The Reaction Studies of α-Chloroformylarylhydrazines with Thiols, Thioureas and α-Cyclodiketones

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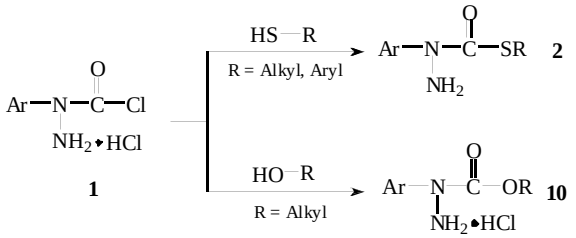
The reactions of α-chloroformylarylhydrazines **1** with various types of mercaptan, thiourea and α-cyclodiketone have been studied intensively. 1-Arylhydrazinecarbothioates **2** were obtained via thioesterization when α-chloroformylarylhydrazines reacted with thiols. On the other hand, compounds **3** were obtained when α-chloroformylarylhydrazines reacted with thio-containing heterocyclic compounds, which suggested a totally different mechanism in these types of reactions. Further studies on the reaction of α-chloroformylarylhydrazines **1** with thiourea compounds confirmed a novel cyclization and de-cyclization mechanism, which led to give 2-arylhydrazinecarboximidamides **5** and 1,3,4-thiadiazolin-5-ones **6**. In addition, various 1,3,4-oxadiazines **9** were obtained by reacting α-chloroformylarylhydrazines with α-cyclodiketones, showing ring cyclization was involved in this type of reaction.

INTRODUCTION

α-Chloroformylarylhydrazines **1** and their derivatives are potent precursors for preparing heterocyclic compounds.[1-2] The nucleophilic substitution reaction of compounds **1** with alcohols[1] and amines[3] has been reported in our previous studies. Since compounds **1** can undergo nucleophilic substitution reactions with potent nucleophilic reagents, it is worthusing compounds **1** as synthons to explore further. In this study by using thiols as nucleophiles, it is found that when compounds **1** react with butylthiol and thiophenol, products **2** (a substitutional product) were obtained (Scheme I); however, when reacting with thio-containing heterocyclic compounds, such as compounds **11**, the expected products (compounds **2'**) were not observed. Instead, compounds **3** (Scheme II) were obtained, which reveals that reaction studies on the compounds **1** with various mercaptans are of importance and of interest.

Scheme I



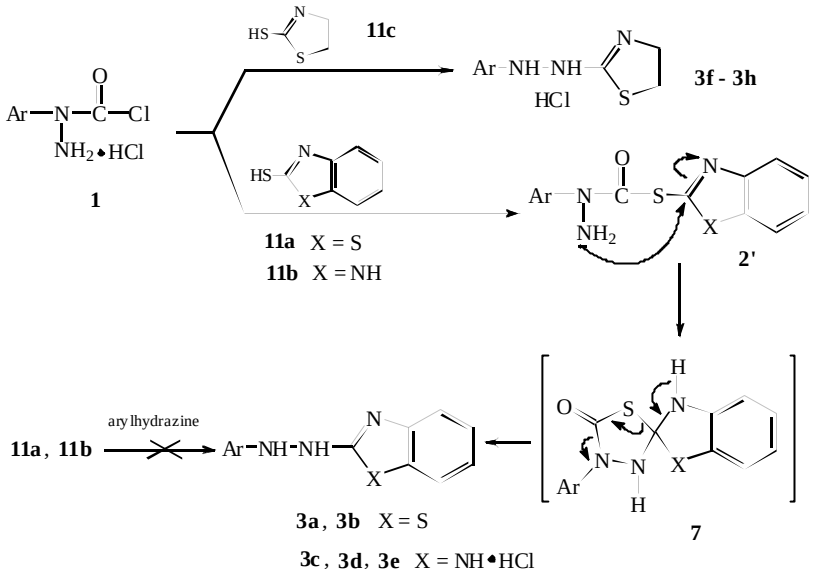
The synthetic methods for preparing 2-arylhydrazinecarboximidamide type compounds, such as compounds **5**,[4,5] and 1,3,4-thiadiazolin-5-one type compounds, such as compounds **6**,[6,7] have been reported earlier. And the derivatives of compounds **5** have been known to possess several biological and pharmacological activities.[8-10] Further study of compounds **1** in this report has led to a better and new synthetic route to these two types compounds by reacting with thioureas.

The synthesis of 1,3,4-oxadiazine type compounds, compounds **9**, have been reported[11,12] and found to possess potential monoamine oxidase inhibitor activity.[13] Our study in this report by reacting compounds **1** with α-cyclodiketones **8** has led to a better method to prepare this type of compound and its derivatives. The detailed discussions of various reactions based on compounds **1** are presented herein.

RESULTS AND DISCUSSION

The preparation of 1-arylhydrazinecarboxylate hydrochlorides **10** were easily accomplished by reacting compounds **1** with alkyl alcohols.[1] Extended synthetic work by using thiols and thiophenols, instead of alcohol, were studied. As shown in Scheme I, 1-arylhydrazinecarbothioates **2,** a direct substitutional product, were obtained with high yields. Based on spectral analysis, compounds **2** were not found in the state of a hydrochloride salt, which is different from the

Scheme II



prod uct ob tained when the nucleophile is alkyl al co hol, in which hy dro chlo ride salt of the com pounds were ob tained.[1] One pos si ble ex pla na tion is that alkoxy groups would better con ju gate with a car bonyl group than alkylthiol groups and thus re sult in a high elec tronic den sity borne by amino ni trogen to form a salt with hy dro chlo ride. Ta ble 1 shows compounds, **2a**~**2f**, ob tained from var i ous thiols re act ing with com pounds **1**. However, some reactions did not proceed when nucleophilic re agents were phe nols (Scheme I). These re sults show that mer cap tans pos sess a better nu cleophilic effect than alkoxy groups.

Fur ther study of thiols re act ing with com pounds **1** has been ex tended to more com pli cated com pounds, such as 2-mercaptobenzothiazole **11a**. The ex pected prod ucts, 1-arylhydrazinecarbothioates **2'**, a prod uct ob tained through a direct nucleophilic sub sti tu tion re ac tion, did not form (Scheme II). In stead, com pounds **3** were ob tained show ing a more com pli cated re ac tion than just a sim ple sub sti tu tion one. In or der to find out whether this prod uct can be ob tained di rectly by substitution reaction through the exchange between arylhydrazine and the sulhydryl moi ety of com pound **11a**, re-ac tions of com pounds **1** with arylhydrazines were car ried out un der the same con di tion; nev er the less, no com pounds **3** were ob served. The pos si ble mech a nism for this type of re action is pro posed as de scribed in Scheme II, i.e. a nucleophilic sub sti tu tion re ac tion takes place first fol lowed by cyclization thus re sult ing in the for ma tion of in ter me di ate **7**, which is then fol lowed by elim i na tion of S=C=O to give com pounds **3**. The same re sults were formed in the re ac tions of 2-mercaptobenzimidazole **11b** and 2-mercaptothiazoline **11c** with compounds **1**. The yields are sum ma rized in Ta ble 2.

In or der to ex am ine whether the re ac tion mech a nism as shown in Scheme II is ap pli ca ble in the thiourea type of compounds, thioureas **4** were used to re act with com pounds **1** under the same con di tion (Scheme III) and we have ob tained the ex pected prod ucts, 2-arylhydrazinecarboximidamides **5** and 4-aryl-2-amino-1,3,4-thiadiazolin-5-ones **6**, showing the pro posed re ac tion mech a nism (Scheme II) is plau si ble. In the

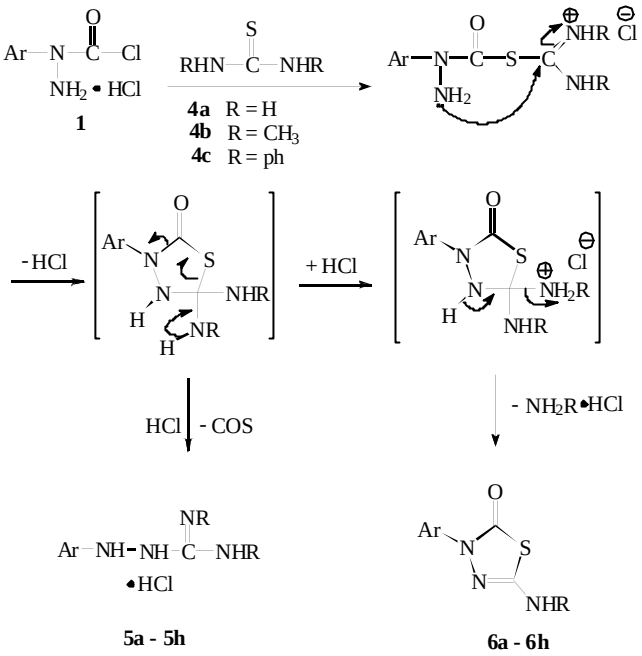
Table 1. Preparation of Compounds **2** from Compounds **1** with Thiols

Compound	Ar	R	Reaction time (hr)	Yield (%)
2a	C_6H_5	n-C_4H_9	1	88
2b	*p*-$CH_3C_6H_4$	n-C_4H_9	1	78
2c	*p*-ClC_6H_4	n-C_4H_9	1	95
2d	C_6H_5	C_6H_5	5	74
2e	*p*-$CH_3C_6H_4$	C_6H_5	5	68
2f	*p*-ClC_6H_4	C_6H_5	5	65

Table 2. Preparation of Compounds **3** from Compounds **1** Reacted with Compounds **11**

Compound	Ar	Reaction time (hr)	Yield (%)
3a	*p*-$CH_3C_6H_4$	1	36
3b	*p*-ClC_6H_4	1	34
3c	C_6H_5	0.5	76
3d	*p*-$CH_3C_6H_4$	0.5	70
3e	*p*-ClC_6H_4	0.5	62
3f	C_6H_5	4	53
3g	*p*-$CH_3C_6H_4$	4	30
3h	*p*-ClC_6H_4	4	30

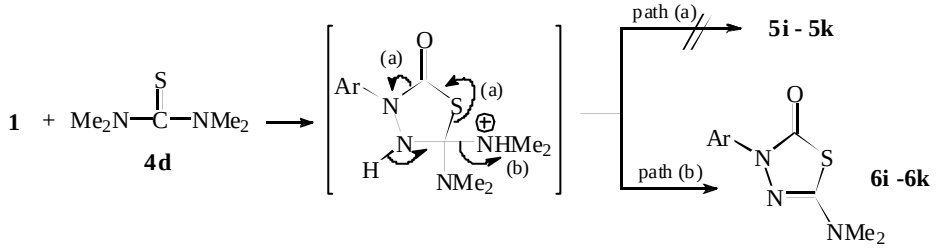
Scheme III



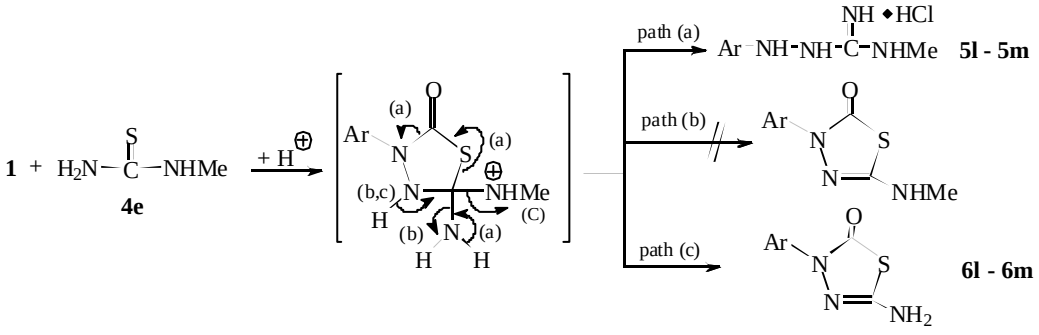
re ac tions of com pounds **1** with thiourea **4a**, 1,3- dimethylthiourea **4b,** and diphenylthiourea **4c** (Scheme III), compounds **5a~5h** were the ma jor prod ucts (40~60%) ob tained through the elim i na tion of S=C=O af ter cyclization, whereas com pounds **6a~6h** were the mi nor prod ucts (10~20%) obtained through deaminonation after cyclization. Further study shows that for the reactions of N,N-tetra methylthiourea **4d** with com pounds **1**, the step of S=C=O elim i nation (Scheme IV, path a) did not proceed; however, the deamination step was ob served to give com pounds **6 (6i~6k)** (Scheme IV, path b). One pos si ble ex pla na tion is that protonation on the elec tron-rich dimethylamino group pre vailed and the large steric ef fects be tween the two dimethylamino groups re sulted in the elim i na tion of the dimethylamino group to give com pounds **6** (**6i~6k**), in stead of elim i na tion of S=C=O to give the more un sta ble com pounds **5i~5k**.

In the re ac tions of 1-methylthiourea **4e** (Scheme V) with com pounds **1**, elim i na tion of S=C=O (Scheme VI, path

Scheme IV



Scheme V



Scheme VI

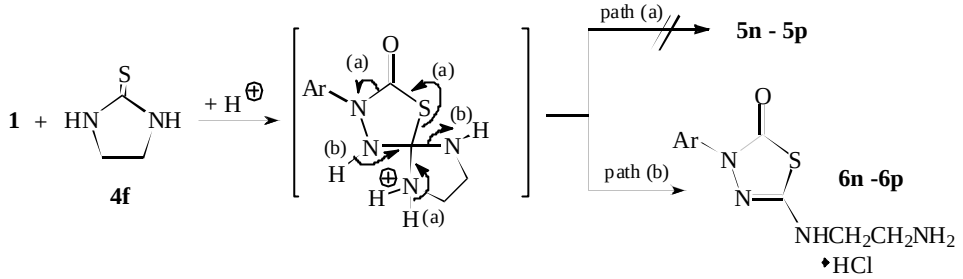


Table 3. Preparation of Compounds **5** and **6** from Compounds **1** Reacted with Compounds **4**

Starting Material	Ar	Reaction Time (hr)	Comp'd 5	Yield (%)	Comp'd 6	Yield (%)
4a	Ph	10	**5a**	44	**6a**	15
4a	*p*-MeC_6H_4	8	**5b**	49	**6b**	13
4a	*p*-ClC_6H_4	9	**5c**	41	**6c**	20
4b	Ph	5	**5d**	60	**6d**	15
4b	*p*-MeC_6H_4	5	**5e**	66	**6e**	20
4b	*p*-ClC_6H_4	6	**5f**	68	**6f**	12
4c	*p*-MeC_6H_4	48	**5g**	58	**6g**	12
4c	*p*-ClC_6H_4	48	**5h**	52	**6h**	10
4d	Ph	48	**5i**	-	**6i**	27
4d	*p*-MeC_6H_4	48	**5j**	-	**6j**	20
4d	*p*-ClC_6H_4	24	**5k**	-	**6k**	45
4e	Ph	4	**5l**	24	**6l = 6a**	16
4e	*p*-ClC_6H_4	3	**5m**	17	**6m = 6c**	20
4f	Ph	20	**5n**	-	**6n**	31
4f	*p*-MeC_6H_4	24	**5o**	-	**6o**	33
4f	*p*-ClC_6H_4	14	**5p**	-	**6p**	24

Table 4. Preparation of Compounds **9** from Compounds **1** Reacted with Compounds **8**

Starting material	Ar	Reaction time (hr)	Compound **9**	Yield (%)
8a	Ph	3	**9a**	21
8a	*p*-ClC_6H_4	3	**9b**	17
8b	Ph	1	**9c**	61
8b	*p*-MeC_6H_4	1	**9d**	60
8b	*p*-ClC_6H_4	1	**9e**	62
8c	Ph	2	**9f**	36
8c	*p*-MeC_6H_4	3	**9g**	44
8c	*p*-ClC_6H_4	3	**9h**	44
8d	Ph	4	**9i**	80
8d	*p*-MeC_6H_4	4	**9j**	72
8d	*p*-ClC_6H_4	4	**9k**	68
8e	Ph	5	**9l**	70
8e	*p*-MeC_6H_4	5	**9m**	68
8e	*p*-ClC_6H_4	5	**9n**	79

a) gives N-methyl-2-arylhydrazinecarboximidamide **5 (5l, 5m)**. In the step of deamination, only com pounds **6** (**6l, 6m**) (through path c), not the com pounds through path b, were ob-tained, show ing that the methylamino group is more likely to give protonation than the amino group, then to be elim i nated. This is ex plain able since the methylamino group bears a higher elec tron den sity than the amino group. In ad di tion, com pounds **1** re acted with ethylenethiourea **4f** to give 2-(β-aminoethyl)amino-1,3,4-thiadiazolin-5-ones **6** (**6n~ 6p**) as the only prod ucts (Scheme VI). The struc tures of com-pounds **5** were con firmed by X-ray crys tal log ra phy. Fig. 1 and Ta ble 5, 6, 7 and 8 are the X-ray struc ture and var i ous spec tral data of com pound **5d**. The re ac tion yields of these types re ac tions are sum ma rized in Ta ble 3.

The re ac tions of com pounds **1** with α-cyclodiketones **8** to form com pounds **9** are well understood. The reaction mech a nism is as fol lows: nucleophilic ad di tion of ni tro gen of

Table 5. Crystal Data of **5d**

Formula	$C_9H_{15}ClN_4$
Formula weight	214.70
Cryst system	Orthorhombic
Space group	P cab
a/Å	9.7956 (16)
b/Å	12.8591 (21)
c/Å	18.059 (4)
V/Å^3	2274.8 (7)
Z	8
D_c/g cm^3	1.254
F_{000}	911.77
λ(Mo-Kα) Å	0.70930
μ/cm^{-1}	0.30
Range/deg	23.26-24.44
Scan type	2θ
$2\theta_{max}$	49.8
Reflections measured	1993
Unique reflections	1993
Observed reflections	1287
Refined parameters	127
R_f for significant reflections	0.048
R_w for significant reflections	0.046
GoF	2.92

amine to car bonyl car bon, then loss of wa ter to form imine together with a nucleophlic sub sti tu tion of the chlo ride by hydroxyl group (see Scheme VII). The re ac tion yields for these types of re ac tions are gen er ally high and are shown in Ta ble 4. As for the re ac tion yield of **9a** and **9b,** in which R_1 is H, are lower than av er age, which can be at trib uted to a comparative hy dro ly sis tak ing place from in ter me di ate **12**, because com pounds **13** (2-arylhydrazino-1-cyclohexanones)

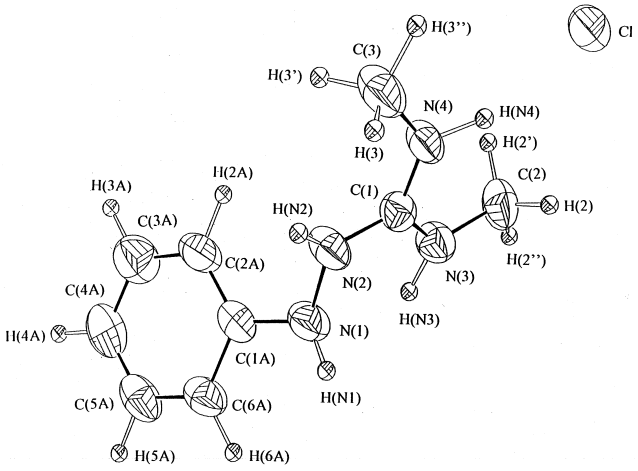


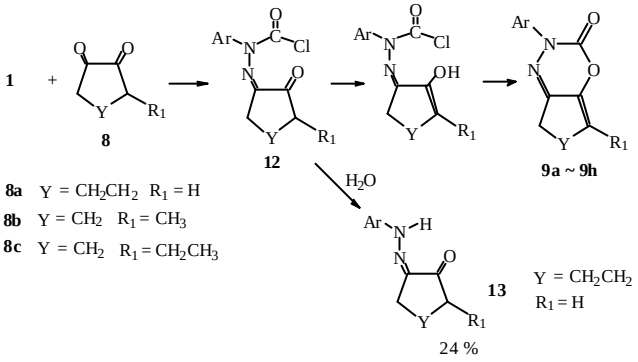
Fig. 1. Molecular structure of N,N'-Dimethyl-2-phenylhydrazinecarboximidamide hydrochloride (**5d**).

Table 6. Bond Distances/Å of **5d**

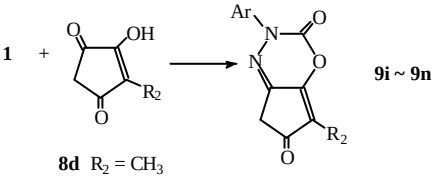
Cl-H(N2)(a)	2.1846(10)	C(3)-H(3)	1.097(4)
Cl-H(N4)	2.1280(10)	C(3)-H(3')	1.099(4)
N(1)-N(2)	1.419(4)	C(3)-H(3'')	1.081(4)
N(1)-C(1A)	1.403(5)	C(1A)-C(2A)	1.378(6)
N(1)-H(N1)	0.962(3)	C(1A)-C(6A)	1.396(5)
N(2)-C(1)	1.349(5)	C(2A)-C(3A)	1.370(6)
N(2)-H(N2)	1.029(3)	C(2A)-H(2A)	1.080(4)
N(3)-C(1)	1.326(5)	C(3A)-C(4A)	1.376(6)
N(3)-C(2)	1.455(5)	C(3A)-H(3A)	1.081(5)
N(3)-H(N3)	1.040(3)	C(4A)-C(5A)	1.372(7)
N(4)-C(1)	1.319(5)	C(4A)-H(4A)	1.081(4)
N(4)-C(3)	1.449(5)	C(5A)-C(6A)	1.384(6)
N(4)-H(N4)	1.070(3)	C(5A)-H(5A)	1.080(4)
C(2)-H(2)	1.081(4)	C(6A)-H(6A)	1.081(4)
C(2)-H(2')	1.093(4)	H(N2)-Cl(b)	2.1846(10)
C(2)-H(2'')	1.092(4)		

Scheme VII

(a)



(b)

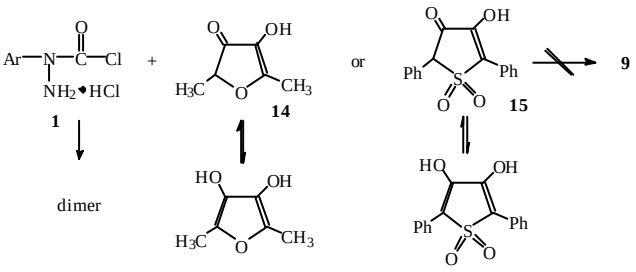


were ob tained. In or der to im prove the re ac tion yields of com pounds **9**, in which R_1 is H, var i ous alkyl type sub stituents were in tro duced into α-cyclodiketones, with which enol for ma tion is in creased to in crease the cyclization through nucleophlic sub sti tu tion of the chlo ride by the hydroxyl group to give com pounds **9**. With this, it is also found that the yields of side prod ucts, com pounds **13**, were re duced to about 5%. We also used com pounds **1** to re act with 4-hydroxy- 5-

Table 7. Bond Angles/deg of **5d**

H(N2)(a)-Cl-H(N4)	125.03(5)	N(4)-C(3)-H(3'')	108.1(3)
N(2)-N(1)-C(1A)	115.5(3)	H(3)-C(3)-H(3')	106.8(3)
N(2)-N(1)-H(N1)	107.9(3)	H(3)-C(3)-H(3'')	110.0(4)
C(1A)-N(1)-H(N2)	118.8(3)	H(3')-C(3)-H(3'')	109.8(4)
N(1)-N(2)-C(1)	117.5(3)	N(1)-C(1A)-C(2A)	123.8(3)
N(1)-N(2)-H(N2)	118.4(3)	N(1)-C(1A)-C(6A)	117.1(4)
C(1)-N(2)-H(N2)	122.2(3)	C(2A)-C(1A)-C(6A)	119.1(4)
C(1)-N(3)-C(2)	123.8(3)	C(1A)-C(2A)-C(3A)	120.3(4)
C(1)-N(3)-H(N3)	114.0(3)	C(1A)-C(2A)-H(2A)	119.9(4)
C(2)-N(3)-H(N3)	121.7(3)	C(3A)-C(2A)-H(2A)	119.8(4)
C(1)-N(4)-C(3)	125.3(3)	C(2A)-C(3A)-C(4A)	121.2(4)
C(1)-N(4)-H(N4)	117.9(3)	C(2A)-C(3A)-H(3A)	119.3(4)
C(3)-N(4)-H(N4)	116.8(3)	C(4A)-C(3A)-H(3A)	119.5(4)
N(2)-C(1)-N(3)	119.2(3)	C(3A)-C(4A)-C(5A)	118.8(4)
N(2)-C(1)-N(4)	119.3(3)	C(3A)-C(4A)-H(4A)	120.4(5)
N(3)-C(1)-N(4)	121.5(3)	C(5A)-C(4A)-H(4A)	120.8(4)
N(3)-C(2)-H(2)	110.4(3)	C(4A)-C(5A)-C(6A)	121.1(4)
N(3)-C(2)-H(2')	109.7(3)	C(4A)-C(5A)-H(5A)	119.4(4)
N(3)-C(2)-H(2'')	107.7(3)	C(6A)-C(5A)-H(5A)	119.5(4)
H(2)-C(2)-H(2')	108.4(3)	C(1A)-C(6A)-C(5A)	119.4(4)
H(2)-C(2)-H(2'')	110.8(3)	C(1A)-C(6A)-H(6A)	120.3(4)
H(2')-C(2)-H(2'')	109.8(4)	C(5A)-C(6A)-H(6A)	120.3(4)
N(4)-C(3)-H(3)	111.0(3)	Cl(b)-H(N2)-N(2)	163.56(17)
C(4)-C(3)-C(3')	111.0(3)	Cl-H(N4)-N(4)	152.11(16)

Scheme VIII



substituted-4-cyclopentene-1,3-diones, com pounds **8d** and **8e**, an enol form type com pound (Scheme VII, b). These re actions do ob vi ously in crease the re ac tion yield. As shown in Ta ble 4 prod ucts **9i**~**9n** have a yield in the range of 68%~ 80%, whereas it is in the range of 17%~62% for prod ucts **9a**~**9e**. How ever, when 2,5-dimethyl-4-hydroxy-3-furanone, **14**, and 4-hydroxy-2,5-diphenyl-3(2H)-thiophenone-1,1-dioxide, **15,** were used to re act with com pounds **1**, the expected prod ucts, 1,3,4-oxadiazine type of prod uct **9** were not ob served. In stead, the self-dimerization of com pounds **1** reac tion was ob served. This is be cause com pound **14** un dergoes enolization to be come a more sta ble ar o matic type compound re sult ing in no re ac tion tak ing place (Scheme VIII).

CONCLUSION

Four heterocyclic com pounds, **3**, **5**, **6** and **9** have been syn the sized by the re ac tions of α-chloroformylaryl hydrazines hy dro chlor ides **1** with thiol, thioureas and α-cyclodiketone, re spec tively. These re sults man i fest that when compounds **1** re acted with sul fur-containing re agents, which possessed ei ther a N=C-S or a N-C=S frag ment, they would proceed through more com pli cated re ac tion routes in clud ing nucleophilic sub sti tu tion, cyclization, and elim i na tion re actions, lead ing to the for ma tion of prod ucts **5** and **6**. In the reac tions of com pounds **1** with α-cyclodiketone, the 1,3,4-oxdiazine type com pounds **9** were ob tained through a sim ple con den sa tion and sub sti tu tion re ac tion. These re sults re veal that one of the car bonyl groups in α-cyclodiketone un der goes enolization be fore pro ceed ing to the sub sti tu tion re ac tion. We have shown that when β-alkylated α-cyclodiketones, which have a higher po ten tial to un dergo enolization, re acted with com pounds **1**, it leads to a higher re ac tion yield of compounds **9**. How ever, β- and δ-dialkylated α-cyclodiketones un dergo enolization to form a more sta ble ar o matic type compound as no re ac tion takes place. Also, the meth ods we de veloped to pre pare com pounds **5**, **6**, and **9** and their de riv a tives are better meth ods when com pared with those pre vi ously reported.[4-7,11-13]

Table 8. Atomic Coordinates of **5d**

Atom	X	Y	Z
Cl	0.11944	0.29382	0.02494*
N(1)	0.06848	-0.19899	0.10746
N(2)	0.15245	-0.11596	0.08289
N(3)	-0.02154	-0.00467	0.11675
N(4)	0.17182	0.05950	0.05982
C(1)	0.10013	-0.01903	0.08618
C(2)	-0.08037	0.09718	0.13138
C(3)	0.30996	0.05263	0.03151
C(1A)	0.13144	-0.27069	0.15501
C(2A)	0.23793	-0.24602	0.20170
C(3A)	0.29045	-0.31941	0.24872
C(4A)	0.24029	-0.41933	0.24982
C(5A)	0.13378	-0.44428	0.20380
C(6A)	0.07907	-0.37162	0.15569
H(N1)	0.01833	-0.22465	0.06543
H(N2)	0.23750	-0.13340	0.05179*
H(N3)	-0.06681	-0.07257	0.13609
H(N4)	0.12303	0.13377	0.05625
H(2)	-0.10369	0.13641	0.08000
H(2')	-0.00750	0.14468	0.16234
H(2'')	-0.17272	0.08562	0.16422
H(3)	0.31320	0.00769	-0.02008
H(3')	0.37718	0.01274	0.07113
H(3'')	0.34664	0.13073	0.02184
H(2A)	0.28025	-0.16847	0.20121
H(3A)	0.37263	-0.29818	0.28572
H(4A)	0.28459	-0.47707	0.28614
H(5A)	0.09165	-0.52186	0.20535
H(6A)	-0.00343	-0.39281	0.11891
H(N2)(a)	0.26250	0.36660	0.05179
	(0.500-X)	(0.500 + Y)	(-Z)
Cl(b)	0.38056	-0.20672	0.02494
	(0.500-X)	(-0.500 + Y)	(-Z)

*Indicates that there are Symmetry Equivalents of an atom.
H(N2)(a) and Cl(b) are the Symmetry Equivalents.

EXPERIMENTAL SECTION

General

Melting points (Buchi 535 apparatus) are uncorrected. IR spectra were recorded on a Hitachi 270-30 infrared spectrometer. NMR spectra were measured on a Bruker AMX-200 NMR spectrometer with tetramethylsilane (TMS) as internal standard and the ^{1}H NMR spectra were measured in DMSO-*d6* for all samples. The mass spectra were measured on a Finnigan MAT TSQ-46C spectrometer at an ionizing potential of 70 eV. Elemental analyses were performed on Heraeus CHN-O-Rapid and Tacussel Coulomax 78 analyzers. X-ray analysis was made with a Nonius CAD-4 diffractometer. Column chromatography was carried out with a silica gel packed open column (Kieselgel 100, 230-400 mesh, E. Merck).

Preparation of 1-arylhydrazine carbonylthioate 2a~2f

0.3 g (1.45 mmol) of α-chloroformylphenylhydrazine hydrochloride **1** in 5 mL of EtOH was added to 0.2 mL of butylthiol (or thiophenol). The reaction mixture was stirred at room temperature. After about 1 hr, the reaction mixture was poured into ice water, then was stirred for 10 min. The precipitation was filtered, then recrystallized with 95% EtOH to give 0.29 g of compound **2a** (88%). The physical properties and spectroscopic data of compounds **2** are as follows:

S-Butyl 1-phenylhydrazinecarbothioate (2a)

Colorless needles; mp 58~59°C, IR (KBr): 3358, 3286, 3058, 2950, 2926, 2896, 2866, 1620 cm^{-1}; ^{1}H NMR, δ = 0.81~0.96 (m, 3H), 1.27~1.61 (m, 4H), 2.68 (t, *J* = 7.0 Hz, 2H), 5.57 (s, 2H), 7.08~7.66 (m, 5H). ^{13}C NMR (DMSO-*d6*): δ = 171.5, 143.8, 128.8, 125.3, 122.2, 32.1, 29.6, 21.9, 13.9. EIMS (70 eV), *m/z* (%): 224 (M$^+$, 60), 135 (14), 107 (100), 77 (34). Anal. Calcd. for $C_{11}H_{16}N_2OS$: C: 58.90, H: 7.12, N: 12.29, S: 14.29. found C: 58.96, H: 7.17, N: 12.33, S: 14.26.

S-Butyl 1-(4-methylphenyl)hydrazinecarbothioate (2b)

Colorless needles; mp 75~76°C, IR (KBr): 3358, 3280, 2956, 2920, 2866, 1662 cm^{-1}; ^{1}H NMR, δ = 0.79~0.94 (m, 3H), 1.25~1.61 (m, 4H), 2.27 (s, 3H), 2.61 (t, *J* = 7.1 Hz, 2H), 5.50 (s, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H). EIMS (70 eV), *m/z* (%): 238 (M$^+$, 42), 222 (5), 149 (6), 121 (100), 91 (24). Anal. Calcd. for $C_{12}H_{18}N_2OS$: C: 60.47, H: 7.60, N: 11.75, S: 13.45. found C: 60.50, H: 7.61, N: 11.74, S: 13.48.

S-Butyl 1-(4-chlorophenyl)hydrazinecarbothioate (2c)

Colorless needles; mp 70~71°C, IR (KBr): 3346, 3280, 3220, 2962, 2926, 2866, 1650 cm^{-1}; ^{1}H NMR, δ = 0.82~0.96 (m, 3H), 1.33~1.53 (m, 4H), 2.86 (t, *J* = 7.0 Hz, 2H), 5.61 (s, 2H), 7.42 (d, *J* = 9.1 Hz, 2H), 7.65 (d, *J* = 9.1 Hz, 2H). EIMS (70 eV), *m/z* (%): 260 (M$^+$+2, 7), 258 (M$^+$, 20), 169 (3), 141 (100), 111 (8). Anal. Calcd. for $C_{11}H_{15}ClN_2OS$: C: 51.06, H: 5.84, N: 10.83, Cl: 13.70, S: 12.39. found C: 50.91, H: 5.85, N: 10.82, Cl: 13.68, S: 12.36.

S-Phenyl 1-phenylhydrazinecarbothioate (2d)

Colorless needles; mp 121~122 °C, IR (KBr): 3358, 3286, 3058, 1662 cm^{-1}; ^{1}H NMR, δ = 5.79 (br, 2H), 7.14~7.64 (m, 10H). ^{13}C NMR (DMSO-*d6*): δ = 169.8, 143.5, 135.6, 132.0, 129.1, 129.0, 128.9, 125.4, 121.9. EIMS (70 eV), *m/z* (%): 244 (M$^+$, 100), 135 (15), 107 (98), 77 (75). Anal. Calcd.

for $C_{13}H_{12}N_2OS$: C: 63.91, H: 4.95, N: 11.47, S: 13.12. found C: 63.74, H: 4.94, N: 11.53, S: 13.15.

S-Phenyl 1-(4-methylphenyl)hydrazinecarbothioate (2e)

Col or less nee dles; mp 75~76℃, IR (KBr): 3352, 3286, 1662 cm^{-1}; ^1H NMR, δ = 2.27 (s, 3H), 5.71 (s, 2H), 7.15 (d, *J* = 8.5 Hz, 2H), 7.33~7.51 (m, 5H), 7.47 (d, *J* = 8.5 Hz, 2H). EIMS (70 eV), *m/z* (%): 258 (M^+, 58), 149 (15), 121 (100), 91 (54), 77 (48). Anal. Calcd. for $C_{14}H_{14}N_2OS$: C: 65.09, H: 5.46, N: 10.84, S: 12.41. found C: 64.95, H: 5.45, N: 10.82, S: 12.39.

S-Phenyl 1-(4-chlorophenyl)hydrazinecarbothioate (2f)

Col or less nee dles; mp 151~152 ℃, IR (KBr): 3358, 3238, 1653 cm^{-1}; ^1H NMR, δ = 5.83 (s, 2H), 7.38~7.49 (m, 5H), 7.42 (d, *J* = 9.1 Hz, 2H), 7.65 (d, *J* = 9.1 Hz, 2H). EIMS (70 eV), *m/z* (%): 280 (M^++2, 15), 278 (M^+, 40), 141 (100), 77 (37). Anal. Calcd. for $C_{13}H_{11}ClN_2OS$: C: 56.01, H: 3.98, N: 10.05, Cl: 12.72, S: 11.50. found C: 55.97, H: 3.96, N: 10.00, Cl: 12.70, S: 11.49.

The preparation of compounds 3a~3h

0.3 g (1.45 mmol) of com pounds **1** in 8 mL of *i*-PrOH was added to 0.24 g (1.45 mmol) of 2-mercaptobenzothiazole **11a**. The re ac tion mix ture was stirred at 80 ℃ for 1 hr. The re-ac tion sol vent was re moved by vac uum, then 10 mL of ac e-tone was added and was stirred for an other 10 min. The pre-cip i ta tion was fil tered and crys tal lized with EtOH to give 0.133 g of com pound **3a** (36%). For the prep a ra tion of com-pounds **3c**~**3e**, 2-mercaptobenzimidazole **11b** was used to re-act with com pounds **1** at the same re ac tion con di tion for 0.5 hr. The crude prod uct ob tained by di rect fil tra tion was fur ther crys tal lized with EtOH to give pure prod ucts **3c**~**3e**.

The preparation of compounds 3f~3h were as follows:

Com pounds **1** (0.3 g, 1.45 mmol) in 8 mL of 1,4-dioxane were added to 0.17 g (1.45 mmol) of 2-mercapto-thiazoline **11c**. The re ac tion mix ture was stirred at 100 ℃ for 4 hr. The crude prod uct that pre cip i tated out af ter cool ing was col lected by di rect fil tra tion, then was crys tal lized with EtOH to give pure com pounds **3f**~**3h**. The phys i cal prop er ties and spec tro scopic data are as fol low ing:

2-[2-(4-Methylphenyl)hydrazino]benzothiazole (3a)

Col or less nee dles; mp 238~239 ℃, IR (KBr): 3292, 3052~2854 cm^{-1}; ^1H NMR, δ = 2.18 (s, 3H), 6.70 (d, *J* = 8.4 Hz, 2H), 6.99 (d, *J* = 8.4 Hz, 2H), 6.97~7.69 (m, 4H), 8.29 (s, 1H), 9.77 (s, 1H). ^{13}C NMR (DMSO-*d6*): δ = 173.6, 153.5, 146.3, 130.6, 129.8, 128.8, 126.0, 121.6, 121.4, 118.8, 113.1, 20.6. EIMS (70 eV), *m/z* (%): 225 (M^+, 100), 239 (11), 222 (19), 150 (48), 149 (20), 106 (97), 91 (29), 77 (42). Anal. Calcd. for $C_{14}H_{13}N_3S$: C: 65.85, H: 5.13, N: 16.46, S: 12.56. found C: 65.84, H: 5.19, N: 16.39, S: 12.51.

2-[2-(4-Chlorophenyl)hydrazino]benzothiazole (3b)

Pale or ange nee dles; mp 247~248 ℃, IR (KBr): 3292, 3076~2830 cm^{-1}; ^1H NMR, δ = 6.81 (d, *J* = 8.8 Hz, 2H), 7.01~7.71 (m, 4H), 7.22 (d, *J* = 8.8 Hz, 2H), 8.60 (s, 1H), 9.87 (s, 1H). EIMS (70 eV), *m/z* (%): 277 (M^++2, 35), 275 (M^+, 100), 259 (8), 242 (19), 150 (44), 149 (84), 129 (20), 127 (59), 113 (12), 111 (43). Anal. Calcd. for $C_{13}H_{10}ClN_3S$: C: 56.62, H: 3.65, N: 15.24, Cl: 12.86, S: 11.63. found C: 56.62, H: 3.68, N: 15.14, Cl: 12.88, S: 11.62.

2-(2-Phenylhydrazinobenzimidazole hydrochloride (3c)

Pale yel low nee dles; mp 234~235 ℃, IR (KBr): 3262~2908 cm^{-1}; ^1H NMR, δ = 6.37~6.47 (m, 3H), 6.75~6.82 (m, 4H), 6.91~6.95 (m, 2H), 8.67 (s, 1H), 11.67 (s, 1H), 13.18 (br, 2H). EIMS (70 eV), *m/z* (%): 224 (M^+, 100), 208 (6), 194 (5), 193 (22), 150 (12), 133 (49), 132 (78), 105 (46), 93 (98), 91 (21), 77 (49). Anal. Calcd. for $C_{13}H_{13}ClN_4$: C: 59.89, H: 5.03, N: 21.49, Cl: 13.60. found C: 59.82, H: 5.04, N: 21.39, Cl: 13.61.

2-[2-(4-Methylphenyl)hydrazino]benzimidazole hydrochloride (3d)

Pale yel low nee dles; mp 211~212 ℃, IR (KBr): 3260~2914 cm^{-1}; ^1H NMR, δ = 2.21 (s, 3H), 6.81 (d, *J* = 8.3 Hz, 2H), 7.06 (d, *J* = 8.3 Hz, 2H), 7.22~7.28 (m, 2H), 7.34~7.40 (m, 2H), 8.48 (s, 1H), 11.05 (s, 1H), 13.11 (br, 2H). EIMS (70 eV), *m/z* (%): 238 (M^+, 83), 222 (20), 208 (13), 207 (42), 150 (7), 133 (7), 132 (67), 107 (100), 91 (61), 77 (46). Anal. Calcd. for $C_{14}H_{15}ClN_4$: C: 61.20, H: 5.50, N: 20.39, Cl: 12.90. found C: 61.17, H: 5.55, N: 20.45, Cl: 12.94.

2-[2-(4-Chlorophenyl)hydrazino]benzimidazole hydrochloride (3e)

Col or less nee dles; mp 228~229 ℃, IR (KBr): 3250~2908 cm^{-1}; ^1H NMR, δ = 6.93 (d, *J* = 8.8 Hz, 2H), 7.21~7.30 (m, 2H), 7.26 (d, *J* = 8.8 Hz, 2H), 7.36~7.41 (m, 2H), 8.87 (s, 1H), 11.25 (s, 1H), 13.22 (br, 2H). ^{13}C NMR (DMSO-*d6*): δ = 152.3, 146.6, 129.8, 128.8, 128.7, 123.8, 123.3, 122.8, 114.8, 114.2, 111.7. EIMS (70 eV), *m/z* (%): 260 (M^++2, 13), 258 (M^+, 43), 242 (3), 228 (4), 227 (13), 133 (51), 132 (100), 127 (75), 111 (28), 105 (52). Anal. Calcd. for $C_{13}H_{12}Cl_2N_4$: C: 52.90, H: 4.10, N: 18.98, Cl: 24.02. found C: 52.94, H: 4.15,

N: 19.06, Cl: 24.03.

2-(2-Phenylhydrazino)thiazoline hydrochloride (3f)

Pale yellow needles; mp > 250 °C, IR (KBr): 3190~2752 cm^{-1}; ^1H NMR, δ = 3.51~3.76 (br, 2H), 3.78~4.11 (br, 2H), 6.59~7.56 (m, 5H), 8.68~9.10 (br, 2H), 10.23~11.75 (br, 1H). EIMS (70 eV), *m/z* (%): 193 (M^+, 100), 133 (15), 105 (13), 92 (36), 77 (63). Anal. Calcd. for $C_9H_{12}ClN_3S$: C: 47.05, H: 5.26, N: 18.29, Cl: 15.43, S: 13.96. found C: 47.24, H: 5.32, N: 18.35, Cl: 15.50, S: 13.93.

2-[2-(4-Methylphenyl)hydrazino]thiazoline hydrochloride (3g)

Colorless needles; mp > 250 °C, IR (KBr): 3184~2740 cm^{-1}; ^1H NMR, δ = 2.21 (s, 3H), 3.41~3.73 (br, 2H), 3.75~4.18 (br, 2H), 6.70 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 7.53~8.90 (br, 2H), 10.08~11.90 (br, 1H). EIMS (70 eV), *m/z* (%): 207 (M^+, 100), 147 (70), 106 (50), 91 (44), 77 (24). Anal. Calcd. for $C_{10}H_{14}ClN_3S$: C: 49.27, H: 5.79, N: 17.24, Cl: 14.54, S: 13.15. found C: 49.36, H: 5.80, N: 17.33, Cl: 14.44, S: 13.10.

2-[2-(4-Chlorophenyl)hydrazino]thiazoline hydrochloride (3h)

Colorless needles; mp > 250 °C, IR (KBr): 3184~2764 cm^{-1}; ^1H NMR, δ = 3.40~3.72 (br, 2H), 3.75~4.10 (br, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 7.30 (d, *J* = 8.8 Hz, 2H), 8.81~9.23 (br, 2H), 10.21~11.78 (br, 1H). EIMS (70 eV), *m/z* (%): 229 (M^++2, 36), 227 (M^+, 100), 167 (7), 125 (14), 113 (8), 111 (24). Anal. Calcd. for $C_9H_{11}Cl_2N_3S$: C: 40.92, H: 4.20, N: 15.91, Cl: 26.84, S: 12.14. found C: 40.87, H: 4.22, N: 15.49, Cl: 26.84, S: 12.10.

The preparation of compounds 5 and 6

(A) Preparation of **5a~5c** and **6a~6c** by reacting compounds **1** with thiourea **4a**

α-Chloroformylphenylhydrazine hydrochloride **1** (1.5 g, 7.25 mmol) in 12 mL of EtOH was added to 0.55 g (7.25 mmol) of thiourea **4a**. The reaction mixture was stirred at room temperature for 10 hr. The reaction solvent was removed under reduced pressure, then 10 mL of THF was added and stirred for 10 min. The precipitation was collected by filtration to give 0.59 g of pure compound **5a** (44%). The filtrate was subjected to chromatography (EtOAc:n-hexane = 1:1). The eluted fractions were pooled and the solvent was removed under reduced pressure to give pure product **6a** (0.22 g, 15%). The physical properties and spectroscopic data of compounds **5** and **6** are as follows:

2-Phenylhydrazinecarboximidamide hydrochloride (5a)

Colorless needles; mp 227~228 °C, IR (KBr): 3442~2836 cm^{-1}; ^1H NMR, δ = 6.72~6.87, 7.19~7.27 (m, 5H), 7.57 (br, 2H), 8.11 (s, 1H), 9.68 (s, 1H). EIMS (70 eV), *m/z* (%): 150 (M^+, 90), 133 (40), 91 (61), 77 (35). Anal. Calcd. for $C_7H_{11}ClN_4$: C: 45.05, H: 5.94, N: 30.02, Cl: 19.00. found C: 45.06, H: 5.96, N: 29.97, Cl: 18.99.

2-(4-Methylphenyl)hydrazinecarboximidamide hydrochloride (5b)

Colorless needles; mp 199~200 °C, IR (KBr): 3460~3034 cm^{-1}; ^1H NMR, δ = 2.21 (s, 3H), 6.66 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 7.51 (br, 4H), 7.93 (s, 1H), 9.62 (s, 1H). ^{13}C NMR (DMSO-*d6*): δ = 159.2, 145.2, 129.4, 129.1, 113.0, 20.2. EIMS (70 eV), *m/z* (%): 164 (M^+, 80), 147 (32), 105 (100), 91 (48), 77 (38). Anal. Calcd. for $C_8H_{13}ClN_4$: C: 47.88, H: 6.53, N: 27.92, Cl: 17.69. found C: 47.71, H: 6.40, N: 27.96, Cl: 17.71.

2-(4-Chlorophenyl)hydrazinecarboximidamide hydrochloride (5c)

Colorless needles; mp 228~229 °C, IR (KBr): 3466~2854 cm^{-1}; ^1H NMR, δ = 6.74 (d, *J* = 9.0 Hz, 2H), 7.28 (d, *J* = 9.0 Hz, 2H), 7.58 (br, 4H), 8.30 (s, 1H), 9.74 (s, 1H). EIMS (70 eV), *m/z* (%): 186 (M^++2, 32), 184 (M^+, 100), 167 (36), 125 (99), 111 (25). Anal. Calcd. for $C_7H_{10}Cl_2N_4$: C: 38.03, H: 4.56, N: 25.34, Cl: 32.07. found C: 37.94, H: 4.55, N: 25.20, Cl: 32.10.

2-Amino-4-phenyl-1,3,4-thiadiazolin-5-one (6a)

Colorless needles; mp 171~172 °C, IR (KBr): 3394, 3304, 3196, 1677 cm^{-1}; ^1H NMR, δ = 6.98 (s, 2H), 7.18~7.25, 7.38~7.43, 7.69~7.74 (m, 5H). EIMS (70 eV), *m/z* (%): 193 (M^+, 77), 133 (49), 91 (100), 77 (47). Anal. Calcd. for $C_8H_7N_3OS$: C: 49.73, H: 3.65, N: 21.75, S: 16.59. found C: 49.73, H: 3.56, N: 21.75, S: 16.40.

2-Amino-4-(4-methylphenyl)-1,3,4-thiadiazolin-5-one (6b)

Colorless needles; mp 151~152 °C, IR (KBr): 3538~3196, 1671 cm^{-1}; ^1H NMR, δ = 2.29 (s, 3H), 6.94 (s, 2H), 7.20 (d, *J* = 8.5 Hz, 2H), 7.58 (d, *J* = 8.5 Hz, 2H). EIMS (70 eV), *m/z* (%): 207 (M^+, 96), 147 (12), 119 (2), 105 (100), 91 (27). Anal. Calcd. for $C_9H_9N_3OS$: C: 52.17, H: 4.35, N: 20.29, S: 15.47. found C: 52.11, H: 4.32, N: 20.31, S: 15.45.

2-Amino-4-(4-chlorophenyl)-1,3,4-thiadiazolin-5-one (6c)

Colorless needles; mp 151~152 °C, IR (KBr): 3466~3190, 1674 cm^{-1}; ^1H NMR, δ = 7.03 (s, 3H), 7.48 (d, *J* = 9.0

Hz, 2H), 7.76 (d, *J* = 9.0 Hz, 2H). EIMS (70 eV), *m/z* (%): 229 (M^++2, 30), 227 (M^+, 92), 167 (57), 139 (7), 127 (54), 125 (100), 111 (31). Anal. Calcd. for $C_8H_6ClN_3OS$: C: 42.20, H: 2.66, N: 18.46. found C: 42.38, H: 2.61, N: 18.56.

(B) Preparation of **5d**~**5f** and **6d**~**6f** by reacting of compounds **1** with reagent **4b**

α-Chloroformylphenylhydrazine hydrochloride **1** (1.5 g, 7.25 mmol) in 12 mL of *i*-PrOH was added to 0.75 g (7.25 mmol) of 1,3-dimethylthiourea **4b**. The reaction mixture was stirred at room temperature for 5 hr. The work-up to give pure products was the same as in step (A).

N,N'-Dimethyl-2-phenylhydrazinecarboximidamide hydrochloride (5d)

Colorless needles; mp 215~216 °C, IR (KBr): 3370~2944 cm^{-1}; ^1H NMR, δ = 2.78 (br, 6H), 6.78~6.88, 7.19~7.27 (m, 5H), 7.94 (br, 2H), 8.16 (s, 1H), 9.67 (s, 1H). EIMS (70 eV), *m/z* (%): 178 (M^+, 56), 147 (13), 108 (8), 91 (29), 77 (33), 71 (100). Anal. Calcd. for $C_9H_{15}ClN_4$: C: 50.35, H: 7.04, N: 26.10, Cl: 16.51. found C: 50.32, H: 7.08, N: 25.97, Cl: 16.44.

N,N'-Dimethyl-2-(4-methylphenyl)hydrazinecarboximidamide hydrochloride (5e)

Pale yellow powder; mp 199~200 °C, IR (KBr): 3466~3130 cm^{-1}; ^1H NMR, δ = 2.22 (s, 3H), 2.79 (br, 6H), 6.70 (d, *J* = 8.4, 2H), 7.04 (d, *J* = 8.4, 2H), 7.90 (br, 4H), 7.99 (s, 1H), 9.61 (s, 1H). EIMS (70 eV), *m/z* (%): 192 (M^+, 80), 164 (38), 147 (32), 105 (100), 91 (48), 77 (38). Anal. Calcd. for $C_{10}H_{17}ClN_4qH_2O$: C: 48.68, H: 7.76, N: 22.71, Cl: 14.37. found C: 48.66, H: 7.77, N: 22.64, Cl: 14.41.

N,N'-Dimethyl-2-(4-chlorophenyl)hydrazinecarboximidamide hydrochloride (5f)

Colorless needles; mp 230~231 °C, IR (KBr): 3472~3118 cm^{-1}; ^1H NMR, δ = 2.79 (br, 6H), 6.81 (d, *J* = 8.8 Hz, 2H), 7.25 (d, *J* = 8.8 Hz, 2H), 7.94 (br, 2H), 8.33 (s, 1H), 9.70 (s, 1H). ^{13}C NMR (DMSO-*d6*): δ = 156.9, 146.7, 128.6, 123.5, 114.7, 27.9. EIMS (70 eV), *m/z* (%):214 (M^++2, 29), 212 (M^+, 89), 181 (20), 142 (7), 125 (59), 111 (21), 71 (100). Anal. Calcd. for $C_9H_{14}Cl_2N_4$: C: 43.35, H: 5.64, N: 22.49, Cl: 28.39. found C: 43.35, H: 5.64, N: 22.38, Cl: 28.39.

2-Methylamino-4-phenyl-1,3,4-thiadiazolin-5-one (6d)

Colorless needles; mp 88~89 °C, IR (KBr): 3316, 1674 cm^{-1}; ^1H NMR, δ = 2.80 (d, *J* = 4.8 Hz, 3H), 7.39~7.46 (br, 1H), 7.19~7.26, 7.39~7.46, 7.75~7.79 (m, 6H). EIMS (70 eV), *m/z* (%): 207 (M^+, 100), 147 (19), 132 (3), 119 (10), 91 (77), 77 (37). Anal. Calcd. for $C_9H_9N_3OS$: C: 52.16, H: 4.38, N: 20.27, S: 15.47. found C: 52.15, H: 4.43, N: 20.12, S: 15.41.

2-Methylamino-4-(4-methylphenyl)-1,3,4-thiadiazolin-5-one (6e)

Colorless needles; mp 128~129 °C, IR (KBr): 3334, 1659 cm^{-1}; ^1H NMR, δ = 2.30 (s, 3H), 2.80 (d, *J* = 4.8 Hz, 3H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.26~7.48 (br, 1H), 7.64 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (DMSO-*d6*): δ = 165.1, 151.3, 135.9, 134.8, 129.2, 120.6, 28.9, 20.5. EIMS (70 eV), *m/z* (%): 221 (M^+, 100), 161 (7), 119 (2), 105 (65), 91 (16). Anal. Calcd. for $C_{10}H_{11}N_3OS$: C: 54.28, H: 5.01, N: 18.99, S: 14.49. found C: 54.39, H: 5.06, N: 19.04, S: 14.39.

2-Methylamino-4-(4-chlorophenyl)-1,3,4-thiadiazolin-5-one (6f)

Pale yellow powder; mp 140~141 °C, IR (KBr): 3418, 1659 cm^{-1}; ^1H NMR, δ = 2.80 (d, *J* = 4.8 Hz, 3H), 7.44~7.45 (br, 1H), 7.49 (d, *J* = 9.0 Hz, 2H), 7.82 (d, *J* = 9.0 Hz, 2H). EIMS (70 eV), *m/z* (%): 243 (M^++2, 37), 241 (M^+, 100), 181 (26), 139 (3), 125 (89), 111 (20). Anal. Calcd. for $C_9H_8ClN_3OS$: C: 44.87, H: 3.34, N: 17.39, Cl: 14.59, S: 13.27. found C: 44.86, H: 3.38, N: 17.36, Cl: 14.59, S: 13.20.

(C) Preparation of **5g**~**5h** and **6g**~**6h** by reacting compounds **1** with reagent **4c**

α-Chloroformyl-(4-methylphenyl)hydrazines hydrochloride **1** (1 g, 4.25 mmol) in 12 mL of acetone was added to 1 g (7.25 mmol) of 1,3-diphenylthiourea **4c**. The reaction mixture was stirred at room temperature for 48 hr. The precipitation was collected by filtration to give 0.93 g of pure product **5g** (58%). The filtrate was poured into ice water and stirred for 10 min. The precipitation was collected by filtration and crystallized with EtOAc to give 0.15 g of product **6g** (12%). The physical properties and spectroscopic data of compounds **5g**~**5h** and **6g**~**6h** are as following:

N,N'-Diphenyl-2-(4-methylphenyl)hydrazinecarboximidamide hydrochloride (5g)

Colorless needles; mp 227~228 °C, IR (KBr): 3220~2926 cm^{-1}; ^1H NMR, δ = 2.21 (s, 3H), 6.85 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 7.15~7.38 (m, 10H), 8.23 (s, 1H), 10.26 (br, 3H). ^{13}C NMR (DMSO-*d6*): δ = 155.2, 145, 129.4, 129.3, 129.1, 126.0, 124.1, 113.5, 20.2. EIMS (70 eV), *m/z* (%): 316 (M^+, 47), 195 (100), 122 (29), 105 (11), 92 (21), 77 (21). Anal. Calcd. for $C_{20}H_{21}ClN_4$: C: 68.08, H: 6.00, N: 15.88, Cl: 10.05. found C: 67.99, H: 6.00, N: 15.83, Cl: 10.00.

N,N'-Diphenyl-2-(4-chlorophenyl)hydrazinecarboximidamide hydrochloride (5h)

Colorless needles; mp 213~214 °C, IR (KBr): 3250~2974 cm^{-1}; ^1H NMR, δ = 6.95 (d, *J* = 9.0 Hz, 2H), 7.27 (d, *J* = 9.0 Hz, 2H), 7.18~7.41 (m, 10H), 8.49 (s, 1H), 10.26 (br, 3H). EIMS (70 eV), *m/z* (%): 338 (M^++2, 32), 336 (M^+, 100), 195 (100), 142 (33), 125 (26), 111 (13), 92 (27), 77 (32). Anal. Calcd. for $C_{19}H_{18}Cl_2N_4$: C: 61.14, H: 4.86, N: 15.01, Cl: 19.00. found C: 61.11, H: 4.75, N: 15.07, Cl: 18.95.

2-Phenylamino-4-(4-methylphenyl)-1,3,4-thiadiazolin-5-one (6g)

Colorless needles; mp 209~210 °C, IR (KBr): 3304, 1668 cm^{-1}; ^1H NMR, δ = 2.32 (s, 3H), 6.95~7.02, 7.25~7.37, 7.46~7.50 (m, 5H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 2H), 10.01 (s, 1H). EIMS (70 eV), *m/z* (%): 283 (M^+, 100), 222 (10), 136 (30), 105 (71), 91 (19), 77 (31). Anal. Calcd. for $C_{15}H_{13}N_3OS$: C: 63.56, H: 4.62, N: 14.83, S: 11.32. found C: 63.56, H: 4.70, N: 14.87, S: 11.30.

2-Phenylamino-4-(4-chlorophenyl)-1,3,4-thiadiazolin-5-one (6h)

Colorless needles; mp 212~213 °C, IR (KBr): 3310, 1668 cm^{-1}; ^1H NMR, δ = 6.98~7.39, 7.46~7.51 (m, 5H), 7.55 (d, *J* = 9.0 Hz, 2H), 7.85 (d, *J* = 9.0 Hz, 2H), 10.07 (s, 1H). EIMS (70 eV), *m/z* (%): 305 (M^++2, 38), 303 (M^+, 100), 243 (14), 125 (66), 111 (13), 77 (30). Anal. Calcd. for $C_{14}H_{10}ClN_3OS$: C: 55.36, H: 3.32, N: 13.85, Cl: 11.67, S: 10.56. found C: 55.40, H: 3.37, N: 13.85, Cl: 11.59, S: 10.47.

(D) Preparation of **6i**~**6k** by reacting compounds **1** with reagent **4d**

α-Chloroformylphenylhydrazine hydrochloride **1** (1.5 g, 7.25 mmol) in 12 mL of i-PrOH was added to 0.96 g (7.25 mmol) of tetramethylthiourea **4d**. The reaction mixture was stirred at room temperature for 48 hr. The reaction solution was added to cool water drop by drop, then was stirred for another 10 min. The precipitation was collected by filtration and crystallized with EtOAc to give 0.43 g of product **6i** (27%). The physical properties and spectroscopic data of compounds **6i**~**6k** are as follows:

2-Dimethylamino-4-phenyl-1,3,4-thiadiazolin-5-one (6i)

Colorless needles; mp 65~66 °C, IR (KBr): 1677 cm^{-1}; ^1H NMR, δ = 2.95 (s, 6H), 7.21~7.28, 7.40~7.47, 7.75~7.80 (m, 5H). EIMS (70 eV), *m/z* (%): 221 (M^+, 100), 161 (4), 118 (22), 91 (32), 88 (61), 77 (21). Anal. Calcd. for $C_{10}H_{11}N_3OS$: C: 54.28, H: 5.01, N: 18.99, S: 14.49. found C: 54.30, H: 5.04, N: 18.96, S: 14.44.

2-Dimethylamino-4-(4-methylphenyl)-1,3,4-thiadiazolin-5-one (6j)

Colorless needles; mp 103~104 °C, IR (KBr): 1665 cm^{-1}; ^1H NMR, δ = 2.30 (s, 3H), 2.93 (s, 6H), 7.23 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ = 166.7, 153.7, 136.1, 135.5, 129.2, 121.1, 39.1, 20.9. EIMS (70 eV), *m/z* (%): 235 (M^+, 100), 175 (3), 132 (13), 105 (50), 91 (12), 88 (57). Anal. Calcd. for $C_{11}H_{13}N_3OS$: C: 56.15, H: 5.57, N: 17.86, S: 13.63. found C: 56.08, H: 5.62, N: 17.90, S: 13.62.

2-Dimethylamino-4-(4-chlorophenyl)-1,3,4-thiadiazolin-5-one (6k)

Colorless needles; mp 91~92 °C, IR (KBr): 1698 cm^{-1}; ^1H NMR, δ = 2.94 (s, 6H), 7.48 (d, *J* = 8.8 Hz, 2H), 7.81 (d, *J* = 8.9 Hz, 2H). EIMS (70 eV), *m/z* (%): 257 (M^++2, 35), 255 (M^+, 100), 195 (7), 160 (18), 125 (47), 111 (9), 88 (58). Anal. Calcd. for $C_{10}H_{10}ClN_3OS$: C: 46.97, H: 3.94, N: 16.43, Cl: 13.86, S: 12.54. found C: 47.07, H: 3.93, N: 16.38, Cl: 13.74, S: 12.54.

(E) Preparation of **5l**~**5m** and **6l**~**6m** by reacting compounds **1** with reagent **4e**

α-Chloroformylphenylhydrazine hydrochloride **1** (1.5 g, 7.25 mmol) in 12 mL of i-PrOH was added to 0.65 g (7.25 mmol) of methylthiourea **4e**. The reaction mixture was stirred at room temperature for 4 hr. The work-up was the same as in step (A) and gave **5l** (0.34 g, 24%) and **6l** (0.22 g, 16%).

N-Methyl-2-phenylhydrazinecarboximidamide hydrochloride (5l)

Colorless needles; mp 153~154 °C, IR (KBr): 3340~2974 cm^{-1}; ^1H NMR, δ = 2.78 (d, *J* = 4.8 Hz, 3H), 6.73~6.87, 7.18~7.26 (m, 5H), 7.73 (s, 2H), 7.94 (br, 1H), 8.07 (s, 1H), 9.57 (s, 1H). EIMS (70 eV), *m/z* (%): 164 (M^+, 100), 147 (17), 108 (33), 91 (57), 77 (38), 57 (63). Anal. Calcd. for $C_8H_{13}ClN_4$: C: 47.88, H: 6.53, N: 27.92, Cl: 17.67. found C: 47.66, H: 6.60, N: 27.75, Cl: 17.63.

N-Methyl-2-(4-chlorophenyl)hydrazinecarboximidamide hydrochloride (5m)

Colorless needles; mp 202~203 °C, IR (KBr): 3370~2902 cm^{-1}; ^1H NMR, δ = 2.77 (d, *J* = 4.8 Hz, 3H), 6.76 (d, *J* = 8.8 Hz, 2H), 7.27 (d, *J* = 8.8 Hz, 2H), 7.77 (s, 2H), 7.97 (br, 1H), 8.27 (s, 1H), 9.66 (s, 1H). ^{13}C NMR ($CDCl_3$): δ = 158.7, 145.1, 129.0, 126.5, 114.8, 27.5. EIMS (70 eV), *m/z* (%): 200 (M^++2, 32), 198 (M^+, 100), 181 (13), 125 (78), 111 (27), 57 (53). Anal. Calcd. for $C_8H_{12}Cl_2N_4$: C: 40.87, H: 5.14, N:

23.83, Cl: 30.16. found C: 40.87, H: 5.15, N: 23.89, Cl: 30.15.

(F) Preparation of **6n~6p** by reacting compounds **1** with reagent **4f**

α-Chloroformylphenylhydrazine hydrochloride **1** (1.5 g, 7.25 mmol) in 12 mL of EtOH was added to 0.74 g (7.25 mmol) of ethylenethiourea **4f**. The reaction mixture was stirred at room temperature for 20 hr. The precipitated out product was collected by filtration and crystallized with EtOAc to give 0.61 g of product **6n** (31%).

2-(β-aminoethyl)amino-4-phenyl-1,3,4-thiadiazolin-5-one (6n)

Pale yellow needles; mp 217~218 °C, IR (KBr): 3262, 3154, 3010, 2884, 1668 cm^{-1}; ^1H NMR, δ = 3.00~3.08 (m, 2H), 3.44~3.53 (m, 2H), 7.21~7.28, 7.40~7.47, 7.75~7.80 (m, 6H), 8.05 (br, 3H). EIMS (70 eV), *m/z* (%): 236 (M^+, 60), 207 (31), 193 (100), 119 (69), 105 (23), 91 (56), 77 (99). Anal. Calcd. for $C_{10}H_{13}ClN_4OS$: C: 44.04, H: 4.80, N: 20.54, Cl: 13.00, S: 11.76. found C: 44.08, H: 4.85, N: 20.51, Cl: 12.99, S: 11.75.

2-(β-aminoethyl)amino-4-(4-methylphenyl)-1,3,4-thiadiazolin-5-one (6o)

Colorless needles; mp > 250 °C, IR (KBr): 3268, 3010, 1674 cm^{-1}; ^1H NMR, δ = 2.30 (s, 3H), 3.00~3.06 (m, 2H), 3.43~3.51 (m, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.75 (t, *J* = 5.4 Hz, 1H), 8.04 (br, 3H). ^{13}C NMR (DMSO-*d6*): δ = 165.1, 150.7, 135.8, 135.0, 129.3, 120.6, 40.1, 37.6, 20.5. EIMS (70 eV), *m/z* (%): 250 (M^+, 100), 221 (57), 207 (71), 133 (51), 105 (40), 91 (60). Anal. Calcd. for $C_{11}H_{15}ClN_4OS$: C: 46.07, H: 5.27, N: 19.54, Cl: 12.36, S: 11.18. found C: 46.04, H: 5.30, N: 19.52, Cl: 12.37, S: 11.14.

2-(β-aminoethyl)amino-4-(4-chlorophenyl)-1,3,4-thiadiazolin-5-one (6p)

Colorless needles; mp > 250 °C, IR (KBr): 3262, 3154, 3004, 1668 cm^{-1}; ^1H NMR, δ = 3.00~3.07 (m, 2H), 3.45~3.51 (m, 2H), 7.49 (d, *J* = 9.0 Hz, 2H), 7.82 (d, *J* = 9.0 Hz, 2H), 7.95 (t, *J* = 5.3 Hz, 1H), 8.12 (br, 3H). EIMS (70 eV), *m/z* (%): 272 (M^++2, 34), 270 (M^+, 91), 243 (23), 241 (64), 229 (35), 227 (93), 155 (14), 153 (40), 127 (13), 125 (40), 113 (16), 111 (49), 69 (100). Anal. Calcd. for $C_{10}H_{12}Cl_2N_4OS$: C: 39.10, H: 3.94, N: 18.23, Cl: 23.08, S: 10.44. found C: 38.99, H: 3.93, N: 18.14, Cl: 23.07, S: 10.43.

Preparation of compounds 9a~9h

(A) Preparation of compounds **9a** and **9b** by reacting compounds **1** with 1,2-cyclohexanedione **8a**

α-Chloroformylphenylhydrazine hydrochloride **1** (1.5 g, 7.25 mmol) in 12 mL of *i*-PrOH was added to 0.81 g (7.25 mmol) of 1,2-cyclohexanedione **8a**. The reaction mixture was stirred at room temperature for 3 hours. The reaction solvent was then removed under reduced pressure. The crude solid was further purified through chromatography (EtOAc: n- hexane = 1:1). The eluted fractions were pooled and the solvent was removed under reduced pressure to give 0.35 g (21%) of compound **9a** and 0.35 g (24%) of 2-phenyl hydrazino-1-cyclohexanone **13**.

2-Phenyl-3-oxo-6,7,8-trihydrocyclohex[e][1,3,4]oxadiazine (9a)

Pale yellow needles; mp 57~58 °C, IR (KBr): 1731 cm^{-1}; ^1H NMR, δ = 1.72~1.84 (m, 2H), 2.23~2.31 (m, 2H), 2.48~2.54 (m, 2H), 5.79 (t, *J* = 4.6 Hz, 1H), 7.26~7.50 (m, 5H). EIMS (70 eV), *m/z* (%): 228 (M^+, 70), 130 (100), 119 (79), 91 (50), 77 (59), 55 (50). Anal. Calcd. for $C_{13}H_{12}N_2O_2$: C: 68.41, H: 5.30, N: 12.27. found C: 68.42, H: 5.35, N: 12.24.

2-(4-Chlorophenyl)-3-oxo-6,7,8-trihydrocyclohex[e][1,3,4]-oxadiazine (9b)

Pale yellow needles; mp 68~69 °C, IR (KBr): 1731 cm^{-1}; ^1H NMR, δ = 1.75~1.84 (m, 2H), 2.23~2.32 (m, 2H), 2.48~2.55 (m, 2H), 5.81 (t, *J* = 4.6 Hz, 1H), 7.54~7.39 (m, 4H). EIMS (70 eV), *m/z* (%): 264 (M^++2, 23), 262 (M^+, 75), 183 (9), 166 (29), 164 (94), 155 (23), 153 (66), 125 (58), 113 (23), 111 (64), 55 (100). Anal. Calcd. for $C_{13}H_{11}ClN_2O_2$: C: 59.44, H: 4.22, N: 10.66, Cl: 13.50. found C: 59.33, H: 4.32, N: 10.54, Cl: 13.55.

2-Phenylhydrazino-1-cyclohexanone (13)

Colorless needles; mp 188~189 °C, IR (KBr): 3250, 1662 cm^{-1}; ^1H NMR, δ = 1.79~1.88 (m, 4H), 2.40~2.57 (m, 4H), 6.87~6.91, 7.21~7.28 (m, 5H), 9.81 (s, 1H). EIMS (70 eV), *m/z* (%): 202 (M^+, 100), 173 (9), 145 (15), 110 (9), 93 (82), 82 (38), 77 (24), 55 (62), 41 (52). Anal. Calcd. for $C_{12}H_{14}N_2O$: C: 71.26, H: 6.98, N: 13.85. found C: 71.25, H: 7.01, N: 13.83.

(B) Preparation of compounds **9c~9e**, **9f~9h**, **9i~9k** and **9l~9n** by reacting compounds **1** with **8b**, **8c**, **8d and 8e**, respectively

α-Chloroformylphenylhydrazine hydrochloride **1** (1 g, 4.83 mmol) in 12 mL of EtOH was added to 0.54 g (4.83 mmol) of 3-methyl-1,2-cyclopentanedione **8b**. In preparing products **9f~9h**, **9i~9k** and **9l~9n**, 0.61 g of **8c**, 0.61 g of **8d,** and 0.91 g of **8e** were used, respectively, to react with 1 g of α-chloroformylphenylhydrazine hydrochloride **1**. The reac-

tion mix ture was stirred at room tem per a ture for 1 hr. The pre cip i ta tion was col lected by fil tra tion, then was washed with cool *i*-PrOH and fi nally was crys tal lized with EtOH to give 0.67 g of pure prod uct **9c** (61%).

5-Methyl-2-phenyl-3-oxo-6,7-dihydrocyclopent[e][1,3,4]-oxadiazine (9c)

Pale yel low pow der; mp 90~91 °C, IR (KBr): 1746 cm^{-1}; ^1H NMR, δ = 1.81 (s, 3H), 2.49~2.65 (m, 4H), 7.27~7.31, 7.38~7.47 (m, 5H). EIMS (70 eV), *m/z* (%): 228 (M^+, 76), 119 (57), 91 (41), 77 (30), 69 (100), 41 (60). Anal. Calcd. for $C_{13}H_{12}N_2O_2$: C: 68.41, H: 5.30, N: 12.27. found C: 68.45, H: 5.35, N: 12.24.

5-Methyl-2-(4-methylphenyl)-3-oxo-6,7-dihydrocyclopent-[e][1,3,4]oxadiazine (9d)

Col or less nee dles; mp 134~135 °C, IR (KBr): 1734 cm^{-1}; ^1H NMR, δ = 1.80 (s, 3H), 2.30 (s, 3H), 2.49~2.65 (m, 4H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H). EIMS (70 eV), *m/z* (%): 242 (M^+, 57), 133 (100), 91 (10), 69 (49), 41 (12). Anal. Calcd. for $C_{14}H_{14}N_2O_2$: C: 69.41, H: 5.82, N: 11.56. found C: 69.48, H: 5.80, N: 11.51.

2-(4-Chlorophenyl)-5-methyl-3-oxo-6,7-dihydrocyclopent-[e][1,3,4]oxadiazine (9e)

Col or less nee dles; mp 118~119 °C, IR (KBr): 1731 cm^{-1}; ^1H NMR, δ = 1.80 (s, 3H), 2.40~2.71 (m, 4H), 7.43 (d, *J* = 9.0 Hz, 2H), 7.49 (d, *J* = 9.0 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ = 157.3, 143.7, 141.2, 139.8, 132.1, 128.9, 128.6, 125.7, 30.7, 24.4, 12.2. EIMS (70 eV), *m/z* (%): 264 (M^++2, 20), 262 (M^+, 63), 155 (15), 153 (48), 127 (9), 125 (29), 113 (4), 111 (12), 69 (100), 41 (62). Anal. Calcd. for $C_{13}H_{11}ClN_2O_2$: C: 59.44, H: 4.22, N: 10.66, Cl: 13.50. found C: 59.37, H: 4.23, N: 10.58, Cl: 13.51.

5-Ethyl-2-phenyl-3-oxo-6,7-dihydrocyclopent[e][1,3,4]-oxadiazine (9f)

Col or less nee dles; mp 88~89 °C, IR (KBr): 1737 cm^{-1}; ^1H NMR, δ = 1.12 (t, *J* = 7.7 Hz, 3H), 2.33 (q, *J* = 7.7 Hz, 2H), 2.56~2.72 (m, 4H), 7.27~7.31, 7.36~7.53 (m, 5H). ^{13}C NMR ($CDCl_3$): δ = 157.2, 143.9, 141.3, 140.5, 133.6, 128.7, 126.9, 124.7, 28.3, 24.3, 19.9, 11.4. EIMS (70 eV), *m/z* (%): 242 (M^+, 85), 119 (38), 91 (29), 83 (100), 77 (21), 55 (67). Anal. Calcd. for $C_{14}H_{14}N_2O_2$: C: 69.41, H: 5.82, N: 11.56. found C: 69.31, H: 5.97, N: 11.53.

5-Ethyl-2-(4-methylphenyl)-3-oxo-6,7-dihydrocyclopent-[e][1,3,4]oxadiazine (9g)

Pale yel low nee dles; mp 102~103 °C, IR (KBr): 1737 cm^{-1}; ^1H NMR, δ = 1.11 (t, *J* = 7.7 Hz, 3H), 2.30 (s, 3H), 2.33 (q, *J* = 7.7 Hz, 2H), 2.55~2.71 (m, 4H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H). EIMS (70 eV), *m/z* (%): 256 (M^+, 45), 133 (98), 105 (15), 91 (28), 83 (91), 77 (25), 55 (100). Anal. Calcd. for $C_{15}H_{16}N_2O_2$: C: 70.29, H: 6.29, N: 10.93. found C: 70.25, H: 6.28, N: 11.07.

5-Ethyl-2-(4-chlorophenyl)-3-oxo-6,7-dihydrocyclopent[e]-[1,3,4]oxadiazine (9h)

Pale yel low nee dles; mp 53~54 °C, IR (KBr): 1740 cm^{-1}; ^1H NMR, δ = 1.12 (t, *J* = 7.7 Hz, 3H), 2.32 (q, *J* = 7.7 Hz, 2H), 2.52~2.72 (m, 4H), 7.35 (d, *J* = 9.0 Hz, 2H), 7.47 (d, *J* = 9.0 Hz, 2H). EIMS (70 eV), *m/z* (%): 278 (M^++2, 6), 276 (M^+, 20), 155 (4), 153 (13), 127 (5), 125 (13), 113 (4), 111 (12), 83 (100), 55 (83). Anal. Calcd. for $C_{14}H_{13}ClN_2O_2$: C: 60.77, H: 4.73, N: 10.12, Cl: 12.81. found C: 60.57, H: 4.70, N: 10.13, Cl: 12.83.

5-Methyl-2-phenyl-3,6-dioxo-6H-cyclopent[e][1,3,4]-oxadiazine (9i)

Pale yel low nee dles; mp 170~171 °C, IR (KBr): 1761, 1722 cm^{-1}; ^1H NMR, δ = 1.76 (s, 3H), 3.29 (s, 2H), 7.36~7.54 (m, 5H). EIMS (70 eV), *m/z* (%): 242 (M^+, 50), 119 (100), 91 (29), 83 (38), 77 (35). Anal. Calcd. for $C_{13}H_{10}N_2O_3$: C: 64.45, H: 4.16, N: 11.56. found C: 64.47, H: 4.15, N: 11.52.

5-Methyl-2-(4-methylphenyl)-3,6-dioxo-6H-cyclopent[e]-[1,3,4]oxadiazine (9j)

Pale yel low nee dles; mp 177~178 °C, IR (KBr): 1764, 1716 cm^{-1}; ^1H NMR, δ = 1.76 (s, 3H), 2.33 (s, 3H), 3.28 (s, 2H), 7.26 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.5 Hz, 2H). EIMS (70 eV), *m/z* (%): 256 (M^+, 70), 133 (100), 105 (17), 91 (36), 83 (36). Anal. Calcd. for $C_{14}H_{12}N_2O_3$: C: 65.62, H: 4.72, N: 10.93. found C: 65.68, H: 4.75, N: 10.83.

2-(4-Chlorophenyl)-5-mthyl-3,6-dioxo-6H-cyclopent[e]-[1,3,4]oxadiazine (9k)

Col or less pow der; mp 200~201 °C, IR (KBr): 1743, 1716 cm^{-1}; ^1H NMR, δ = 1.76 (s, 3H), 3.30 (s, 2H), 7.54 (s, 4H). ^{13}C NMR ($CDCl_3$): δ = 195.8, 160.7, 146.6, 141.5, 138.6, 133.5, 129.0, 125.6, 124.8, 36.1, 6.1. EIMS (70 eV), *m/z* (%): 278 (M^++2, 16), 276 (M^+, 48), 155 (100), 127 (8), 125 (28), 113 (8), 111 (26), 83 (44). Anal. Calcd. for $C_{13}H_9ClN_2O_3$: C: 56.43, H: 3.28, N: 10.12, Cl: 12.81. found C: 56.45, H: 3.28, N: 10.09, Cl: 12.88.

2,5-Diphenyl-3,6-dioxo-6H-cyclopent[e][1,3,4]oxadiazine (9l)

Pale yel low nee dles; mp 209~210 °C, IR (KBr): 1761,

1713 cm^{-1}; ^1H NMR, δ = 3.45 (s, 2H), 7.39~7.57, 7.90~7.95 (m, 10H). EIMS (70 eV), *m/z* (%): 304 (M^+, 59), 185 (11), 145 (100), 119 (45), 117 (27), 91 (28), 89 (85), 77 (37). Anal. Calcd. for $C_{18}H_{12}N_2O_3$: C: 71.05, H: 3.97, N: 9.21. found C: 71.07, H: 3.98, N: 9.21.

2-(4-Methylphenyl)-5-phenyl-3,6-dioxo-6H-cyclopent[e]-[1,3,4]oxadiazine (9m)

Pale yel low nee dles; mp 160~161°C, IR (KBr): 1755, 1713 cm^{-1}; ^1H NMR, δ= 2.34 (s, 3H), 3.45 (s, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.39~7.56, 7.90~7.95 (m, 7H). ^{13}C NMR ($CDCl_3$): δ = 194.8, 159.1, 145.5, 141.6, 138.2, 137.7, 130.0, 129.8, 129.6, 128.6, 127.5, 124.4, 122.4, 36.8, 21.1. EIMS (70 eV), *m/z* (%): 318 (M^+, 80), 185 (10), 145 (81), 133 (100), 117 (22), 91 (22), 89 (77), 77 (21). Anal. Calcd. for $C_{19}H_{14}N_2O_3$: C: 71.69, H: 4.43, N: 8.80. found C: 71.64, H: 4.47, N: 8.78.

2-(4-Chlorophenyl)-5-phenyl-3,6-dioxo-6H-cyclopent[e]-[1,3,4]oxadiazine (9n)

Pale yel low nee dles; mp 187~188°C, IR (KBr): 1773, 1704 cm^{-1}; ^1H NMR, δ = 3.49 (s, 2H), 7.43~7.56, 7.90~7.95 (m, 5H), 7.58 (s, 4H). EIMS (70 eV), *m/z* (%): 340 (M^++2, 16), 338 (M^+, 49), 185 (11), 155 (10), 153 (33), 145 (100), 127 (14), 125 (21), 117 (27), 113 (5), 111 (14), 89 (91), 77 (11). Anal. Calcd. for $C_{18}H_{11}ClN_2O_3$: C: 63.82, H: 3.27, N: 8.27, Cl: 10.47. found C: 63.88, H: 3.30, N: 8.24, Cl: 10.36.

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Key Words

α-Chloroformylarylhydrazine;
1-Arylhydrazinecarbothioate;
2-Arylhydrazinecarboximidamide;
1,3,4-Thiadiazolin-5-one; 1,3,4-Oxadiazine.

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