August, 1988] *Bull. Chem. Soc. Jpn., 61, 2913—2916 (1988)*

Novel Syntheses of Arylcarbamic Esters from Carbon Dioxide and Aromatic Amine via a Zinc Carbamate

Yasuhiko YOSHIDA,* Shigeru ISHII, Akinori KAWATO, Tadataka YAMASHITA,
Masahiro YANO,† and Shohei INOUE†
Department of Applied Chemistry, Faculty of Engineering, Toyo University, Kawagoe, Saitama 350
†Department of Synthetic Chemistry, Faculty of Engineering, The University of Tokyo, Bunkyo-ku, Hongo, Tokyo 113
(Received March 12, 1988)

Arylcarbamic esters were synthesized directly from carbon dioxide and an aromatic amine via a zinc carbamate. The alkylation of the reaction mixture of carbon dioxide, an aromatic amine, and diethylzinc with dialkyl sulfate formed alkyl arylcarbamate in a high yield. Also, 2-hydroxycyclohexyl diphenylcarbamate was obtained selectively in a good yield by the reaction of carbon dioxide, epoxycyclohexane, and ethylzinc diphenylamide. Other arylcarbamates of 1,2-cyclohexanediol were obtained by the reactions of carbon dioxide, an aromatic amine, diethylzinc, and epoxycyclohexane.

The carbamic esters are used industrially as plasticizers for rubbers and melamine alkyd resins, fuel additives, and agricultural chemicals such as insecticide and herbicide. The process to synthesize carbamic esters uses isocyanate, carbamoyl chloride, or chloroformate, which are obtained by the reaction using phosgene as a starting material.[1] Since phosgene is toxic and corrosive, and its use produces a large quantity of HCl, it is of interest to develop the novel synthetic methods of carbamic ester without phosgene.

The interest in the fixation of carbon dioxide has led us to investigate the direct synthetic reaction of carbamic ester from carbon dioxide as a starting material.[2–6] Alkylcarbamic esters of 1,2-diol or hemiacetal can be synthesized directly by the reaction of carbon dioxide, primary or secondary aliphatic amines, and epoxides or vinyl ethers, respectively. An analogous reaction by using aromatic amines did not occur, since their basicities are evidently lower.

On the other hand, it is well-known that carbon dioxide inserts to the nitrogen-metal bond to form the salt of carbamic acid.[7–25]

$$\mathrm{R_2N\text{-}M + CO_2 \rightarrow R_2NCOO\text{-}M} \qquad (1)$$

(M: Ti,Zr,V,Nb,Ta,W,Sn,Si,Ge,P,As,Sb,Zn,Al)

Hydrolysis of the salt, however, forms metal hydroxide and releases amine with evolution of carbon dioxide. Since carbamic acid is unstable, the fixation of carbon dioxide may not be accomplished by this reaction only.

We reported that the reactions of carbon dioxide, epoxycyclohexane, and metal dimethylamides, such as $Ti(NMe_2)_4$, $TiCp_2(NMe_2)_2$, or $W(NMe_2)_6+W_2(NMe_2)_6$, proceeded to afford dimethylcarbamate of 1,2-cyclohexanediol in high yields.[5,6] Similar reaction using metal arylamide, however, has not been reported. This paper reports a novel synthesis of arylcarbamic esters by the reaction of carbon dioxide with zinc arylamides followed by alkylation with dialkyl sulfates or an epoxide.

Results and Discussion

Synthesis of Arylcarbamic Esters by the Reaction of Zinc Carbamate with Dialkyl Sulfate. The reaction of *N*-methylaniline, diethylzinc, and carbon dioxide at 120 °C for 5 h was confirmed to give the corresponding ethylzinc carbamate quantitatively, as observed by the NMR spectral analysis of the reaction mixture.

$$\mathrm{PhMeNH + Et_2Zn + CO_2 \rightarrow PhMeNCOO\text{-}Zn\text{-}Et} \qquad (2)$$

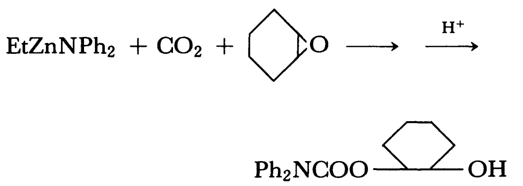
When the reaction of *N*-methylaniline, diethylzinc, and carbon dioxide was followed by the alkylation of the product with diethyl sulfate at 140—160 °C for 20 h, ethyl methylphenylcarbamate was obtained in 93—96% yield (Eq. 3).

$$\mathrm{PhMeNCOO\text{-}Zn\text{-}Et + Et_2SO_4 \rightarrow PhMeNCOOEt} \qquad (3)$$

Attempted alkylation of zinc carbamate with diethyl sulfate at a temperature below 100°C hardly occurred (Table 1, Runs 1—5). The results of the synthesis of carbamic esters using various aromatic amines are shown in Table 1. By this method, aromatic amines gave the corresponding alkyl arylcarbamates in good yields.

Synthesis of Arylcarbamic Esters by the Reaction of Zinc Carbamate with Epoxycyclohexane. 2-Hydroxycyclohexyl arylcarbamates were found to be obtained selectively in good yields by the reaction of epoxycyclohexane with zinc arylcarbamates.

Carbon dioxide (50 atm) was reacted with an equimolar mixture of epoxycyclohexane and ethylzinc diphenylamide ($EtZnNPh_2$) in benzene solution at 80 °C for 120 h, to give selectively *trans*-2-hydroxycyclohexyl diphenylcarbamate in 48% yield (Table 2, Run 10).



(4)

Table 1. Reaction of Aromatic Amine, Et_2Zn, and CO_2,[a] Followed by the Reaction of the Product with R_2SO_4[b]

Run	Aromatic amine	R_2SO_4	Temp	Product	
			°C	Carbamate	Yield/%[e]
1	PhMeNH	Et_2SO_4	100	PhMeNCOOEt	4[f]
2	PhMeNH	Et_2SO_4	110	PhMeNCOOEt	16[f]
3	PhMeNH	Et_2SO_4	120	PhMeNCOOEt	60[f]
4	PhMeNH	Et_2SO_4	140	PhMeNCOOEt	93[f]
5	PhMeNH	Et_2SO_4	160	PhMeNCOOEt	96[f]
6	Ph_2NH	Et_2SO_4	140	$Ph_2NCOOEt$	46[g]
7	PhNpNH[c]	Et_2SO_4	140	PhNpNCOOEt	26[g]
8	*p*-$MeC_6H_4(Et)NH$[d]	Et_2SO_4	140	*p*-$MeC_6H_4(Et)NCOOEt$	79[h]
9	*p*-$MeC_6H_4(Et)NH$[d]	Me_2SO_4	140	*p*-$MeC_6H_4(Et)NCOOMe$	50[h]

a) Aromatic amine; 50 mmol, $ZnEt_2$; 50 mmol, CO_2; 50 atm, benzene; 30 ml, 120 °C, 5 h. b) R_2SO_4; 110 mmol, 20 h. c) 2-Naphthylphenylamine. d) *N*-Ethyl-*p*-toluidine. e) The yields of carbamates were based on amine. f) Yield by GLC of the reaction mixture of Et_2SO_4 and zinc carbamate for 15 h. g) Isolated yield by recrystallization from 1-pentanol. h) Isolated yield by distillation.

Table 2. The Reaction of Aromatic Amine, Et_2Zn, CO_2, and Epoxycyclohexane[a]

Run	Aromatic amine	Time	Temp	Product
		h	°C	Arylcarbamate/%[b]
1	Ph_2NH	16	40	0
2	Ph_2NH	16	60	15
3	Ph_2NH	16	80	32
4	Fh_2NH	16	100	40
5	Ph_2NH	2	80	21
6	Ph_2NH	4	80	23
7	Ph_2NH	8	80	29
8	Ph_2NH	32	80	37
9	Ph_2NH	44	80	44
10	Ph_2NH	120	80	48
11	PhMeNH	68	80	65
12	PhEtNH	48	80	34
13	PhNpNH	72	80	27

a) Aromatic amine; 40 mmol, $ZnEt_2$; 40 mmol, CO_2; 50 atm, epoxycyclohexane; 40 mmol, benzene; 40 ml. For Runs 1—10, ethylzinc diphenylamide prepared from Ph_2NH and $ZnEt_2$, was reacted with CO_2 and epoxycyclohexane. b) The isolated yields of arylcarbamates based on amine.

Although arylcarbamic ester was not formed in the reaction for 16 h at 40 °C, the yields of arylcarbamic ester increased to 40% at a high temperature such as 100°C (Table 2, Runs 1—4). No side products, such as polyether (homopolymer of epoxide), polycarbonate (copolymer of carbon dioxide and epoxide), or cyclic carbonate (the equimolar reaction product of epoxide and carbon dioxide), could be detected even in the reaction at 100 °C.

The reactions of epoxycyclohexane with carbon dioxide, diethylzinc, and an aromatic amine, without isolation of the zinc aromatic amide, were found to give the corresponding 2-hydroxycyclohexyl arylcarbamate, as shown in Table 2. In the case of secondary aromatic amines (PhMeNH, PhEtNH, and PhNpNH), arylcarbamic esters were obtained in good yields (Table 2, Runs 11—13), but the yields of arylcarbamic ester from primary aromatic amines were low.

A similar reaction of carbon dioxide, epoxycyclohexane, and diethylaluminum diphenylamide (Et_2AlNPh_2)[26] instead of $EtZnNPh_2$ also gave diphenylcarbamic ester in a low yield (9%), and simultaneously yielded polycarbonate.

Experimental

General. Commercially available aromatic amines, epoxycyclohexane, benzene, diethylzinc, and triethylaluminium were purified by recrystallization or distillation, and stored in a nitrogen atmosphere. Dialkyl sulfates were used without further purification. Commercial high-purity carbon dioxide gas was introduced into an autoclave directly from a gas cylinder without further purification.

Measurements. IR spectra were recorded on a Hitachi EPI-G3 apparatus, and NMR spectra were measured by using Hitachi 24B spectrometer operating at 60 MHz and JEOL FX90Q at 90 MHz, using hexamethyldisiloxane (HMDS) as internal standard. GC-MS spectra were measured by using a Shimadzu QP-1000 GC-MS spectrometer, and gas liquid chromatogram (GLC) were recorded on a Shimadzu GC-4C apparatus with a thermal conductor.

Reaction of Carbon Dioxide with the Reaction Mixture of Diethylzinc and *N*-Methylaniline. A 100 cm^3 stainless autoclave was swept free of air by displacement with nitrogen. Into the autoclave was added a solution of Et_2Zn (10 cm^3, 100 mmol) and *N*-methylaniline (10.8 cm^3, 100 mmol) in 30 cm^3 of benzene, and CO_2 gas was introduced directly from gas cylinder until the pressure reached 50 atm (5.1×10^6 Pa). After the autoclave was allowed to stand in an oil bath controlled at 120 °C for 5 h, the excess of CO_2 gas was released, and IR and ^1H NMR of the reaction mixture was measured. The IR spectrum of the reaction mixture showed a new absorption at 1565 cm^{-1} to suggest the presence of carboxylate group. ^1H NMR spectrum of the reaction mixture in $CDCl_3$ showed signals at δ 0.2 (2H, q), 1.4 (3H, t), 3.1 (3H, s, $NC\underline{H}_3$), and 7.0 (5H, $C_6\underline{H}_5N$), while ethyl group bonded to zinc such as ethylzinc diethylamide is known to show signals at δ 0.4 (2H, q, $CH_3C\underline{H}_2Zn$) 1.4 (3H, t, $C\underline{H}_3CH_2Zn$).[27]

Synthesis of Arylcarbamate. Reaction of Et_2Zn, aromatic amine, and CO_2, followed by the reaction of the product with dialkyl sulfate: A typical example for the synthesis of ethyl ethyl(4-methylphenyl)carbamate is as follows.

A 100 cm^3 stainless autoclave was swept free of air by displacement with nitrogen. Into the autoclave was added a solution of Et_2Zn (5.1 cm^3, 50 mmol) and *N*-ethyl-*p*-toluidine (7.2 cm^3, 50 mmol) in 30 cm^3 of benzene, and CO_2 gas was introduced directly from gas cylinder until the pressure reached 50 atm. After the autoclave was allowed to stand in an oil bath controlled at 120 °C for 5 h, the excess of CO_2 gas was released, and diethyl sulfate (14.4 cm^3, 110 mmol) was added into the reaction mixture in the autoclave. After the reaction mixture was heated at 140 °C for 20 h, the contents of the reaction mixture was washed with diluted hydrochloric acid, then with water, and subjected to distillation under a reduced pressure to give the product, ethyl ethyl(4-methylphenyl)carbamate, 100 °C/1.5 mmHg (1 mmHg=133.322 Pa), 8.15 g (79%).

Preparations of other alkyl arylcarbamates were carried out by a similar procedure.

Synthesis of 2-Hydroxycyclohexyl Arylcarbamate: A typical example for the synthesis of 2-hydroxycyclohexyl diphenylcarbamate is as follows.

A 100 cm^3 stainless autoclave was swept free of air by displacement with nitrogen. Into the autoclave was added a solution of $EtZnNPh_2$[24] (10 g, 40 mmol) and epoxycyclohexane (4.0 cm^3, 40 mmol) in 40 cm^3 of benzene, and CO_2 gas was introduced directly from gas cylinder until the pressure reached 50 atm. After the autoclave was allowed to stand in an oil bath controlled at 80 °C for 16 h, the excess of CO_2 gas was released and the contents of the reaction mixture was washed with diluted hydrochloric acid, then with water, and subjected to freeze drying to give a white powder. The white powder was recrystallized from hexane to yield 3.8 g (32%) of 2-hydroxycyclohexyl diphenylcarbamate, mp 133 °C. This carbamate was confirmed to be of trans form, since *trans*-1,2-cyclohexanediol was obtained quantitatively by the hydrolysis of the carbamic ester with methanolic sodium hydroxide.

Preparations of other 2-hydroxycyclohexyl arylcarbamates were carried out by using Et_2Zn and an aromatic amine instead of $EtZnNPh_2$.

Reaction of Et_2AlNPh_2, CO_2, and Epoxycyclohexane: Diethylaluminum diphenylamide (Et_2AlNPh_2)[26] (11 g) in benzene solution (40 cm^3) was heated with epoxycyclohexane (3.9 g) at 80 °C for 87 h under a carbon dioxide pressure (50 atm) in a 100 cm^3 stainless autoclave. The reaction mixture was washed with diluted hydrochloric acid, then with water, and poured to methanol (500 cm^3) to give a white powdery precipitate (polycarbonate; 1.4 g). Evaporation of the solvent from the filtrate left a white residue, which was recrystallized from hexane to give 1.1 g (9%) of 2-hydroxycyclohexyl diphenylcarbamate.

Identification of the Products. Ethyl Methylphenylcarbamate: Bp 79—80 °C/0.45 mmHg (lit,[28,29] 79—80 °C/1 mmHg); IR(neat) 1700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.15 (3H, t, $OCH_2C\underline{H}_3$), 3.2 (3H, s, $NC\underline{H}_3$), 4.1 (2H, q, $OC\underline{H}_2CH_3$), 7.2 (5H, $NC_6\underline{H}_5$); MS (70 eV) m/z=179 (M^+).

Ethyl Diphenylcarbamate: Mp 69—70 °C (lit,[29] mp 72—73 °C); IR (KBr pellet) 1695 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.1 (3H, t, $OCH_2C\underline{H}_3$), 4.1 (2H, q, $OC\underline{H}_2CH_3$), 7.1 (10H, s, $N(C_6\underline{H}_5)_2$); MS (70 eV) m/z=241 (M^+).

Ethyl (2-Naphthyl)phenylcarbamate: Mp 87—89 °C (lit,[30] mp 93 °C); IR (KBr pellet) 1708 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.4 (3H, t, $OCH_2C\underline{H}_3$), 4.1 (2H, q, $OC\underline{H}_2CH_3$), 7.2 (5H, s, $NC_6\underline{H}_5$), 7.1—7.8 (7H, m, naphthyl group); MS (70 eV) m/z=291 (M^+).

Ethyl Ethyl(4-methylphenyl)carbamate: Bp 100 °C/1.5 mmHg; IR (neat) 1710 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.9—1.2 (6H, methyl groups of NC_2H_5 and OC_2H_5), 2.1 (3H, s, CH_3 of 4-methylphenyl group), 3.6 (2H, q, $NC\underline{H}_2CH_3$), 4.0 (2H, q, $OC\underline{H}_2CH_3$), 7.0 (4H, aromatic ring); MS (70 eV) m/z=207 (M^+); EA,Found: C, 69.54; H, 8.26; N, 6.76%. Calcd for $C_{12}H_{17}NO_2$: C, 69.69; H, 8.34; N, 6.73%.

Methyl Ethyl(4-methylphenyl)carbamate: Bp 83.3—83.4 °C/0.5 mmHg; IR (neat) 1695 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.0 (3H, t, $NCH_2C\underline{H}_3$), 2.2 (3H, s, CH_3 of 4-methylphenyl group), 3.5 (3H, s, $OC\underline{H}_3$), 3.6 (2H, q, $NC\underline{H}_2CH_3$), 7.0 (4H, aromatic ring); MS (70 eV) m/z=193 (M^+); EA,Found: C, 68.37; H, 7.82; N, 7.25%. Calcd for $C_{11}H_{15}NO_2$: C, 68.35; H, 7.81; N, 7.21%.

2-Hydroxycyclohexyl Diphenylcarbamate: Mp 133 °C (recrystallized from hexane); IR (KBr pellet) 3500 and 1695 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.0—2.1 (8H, methylenes of cyclohexane ring), 2.6 (1H, $O\underline{H}$), 3.4 (1H, $C\underline{H}$-OH), 4.4 (1H, $C\underline{H}$-O(C=O)), 7.2 (10H, $N(C_6\underline{H}_5)_2$); EA, Found: C, 72.93; H, 6.89; N, 4.48%. Calcd for $C_{19}H_{21}NO_3$: C, 73.29; H, 6.80; N, 4.50%.

2-Hydroxycyclohexyl Methylphenylcarbamate: Mp 100 °C (recrystallized from hexane); IR (KBr pellet) 3500 and 1695 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.0—2.1 (8H, methylenes of cyclohexane ring), 3.2 (4H, $NC\underline{H}_3$ and $O\underline{H}$), 3.5 (1H, $C\underline{H}$-OH), 4.4 (1H, $C\underline{H}$-O(C=O)), 7.2 (5H, $NC_6\underline{H}_5$); EA, Found: C, 67.35; H, 7.90; N, 5.61%. Calcd for $C_{14}H_{19}NO_3$: C, 67.45; H, 7.68; N, 5.62%.

2-Hydroxycyclohexyl Ethylphenylcarbamate: Bp 66 °C/7 mmHg; IR (neat) 3500 and 1695 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.9—2.1 (8H, methylenes of cyclohexane ring), 1.0 (3H, t, $NCH_2C\underline{H}_3$), 3.1—3.6 (2H, $C\underline{H}$-$C\underline{H}$), 3.6 (2H, q, $NC\underline{H}_2CH_3$), 4.4 (1H, m, $C\underline{H}$-O(C=O)), 7.2 (5H, $NC_6\underline{H}_5$); EA,Found: C, 68.19; H, 8.37; N, 5.15%. Calcd for $C_{15}H_{21}NO_3$: C, 68.41; H, 8.03; N, 5.31%.

2-Hydroxycyclohexyl (2-Naphthyl)phenylcarbamate: Mp 175 °C (recrystallized from hexane); IR(KBr pellet) 3500 and 1695 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.0—2.1 (8H, methylenes of cyclohexane ring), 2.6 (1H, $O\underline{H}$), 3.4 (1H, $C\underline{H}$-OH), 4.6 (1H, $C\underline{H}$-O(C=O)), 6.8—7.9 (12H, phenyl and 2-naphthyl groups); EA,Found: C, 76.61; H, 6.39; N, 3.91%. Calcd for $C_{23}H_{23}NO_3$: C, 76.43; H, 6.41; N, 3.87%.

References

1) P. Adams and F. A. Baron, *Chem. Rev.*, **65**, 567 (1965).

2) Y. Yoshida and S. Inoue, *Chem. Lett.*, **1977**, 1375.

3) Y. Yoshida and S. Inoue, *Chem. Lett.*, **1978**, 139.

4) Y. Yoshida and S. Inoue, *J. Chem. Soc., Perkin Trans. 1*, **1979**, 3146.

5) Y. Yoshida and S. Inoue, *Bull. Chem. Soc. Jpn.*, **51**, 559 (1978).

6) Y. Yoshida and S. Inoue, *Polym. J.*, **12**, 763 (1980).

7) J. Chandra, A. D. Jenkins, M. F. Lappert, and R. C. Srivastava, *J. Chem. Soc. A*, **1970**, 2550.

8) R. F. Dalton and K. Jones, *J. Chem. Soc. A.*, **1970**, 590.

9) M. H. Chisholm and M. W. Extine, *J. Am. Chem. Soc.*, **96**, 6214 (1974).

10) M. H. Chisholm and M. W. Extine, *J. Chem. Soc., Chem. Commun.*, **1975**, 438.

11) M. H. Chisholm and M. W. Extine, *J. Am. Chem. Soc.*, **97**, 1623 (1975).

12) M. H. Chisholm and M. W. Extine, *J. Am. Chem. Soc.*, **97**, 5625 (1975).

13) M. H. Chisholm and M. W. Extine, *J. Am. Chem. Soc.*, **99**, 782, 792 (1977).

14) H. Breederveld, *Rec. Trav. Chim.*, **81**, 276 (1962).

15) G. Oetel, H. Marz, and H. Holtschmidt, *Chem. Ber.*, **97**, 891 (1964).

16) R. H. Crag and M. F. Lappert, *J. Chem. Soc. A*, **1966**, 82.

17) L. K. Peterson and K. I. The, *Can. J. Chem.*, **50**, 562 (1972).

18) J. Satge, M. Lesbre, and M. Baudet, *Compt. Rend.*, **259**, 4733 (1964).

19) M. R. Baudet and J. Satge, *Bull. Soc. Chim. Fr.*, **1969**, 1356.

20) T. A. George, K. Jones, and M. F. Lappert, *J. Chem. Soc.*, **1965**, 2157.

21) A. J. Bloodworth, A. G. Davies, and S. C. Vasishtha, *J. Chem. Soc. C*, **1967**, 1309.

22) A. G. Davies and P. G. Harrison, *J. Chem. Soc. C*, **1967**, 1313.

23) J. Koketsu and Y. Ishii, *J. Chem. Soc. C*, **1971**, 511.

24) J. G. Noltes, *Rec. Trav. Chim.*, **84**, 126 (1965).

25) S. Inoue and Y. Yokoo, *Bull. Chem. Soc. Jpn.*, **45**, 3651 (1972).

26) S. Murahashi, T. Niki, T. Obokata, H. Yuki, and K. Hatada, *Kobunshi Kagaku*, **24**, 198 (1967); H. Yuki, K. Hatada, T. Ninomi, and Y. Kikuchi, *Polym. J.*, **1**, 36 (1970).

27) Y. Yoshida, S. Asano, and S. Inoue, *Chem. Lett.*, **1984**, 1073.

28) O. Schmidt, *Z. Physik. Chem.*, **58**, 513 (1907).

29) R. L. Dannley, M. Lukin, and J. Shapiro, *J. Org. Chem.*, **20**, 92 (1955).

30) V. Merz, *Ber. Bunzeneges. Physik. Chem.*, **24**, 2905 (1920).