Metallation of Diazines II.

First Metallation of Pyridazine, Metallation of 2,4-Dichloropyrimidine

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3,6-Dichloropyridazine was ortho-lithiated by lithium 2,2,6,6-tetramethylpiperidide. The resulting lithio compound was reacted with carbonyl derivatives iodine and trimethylchlorosilane. An azaxanthone was synthesised. An unusual regioselectivity for the lithiation of 2,4-dichloropyrimidine was studied.

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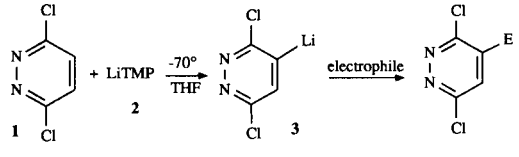
There are few reports about metallation of diazines. Only some pyrimidines have been metalled. In a previous communication [1] we described the first preparative metallation of a pyrazine and to our knowledge there is no reports on the metallation of pyridazines. We present here the direct lithiation of 3,6-dichloropyridazine and a surprising regioselectively for the metallation of 2,4-dichloropyrimidine.

Pyridazine derivatives are in general troublesome to prepare; a good preparative method, based upon the Minisci reaction [2,3] has been developed by Heinisch and coworkers [4] nevertheless this reaction presents in some cases a poor regioselectivity.

The most affordable derivative of pyridazine is maleic hydrazide a well known plant growth regulator which leads easily to 3,6-dichloropyridazine (**1**). Lithiations of **1** (Scheme I) was performed with lithium 2,2,6,6-tetramethylpiperidide (**2**) and the lithio derivative **3** was reacted with various electrophiles.

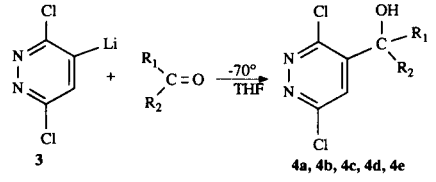
Scheme I



Synthesis of Pyridazinyl Alcohols and Ketones.

Table I shows the results obtained with some aldehydes and benzophenone (Scheme II).

Scheme II

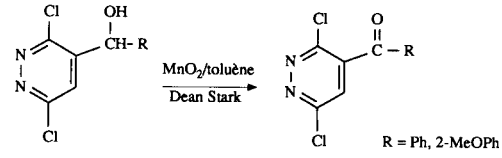


The secondary alcohols **4b** and **4d** were readily oxidized with manganese IV oxide [5] (Scheme III) affording the dichloropyridazinyl ketones **5b** and **5d** in good yields (68-84%).

TABLE I

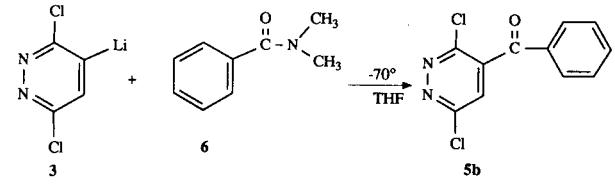
R_1	R_2	Compound	Yield
H	Me	**4a**	65 %
H	Ph	**4b**	60 %
H	4-MeOPh	**4c**	50 %
H	2-MeOPh	**4d**	60 %
Ph	Ph	**4e**	45 %

Scheme III



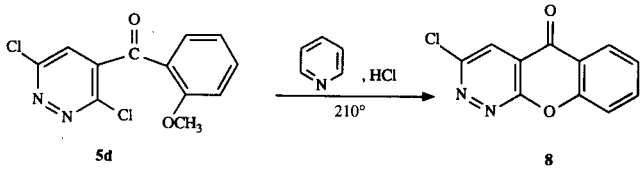
A more straightforward access to ketone **5b** was tested by reaction of **3** with *N,N*-dimethylbenzamide (**6**) [6] (Scheme IV) but the yield was poor (28%) and the first method was preferred to prepare compound **5b**. Ketone **5b** has been recently prepared [7] by Friedel and Crafts acylation of benzene with 3,6-dichloro-4-pyridazinecarbonyl chloride but our method starts from much more easily affordable materials.

Scheme IV



Cyclisation of **5d** by the method of Royer [8] led to an azaxanthone, 3-chloro-5-oxo-5H benzopyrano[2,3-*c*]pyridazine (**8**) (Scheme V).

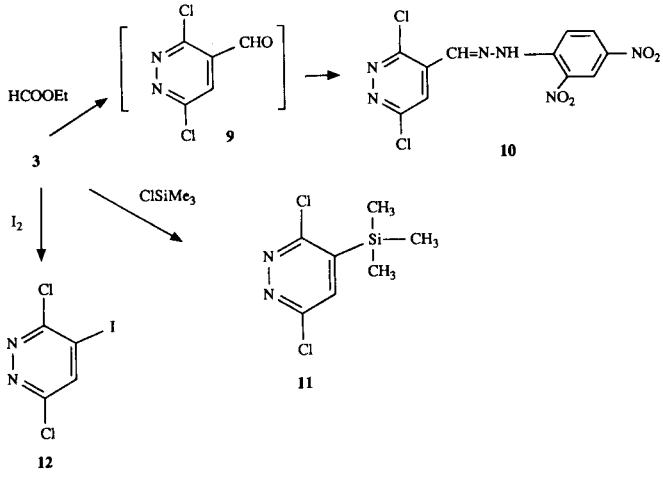
Scheme V



The synthetic interest of *o*-chloroaldehydes prompted us to synthesize 3,6-dichloro-4-formylpyridazine (**9**) by reaction of **3** with ethyl formate. Great difficulties were encountered to isolate **9** due to its poor stability *versus* air and light and it could only be characterized by way of the 2,4-dinitrophenylhydrazine derivative **10** (Scheme VI).

Reaction of chlorotrimethylsilane with the lithio derivative **3** led us to the trimethylsilyl **11** with a poor yield (20%) (Scheme VI). Such a poor yield with silanes was previously observed with chloropyrazine [1]. Reaction of iodine with **3** afforded the iodo derivative **12**.

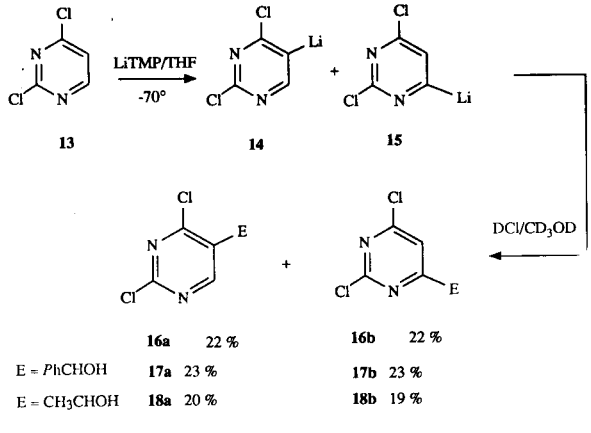
Scheme VI



In the pyrimidine system there are few reports dealing with *ortho* directed lithiation [9-12] of pyrimidine having an *ortho* activating group.

We wish to report here the metallation of 2,4-dichloropyrimidine with lithium 2,2,6,6-tetramethylpiperidide (LiTMP).

Scheme VII



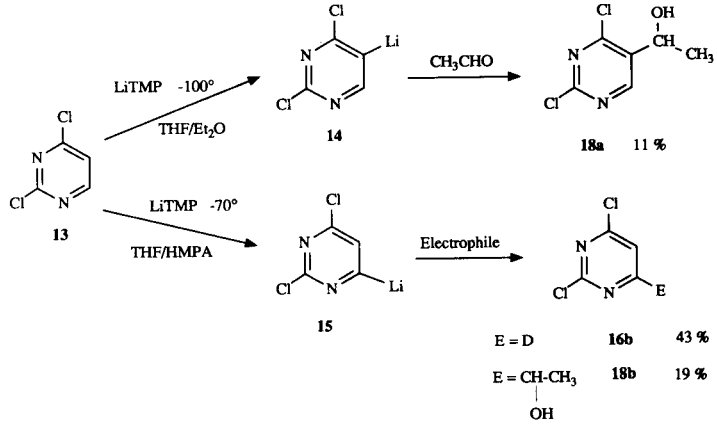
Treatment of 2,4-dichloropyrimidine **13** (Scheme VII) in tetrahydrofuran with 1.1 equivalent of LiTMP at -70° for two hours followed by quenching the reaction with deuterium chloride/perdeuteriomethanol afforded a mixture of two deutero compounds **16a** and **16b** in equal amounts identified by their nmr spectra. This experimental data indicated the formation of the two lithio derivatives **14** and **15**. These lithio derivatives were also reacted with benzaldehyde and acetaldehyde. In each case the two expected hydroxy compounds **17a** and **17b**, **18a** and **18b** were obtained in equal amounts with only modest total yield and no recovery of the starting material.

These results indicate an *ortho*-lithiation at C-5 position directed by the 4-chlorine group in competition with a metallation at C-6 position. Such a metallation at C-6 position without any *o*-directing groupe is very uncommon. In the azines series, metallation without *ortho*-directing group has been performed on pyridine itself but with much more drastic conditions [14] [15].

It must be noticed that this can be correlated with the fact that the C-6 position in the pyrimidine ring is strongly activated toward nucleophilic attack by the electron withdrawing effects of both nitrogen atoms.

Furthermore when metallation of **13** was performed at lower temperature (-100°) (Scheme VIII) with LiTMP in tetrahydrofuran (THF)-diethylether (1:1, v/v) subsequent reaction with acetaldehyde gave **18a** proving that metallation occurred exclusively at C-5 position (lithio derivative **14**).

Scheme VIII



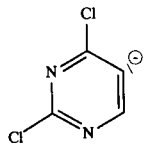
A complete regioselectivity was also obtained by the influence of a strong polar agent such as hexamethylphosphoramide (HMPA). The lithio derivative was prepared for 1.5 hours in THF at -70° with two equivalents of HMPA. Further reaction with deuterium chloride or acetaldehyde afforded respectively **16b** and **18b** which indicated the formation of the lithio derivative **15** exclusively.

Attempts were made to study 2,6-dichloropyrimidine reactivity toward lithiation by use of the quantum semi-empirical method MNDO.

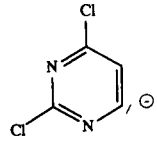
The net charge Q_r determined for $H_{(4)}$ and $H_{(5)}$ are close ($Q_4 = 0.89552$, $Q_5 = 0.89439$) and this can account

for the competition between the two sites of lithiation.

The total energy of both carbanions were estimated also by the MNDO method. The carbanion at the C-6 position of **19b** is more stable than **19a** (C-5 position) ($\Delta E \sim 4$ kcal).



19a



19b

The regioselectivity of lithiation can be discussed in terms of kinetic and thermodynamic control of the reaction. At lower temperature (-100°) lithiation of **13** could be kinetically controlled and lithiation occurred exclusively at C-5 position. At higher temperatures the C-5 carbanion **19a** equilibrates with the thermodynamically more stable C-6 carbanion **19b**, so competition is observed at -70° in THF.

In the presence of HMPA the shift from the C-5 carbanion **19a** to the C-6 carbanion **19b** was facilitated likely due to the strong coordinating power of HMPA which induces formation of the more stable carbanion **19b**. So under these conditions the lithiation could be thermodynamically controlled.

EXPERIMENTAL

Melting points were determined on a Kofler hot stage and are uncorrected. The ^{1}H nmr spectra were recorded in deuteriochloroform with tetramethylsilane as the internal standard or in deuterated dimethyl sulfoxide with hexamethyldisiloxane as the internal standard on a Varian EM 360 L spectrometer. Microanalyses were performed on a Carlo Erba CHNOS 1106 apparatus. The ir spectra were obtained as potassium bromide pellets with a Perkin Elmer R12 spectrophotometer.

Tetrahydrofuran was distilled from benzophenone-sodium and used immediately. The water content of the solvent was estimated by the modified Karl-Fischer method (THF with less than 50 ppm of water).

Metallations were performed under an argon atmosphere whose water content was checked. Reagents were handled with syringes through septa.

General Procedure for Metallation.

A solution of butyllithium (1.6 *M* in hexane, 3 ml, 4.8 mmoles) was added to cold (-30°), stirred, anhydrous tetrahydrofuran (40 ml) under an atmosphere of dry argon. The mixture was warmed to 0° and 2,2,6,6-tetramethylpiperidine (0.91 ml, 5.4 mmoles) was added and the solution was allowed to stand kept at 0° for 30 minutes. It was then cooled to -70°, 3,6-dichloropyridazine or 2,4-dichloropyrimidine was added and this mixture was stirred for 1.5 hour at -70°. The electrophile was added and stirring was continued for 1 hour at -70°. Hydrolysis was then carried out at -70° using a mixture of 35% aqueous hydrochloric acid (2 ml), ethanol (2 ml) and tetrahydrofuran (8 ml). The solution was then gently warmed to room temperature, made slightly basic with a saturated sodium hydrogen carbonate solution (10 ml) and evaporated under vacuum nearly to dryness. The residue was extracted with dichloromethane (3 x 50 ml). The organic extract was dried (magnesium sulphate) and evaporated. The crude product was purified by column chromatography on silica gel using dichloromethane as an eluent.

(3,6-Dichloro-4-pyridazinyl)ethanol (**4a**).

Metallation of 3,6-dichloropyridazine (**1**) (0.5 g, 3.4 mmoles) according to the general procedure and reaction with acetaldehyde (2 ml, 36 mmoles) gave 0.43 g (65%) of **4a**, mp 80°; ^{1}H nmr (deuteriochloroform): δ 1.56 (d, 3H, J = 7 Hz), 3.47 (m, 1H, OH), 5.17 (q, 1H, CH, J = 7 Hz), 7.9 (s, 1H, H_5) ppm; ir (potassium bromide): ν 3270, 2980, 1570 cm^{-1}.

Anal. Calcd. for $C_6H_6Cl_2N_2O$: C, 37.31; N, 14.51; H, 3.11. Found: C, 37.7; N, 14.3; H, 3.1.

(3,6-Dichloro-4-pyridazinyl)phenylmethanol (**4b**).

Metallation of **1** (0.5 g, 3.4 mmoles) according to the general procedure and reaction with benzaldehyde (0.42 ml, 4 mmoles) gave 0.52 g (60%) of **4b**, mp 148°; ^{1}H nmr (DMSO-d_6): δ 5.75 (d, 1H, CH), 6.50 (d, 1H, OH), 7.30 (s, 5H, Phenyl), 8.05 (s, 1H, H_5) ppm; ir (potassium bromide): ν 3240, 1560 cm^{-1}.

Anal. Calcd. for $C_{11}H_8Cl_2N_2O$: C, 51.76; N, 10.98; H, 3.14. Found: C, 51.9; N, 11.1; H, 3.0.

(3,6-Dichloro-4-pyridazinyl)-4-methoxyphenylmethanol (**4c**).

Metallation of **1** (0.5 g, 3.4 mmoles) according to the general procedure and reaction with 4-methoxybenzaldehyde (0.41 ml, 3.4 mmoles) gave 0.48 g (50%) of **4c**, mp 156°; ^{1}H nmr (DMSO-d_6): δ 3.71 (s, 3H, OCH_3), 5.76 (d, 1H, OH, J = 4 Hz), 6.37 (d, 1H, CH, J = 4 Hz), 6.83 (d, 2H, H phenyl, J = 9 Hz), 7.23 (d, 2H, H phenyl, J = 9 Hz), 8.07 (s, 1H, H_5 pyridazine) ppm; ir (potassium bromide): ν 3230, 1610 cm^{-1}.

Anal. Calcd. for $C_{12}H_{10}N_2Cl_2O_2$: C, 50.53; N, 9.82; H, 3.51. Found: C, 50.5; N, 9.8; H, 3.4.

(3,6-Dichloro-4-pyridazinyl)-2-methoxyphenylmethanol (**4d**).

Metallation of **1** (0.65 g, 4.4 mmoles) according to the general procedure and reaction with 2-methoxybenzaldehyde (0.53 ml, 4.4 mmoles) gave 0.75 g (60%) of **4d**, mp 150°; ^{1}H nmr (DMSO-d_6): δ 3.7 (s + m, 4H, OCH_3 + OH), 6.03 (s, 1H, CH), 7.03 (m, 4H, H phenyl), 7.87 (s, 1H, H_5 pyridazine) ppm; ir (potassium bromide): ν 3420, 1600 cm^{-1}.

Anal. Calcd. for $C_{12}H_{10}N_2Cl_2O_2$: C, 50.53; N, 9.82; H, 3.51. Found: C, 50.5; N, 9.8; H, 3.3.

(3,6-Dichloro-4-pyridazinyl)diphenylmethanol (**4e**).

Metallation of **1** (0.5 g, 3.4 mmoles) according to the general procedure and reaction with benzophenone (0.77 g, 4.2 mmoles) gave 0.51 g (45%) of **4e**, mp 141°; ^{1}H nmr (DMSO-d_6): δ 7.07 (s, 1H, OH), 7.27 (s, 10H, H phenyl), 7.45 (s, 1H, H_5 pyridazine) ppm; ir (potassium bromide): ν 3350, 1605, 1350, 1140 cm^{-1}.

Anal. Calcd. for $C_{17}H_{12}Cl_2N_2O$: C, 61.63; N, 8.46; H, 3.63. Found: C, 61.7; N, 8.4; H, 3.6.

(3,6-Dichloro-4-pyridazinyl)phenylmethanone (**5b**).

A suspension of **4b** (0.3 g, 1.2 mmoles), 100 ml of dry toluene and manganeseIV oxide (3 g) was heated at reflux with a Dean Stark apparatus. After the disappearance of **4b** (tlc, uv, 254 nm) (3 hours). The mixture was filtered, manganese oxide was washed with chloroform (30 ml) and solvents evaporated under vacuum

yielding 0.21 g (68%) of **5b** identical to the product described by T. A. Eichhorn, S. Piesch and W. Ried [7].

Anal. Calcd. for $C_{11}H_6N_2Cl_2O$: C, 52.17; N, 11.07; H, 2.37. Found: C, 52.0; N, 10.9; H, 2.5.

(3,6-Dichloro-4-pyridazinyl)-2 methoxyphenylmethanone (**5d**).

Same procedure as above for **4d** (0.28 g, 1 mmole) yielding 0.24 g (84%) of a pale yellow solid, mp 72°; ^{1}H nmr (deuteriochloroform): δ 3.65 (s, 3H, OCH_3), 6.8 to 8.0 (m, 4H, H phenyl), 7.43 (s, 1H, H_5 pyridazine) ppm; ir (potassium bromide): ν 3050, 1660 cm^{-1}.

Anal. Calcd. for $C_{12}H_8N_2Cl_2O_2$: C, 50.88; N, 9.89; H, 2.83. Found: C, 51.0; N, 9.8; H, 2.7.

(3,6-Dichloro-4-pyridazinyl)phenylmethanone (**5b**). Direct Method.

Metallation of **1** (1.06 g, 7.1 mmoles) according to the general procedure (except butyllithium: 5 ml and tetramethylpiperidine 1.3 ml) and reaction with *N*,*N*-dimethylbenzamide (**6**) (1.06 g, 7.1 mmoles) gave 0.5 g (28%) of **5b** which was identical to the previously obtained product.

3-Chloro-5-oxo-5*H*-benzopyrano[2,3-*c*]pyridazine (**8**).

A solution of **5d** (0.08 g, 0.28 mmole) in hot anhydrous pyridinium hydrochloride (20 g) was heated at 210° for 15 minutes. The hot solution was poured onto ice (50 g) and this mixture was extracted with chloroform (3 x 20 ml). The extract was dried (magnesium sulphate) and evaporated to dryness. The crude product was purified by column chromatography on silica gel using dichloromethane as an eluent. The product was then sublimed (150°, 0.8 torr) and gave 0.037 g (60%) of **8**, mp 209°; ^{1}H nmr (deuteriochloroform): δ 7.4-7.9 (m, 3H, $H_{7,8,9}$), 8.3 (d, 1H, H_6), 8.33 (s, 1H, H_4) ppm.

Anal. Calcd. for $C_{10}H_5ClN_2O_2$: C, 56.77; N, 12.04; H, 2.15. Found: C, 57.1; N, 11.6; H, 2.1.

3,6-Dichloro-4-formylpyridazine-2,4-Dinitrophenylhydrazone (**10**).

Compound **1**, (0.65 g, 4.4 mmoles) was metallated according to the general procedure and reaction with ethyl formate (0.4 ml, 5 mmoles). After column chromatography the resulting product was reacted with a solution of 2,4-dinitrophenylhydrazine (1 g, 5 mmoles) in 20 ml of methanol and 2 ml of sulfuric acid. After 15 minutes **10** separated as a yellow solid, yield 0.31 g (20%), mp 259°; ^{1}H nmr (DMSO-d_6): δ 8.18 (m, 2H, H_5 pyridazine and H_6 phenyl), 8.33 (s, 1H, -CH=); 8.72 (m, 1H, H_5 phenyl), 8.7 (s, 1H, H_3 phenyl), 12.13 (s, 1H, NH) ppm; ir (potassium bromide): ν 3220, 1620, 1330 cm^{-1}.

Anal. Calcd. for $C_{11}H_6Cl_2N_6O_4$: C, 36.97; N, 23.53; H, 1.68. Found: C, 36.7; N, 23.3; H, 1.6.

4-Formyl-3,6-dichloropyridazine (**9**).

This compound had ^{1}H nmr (deuteriochloroform): δ 7.87 (s, 1H, H_5), 10.4 (s, 1H, CHO).

3,6-Dichloro-4-trimethylsilylpyridazine (**11**).

Metallation of **1** (0.5 g, 3.4 mmoles) according to the general procedure and reaction with chlorotrimethylsilane (1.25 ml, 10 mmoles) gave 0.15 g (20%) of colourless liquid **11**; ^{1}H nmr (deuteriochloroform): δ 0.45 (s, 9H, $Si(CH_3)_3$), 7.5 (s, 1H, H_5); ir: ν 2960, 1330, 1280, 1145 cm^{-1}.

Anal. Calcd. for $C_7H_{10}SiCl_2N_2$: C, 38.01; N, 12.67; H, 4.52. Found: C, 37.8; N, 12.9; H, 4.7.

3,6-Dichloro-4-iodopyridazine (**12**).

Metallation of **1** (1.05 g, 7 mmoles) according to the general procedure and reaction with iodine (2.01 g, 7.9 mmoles) gave 0.62 g (32%) of **12**, mp 135°; ^{1}H nmr (deuteriochloroform): δ 8.10 (1H, s, H_5) ppm; ir (potassium bromide): ν 3090, 1520, 1335 cm^{-1}.

Anal. Calcd. for $C_4HN_2Cl_2I$: C, 17.45; N, 10.18; H, 0.36. Found: C, 17.6; N, 10.0; H, 0.3.

5- And 6-Deutero-2,4-dichloropyrimidine **16a** and **16b**.

Metallation of 2,4-dichloropyrimidine (**13**) (0.65 g, 4.4 mmoles) according to the general procedure and reaction with 1 ml of mixture perdeuteriomethanol/deuterium chloride 1:1 gave a mixture of two deuterio derivatives **16a**-**16b** in equal amounts identified by their ^{1}H nmr spectra, total yield 43%; **16a**, ^{1}H nmr (deuteriochloroform): δ 8.56 (1H, s, H_6) ppm; **16b**, ^{1}H nmr (deuteriochloroform): δ 7.43 (1H, s, H_5) ppm.

(2,4-Dichloro-5-pyrimidinyl)phenylmethanol (**17a**).

Metallation of **13** (0.65 g, 4.4 mmoles) according to the general procedure and reaction with benzaldehyde (0.42 ml, 4.0 mmoles) gave after purification by column chromatography on silica gel with dichloromethane as an eluent, 200 mg (23%) of **17a**, mp 30°; ^{1}H nmr (deuteriochloroform): δ 4.86 (m, 1H, OH), 6.13 (s, 1H, CH), 7.43 (m, 5H, phenyl), 9.0 (s, 1H, H_6) ppm; ir (potassium bromide): ν 3400, 1555, 1525 cm^{-1}.

Anal. Calcd. for $C_{11}H_8Cl_2N_2O$: C, 51.76; N, 10.98; H, 3.14. Found: C, 51.8; H, 10.8; N, 3.3.

(2,4-Dichloro-6-pyrimidinyl)phenylmethanol (**17b**).

Metallation of **13** (0.65 g, 4.4 mmoles) according to the general procedure and reaction with benzaldehyde (0.42 ml, 4.0 mmoles) gave after purification by column chromatography on silica gel with a mixture of dichloromethane/ethyl acetate 95:5 as an eluent, 200 mg (23%) of **17b**, mp 30°; ^{1}H nmr (deuteriochloroform): δ 4.0 (d, 1H, J = 6 Hz), 5.7 (d, 1H, CH, J = 6 Hz), 7.4 (s, 5H, phenyl), 7.45 (s, 1H, H_5) ppm; ir (potassium bromide): ν 3400, 1540 cm^{-1}.

Anal. Calcd. for $C_{11}H_8Cl_2N_2O$: C, 51.76; N, 10.98; H, 3.14. Found: C, 52.1; N, 10.8; H, 3.4.

(2,4-Dichloro-5-pyrimidinyl)ethanol (**18a**).

Method a.

Metallation of **13** (0.48 g, 3.2 mmoles) according to the general procedure and reaction with acetaldehyde (2 ml, 36 mmoles) gave after purification by column chromatography on silica gel with a mixture of dichloromethane/ethyl acetate (9:1) as an eluent 129 mg (20%) of **18a** as a colourless liquid; ^{1}H nmr (deuteriochloroform): δ 1.56 (d, 3H, CH_3, J = 8 Hz), 3.9 (s, 1H, OH), 5.23 (q, 1H, CH, J = 8 Hz), 8.8 (s, 1H, H_6) ppm; ir (potassium bromide): ν 3400, 1530, 1560 cm^{-1}.

Anal. Calcd. for $C_6H_6Cl_2N_2O$: C, 37.31; N, 14.50; H, 3.11. Found: C, 37.3; N, 14.4; H, 3.3.

Method b.

A solution of butyllithium (1.6 *M* in hexane, 3 ml, 4.8 mmoles) was added to a cold (-10°) stirred mixture of anhydrous tetrahydrofuran (20 ml) and diethyl ether (20 ml) under an atmosphere of dry argon. The mixture was cooled to -70°, 2,2,6,6-tetramethylpiperidine (0.91 ml, 5.4 mmoles) was added, and the solution was warmed to 0° and allowed to stand at 0° for 30 minutes. It was then cooled to -100°, 2,4-dichloropyrimdine was added and this mixture was stirred for 1.5 hour at -100°. The

acetaldehyde was added and stirring was continued for 1.5 hour at -100°. Hydrolysis was then carried out at -100° using a mixture of 35% aqueous hydrochloric acid (2 ml), ethanol (2 ml) and tetrahydrofuran (8 ml). The solution was then treated according to the general procedure. After purification 81 mg (11%) of **18a** was obtained.

(2,4-Dichloro-6 pyrimidinyl)ethanol **18b**.

Method a.

The same procedure for **18a** (Method a) yields 120 mg (19%) of **18b**, as a colorless liquid; ^{1}H nmr (deuteriochloroform): δ 1.56 (d, 3H, CH_3, J = 9 Hz), 3.3 (s, 1H, OH), 4.9 (q, 1H, CH, J = 9 Hz), 7.5 (s, 1H, H_5) ppm; ir (potassium bromide): ν 3280, 1630, 1555, 1525 cm^{-1}.

Anal. Calcd. for $C_6H_6Cl_2N_2O$: C, 37.31; N, 14.50; H, 3.11. Found: C, 37.3; N, 14.2; H, 3.5.

Method b.

Metallation of **13** (0.5 g, 3.4 mmoles) according to the general procedure with 2 ml of HMPA (13 mmoles) and reaction with acetaldehyde gave **18b** identified by ^{1}H nmr.

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