BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 2898—2902 (1972)

Electrocatalytic Chemistry of the Transition Metal Complexes. II. Dehydrogenation of Cyclohexene Catalyzed by the Electroreduced Cobalt Complex of α,β,γ,δ-Tetraphenylporphine

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(Received December 17, 1971)

The metal complexes of α,β,γ,δ-tetraphenylporphine (M(TPP), M=Co(II), Ni(II), FeCl(III), Pd(II), Pt(II), Cu(II), MnCl(III), and V(IV)O) were electrolyzed at −2.0 V *vs.* Ag wire in the presence of cyclohexene under nitrogen atmosphere. The cobalt complex only had the catalytic activity of dehydrogenating cyclohexene to 1,3- and 1,4-cyclohexadiene and benzene. With the use of dimethylformamide, dioxane, and hexamethylphosphoric triamide as solvent, cyclohexadienes were produced, and with that of benzonitrile, and dimethyl sulfoxide, benzene was produced and cyclohexadienes were scarcely produced at all. In all cases, the current efficiency of the products was much higher than 100%, indicating that the dehydrogenation reaction is catalytic. The composition of the products also varied with the reaction temperature. When ethanol was added to the reaction solution, the amount of cyclohexadienes increased with benzonitrile used as solvent. The ESR spectrum observed at g=2.003 under electrolysis at the second wave potential is due to the anion radical of cobalt(I) tetraphenylporphine. From polarographic data and other experiments, the species is considered to be an intermediate for dehydrogenation of cyclohexene. The active sites for dehydrogenation are considered to be both the central metal atom and the conjugated ring.

The chemistry of metal complexes of α,β,γ,δ-tetraphenylporphine has currently received much interest with respect to their catalysis. Some works have been carried out in which these complexes were used as catalysts such as synthesis of ammonia from hydrogen and nitrogen,[1] isomerization from quadricyclene to norbornadiene,[2] oxidation of olefins,[3] syntheses of aniline and benzene from 1,4-cyclohexadiene and nitrobenzene.[4]

While there are many reports on the electrochemical studies of the transition metal complexes, only a few have appeared in which electroreduced metal complexes were used as catalysts such as oligomerization of butadiene and polymerization of acrylonitrile catalyzed by the electroreduced tetrakis(pyridine)dichloronickel(II),[5] oligomerization of butadiene catalyzed by the electroreduced nickel acetylacetonate.[6]

The electroreduced species in the above two cases were very stable after the current was cut off. It is well-known that an analogous species is produced by the reduction of nickel acetylacetonate with chemical reagents such as $AlEt_3$, $LiAlH_4$.[7]

In a previous paper,[8] the authors briefly reported that the electroreduced cobalt complex of α,β,γ,δ-tetraphenylporphine had the catalytic activity of dehydrogenating cyclohexene to cyclohexadienes and benzene, and the electroreduced species was unstable. In this paper a detailed study of the catalytic reaction is given.

Experimental

Materials. All solvents were purified by refluxing over dehydrating agents and distilled several times. Cyclohexene was purified by refluxing over $CaSO_4$ and fractionally distilled twice. Tetra-*n*-butylammonium perchlorate (TBAP) used as a supporting electrolyte was obtained by adding hydroperchloric acid to aqueous tetra-*n*-butylammonium bromide and was recrystallized from ethanol three times after washing with water.

α,β,γ,δ-Tetraphenylporphine free base (H_2(TPP)) was prepared from benzaldehyde and pyrrole according to the method of Ball *et al.*[9]

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[1] M. Ichikawa, *Kagaku no Ryoiki*, **24**, 863 (1970).

[2] J. Manassen, *J. Catal.*, **18**, 38 (1970).

[3] US 2950237, Aug. 23 (1960).

[4] J. Manassen and A. Bar-Ilan, *J. Catal.*, **17**, 86 (1970).

[5] N. Yamazaki and S. Murai, *Chem. Commun.*, **1968**, 147.

[6] H. Lehmkuhl and W. Leuchte, *J. Organometal. Chem.*, **23**, C30 (1970).

[7] G. Wilke, *Angew. Chem.*, **69**, 397 (1957).

[8] H. Kageyama, M. Hidai, and Y. Uchida, *Chem. Lett.*, **1972**, 139.

[9] R. H. Ball, G. D. Dorough, and M. Calvin, *J. Amer. Chem. Soc.*, **68**, 2278 (1946).

The cobalt complex of TPP (Co(TPP)) was prepared from cobalt acetate and H_2(TPP).[10] Ni(TPP), Cu(TPP), and MnCl(TPP) were obtained by a similar method.[10] Pd(TPP), Pt(TPP), and VO(TPP) were prepared by using $PdCl_2$, K_2PtCl_4, and vanadyl acetylacetonate, respectively.[11,12]

Reaction Apparatus. The reaction apparatus is an H type cell with an arm to enable the insertion of the reference electrode. The platinum coil, platinum plate (electrode area, 2.7 cm^2), and silver coil were used as cathode, anode, and reference electrode, respectively.

Procedure. M(TPP), 1.0×10^{-4} mol and TBAP, 2.0×10^{-3} mol were dissolved in 10.0 m*l* of the solvent under nitrogen atmosphere, and 2.0 m*l* (*ca* 2×10^{-2} mol) of cyclohexene was added to the solution. After stirring for 30 min at room temperature, the solution was introduced into the electrolytic cell. The cathode potential was set up and controlled *vs.* silver wire using a Yanagimoto Controlled Potential Electrolyzer Model VE-3.

Electrolysis was carried out for 6—24 hr at room temperature. After the reaction the solution was analyzed by gas chromatography. The current was measured by a copper coulometer.

Analysis. The polarograph used was a Yanagimoto Model PB-105. Polarography was carried out by using an H type cell. The cathode and anode were a dropping mercury electrode and a mercury pool, respectively. The concentration of the metal complexes and TBAP were 5.0×10^{-3} mol/*l* and 2.0×10^{-1} mol/*l*, respectively.

Quantitative analysis of the dehydrogented products was carried out by gas chromatography. Column, Carbowax 1500 (10%) on Diasolid M (60—80 mesh) 2 m; Column temperature, 40°C; Carrier gas, H_2 30 cc/min; Detector, Thermal conductivity cell.

Detection of hydrogen evolved was carried out by gas chromatography. Column, Molecular sieve 5A 2 m; Column temperature, 20 °C; Carrier gas. N_2 5 cc/min.

ESR Measurement. The ESR spectra were recorded using a JEOL JS-3BS-X Spectrometer. The cathode, anode and reference electrode were a mercury pool, platinum wire and silver wire, respectively. The ESR spectra were measured under controlled potential electrolysis under nitrogen atomosphere.

Visible Spectra. The visible spectra of the complexes were measured using a Shimadzu MPS-50L Spectrophotometer. All operations were carried out under nitrogen atmosphere.

Results and Discussion

Electrolysis of the Metal Complexes in the Presence of Cyclohexene. The half wave potentials of Co(TPP), Ni(TPP), Pd(TPP), Pt(TPP), Cu(TPP), FeCl(TPP), and MnCl(TPP) used as the metal complexes are shown in Table 1. The electrolysis of the above-mentioned complexes and VO(TPP) were carried out at —2.0 V *vs.* Ag wire which was more negative than the second wave potential of all complexes, in a dimethylformamide(DMF) solution of cyclohexene for 6 hr at room temperature.

TABLE 1. THE HALF WAVE POTENTIALS OF THE METAL COMPLEXES

Complex	Prewave	$E_{1/2}$ (1)	$E_{1/2}$ (2)	Δ[b]
H_2 (TPP)[a]	−0.70	−1.05	−1.47	0.42
Co (TPP)[a]	—	−0.82	−1.87	1.05
Ni (TPP)[a]	—	−1.18	−1.75	0.57
Pd (TPP)	—	−1.00	−1.53	0.53
Pt (TPP)	—	−1.18	−1.71	0.53
Cu (TPP)[a]	−0.72	−1.20	−1.68	0.48
MnCl (TPP)	−0.09	−1.52	−1.91	0.39
FeCl (TPP)	−0.18, −0.82	−1.07	−1.68	0.61

conditions: concentration of the metal complex, 5.0×10^{-3} mol/*l*; supporting electrolyte, TBAP, 2.0×10^{-1} mol/*l*; solvent, DMF; potential *vs.* Hg pool.

a) Ref. 9. b) $\Delta=E_{1/2}(1)-E_{1/2}(2)$.

Only when the cobalt complex was electrolyzed in the presence of cyclohexene, cyclohexene was dehydrogenated to 1,3- and 1,4-cyclohexadiene with evolution of hydrogen, no cyclohexane being observed in the reaction mixture. The subsequent experiments were carried out by using the cobalt complex as the metal complex.

Dehydrogenation of Cyclohexene Catalyzed by the Electroreduced Co(TPP) in a Variety of Solvents. The current efficiency for the formation of 1,3-cyclohexadiene(1,3-CHD) and 1,4-cyclohexadiene(1,4-CHD), benzene(Bz) was defined as follows:

$$\eta_{\mathrm{CHD}} = (\text{Amount of CHD(mol)} \times 2/\text{Current passage(Faraday)}) \times 100$$

TABLE 2. DEHYDROGENATION OF CYCLOHEXENE CATALYZED BY THE ELECTROREDUCED Co(TPP) IN VARIOUS SOLVENTS

Solvent	cC_6'/Co mole ratio	Yield (%)		CHD/Co mole ratio	Bz/Co mole ratio	η_{CHD}[c] (%)	η_{Bz}[d] (%)	Dielectric constant
		CHD[a]	Bz[b]					
Dioxane	195	6.88	0	14.3	0	277	0	2.28
Pyridine	204	trace	trace	~0	~0	~0	~0	12.3
PhCN	212	trace	11.0	~0	23.3	~0	872	25.2
HMPT	204	2.02	0	4.11	0	180	0	30
DMF	202	4.73	0	9.52	0	160	0	36.7
DMSO	204	trace	3.23	~0	6.58	~0	274	49

Conditions: anode, Pt coil; cathode, Pt plate; reference electrode, Ag coil; supporting electrolyte, TBAP, 2.0×10^{-1} mol/*l*; concentration of Co(TPP), 1.0×10^{-2} mol/*l*; electrolysis at —2.0 V *vs.* Ag wire for 24 hr at room temperature (19—23°C).

a) total amount of 1,3- and 1,4-cyclohexadiene. b) benzene

d) current efficiency for formation of CHD. c) current efficiency for formation of Bz.

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10) P. Rothermund and A. R. Menotti, *ibid.*, **70**, 1808 (1948).

11) D. W. Thomas and A. E. Martel, *ibid.*, **81**, 5111 (1959).

12) J. T. Horeczy, B. N. Hill, A. E. Walters, H. G. Shutze, and W. H. Bonner, *Anal. Chem.*, **27**, 1899 (1955).

$$\eta_{Bz} = (\text{Amount of Bz(mol)} \times 4/\text{Current passage(Faraday)}) \times 100$$

We see from Table 2 that 1,3-CHD and 1,4-CHD were formed when DMF, dioxane, and hexamethylphosphoric triamide(HMPT) were used as solvent. When dimethyl sulfoxide(DMSO) and benzonitrile (PhCN) were used as solvent, benzene and only a little cyclohexadienes were obtained. When pyridine was used as solvent, only a little of the dehydrogenated products were obtained. This may be ascribed to the strong coordination of pyridine to cobalt atom thus preventing the coordination of cyclohexene.

When DMF, dioxane, DMSO, HMPT, and PhCN were used as solvent, the current efficiency of the dehydrogenated products was much higher than 100%, indicating that the dehydrogenation reaction is catalytic.

No direct relation was found between the dielectric constants of the solvents and the current efficiency of the products.

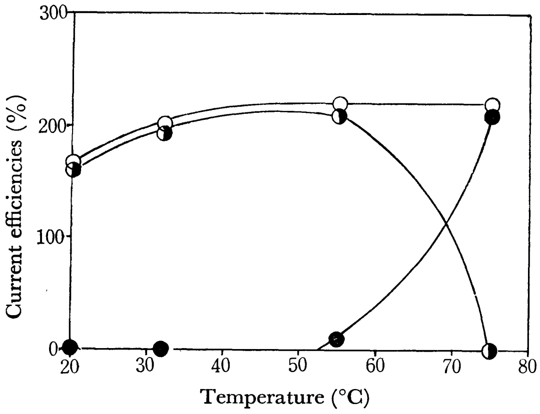

Fig. 1. Effects of the reaction temperature in DMF.
-○- $\eta_{Bz}+\eta_{CHD}$ -●- η_{Bz} -◑- η_{CHD}
η_{Bz}: current efficiency for the formation of benzene
η_{CHD}: current efficiency for the formation of cyclohexadienes

Effects of the Reaction Temperature. The current efficiency of CHD and Bz varied with the reaction temperature when DMF was used as solvent. The results are shown in Fig. 1. Only cyclohexadienes were obtained at 20 and 32°C, cyclohexadienes and benzene at 55°C and only benzene at 75°C. The maximum value of η_{CHD} was 220% at 50°C.

TABLE 3. EFFECTS OF ADDITION OF ETHANOL

Solvent	cC_6'/Co mole ratio	Yield (%) CHD a)	Bz	η_{CHD} b) (%)	η_{Bz} c) (%)	η d) (%)
PhCN	226	2.2	24.0	8.6	188	197
HMPT	199	trace	trace	~0	~0	~0

Conditions: concentration of Co (TPP), 1.0×10^{-2} mol/*l*; TBAP, 2.0×10^{-1} mol/*l*; EtOH, 1.0 m*l*; potential, −2.0 V *vs.* Ag wire; time, 24 hr; temp., room temp.; solvent, 10.0 m*l*.

a) total amount of 1,3- and 1,4-cyclohexadiene
b) current efficiency for formation of cyclohexadienes
c) current efficiency for formation of benzene
d) $\eta=\eta_{CHD}+\eta_{Bz}$

Effects of the Addition of Ethanol to the Reaction Solution. η_{CHD} and η_{Bz} varied with the addition of 1.0 m*l* of dry ethanol to the reaction solution of HMPT and PhCN. The results are given in Table 3.

When ethanol was added to the HMPT solution, η_{CHD} was about 0%, and by adding ethanol to the PhCN solution, η_{Bz} was much lower than that when ethanol was not added. Addition of ethanol thus prevented the formation of CHD in the case of HMPT solution, and that of benzene in the case of PhCN solution.

The ESR Spectra of the Reaction Solution. When the ESR spectra of the DMF solution of Co(TPP) were measured during electrolysis at the first wave potential, no signal was observed in any of the cases. However, at the second wave potential a signal (g=2.003, peak-to-peak width 5.7 gauss, total width 12 gauss) was observed.

In general, the reduction steps of the metalloporphyrins(MP) are described as follows:

$$\text{MP} \xrightarrow{e^-} \text{MP}^- \xrightarrow{e^-} \text{MP}^{2-} \xrightarrow{e^-} \text{MP}^{3-} \xrightarrow{e^-} \text{MP}^{4-}$$

The paramagnetic species are the metalloporphyrin monoanion(MP^-) and trinegative ion(MP^{3-}).

Felton and Linschitz reported[13] that in the case of Co(TPP), one electron was transferred into the central metal atom to geve $[\text{Co}^{\text{I}}(\text{TPP})]^-$ under electrolysis at the first wave potential, while in other metal complexes of TPP, the electron was transferred into the conjugated ring of TPP at the first wave potential, because there is a big difference between the first wave potential ($E_{1/2}$ (1)) and the second ($E_{1/2}$ (2)), *viz.*, Δ was 1.05 V as shown in Table 1, and the visible spectra of the Co(TPP) electroreduced at the first wave potential differed a great deal from the typical spectra of the monoanion of M(TPP), *viz.*, M(TPP)^- (M=Zn, Cd, Mg, and H_2)[13] whose electrons were delocalized on the conjugated ring of TPP.

The signal observed when the Co(TPP) was electrolyzed at the second wave potential was similar to that of M(TPP)^- as shown in Table 4. On the trinegative ion, Hush and Rowland reported[14] that the ESR spectra of the metal porphyrins such as zinc tetrabenzporphine, zinc etioporphyrin I reduced with sodium in tetrahydrofuran showed hyper fine structure,

TABLE 4. ESR SPECTRAL CHARACTERISTICS OF M(TPP)^-

Compound	g value	Peak-to-peak width(gauss)	Total width (gauss)
Zn $(\text{TPP})^-$ a)	2.0000	20	100
Cd $(\text{TPP})^-$ a)	2.0025	7	22
Mg $(\text{TPP})^-$ a)	2.0024	4.7	15
H_2 $(\text{TPP})^-$ a)	2.0027	3.8	15
$[\text{Co (TPP)}^{\overline{\cdot}}]^-$	2.003	5.7	12

Conditions: concentration of Co (TPP), 5.0×10^{-3} mol/*l*; supporting electrolyte, TBAP, 2.0×10^{-1} mol/*l*; solvent, DMF; cathode, Hg pool; anode, Pt wire; reference electrode, Ag wire; potential −2.0 V *vs.* Ag wire.

a) Ref. 9

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[13] R. H. Felton and H. Linschitz, *J. Amer. Chem. Soc.*, **88**, 1113 (1966).

[14] N. S. Hush and J. R. Rowlands, *ibid.*, **89**, 2976 (1967).

and the paramagnetic species was considered to be either a trinegative ion of the porphyrin or a phlorin dianion in which hydrogen atom was attached to a methine carbon atom of the porphyrin skelton. (*cf.* Fig. 2)

The signal observed at the second wave potential was singlet and no hyper fine structure was observed. The ESR characteristics of the signal observed at the second wave potential indicates that electron is delocalized on the conjugated ring of porphyrin. Thus it is reasonable to conclude that the signal observed at the second wave potential is due to the anion radical of Co(I), *viz.*, $[Co^I(TPP)^{\cdot-}]^-$.

It is assumed that the reaction steps in the electroreduction of Co(TPP) dissolved in DMF are described as follows:

$$\text{1st step}\ Co^{II}(TPP) \xrightarrow{e^-} [Co^I(TPP)]^- \quad E_{1/2} = -0.82\,V$$

$$\text{2nd step}[Co^I(TPP)]^- \xrightarrow{e^-} [Co^I(TPP)^{\cdot-}]^- \quad E_{1/2} = -1.87\,V$$

The color of $[Co^I(TPP)]^-$ dissolved in tetrahydrofuran[15] and also that of $[Co^I(TPP)^{\cdot-}]^-$ is green.

The Intermediate for Dehydrogenation of Cyclohexene. The dehydrogenated products were not considered to be derived from the decomposition of the metal complex, since the molar ratio of the products to the metal complex was over 4. The products were obtained only when the reaction solution was electrolyzed at −2.0 V *vs.* Ag wire. No products were formed when the reaction solution was not electrolyzed and kept at room temperature under nitrogen or oxygen, or when the electrolysis was performed at −1.5 V *vs.* Ag wire (the first wave potetential) under nitrogen atmosphere. The results indicate that the dehydrogenation reaction was not catalyzed by $Co^{II}(TPP)$ or $[Co^I(TPP)]^-$.

When a cell with diaphragm (glass filter) was used and the electrolysis was carried out in DMF at −2.0 V *vs.* Ag wire, the dehydrogenated products were detected only in catholyte, and none in anolyte. On the other hand, when the electrolysis was carried out at −2.0 V *vs.* Ag wire under oxygen atmosphere, no products were obtained.

Thus the products were not formed by the electrooxidation of cyclohexene. It is reasonable to conclude that the species electroreduced at the second wave potential had catalytic activity for dehydrogenating cyclohexene to cyclohexadienes and benzene, $[Co^I(TPP)^{\cdot-}]^-$ being reaction intermediate.

Felton *et al.* reported that in the cases of metal complexes (M=Ni, Cu, Pb, Mg *etc.*) except for the cobalt complex, the difference between the first wave potential and the second, Δ was constant 0.44±0.04 V. Thus one electron was transferred to the ring of porphyrin rather than the central metal atom to give the monoanion of M(TPP) at the first wave potential and the dianion of M(TPP) at the second wave potential.

In the cases of Pd(TPP), Pt(TPP), FeCl(TPP), and MnCl(TPP), Δ was much lower than Δ in the case of Co(TPP) (1.05 V) as shown in Table 1. Thus it is considered that the dianion of these complexes was produced under electrolysis at the second wave potential.

It should be noted that the metal complexes except for the cobalt complex in which electrons were transferred to the conjugated ring of TPP under electrolysis had no activity for the dehydrogenation of cyclohexene.

The Active Sites of the Reaction Intermediate for the Dehydrogenation of Cyclohexene. No products were detected when the electrolysis was carried out in pyridine solution. This might be ascribed to the strong coordination of pyridine to the cobalt atom preventing the coordination of cyclohexene. One of the active sites is therefore considered to be the central metal atom.

No products were detected when the electrolysis of H_2TPP in HMPT solution was carried out at the first wave potential (−1.2 V *vs.* Ag wire). Thus the dehydrogenation reaction of cyclohexene was not catalyzed by H_2TPP^- which had only the conjugated ring of TPP.

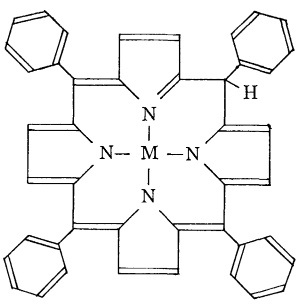

Fig. 2. The structure of tetraphenylphlorin.

Closs and Closs reported[16] that $[Zn(TPP)]^{2-}$ obtained by the reduction of Zn(TPP) with anthracene negative ion was reacted with equimolecular methanol to give the monoanion of zinc tetraphenylphlorin as shown in Fig. 2. When $[Zn(TPP)]^{2-}$ is reacted with excess methanol, the monoanion of zinc tetraphenylchlorin in which two hydrogen atoms are attached to a pyrrole fragment of porphyrin skeleton is produced.[16] Thus it may be reasonable to assume that added alcohol

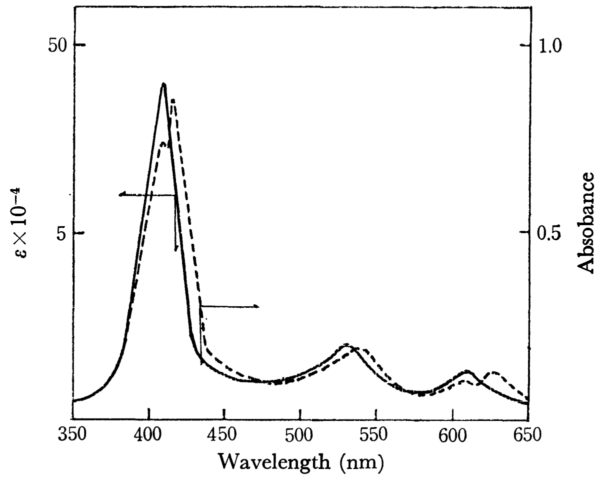

Fig. 3. The visible spectrum of the reaction solution after electrolysis.
solid line: Co(TPP) in dioxane solution
dashed line: the dioxane solution after electrolysis

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[15] H. W. Whitlock, Jr., and B. K. Bower, *Tetrahedron Lett.*, **52**, 4827 (1965).

[16] G. L. Closs and L. E. Closs, *J. Amer. Chem. Soc.*, **85**, 818 (1963).

reacts with the conjugated ring of the porphyrin skeleton to cleave or weaken the conjugated ring, and the composition of the dehydrogenated products changes with the addition of ethanol.

On the other hand, Ichikawa *et al.* reported[17] that the active site for the exchanging reaction of H_2 and D_2 catalyzed by the Na-phthalocyanine electron donor-acceptor complexes may be the conjugated ring of the phthalocyanines[17]. Thus the active sites for the dehydrogenation of cyclohexene are considered to be both the central metal atom and the conjugated ring of $[\mathrm{Co^{I}}\text{-}(\mathrm{TPP})^{\cdot}]^{-}$.

The visible spectrum of the reaction solution after electrolysis is shown in Fig. 3. The band at 620 nm assigned to that of the cobalt complex of tetraphenylchlorin,[18,19] and free hydrogen molecule was detected by gas chromatography. It might be considered that the hydrogen molecule extracted from cyclohexene hydrogenated the conjugated ring of porphyrin giving rise to the evolution of hydrogen molecule.

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17) M. Ichikawa, M. Soma, T. Onishi, and K. Tamaru, *J. Amer. Chem. Soc.*, **91**, 1538 (1969).

18) G. D. Dorough and F. M. Huennekens, *ibid.*, **74**, 3974 (1952).

19) T. Araki, K. Yamamoto, and S. Sotomura, *Rikagaku Kenkyu-jo Hokoku*, **39**, 156 (1963).