Studies of Reduction of Various Organic Compounds with the Nickel(II) Chloride–Zinc System

Atsuko Nose and Tadahiro Kudo*

Daiichi College of Pharmaceutical Sciences, 22-1 Tamagawa-cho, Minami-ku, Fukuoka 815, Japan. *Received Novermber 27, 1989*

The reduction of a variety of functional groups with the nickel(II) chloride–zinc system was investigated. This system reduced aldehydes, ketones, olefins, nitriles, oxime, nitro and heterocyclic compounds under mild conditions in good yields. It is of interest that some cases of reduction of ketones afforded the corresponding olefins and the saturated products, and the reduction of nitriles afforded the corresponding primary alcohols with the primary and secondary amines. The selective reduction of olefin and nitro functionalities in some compounds bearing carbonyl, ester and carboxyl functionalities was observed with this system.

Keywords reduction; nickel(II) chloride–zinc system; aldehyde; ketone; olefin; nitrile; nitro compound; selective reduction; heterocyclic compound

The chemistry of activated metal species has attracted much attention from the standpoint of their great affinity for various functional groups. A number of nickel catalysts that are active for the oligomerization and isomerization of olefins are also active hydrogenation catalysts. Nickel salts, with or without additional ligands, can be used as hydrogenation catalysts, but in general, their activity is low and elevated temperature is necessary.[1a–d] More active catalysts may be prepared by treating nickel salts whith Grignard reagents,[2] alkylaluminums,[3a–c] butyllithium[4] or sodium borohydride.[5a,b] Furthermore, finely divided nickel with high catalytic activity can also be obtained by the treatment of nickel salts with zinc (Zn) dust[6a–e,g] or alkali metal.[6f] The latter nickel catalyst was proved to be useful for the catalytic hydrogenation of a variety of organic functionalities[6a,e] and for other organic catalytic reactions.[7a–h]

In the previous papers, we reported the reduction of a variety of organic functionalities by the use of dimethoxyborane–nickel(II) chloride ($NiCl_2$),[8a] sodium borohydride–nickel boride,[8b] nickel boride–HCl or NH_4OH[8c] and dimethoxyborane–nickel boride systems.[8d] As a continuation of these studies, the present paper deals with the reduction of aldehyde, ketone, olefin, nitrile, nitro and heterocyclic compounds with the $NiCl_2$–Zn system in methanol solution.

As shown in Table I, aldehydes (**1**—**4**) were reduced with the $NiCl_2$–Zn system in refluxing methanol to afford the corresponding alcohols (**5**—**8**) in good yields.

The reductions of ketones (**9**—**12**) afforded the corresponding secondary alcohols (**15**—**18**) as the major products (Table II) together with the dehydrated products (**19** and **20**) and the ethylbenzenes (**21**—**24**) as by-products. Interestingly, in the reduction of *p*-methylacetophenone (**10**), the secondary alcohol (**16**) and other by-products were obtained, while the reduction of *p*-chloroacetophenone (**11**) using 10 eq of Zn unexpectedly afforded *p*-chloroethylbenzene (**23**) as a major product. Similar treatments of 2-octanone (**13**) and 6-methyl-2-heptanone (**14**) resulted in recovery of the starting materials, respectively, and lower aliphatic ketones, such as acetone and 2-butanone, afforded the condensation products under similar conditions, in contrast to the result with cyclohexanone (**12**).

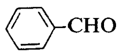
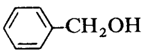
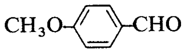
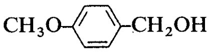
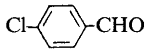
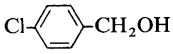
Olefins (**25**—**27** and **20**) were easily reduced to the corresponding saturated compounds (**22**, **23**, **28** and **29**) in good yields under similar conditions. In the reduction of stilbene (**27**), the yield of 1,2-diphenylethane (**29**) was excellent when 2—4 eq mol of $NiCl_2$ and 8 eq mol of Zn were used.

Nitriles (**30**—**33**) and benzaldehyde oxime (**58**) were converted to the corresponding primary amines (**34**—**37**), secondary amines (**38**—**41**) and primary alcohols (**5**, **7**, **42** and **43**) (Table IV). It was interesting that the primary alcohols were obtained in these reductions since the formation of alcohols provides a clue to the reduction mechanism of nitriles with this system. Taking into account the agreement between the results with the oxime (**58**) and those with nitriles, it appears that the oxime (**58**) was partially hydrolyzed under the tested conditions to the aldehyde, which was further reduced to the alcohol.

Nitro compounds (**44**—**47**) were easily reduced to the corresponding amines (**48**—**51**) with this system (Table V).

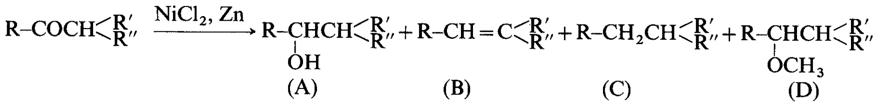
As shown in Table VI, 1,2,3,4-tetrahydroquinoline (**56**) was obtained from quinoline (**52**) in 69.7% yield and

Table I. Reduction of Aldehydes with the $NiCl_2$–Zn System

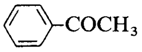
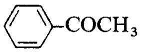
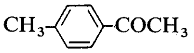
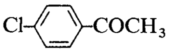
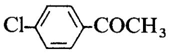
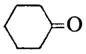
Compound (No.)	$NiCl_2 \cdot 6H_2O$ eq mol	Zn eq mol	Time[a] (h)	Product (No.)	Yield (%)
 (1)	2	8	1	 (5)	75.6
 (2)	3	8	1	 (6)	83.4
 (3)	3	8	1	 (7)	74.7
$CH_3(CH_2)_6CHO$ (4)	3	8	5	$CH_3(CH_2)_6CH_2OH$ (8)	73.3

a) The reaction mixture was refluxed in methanol.

TABLE II. Reduction of Ketones with the $NiCl_2$–Zn System

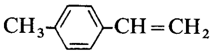
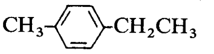
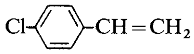
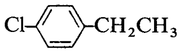
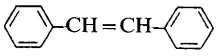


$$\mathrm{R{-}COCH{<}^{R'}_{R''}} \xrightarrow{\mathrm{NiCl_2,\ Zn}} \underset{\text{(A)}}{\mathrm{R{-}\underset{OH}{C}HCH{<}^{R'}_{R''}}} + \underset{\text{(B)}}{\mathrm{R{-}CH{=}C{<}^{R'}_{R''}}} + \underset{\text{(C)}}{\mathrm{R{-}CH_2CH{<}^{R'}_{R''}}} + \underset{\text{(D)}}{\mathrm{R{-}\underset{OCH_3}{C}HCH{<}^{R'}_{R''}}}$$

Compound (No.)	$NiCl_2 \cdot 6H_2O$ eq mol	Zn eq mol	Time[a] (h)	Product (No.) Yield (%)			
				(A)	(B)	(C)	(D)
 (9)	2	8	1	(15) 75.6			
 (9)	3	8	1	(15) 64.7	(19) 1.4	(21) 14.7	
 (10)	3	12	12	(16) 65.1	(20) 1.1	(22) 3.5	(24) 13.9
 (11)	3	8	1	(17) 36.2		(23) 19.7	
 (11)	3	10	1	(17) 12.3		(23) 43.7	
 (12)	3	10	1	(18) 69.1			
$CH_3CO(CH_2)_5CH_3$ (13)	3	12	12		Recovery		
$CH_3CO(CH_2)_3CH(CH_3)_2$ (14)	3	12	8		Recovery		

a) The reaction mixture was refluxed in methanol.

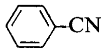
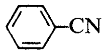
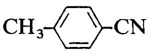
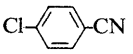
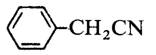
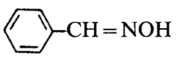
TABLE III. Reduction of Olefins with the $NiCl_2$–Zn System

Compound (No.)	$NiCl_2 \cdot 6H_2O$ eq mol	Zn eq mol	Time[a] (h)	Product (No.)	Yield (%)
$CH_3(CH_2)_8CH{=}CH_2$ (25)	2	8	1	$CH_3(CH_2)_9CH_3$ (28)	78.1
$CH_3(CH_2)_8CH{=}CH_2$ (25)	6	8	1	$CH_3(CH_2)_9CH_3$ (28)	87.8
 (20)	1	6	1	 (22)	65.5
 (26)	1	6	1	 (23)	61.5
 (27)	4	8	1	 (29)	80.7

a) The reaction mixture was refluxed in methanol.

TABLE IV. Reduction of Nitriles and Benzaldehyde Oxime (58) with the $NiCl_2$–Zn System

$$\mathrm{R{-}CN} \xrightarrow{\mathrm{NiCl_2,\ Zn}} \underset{\text{(A)}}{\mathrm{R{-}CH_2NH_2}} + \underset{\text{(B)}}{\mathrm{(R{-}CH_2)_2NH}} + \underset{\text{(C)}}{\mathrm{R{-}CH_2OH}}$$

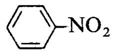
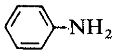
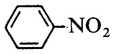
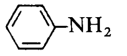
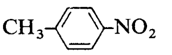
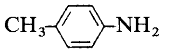
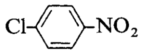
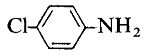
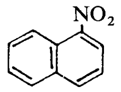
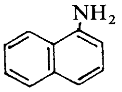
Compound (No.)	$NiCl_2 \cdot 6H_2O$ eq mol	Zn eq mol	Time[a] (h)	Product (No.) Yield (%)		
				(A)	(B)	(C)
 (30)	2	8	7	(34) 20.8	(38) 14.6	(5) 37.9
 (30)	3	12	1	(34) 29.3	(38) 9.7	(5) 35.7
 (31)	3	8	1	(35) 24.2	(39) 3.8	(42) 29.2
 (32)	3	8	4	(36) 37.4	(40) 5.0	(7) 39.2
 (33)	3	12	1	(37) 51.9	(41) 13.5	(43) 27.8
 (58)	3	8	1	(34) 31.2	(38) 35.6	(5) 9.2

a) The reaction mixture was refluxed in methanol.

1,2,3,4-tetrahydroquinaldine (57) was similarly obtained from quinaldine (53) in 54% yield with this system. However, lepidine (54) and isoquinoline (55) were inert to this system even when the reaction time was extended to 12 h.

On the other hand, benzamide, benzoic acid and ethyl

Table V. Reduction of Nitro Compounds with the $NiCl_2$–Zn System

Compound (No.)	$NiCl_2 \cdot 6H_2O$ eq mol	Zn eq mol	Time[a] (h)	Product (No.)	Yield (%)
 **(44)**	2	8	1	 **(48)**	80.1
 **(44)**	3	6	1	 **(48)**	84.6
 **(45)**	3	8	1	 **(49)**	68.9
 **(46)**	6	8	1	 **(50)**	78.0
 **(47)**	2	8	1	 **(51)**	90.3

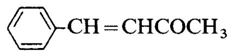
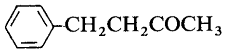
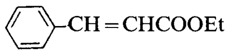
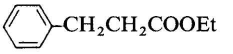
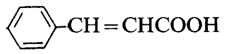
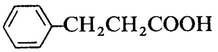
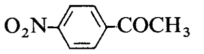
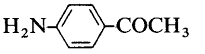
a) The reaction mixture was refluxed in methanol.

Table VI. Reduction of Heterocyclic Compounds with the $NiCl_2$–Zn System

Compound (No.)	$NiCl_2 \cdot 6H_2O$ eq mol	Zn eq mol	Time[a] (h)	Product (No.)	Yield (%)
Quinoline **(52)**	3	10	12	1,2,3,4-Tetrahydroquinoline **(56)**	69.7
Quinaldine **(53)**	3	8	1	1,2,3,4-Tetrahydroquinaldine **(57)**	54.1
Quinaldine **(53)**	6	8	6	1,2,3,4-Tetrahydroquinaldine **(57)**	35.4
Lepidine **(54)**	3	8	12	Recovery	
Isoquinoline **(55)**	3	8	12	Recovery	

a) The reaction mixture was refluxed in methanol.

Table VII. Selective Reduction with the $NiCl_2$–Zn System

Compound (No.)	$NiCl_2 \cdot 6H_2O$ eq mol	Zn eq mol	Time[a] (h)	Product (No.)	Yield (%)
 **(59)**	2	8	1	 **(63)**	71.8
 **(60)**	2	8	1	 **(64)**	89.4
 **(61)**	2	8	1	 **(65)**	86.0
 **(62)**	1	6	1	 **(66)**	87.3

a) The reaction mixture was refluxed in methanol.

decanoate were unaffected with this system and the starting compounds were recovered. These results suggested the possibility of selective reduction of various organic compounds bearing other functional groups. As may be seen in Table VII, olefins bearing other functionalities (**59**—**61**) and *p*-nitroacetophenone (**62**) were selectively reduced to give the corresponding products (**63**—**66**). These results show that this system possesses selective reducing ability for the carbon–carbon double bond and nitro group.

The reaction of $NiCl_2$ with Zn in methanol is exothermic and instantly deposits a black precipitate of a low-valent nickel catalyst through an ion-exchange reaction. Though the reduction mechanism of this system has not been elucidated in detail, it appears that the water of crystallization of $NiCl_2$ plays an important role by supplying hydrogen for the present catalytic reduction and the excess Zn in this system protects the nickel catalyst from oxidation.[9] Taking into account the by-products detected in the reduction of ketones, though the nature of any intermediates is highly speculative, it appears that low-valent nickel and water attack the carbonyl group to afford the α-hydroxyalkylnickel species and a second reductive step is ultimately necessary in order to form an organonickel species capable of undergoing protolysis to the hydrocarbon products. In the reduction of nitriles, it is presumed that the intermediate is the aldimine which reacts with the primary amine to give the secondary amine, or is further reduced to afford the primary alcohol.

As described above, the $NiCl_2$–Zn system reduced aldehyde, ketone, olefin, nitrile, oxime, nitro and some heterocyclic compounds, and olefin and nitro derivatives bearing carbonyl, ester or carboxyl functionality were reduced selectively with this system. These reductions can be performed under mild and neutral conditions, so this system provides a useful and simple synthetic route for the selective reduction of olefin and nitro derivatives.

Experimental

Commercially available $NiCl_2 \cdot 6H_2O$ and Zn dust were used throughout this work. Melting points were determined on a Yanagimoto micro-melting point apparatus, model MP-S3, and are uncorrected. Infrared (IR) spectra were measured in Nujol mulls or as liquid films with a JASCO A-100 (Nihon Bunko) infrared spectrometer, and ultraviolet (UV) spectra were recorded on a JASCO Uvidec-505 (Nihon Bunko) ultraviolet spectrometer. Gas chromatography (GC) was done on a JEOL JGC-20K (Nihon Denshi) gas chromatograph, yields of amines were calculated by GC on a glass column, packed with SE-30, at 140 °C (column temperature) and 0.8 kg/cm^2 nitrogen pressure, by comparison with standard amounts of authentic samples. Chromatography columns of alumina were prepared with Aluminum oxide 90 (70—230 mesh ASTM, Merck). Nuclear magnetic resonance (NMR) spectra were recorded on a Hitachi R20-A spectrometer.

Reduction of Benzaldehyde (1) Compound **1** (1.06 g, 10 mmol) and $NiCl_2 \cdot 6H_2O$ (4.75 g, 20 mmol) were suspended in methanol (50 ml), and Zn (5.23 g, 80 mmol) were added in portions with stirring. Then, the methanol solution was refluxed for 1 h. The precipitate was separated by filteration while hot, and washed with methanol. The filtrate and the washing were combined and the solvent was evaporated off. Water (10 ml) was added, the mixture was extracted with ether and the ether solution was dried over anhydrous magnesium sulfate. After removal of the ether, the residue was distilled under reduced pressure to give 0.82 g (75.6%) of benzyl alcohol (**5**), bp 104—105 °C (20 mmHg).

The following products were similarly obtained, and their yields are listed in Table I; *p*-methoxybenzyl alcohol (**6**), bp 129—131 °C (20 mmHg) (lit.[10] bp 150—151 °C (27 mmHg)); *p*-chlorobenzyl alcohol (**7**), mp 71—72 °C (from ethanol) (lit.[11] mp 69—71 °C); l-octanol (**8**), bp 100—101 °C (20 mmHg) (lit.[12] bp 195.28 °C). These products were identical with authentic samples on the basis of comparisons of their IR and mass spectra.

Reduction of Acetophenone (9) Zn (5.23 g, 80 mmol) was added to a suspension of compound **9** (1.06 g, 10 mmol) and $NiCl_2 \cdot 6H_2O$ (7.13 g, 30 mmol) in methanol (60 ml) in portions with stirring. After refluxing followed by treatment in the manner described above, the residue was chromatographed on a neutral alumina column using petroleum ether as the eluent. The initial eluate was evaporated and the residue was distilled to give 0.16 g (14.7%) of ethylbenzene (**21**), bp 131—135 °C (lit.[13] bp 136.15 °C). The later eluate was evaporated and the residue was distilled to give 15 mg (1.4%) of styrene (**19**). The benzene eluate was evaporated and the residue was distilled to afford 0.79 g (64.7%) of 1-phenylethanol (**15**), bp 88—90 °C (8 mmHg) (lit.[14] bp 93 °C (12 mmHg)).

The following products were similarly obtained, and their yields are listed in Table II: 1-(*p*-tolyl)ethanol (**16**), bp 107—108 °C (15 mmHg) (lit.[15] bp 120 °C (19 mmHg)); 4-methylstyrene (**20**), bp 63—66 °C (18 mmHg) (lit.[15] bp 63 °C (18 mmHg)); *p*-tolylethane (**22**), bp 155—158 °C (lit.[16] bp 159—160 °C (750 mmHg)); 1-methoxy-1-(*p*-tolyl)ethane (**24**), bp 71—74 °C (10 mmHg) (lit.[17] bp 72—73 °C (8 mmHg)); 1-(*p*-chlorophenyl)ethanol (**17**), bp 123—124 °C (15 mmHg) (lit.[18] bp 125 °C (15 mmHg)); *p*-chloroethylbenzene (**23**), bp 183—184 °C (lit.[19] bp 178—180 °C (748 mmHg)). These products were identical with authentic samples on the basis of comparisons of their IR, NMR and mass spectra.

Reduction of Olefins (25—27 and 20) The reaction procedure and treatment were almost the same as those described above. The following products were obtained, and their yields are listed in Table III: undecane (**28**), bp 195—196 °C; 1,2-diphenylethane (**29**), mp 52.5—53 °C (from ethanol) (lit.[20] mp 52.5—53 °C). The products (**22**, **23**, **28** and **29**) were identical with authentic samples on the basis of comparisons of their IR, NMR and mass spectra.

Reduction of Benzyl Cyanide (33) The reaction procedure was almost the same as that described above (see Table IV). After removal of the solvent, 10% hydrochloric acid (20 ml) was added at 0 °C, and the precipitate was collected and washed with ether. The precipitate was recrystallized from ethanol to give diphenethylamine (**41**) hydrochloride, mp 268.5—269.5 °C (lit.[21] mp 271 °C). This precipitate was suspended in water, and the suspension was basified by the addition of 10% sodium hydroxide, followed by extraction with ether. The extract was dried over anhydrous magnesium sulfate. After removal of the ether, the residue was distilled under reduced pressure to give diphenethylamine (**41**) (13.5%), bp 171—173 °C (8 mmHg) (lit.[22] bp 170—175 °C (8 mmHg)); picrate (from ethanol), mp 150—152 °C (lit.[23] mp 151—152 °C). The acidic aqueous layer treated above was extracted with ether, and the extract was dried over anhydrous magnesium sulfate. After removal of the ether, the residue was distilled to give 2-phenylethanol (**43**) (27.8%), bp 97—99 °C (10 mmHg). The acidic aqueous layer was basified by the addition of 10% sodium hydroxide, followed by extraction with ether. The extract was dried over anhydrous magnesium sulfate. After removal of the ether, the residue was distilled to give phenethylamine (**37**), bp 196—198 °C. These products were identical with authentic samples based on comparisons of IR, UV and NMR spectra, and gas chromatographic behavior.

Similarly, compounds **30**—**32** were reduced to the following products (the results and yields are listed in Table IV): benzylamine (**34**), bp 184 °C; dibenzylamine (**38**), bp 151—154 °C (4 mmHg) (lit.[24] bp 113—114 °C (0.1 mmHg)); *p*-methylbenzylamine (**35**), bp 81—82 °C (15 mmHg); di-*p*-methylbenzylamine (**39**), bp 186—188 °C (2 mmHg) (lit.[24] bp 135—137 °C (0.1 mmHg)), mp 34—35 °C (from cyclohexane) (lit.[24] mp 34.5—36.5 °C); *p*-methylbenzyl alcohol (**42**), bp 116—117 °C (19 mmHg), mp 58—60 °C (from heptane); *p*-chlorobenzylamine (**36**), bp 105—106 °C (15 mmHg)); di-(*p*-chlorobenzyl)amine (**40**), bp 227—229 °C (15 mmHg) (lit.[25] bp 230 °C (15 mmHg)), mp 30—31 °C (lit.[25] mp 31 °C); picrate, mp 187 °C (from ethanol) (lit.[25] mp 187 °C); *p*-chlorobenzyl alcohol (**7**), mp 70—71 °C (lit.[11] mp 69—71 °C). These products were identical with authentic samples based on comparisons of IR, UV and NMR spectra, and gas chromatographic behavior.

Reduction of Nitro Compounds (44—47) The reaction procedure and treatment were almost the same as those described above. The products (**48**—**51**) and their yields are listed in Table V.

Reduction of Quinoline (52) and Quinaldine (53) Compounds **52** and **53** were reduced similarly under the conditions shown in Table VI followed by treatment in the manner described above. Products: 1,2,3,4-tetrahydroquinoline (**56**), bp 108—109 °C (7 mmHg) (lit.[26] bp 251 °C); picrate (from ethanol), mp 141 °C (lit.[27] mp 141 °C); 1,2,3,4-tetrahydroquinalidine (**57**), bp 104—106 °C (9 mmHg) (lit.[28] bp 115—116 °C (12 mmHg)), picrate mp 148—150 °C (from ethanol) (lit[28] mp 150 °C). These products were identical with authentic samples based on comparisons of IR, UV and NMR spectra, and gas chromatographic behavior.

Selective Reduction of Compounds 59—62 Compounds **59**—**62** were similarly reduced under the conditions shown in Table VII followed by treatment in the manner described above. The products (**63**—**66**) and their yields are listed in Table VII: 4-phenyl-2-butanone (**63**), bp 111—112 °C (12 mmHg) (lit.[29] bp 63 °C (0.7 mmHg)); ethyl 3-phenylpropanoate (**64**), bp 127—128 °C (22 mmHg) (lit.[30] bp 82 °C (0.7 mmHg)); 3-phenylpropanoic acid (**65**), mp 46—47 °C (from petroleum ether) (lit.[31] mp 46—47 °C); *p*-aminoacetophenone (**66**), mp 105—106 °C (from water) (lit.[32] mp 106 °C). These products were identical with authentic samples based on comparisons of IR, UV and NMR spectra, and gas chromatographic behavior.

References and Notes

1) *a*) H. Itatani and J. C. Bailar, Jr., *Ind. Eng. Cham., Prod. Res. Develop.*, **11**, 146 (1972); *b*) E. A. Emken, E. N. Frankel, and R. O. Butterfield, *J. Am. Oil Chem. Soc.*, **43**, 14 (1966); *c*) E. N. Frankel, H. Itatani, and J. C. Bailar, Jr., *J. Am. Oil Chem. Soc.*, **49**, 132 (1972); *d*) H. Itatani and J. C. Bailar Jr., *J. Am. Chem. Soc.*, **89**, 1600 (1967).

2) Y. Takegami, T. Ueno, and T. Sakata, *Kogyo Kagaku Zasshi*, **68**, 2373 (1965).

3) *a*) M. F. Sloan, A. S. Matlack, and D. S. Breslow, *J. Am. Chem. Soc.*, **85**, 4014 (1963); *b*) Y. Takegami, T. Ueno, and T. Fujii, *Bull. Chem. Soc. Jpn.*, **42**, 1663 (1969); *c*) Y. Tajima and E. Kunioka, *J. Org. Chem.*, **33**, 1689 (1968).

4) J. C. Falk, *J. Org. Chem.*, **36**, 1445 (1971).

5) *a*) H. Samejima, T. Mizuta, H. Yamamoto, and T. Kwan, *Bull. Chem. Soc. Jpn.*, **42**, 2722 (1969); *b*) P. Abley and F. J. McQuillin, *J. Catal.*, **24**, 536 (1972).

6) *a*) K. Hata and S. Taira, *Yuki Gosei Kagaku Kyokai Shi*, **16**, 596 (1958); *b*) K. Sakai and K. Watanabe, *Bull. Chem. Soc. Jpn.*, **40**, 1548 (1967); *c*) K. Sakai, T. Ito, and K. Watanabe, *ibid.*, **40**, 1660 (1967); *d*) K. Sakai, M. Ishige, H. Kono, I. Motoyama, K. Watanabe, and K. Hata, *ibid.*, **41**, 1902 (1668); *e*) M. Kajitani, A. Sugimori, K. Sakai, M. Ishige, and M. Shiota, *Yuki Gosei Kogaku Kyokai Shi.*, **32**, 951 (1974); *f*) R. D. Rieke, A. V. Kavaliunas, L. D. Rhyne, and D. J. J. Fraser, *J. Am. Chem. Soc.*, **101**, 246 (1979); *g*) K. Takagi and Y. Sakakibara, *Chem. Lett.*, **1989**, 1957.

7) *a*) K. Watanabe, *Bull. Chem. Soc. Jpn.*, **32**, 1280 (1959); *b*) K. Watanabe and K. Sakai, *ibid.*, **39**, 8 (1966); *c*) K. Takagi, N. Hayama, and S. Inokawa, *Chem. Lett.*, **1979**, 917; *e*) M. Onaka, Y. Matsuoka, and T. Mukaiyama, *ibid.*, **1981**, 531; *f*) T. Goto, M. Onaka, and T. Mukaiyama, *ibid.*, **1980**, 709; *g*) T. T. Tsou and J. K. Kochi, *J. Org. Chem.*, **45**, 1930 (1980); *h*) K. Takagi, N. Hayama, and S. Inokawa,

Bull. Chem. Soc. Jpn., **53**, 3691 (1980).

8) *a*) A. Nose and T. Kudo, *Chem. Pharm. Bull.*, **37**, 808 (1989); *b*) *Idem, ibid.*, **36**, 1529 (1988); *c*) *Idem, ibid.*, **37**, 816 (1989); *d*) *Idem, ibid.*, **38**, 1720 (1990).

9) It has been reported that the $NiCl_2$–Zn system in water contains Ni, Zn, ZnO, Zn(OH)Cl and Zn $(OH)_2$: Y. Urushibara, S. Yamaguchi, and M. Kobayashi, *Bull. Chem. Soc. Jpn.*, **29**, 815 (1956); Y. Urushibara, M. Kobayashi, S. Nishimura, and H. Uebara, *Shokubai* (Tokyo), **12**, 111 (1956).

10) R. Mozingo and K. Folkers, *J. Am. Chem. Soc.*, **79**, 229 (1948).

11) A. McKillop and M. F. Ford, *Tetrahedron*, **30**, 2467 (1974).

12) G. L. Dorough, H. B. Glass, T. L. Gresham, G. B. Malone, and E. E. Reid, *J. Am. Chem. Soc.*, **63**, 3100 (1941).

13) M. Lacat, *Recl. Trav. Chim. Pays-Bas*, **46**, 243 (1927).

14) H. Wieland, C. Schoph, and W. Hermsen, *Justus Liebigs Ann. Chem.*, **444**, 40 (1925).

15) M. Sulzbacher and E. Bergmann, *J. Org. Chem.*, **13**, 303 (1948).

16) F. Eisenlohr and L. Schulz, *Chem. Ber.*, **57**, 1817 (1924).

17) I. I. Lapkin and O. M. Lakina, *Zh. Obshch. Khim.*, **22**, 1602 (1952) [*Chem. Abstr.*, **45**, 9293*f* (1953)].

18) K. B. Wiberg and T. M. Shryne, *J. Am. Chem. Soc.*, **77**, 2774 (1955).

19) G. Lock and K. Stach, *Chem. Ber.*, **77**, 293 (1944).

20) H. A. Smith, D. M. Alderman Jr., C. D. Shacklett, and C. M. Welch, *J. Am. Chem. Soc.*, **71**, 3772 (1949).

21) K. Kinder and K. Schrader, *Justus Liebigs Ann. Chem.*, **564**, 49 (1949).

22) C. F. Winans and H. Adkins, *J. Am. Chem. Soc.*, **55**, 4167 (1933).

23) W. Barr and J. W. Cook, *J. Chem. Soc.*, **1945**, 428.

24) R. Juday and H. Adkins, *J. Am. Chem. Soc.*, **77**, 4559 (1955).

25) J. v. Braun, M. Kühn, and J. Weismantel, *Justus Liebigs Ann. Chem.*, **449**, 249 (1926).

26) R. E. Rindfusz and V. L. Harnack, *J. Am. Chem. Soc.*, **42**, 1720 (1920).

27) J. v. Broun, W. Gmelin, and A. Petzold, *Chem. Ber.*, **55**, 3779 (1922).

28) J. v. Broun, W. Gmelin, and A. Schultheiss, *Chem. Ber.*, **56**, 1338 (1923).

29) B. J. Bestman and B. Arnason, *Chem. Ber.*, **95**, 1513 (1962).

30) M. L. Bender and K. C. Kemp, *J. Am. Chem. Soc.*, **79**, 111 (1957).

31) E. Schwenk and D. Papa, *J. Org. Chem.*, **11**, 798 (1946).

32) S. Chodroff and H. C. Klein, *J. Am. Chem. Soc.*, **70**, 1647 (1948).