1 H), 2.23 (dt, J = 15.1, 3.4 Hz, 1 H), 2.33 (d, J = 10.5 Hz, 1 H), 2.4–2.5 (m, 1 H), 3.51 and 3.76 (AB q, J = 11.6 Hz, 2 H), 3.57 and 4.02 (AB q, J = 11.9 Hz, 2 H), 4.75 (br s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) 18.0, 20.0, 21.7, 23.4, 24.2, 24.6, 32.7, 34.8, 36.7, 62.3, 68.5, 72.1, 177.9. Anal. Calcd for $C_{13}H_{22}NO_2I$: C, 44.46; H, 6.31; N, 3.99 Found: C, 44.46; H, 6.49; N, 3.87.

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Stereoselective Formation of (Porphinato)aluminum Enolates

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(Porphinato)aluminum enolates ((P)AlOCR^1=CHR^2) were formed by the hydrogen abstraction from a ketone by (porphinato)aluminum diethylamide ((P)AlNEt$_2$), quantitatively. (Porphinato)aluminum enolates were also formed by the conjugate addition of (porphinato)aluminum ethyl ((P)AlEt) or thiolate ((P)AlSR) to an α,β-unsaturated ketone. The NMR spectra of (porphinato)aluminum enolates showed that only one of the geometrical isomers was formed invariably, and the structure was found to be Z form by ^{1}H NMR spectroscopy and by the derivation to the corresponding silyl enol ether. It is of particular interest that the enolate groups exchange between the aluminum porphyrin molecules reversibly, where the Z forms are retained.

The reactions of metalloporphyrins are of interest in relation to a variety of biochemical reactions and biomimetic syntheses. The reactions of the axial ligand bound to the metal covalently, ionically, or by coordination (e.g., oxygen, olefin) are the subjects of particular interest, together with the possible effect of the photoexcitation of the metal–axial ligand bond. In these reactions, specificity in stereochemical aspects is expected because of the reactions taking place on a rigid macrocycle of porphyrin.

Recently, we have made extensive studies on the reactions of aluminum porphyrins and found some interesting catalytic behaviors. Catalytic fixations of carbon dioxide[1,2] and a catalytic reaction taking place on both sides of the porphyrin ring[3] are the examples. More recently, we found a novel catalytic formation of carbon–carbon bond induced by visible light.[4] The reaction is the polymerization of methacrylic esters initiated by (tetraphenylporphinato)aluminum methyl, and the reactive species involved is a (porphinato)aluminum enolate.

In the present paper, we report that the (porphinato)aluminum enolates formed by various routes are invariably in Z form with very high selectivity. Of particular interest is the fact that the intermolecular exchange of the enolate group on aluminum porphyrin takes place, in which the selectivity in geometrical isomerism is also retained. This is the first example with evidence as to the exchange of enolates groups on metal.

Results and Discussion

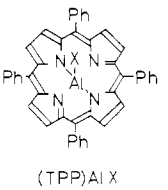
1. Formation of (Porphinato)aluminum Enolate. (Porphinato)aluminum enolates can be formed either by the hydrogen abstraction from a ketone by (porphinato)aluminum diethylamide or by the conjugate addition of (porphinato)aluminum ethyl or thiolate to an α,β-unsaturated ketone.

$$(P)AlNEt_2 + R^1COCH_2R^2 \xrightarrow{-HNEt_2} (P)AlOCR^1{=}CHR^2 \quad (1)$$

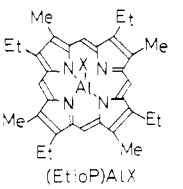
$$(P)AlX + R^1COCH{=}CH_2 \rightarrow (P)AlOCR^1{=}CHCH_2X \quad (2)$$

$$X = Et,SR$$

Formation of (Porphinato)aluminum Enolates by the Reaction of (Porphinato)aluminum Diethylamide with Ketone. First, (tetraphenylporphinato)aluminum diethylamide ((TPP)AlNEt$_2$, **2**) was formed by the equimolar reaction of (tetraphenylporphinato)aluminum chloride ((TPP)AlCl, **1**) and lithium diethylamide (eq 3).



(TPP)AlX



(Et$_8$oP)AlX

$$\underset{\mathbf{1}}{(TPP)AlCl} + LiNEt_2 \xrightarrow{-LiCl} \underset{\mathbf{2}}{(TPP)AlNEt_2} \quad (3)$$

The formation of (TPP)AlNEt$_2$ (**2**) was confirmed by the ^{1}H NMR spectrum of the reaction mixture in C_6D_6. In the high magnetic field, a signal of CH_2 (δ −1.32, q) and a signal of CH_3 (δ −1.38, t) of the NEt$_2$ group appeared. These characteristic signals at unusually high magnetic field region are due to the strong shielding effect of the porphyrin ring.[5] The upfield shifts of the signals of NEt$_2$ group from those of Et$_2$AlNEt$_2$ are 4.3 ppm for CH_2 and

(1) Aida, T.; Inoue, S. *J. Am. Chem. Soc.* **1983**, *105*, 1304.
(2) Kojima, F.; Aida, T.; Inoue, S. *J. Am. Chem. Soc.* **1986**, *108*, 391.
(3) Aida, T.; Inoue, S. *J. Am. Chem. Soc.* **1985**, *107*, 1358.
(4) Kuroki, M.; Aida, T.; Inoue, S. *J. Am. Chem. Soc.* **1987**, *109*, 4737.
(5) Scheer, H.; Kats, J. J. In *Porphyrins and Metalloporphyrins*; Smith, K. M., Ed.; Elsevier: New York, 1975; pp 399–524.

0022-3263/89/1954-0414$01.50/0

Table I. Selected ^{1}H NMR Data of (Porphinato)aluminum Enolates (P)AlOCR^1=CHR^2 in $CDCl_3$ (in ppm)

enolates	porphyrin ligand	R^1	R^2	vinyl	R^1	
					o-Ph	^{t}Bu
3a	TPP	Ph	H	2.36, −0.04	4.61	
3b	TPP	Ph	Me	2.84	4.42	
3c	TPP	Ph	Et	2.64	4.36	
3d	TPP	Et	Me	1.98		
3e	TPP	^{n}Pr	Et	1.86		
3f	TPP	Ph	Ph	3.60	4.45	
6b	EtioP	Ph	Me	2.30	3.98	
6c	EtioP	Ph	Et	2.17	4.01	
6d	EtioP	Et	Me	1.61		
8	TPP	^{t}Bu	^{n}Pr	1.95		−1.46
11a	TPP	Ph	CH_2SEt	2.77	4.29	
11b	TPP	^{t}Bu	CH_2S^nPr	2.03		−1.48
11c	TPP	^{t}Bu	CH_2SPh	2.08		−1.55

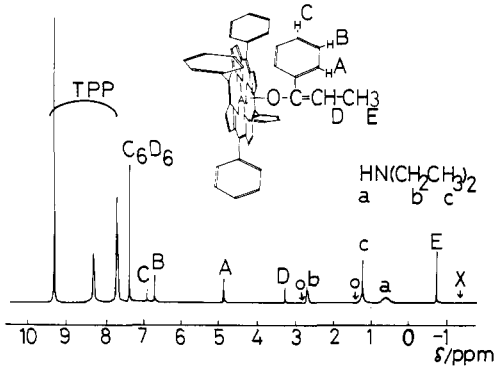


Figure 1. ^{1}H NMR spectrum of the reaction mixture between (TPP)AlNEt$_2$ (**2**) and propiophenone (1:1) in C_6D_6, 20 min after mixing. (×) and (○) indicate the position of the signals due to **2** and those of the signals due to propiophenone, respectively.

2.9 ppm for CH_3, respectively.[6] Relative intensity of the signals due to the NEt_2 group to those of the porphyrin ligand (δ 9.3, 8.4, 7.7) showed that (TPP)AlNEt$_2$ (**2**) was generated quantitatively.

To a solution of **2** in C_6D_6 thus obtained was added an equimolar amount of propiophenone at room temperature, and this reaction mixture was immediately subjected to ^{1}H NMR analysis (Figure 1). The signals of the NEt_2 group of **2** (δ −1.32 and −1.38) disappeared, and the signals of propiophenone (δ 2.70 (CH_2), 1.34 (CH_3)) were not observed. Instead, the signals due to diethylamine (a–c) in an equivalent amount to **2** were newly detected. Other new signals in this spectrum (A–E) are assigned to the enolate group as the axial ligand of the aluminum porphyrin on the basis of the chemical shifts, modes of splitting, and relative intensities.

A set of the signals A–C are assigned to the phenyl group shifted to the higher magnetic field (A, δ 4.82, ortho; B, 6.71, meta; C, 6.92, para) from the positions of the corresponding signals of propiophenone (δ 7.3, meta and para, 8.0, ortho). The doublet peak appeared at unusually high magnetic field (E, δ −0.75, 3 H) and is assigned to the methyl protons, also shielded strongly by the porphyrin ring current and shifted from the signal of the methyl group of propiophenone (δ 1.34). The signal D (δ 3.25, 1 H, q) is assigned to the vinyl proton of the enolate **3**, R^1 = Ph, R^2 = Me. All these findings indicate that propiophenone was converted to the enolate as the axial ligand of the aluminum porphyrin. The relative intensities of the signals A–E to the signals of the porphyrin ligand revealed that this enolization reaction of propiophenone proceeded quantitatively (eq 4).

$$\underset{\mathbf{2}}{(TPP)AlNEt_2} + R^1COCH_2R^2 \xrightarrow{-HNEt_2} (TPP)AlOCR^1{=}CHR^2$$

3a: R^1 = Ph; R^2 = H
3b: R^1 = Ph; R^2 = Me
3c: R^1 = Ph; R^2 = Et
3d: R^1 = Et; R^2 = Me
3e: R^1 = ^{n}Pr; R^2 = Et (4)

Acetophenone, butyrophenone, 3-pentanone, and 4-hexanone were also converted to the corresponding enolates quantitatively. ^{1}H NMR data are summarized in Table I.

When hydrogen chloride was introduced to the solution of **3d** in chloroform, absorption at 1651 cm^{-1} due to $\nu_{C=C}$ of the enolate[7] disappeared, and a new absorption at 1709 cm^{-1} assigned to $\nu_{C=O}$ of 3-pentanone appeared. Quantitative liberation of 3-pentanone was also confirmed by ^{1}H NMR spectroscopy.

When etioporphyrin I was employed as a porphyrin ligand instead of tetraphenylporphyrin, (etioporphinato)aluminum enolates of propiophenone, **6b**, butyrophenone, **6c**, and 3-pentanone, **6d**, were formed quantitatively, starting from the corresponding chloroaluminum complex of etioporphyrin I, (EtioP)AlCl **4** (eq 5).

$$\underset{\mathbf{4}}{(EtioP)AlCl} \xrightarrow[-LiCl]{LiNEt_2} \underset{\mathbf{5}}{((EtioP)AlNEt_2)} \xrightarrow[-HNEt_2]{R^1COCH_2R^2} (EtioP)AlOCR^1{=}CHR^2$$

6b: R^1 = Ph; R^2 = Me
6c: R^1 = Ph; R^2 = Et
6d: R^1 = Et; R^2 = Me (5)

The possibility that the reaction product between (TPP)AlNEt$_2$ (**2**) and ketone be α-metallo ketone, but not enolate, could be excluded by ^{13}C NMR analysis. The enol stannane (tin enolate) of propiophenone, obtained by the reaction of the corresponding enol acetate and organotin methoxide, are reported to exist as an equilibrium mixture of O–Sn and C–Sn forms. These two compounds can be distinguished by ^{13}C NMR spectroscopy. The chemical shifts of the α-carbon for the two structures,

(6) Et_2AlNEt_2 was synthesized by the reaction between Et_3Al and diethylamine: Inoue, S.; Yokoo, Y. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 3651. ^{1}H NMR (C_6D_6): δ 2.93 (4 H, q, NCH_2CH_3), 1.55 (6 H, t, NCH_2CH_3).

(7) For the trimethylsilyl enol ether of 3-pentanone, 1665 cm^{-1} for the *E* isomer and 1676 cm^{-1} for the *Z* isomer: Friedrich, E.; Kalinowski, H.-O.; Luts, W. *Tetrahedron* **1980**, *36*, 1051. For $Et_2BOCEt{=}CHMe$, 1685 cm^{-1}; Fenzl, W.; Köster, R. *Justus Liebigs Ann. Chem.* **1975**, 1322.

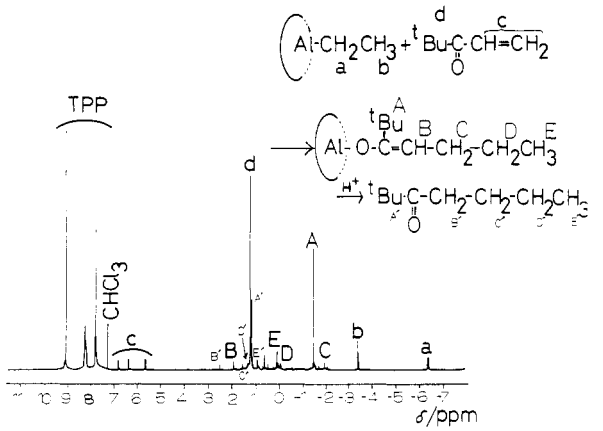


Figure 2. ^{1}H NMR spectrum of the reaction mixture of (TPP)AlEt (**7**) and *tert*-butyl vinyl ketone (1:1) in $CDCl_3$ after 2 h of irradiation in visible light.

$Bu_3SnOCPh{=}CHMe$ and $Bu_3SnCHMeCOPh$, are reported to be 100.59 and 31.58 ppm, respectively.[8] The trimethylsilyl enol ether of propiophenone (*Z* form) exhibits the signal due to $PhC(OTMS){=}CHMe$ at 105.2 ppm.[9] On the other hand, the reaction product between (EtioP)AlNEt_2 (**5**) and propiophenone, for instance, shows a signal at δ 95.70 assigned to the enolate structure **6b**. No signal was observed in the region corresponding to α-metallo ketone.[10]

(Porphinato)aluminum enolate could be also formed by hydrogen abstraction of a ketone by (tetraphenylporphinato)aluminum ethyl, (TPP)AlEt (**7**), under irradiation of visible light, although some side reactions accompanied (eq 6).

$$\underset{\mathbf{7}}{(TPP)AlEt} + R^1COCH_2R^2 \xrightarrow{-EtH} (TPP)AlOCR^1{=}CHR^2 \quad (6)$$

3b: R^1 = Ph; R^2 = Me

3f: R^1 = Ph; R^2 = Ph

Formation of (Porphinato)aluminum Enolate by the Addition of (Porphinato)aluminum Ethyl or Thiolate to α,β-Unsaturated Ketone. Under the irradiation of visible light, (tetraphenylporphinato)aluminum ethyl undergoes the conjugate addition reaction with some α,β-unsaturated ketones.

In the ^{1}H NMR spectrum of the reaction mixture of (TPP)AlEt (**7**) and an equimilar amount of *tert*-butyl vinyl ketone in $CDCl_3$ after 2 h irradiation (Figure 2), the signals due to the ethyl group of **7** (a, δ −6.35, CH_2; b, −3.41, CH_3) and the signals due to *tert*-butyl vinyl ketone (c, d, δ 6.80, 6.33, 5.64, 1.21) decreased in intensity. The most remarkable new signal is that at δ −1.46 (A), which is assigned to the *tert*-butyl group present in the vicinity of porphyrin ring and affected by the ring current.[11] A set of new signals coupled with this is observed (B–E), and these signals are assigned to (TPP)Al enolate **8**, resulting from the conjugate addition of (TPP)AlEt (**7**) to *tert*-butyl vinyl ketone. Another set of small signals (A′ ~ E′) indicates the presence of a small amount of 2,2-dimethyl-3-heptanone (**9**), the final product of the conjugate addition, in the reaction mixture (eq 7).[12]

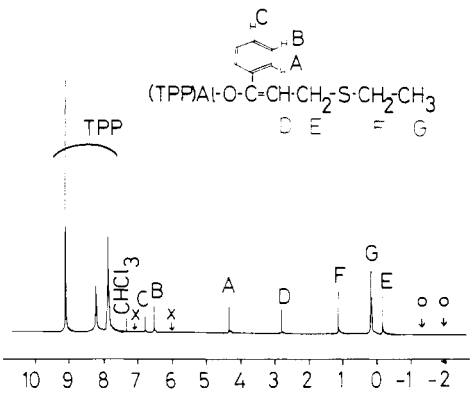


Figure 3. ^{1}H NMR spectrum of the reaction mixture between (TPP)AlSEt (**10a**) and phenyl vinyl ketone (1:1) after 2 h in $CDCl_3$. (○) and (×) indicate the positions of the signals of **10a** and those of the signals of phenyl vinyl ketone, respectively.

$$\underset{\mathbf{7}}{(TPP)AlEt} + t\text{-}BuCOCH{=}CH_2 \rightarrow \underset{\mathbf{8}}{(TPP)AlOC\text{-}t\text{-}Bu{=}CHCH_2Et} \xrightarrow{H^+} O{=}C\text{-}t\text{-}BuCH_2CH_2Et \quad (7)$$

9

When hydrogen chloride was bubbled into the reaction mixture after the completion of the reaction, the signals of **8** disappeared while the signals of **9** increased in intensity corresponding to about 80% of the enolate group. On the other hand, no signals due to 4,4-dimethyl-3-ethyl-1-penten-3-ol, the expected product of carbonyl addition, were detected.[13]

Addition of an equimolar amount of phenyl vinyl ketone to (tetraphenylporphinato)aluminum ethanethiolate (TPP)AlSEt (**10a**) was found to bring about the conjugate addition to generate (TPP)Al enolate **11a** quantitatively (eq 8).

$$\underset{\mathbf{10}}{(TPP)AlSR^1} + O{=}CR^2CH{=}CH_2 \rightarrow \underset{\mathbf{11}}{(TPP)AlOCR^2{=}CHCH_2SR^1} \quad (8)$$

10a, **11a**: R^1 = Et; R^2 = Ph

10b, **11b**: R^1 = ^{n}Pr; R^2 = ^{t}Bu

10c, **11b**: R^1 = Ph; R^2 = ^{t}Bu

In Figure 3 is shown the ^{1}H NMR spectrum of the reaction mixture between (TPP)AlSEt (**10a**) and phenyl vinyl ketone (1:1) after 2 h. The signals due to (TPP)AlSEt (**10a**) (δ −1.99 (CH_2), −1.13 (CH_3)) and the signals due to phenyl vinyl ketone (δ 7.95, 7.59, 7.49, (Ph); 7.16, 6.47, 5.39 (vinyl) disappeared. The signals assigned to the phenyl group were shifted to the higher magnetic field (A, δ 4.29, ortho, B, 6.45, meta, C, 6.73, para) from the positions of phenyl vinyl ketone, indicating that the phenyl group is affected by the ring current of the porphyrin ligand. The signals due to EtS group appeared in the region of somewhat lower magnetic field (F, δ 1.09, SCH_2CH_3; G, 0.10, SCH_2CH_3) than those of **10a**. On the other hand, the

(8) Labadie, S. S.; Stille, J. K. *Tetrahedron* **1984**, *40*, 2329.

(9) Heathcock, C. H.; Buse, C. T.; Kleschick, W. A.; Pirrung, M. C.; Sohn, J. E.; Lampe, J. *J. Org. Chem.* **1980**, *45*, 1066.

(10) In ^{13}C NMR spectrum, the effect of the porphyrin ring current seems to be relatively small. For instance, (TPP)AlOEt, δ 53 (OCH_2CH_3), 16.6 (OCH_2CH_3); Et_2AlOEt, δ 58.9 (OCH_2CH_3), 18.3 (OCH_2CH_3); (TPP)AlEt, δ 5.6 (CH_3); Et_3Al, δ 8.7 (CH_3).

(11) For (TPP)AlOCH(^{t}*Bu*)CH_2Cl, δ −1.48. See ref 1.

(12) The chemical shifts of the signals (A′–E′) are in agreement with those reported for ^{t}BuC(=O)$CH_2CH_2CH_2CH_3$: Heathcock, C. H.; Lampe, J. *J. Org. Chem.* **1983**, *48*, 4330.

(13) For preliminary communication: Murayama, H.; Inoue, S. *Chem. Lett.* **1985**, 1377.

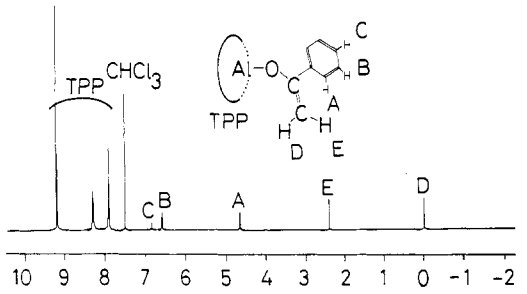


Figure 4. ^{1}H NMR spectrum of the (TPP)Al enolate of acetophenone **3a** in $CDCl_3$.

signals of the EtS group of ethanethiol appears in a still lower magnetic field (δ 2.59, CH_2; 1.37, CH_3). These facts indicate that the EtS group in the reaction mixture is still affected by the porphyrin ring current, but the insertion of phenyl vinyl ketone to the Al–S bond of (TPP)Al–SEt (**10a**) made the distance between the EtS group and the porphyrin ligand longer than in **10a**, so that the shielding effect on the EtS group was weakened. The signal at δ 2.77 (D, 1 H, t) has a chemical shift very close to that of the vinyl proton of **3b** (δ 2.84 in $CDCl_3$), the enolate obtained by the reaction of (TPP)$AlNEt_2$ (**2**) and propiophenone. Considering the mode of splitting and the relative intensity, signal D is assigned to the vinyl proton of an enolate. All these observations indicate the quantitative formation of (porphinato)aluminum enolate **11a**.

When hydrogen chloride was introduced to the reaction mixture, the signals of **11a** disappeared, and the signals due to the corresponding ketone were observed quanitatively (eq 9).

$$\underset{\textbf{11a}}{(TPP)AlOCPh{=}CHCH_2SEt} \xrightarrow{H^+} O{=}CPhCH_2CH_2SEt \quad (9)$$

The reaction of *tert*-butyl vinyl ketone with (TPP)AlSR (R = alkyl, aryl) also took place readily to give (TPP)Al enolates **11b**, **11c**.[14]

2. Stereochemical Aspects of (Porphinato)aluminum Enolates. Organoaluminum enolate, synthesized by the addition reaction of trimethylaluminum to mesityl oxide, was reported to exist as a mixture of *Z* and *E* isomers. These isomers were separated by distillation and showed different ^{1}H NMR and IR spectra.[15] More recently, the proton abstraction reaction of alkyl ketones by trimethyl-, triethyl-, and triisobutylaluminum was reported.[16] In some cases two geometrical isomers were formed and also showed two signals in ^{1}H NMR spectra.

(Porphinato)aluminum enolates, **3b–f**, **6b–d**, **8** and **11a–c**, may also exist as a mixture of two isomers. In this respect, it is of much interest to note that only one set of signals was observed in every (porphinato)aluminum enolate in the ^{1}H and ^{13}C NMR spectra as described below in detail. This fact indicates that only one of the two possible isomers of the enolate was generated stereoselectively on aluminum porphyrin, by the proton abstraction reaction from ketones by (porphinato)$AlNEt_2$, or by the 1,4-addition reaction of (porphinato)AlEt or AlSR to α,β-unsaturated ketones. In order to determine the geometrical structure of (porphinato)aluminum enolate, *Z* or *E*, ^{1}H NMR analysis and the derivation to silyl enol ether were carried out.

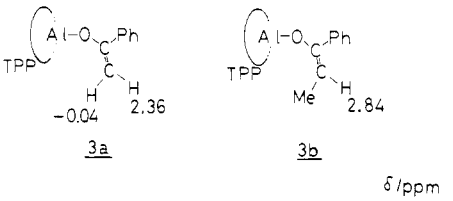
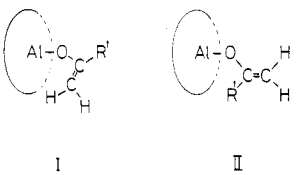


Figure 5. Structures of two enolates.

^{1}H NMR Investigation. In Figure 4 is shown the ^{1}H NMR spectrum of (TPP)aluminum enolate of acetophenone **3a**. Three signals at δ 6.79 (C), 6.53 (B), 4.61 (A) are due to phenyl protons, shifted to higher magnetic field from the signals of phenyl group of acetophenone. The chemical shifts of these phenyl signals are almost the same as those of the phenyl group of the (TPP)aluminum enolate of propiophenone **3b**.

Each of the two other signals at δ 2.36 (E) and δ −0.04 (D) is a singlet, and their relative intensities with respect to (TPP) ligand are 1 H, respectively. These signals are reasonably assigned to the vinyl protons of the enolate. For the trimethylsilyl enol ether of acetophenone, the reported resonances of vinyl protons are at δ 4.27 and δ 4.73.[17] For other examples of metal enolates of acetophenone, vinyl protons of Cp_2ClZr enolates were reported to show their resonances at δ 4.12 and 4.75.[18]

As for the enolate group on aluminum porphyrin, there are considered two representative conformations I and II.



Among these, conformation II with bulky R^1 group (R^1 = phenyl for **3a**) in proximity with the porphyrin ring is unlikely. In the more likely conformation I, one of the two vinyl protons is much closer to the porphyrin ring than the other. In this respect, it is of much interest to note that in the (TPP) aluminum enolate of acetophenone **3a**, the resonances of the two vinyl protons differ from each other by 2.40 ppm in chemical shifts, much more than ever reported. This is the result of ring current effect of porphyrin ring. The proton closer to the ring is affected more; the signal is shifted to a higher magnetic field in the ^{1}H NMR spectrum. Therefore, the resonance at δ −0.04 (D) is considered to be due to the proton cis to aluminum, and the distance between this proton and porphyrin ring must be very short. The other resonance at δ 2.36 (E) is assigned to the vinyl proton trans to aluminum.

Now, the (porphinato)aluminum enolate of propiophenone **3b** shows its signal of vinyl proton at δ 2.84 in $CDCl_3$. Since this chemical shift is similar to that of the trans vinyl proton of **3a** (δ 2.36), the vinyl proton of **3b** is considered to be located in almost the same position as the trans vinyl proton of **3a** with respect to the porphyrin ring. Therefore, **3b** is concluded to be of the *Z* form as depicted in Figure 5.

In Table I are listed the chemical shifts of the (porphinato)aluminum enolates. All the enolates show their vinyl protons in the range from δ 1.61 to 3.60 in the ^{1}H

(14) For the addition of Me_2AlSPh to α,β-unsaturated ketones, see: Itoh, A.; Ozawa, S.; Oshima, K.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 274.

(15) Jeffery, E. A.; Meisters, A.; Mole, T. *J. Organomet. Chem.* **1974**, *74*, 365 and 373.

(16) Yasuda, H.; Fukui, M.; Araki, T.; Nakamura, A. *Nippon Kagaku Kaishi* **1985**, 317.

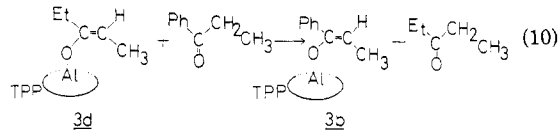
(17) House, H. O.; Czuba, L. J.; Gall, M.; Olmstead, H. D. *J. Org. Chem.* **1969**, *34*, 2324.

(18) Yamamoto, Y.; Maruyama, K. *J. Am. Chem. Soc.* **1982**, *104*, 2323.

NMR spectra.[19,20] The signals of R^1, phenyl, and *tert*-butyl, respectively, are also similar to each other for various enolates. Thus, all these (porphinato)aluminum enolates are the *Z* isomers, regardless of the procedure of their formation, the porphyrin ligand, and the bulkiness of the R^1 group.

Silylation of (Porphinato)aluminum Enolate. In order to confirm the geometrical structure of the enolate, the silylation of the enolate was carried out. Although the attempted reaction of (TPP)aluminum enolate of 3-pentanone **3d** with Me_3SiCl was too sluggish, the use of Me_3SiI (1 equiv) gave a quantitative amount of the corresponding silyl enol ether at least after 20 min. Two geometrical isomers of silyl enol ether were detected by ^1H NMR analysis, and the ratio *Z*/*E* was found to be 86/14. When 5 equiv of Me_3SiBr were used with a prolonged reaction time (24 h), the silyl enol ether was obtained in 83% yield, with the *Z*/*E* ratio of 94/6. These results confirm the *Z* form of the (porphinato)aluminum enolate.[21]

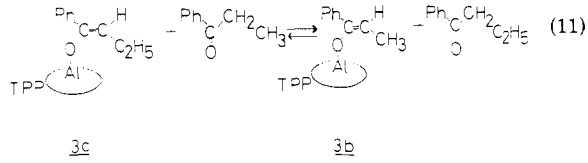
3. "Transenolization Reaction" of (Porphinato)aluminum Enolate with Ketone. When an excess amount of propiophenone was added to the (TPP)aluminum enolate of 3-pentanone **3d**, 3-pentanone was liberated within 2 h, and the *Z* form of the enolate of propiophenone **3b** was formed quantitatively (eq 10). This



(10)

reaction is regarded as the proton abstraction reaction by **3d** as a base similar to (TPP)AlNEt$_2$ (**2**). In contrast, the addition of an excess of 3-pentanone to the enolate of propiophenone **3b** caused no reaction even after 7 days.

The addition of propiophenone to the enolate of butyrophenone **3c** was found to lead to a different result. Although 30 equiv of propiophenone to **3c** was added, the amount of **3b** generated was about 80% with respect to the aluminum porphyrin, and the rest of **3c** remained unreacted. Addition of butyrophenone to **3b** gave a similar result; the amount of **3c** formed was 70% with respect to the starting **3b**, and unreacted **3b** (30%) was also observed. All enolates (**3b**, **3c**) existing in this system were found to be *Z* isomers (eq 11).



(11)

4. "Enolate Exchange Reaction" between Two (Porphinato)aluminum Enolates. Of particular interest is the "enolate exchange reaction" between two (porphinato)aluminum enolates. When equimolar amounts of the (TPP)aluminum enolate of propiophenone **3b** in $CDCl_3$ and the (EtioP)aluminum enolate of 3-pentanone **6d** in $CDCl_3$ were mixed in a sealed tube and the mixture was subjected to ^1H NMR analysis after 2 h, only four signals due to these two enolates were observed in the magnetic field higher than 0 ppm; δ −1.22 (d, $CHCH_3$ of **3b**), −1.65 (t, CH_2CH_3 of **6d**), −1.77 (d, $CHCH_3$ of **6d**), and −2.24 (m, CH_2CH_3 of **6d**) (Figure 6A). After 90 h after mixing, four other signals were newly observed in addition to the signals of **3b** and **6d**. The signal at δ −1.67 (d) is assigned to the methyl group of **6b**, those at δ −1.33 (t), −1.36 (d), and −1.80 (q) agree with the signals of CH_2CH_3, $CHCH_3$, CH_2CH_3 of **3d**, respectively (Figure 6B).

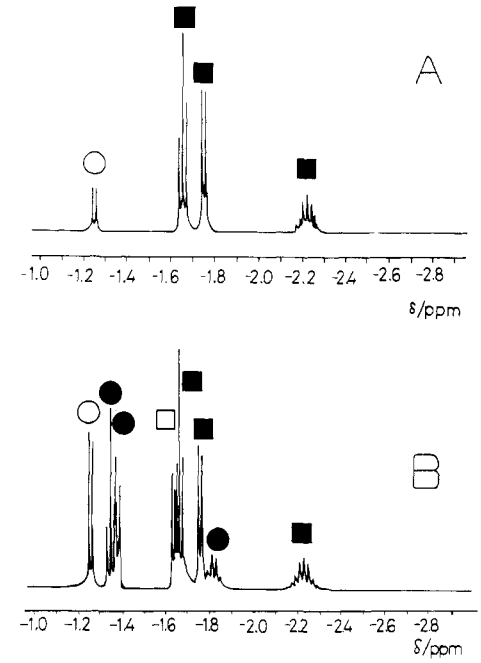


Figure 6. ^1H NMR spectra of the mixture of (TPP)AlOCPh=CHMe (**3b**) (○) and (EtioP)AlOCEt=CHMe **6d** (■) in $CDCl_3$; after 2 h (A) and after 90 h (B). (●) and (□) represent the signals due to (TPP)AlOCEt=CHMe (**3d**) and (EtioP)AlOCPh=CHMe (**6b**), respectively.

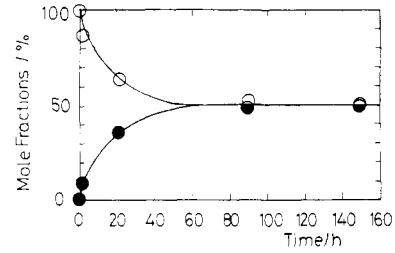
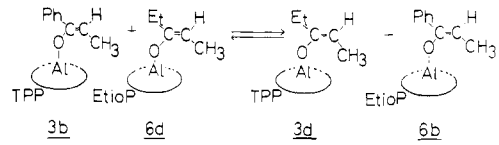


Figure 7. Mole fractions of (TPP)AlOCPh=CHMe (**3b**, ○) and (TPP)AlOCEt=CHMe (**3d**, ●) in the reaction mixture of (TPP)AlOCPh=CHMe (**3b**) and (EtioP)AlOCEt=CHMe (**6d**).

Thus the enolate ligand of aluminum porphyrin was found to exchange between the molecules of (porphinato)aluminum enolate (eq 12).



(12)

Mole fractions of **3b**, **6d**, **3d**, and **6b** were estimated by the relative signal intensities of the enolate ligands and the porphyrin ligands. As shown in Figure 7, **3d** was

(19) Of course, there is the effect of R^2 group on the chemical shift of the vinyl proton. In this connection, it is of interest to note that the difference [δ(vinyl H of enolate) − δ(α-H of ketone)] is almost the same for acetophenone (δ(α-H) = 2.62, $\Delta\delta$ = −0.26 ppm for trans proton of enolate), propiophenone ($\Delta\delta$ = −0.19), 3-pentanone ($\Delta\delta$ = −0.47), and phenyl benzyl ketone ($\Delta\delta$ = −0.69).

(20) The signals of the axial ligands of (EtioP)Al complexes are in a little higher magnetic field than the corresponding complex of (TPP)Al. For example, (EtioP)AlOCH$_2$CH$_3$, δ −1.7 (CH_2), −2.4 (CH_3); (TPP)AlOCH$_2$CH$_3$, δ −1.3 (CH_2), −2.1 (CH_3).

(21) For examples of the specific formation of *Z* isomers of lithium and boron enolates, see ref 17 and (a) Ireland, R. E.; Mueller, R. H.; Willard, A. K. *J. Am. Chem. Soc.* **1976**, *98*, 2868. (b) Fataftah, Z. A.; Kopka, I. E.; Rathke, M. W. *J. Am. Chem. Soc.* **1980**, *102*, 3959. (c) Evans, D. A.; Nelson, J. V.; Vogel, E.; Taber, T. R. *J. Am. Chem. Soc.* **1981**, *103*, 3099; see also, ref 9.

generated and increased at the expense of **3b** to attain the equilibrium in about 60 h after mixing. The same observation was made as to the mole fraction of (EtioP)-aluminum enolates **6d** and **6b**.

Since it was confirmed that **3b** does not react with 3-pentanone to generate **3d** as described above, the generation of **3d** and **6b** is not due to the any concomitant presence of 3-pentanone or propiophenone but is the result of the direct "enolate exchange reaction.[22] All enolates, **3b**, **6d**, **3d**, and **6b**, existing in this reaction system were found to be *Z* isomers.

Conclusion

Highly stereoselective formation of (porphinato)aluminum enolates takes place in the hydrogen abstraction of ketones by (porphinato)aluminum diethylamide and in the conjugate addition of (porphinato)aluminum ethyl or thiolate to α,β-unsaturated ketones. Irrespective of the procedure of the formation and the bulkiness of the α-alkyl and -aryl substituent groups of the ketone, *Z* isomers of the enolates are formed with high selectivity. Of particular interest is the fact that the enolate groups exchange between the aluminum porphyrin molecules reversibly, where the *Z* forms are retained. The present findings indicate the possibility of other stereoselective reactions on aluminum porphyrin. In our preliminary studies on the reaction of (TPP)aluminum enolate of 3-pentanone **3d** with benzaldehyde, the preferred formation of the erythro isomer of the corresponding aldol was indicated.

Experimental Section

Materials. 5,10,15,20-Tetraphenylporphine ($TPPH_2$) was synthesized by the reaction of pyrrole and benzaldehyde in propionic acid and recrystallized from chloroform/methanol.[23] Etioporphyrin I ($EtioPH_2$) was synthesized from *tert*-butyl 4-ethyl-3,5-dimethylpyrrole-2-carboxylate, as reported by Barnett and Smith.[24]

Triethylaluminum (Et_3Al) and diethylaluminum chloride (Et_2AlCl) were purified by distillation under reduced pressure in nitrogen. Commercially available hexane solution of butyllithium (^nBuLi) (Aldrich, 1.6 mol cm^{-3}) was filtered in a nitrogen atmosphere to remove a small amount of insoluble materials, and the concentration was determined by Gilman's double titration.[25] Trimethylbromosilane (Me_3SiBr) and trimethyliodosilane (Me_3SiI) were distilled after refluxing over a mixture of calcium hydride and copper powder just prior to use in a nitrogen atmosphere.

3-Pentanone and 4-hexanone were distilled after refluxing over calcium hydride in nitrogen atmosphere. Acetophenone, propiophenone, and butyrophenone were distilled over P_2O_5 under a reduced pressure in nitrogen. Phenyl benzyl ketone was recrystallized from ethanol. *tert*-Butyl vinyl ketone was prepared from pinacolone, paraformaldehyde, and dimethylamine hydrochloride.[26] Phenyl vinyl ketone was synthesized from β-chloropropiophenone.[27] These two vinyl ketones were purified by repeated distillation over calcium hydride under reduced pressure of nitrogen just prior to use.

Diethylamine was distilled after being refluxed over a mixture of calcium hydride and potassium hydroxide in a nitrogen atmosphere. Ethanethiol and 1-propanethiol were distilled after being refluxed over calcium sulfate in nitrogen. Benzenethiol was distilled over calcium sulfate under reduced pressure in nitrogen. Benzene and hexane were washed with sulfuric acid, neutralized, dried, and distilled over sodium benzophenone ketyl in nitrogen atmosphere. Deuteriated benzene (C_6D_6) was distilled over sodium benzophenone ketyl. Dichloromethane and chloroform were washed with sulfuric acid, neutralized, dried, and distilled over calcium hydride in a nitrogen atmosphere. Deuteriated chloroform ($CDCl_3$) was distilled over calcium hydride in a nitrogen atmosphere. Diethyl ether was refluxed over lithium aluminum hydride and then distilled in a nitrogen atmosphere.

Procedures. All operations using aluminum complexes were carried out under a dry nitrogen atmosphere in a Pyrex flask fitted with a three-way stopcock. Solvent and liquid materials were introduced with a hypodermic syringe through the cock. The irradiation with visible light was carried out with 500-W Xe lamp (USIO UXL-500 D-0). A cutoff filter was used to avoid the irradiation below 420 nm; the reaction vessel was dipped in a water bath thermostated at 20 °C.

^1H and ^{13}C NMR spectra were measured in a sealed tube with a JEOL Type JNM GX-400 spectrometer operating at 399.7 MHz (^1H) and 100.5 MHz (^{13}C), respectively. Chemical shifts were determined with respect to $CHCl_3$ (δ 7.28) or C_6H_6 (δ 7.40) for ^1H NMR, and with respect to $CDCl_3$ (δ 77.10) for ^{13}C NMR. Mass spectra were obtained with a Hitachi RMU-6MG mass spectrometer (EI, 70 eV). Solid sample was introduced to the preheated (200 °C) probe. Infrared spectra were measured in a KBr fixed cell, with a Hitachi 260-30 infrared spectrometer.

Formation of (TPP)AlNEt$_2$ (2) (eq 3). (TPP)AlCl (1) was prepared by the reaction of Et_2AlCl with $TPPH_2$ as described previously.[28] $TPPH_2$ (614 mg, 1.0 mmol) was placed in a Pyrex flask fitted with a three-way stopcock and purged by dry nitrogen. Dichloromethane (20 cm^3) was introduced to dissolve the porphyrin, and to this solution was added Et_2AlCl (1.2 mmol) at room temperature, and the mixture was allowed to stand for about 2 h with magnetic stirring. Volatile materials were removed under reduced pressure to give 1 as a purple solid; 1 was dissolved in benzene (40 mL) to give a dark red solution.

To a solution of 1.1 cm^3 (11 mmol) of diethylamine in 19 cm^3 of diethyl ether was added dropwise 6.0 cm^3 of a solution of ^nBuLi in hexane (1.63 mol dm^{-3}, 9.8 mmol) at −78 °C with vigorous stirring. After 60 min the solution was allowed to warm to 0 °C and was kept at this temperature for more 60 min. Then the solution was warmed to room temperature, and 2.7 cm^3 (1.0 mmol as $LiNEt_2$) was transferred to the vigorously stirred solution of (TPP)AlCl (1) (1.0 mmol) in benzene (40 cm^3). The color of the solution changed immediately from dark red to bright red, and a slight precipitate (LiCl) emerged.

A small amount (2.0 cm^3, 0.05 mmol) of the reaction mixture was transferred to another flask, and the solution was evaporated under a reduced pressure. The resulting purple solid was dissolved in C_6D_6 (1 cm^3), and 0.7 cm^3 of this solution was transferred to a Pyrex NMR tube (o.d. = 5 mm) by a syringe, and the tube was sealed in 1 atm of nitrogen and subjected to ^1H NMR analysis.

Since it was confirmed that (TPP)AlCl (1) reacts fast and stoichiometrically with $LiNEt_2$, $LiNEt_2$ was often used in an amount a little less than that of (TPPAlCl (1) (ca. 95%), in order to exclude the existence of a trace of unreacted $LiNEt_2$ in the subsequent reaction.

Reaction of (TPP)AlNEt$_2$ (2) with Ketone (eq 4). For example, to a solution of (TPP)$AlNEt_2$ (2) (1.0 mmol) in 40 cm^3 of benzene was added 1.1 mmol (0.12 cm^3) of 3-pentanone at room temperature. The color of the solution immediately changed from bright red to orange red. After 30 min a small portion of the solution was transferred to another flask and evaporated under reduced pressure, the resulting purple solid was dissolved in C_6D_6 or $CDCl_3$, and the solution was subjected to NMR analysis. (TPP)AlOCEt=CHMe (**3d**): ^1H NMR ($CDCl_3$) δ 1.98 (1 H, q, C*H*), −1.33 (3 H, t, CH_3CH_2), −1.36 (3 H, d, CH_3CH), −1.80 (2 H, q, CH_2CH_3); ^{13}C NMR ($CDCl_3$) δ 90.99 (d, *C*H), 26.46 (t, CH_2), 9.66 (q, CH_3), 6.91 (q, CH_3); IR ($CHCl_3$) 1651 cm^{-1} ($\nu_{C=C}$). (TPP)AlOCPh=CHMe (**3b**): ^{13}C NMR ($CDCl_3$) δ 96.06 (d, C=

(22) Such an interesting exchange of axial ligands on aluminum porphyrin was also observed for (porphinato)aluminum alkoxides and carboxylates. Asano, S.; Aida, T.; Inoue, S. *Macromolecules* **1985**, *18*, 2057.

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(28) Aida, T.; Mizuta, R.; Yoshida, Y.; Inoue, S. *Makromol. Chem.* **1981**, *182*, 1073.

CH), 7.50 (q, $CHCH_3$); MS (70eV), *m/e* (relative intensity) 774 (3), 773 (7), 772 (M^+, 10), 639 ((TPP)Al^+, 100), 562 (((TPP)Al - C_6H_5)$^+$, 2), 386 (M^{2+}, 4), 319.5 ((TPP)Al^{2+}, 28).

Formation of (EtioP)aluminum Enolate (eq 5). To a solution of (EtioP)AlCl (**4**) (0.5 mmol), synthesized in a similar manner to **1** in benzene (40 cm^3), was added a solution of $LiNEt_2$ (0.5 mmol in 1.35 cm^3) in hexane/diethyl ether. After 1 h, a ketone was added (0.6 mmol), the mixture was allowed to stand for one more hour, and the solution was evaporated to dryness under reduced pressure to give a red solid. This reaction product was analyzed by NMR spectroscopy. For example, (EtioP)-AlOCPh=CHMe (**6b**): ^1H NMR ($CDCl_3$) δ 6.71 (1 H, t, *p*-Ph), 6.37 (2 H, t, *m*-Ph), 3.98 (2 H, d, *o*-Phe, 2.30 (1 H, q, C*H*), -1.67 (3 H, d, CH_3); ^{13}C NMR ($CDCl_3$) δ 148.14 (s, *C*Ph=CHMe), 95.70 (d, CPh=*C*HMe), 6.75 (q, CPh=CHCH_3); MS (70 eV), *m/e* (relative intensity), 637 (1), 636 (M^+, 2), 524 (12), 480 (100).

Reaction of (TPP)AlSR with α,β-Unsaturated Ketone (eq 8, 9). (TPP)AlEt (**7**) (1.0 mmol) was prepared by the equimolar reaction between $TPPH_2$ and Et_3Al in benzene (20 cm^3) at room temperature.[29] To this reaction mixture was added a large excess (30 mmol) of a thiol, and the solution was magnetically stirred for 12 h under the irradiation of visible light. The green solution of **7** became dark blue when the thiol was added and then turned to brown red, characteristic of the solution of (TPP)AlSR (**10**).

The volatile materials were removed under reduced pressure; the resulting purple solid was dissolved in chloroform (10 cm^3). When nonvolatile thiol (benzenethiol) was used, hexane (20 cm^3) was added to the chloroform solution, and the precipitates formed were collected by filtration in a nitrogen atmosphere and washed with hexane to leave reddish purple solids, which were dissolved in chloroform. For example, (TPP)AlSPh (**10c**): ^1H NMR ($CDCl_3$) δ 6.58 (1 H, t, *p*-Ph), 6.23 (2 H, t, *m*-Ph), 3.93 (2 H, d, *o*-Ph).

To a solution of (TPP)AlSEt (**10a**) (0.16 mmol) in 5.0 cm^3 of $CDCl_3$ was added a solution of an equimolar amount of phenyl vinyl ketone (0.16 mmol, freshly distilled) in $CDCl_3$ (0.32 cm^3) at room temperature. The solution turned from brown red to orange red, and NMR analysis was performed. (TPP)-AlOCPh=$CHCH_2SEt$ (**11a**): ^1H NMR ($CDCl_3$) δ 6.73 (1 H, t, *p*-Ph), 6.45 (2 H, t, *m*-Ph), 4.29 (2 H, d, *o*-Ph), 2.77 (1 H, t, CH), 1.09 (2 H, q, CH_2CH_3), 0.10 (3 H, t, CH_2CH_3), -0.21 (2 H, d, $CHCH_2$); ^{13}C NMR ($CDCl_3$) δ 150.19 (*C*Ph=CH), 97.45 (CPh=*C*H), 23.58 (CH_2), 23.37 (CH_2), 13.84 (CH_3).

When dry HCl gas was introduced to a solution of **11a** in $CDCl_3$, the orange red solution immediately turned to dark red. ^1H NMR spectrum of this mixture showed the signals to be identical with those of β-ethylthiopropiophenone synthesized separately.[30]

(29) Inoue, S.; Takeda, N. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 984.

In order to isolate the product, β-ethylthiopropiophenone, the reaction mixture (phenyl vinyl ketone 0.19 mmol (25 mg), (TPP)AlSEt (**10a**) 0.20 mmol, benzene (4.4 mL), room temperature, 1 h) was poured into water and extracted successively by $CHCl_3$. The organic layer was dried by Na_2SO_4, and evaporated to leave a purple solid. This solid was chromatographed over silica (Wakogel C-300), eluted by ethyl ether/hexane (1:1). The first red band contained β-ethylthiopropiophenone, together with some porphyrins. The fraction corresponding to this band was evaporated to give a purple solid, which was again chromatographed over silica with CH_2Cl_2 as eluent. A fast moving, slightly yellow band was collected to obtain β-ethylthiopropiophenone, as identified by ^1H NMR spectrum; yield 34.0 mg (92%).

Reaction of (TPP)AlOCEt=CHMe 3d with Me_3SiI. To a vigorously stirred solution of **3d** (0.40 mmol) in $CDCl_3$ (4.0 cm^3) was added 0.06 cm^3 (0.42 mmol) of freshly distilled Me_3SiI at room temperature, and the solution was immediately sealed in a NMR tube (o.d. = 5 mm) under 1 atm of nitrogen. After 20 min, the ratio of the isomers of the silyl enol ether was determined by the intensities of the corresponding signals, assignments of which were made by using the authentic sample.[9]

Acknowledgment. We wish to thank Dr. Takuzo Aida for his helpful discussions and comments throughout this work, Fumitoshi Kojima for the preliminary experiments on the formation of (TPP)$AlNEt_2$, and Shizuo Mohara at Sagami Chemical Research Center for the measurement of the mass spectra.

Registry No. **1**, 71102-37-9; **2**, 118102-14-0; **3a**, 118102-15-1; **3b**, 118102-16-2; **3c**, 118102-17-3; **3d**, 118102-18-4; **3e**, 118102-19-5; **3f**, 118102-20-8; **4**, 55940-13-1; **6b**, 118102-21-9; **6c**, 118102-22-0; **6d**, 118102-23-1; **7**, 63256-30-4; **8**, 118102-24-2; **9**, 19078-97-8; **10a**, 118102-25-3; **10b**, 118102-26-4; **10c**, 118102-27-5; **11a**, 118102-27-5; **11b**, 118102-30-0; **11c**, 118102-29-7; $PhC(O)CH_3$, 98-86-2; $PhC(O)CH_2CH_3$, 93-55-0; $PhC(O)(CH_2)_2CH_3$, 495-40-9; $CH_3CH_2C(O)CH_2CH_3$, 96-22-0; $CH_3(CH_2)_2C(O)(CH_2)_2CH_3$, 123-19-3; $PhC(O)CH_2Ph$, 451-40-1; EtSH, 75-08-1; PrSH, 79869-58-2; PhSH, 108-98-5; $PhC(O)CH=CH_2$, 768-03-6; (*E*)-$CH_3CH_2C(OH)=CHCH_3$, 57643-01-3; (*Z*)-$CH_3CH_2C(OH)=CHCH_3$, 57643-02-4; *tert*-butyl vinyl ketone, 2177-30-2; β-(ethylthio)propiophenone, 55101-14-9.

(30) To a solution of phenyl vinyl ketone (3 mmol) in dichloromethane was added 3.1 mmol of ethanethiol at room temperature in a nitrogen atmosphere. After 4 days, volatile materials were evaporated to give β-ethylthiopropiophenone as a white solid: mp 44.5-45.0 °C (methanol); lit. mp (a) 47.0-47.5 °C (Weiss, M. J.; O'Donoghue, M. D. *J. Am. Chem. Soc.* **1957**, *79*, 4771); (b) 45-46 °C (Böhme, H.; Heller, P. *Chem. Ber.* **1953**, *86*, 443).

Tandem 1,3-Dipolar Cycloadditions of Pyridinium or Isoquinolinium Methylides with Olefinic Dipolarophiles Leading to Cycl[3.2.2]azines. "Enamine Route" as a New Generation Method of Azomethine Ylides

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Pyridinium or isoquinolinium methylides undergo tandem 1,3-dipolar cycloadditions with two molecules of olefins to produce cycl[3.2.2]azine derivatives in a highly regioselective, stereoselective, and face-selective manner. A new generation of azomethine ylides is involved in the second cycloaddition, which consists of a thermal tautomerization of dienamines or enamines.

Cycloadditions of pyridinium methylides as representatives of heteroaromatic *N*-ylides[1] with electron-deficient olefins where the substituent R^1 is electron-withdrawing produce tetrahydro derivatives of indolizine in a highly

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