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Introduction.

Since the first preparation of pyridazines by Fischer, [1] major attention has been devoted to their chemistry only in the early few decades. However, pyridazin-3(2*H*)-ones and their fused ring derivatives have recently received much more attention to possess various biological activities [2-5] and also to use the asymmetric dihydroxylation catalysts and the ligands for metal complexes [2].

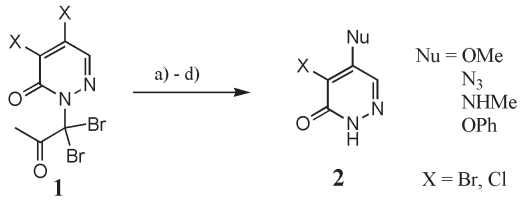
The first synthesis of 4,5-dihalopyridazin-3(2*H*)-ones was achieved by Bistrycki *et al*. [6, 7].

Mono- and multihalopyridazin-3(2*H*)-ones are useful intermediates for the synthesis of pyridazine derivatives such as multisubstituted-pyridazin-3(2*H*)-ones and fused heterocycles involving pyridazin-3(2*H*)-one. Therefore, our research group became interested in the functionalization and the synthetic application of pyridazin-3(2*H*)-ones.

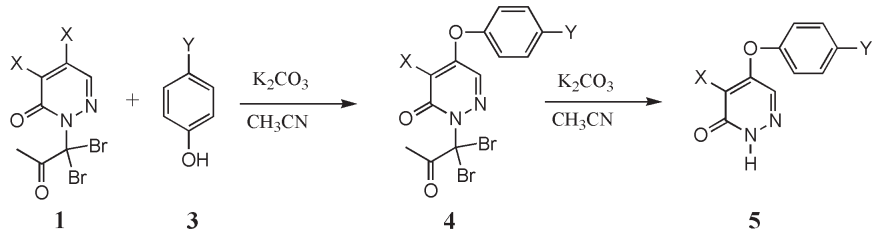
Functionalization of 4,5-Dihalopyridazin-3(2*H*)-ones.

The functionalization of free pyridazin-3(2*H*)-ones is difficult because of the acidity for hydrogen at the N-2 position. The nucleophilic reactivity and regiochemistry of the ring carbons in pyridazin-3(2*H*)-ones also depends on the followings; 1) structural factors such as the kind, the position and the number of the substitutes on the ring carbon and the nitrogens. 2) the reaction condition factors such as the reaction temperature, the solvent, the kind of the nucleophile and the base. Therefore, to increase the reactivity and regioselectivity, the introduction of a protecting group at the N-2 position is favorable. The preconditions for the functionalization using the protecting group are the followings: 1) the reactivity and regioselectivity on the ring must be increased by the introduction of a protecting group, 2) the introduction and the removal of the protecting group must be easy under mild condition, 3) the substitution on the ring must also be faster than the cleavage of the protecting group. Bryant *et al*. [8] synthesized 5-methoxypyridazin-3(2*H*)-one from 4,5-dichloropyridazin-3(2*H*)-one using dihydropyran as the protecting group *via* four steps. In the previous papers [9, 10], we reported the decomposition of 2-(2-oxopropyl)-4,5-dichloropyridazin-3(2*H*)-one and 2-(1,1-dibromo-2-oxopropyl)-4,5-dichloropyridazin-3(2*H*)-one with bases to the corresponding multisubstituted-pyridazin-3(2*H*)-ones. Therefore, we investigated the functionalization of 4,5-dihalopyridazin-

Scheme 1



a) MeOH, $4K_2CO_3$, room temp. b) $4NaN_3$, MeOH, reflux.
c) $4MeNH_2.HCl$, $8Et_3N$, MeOH, reflux.
d) i) PhOH, K_2CO_3, CH_3CN, reflux. ii) K_2CO_3, H_2O, reflux.



X = Cl, Br Y = NO_2, CN, OMe, Cl

3(2*H*)-ones using 1,1-dibromo-2-oxopropyl group as a protecting group.

2-(1,1-Dibromo-2-oxopropyl)-4,5-dihalopyridazin-3(2*H*)-ones [10, 11] were reacted with some nucleophiles such as potassium methoxide ($MeOH/K_2CO_3$) [12], sodium azide, methylamine and potassium phenoxides to give regioselectively the corresponding 5-substituted-pyridazin-3(2*H*)-ones in good to excellent yields [13]. According to our observations, the *p*-substituents on the phenyl ring and/or halogens on the pyridazinone affect the rate of the substitution and the dealkylation, *i.e.*, 1) the substitution of **1** with 4-substituted-phenol containing the electron withdrawing groups such as nitro and cyano is easier than 4-substituted-phenol containing the electron donating group (OMe, Cl). The dealkylation for the **4** isomers containing *p*-OMe or *p*-Cl is also faster than it for the **4** isomers containing *p*-NO_2 and *p*-CN. 3) The rate of the dealkylation is faster generally for bromopyridazinones than for chloropyridazinones

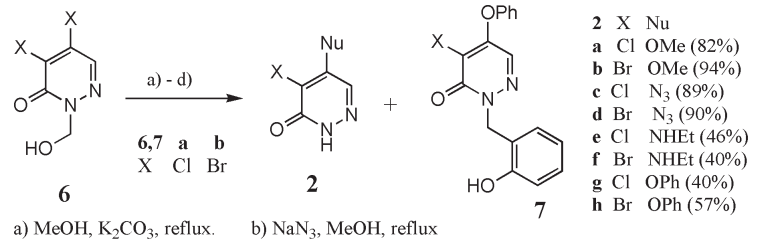
Although the 1,1-dibromo-2-oxopropyl group is useful for the functionalization of 4,5-dihalopyridazin-3(2*H*)-ones, the introduction of this group is difficult. According to the literatures [14-16], 2-hydroxymethylpyridazin-3(2*H*)-ones are a good 1-*O*, 3-*N*, 5-*O* ene-adduct. The retro-ene reaction of 2-hydroxymethylpyridazin-3(2*H*)-ones also is promoted by a base and/or the heat. Because dehydroxymethylation and the introduction of 2-hydroxymethyl group are facile, we tried the functionalization by the retro-ene reaction of 2-hydroxymethylpyridazin-3(2*H*)-ones.

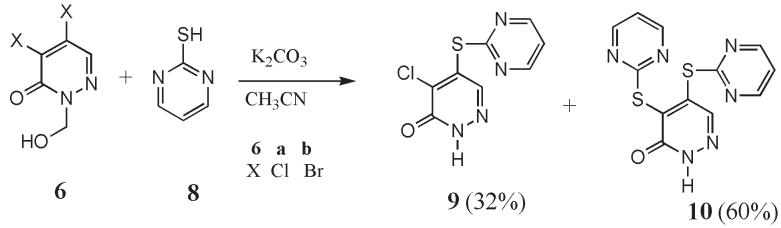
Functionalization of 2-hydroxymethyl-4,5-dihalopyridazin-3(2*H*)-ones *via* a retro-ene reaction with some nucleophiles such as potassium methoxide [12], sodium azide, ethylamine, potassium phenoxide, 2-mercaptopyrimidine in acetonitrile gave regioselectively only the corresponding 4-halo-5-substituted-pyridazin-3(2*H*)-ones except when 2-mercaptopyrimidine is used [17].

Reaction of **6** with phenol (1 equivalent) in the presence of potassium carbonate in refluxing acetonitrile gave the corresponding 5-phenoxy derivatives **2g** and **2h**, whereas treatment of **6** with excess phenol (2 equivalents) in the presence of potassium carbonate (2 equivalents) afforded **2g** and **2h** as the main product and **7a** and **7b** as the minor product. On the other hand, reaction of **6a** with 2-mercaptopyrimidine (**8,** 2 equivalents) in the presence of potassium carbonate (2 equivalents)) afforded **9** (32%) and **10** (60%), whereas, treatment of **6b** with **8** under the same condition gave only **10** (90%) [17].

This functionalization may be regarded as reaction *via* two steps; *i.e.*, the replacement of the halogens by nucleophiles occurs in the first step and then fragmentation at the N-2 position occurs by the retro-ene reaction. In the case of the slow reaction under this condition, however, the retro-ene reaction of **6** occurs before the substitution of the nucleophiles. Thus the reaction yield is low. Because of the easy retro-ene reaction of this ene-adduct, the synthesis and storage of **6** are also difficult. In order to overcome the problems, we introduced the acetyloxymethyl group at the N-2 position of 4,5-dichloropyridazin-3(2*H*)-one instead of the hydrox-

Scheme 2





ymethyl group. According to Chung, *et al*.[18], the treatment of 2-acetyloxymethyl-4-chloro-5-phenoxypyridazin-3(2*H*)-one with aqueous potassium carbonate solution gives 4-chloro-5-phenoxypyridazin-3(2*H*)-one *via* the retro-ene reaction. The retro-ene reaction of 2-acetyloxymethylpyridazinones is slower than 2-hydroxymethylpyridazinones because the retro-ene reaction of 2-acetyloxymethylpyridazinones occurs *via* two steps; *i.e.*, the hydrolysis of the ester occurs firstly, and then the retro-ene reaction occurs.

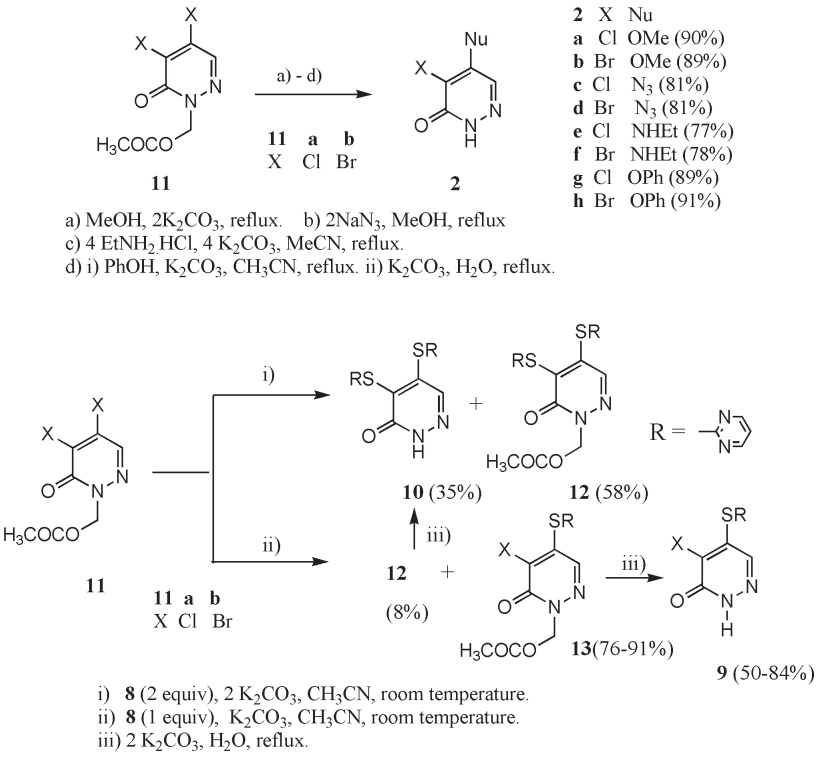
Functionalization of 2-acetyloxymethyl-4,5-dihalopyridazin-3(2*H*)-ones **11** with some nucleophiles also gave regioselectively only 4-halo-5-substituted-pyridazin-3(2*H*)-ones **2** in good yields.[19]

nucleophilicity in a suitable solvent to achieve the direct functionalization of 4,5-dihalopyridazin-3(2*H*)-ones. We carried out the regioselective functionalization of 4,5-dichloropyridazin-3(2*H*)-one with some nucleophiles such as sodium azide, ethylamine, methanol, phenol and arylmercaptan in seven solvent systems such as tetrahydrofuran, tetrahydrofuran/water, acetonitrile, acetonitrile/water, methanol, methanol/water and water [20]. Among the seven solvent systems, water is the most useful and eco-friendly solvent for the direct functionalization.

Chlorination of some pyridazin-3(2*H*)-ones.

The preparation of multichloropyridazines from the corresponding pyridazinones using phosphorus oxychlo-

Scheme 3

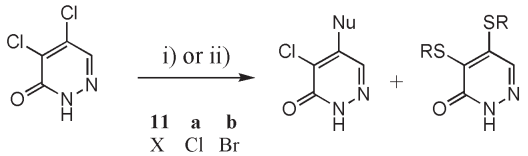


Compound **11** was reacted with 2-mercaptopyrimidine (**8**, 2 equivalents) in the presence of potassium carbonate (2 equivalents) in acetonitrile to give **10** (35%) and **12** (58%), whereas reaction of **11** with **8** (1 equivalent) and potassium carbonate (1 equivalent) in acetonitrile afforded **12** (8%) and **13** (76% for **13a**, 91% for **13b**)

Although the functionalization using 1-*O*, 3-*N*, 5-*O* ene-adduct can be achieved, we continually studied on a simple, convenient and eco-friendly functionalization of 4,5-dihalopyridazin-3(2*H*)-ones. A nucleophile has the high

ride and/or phosphorus pentachloride has been reported [21]. Coad, *et al*.[22] reported the formation of 6-chloro-2-(6-chloropyridazin-3-yl)pyridazin-3(2*H*)-one as a by-product during the chlorination of pyridazin-3,6-dione with phosphorus oxychloride. Therefore, we investigated the synthesis of multichloropyridazinylpyridazin-3(2*H*)-ones from some pyridazin-3(2*H*)-ones using $POCl_3$ or PCl_5 [23, 24].

Scheme 4



11 2 10

i) For NaN_3, $EtNH_2$.HCl; Nucleophile, solvent, reflux.
ii) For ROH, RSH; Nucleophile, K_2CO_3, solvent, reflux.

Nu	THF	THF/H_2O	MeOH	EtOH	MeCN	MeCN/H_2O	H_2O
N_3	71(%)	92(%)	64(%)	70(%)	69(%)	82(%)	75(%)
EtNH	56	58	19[a]	46[b]	52	76	48
OMe	NR[c]	62	91	NR[c]	NR[c]	slow	90
OPh	NR[c]	90	_[d]	52[e]	NR[c]	87	82
SR[f]	98	76[g]	76[g]	65	91	65[g]	85[g]

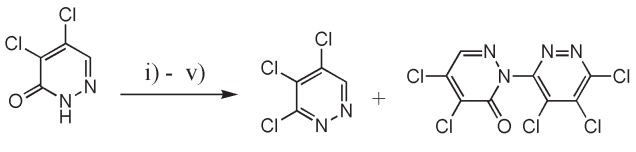
[a] 5-MeO- (52%) was isolated. [b]5-EtO- (23%) was isolated. [c]No reaction. [d]5-MeO- (98%) was isolated. [e]5-EtO-(14%) was isolated. [f]**10** is the main product. [g]5-RS was isolated in 8% (THF/H_2O), 3% (MeOH), 6%(MeCN /H_2O) and 3% (H_2O) yields, respectively.

Reaction of **11** with phosphorus oxychloride (method A and B) or phosphorus pentachloride in refluxing acetonitrile (Method E) gave only 3,4,5-trichloropyridazine (**14**). Whereas, **11** was reacted with phosphorus pentachloride at reflux temperature to give **14** (36%) and **15** (46%) (Method C). On the other hand, treatment of **11** with phosphorus pentachloride in refluxing toluene afforded only **15** in 81% yield [23].

Reaction of 4,5,6-trichloropyridazin-3(2*H*)-one (**16**) with PCl_5 at reflux temperature without the solvent also gave only 3,4,5,6-tetrachloropyridazine (**17**) in 81% yield (Method A). Compound **16** was reacted with PCl_5 in refluxing cyclohexane gave only **18** (81%) (Method F). Whereas, treatment of 16 with PCl_5 in refluxing toluene or in refluxing chlorobenzene afforded **17** (11 - 60%) and **18** (23 - 61%) (Method B – E) [24].

On the other hand, we investigated the reaction of **19** with dimethylchloromethyleneammonium chloride {DCMAC, $[(CH_3)_2NCHCl]^+Cl^-$} (Scheme 7) [25]. Dimethylchloromethyleneammonium chloride {$[(CH_3)_2$-

Scheme 5

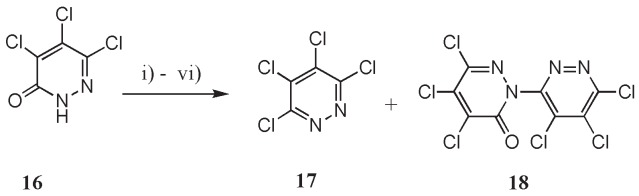


11 14 15

i) Method A; $POCl_3$, reflux ii) Method B; $POCl_3$, toluene, reflux
iii) Method C; PCl_5, reflux iv) Method D; PCl_5, toluene, reflux
v) Method E; PCl_5, acetonitrile, reflux.

Method	A	B	C	D	E
14 (%)	67	67	36	—	51
15 (%)	—	—	46	81	—

Scheme 6



16 17 18

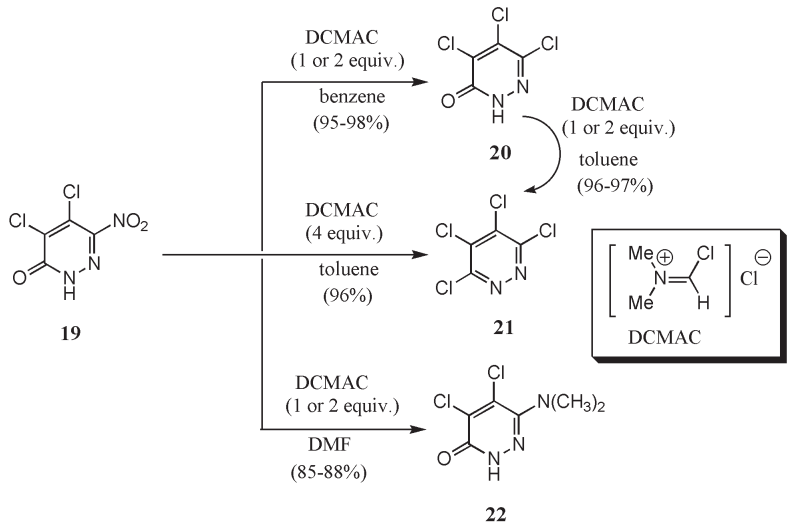
i) Method A; $POCl_3$, reflux. ii) Method B; PCl_5 (2 equiv), reflux.
iii) Method C; PCl_5 (1.2 equiv.), toluene, reflux.
iv) Method D; PCl_5 (2.05 equiv.), toluene, reflux.
v) Method E; PCl_5 (1.2 equiv.), chlorobenzene, reflux.
vi) Method F; PCl_5 (1.2 equiv.), cyclohexane, reflux.

Method	A	B	C	D	E	F
17 (%)	81	60	11	27	43	—
18 (%)	—	23	61	45	43	81

NCHCl]$^+$Cl$^-$}, readily available by the reaction of phosgene, phosphorus oxychloride or thionyl chloride with dimethylformamide, is a highly reactive chlorinating agent [26-28].

In all mixtures of a hindered amine and a less-hindered amine, *N*-acylation occurs generally at the less-hindered amino group. This selectivity may be due to the steric bulkiness around the acyl carbonyl group in compound **23**.

Scheme 7



Treatment of **19** with dimethylchloromethyleneammonium chloride (1 or 2 equivalents) in dry benzene gave only **20** in 95-98% yields. Compound **19** was also reacted with dimethylchloromethyleneammonium chloride (4 equivalents) in dry toluene to afford only **21** in excellent yield. However, **19** was treated with dimethylchloromethyleneammonium chloride (1 or 2 equivalents) in dry dimethylformamide to give unusually only **22** in 85-88% yields.

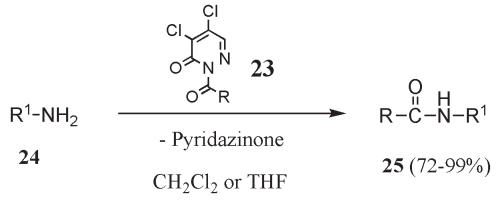
In these reactions, we isolated reusable 4,5-dichloropyridazin-3(2*H*)-one in quantitative yield.

Synthetic application of pyridazin-3(2*H*)-ones.

Pyridazin-3(2*H*)-ones are a good electron acceptable and stable leaving group [17, 19, 29]. The sufficient steric bulkiness would be provided around the N2-Cα bond [29]. Also pyridazin-3(2*H*)-ones have the moderate solubility in the organic solvents. Therefore, we attempted to develop the electrophilic agents using some 2-substituted-pyridazin-3(2*H*)-ones.

Firstly, we evaluate the *N*-acyl transfer potentiality of 2-acyl-4,5-dichloropyridazin-3(2*H*)-ones **23**, which was prepared by reaction of 4,5-dichloropyridazin-3(2*H*)-one with acyl chloride in the presence of triethylamine in methylene chloride [29]. 2-Acyl-4,5-dichloropyridazin-3(2*H*)-ones **23** served as excellent, convenient and chemoselective *N*-acylating agents for amines under neutral conditions in organic solvents (Scheme 8). We also investigated the selectivity in the benzoylation of a mixture (1: 1 equiv) of a hindered amine and a less-hindered amine with 2-(4-methoxybenzoyl)-4,5-dichloropyridazin-3(2*H*)-one (**23**).

Scheme 8

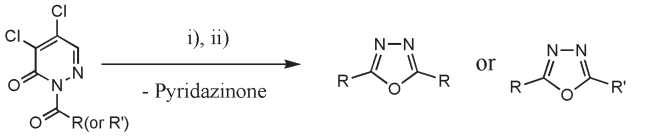


R = Me, C_6H_5, $CH_3(CH_2)_4$, 4-$MeOC_6H_4$, 4-ClC_6H_4, C_6H_{11}
R^1 = C_6H_5, 4-$MeC_6H_4CH_2$, 4-$HOCH_2CH_2C_6H_4$, $HOOCCH_2$, 3-$HO_2CC_6H_4$, Naphth-1-ol-5-yl

Also, we successfully synthesized both symmetrically and unsymmetrically 2,5-disubstituted 1,3,4-oxadiazoles by using 2-acyl-4,5-dichloropyridazin-3(2*H*)-ones **23** as acylating agents (Scheme 9) [30].

On the other hand, a facile synthetic method of carboxylic anhydrides from carboxylic acid using 4,5-dichloro-2-[(4-nitrophenyl)sulfonyl]pyridazin-3(2*H*)-one (**28**) was developed. Treatment of aliphatic or aromatic carboxylic acids with **28** in the presence of base such as potassium carbonate, triethylamine and *N*,*N*-dimethylaminopyridine in organic solvents gave the corresponding anhydrides in good to excellent yields (Scheme 10) [31].

Scheme 9

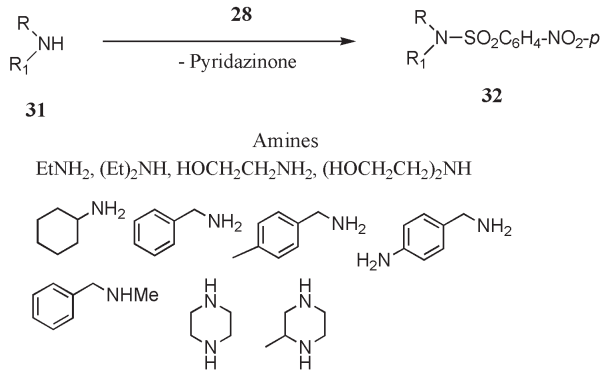


23 **26**(81-96%) **27**(74-95%)

i) $NH_2NH_2.H_2O$ ii) $BF_3.OEt_2$, dioxane or polyphosphoric acid

R = Et, C_6H_5, 4-MeC_6H_4, 4-ClC_6H_4, 2,4-$Cl_2C_6H_3$, 4-$C_6H_5C_6H_4$, 4-$MeOC_6H_4$, 2-Furyl
R' = Et, 4-MeC_6H_4, 4-ClC_6H_4, 2,4-$Cl_2C_6H_3$, 2-Furyl

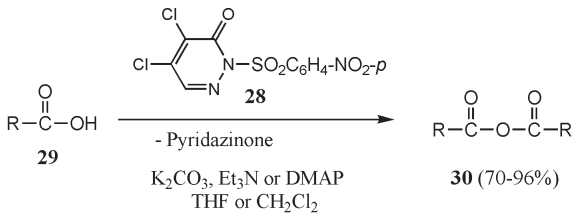
Scheme 11



Chemoselective *N*-benzenesulfonylation of aliphatic amines using **28** also gave the corresponding 4-nitrobenzenesulfonamides **32** in good to excellent yields (Scheme 11) [32].

We also attempted to develop the nitrating agent using pyridazin-3(2*H*)-ones (Scheme 12) [33]. Firstly, the direct nitration of 4,5-disubstituted-pyridazin-3(2*H*)-ones with $Cu(NO_3)_2$ in acetic anhydride afforded the corresponding 2-nitro derivatives **33** in good yields. According to the preliminary experiments for the evaluation of *N*-nitro transfer potentiality, we selected 4-chloro-2-nitro-5-methoxypyridazin-3(2*H*)-one as a nitrating agent and dichloromethane as a suitable solvent. *N*-Nitration of some secondary amines with 4-chloro-2-nitro-5-methoxypyridazin-3(2*H*)-one in dichloromethane at room temperature gave the corresponding *N*-nitroamines in good yields. Therefore, 4-chloro-2-nitro-5-methoxypyridazin-3(2*H*)-one is stable, mild and efficient reagent as a source for the delivery of nitronium ion (NO_2^+) under mild, neutral and homogeneous conditions.

Scheme 10



R = C_6H_5, 4-MeC_6H_4, 4-$C_6H_5C_6H_4$, 3-ClC_6H_4, 4-$MeOC_6H_4$, 4-$(CH_2{=}CH)C_6H_4$, 4-(*n*-Pr)C_6H_4, (*E*)-PhCH=CH, $Me_2C{=}CH$, $CH_3(CH_2)_{14}$, Thianapthene-2-yl.

Conclusion.

From all given examples on the functionalization and the synthetic application, we can conclude the followings; i) Water or water/organic solvent systems are useful and eco-friendly solvent for the direct functionalization of pyridazin-3(2*H*)-ones with a nucleophile. ii) Dimethylchloromethyleneammonium chloride may also be a useful, effective and eco-friendly chlorinating agent for the pyridazin-3(2*H*)-ones. iii) The product distribution of the chlorination using $POCl_3$, PCl_5 and dimethylchloromethyleneammonium chloride depends on the kind and amounts of chlorinating agent and the reaction solvent. iv) 2-Acyl-4,5-dichloropyridazin-3(2*H*)-one is a useful, efficient and stable acylating agent. v) 2-(4-Nitrobenzenesulfonyl)-4,5-dichloropyridazin-3(2*H*)-one is an efficient and facile electrophilic sulfonyl group transfer reagents for the carboxylic acid and the aliphatic amine. vi) 4-Chloro-5-methoxy-2-nitropyridazin-3(2*H*)-one also is a stable, efficient and mild nitration agent. Other examples for the synthetic application of pyridazin-3(2*H*)-one derivatives will follow soon.

Acknowledgments.

The author thanks all his collaborators whose names appear in the references. This work was supported by a grant from the Korea Science and Engineering Foundation (KOSEF) to the Environmental Biotechnology Research Center (grant #: R15-2003-002-01001-0) & by a grant from the Chinju National University of Education 2003.

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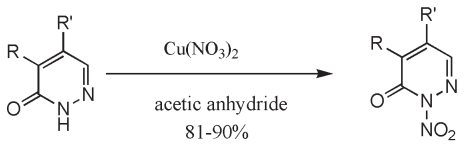
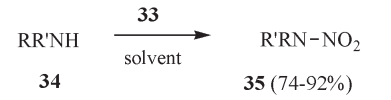
Scheme 12

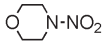
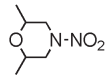
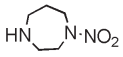
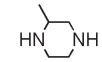
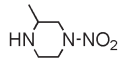


33 **33**

R = Cl, Br R' = Cl, Br, OMe, OPh, OEt, N_3



34 **35** (74-92%)

34	2° Amines	**35**	Nitramines
a	$C_6H_5CH_2NHMe$	**a**	$C_6H_5CH_2N(NO_2)Me$
b	$C_6H_5CH_2NH(i\text{-}Pr)$	**b**	$C_6H_5CH_2N(NO_2)(i\text{-}Pr)$
c	Et_2NH	**c**	$Et_2N\text{-}NO_2$
d	$(c\text{-}C_6H_{11})_2NH$	**d**	$(c\text{-}C_6H_{11})_2N\text{-}NO_2$
e		**e**	
f		**f**	
g		**g**	
h		**h**	
i		**i**	
j		**j**	

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