the presence of  $\text{Pb}(\text{OAc})_2$  in the temperature range between 413 and 473 K. The results are shown in Fig. 5. The conversion of **2**

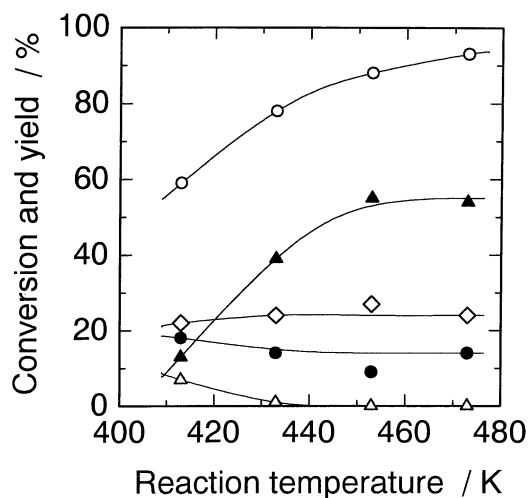


FIG. 5. Effect of reaction temperature on the product distribution in the reaction of **2** with DMC. Reaction time = 3 h; **2** = 3 mmol, DMC = 6 mmol,  $\text{Pb}(\text{OAc})_2$  = 0.3 mmol. Conversion of **2** (○); yields of **4** (●), **6** (▲), *N,N*-dimethylanisidine (◇), and *N,N*-dimethyl-*o*-aminophenol + *N*-methyl-*o*-anisidine products (△).

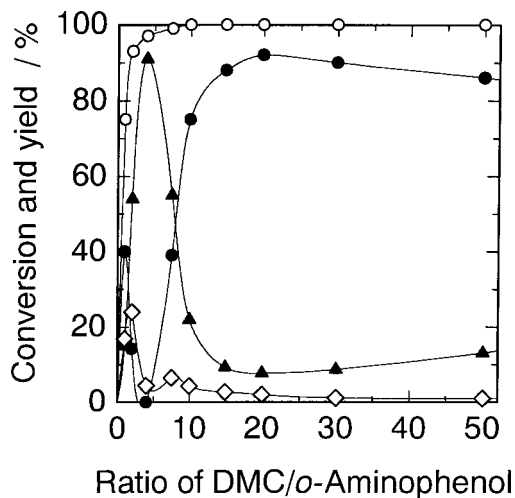


FIG. 6. Effect of the ratio of DMC/**2** on the product distribution in the reaction of **2** with DMC. Reaction temperature = 473 K; reaction time = 3 h; **2** = 3 mmol,  $\text{Pb}(\text{OAc})_2$  = 0.3 mmol. Conversion of **2** (○); yields of **4** (●), **6** (▲), and methylated products (◇).

increased from 59% to 97% with increasing reaction temperature. The main products were **4**, **6**, and *N,N*-dimethyl-*o*-anisidine. Doubly methylated products (*N,N*-dimethyl-*o*-aminophenol and *N*-methyl-*o*-anisidine) were also formed in a small amount at lower temperatures. The yield of **4** was 14% and did not change with temperature, while the yield of **6** increased from 13% to 54% with increasing reaction temperature. The yield of *N,N*-dimethyl-*o*-anisidine was slightly increased from 22% to 25%.

(b) *Effect of ratio of DMC/**2** on the product distribution.* The effect of the DMC/**2** molar ratio was examined in the range between 1 and 50 at 473 K, using  $\text{Pb}(\text{OAc})_2$  as a catalyst. The amount of **2** was kept constant, 3 mmol. The ratio greatly affected the product composition as shown in Fig. 6. The conversion of **2** was 74% at a DMC/**2** ratio of 1 and it increased with the ratio and reached 100% at a ratio of 7.5. The products were mostly **4** and **6**. At lower DMC/**2** values, the methylation products of **2** such as *N,N*-dimethyl-*o*-anisidine was formed as described in the previous section.

The yield of **4** was about 40% at a DMC/**2** ratio of 1. It decreased with increasing the ratio up to 5, where the yield became zero. The yield of **4** again increased as the ratio was increased and became a constant value of 89% in the range between 5 and 20. The yield of **4** again decreased slightly with further increasing the DMC/**2** ratio.

The yield of **6** was just opposite to that of **2**. It first increased and reached a maximum value of 92% at a DMC/**2** ratio of 5, where the conversion of **2** was 97%. The yield of **6** decreased at higher ratios, to 9% at a ratio of 20. It then gradually increased at higher ratios.

The results described above show that the rates of carbonylation and methylation depend greatly on the ratio of DMC and **2**. The lower DMC/**2** or higher concentration of **2** facilitates methylation. At low DMC/**2** ratio, methylation of **2** occurs to give *N,N*-dimethylanisidine together with a carbonylation/methylation product **6**. At a DMC/**2** ratio of 5, direct methylation of **2** becomes slower and **2** undergoes carbonylation to give **4**, which is readily methylated to give **6** as a main product. At a DMC/**2** ratio of 20, methylation becomes slower and the methylation of the primary carbonylation product **4** does not occur extensively and the main product at this stage becomes **4**. The slight increase in the yield of **6** at higher DMC/**2** ratios may be simply due to higher concentration of the methylating agent, DMC.

There is a possibility that the methylation at lower DMC/**2** values is catalyzed by the reactant itself, namely, *o*-aminophenol, which might serve as a base catalyst. It has been shown that methylation of phenol proceeds selectively in the presence of base catalysts such as  $\text{K}_2\text{CO}_3$  and  $\text{CsOH}/\text{Al}_2\text{O}_3$  (11).

(c) *Effect of reaction time on the product distribution.* Figure 7 shows the effect of the reaction time on the yield of **4**. The reaction was carried out at 273 K with a DMC/**2** ratio of 15 using  $\text{Pb}(\text{OAc})_2$  as a catalyst. Under these conditions, the product was mainly **4**. At a reaction time of 0.25 h, the yield was 83% and it increased to 89% at 0.5 h, and did not change at longer reaction times. The greatest part of the other products was **6**, the yield being below 3%.

(d) *Effect of the catalyst amount.* Figure 8 shows the effect of the ratio of  $\text{Pb}(\text{OAc})_2$ /**2** on the yield of **4** at 473 K

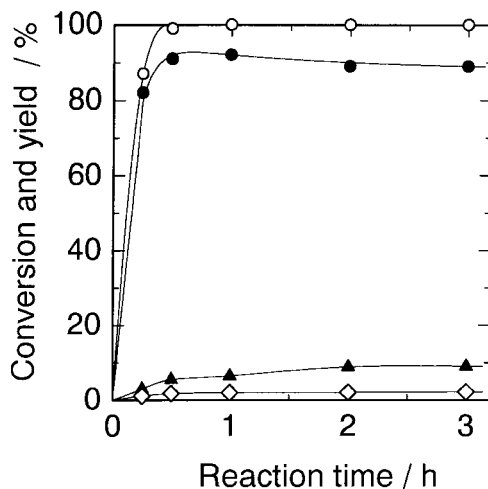


FIG. 7. Effect of the reaction time on the yield of **4** in the reaction of **2** with DMC. Reaction temperature = 473 K; **2** = 3 mmol, DMC = 45 mmol,  $\text{Pb}(\text{OAc})_2$  = 0.3 mmol. Conversion of **2** (○); yields of **4** (●), **6** (▲), and methylated products (◇).

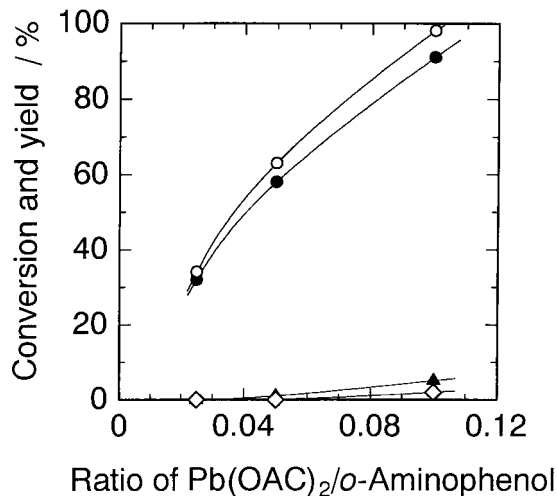


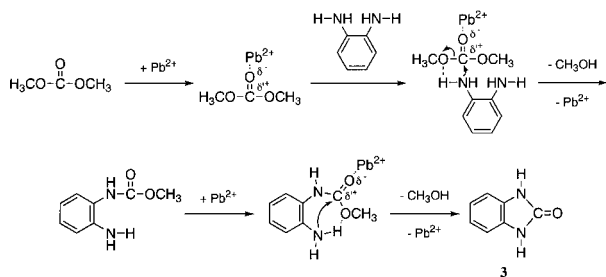
FIG. 8. Effect of the ratio of  $\text{Pb}(\text{OAc})_2/2$  on the yield of **4** in the reaction of **2** with DMC. Reaction temperature = 473 K; reaction time = 0.5 h; **2** = 3 mmol, DMC = 45 mmol. Conversion of **2** (○), yields of **4** (●), **6** (▲), and methylated products (◇).

at a reaction time of 0.5 h. The  $\text{Pb}(\text{OAc})_2/2$  ratio was varied between 0.025 and 0.1 by changing the amount of the catalyst. The yield of **4** increased from 33% to 89% by increasing from 0.025 to 0.1. The product distribution hardly changed with the  $\text{Pb}(\text{OAc})_2/2$  ratio.

The yield of **4** could be increased to 89% even at the lowest  $\text{Pb}(\text{OAc})_2/2$  ratio, 0.025, by prolonging the reaction time to 3 h.

### Reaction Mechanism

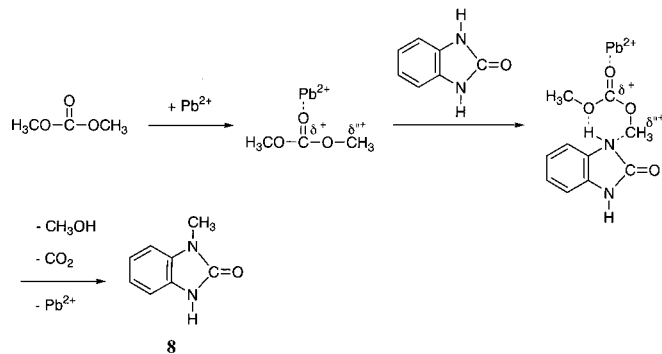
The plausible reaction mechanism for the carbonylation of **1** is expressed as follows:



Here, the Pb species serves as a Lewis acid to enhance the polarization of the carbonyl group of DMC, which interacts with the amino group of **1**. The carbonylation of **2** plausibly proceeds in a similar mechanism.

The methylation of **3** with DMC in the presence of a Pb compound is considered to proceed in the following

scheme:



The activities for carbonylation and methylation of a catalyst probably depend on the ligand and/or counteranion of  $\text{Pb}^{2+}$  ions. Reactant or intermediate amines can be the ligand to possibly modify the catalytic nature of metal cations. The balance of the two functions, carbonylation and methylation, decides the distribution of the products. As described above, *o*-aminophenol seems to serve as a base catalyst for its own methylation with DMC.

### CONCLUSION

Lead compounds are very effective agents for carbonylation of **1** and **2** with DMC. The reaction of **1** with DMC afforded **3** in an 88% yield at 443 K, using  $\text{Pb}(\text{NO}_3)_2$  as a catalyst. When the DMC/**1** ratio was high enough, the reaction of **1** with DMC quantitatively gave **5** in the presence of  $\text{Pb}(\text{OAc})_2$  at 473 K. The reaction proceeded successively. Thus, **3** is the primary product formed by carbonylation of **1**, while **5** was the secondary product formed by the methylation of **3**. In this case, DMC serves as a reagent for methylation as well as carbonylation.

The reaction of **2** with DMC at a DMC/**2** ratio of 15 gave **4** in an 89% yield at 473 K, while **6** was obtained in a 92% yield when the DMC/**2** ratio was 5 in the presence of  $\text{Pb}(\text{OAc})_2$ . In the latter case, the reactant itself, **2** serves as a base catalyst for the methylation, while the carbonylation of **2** is catalyzed by  $\text{Pb}(\text{OAc})_2$ .

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