

afforded an oil (2.96 g), which was chromatographed on silica gel (110 g, activity II-III). Elution with 95:5 CH₂Cl₂:Et₂O (fractions 11-28) gave **24** (1.35 g, 49%); IR 3610 (m), 3100 (w), 2950 (s), 1700 (s), 1650 (w), 1070 (w), 1050 (w), 882 (m) cm⁻¹; NMR (60 MHz) δ 4.67 (br s, 2 H), 4.00-3.37 (m, 2 H), 2.83-1.00 (m with br s at 1.7, 1.4 H). Treatment of the ketol (368.4 mg, 2.02 mmol) with *p*-TsCl (564 mg, 2.96 mmol) in pyridine (5 mL) in the usual way afforded the tosylate (643 mg, 95%). Without further purification, a solution of the tosylate in Et₂O (15 mL) was cooled to 0 °C and treated with 1,5-diazabicyclo[4.3.0]non-5-ene (475 μ L) for 0.75 h. The mixture was diluted with pentane, washed with H₂O, dilute aqueous acetic acid, H₂O, and NaHCO₃, and dried. All operations were carried out with precooled reagents in a cold room. Removal of solvent in vacuo at 0 °C afforded **11** (317 mg, 100%); IR 3095 (m), 2955 (s), 1695 (s), 1647 (m), 1615 (m), 1445 (m), 930 (m), 885 (s) cm⁻¹; NMR (60 MHz) δ 5.67 (dd, $J_1 = J_2 = 1.5$ Hz, 1 H), 5.00 (dd, $J_1 = J_2 = 1.5$ Hz, 1 H), 4.73 (br s, 1 H), 4.65 (br s, 1 H), 3.00-1.33 (m with br s at 1.73, 1.2 H).

Photolysis of 11. A solution of **11** (317 mg) in pentane (150 mL) containing a small amount of NaHCO₃ was irradiated at -20 °C through Pyrex glass. The disappearance of **11** and formation of one product were detected by VPC analysis (column A, 145 °C). After 34.5 h, product destruction was noted, and the photolysis was ended. Preparative VPC (column H, 150 °C) gave three components. The first was identified as **11a** (40% based on unrecovered **11**): IR 2960 (s), 2880 (s), 1705 (s), 1450 (m), 1378 (m), 1345 (m), 1176 (w), 1133 (w) cm⁻¹; NMR²⁸ (300 MHz) δ 2.35-2.20 (m, 4 H), 2.10-1.99 (m, 1 H), 1.97-1.63 (m with dd at 1.83, H_A, $J_{AB} = 6.2$, $J_{AA'} = 9.5$ Hz and dd at 1.65, H_B, $J_{A'B'} = 6.8$, $J_{BD} = 2.5$ Hz, 4 H), 1.53 (dddd, $J = 3.4, 12.6, 12.6, 12.8$ Hz, 1 H), 1.39 (ddd, H_B, $J_{AB} = 6.2$, $J_{BE} = 2.3$, $J_{BE'} = 1.4$ Hz), 1.30 (ddd, H_E, $J_{DE} =$

10.8, $J_{EE'} = 3.7$, $J_{BE} = 2.8$ Hz), 1.18 (s, 3 H), 1.17 (dd, H_A, $J_{A'B'} = 6.7$, $J_{AA'} = 9.5$ Hz). Anal. (C₁₁H₁₆O) C, H. The second component was **8a** (1%) and the third **8** (36%) arising from thermal Cope rearrangement on gas chromatography of unreacted **11**.

A sealed, evacuated tube containing **11a** (~10 mg) in C₆H₆ (1 mL) was heated at 190 °C for 3 h. VPC analysis indicated neither destruction of **11a** nor formation of other products.

Acknowledgment. We thank the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We are indebted to Eric Orava for technical assistance, to Bodil Braren and Francis Picart for 300-MHz spectra, and to S. T. Bella for microanalyses. The 300-MHz NMR spectrometer was purchased with assistance from the National Science Foundation and from the Camille and Henry Dreyfus Foundation.

Registry No. **6**, 42809-06-3; **6a**, 42809-42-7; **7**, 84433-82-9; **7a**, 84433-86-3; **7D**, 84433-94-3; **8**, 84433-83-0; **8a**, 84433-87-4; **8b**, 57428-66-7; **8c**, 84433-88-5; **9**, 84433-84-1; **9a**, 84433-89-6; **9b**, 84433-90-9; **9D**, 84433-97-6; **10**, 84433-85-2; **10a**, 84433-91-0; **11**, 82880-50-0; **11a**, 84433-92-1; **13**, 81762-94-9; **14**, 84433-93-2; **15**, 82880-47-5; **16**, 84433-95-4; **17**, 68241-78-1; **19**, 84434-02-6; **21**, 84433-98-7; **22**, 18926-99-3; **23**, 84434-00-4; **24**, 84434-01-5; **25**, 84433-96-5; 4-bromo-2-methyl-1-butene, 20038-12-4; ethyl acetoacetate, 141-97-9; cyclohexanone dimethylhydrazone, 10424-93-8; 4,4-dimethyl-3-methylene-1-pentanol, 84433-99-8; 3-ethoxycyclohex-2-enone, 5323-87-5; methallyl chloride, 563-47-3.

Activation of Carbon Dioxide with Aluminum Porphyrin and Reaction with Epoxide. Studies on (Tetraphenylporphinato)aluminum Alkoxide Having a Long Oxyalkylene Chain as the Alkoxide Group

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Abstract: (Tetraphenylporphinato)aluminum alkoxide ((TPP)AlOR) having a long oxyalkylene chain as the alkoxide group was prepared by the polymerization of epoxide with (tetraphenylporphinato)aluminum chloride as catalyst. The reactivity of this aluminum alkoxide toward carbon dioxide was markedly enhanced in the presence of 1-methylimidazole. Carbon dioxide thus trapped with the (porphinato)aluminum alkoxide was found to be activated enough to react with epoxide to afford cyclic carbonate. The spectroscopic investigation of the reaction system, favored by the enhanced solubility of the metalloporphyrin due to the long oxyalkylene chain, indicated that cyclic carbonate was formed by the insertion of carbon dioxide followed by that of epoxide into the aluminum-oxygen bond of (TPP)AlOR to give the aluminum alkoxide (TPP)Al-O-CHR-CH₂-O-CO-OR and subsequent intramolecular attack of this aluminum alkoxide toward the adjacent linear carbonate linkage, regenerating the starting alkoxide, (TPP)AlOR.

Chemical fixation of carbon dioxide is of great interest in connection with resource utilization and in relation to biochemical photosynthesis. Fundamental studies on the reactions of carbon dioxide have made much progress in recent years,¹ but the examples of catalytic reactions have been rather limited. An interesting reaction with potential utility is the reaction of carbon dioxide and epoxide using organometallic catalyst systems to give alternating copolymer, an aliphatic polycarbonate, from these monomers.^{2,3} In the series of our studies on this and the related

reactions of carbon dioxide, we found a remarkable effect of visible light on the reaction of (tetraphenylporphinato)aluminum ethyl (**1a**) with carbon dioxide.⁴ Such an effect is considered to be related to electron transfer in the initial stage of photosynthesis.

Another interesting finding we made is on the reactivity of (tetraphenylporphinato)aluminum methoxide ((TPP)AlOMe, **1b**) with carbon dioxide.⁵ (TPP)AlOMe traps carbon dioxide readily and reversibly at room temperature in the presence of 1-methylimidazole. The trapped carbon dioxide is activated enough to react with epoxide at room temperature to afford the corre-

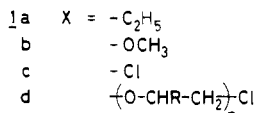
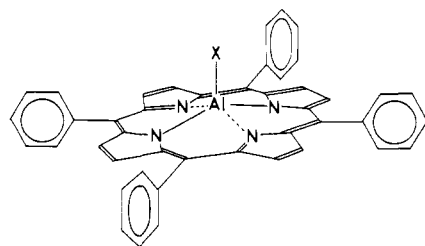
(1) (a) Inoue, S., Yamazaki, N., Eds. "Organic and Bioorganic Chemistry of Carbon Dioxide"; Kodansha: Tokyo, 1981. (b) Vol'pin, M. E.; Kolomnikov, I. S. *Organomet. React.* **1975**, *5*, 313.

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sponding alkylene carbonate. Thus, the (TPP)AlOMe-1-methylimidazole system is a good catalyst for the synthesis of alkylene carbonate from carbon dioxide and epoxide under mild conditions.⁶

Although it is of much interest to elucidate the mechanism of the trap and the activation of carbon dioxide, the very limited solubility of (TPP)AlOMe has prevented detailed investigation. More recently, we succeeded in the preparation of an aluminum porphyrin carrying a long poly(oxyalkylene) chain bound to the aluminum atom as an aluminum alkoxide (**1d**)^{7,8}. This novel aluminum porphyrin is obtained by the polymerization of epoxide by using (tetraphenylporphinato)aluminum chloride ((TPP)AlCl, **1c**) as initiator or catalyst (Scheme I). When the molar ratio of the epoxide to (TPP)AlCl is changed, the length of the poly(oxyalkylene) chain can be regulated. This (porphinato)aluminum alkoxide is characterized by a much improved solubility in organic solvents compared to that of (TPP)AlOMe by the virtue of the long poly(oxyalkylene) chain and is suitable for spectroscopic investigation. Furthermore, the part of the poly(oxyalkylene) chain close to the aluminum porphyrin moiety exhibits NMR signals at unusually high magnetic field due to the strong shielding effect of the porphyrin ring,⁹ and the reaction of the aluminum alkoxide may be followed conveniently by the characteristic signals without being overlapped by other usual signals.

The present paper describes the results of our studies on (1) the interaction of the (porphinato)aluminum alkoxide (**1d**) with 1-methylimidazole, (2) the reaction of the (porphinato)aluminum alkoxide-1-methylimidazole system with carbon dioxide, and (3) the reaction of the above system with epoxide. The mechanism of the trap of carbon dioxide and the reaction with epoxide will be discussed.

Experimental Section

Materials. 5,10,15,20-Tetraphenylporphine (TPPH₂) was synthesized from pyrrole and benzaldehyde in propionic acid and recrystallized from chloroform/methanol.¹⁰ *tert*-Butylethylene oxide (*t*-BuO) was synthesized from 1-bromo-3,3-dimethyl-2-butanone, through reduction with sodium borohydride, followed by ring closure of the resulting bromohydrin in concentrated aqueous solution of potassium hydroxide.¹¹ Propylene oxide (PO) and *t*-BuO were distilled after refluxing over a mixture of calcium hydride and potassium hydroxide. Ethylene oxide (EO), stirred with a mixture of calcium hydride and potassium hydroxide at room temperature, was degassed to remove air and then collected in a trap cooled in a liquid nitrogen bath. Dichloromethane and chloroform

(6) Formation of alkylene carbonate from carbon dioxide and epoxide with other organometallic systems requires more rigorous conditions. For example: (a) Tsuda, T.; Chujo, Y.; Saegusa, T. *J. Chem. Soc., Chem. Commun.* **1976**, 415. (b) Matsuda, H.; Ninagawa, R.; Nomura, R.; Tsuchida, T. *Chem. Lett.* **1979**, 1261.

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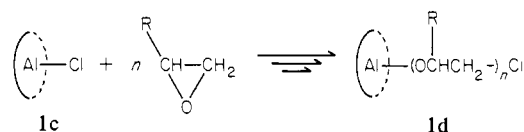
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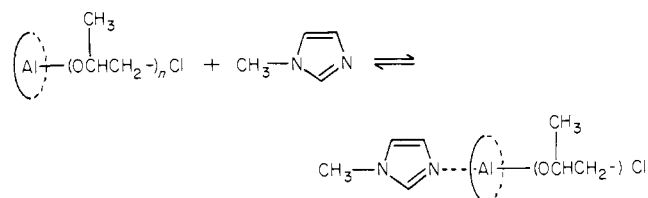
(11) Hurst, S. J.; Bruce, J. M. *J. Chem. Soc.* **1963**, 1321.

(12) Another observation to support this postulation is as follows:⁵ The reaction of carbon dioxide and epoxide catalyzed by **1b** in the absence of MeIm proceeds slowly to give a linear polymer product with carbonate linkage but not cyclic carbonate. Upon addition of MeIm to this system, from which unreacted carbon dioxide and epoxide have been removed, the formation of cyclic carbonate is observed at the expense of the polymeric linear carbonate.

Scheme I



Scheme II



were dried by refluxing over calcium hydride and distilled in a dry nitrogen atmosphere. 1-Methylimidazole (MeIm) was stirred with calcium hydride and then distilled under reduced pressure in a nitrogen atmosphere. Commercial carbon dioxide (99.99%) was dried by passing through the column packed with molecular sieve, then through the column packed with phosphorus pentoxide, before use. Diethylaluminum chloride (Et₂AlCl) was purified by fractional distillation under reduced pressure in a nitrogen atmosphere.

Procedure. (i) **Preparation of (TPP)AlCl (1c) and (TPP)Al-(O-CHR-CH₂)_nCl (1d).** The detailed procedure for the preparation of **1c** and **1d** was described in the previous paper.⁷ **1c** was obtained by the equimolar reaction of (TPP)₂H₂ with Et₂AlCl in CH₂Cl₂ at room temperature in a dry nitrogen stream. **1d** was prepared by the polymerization reaction of the corresponding epoxide with **1c** in CH₂Cl₂ at room temperature under a nitrogen atmosphere. After an appropriate reaction time, the volatile fractions (residual unreacted epoxide and solvent) were removed under reduced pressure to give **1d** as the residue, and then CH₂Cl₂ or CDCl₃ was added to dissolve the product for spectroscopic investigations and further reactions. The average number of the repeating oxyalkylene units -O-CHR-CH₂- of the alkoxide group of **1d** obtained from ethylene oxide and propylene oxide can be controlled by the ratio of the epoxide to **1c** in the polymerization reaction. The distribution as to the number of the repeating units of the polymer molecules has been confirmed to be very narrow.^{7,8} On the other hand, the reaction of *t*-BuO with **1c** under similar conditions afforded (tetraphenylporphinato)aluminum 1-chloro-3,3-dimethyl-2-butoxide ((TPP)Al-*t*-BuO, **1d**, R = *t*-Bu, n = 1). In the present studies were mainly employed **1d** with the number of repeating oxyalkylene units (n) of 2-7 for R = CH₃ ((TPP)AlPPO) and R = H ((TPP)AlPEO).

(ii) **Reaction of CO₂ and Epoxide with the (Tetraphenylporphinato)aluminum Alkoxide (1d)-1-Methylimidazole (MeIm) System.** To a 50-mL flask equipped with a three-way cock containing the dichloromethane or chloroform solution (20 mL) of (tetraphenylporphinato)aluminum alkoxide (**1d**) (1 mmol) was added by a hypodermic syringe, with stirring magnetically, 3 mmol of MeIm ((TPP)AlOR-MeIm system). Then carbon dioxide was bubbled through the needle of the hypodermic syringe in the above system under atmospheric pressure at room temperature for 5 min to prepare the (TPP)AlOR-MeIm system saturated with carbon dioxide ((TPP)AlOR-MeIm-CO₂ system). Into this reaction mixture was bubbled nitrogen gas at room temperature for 5 min in order to remove dissolved, free CO₂, leaving the "trapped CO₂" in the (TPP)AlOR-MeIm system. The reaction of the system thus obtained and epoxide was carried out at room temperature by adding 20 mmol of epoxide.

(iii) **Measurements.** ¹H NMR spectra of the reaction system were measured in a sealed tube with a JEOL Type 4H-A spectrophotometer operating at 100 MHz. Infrared spectra of the reaction system were measured in a KBr fixed cell, with a Hitachi 260-30 infrared spectrophotometer. Visible spectra were measured in a quartz cell of length 1 cm with a Shimadzu RSP-7B spectrophotometer.

Results and Discussion

(Tetraphenylporphinato)aluminum Alkoxide-1-Methylimidazole System. The ¹H NMR signals due to the terminal unit of the alkoxide group (poly(oxyalkylene) chain) of **1d** appear at unusually high magnetic field, due to the strong shielding effect of the porphyrin ring. An example is shown by the ¹H NMR spectrum of (TPP)AlPPO (**1d**, R = CH₃) in CDCl₃ (Figure 1A), in which the signal due to the terminal methyl protons appears at δ -2.0 separately from those due to the other, usual methyl protons of the oxymethylethylene group (δ 1.1).

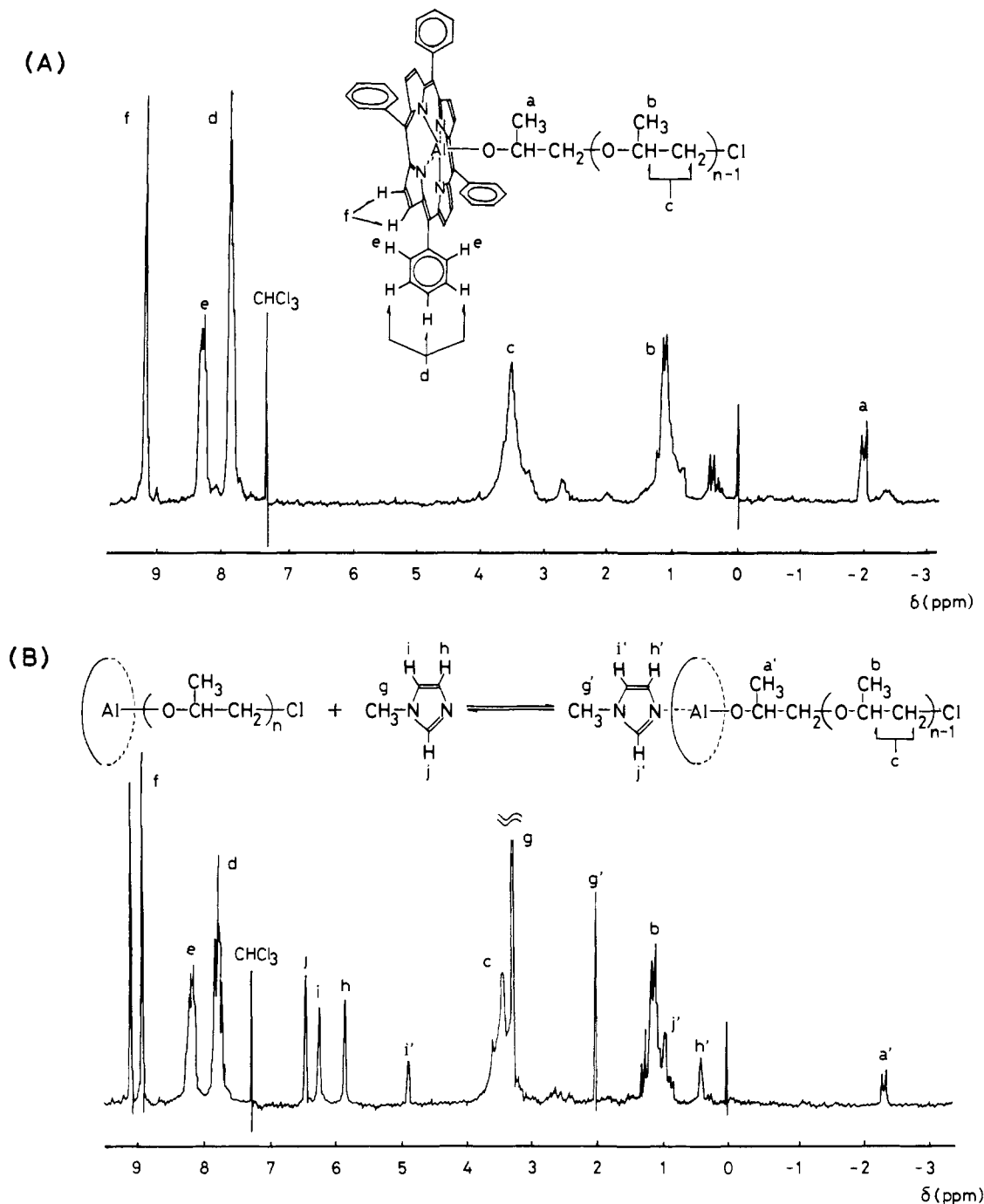


Figure 1. ^1H NMR spectra of (TPP)AlPPO (A) and the (TPP)AlPPO-MeIm (1/3) system (B) in CDCl_3 at room temperature. $[(\text{TPP})\text{AlPPO}]_0 = 50 \text{ mmol L}^{-1}$.

Addition of MeIm to the solution of (TPP)AlPPO brought about the change in the visible spectrum as shown in Figure 2, where the absorption maximum at 548 nm decreased in its intensity with the increase in the mole ratio of MeIm to (TPP)AlPPO, while new absorption bands appeared at 566 and 606 nm.

Figure 1B shows the ^1H NMR spectrum of the (TPP)AlPPO-MeIm (1/3) system in CDCl_3 . The signal due to the methyl protons at the terminal unit of the alkoxide group was observed to shift from $\delta -2.0$ (a in Figure 1A) to -2.3 (a' in Figure 1B). For MeIm, the two sets of signals were observed. One of these (g, δ 3.3; h, δ 5.9; i, δ 6.2; j, δ 6.5) corresponds to the signals of MeIm in CDCl_3 at δ 3.67, 6.86, 7.05, and 7.41 in the absence of (TPP)AlPPO. The other set appears at much higher magnetic field (g' , δ 2.0; h' , δ 0.4; i' , δ 4.9; j' , δ 1.0), which is considered to be due to the coordinated MeIm as an axial ligand of (TPP)AlPPO, taking into account the large shielding effect of the porphyrin ring. The integration of the signals a' and g' indicated

the formation of a 1:1 complex between (TPP)AlPPO and MeIm. These observations together with the visible spectral profile of the (TPP)AlPPO-MeIm system shown in Figure 2 strongly indicate the existence of the equilibrium in Scheme II.

Table I summarizes the NMR data of the (tetraphenylporphinato)aluminum alkoxide-MeIm system. In the ^1H NMR spectrum of (TPP)AlPEO, the signals due to the methylene protons of the terminal and the penultimate oxyethylene units appeared at higher magnetic field (k, δ -1.4; l, δ -0.1; m, δ 1.9; and n, δ 2.7) with respect to those due to the other, usual oxyethylene protons of the alkoxide group (δ 3.4). It is of interest to note that the coordination of MeIm to (TPP)AlPEO induced not only the shift of the signals due to the terminal unit but also that of the penultimate unit of the poly(oxyethylene) chain. Since the effect of the (tetraphenylporphinato)aluminum group on the chemical shifts of the oxyalkylene units other than the terminal unit of the alkoxide group is considered not to be transferred

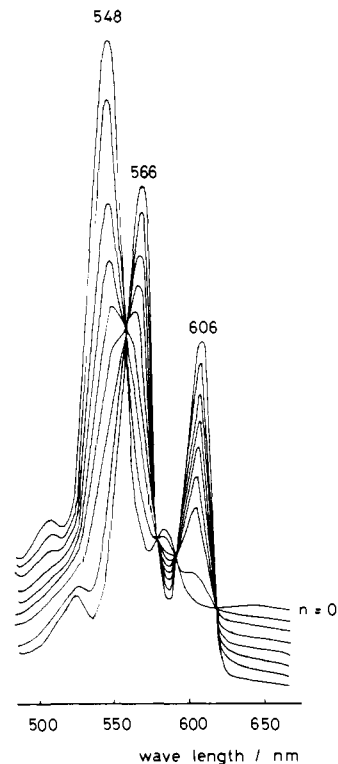


Figure 2. Visible spectra of the (TPP)AlPPO-MeIm system in CH_2Cl_2 at room temperature. n represents the mole ratio of MeIm to (TPP)-AlPPO.

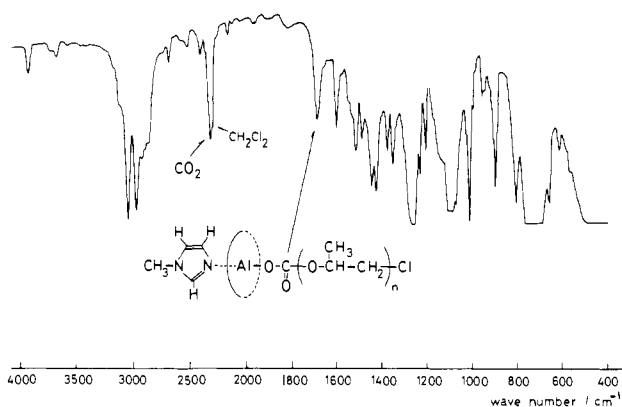
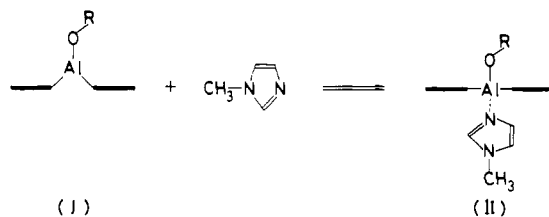


Figure 3. Infrared spectrum of the (TPP)AlPPO-MeIm (1/3) system in CH_2Cl_2 saturated with CO_2 . $[(\text{TPP})\text{AlPPO}]_0 = 50 \text{ mmol L}^{-1}$.

“through bond” but exclusively “through space”, this observation suggests that the coordination of MeIm to (TPP)AlOR is accompanied by the change in the structure of (TPP)AlOR from the square pyramidal (I) to the square planar (II), which allows the alkoxide group (OR) to come closer to the porphyrin plane.



Side view of TPPAlOR

Reaction of Carbon Dioxide with (Tetraphenylporphinato)aluminum Alkoxide. Upon introducing carbon dioxide to the solution of (TPP)AlPPO in the presence of MeIm, an infrared absorption assignable to the metal carbonate bond appeared at 1680 cm^{-1} together with that of dissolved carbon dioxide (2340 cm^{-1}) as

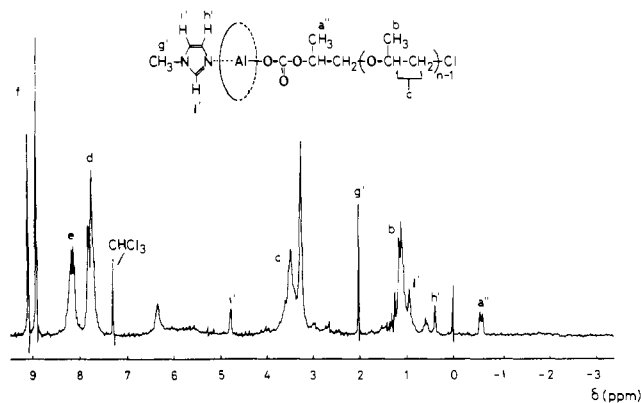


Figure 4. ^1H NMR spectrum of the (TPP)AlPPO-MeIm (1/3) system in CH_2Cl_2 saturated with CO_2 at room temperature. $[(\text{TPP})\text{AlPPO}]_0 = 50 \text{ mmol L}^{-1}$.

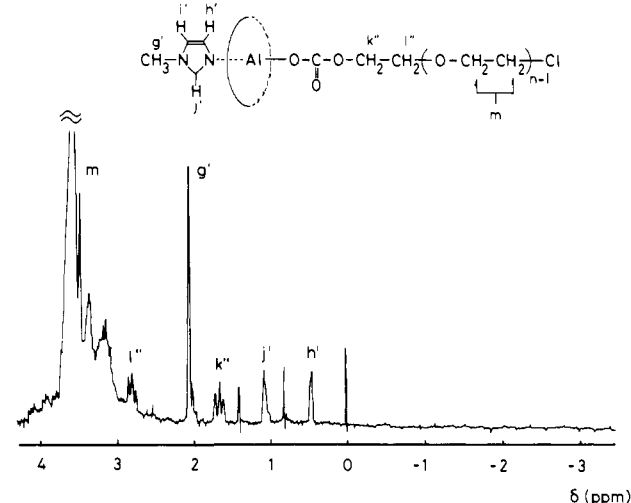
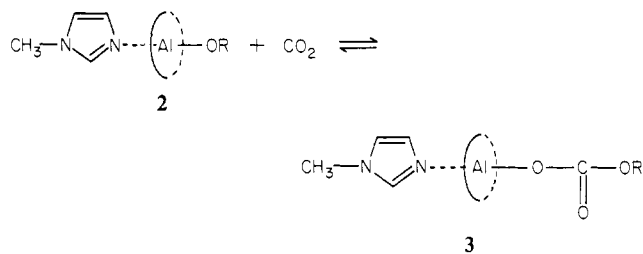


Figure 5. ^1H NMR spectrum of the (TPP)AlPEO-MeIm (1/3) system in CH_2Cl_2 saturated with CO_2 at room temperature. $[(\text{TPP})\text{AlPEO}]_0 = 50 \text{ mmol L}^{-1}$.

Scheme III



shown in Figure 3. Furthermore, the ^1H NMR signal assigned to the methyl proton at the terminal unit of the alkoxide group of (TPP)AlPPO showed a large downfield shift from $\delta -2.3$ (a' in Figure 1B) to -0.5 (a''), while the coordinated MeIm (axial ligand of TPPAlPPO; g' , h' , i' , and j') remained unchanged, as shown in Figure 4. These observations strongly indicate that carbon dioxide inserted into the Al-O bond of (TPP)AlPPO to form a (tetraphenylporphinato)aluminum carbonate (“trapped CO_2 ”), as in Scheme III. In accordance with this observation, in the ^1H NMR spectrum of the (TPP)AlPEO-MeIm (1/3) system saturated with carbon dioxide (Figure 5) two triplet signals assignable to the structure corresponding to 3 appeared at $\delta 1.7$ (k'') and 2.9 (l''), while the signals due to the terminal and the penultimate oxyethylene units of the starting alkoxide (2; Table I, ii) completely disappeared.

On the other hand, in the absence of MeIm, the infrared and ^1H NMR spectra of (TPP)AlPPO did not change even after the bubbling of carbon dioxide. Thus, MeIm as the axial ligand is

Table I. Chemical Shifts of (TPP)AlOR and Their Complexes with MeIm in CH₂Cl₂ at Room Temperature^a

(i) (TPP)AlPO	
(ii) (TPP)AlPEO	
(iii) (TPP)Alr-BuO	

^a [(TPP)AlOR]₀ = 50 mmol L⁻¹; [MeIm]₀/[(TPP)AlOR]₀ = 3.

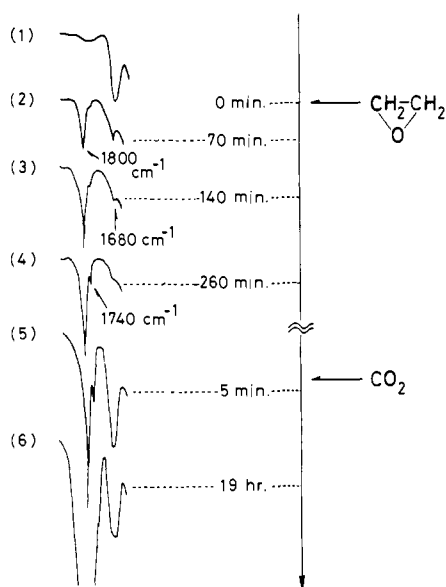


Figure 6. Reaction of CO₂ and ethylene oxide (EO) with the (TPP)-AlPPO-MeIm (1/3) system in CH₂Cl₂ at room temperature. Infrared profile of the reaction at the carbonyl region. [(TPP)AlPPO]₀ = 47.6 mmol L⁻¹, [EO]₀/[(TPP)AlPPO]₀ = 20. (1) TPPAlPPO-MeIm-CO₂ system deficient in the dissolved CO₂.

considered responsible for enhancing the nucleophilic reactivity of the (porphinato)aluminum alkoxide toward carbon dioxide and stabilizing the resulting carbonate.

The ¹H NMR signals (a'') and the infrared absorption at 1680 cm⁻¹, corresponding to the "trapped CO₂", did not change even after removal of the dissolved, free CO₂ from the (TPP)AlPPO-MeIm-CO₂ system by bubbling nitrogen gas. When the above system was allowed to stand for 1 month, the signal a'' was observed to decrease to one-half in its intensity, while a new signal corresponding to the starting alkoxide appeared at δ -2.3. Thus, very slow release of the "trapped CO₂" takes place from the (tetraphenylporphinato)aluminum carbonate 3 in the absence of free CO₂ to regenerate the starting alkoxide 2.

This stability of the "trapped CO₂" by the (TPP)AlPPO-MeIm system is in contrast to that by the (TPP)AlOMe (1b)-MeIm system, where the "trapped CO₂" was readily removed by bubbling nitrogen gas into the reaction mixture.⁵ Higher stability of the "trapped CO₂" by the (TPP)AlPPO-MeIm system enabled us to study the reactivity of the "trapped CO₂" in the absence of free CO₂.

Reaction of Carbon Dioxide and Epoxide with (Tetraphenylporphinato)aluminum Alkoxide in the Presence of 1-Methylimidazole. When ethylene oxide was added to the (TPP)AlPPO-MeIm-CO₂ system after removing the dissolved, free CO₂,

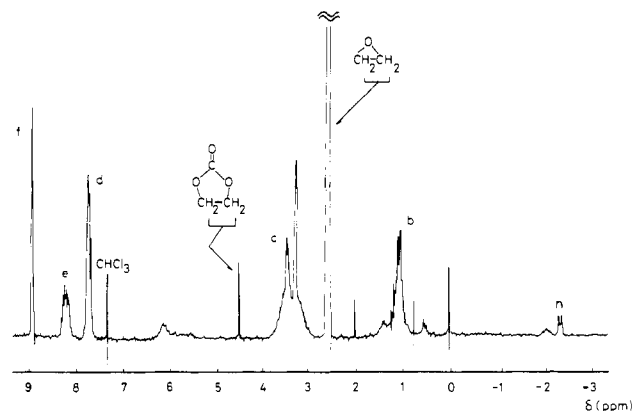


Figure 7. Reaction of CO₂ and ethylene oxide (EO) with the TPPAlPPO-MeIm (1/3) system in CDCl₃ at room temperature. ¹H NMR spectrum of the reaction system without dissolved CO₂. [(TPP)AlPPO]₀ = 47.6 mmol L⁻¹, [EO]₀/[(TPP)AlPPO]₀ = 20.

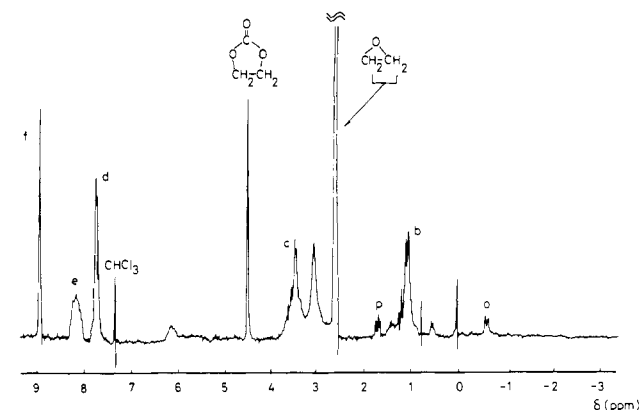
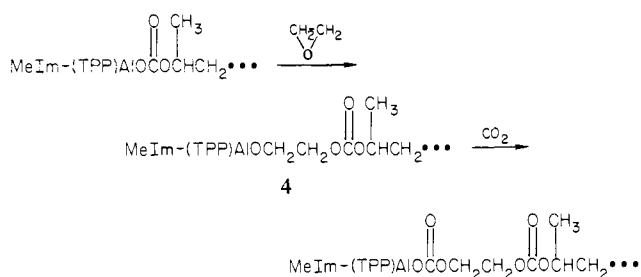


Figure 8. Reaction of CO₂ and ethylene oxide (EO) with the (TPP)-AlPPO-MeIm (1/3) system in CDCl₃ at room temperature. ¹H NMR spectrum of the reaction system with a sufficient amount of CO₂. [(TPP)AlPPO]₀ = 47.6 mmol L⁻¹, [EO]₀/[(TPP)AlPPO]₀ = 20.

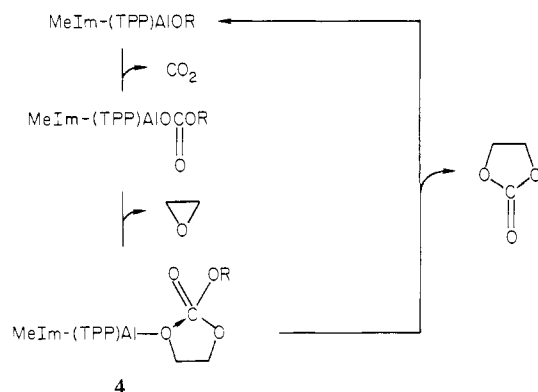
the infrared spectrum of the reaction system showed a new carbonyl absorption due to ethylene carbonate at 1800 cm⁻¹, which increased at the expense of the absorption due to the "trapped CO₂" (Figure 6, 1-4). As shown in Figure 7, the ¹H NMR spectrum of the reaction system after the complete diminishing of the infrared absorption due to the "trapped CO₂" showed a doublet signal (n) attributable to the (TPP)AlPPO-MeIm system, the starting alkoxide before trapping CO₂. Thus, the "trapped CO₂" was actually used for the formation of cyclic carbonate, and consequently the starting alkoxide was reproduced.

When a sufficient amount of carbon dioxide was supplied here to this system, the infrared absorption due to the "trapped CO₂"

Scheme IV



Scheme V



appeared again and ethylene carbonate was additionally formed (Figure 6, 5 and 6). In conformity with this observation, the ^1H NMR spectrum of the reaction system with a sufficient amount of CO_2 (Figure 8) showed a doublet signal (o, $\delta -0.5$) corresponding to the "trapped CO_2 " (see Figure 4), while the signal at $\delta -2.3$ due to the starting alkoxide was not observed. Therefore,

(tetraphenylporphinato)aluminum alkoxide reproduced as the result of the cyclic carbonate formation may react instantaneously with the dissolved CO_2 to serve again the "trapped CO_2 " for the repeated reaction, as long as a sufficient amount of CO_2 exists in the reaction system.

It should be noted here that the ^1H NMR spectrum of the $(\text{TPP})\text{AlPPO}-\text{MeIm}-\text{CO}_2$ -ethylene oxide system (Figure 8) also shows a triplet signal (p) assignable to the structure $\text{MeIm}-(\text{TPP})\text{Al}-\text{O}-\text{CO}-\text{O}-\text{CH}_2-\text{CH}_2\cdots$ (see Figure 5, k''). Together with the fact that an infrared absorption due to linear carbonate linkage is observed at 1740 cm^{-1} in this system (Figure 6), the reaction in Scheme IV is considered also to take place. Thus the participation of linear carbonate as the intermediate is indicated in the formation of cyclic carbonate.¹² As illustrated in Scheme V, cyclic carbonate is considered to be formed at least partly, by the intramolecular nucleophilic attack of aluminum alkoxide group on the adjacent linear carbonate linkage of **4**.

Conclusion

The fixation reaction of carbon dioxide with a (porphinato)-aluminum alkoxide was first investigated by the spectroscopic methods using (tetraphenylporphinato)aluminum alkoxide having a long oxyalkylene chain as an alkoxide group, taking advantage of the good solubility. This alkoxide with unique structure was found to behave as a "carrier" of carbon dioxide activated enough to react under mild conditions with epoxide in the presence of 1-methylimidazole to afford cyclic carbonate.

Registry No. **1c**, 71102-37-9; **1d** (R = Me), 84279-80-1; **1d** (R = H), 84279-82-3; **1d** (R = *t*-Bu; $n = 1$), 84279-77-6; $\text{MeIm}(\text{TPP})\text{Al}(\text{OC}_2\text{H}_5)_n\text{OH}$, 84279-81-2; $\text{MeIm}(\text{TPP})\text{Al}(\text{OCH}_2\text{CH}_2)_n\text{OH}$, 84279-83-4; $\text{MeIm}(\text{TPP})\text{AlOCH}(\text{CH}_2\text{Cl})\text{C}(\text{CH}_3)_3$, 84279-78-7; $\text{MeIm}(\text{TPP})\text{AlPPO}-\text{CO}_2$, 84332-50-3; $\text{MeIm}(\text{TPP})\text{AlPEO}-\text{CO}_2$, 84279-79-8; *tert*-butylene oxide, 2245-30-9; ethylene oxide, 75-21-8; propylene oxide, 75-56-9; carbon dioxide, 124-38-9; 1-methylimidazole, 616-47-7; ethylene carbonate, 96-49-1; propylene carbonate, 108-32-7; carbonic acid, 463-79-6.

Photochemistry of Diastereomeric 2,4-Diphenylpentan-3-ones and Related Ketones in "Super-Cage" Environments Provided by Micelles, Porous Glass, and Porous Silica: Temperature and Magnetic Field Effects

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Abstract: The photochemistry of the meso and *d,l* isomers of 2,4-diphenylpentan-3-one (DPP), of 1,3,4-triphenylbutan-2-one (TPB), and of 1,3-diphenylbutan-2-one (α -MeDBK) has been investigated in homogeneous solvents and in "super-cage" environments that impose constraints on the diffusional displacements of the components of geminate radical pairs and thereby enhance the efficiency of cage reactions of geminate pairs. Solutions of ionic detergents containing micelles, porous glass, and porous silica provide examples of such super-cage environments. The major course of reaction in the photolysis of DPP in pentane or benzene is decarbonylation followed by coupling ($\approx 93\%$) or disproportionation ($\approx 3\%$) of PhCHCH_3 radicals. In super-cage environments, the extent of disproportionation increases significantly, as does diastereomeric interconversion. Although temperature effects (in the range 25 to -77°C) on the product of DPP are small for photolysis in homogeneous solution, substantial variations in product ratios with variation in temperature can be achieved when the photolyses are conducted in super-cage environments. Similarly, although magnetic field effects on the product distributions are negligibly small for photolysis in homogeneous solutions, significant variations are found for photolysis of DPP in super-cage environments. The general features of the results with DPP are analogous to those observed for photolysis of TPB and α -MeDBK. A scheme based on the established photochemistry of dibenzyl ketone is proposed which provides a working mechanism that is consistent with all of the observations of this investigation.

The homolytic α cleavage (type I) of ketones is among the most scrutinized of organic photoreactions.¹ The paradigm mechanism

for α cleavage of a ketone involves photoexcitation to a singlet state followed by intersystem crossing to an n,π^* triplet, $^3\text{RCOR}$,