The Syntheses of 4-Arylamino-1,2,3-triazoles and Stable 6-Sydnonyl verdazyls from Sydnone Derivatives and Their Fragments

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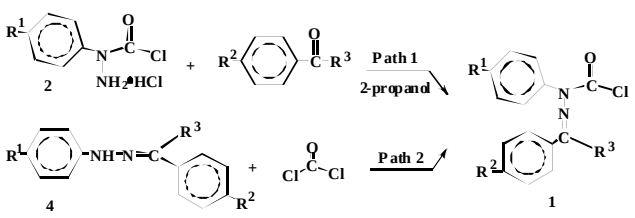
α-Chloroformylarylhydrazones **1** and α-chloroformylarylhydrazones of sydnonecarbaldehydes **3** have been prepared by a new synthetic route: α-chloroformylarylhydrazines hydrochlorides **2** reacted with corresponding carbonyl compounds. Reactions of compounds **3** with various hydrazines to give 6-sydnonyl-1,2,4,5-tetrazinan-3-ones **7** and/or carbazones **8** were also investigated. By oxidization with lead dioxide, compounds **7** were transformed to stable 6-sydnonyl-3,4-dihydro-3-oxo-1,2,4,5-tetrazin-1(2*H*)-yl radical derivatives **9** (sydnonyl verdazyls). Furthermore, sydnonecarbaldehydes arylhydrazones **5** through acidic conditions could be transferred to 4-arylamino-1,2,3-triazoles **6** which were also obtained by means of acidic decompositions of 4-formylsydnones **10**.

INTRODUCTION

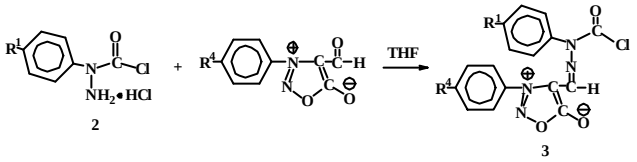
α-Chloroformylarylhydrazones **1** are potent precursors[1-2] of antiinflammatory drugs and many heterocyclic compounds. In this study, compounds **1** were prepared with good yields (Scheme I, path 1) by treatment of the α-chloroformylarylhydrazines hydrochlorides **2** with corresponding aromatical dehydes and ketones. Sydnone carbaldehyde α-chloroformylarylhydrazones **3** were also prepared (Scheme II) in high yields. Both condensation reactions were fast (within 40 min.) and proceeded at room temperature. In addition, the acidic decomposition of sydnonecarbaldehydes arylhydrazones **5** to obtain 4-arylamino-1,2,3-triazoles **6** is a new synthetic route for preparation of compounds **6** and is quite different from traditional methods.[3-5] The examination of acidic decomposition of 4-formylsydnone **10** which would produce compounds **6** has also been studied in this report.

Scheme I



Phosgene reacted with hydrazones **4** to give compounds **1** (Scheme I, path 2) had been reported in good yield by Milcent et al.[2] In their method, however, the reagent, phosgene, is an expensive and dangerous contraband, and reaction conditions require heating and anhydrous conditions. Hence we developed a new synthetic method (path 1) to prepare α-chloroformylarylhydrazones **1**.

Scheme II



According to the literature, 1,2,4,5-tetrazinan-3-ones and their oxidized products, verdazyls, possess liquid-crystal properties[6] and are nuclear magnetic resonance tomography contrast agents.[7] Also, sydnone compounds are well-known in their biological, pharmacological activities and their extremely special electronic structure. However, synthetic reactions using sydnones are experimentally demanding as these compounds are unstable toward both acidic and basic media. As a consequence, the synthesis must be carried out with careful consideration of temperature, reaction path, reagents, etc.[8]

For reasons mentioned above, we employed only sydnonecarbaldehyde α-chloroformylarylhydrazones **3** to prepare 6-sydnonyl-1,2,4,5-tetrazinan-3-ones **7** which were oxidized to give corresponding 6-sydnonyl-3,4-dihydro-3-oxo-1,2,4,5-tetrazin-1(2H)-yl radical derivatives, sydnonyl verdazyls **9**. These compounds are new molecules possessing

si mul ta neously a mesoionic group (sydnone) and a rad i cal group (verdazyls) as dis played in Scheme IV.

RE SULTS AND DIS CUS SION

In the re ac tion of com pounds **2** with al de hydes or ketones, the se lec tion of sol vent is ex tremely im por tant be cause com pounds **2** pos sess both nucleophilc (-NH_2) and electrophilc (-COCl) groups and hence it easily un der goes self-dimerization in sol vent.[9] THF and 2-propanol were suit able sol vents to pre pare com pounds **1** af ter a se quence of var i ous solvent studies. The former would dissolve the products (com pounds **1**), and re sulted in in con ve nient iso la tion and un satis fy ing yields. Using 2-propanol as sol vent, on the other hand, the prod ucts pre cip i tated and were con sid er ably pure as con firmed by el e ment anal y sis. Pres ented in Ta ble 1 are the syn thetic re sults.

Con trary to the above re sults, sydnonecarbaldehydes were quite in sol u ble in 2-propanol and did not re act with com pounds **2**, sydnonecarbaldehyde α-chloroformyl aryl-hydrazones **3** were prepared in THF at acid condition (Scheme II). Pu ri fi ca tion of each prod uct was also eas ily per-formed by sim ple fil tra tion from the re ac tion so lu tion and recrystallization from THF (Ta ble 2).

In view of the poor sta bil ity of sydnone ring, 4- aryl-amino-1,2,3-triazoles **6** might be ob tained by means of the acidic de com po si tion of com pounds **5** (Scheme III, (a)). After add ing $HCl_{(aq)}$ to the so lu tions of com pounds **5** in EtOAc and heat ing to 60 °C; the sydnone ring open ing and decarboxylation pro ceeded se quen tially to pro duce 4-arylamino-1,2,3-triazoles **6** (Ta ble 3, **6a-6i**). The re ac tion mech a nism pro posed in Scheme III is re ferred to as a photolysis mech a-nism of sydnone ring re ported by Marky[5] and the struc tures of com pounds **6** were iden ti fied by var i ous spec tral data and X-ray dif frac tion anal y sis (Fig. 1, Ta bles 6, 7, 8). An al ter na-tive method to syn the size com pounds **6** was ac com plished by acidic de com po si tion of 4-formylsydnones **10** (Scheme III, (b)) in the pres ence of HCl (in EtOAc at 60 °C); some mol e-cules of 4-formylsydnones trans ferred to arylhydrazine by acidic de com po si tion and con densed with other 4-formyl-sydnone mol e cules to form com pounds **5'**, which would be fur ther de com posed in the acidic con di tions to give com-pounds **6** (Ta ble 3, **6h-6k**). It is note wor thy that the same prod ucts (Ta ble 3, **6j-6k**) could be ob tained through acidic de com po si tion of sydnonecarbaldehyde alkylhydrazones **11** (R^6 = CH_3, H). When com pounds **11** (Scheme III, (c)) were adopted as start ing ma te ri als, acidic de com po si tion did not give the ex pected prod ucts, 4-arkylamino-1,2,3-triazoles **12**, but 4-arylamino-1,2,3-triazoles **6** were produced in low yields. These ob ser va tions can ac count for the hy dro ly sis of com pounds **11** that would give com pounds **10**. Acidic de-com po si tion and con den sa tion of com pound **10** gave com-pound **5'**, which was trans ferred to com pound **6** af ter fur ther acidic de com position.

Milcent[2] and Neugebauer[10] ob tained 1,2,4,5-tetra zinan-3-ones by the reaction of com pounds **1** with substituted hydrazines and fol lowed by ox i di za tion to give verdazyls de-riv a tives. We have also un der taken re ac tion stud ies of com-pounds **3** with hydrazine hy drate, methylhydrazine and var i-ous arylhydrazines hy dro chlor ides in the pres ence of tri-ethylamine. It was found that the com pounds **7** and/or sydnonecarbaldehyde carbazones **8** (Scheme IV) can be pro-vided. The re ac tions of com pounds **3** with hydrazine hy drate in eth a nol were con verted ex clu sively into the cor re spond ing

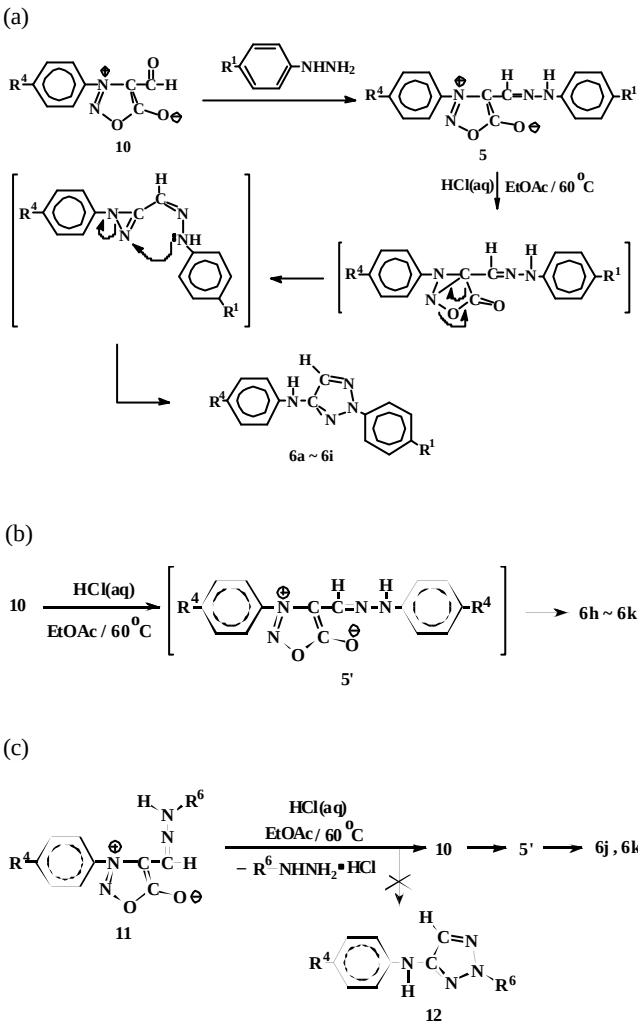
Table 2. Preparation of Compound **3** from Compound **2** in THF

Compound	R^1	R^4	Yield (%)
3a	H	H	78
3b	CH_3	H	80
3c	H	CH_3	88
3d	CH_3	CH_3	90
3e	Cl	CH_3	81
3f	H	CH_3O	76
3g	Cl	CH_3O	80
3h	CH_3O	CH_3O	85

Table 1. Preparation of Compound **1** from Compound **2** in 2-Propanol

Compound	R^1	R^2	R^3	Yield (%)	Mp (°C)	Mp (°C, liter.)
1a	H	H	H	78	101-102	101-102[2]
1b	H	CN	H	80	126.5-127.5	-
1c	H	CH_3O	H	77	91.5-92.5	92[2]
1d	Cl	CH_3O	H	82	112-113	-
1e	CH_3	H	CH_3	92	129-130	-
1f	CH_3O	H	CH_3	91	123-124	-
1g	Cl	H	CH_3	88	108-109	-

Scheme III



carbazones **8**, whereas only cy clic prod ucts **7** were ob tained by the re ac tion with methylhydrazine.

In ad di tion, when arylhydrazines were em ployed to react with com pounds **3**, the re ac tions pro ceeded via 1-N and/or 2-N-acylations of arylhydrazines and gave com pounds **7** and/or **8**. The yield ra tios of com pounds **7/8** were de pend ent on the electronic ef fects of the sub stitu ents borne by the arylhydrazines. Phenyl-, 4-methylphenyl- and 4-ethoxyphen yl hydrazines re acted with com pounds **3** to give compounds **7** and **8** in good yields and the yield ra tios of compounds **7**/**8** were 1/1, 1/1 and 8/1, re spec tively. For re ac tion of 4-ethoxycarbonyl-phenylhydrazine hy dro chlo ride with compounds **3**, 1-N-acylation could not pro ceed and were converted only into the cor re spond ing carbazones **8** since the elec tron den sity of 1-N de creased due to the π-withdrawing na ture of the ethoxycarbonyl group. How ever, when 4- fluoro phenyl hydrazine re acted with com pounds **3**, the yield ra-

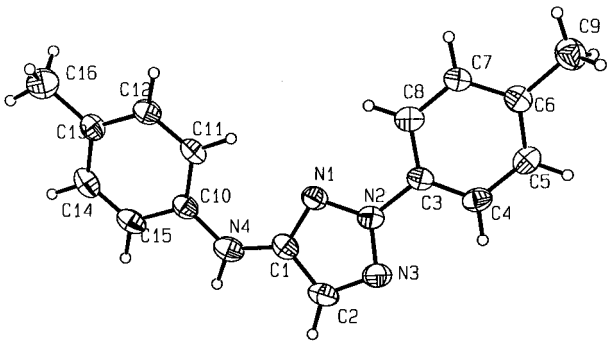


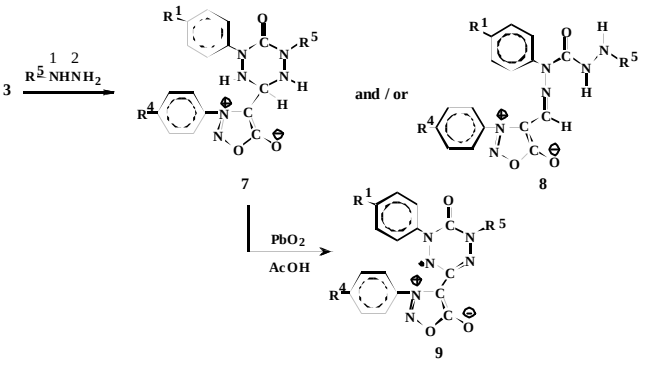
Fig. 1. Mo lec u lar struc ture of 2-(4-methylphenyl)-4-(4-methylphenylamino)-2*H*-1,2,3-triazole (**6h**).

Table 3. Preparation of Compounds **6** from Compounds **5**, **10**, **11**

Compound	R^1	R^4	Yield%[1]	Yield%[2]	Yield%[3]
6a	*p*-CH_3	*p*-EtO	52	-	-
6b	*p*-CH_3	*p*-CH_3O	81	-	-
6c	*p*-CH_3	H	61	-	-
6d	H	*p*-EtO	40	-	-
6e	H	*p*-CH_3O	59	-	-
6f	H	*p*-CH_3	60	-	-
6g	*p*-Cl	*p*-CH_3O	70	-	-
6h	*p*-CH_3	*p*-CH_3	61	70	-
6i	H	H	72	30	-
6j		*p*-EtO	-	62	10*[1]
6k		*p*-CH_3O	-	57	10*[2]

Starting material: [1] = compound **5**, [2] = compound **10**, [3] = compound **11**.
*1: R_6 = CH_3. *2: R_6 = H.

Scheme IV



tios of **7**/**8** were ap prox i mately 2/1, which were higher than **7**/**8** ra tios of phenylhydrazine re acted with com pounds **3**, even though the flu o ride is σ-with draw ing group and would de mote the charge den sity of 1-N. All the yields of compounds **7** and **8** are pre sented in Ta ble 4.

Ox i da tions of 6-sydnoyl-1,2,4,5-tetrazinan-3-ones **7** with lead di ox ide into sta ble sydnonyl-3-oxo-1,2,4,5- tetrazinyl rad i cal, sydnonyl-verdazyls **9** (Scheme IV), were performed in CH_2Cl_2 with acetic acid (Table 5). Sydnonyl verdazyls **9** are new mol e cules of rad i cal with high sta bil ity, i.e., de com po si tion of these com pounds was not ob served after one year at room tem per a ture. Struc ture iden ti fi ca tion of these mol e cules is based on the fol low ing spec tro scopic data. No pro ton sig nal ex cept wa ter and DMSO-d_6 peaks pre sented at ^{1}H NMR spec tra and there was not an N-H stretch ing sig nal in the IR spec tra. The mo lec u lar weight and com po si tion anal y sis were iden ti fied by both mass spec tros copy and el e-mentanalysis.

CONCLUSION

4-Arylamino-1,2,4-triazoles **6** could be syn the sized by acidic de com po si tions of ei ther sydnonecarbaldehydes aryl-hydrazones **5** or 4-formylsydnones **10**. Using α-Chloro for-mylarylhydrazines **2** as start ing ma te ri als, α-chloro formyl-hydrazones of al de hydes, ke tones and sydnonecarbaldehydes might be pre pared more eas ily and safely. In the syn thetic study of sydnonylverdazyls **9**, these re sults pre sented that the methyl- and methoxyphenyl hydrazines were better re agents to pre pare com pounds **7** and the par ti tions of in ter me di ates **7**/**8** were ex tremely de pend ent on the elec tronic ef fects of the sub stitu ents borne by the arylhydrazines. By ox i di za tion, com pounds **7** were trans formed into sydnonylverdazyls **9**, pos sess ing both mesoionic and rad i cal struc ture at trib utes.

EXPERIMENTAL SECTION

General

Melting points (Buchi 535 ap pa ra tus) are un cor rected. IR spec tra were re corded on a Hitachi 270-30 in fra red spec-

Table 4. Preparation of Compounds **7** and **8** from Compounds **3**

Starting material	R^1	R^4	R^5	Yield (%)			
				Compound **7**		Compound **8**	
3f	H	CH_3O	H	**7a**	-	**8a**	80
3h	CH_3O	CH_3O	H	**7b**	-	**8b**	83
3f	H	CH_3O	CH_3	**7c**	76	**8c**	-
3g	Cl	CH_3O	CH_3	**7d**	81	**8d**	-
3h	CH_3O	CH_3O	CH_3	**7e**	88	**8e**	-
3f	H	CH_3O	*p*-$CH_3OC_6H_4$	**7f**	79	**8f**	10
3f	H	CH_3O	*p*-$CH_3C_6H_4$	**7g**	51	**8g**	30
3b	CH_3	H	C_6H_5	**7h**	44	**8h**	38
3d	CH_3	CH_3	C_6H_5	**7i**	48	**8i**	41
3e	Cl	CH_3	C_6H_5	**7j**	43	**8j**	44
3f	H	CH_3O	C_6H_5	**7k**	50	**8k**	37
3g	Cl	CH_3O	C_6H_5	**7l**	51	**8l**	37
3h	CH_3O	CH_3O	C_6H_5	**7m**	53	**8m**	36
3c	H	CH_3	*p*-FC_6H_4	**7n**	56	**8n**	29
3d	CH_3	CH_3	*p*-FC_6H_4	**7o**	54	**8o**	30
3d	CH_3	CH_3	*p*-$EtOCOC_6H_4$	**7p**	-	**8p**	82
3e	Cl	CH_3	*p*-$EtOCOC_6H_4$	**7q**	-	**8q**	85

Table 5. Preparation of Compound **9** from Compound **7**

Compound **9**	R^1	R^4	R^5	Yield%
9a	CH_3	H	C_6H_5	65
9b	CH_3	CH_3	C_6H_5	62
9c	Cl	CH_3	C_6H_5	68
9d	H	CH_3O	C_6H_5	70
9e	Cl	CH_3O	C_6H_5	71
9f	CH_3O	CH_3O	C_6H_5	67

trometer. ^{1}H NMR spectra were measured on a Bruker AMX-200 NMR spectrometer with tetramethylsilane as internal standard, ^{13}C NMR spectra were run on a Bruker AC-300 in DMSO-d_6. The mass spectra were registered on a Finnigan MAT TSQ-46C spectrometer at an ionizing potential 70 eV. Elemental analyses were performed on Heraeus CHN- O-Rapid and Tacussel Coulomax 78 analyzers. UV spectra were taken on a Hitachi U-2000 Spectrophotometer. X-ray intensity data was collected with a Nonius CAD-4 diffractometer. Column chromatography was carried out on silica gel (Kieselgel 100, 230-400 mesh, E. Merck).

Preparation of α-Chloroformylarylhydrazones of Aldehydes 1a~1d and ketones 1e~1g

A solution of α-chloroformylarylhydrazine hydrochloride **1a** (0.828 g, 4 mmol) and benzaldehyde (0.467 g, 4.4 mmol) in 10 mL of *i*-PrOH (1 drop of H_2SO_4 was added for reaction of **1e~1g**) was stirred at room temperature for 30 minutes. The precipitating solid was collected by filtration, washed with cold *i*-PrOH and dried to afford pure powder product **1a** (0.833 g, 81%).

Table 6. Crystal Data of **6h**

Formula	$C_{16}H_{16}N_4$
Formula weight	264.33
Cryst system	Orthorhombic
Space group	P-$2_12_12_1$
a/Å	6.224 (7)
b/Å	7.586 (8)
c/Å	29.150 (7)
V/Å^3	1376.4 (22)
Z	4
D_c/g cm^3	1.271
F_{000}	556.19
λ (Mo-Kα) Å	0.70930
μ/cm^{-1}	0.07
Range/deg	12.64-26.10
Scan type	2θ
$2\theta_{max}$/deg.	44.9
Reflections measured	3964
Unique reflections	1807
Observed reflections	1559
Refined parameters	182
R_f for significant reflections	0.035
R_w for significant reflections	0.048
GoF	1.41

Table 7. Bond Distances/Å of **6h**

C(1)-C(2)	1.394(8)	C(9)-H(9c)	0.951
C(1)-N(1)	1.319(7)	C(10)-C(11)	1.387(7)
C(1)-N(4)	1.351(7)	C(10)-C(15)	1.382(7)
C(2)-N(3)	1.328(7)	C(10)-N(4)	1.409(8)
C(2)-H(2)	0.952(5)	C(11)-C(12)	1.371(8)
C(3)-C(4)	1.352(7)	C(11)-H(11)	0.952
C(3)-C(8)	1.373(7)	C(12)-C(13)	1.388(7)
C(3)-N(2)	1.434(6)	C(12)-H(12)	0.952
C(4)-C(5)	1.401(8)	C(13)-C(14)	1.382(9)
C(4)-H(4)	0.950	C(13)-C(16)	1.505(8)
C(5)-C(6)	1.380(8)	C(14)-C(15)	1.369(9)
C(5)-H(5)	0.951	C(14)-H(14)	0.952
C(6)-C(7)	1.395(7)	C(15)-H(15)	0.951
C(6)-C(9)	1.469(7)	C(16)-H(16a)	0.951
C(7)-C(8)	1.367(7)	C(16)-H(16b)	0.949
C(7)-H(7)	0.952	C(16)-H(16c)	0.950
C(8)-H(8)	0.952	N(1)-N(2)	1.367(6)
C(9)-H(9a)	0.950	N(2)-N(3)	1.318(6)
C(9)-H(9b)	0.950	N(4)-H(N4)	0.952

Benzaldehyde α-chloroformylphenylhydrazone (1a)

White powder, IR (KBr), cm^{-1}: 1728 (ν C=O), 1593 (ν C=N), ^{1}H NMR (Acetone-d_6), δ = 7.74~7.60 (m, *J* = 5H), 7.50 (s, 1H), 7.47~7.42 (m, 5H), EIMS (70 eV) *m/z* (%): 260 (M^++2, 8), 258 (M^+, 25), 221 (5), 195 (100), 167 (34), 155 (21), 120 (30), 104 (30), 89 (38), 77 (77). Anal. Calcd for $C_{14}H_{11}N_2OCl$ (258.70): C: 65.00, H: 4.29, N: 10.83. found C: 64.97, H: 4.31, N: 10.86.

4-Cyanobenzaldehyde α-chloroformylphenylhydrazone (1b)

Yellow powder, IR (KBr), cm^{-1}: 2224 (ν CN), 1734 (ν C=O), 1602 (ν C=N), ^{1}H NMR (Acetone-d_6), δ = 7.94 (d, *J* = 8.5 Hz, 2H), 7.83 (d, *J* = 8.5 Hz, 2H), 7.73~7.62 (m, 3H), 7.56 (s, 1H), 7.46 (dd, *J* = 7.9, 2.0 Hz, 2H). EIMS (70 eV) *m/z* (%): 285 (M^++2, 8), 283 (M^+, 24), 248 (7), 220 (100), 192 (18), 155 (12), 119 (29), 102 (25), 91 (24), 77 (59). Anal. Calcd for $C_{15}H_{10}N_3OCl$ (283.71): C: 63.50, H: 3.55, N: 14.81. found C: 63.52, H: 3.69, N: 14.72.

4-Methoxybenzaldehyde α-chloroformylphenylhydrazone (1c)

Yellow powder, IR (KBr), cm^{-1}: 1725 (ν C=O), 1611 (ν C=N), ^{1}H NMR (Acetone-d_6), δ = 7.68~7.56 (m, 5H), 7.45~

Table 8. Bond Angles/deg of **6h**

C(2)-C(1)-N(1)	109.1(5)	C(11)-C(10)-N(4)	124.3(4)
C(2)-C(1)-N(4)	126.0(5)	C(15)-C(10)-N(4)	117.5(5)
N(1)-C(1)-N(4)	124.9(5)	C(10)-C(11)-C(12)	120.2(4)
C(1)-C(2)-N(3)	109.3(3)	C(10)-C(11)-H(11)	121.1
C(1)-C(2)-H(2)	124.8	C(12)-C(11)-H(11)	118.8
N(3)-C(2)-H(2)	125.9	C(11)-C(12)-C(13)	122.1(5)
C(4)-C(3)-C(8)	121.0(5)	C(11)-C(12)-H(12)	117.2
C(4)-C(3)-N(2)	120.4(5)	C(13)-C(12)-H(12)	120.6
C(8)-C(3)-N(2)	118.6(4)	C(12)-C(13)-C(14)	117.0(5)
C(3)-C(4)-C(5)	119.5(5)	C(12)-C(13)-C(16)	121.2(5)
C(3)-C(4)-H(4)	118.8	C(14)-C(13)-C(16)	121.8(5)
C(5)-C(4)-H(4)	121.6	C(13)-C(14)-C(15)	121.4(5)
C(4)-C(5)-C(6)	120.9(4)	C(13)-C(14)-H(14)	120.0
C(4)-C(5)-H(5)	119.7(6)	C(15)-C(14)-H(14)	118.6
C(6)-C(5)-H(5)	119.4(6)	C(10)-C(15)-C(14)	121.2(5)
C(5)-C(6)-C(7)	117.2(5)	C(10)-C(15)-H(15)	119.6
C(5)-C(6)-C(9)	122.6(5)	C(14)-C(15)-H(15)	119.2
C(7)-C(6)-C(9)	120.2(5)	C(13)-C(16)-H(16a)	110.6
C(6)-C(7)-C(8)	121.9(5)	C(13)-C(16)-H(16b)	112.7
C(6)-C(7)-H(7)	120.4	C(13)-C(16)-H(16c)	109.9
C(8)-C(7)-H(7)	117.7	H(16a)-C(16)-H(16c)	108.7
C(3)-C(8)-C(7)	119.4(5)	H(16a)-C(16)-H(16c)	105.6
C(3)-C(8)-H(8)	118.5	H(16b)-C(16)-H(16c)	109.2
C(7)-C(8)-H(8)	122.1	C(1)-N(1)-N(2)	102.9(4)
C(6)-C(9)-H(9a)	112.5	C(3)-N(2)-N(1)	123.1(4)
C(6)-C(9)-H(9b)	111.5	C(3)-N(2)-N(3)	121.8(4)
C(6)-C(9)-H(9c)	109.6	N(1)-N(2)-N(3)	115.0(4)
H(9a)-C(9)-H(9b)	109.7	C(2)-N(3)-N(2)	103.7(4)
H(9a)-C(9)-H(9c)	107.3	C(1)-N(4)-C(10)	129.3(4)
H(9b)-C(9)-H(9c)	105.9	C(1)-N(4)-H(N4)	115.7
C(11)-C(10)-C(15)	118.2(5)	C(10)-N(4)-H(N4)	115.0

7.40 (m, 3H), 6.98 (d, J = 8.8 Hz, 2H), 3.83 (s, 3H). EIMS (70 eV) *m/z* (%): 290 (M^++2, 13), 288 (M^+, 42), 225 (68), 210 (11), 182 (56), 155 (20), 134 (40), 119 (27), 91 (53), 77 (100), 63 (49). Anal. Calcd for $C_{15}H_{13}N_2O_2Cl$ (288.73): C: 62.40, H: 4.54, N: 9.70. found C: 62.41, H: 4.59, N: 9.81.

4-Methoxybenzaldehyde α-chloroformyl-4-chlorophenylhydrazone (1d)

White pow der, IR (KBr), cm^{-1}: 1713 (ν C=O), 1605 (ν C=N), ^{1}H NMR (Ac e tone-d_6), δ = 7.71~7.65 (m, 4H), 7.52 (d, J = 8.9 Hz, 2H), 7.46 (s, 1H), 6.98 (d, J = 8.9 Hz, 2H), 3.84 (s, 3H). EIMS (70 eV) *m/z* (%): 326 (M^++4, 7), 324 (M^++2, 36), 322 (M^+, 54), 261 (32), 259 (100), 224 (32), 216 (40), 153 (40), 134 (77), 111 (48), 91 (50), 77 (74). Anal. Calcd for $C_{15}H_{12}N_2O_2Cl_2$ (323.18): C: 55.75, H: 3.74, N: 8.67. found C: 55.80, H: 3.83, N: 8.87.

Acetophenone α-chloroformyl-4-methylphenylhydrazone (1e)

White pow der, IR (KBr), cm^{-1}: 1722 (ν C=O), ^{1}H NMR (DMSO-d_6), δ = 7.88 (d, J = 8.0 Hz, 2H), 7.53 (d, J = 7.8 Hz, 2H), 7.51 (m, 1H), 7.42 (d, J = 7.8 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 2.38 (s, 3H), 2.32 (s, 3H), FABMS (1.13 eV) *m/z* (%): 287 (M^++1, 36), 286 (M^+, 24). Anal. Calcd for $C_{16}H_{15}N_2OCl$ (286.76): C: 67.01, H: 5.27, N: 9.76. found C: 66.93, H: 5.29, N: 9.74.

Acetophenone α-chloroformyl-4-methoxyphenylhydrazone (1f)

Pale yel low pow der; IR (KBr), cm^{-1}: 1728 (ν C=O), ^{1}H NMR (DMSO-d_6), δ = 7.85 (d, J = 8.0 Hz, 2H), 7.53-7.41 (m, 5H), 7.00 (d, J = 8.1 Hz, 2H), 3.76 (s, 3H), 2.39 (s, 3H), FABMS (1.26 eV) *m/z* (%): 305 (M^++3, 34), 304 (M^++2, 31), 303 (M^++1, 77), 302 (M^+, 68). Anal. Calcd for $C_{16}H_{15}N_2O_2Cl$ (302.76): C: 63.47, H: 4.99, N: 9.25. found C: 63.42, H: 5.09, N: 9.31.

Acetophenone α-chloroformyl-4-chlorophenylhydrazone (1g)

White pow der; IR (KBr), cm^{-1}: 1713 (ν C=O), ^{1}H NMR (DMSO-d_6), δ = 7.77 (d, J = 8.2 Hz, 2H), 7.51-7.48 (m, 5H), 7.23 (d, J = 8.2 Hz, 2H), 2.24 (s, 3H), FABMS (1.26 eV) *m/z*

(%): 309 (M^++3, 32), 307 (M^++1, 50). Anal. Calcd for $C_{15}H_{12}N_2OCl_2$ (307.18): C: 58.70, H: 4.08, N: 9.46. found C: 58.81, H: 4.07, N: 9.37.

Preparation of sydnonecarbaldehyde α-chloroformyl-arylhydrazones 3a~3h

A solution of α-chloroformylphenylhydrazine hydrochloride (0.327 g, 1.58 mmol) and 0.3 g (1.58 mmol) of 3-phenylsydnonecarbaldehyde in THF (5 mL) was stirred at room temperature for 30 minutes. The precipitating solid was collected by filtration and the filtrate was removed under reduced pressure. 10 mL of *i*-PrOH was added, stirred and then filtered. The solid products were combined and recrystallized with THF to obtain 3-phenylsydnonecarbaldehyde α-chloroformylphenylhydrazone **3a** (0.481 g, 78%).

3-Phenylsydnon-4-ylformaldehyde α-chloroformyl-4-methylphenylhydrazone (3a)

Yellow needles; mp 201-202°C, IR (KBr), cm^{-1}: 1779, 1716 (ν C=O), ^{1}H NMR (Acetone-d_6), δ = 7.81-7.68 (m, 5H), 7.61-7.29 (m, 5H), 7.02 (s, 1H). EIMS (70 eV) *m/z* (%): 344 (M^++2, 8), 342 (M^+, 44), 284 (100), 249 (3), 221 (12), 119 (49), 104 (69), 77 (79). Anal. Calcd for $C_{17}H_{13}O_3N_4Cl$: (342.74) C: 56.07, H: 3.23, N: 16.35. found C: 56.07, H: 3.24, N: 16.31.

3-Phenylsydnon-4-ylformaldehyde α-chloroformyl-4-methylphenylhydrazone (3b)

Yellow needles; mp 209-210°C, IR (KBr), cm^{-1}: 1758, 1737 (ν C=O), ^{1}H NMR (Acetone-d_6), δ = 7.70-7.51 (m, 5H), 7.42 (d, *J* = 8.3 Hz, 2H), 7.18 (d, *J* = 8.3 Hz, 2H), 7.04 (s, 1H), 2.39 (s, 3H), EIMS (70 eV), *m/z* (%): 358 (M^++2, 12), 356 (M^+, 37), 298 (100), 235 (8), 133 (50), 104 (55), 91 (29), 77 (41). Anal. Calcd for $C_{17}H_{13}O_3N_4Cl$: (356.76) C: 57.23, H: 3.67, N: 15.70. found C: 57.15, H: 3.71, N: 15.66.

3-(4-Methylphenyl)sydnon-4-ylformaldehyde α-chloroformylphenylhydrazone (3c)

Yellow powder; mp 199-200°C, IR (KBr), cm^{-1}: 1773, 1734 (ν C=O), ^{1}H NMR (Acetone-d_6), δ = 7.70-7.38 (m, 5H), 7.42 (d, *J* = 8.3 Hz, 2H), 7.18 (d, *J* = 8.3 Hz, 2H), 6.77 (s, 1H), 2.39 (s, 3H), EIMS (70 eV), *m/z* (%): 358 (M^++2, 11), 356 (M^+, 33), 298 (100), 235 (7), 119 (34), 105 (4), 91 (51), 77 (28). Anal. Calcd. for $C_{17}H_{13}O_3N_4Cl$: C: 57.23, H: 3.67, N: 15.70. found C: 57.17, H: 3.70, N: 15.66.

3-(4-Methylphenyl)sydnon-4-ylformaldehyde α-chloroformyl-4-methylphenyl-hydrazone (3d)

Yellow needles; mp 208-209°C, IR (KBr), cm^{-1}: 1755, 1731 (ν C=O), ^{1}H NMR (Acetone-d_6), δ = 7.67 (d, *J* = 8.3 Hz, 2H), 7.51 (d, *J* = 8.3 Hz, 2H), 7.40 (s, 1H), 6.92 (d, *J* = 8.3 Hz, 2H), 6.54 (d, *J* = 8.3 Hz, 2H), 2.07 (s, 3H), 2.06 (s, 3H), EIMS (70 eV), *m/z* (%): 372 (M^++2, 14), 370 (M^+, 40), 312 (100), 249 (10), 133 (28), 118 (44), 105 (16), 91 (44), 77 (69). Anal. Calcd. for $C_{18}H_{15}O_3N_4Cl$: C: 58.31, H: 4.08, N: 15.11. found C: 58.31, H: 4.15, N: 15.00.

3-(4-Methylphenyl)sydnon-4-ylformaldehyde α-chloroformyl-4-chlorophenyl-hydrazone (3e)

Yellow needles; mp 214-215°C, IR (KBr), cm^{-1}: 1776, 1737 (ν C=O), ^{1}H NMR (Acetone-d_6), δ = 7.68 (d, *J* = 8.3 Hz, 2H), 7.44 (d, *J* = 8.3 Hz, 2H), 7.40 (s, 1H), 6.88 (d, *J* = 7.7 Hz, 2H), 6.56 (d, *J* = 7.7 Hz, 2H), 2.07 (s, 3H), EIMS (70 eV), *m/z* (%): 394 (M^++4, 5), 392 (M^++2, 22), 390 (M^+, 33), 322 (100), 269 (6), 153 (33), 118 (95), 91 (36). Anal. Calcd. for $C_{17}H_{12}O_3N_4Cl_2$: C: 52.19, H: 3.09, N: 14.32. found C: 52.13, H: 3.13, N: 14.16.

3-(4-Methoxyphenyl)sydnon-4-ylformaldehyde α-chloroformylphenylhydrazone (3f)

Yellow powder; mp 168-169°C, IR (KBr), cm^{-1}: 1779, 1725 (ν C=O), ^{1}H NMR (Acetone-d_6), δ = 7.80-7.52 (m, 5H), 7.55 (d, *J* = 8.3 Hz, 2H), 7.20 (d, *J* = 8.3 Hz, 2H), 6.94 (s, 1H), 3.98 (s, 3H), EIMS (70 eV), *m/z* (%): 374 (M^++2, 10), 372 (M^+, 20), 314 (100), 251 (7), 134 (633), 119 (24), 77 (35). Anal. Calcd. for $C_{17}H_{13}O_4N_4Cl$: C: 54.78, H: 3.51, N: 15.03. found C: 54.82, H: 3.50, N: 15.05.

3-(4-Methoxyphenyl)sydnon-4-ylformaldehyde α-chloroformyl-4-chlorophenyl-hydrazone (3g)

Yellow needles; mp 200-201°C, IR (KBr), cm^{-1}: 1776, 1740 (ν C=O), ^{1}H NMR (Acetone-d_6), δ = 7.42 (d, *J* = 8.2 Hz, 2H), 7.16 (d, *J* = 8.2 Hz, 2H), 7.04 (s, 1H), 6.88 (d, *J* = 7.4 Hz, 2H), 6.54 (d, *J* = 7.4 Hz, 2H), 4.01 (s, 3H), EIMS (70 eV), *m/z* (%): 410 (M^++4, 1), 408 (M^++2, 5), 406 (M^+, 8), 348 (29), 286 (21), 134 (100), 125 (24), 111 (30). Anal. Calcd. for $C_{17}H_{12}O_4N_4Cl_2$: C: 50.14, H: 2.97, N: 13.76. found C: 50.05, H: 2.87, N: 13.67.

3-(4-Methoxyphenyl)sydnon-4-ylformaldehyde α-chloroformyl-4-methoxyphenyl-hydrazone (3h)

Yellow needles; mp 188.5-189.5 °C, IR (KBr), cm^{-1}: 1782, 1725 (ν C=O), ^{1}H NMR (Acetone-d_6), δ = 7.70 (d, *J* = 9.0 Hz, 2H), 7.26~7.09 (m, 6H), 7.06 (s, 1H), 3.93 (s, 3H), 3.87 (s, 3H), EIMS (70 eV), *m/z* (%): 404 (M^++2, 10), 402 (M^+, 29), 346 (29), 344 (87), 309 (15), 281 (11), 168 (13), 149 (100), 134 (92), 121 (31), 107 (27), 92 (20). Anal. Calcd. for $C_{18}H_{15}O_5N_4Cl$: C: 53.67, H: 3.75, N: 13.91. found C: 53.44, H: 3.77, N: 13.85.

Preparation of 4-Arylamino-1,2,3-triazoles 6a~6k

A solution of 3-(4-ethoxyphenyl)sydnonecarbaldehyde

4-methylphenylhydrazone (0.3 g, 0.9 mmol) in EtOAc (5 mL) and aque ous HCl (0.5 mL, 12 M) was heated at 60 °C for 1 hr. The sol vent was re moved un der re duced pres sure. 6 mL of *i*-PrOH was added to the vis cous so lu tion, decolorized with char coal and fil tered. The fil trate was then dropped into 20 mL of wa ter, and crude prod uct was col lected by fil tra tion. Recrystallization us ing EtOAc-hexane af forded 0.14 g of **6a** (52%).

Preparation of com pounds **6i-6k** from 4-formyl-sydnones **10** or sydnonecarbaldehydes alkylhydrazones was ac cord ing to the above pro ce dure.

2-(4-Methylphenyl)-4-(4-ethoxyphenylamino)-2*H*-1,2,3-triazole (6a)

Yel low pow der; mp 96.5~97.5°C, IR (KBr), cm^{-1}: 3328 (ν N-H), 1596 (ν C=N), ^1H NMR (DMSO-d_6), δ = 8.89 (s, 1H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.54 (s, 1H), 7.37 (d, *J* = 8.9 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 8.9 Hz, 2H), 3.95 (q, *J* = 6.9 Hz, 2H), 1.29 (s, 3H), 1.29 (t, *J* = 6.9 Hz, 3H), EIMS (70 eV), *m/z* (%): 294 (M^+, 100), 265 (77), 149 (3), 134 (7), 105 (15), 91 (18), 69 (7), 65 (7). Anal. Calcd. for $C_{17}H_{18}N_4O$: C: 69.37, H: 6.16, N: 19.03. found C: 69.25, H: 6.18, N: 19.17.

2-(4-Methylphenyl)-4-(4-methoxyphenylamino)-2*H*-1,2,3-triazole (6b)

Yel low pow der; mp 75.5~76.5°C, IR (KBr), cm^{-1}: 3352 (ν N-H), 1596 (ν C=N), ^1H NMR (DMSO-d_6), δ = 8.89 (s, 1H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.54 (s, 1H), 7.39 (d, *J* = 8.9 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 8.9 Hz, 2H), 3.70 (s, 3H), 2.33 (s, 3H), EIMS (70 eV), *m/z* (%): 280 (M^+, 100), 265 (45), 188 (3), 165 (4), 133 (11), 105 (32), 91 (22), 77 (16). Anal. Calcd. for $C_{16}H_{16}N_4$: C: 72.70, H: 6.10, N: 21.20. found C: 72.56, H: 6.18, N: 21.23.

2-(4-Methylphenyl)-4-phenylamino-2*H*-1,2,3-triazole (6c)

Yel low pow der; mp 97.5~98.8°C, IR (KBr), cm^{-1}: 3322 (ν N-H), 1605 (ν C=N), ^1H NMR (DMSO-d_6), δ = 9.15 (s, 1H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.63 (s, 1H), 7.46 (d, *J* = 7.7 Hz, 2H), 7.35~7.24 (m, *J* = 4H), 6.86 (t, *J* = 7.3 Hz, 1H), 2.34 (s, 3H), EIMS (70 eV), *m/z* (%): 250 (M^+, 100), 222 (4), 118 (7), 105 (29), 104 (14), 91 (17), 77 (13). Anal. Calcd. for $C_{15}H_{14}N_4$: C: 71.98, H: 5.64, N: 22.38. found C: 71.98, H: 5.65, N: 22.38.

4-(4-Ethoxyphenylamino)-2-phenyl-2*H*-1,2,3-triazole (6d)

Yel low pow der; mp 70.5~71.5°C, IR (KBr), cm^{-1}: 3348 (ν N-H), 1598 (ν C=N), ^1H NMR (DMSO-d_6), δ = 8.96 (s, 1H), 7.92 (d, *J* = 8.2 Hz, 2H), 7.59 (s, 1H), 7.56~7.38 (m, 4H), 7.28 (t, *J* = 7.4 Hz, 1H), 6.88 (d, *J* = 9.0 Hz, 2H), 3.94 (q, *J* = 6.9 Hz, 2H), 1.28 (t, *J* = 6.9 Hz, 3H), EIMS (70 eV), *m/z* (%): 280 (M^+, 100), 264 (12), 252 (29), 251 (88), 134 (11), 92 (21), 91 (29), 77 (69). Anal. Calcd. for $C_{16}H_{16}N_4O$: C: 68.55, H: 5.75, N: 19.98. found C: 68.41, H: 5.90, N: 20.00.

4-(4-Methoxyphenylamino)-2-phenyl-2*H*-1,2,3-triazole (6e)

Yel low pow der; mp 79.5~80.5°C, IR (KBr), cm^{-1}: 3348 (ν N-H), 1598 (ν C=N), ^1H NMR (DMSO-d_6), δ = 8.94 (s, 1H), 7.91 (d, *J* = 7.8 Hz, 2H), 7.58 (s, 1H), 7.52 (t, *J* = 7.8 Hz, 2H), 7.41 (d, *J* = 8.9 Hz, 2H), 7.29 (t, *J* = 7.8 Hz, 1H), 6.90 (d, *J* = 8.9 Hz, 2H), 3.70 (s, 3H), EIMS (70 eV), *m/z* (%): 266 (M^+, 100), 251 (71), 252 (10), 148 (12), 133 (36), 105 (25), 91 (40), 91 (40), 77 (95). Anal. Calcd. for $C_{15}H_{14}N_4O$: C: 67.65, H: 5.30, N: 21.04. found C: 67.53, H: 5.41, N: 20.97.

4-(4-Methylphenylamino)-2-phenyl-2*H*-1,2,3-triazole (6f)

Yel low pow der; mp 73.5~75.0°C, IR (KBr), cm^{-1}: 3340 (ν N-H), 1605 (ν C=N), ^1H NMR (DMSO-d_6), δ = 9.06 (s, 1H), 7.94 (d, *J* = 8.3 Hz, 2H), 7.64 (s, 1H), 7.54 (t, *J* = 8.3 Hz, 2H), 7.39~7.31 (m, *J* = 3H), 7.11 (t, *J* = 8.4 Hz, 2H), 2.25 (s, 3H), EIMS (70 eV), *m/z* (%): 250 (M^+, 100), 222 (11), 194 (4), 131 (7), 118 (6), 107 (5), 91 (26). Anal. Calcd. for $C_{15}H_{14}N_4$: C: 71.98, H: 5.64, N: 22.38. found C: 71.95, H: 5.68, N: 22.17.

2-(4-Chlorophenyl)-4-(4-methoxyphenylamino)-2*H*-1,2,3-triazole (6g)

Yel low pow der; mp 96.5~97.5°C, IR (KBr), cm^{-1}: 3328 (ν N-H), 1605 (ν C=N), ^1H NMR (DMSO-d_6), δ = 9.01 (s, 1H), 7.91 (d, *J* = 9.0 Hz, 2H), 7.61 (s, 1H), 7.57 (d, *J* = 9.1 Hz, 2H), 7.41 (d, *J* = 9.0 Hz, 2H), 6.90 (d, *J* = 9.1 Hz, 2H), 3.70 (s, 3H), EIMS (70 eV), *m/z* (%): 302 (M^++2, 37), 300 (M^+, 100), 285 (48), 148 (8), 133 (15), 125 (12), 111 (16), 90 (10). Anal. Calcd. for $C_{15}H_{13}N_4OCl$: C: 59.91, H: 4.36, N: 18.63. found C: 59.77, H: 4.50, N: 18.64.

4-(4-Methylphenylamino)-2-(4-methylphenyl)-2*H*-1,2,3-triazole (6h)

Yel low pow der; mp 149.5~150.0 °C, IR (KBr), cm^{-1}: 3406 (ν N-H), 1614 (ν C=N), ^1H NMR (DMSO-d_6), δ = 9.00 (s, 1H), 7.80 (d, *J* = 8.5 Hz, 2H), 7.58 (s, 1H), 7.36~7.29 (m, 4H), 7.09 (d, *J* = 8.4 Hz, 2H), 2.34 (s, 3H), 2.23 (s, 3H). EIMS (70 eV), *m/z* (%): 264 (M^+, 100), 131 (9), 118 (6), 106 (14), 105 (31), 91 (35), 78 (12). Anal. Calcd. for $C_{16}H_{16}N_4$: C: 72.70, H: 6.10, N: 21.20. found C: 72.55, H: 6.19, N: 21.24.

4-Phenylamino-2-phenyl-2*H*-1,2,3-triazole (6i)

Yel low pow der; mp 85~86 °C, IR (KBr), cm^{-1}: 3328 (ν N-H), 1605 (ν C=N), ^1H NMR (DMSO-d_6), δ = 9.20 (s, 1H), 7.94 (d, *J* = 8.0 Hz, 2H), 7.67 (s, 1H), 7.58~7.25 (m, 7H), 6.86 (t, *J* = 7.6 Hz, 1H). EIMS (70 eV), *m/z* (%): 236 (M^+, 100), 208 (13), 180 (6), 118 (7), 104 (8), 91 (48), 77 (57). Anal. Calcd. for $C_{14}H_{12}N_4$: C: 71.17, H: 5.12, N: 23.71. found C: 71.10, H: 5.16, N: 23.70.

2-(4-Ethoxyphenyl)-4-(4-ethoxyphenylamino)-2*H*-1,2,3-triazole (6j)

Yellow powder; mp 116.5~117 °C, IR (KBr), cm^{-1}: 3404 (ν N-H), 1596 (ν C=N), ^1H NMR (DMSO-d_6), δ = 8.82 (s, 1H), 7.80 (d, *J* = 8.7 Hz, 2H), 7.50 (s, 1H), 7.35 (d, *J* = 8.5 Hz, 2H), 7.04 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.5 Hz, 2H), 4.05 (q, *J* = 7.3 Hz, 2H), 3.94 (q, *J* = 7.2 Hz, 2H), 1.32 (t, *J* = 7.3 Hz, 3H), 1.29 (t, *J* = 7.2 Hz, 3H), EIMS (70 eV), *m/z* (%): 324 (M^+, 100), 295 (66), 134 (12), 121 (6), 107 (9), 69 (20). Anal. Calcd. for $C_{18}H_{20}N_4O_2$: C: 66.65, H: 6.21, N: 17.27. found C: 66.59, H: 6.35, N: 17.33.

2-(4-Methoxyphenyl)-4-(4-methoxyphenylamino)-2*H*-1,2,3-triazole (6k)

Yel low pow der; mp 129.5~130.5 °C, IR (KBr), cm^{-1}: 3352 (ν N-H), 1598 (ν C=N), ^1H NMR (DMSO-d_6), δ = 8.85 (s, 1H), 7.83 (d, *J* = 7.0 Hz, 2H), 7.52 (s, 1H), 7.38 (d, *J* = 9.0 Hz, 2H), 7.07 (d, *J* = 7.0 Hz, 2H), 6.89 (d, *J* = 9.0 Hz, 2H), 3.94 (s, 3H), 3.79 (s, 3H). EIMS (70 eV), *m/z* (%): 296 (M^+, 100), 281 (27), 148 (9), 121 (14), 107 (5), 78 (4). Anal. Calcd. for $C_{16}H_{16}N_4O_2$: C: 64.85, H: 5.44, N: 18.91. found C: 64.64, H: 5.60, N: 18.80.

Prep a ra tion of 6-Sydnonyl-1,2,4,5-tetrazinan-3-one 7 and/or Sydnonecarbaldehyde Carbazone 8

To a stirred so lu tion of 6 mmol of phenylhydrazine, hydrazine hy drate, methylhydrazine (or 3 mmol of aryl hydrazine hy dro chlo ride and 6 mmol triethylamine) in 10 mL of eth a nol, 3 mmol of α-chloroformylarylhydrazone **3a**~**h** was added. The re ac tion so lu tion was stirred at room tem per a ture for 15 min utes. In the cases of ei ther phenylhydrazine or 4-methoxyphenyl-hydrazine, the pre cip i tat ing solid was collected by fil tra tion and recrystallization from eth a nol to obtain cy clic com pounds **7**. The fil trate was con cen trated un der re duced pres sure, then the crude solid was sub jected to chroma tog ra phy (EtOAc: n-hexane = 1:2) to ob tain com pounds **7** and **8**. In the case of 4-fluorophenylhydrazine, the pre cip i tating solid was col lected by fil tra tion and recrystallization from eth a nol to ob tain cy clic com pounds **7n** and **7o**. The filtrate was con cen trated un der re duced pres sure to af ford pure solid prod uct **8n** and **8o** by recrystallization from eth a nol. In the other cases, the so lu tion was poured into 100 mL of wa ter. Tetrazinan-3-one **7** or carbazone **8** pre cip i tated, and was then pu ri fied by recrystallization from eth a nol.

3-(4-Methoxyphenyl)-sydnon-4-ylaldehyde 2-phenylcarbazone (8a)

Yel low pow der; mp 160~161 °C, IR (KBr), cm^{-1}: 3430, 3334, 3232 (ν N-H), 1746, 1707 (ν C=O), 1605 (ν C=N), ^1H NMR (DMSO-d_6), δ = 7.00 (d, *J* = 9.0 Hz, 2H), 7.55~7.43 (m, 3H), 7.18 (d, *J* = 9.0 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 6.82 (br, 1H), 6.66 (s, 1H), 4.15 (br, 2H), 3.87 (s, 3H). EIMS (70 eV), *m/z* (%): 368 (M^+, 3), 310 (18), 266 (14), 252 (42), 134 (91), 108 (50), 92 (100), 77 (96), 65 (63). Anal. Calcd. for $C_{17}H_{16}N_6O_4$ (368.35) C: 55.43, H: 4.38, N: 22.81. found C: 55.38, H: 4.40, N: 22.81.

3-(4-Methoxyphenyl)-sydnon-4-ylaldehyde 2-(4-methoxyphenyl)carbazone (8b)

Yel low pow der; mp 191~192 °C, IR (KBr), cm^{-1}: 3442, 3328, 3226 (ν N-H), 1749, 1704 (ν C=O), 1611 (ν C=N), ^1H NMR (DMSO-d_6), δ = 7.71 (d, *J* = 9.0 Hz, 2H), 7.20 (d, *J* = 9.0 Hz, 3H), 7.04 (s, 4H), 6.79 (br, 1H), 6.67 (s, 1H), 4.39 (br, 2H), 3.87 (s, 3H), 3.87 (s, 3H). EIMS (70 eV), *m/z* (%): 398 (M^+, 5), 340 (19), 309 (6), 282 (29), 162 (9), 149 (27), 134 (100), 122 (96), 107 (40), 92 (37), 77 (37). Anal. Calcd. for $C_{18}H_{18}N_6O_5$ (398.37) C: 54.27, H: 4.55, N: 21.09. found C: 54.27, H: 4.63, N: 20.93.

2-Methyl-6-[3-(4-methoxyphenyl)sydnon-4-yl]-4-phenyl-1,2,4,5-tetrazinan-3-one (7c)

Yel low nee dles; mp 176.5~177.5 °C, IR (KBr), cm^{-1}: 3256 (ν N-H), 1743, 1632 (ν C=O), ^1H NMR (DMSO-d_6), δ = 7.75 (d, *J* = 8.9 Hz, 2H), 7.19 (d, *J* = 8.9 Hz, 2H), 7.15~7.10 (m, 5H), 6.22 (d, *J* = 9.5 Hz, 1H), 6.09 (d, *J* = 9.5 Hz, 1H), 4.99 (t, *J* = 9.5 Hz, 1H), 3.85 (s, 3H), 2.99 (s, 3H). ^{13}C NMR, δ = 165.66, 161.97, 154.17, 142.98, 127.76, 126.69, 126.21, 123.22, 121.23, 115.02, 103.31, 63.66, 55.90, 36.72. EIMS (70 eV), *m/z* (%): 382 (M^+, 22), 324 (6), 308 (5), 280 (4), 252 (20), 191 (13), 175 (25), 159 (16), 146 (41), 134 (88), 119 (34), 107 (67), 92 (50), 77 (100). Anal. Calcd. for $C_{18}H_{18}N_6O_4$ (382.37) C: 56.54, H: 4.74, N: 21.98. found C: 56.50, H: 4.71, N: 22.01.

2-(4-Chlorophenyl)-6-[3-(4-methoxyphenyl)sydnon-4-yl]-4-methyl-1,2,4,5-tetrazinan-3-one (7d)

Yel low pow der; mp 153.5~154.5 °C, IR (KBr), cm^{-1}: 3256 (ν N-H), 1743, 1632 (ν C=O), ^1H NMR (DMSO-d_6), δ = 7.76 (d, *J* = 8.9 Hz, 2H), 7.28~7.11 (m, 6H), 6.28 (d, *J* = 9.4 Hz, 1H), 6.11 (d, *J* = 9.4 Hz, 1H), 5.00 (t, *J* = 9.4 Hz, 1H), 3.86 (s, 3H), 2.99 (s, 3H). ^{13}C NMR, δ = 165.59, 161.96, 157.55, 154.11, 141.87, 127.57, 126.67, 126.13, 122.21, 115.03, 103.29, 63.53, 55.87, 36.61. EIMS (70 eV), *m/z* (%): 416 (M^++2, 7), 416 (M^+, 22), 358 (3), 342 (3), 286 (6), 225 (8), 209 (15), 190 (9), 146 (30), 134 (100), 125 (31), 107 (55), 92 (41), 77 (73). Anal. Calcd. for $C_{18}H_{17}N_6O_4Cl$ (416.83) C: 51.87, H: 4.11, N: 20.16. found C: 51.99, H: 4.12, N: 20.16.

2-Methyl-6-[3-(4-methoxyphenyl)sydnon-4-yl]-4-(4-methoxyphenyl)-1,2,4,5-tetrazinan-3-one (7e)

Yel low nee dles; mp 151.5~152.5 °C, IR (KBr), cm^{-1}: 3226 (ν N-H), 1746, 1641 (ν C=O), ^1H NMR (DMSO-d_6), δ =

7.78 (d, *J* = 9.0 Hz, 2H), 7.23 (d, *J* = 9.0 Hz, 2H), 7.18 (d, *J* = 9.0 Hz, 5H), 6.78 (d, *J* = 9.0 Hz, 2H), 6.22 (d, *J* = 9.4 Hz, 1H), 6.08 (d, *J* = 9.4 Hz, 1H), 5.00 (t, *J* = 9.4 Hz, 1H), 3.90 (s, 3H), 3.73 (s, 3H), 3.01 (s, 3H). ^{13}C NMR, δ = 165.65, 161.94, 155.64, 153.71, 136.24, 126.68, 126.19, 123.71, 114.99, 112.93, 103.13, 63.41, 55.89, 55.16, 36.88. EIMS (70 eV), *m/z* (%): 412 (M^+, 15), 354 (2), 337 (3), 310 (2), 282 (12), 248 (7), 205 (14), 190 (15), 162 (14), 149 (75), 134 (100), 121 (51), 107 (60), 92 (47), 77 (58). Anal. Calcd. for $C_{19}H_{20}N_6O_5$ (412.40) C: 55.34, H: 4.89, N: 20.38. found C: 55.39, H: 4.90, N: 20.29.

2-(4-Methoxyphenyl)-6-[3-(4-methoxyphenyl)sydnon-4-yl]-4-phenyl-1,2,4,5-tetrazinan-3-one (7f)

Yel low pow der; mp 143.5~144.5 °C, IR (KBr), cm^{-1}: 3256 (ν N-H), 1737, 1668 (ν C=O), ^{1}H NMR (DMSO-d_6), δ = 7.79 (d, *J* = 8.8 Hz, 2H), 7.34~7.18 (m, 8H), 7.03 (t, *J* = 6.9 Hz, 1H), 6.83 (d, *J* = 8.8 Hz, 2H), 6.44 (d, *J* = 9.7 Hz, 2H), 5.22 (t, *J* = 9.7 Hz, 1H), 3.86 (s, 3H), 3.72 (s, 3H). ^{13}C NMR, δ = 165.67, 161.97, 156.11, 154.42, 142.48, 135.42, 127.85, 126.77, 126.19, 124.31, 123.61, 121.69, 115.04, 113.14, 103.52, 65.06, 55.89, 55.21. EIMS (70 eV), *m/z* (%): 474 (M^+, 4), 457 (5), 416 (2), 399 (12), 309 (35), 279 (23), 252 (18), 149 (71), 108 (86), 91 (61), 77 (100), 65 (40). Anal. Calcd. for $C_{24}H_{22}N_6O_5$ (474.47) C: 60.75, H: 4.67, N: 17.71. found C: 60.68, H: 4.73, N: 17.66.

3-(4-Methoxyphenyl)sydnon-4-ylaldehyde 5-(4-methoxyphenyl)-2-phenylcarbazone (8f)

Yel low nee dles; mp 181.5~182.5 °C, IR (KBr), cm^{-1}: 3346, 3286 (ν N-H), 1755, 1695 (ν C=O), 1605 (ν C=N), ^{1}H NMR (DMSO-d_6), δ = 7.75 (d, *J* = 9.0 Hz, 2H), 7.56~7.35 (m, 6H), 7.18 (d, *J* = 1.7 Hz, 1H), 7.14 (d, *J* = 9.0 Hz, 2H), 6.78 (d, *J* = 9.0 Hz, 2H), 6.72 (s, 1H), 6.59 (d, *J* = 9.0 Hz, 3H), 3.66 (s, 3H), 3.64 (s, 3H). EIMS (70 eV), *m/z* (%): 474 (M^+, 2), 443 (23), 416 (1), 399 (4), 293 (33), 252 (14), 191 (21), 164 (12), 134 (50), 123 (93), 108 (39), 92 (59), 77 (100). Anal. Calcd. for $C_{24}H_{22}N_6O_5$ (474.48) C: 60.75, H: 4.67, N: 17.71. found C: 60.81, H: 4.74, N: 17.75.

2-(4-Methylphenyl)-6-[3-(4-methoxyphenyl)sydnon-4-yl]-4-phenyl-1,2,4,5-tetrazinan-3-one (7g)

Yel low pow der; mp 155~156 °C, IR (KBr), cm^{-1}: 3232, 3172 (ν N-H), 1758, 1644 (ν C=O), ^{1}H NMR (DMSO-d_6), δ = 7.80 (d, *J* = 8.9 Hz, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.28~7.18 (m, 6H), 7.06 (d, *J* = 8.2 Hz, 2H), 6.46 (d, *J* = 9.7 Hz, 2H), 5.22 (t, *J* = 9.7 Hz, 1H), 3.87 (s, 3H), 2.25 (s, 3H). ^{13}C NMR, δ = 165.65, 161.96, 155.09, 142.33, 139.81, 132.88, 128.37, 127.87, 126.75, 126.17, 123.62, 121.92, 121.58, 115.03, 103.68, 65.33, 55.88, 20.42. EIMS (70 eV), *m/z* (%): 458 (M^+, 16), 400 (2), 310 (4), 266 (12), 252 (10), 162 (12), 146 (14), 134 (64), 121 (32), 107 (75), 91 (100), 77 (88). Anal. Calcd. for $C_{24}H_{22}N_6O_4$ (458.47) C: 62.87, H: 4.84, N: 18.33. found C: 62.72, H: 4.95, N: 18.30.

3-(4-Methoxyphenyl)sydnon-4-ylaldehyde 5-(4-methylphenyl)-2-phenylcarbazone (8g)

Yel low pow der; mp 144~145 °C, IR (KBr), cm^{-1}: 3412, 3323 (ν N-H), 1758, 1701 (ν C=O), 1605 (ν C=N), ^{1}H NMR (DMSO-d_6), δ = 7.75 (d, *J* = 8.9 Hz, 2H), 7.55~7.48 (m, 4H), 7.35 (d, *J* = 2.3 Hz, 1H), 7.18 (d, *J* = 2.3 Hz, 1H), 7.14~7.09 (m, 3H), 6.97 (d, *J* = 8.2 Hz, 2H), 6.74 (s, 1H), 6.55 (d, *J* = 8.2 Hz, 2H), 3.62 (s, 3H), 2.18 (s, 3H). EIMS (70 eV), *m/z* (%): 458 (M^+, 8), 400 (2), 310 (28), 293 (10), 280 (13), 252 (43), 162 (23), 148 (19), 134 (100), 119 (45), 106 (77), 91 (99), 77 (89). Anal. Calcd. for $C_{24}H_{22}N_6O_4$ (458.48) C: 62.87, H: 4.84, N: 18.33. found C: 62.76, H: 4.94, N: 18.20.

2-(4-Methylphenyl)-6-(3-phenylsydnon-4-yl)-4-phenyl-1,2,4,5-tetrazinan-3-one (7h)

Yel low pow der; mp 129~130 °C, IR (KBr), cm^{-1}: 3208 (ν N-H), 1734, 1659 (ν C=O), ^{1}H NMR (DMSO-d_6), δ = 7.89~7.70 (m, 5H), 7.33~7.18 (m, 7H), 7.03 (d, *J* = 8.1 Hz, 2H), 6.46 (d, *J* = 9.7 Hz, 1H), 6.44 (d, *J* = 9.7 Hz, 1H), 5.25 (t, *J* = 9.7 Hz, 1H), 2.24 (s, 3H). EIMS (70 eV), *m/z* (%): 428 (M^+, 10), 370 (1), 236 (16), 222 (13), 149 (11), 132 (30), 119 (26), 104 (69), 91 (93), 77 (100). Anal. Calcd. for $C_{23}H_{20}N_6O_3$ (458.47) C: 64.48, H: 4.71, N: 19.61. found C: 64.29, H: 4.75, N: 19.50.

3-Phenylsydnon-4-ylaldehyde 2-(4-methylphenyl)-5-phenylcarbazone (8h)

Yel low pow der; mp 175.5~176.5 °C, IR (KBr), cm^{-1}: 3364 (ν N-H), 1752, 1725 (ν C=O), 1605 (ν C=N), ^{1}H NMR (DMSO-d_6), δ = 7.85~7.80 (m, 2H), 7.65~7.59 (m, 4H), 7.33~7.12 (m, 5H), 7.03 (d, *J* = 8.1 Hz, 2H), 6.75 (s, 1H), 6.72 (t, *J* = 7.4 Hz, 1H), 6.62 (d, *J* = 8.1 Hz, 2H), 2.32 (s, 3H). EIMS (70 eV), *m/z* (%): 428 (M^+, 7), 384 (6), 370 (2), 236 (21), 134 (27), 106 (60), 91 (96), 77 (100), 65 (96). Anal. Calcd. for $C_{23}H_{20}N_6O_3$ (458.48) C: 64.48, H: 4.71, N: 19.62. found C: 64.31, H: 4.73, N: 19.56.

2-(4-Methylphenyl)-6-[3-(4-methylphenyl)sydnon-4-yl]-4-phenyl-1,2,4,5-tetrazinan-3-one (7i)

Yel low pow der; mp 181.5~182.5 °C, IR (KBr), cm^{-1}: 3236 (ν N-H), 1740, 1677 (ν C=O), ^{1}H NMR (DMSO-d_6), δ = 7.75 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.36~7.20 (m, 6H), 7.07~7.00 (m, 3H), 6.46 (d, *J* = 9.4 Hz, 2H), 5.23 (t, *J* = 9.4 Hz, 1H), 2.44 (s, 3H), 2.25 (s, 3H). ^{13}C NMR, δ = 160.59, 155.09, 142.77, 142.31, 139.78, 132.85, 131.16, 130.37, 128.35, 127.84, 124.94, 123.58, 121.89, 121.54,

103.60, 65.30, 20.90, 20.41. EIMS (70 eV), *m/z* (%): 442 (M^+, 30), 384 (6), 308 (8), 294 (10), 250 (11), 133 (30), 119 (33), 106 (36), 91 (100), 77 (47). Anal. Calcd. for $C_{24}H_{22}N_6O_3$ (442.48) C: 65.15, H: 5.01, N: 18.99. found C: 65.18, H: 5.03, N: 18.91.

3-(4-Methylphenyl)sydnon-4-ylaldehyde 2-(4-methylphenyl)-5-phenyl-carbazone (8i)

Yel low nee dles; mp 192~193 °C, IR (KBr), cm^{-1}: 3418, 3304 (ν N-H), 1761, 1698 (ν C=O), 1605 (ν C=N), ^{1}H NMR (DMSO-d_6), δ = 7.70 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 2.0 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.16 (t, *J* = 7.8 Hz, 2H), 7.02 (d, *J* = 8.2 Hz, 2H), 6.94 (d, *J* = 2.0 Hz, 1H), 6.73 (s, 1H), 6.73 (t, *J* = 7.2 Hz, 1H), 6.58 (d, *J* = 7.6 Hz, 2H), 2.34 (s, 3H), 2.11 (s, 3H). EIMS (70 eV), *m/z* (%): 442 (M^+, 13), 384 (5), 308 (13), 250 (21), 134 (33), 106 (66), 91 (100), 77 (85), 65 (59). Anal. Calcd. for $C_{24}H_{22}N_6O_3$ (442.48) C: 65.15, H: 5.01, N: 18.99. found C: 65.03, H: 5.02, N: 18.94.

2-(4-Chlorophenyl)-6-[3-(4-methylphenyl)sydnon-4-yl]-4-phenyl-1,2,4,5-tetrazinan-3-one (7j)

Yel low pow der; mp 149~150 °C, IR (KBr), cm^{-1}: 3256 (ν N-H), 1731, 1674 (ν C=O), ^{1}H NMR (DMSO-d_6), δ = 7.74 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 8.3 Hz, 2H), 7.42~7.22 (m, 8H), 7.09~7.06 (m, 1H), 6.55 (d, *J* = 9.5 Hz, 1H), 6.50 (d, *J* = 9.5 Hz, 1H), 5.24 (t, *J* = 9.5 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR, δ = 165.55, 155.99, 142.80, 141.98, 141.14, 131.13, 130.39, 127.96, 127.72, 127.17, 124.94, 123.75, 122.58, 121.34, 103.79, 65.49, 20.89. EIMS (70 eV), *m/z* (%): 464 (M^++2, 11), 462 (M^+, 40), 404 (8), 328 (12), 294 (12), 270 (15), 236 (21), 153 (32), 118 (53), 91 (100), 77 (80). Anal. Calcd. for $C_{23}H_{19}N_6O_3Cl$ (462.90) C: 59.68, H: 4.14, N: 18.16. found C: 59.64, H: 4.01, N: 18.19.

3-(4-Methylphenyl)sydnon-4-ylaldehyde 2-(4-chlorophenyl)-5-phenylcarbazone (8j)

Yel low pow der; mp 186.5~187.5 °C, IR (KBr), cm^{-1}: 3418, 3304 (ν N-H), 1758, 1701 (ν C=O), 1605 (ν C=N), ^{1}H NMR (DMSO-d_6), δ = 7.71 (d, *J* = 8.1 Hz, 2H), 7.59 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 8.1 Hz, 2H), 7.25~7.13 (m, 4H), 7.08 (d, *J* = 1.6 Hz, 1H), 6.76 (s, 1H), 6.74 (t, *J* = 7.3 Hz, 1H), 6.61 (d, *J* = 7.8 Hz, 2H), 2.14 (s, 3H). EIMS (70 eV), *m/z* (%): 464 (M^++2, 3), 462 (M^+, 10), 404 (3), 328 (16), 286 (9), 270 (27), 153 (16), 118 (52), 91 (100), 77 (99), 65 (82). Anal. Calcd. for $C_{23}H_{19}N_6O_3Cl$ (462.90) C: 59.68, H: 4.14, N: 18.19. found C: 59.55, H: 4.18, N: 18.15.

2,4-Diphenyl-6-[3-(4-methylphenyl)sydnon-4-yl]-1,2,4,5-tetrazinan-3-one (7k)

Yel low pow der; mp 192.5~193.5 °C, IR (KBr), cm^{-1}: 3250, 3214 (ν N-H), 1740, 1638 (ν C=O), ^{1}H NMR (DMSO-d_6), δ = 7.80 (d, *J* = 8.8 Hz, 2H), 7.39~7.18 (m, 10H), 7.09~7.00 (m, 2H), 6.49 (d, *J* = 9.6 Hz, 2H), 5.24 (t, *J* = 9.6 Hz, 2H), 3.86 (s, 3H). ^{13}C NMR, δ = 165.64, 161.97, 155.53, 142.23, 127.90, 126.76, 126.17, 123.67, 121.52, 115.04, 103.78, 65.48, 55.89. EIMS (70 eV), *m/z* (%): 444 (M^+, 54), 386 (8), 310 (11), 279 (12), 252 (22), 134 (39), 119 (40), 107 (39), 91 (44), 77 (100), 65 (18). Anal. Calcd. for $C_{23}H_{20}N_6O_4$ (444.45) C: 62.15, H: 4.54, N: 18.91. found C: 61.92, H: 4.61, N: 18.80.

3-(4-Methoxyphenyl)sydnon-4-ylaldehyde 2,5-diphenyl-carbazone (8k)

Yel low pow der; mp 161~162 °C, IR (KBr), cm^{-1}: 3364, 3298 (ν N-H), 1746, 1698 (ν C=O), 1605 (ν C=N), ^{1}H NMR (DMSO-d_6), δ = 7.75 (d, *J* = 9.0 Hz, 2H), 7.71 (d, *J* = 1.6 Hz, 1H), 7.56~7.45 (m, 3H), 7.37 (d, *J* = 1.6 Hz, 1H), 7.19~7.08 (m, 6H), 6.74 (s, 1H), 6.72 (t, *J* = 7.3 Hz, 1H), 6.63 (d, *J* = 7.7 Hz, 2H), 3.60 (s, 3H). EIMS (70 eV), *m/z* (%): 444 (M^+, 15), 386 (2), 384 (7), 310 (12), 252 (17), 134 (25), 120 (12), 107 (18), 92 (47), 77 (100), 65 (34). Anal. Calcd. for $C_{23}H_{20}N_6O$ (444.45) C: 62.15, H: 4.54, N: 18.91. found C: 62.04, H: 4.61, N: 18.85.

2-(4-Chlorophenyl)-6-[3-(4-methoxyphenyl)sydnon-4-yl]-4-phenyl-1,2,4,5-tetrazinan-3-one (7l)

Pale yel low pow der; mp 159~160 °C, IR (KBr), cm^{-1}: 3256 (ν N-H), 1746, 1668 (ν C=O), ^{1}H NMR (DMSO-d_6), δ = 7.79 (d, *J* = 8.9 Hz, 2H), 7.43~7.18 (m, 10H), 7.05 (t, *J* = 7.2 Hz, 1H), 6.55 (d, *J* = 9.4 Hz, 1H), 6.50 (d, *J* = 9.4 Hz, 1H), 5.23 (t, *J* = 9.4 Hz, 1H), 3.86 (s, 3H). ^{13}C NMR, δ = 165.57, 161.95, 155.95, 141.99, 141.15, 127.95, 127.70, 127.17, 126.73, 126.12, 123.75, 122.57, 121.34, 115.02, 103.84, 65.50, 55.86. EIMS (70 eV), *m/z* (%): 480 (M^++1, 6), 478 (M^+, 17), 420 (3), 344 (6), 310 (10), 286 (12), 252 (9), 153 (28), 134 (45), 108 (35), 91 (46), 77 (100). Anal. Calcd. for $C_{23}H_{19}N_6O_4Cl$ (478.90) C: 57.69, H: 4.00, N: 17.55. found C: 57.61, H: 4.02, N: 17.51.

3-(4-Methoxyphenyl)sydnon-4-ylaldehyde 2-(4-chlorophenyl)-5-phenylcarbazone (8l)

Yel low pow der; mp 159.5~160.5 °C, IR (KBr), cm^{-1}: 3418, 3310 (ν N-H), 1758, 1701 (ν C=O), 1605 (ν C=N), ^{1}H NMR (DMSO-d_6), δ = 7.75 (d, *J* = 8.9 Hz, 2H), 7.71 (d, *J* = 2.2 Hz, 1H), 7.59 (d, *J* = 8.6 Hz, 2H), 7.39 (d, *J* = 2.2 Hz, 1H), 7.25~7.09 (m, 6H), 6.77 (s, 1H), 6.72 (t, *J* = 7.3 Hz, 1H), 6.63 (d, *J* = 7.5 Hz, 2H), 3.61 (s, 3H). EIMS (70 eV), *m/z* (%): 480 (M^++2, 1), 478 (M^+, 4), 418 (2), 344 (7), 286 (16), 153 (8), 134 (46), 111 (30), 92 (46), 77 (100), 65 (43). Anal. Calcd. for $C_{23}H_{19}N_6O_4Cl$ (478.90) C: 57.69, H: 4.00, N: 17.55. found C:

57.55, H: 4.04, N: 17.51.

2-(4-Methoxyphenyl)-6-[3-(4-methoxyphenyl)sydnon-4-yl]-4-phenyl-1,2,4,5-tetrazinan-3-one (7m)

Yel low pow der; mp 143.5~144.5 °C, IR (KBr), cm^{-1}: 3256 (ν N-H), 1737, 1668 (ν C=O), ^{1}H NMR (DMSO-d_6), δ = 7.79 (d, *J* = 8.8 Hz, 2H), 7.34~7.18 (m, 8H), 7.03 (t, *J* = 6.9 Hz, 1H), 6.83 (d, *J* = 8.8 Hz, 2H), 6.44 (d, *J* = 9.7 Hz, 2H), 5.22 (t, *J* = 9.7 Hz, 1H), 3.86 (s, 3H), 3.72 (s, 3H). EIMS (70 eV), *m/z* (%): 474 (M^+, 4), 457 (5), 416 (2), 399 (12), 309 (35), 279 (23), 252 (18), 149 (71), 108 (86), 91 (61), 77 (100), 65 (40). Anal. Calcd. for $C_{24}H_{22}N_6O_5$ (474.47) C: 60.75, H: 4.67, N: 17.71. found C: 60.68, H: 4.73, N: 17.66.

3-(4-Methoxyphenyl)sydnon-4-ylaldehyde 2-(4-methoxyphenyl)-5-phenylcarbazone (8m)

Yel low pow der; mp 160.5~161.5 °C, IR (KBr), cm^{-1}: 3430, 3310 (ν N-H), 1752, 1713 (ν C=O), 1605 (ν C=N), ^{1}H NMR (DMSO-d_6), δ = 7.75 (d, *J* = 8.9 Hz, 2H), 7.68 (d, *J* = 2.3 Hz, 1H), 7.27 (d, *J* = 2.3 Hz, 1H), 7.19~7.06 (m, 8H), 6.75 (s, 1H), 6.68 (t, *J* = 7.3 Hz, 1H), 6.62 (d, *J* = 7.7 Hz, 2H), 3.78 (s, 3H), 3.59 (s, 3H). EIMS (70 eV), *m/z* (%): 474 (M^+, 3), 414 (1), 340 (5), 309 (26), 282 (8), 257 (16), 149 (39), 122 (72), 108 (100), 93 (47), 77 (92). Anal. Calcd. for $C_{24}H_{22}N_6O_5$ (474.47) C: 60.75, H: 4.67, N: 17.71. found C: 60.58, H: 4.74, N: 17.60.

2-(4-Fluorophenyl)-6-[3-(4-methylphenyl)sydnon-4-yl]-4-phenyl-1,2,4,5-tetrazinan-3-one (7n)

Pale green nee dles; mp 181.5~182.5 °C, IR (KBr), cm^{-1}: 3256 (ν N-H), 1734, 1674 (ν C=O), ^{1}H NMR (DMSO-d_6), δ = 7.74 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.40~7.20 (m, 6H), 7.15~7.01 (m, 3H), 6.53 (d, *J* = 9.6 Hz, 1H), 6.47 (d, *J* = 9.6 Hz, 1H), 5.25 (t, *J* = 9.6 Hz, 1H), 2.44 (s, 3H). EIMS (70 eV), *m/z* (%): 446 (M^+, 14), 388 (2), 254 (11), 236 (20), 137 (27), 118 (80), 109 (53), 95 (56), 91 (100), 77 (99), 65 (49). Anal. Calcd. for $C_{23}H_{19}N_6O_3F$ (446.45) C: 61.88, H: 4.29, N: 18.82. found C: 61.87, H: 4.38, N: 18.85.

3-(4-Methylphenyl)sydnon-4-ylaldehyde 5-(4-fluorophenyl)-2-phenylcarbazone (8n)

Yel low pow der; mp 178.5~179.5 °C, IR (KBr), cm^{-1}: 3352, 3310 (ν N-H), 1752, 1701 (ν C=O), 1614 (ν C=N), ^{1}H NMR (DMSO-d_6), δ = 7.71 (d, *J* = 8.3 Hz, 2H), 7.67 (d, *J* = 2.0 Hz, 1H), 7.58~7.40 (m, 5H), 7.19~7.02 (m, 4H), 6.97 (d, *J* = 2.0 Hz, 1H), 6.74 (s, 1H), 6.64~6.58 (m, 2H), 2.15 (s, 3H), EIMS (70 eV), *m/z* (%): 446 (M^+, 33), 294 (25), 236 (36), 146 (16), 126 (41), 106 (49), 91 (100), 77 (88), 65 (53). Anal. Calcd. for $C_{23}H_{19}N_6O_2F$ (446.44) C: 61.88, H: 4.29, N: 18.83. found C: 61.83, H: 4.38, N: 18.79.

2-(4-Fluorophenyl)-4-(4-methylphenyl)-6-[3-(4-methylphenyl)sydnon-4-yl]-1,2,4,5-tetrazinan-3-one (7o)

Pale green nee dles; mp 199~200 °C, IR (KBr), cm^{-1}: 3232, 3184 (ν N-H), 1756, 1644 (ν C=O), ^{1}H NMR (DMSO-d_6), δ = 7.74 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 8.3 Hz, 2H), 7.38~7.29 (m, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.14~6.95 (m, 4H), 6.49 (d, *J* = 9.8 Hz, 1H), 6.43 (d, *J* = 9.8 Hz, 1H), 5.24 (t, *J* = 9.8 Hz, 1H), 2.44 (s, 3H), 2.36 (s, 3H). EIMS (70 eV), *m/z* (%): 460 (M^+, 7), 402 (1), 385 (3), 308 (4), 250 (11), 133 (23), 118 (47), 106 (40), 95 (34), 91 (100), 77 (42). Anal. Calcd. for $C_{24}H_{21}N_6O_3F$ (460.47) C: 62.60, H: 4.60, N: 18.25. found C: 62.62, H: 4.67, N: 18.33.

3-(4-Methylphenyl)sydnon-4-ylaldehyde 5-(4-fluorophenyl)- 2-(4-methylphenyl)-carbazone (8o)

Yel low pow der; mp 126.5~127.5 °C, IR (KBr), cm^{-1}: 3532, 3340 (ν N-H), 1749, 1692 (ν C=O), 1599 (ν C=N), ^{1}H NMR (DMSO-d_6), δ = 7.71 (d, *J* = 8.3 Hz, 2H), 7.65 (d, *J* = 2.3 Hz, 1H), 7.41 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.05~6.95 (m, 5H), 6.73 (s, 1H), 6.62~6.55 (m, 2H), 2.34 (s, 3H), 2.14 (s, 3H), EIMS (70 eV), *m/z* (%): 460 (M^+, 9), 308 (20), 294 (12), 250 (36), 236 (19), 150 (16), 106 (61), 91 (100), 77 (49), 65 (50). Anal. Calcd. for $C_{24}H_{21}N_6O_3F$ (460.46) C: 62.60, H: 4.60, N: 18.46. found C: 62.61, H: 4.62, N: 18.36.

3-(4-Methylphenyl)sydnon-4-ylaldehyde 5-(4-ethoxycarbonylphenyl)-2-(4-methylphenyl)carbazone (8p)

Yellow pow der; mp 233~233.5 °C, IR (KBr), cm^{-1}: 3370, 3316 (ν N-H), 1764, 1710, 1680 (ν C=O), 1608 (ν C=N), ^{1}H NMR (DMSO-d_6), δ = 8.38 (d, *J* = 1.2 Hz, 1H), 7.79 (d, *J* = 8.8 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.05 (d, *J* = 8.2 Hz, 2H), 6.97 (d, *J* = 1.2 Hz, 1H), 6.74 (s, 1H), 6.63 (d, *J* = 8.8 Hz, 2H), 4.24 (q, *J* = 7.1 Hz, 2H), 2.34 (s, 3H), 2.10 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H), FABMS, *m/z* (%): 515 (M^++1, 86), Anal. Calcd. for $C_{27}H_{26}N_6O_5$ (514.55) C: 63.03, H: 5.09, N: 16.33. found C: 63.07, H: 5.13, N: 16.20.

3-(4-Methylphenyl)sydnon-4-ylaldehyde-5-(4-ethoxycarbonylphenyl)-2-(4-chlorophenyl)carbazone (8q)

Yel low pow der; mp 192-193 °C, IR (KBr), cm^{-1}: 3370, 3316 (ν N-H), 1767, 1716, 1695 (ν C=O), 1608 (ν C=N), ^{1}H NMR (DMSO-d_6), δ = 8.40 (d, *J* = 1.2 Hz, 1H), 7.80 (d, *J* = 8.7 Hz, 2H), 7.71 (d, *J* = 8.2 Hz, 2H), 7.60 (d, *J* = 8.7 Hz, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 8.7 Hz, 2H), 7.12 (d, *J* = 1.2 Hz, 1H), 6.77 (s, 1H), 6.64 (d, *J* = 8.7 Hz, 2H), 4.24 (q, *J* = 7.1 Hz, 2H), 2.13 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H), FABMS *m/z* (%): 535 (M^++1, 83), Anal. Calcd. for $C_{26}H_{23}N_6O_5Cl$

(534.96) C: 58.38, H: 4.33, N: 15.71. found C: 58.51, H: 4.37, N: 15.68.

Preparation of 6-Sydnonyl-3,4-dihydro-3-oxo-1,2,4,5-tetrazin-1(2*H*)-yl Radical 9a~9f

To a solution of 0.414 g (1 mmol) of **7i** in 10 mL dichloro methane and 1 mL of acetic acid was added 0.29 g (1.2 mmol) of lead dioxide. The solution was stirred at room temperature for 8 hours. After filtration, the filtrate was washed with water until it was neutral. The organic layer was dried with magnesium sulfate, then evaporated. The crude product was recrystallized with acetonitrile to obtain **9a** (0.27g, 65%).

2-(4-Methylphenyl)-4-phenyl-6-(3-phenylsydnon-4-yl)-3,4-dihydro-3-oxo-1,2,4,5-tetrazin-1(2*H*)-yl radical (9a)

Dark green powder; mp 172~173 °C, IR (KBr), cm^{-1}: 1761, 1713 (ν C=O), UV λ_{max} (EtOAc) 265, 306, 350, 439, 578 nm. EIMS (70 eV), *m/z* (%): 426 (M^++1, 18), 425 (M^+, 6), 368 (13), 367 (18), 133 (29), 119 (31), 104 (45), 91 (70), 77 (100), 65 (25). Anal. Calcd. for $C_{23}H_{17}N_6O_3$ (425.43) C: 64.94, H: 4.03, N: 19.75. found C: 64.81, H: 4.16, N: 19.79.

2-(4-Methylphenyl)-6-[3-(4-methylphenyl)sydnon-4-yl]-4-phenyl-3,4-dihydro-3-oxo-1,2,4,5-tetrazin-1(2*H*)-yl radical (9b)

Dark green powder; mp 164~164.5 °C, IR (KBr), cm^{-1}: 1761, 1713 (ν C=O), UV λ_{max} (EtOAc) 259, 320, 343, 455, 580 nm. EIMS (70 eV), *m/z* (%): 440 (M^++1, 21), 439 (M^+, 9), 382 (11), 381 (16), 226 (8), 133 (46), 119 (61), 105 (22), 91 (100), 77 (57). Anal. Calcd. for $C_{24}H_{19}N_6O_3$ (439.46) C: 65.60, H: 4.36, N: 19.12. found C: 65.61, H: 4.36, N: 19.17.

2-(4-Chlorophenyl)-6-[3-(4-methylphenyl)sydnon-4-yl]-4-phenyl-3,4-dihydro-3-oxo-1,2,4,5-tetrazin-1(2*H*)-yl radical (9c)

Dark green powder; mp 188.5~189.5 °C, IR (KBr), cm^{-1}: 1767, 1701 (ν C=O), UV λ_{max} (EtOAc) 264, 315, 350, 442, 586 nm. EIMS (70 eV), *m/z* (%): 462 (M^++3, 10), 461 (M^++2, 5), 460 (M^++1, 33), 459 (M^+, 15), 402 (18), 401 (35), 153 (44), 118 (72), 91 (100), 77 (54), 65 (29). Anal. Calcd. for $C_{23}H_{16}N_6O_3Cl$ (459.87) C: 60.07, H: 3.51, N: 18.27. found C: 59.97, H: 3.61, N: 18.18.

6-[3-(4-Methoxyphenyl)sydnon-4-yl]-2,4-diphenyl-3,4-dihydro-3-oxo-1,2,4,5-tetrazin-1(2*H*)-yl radical (9d)

Dark green powder; mp 219~220 °C, IR (KBr), cm^{-1}: 1776, 1707 (ν C=O), UV λ_{max} (EtOAc) 265, 309, 347, 448, 576 nm. EIMS (70 eV), *m/z* (%): 442 (M^++1, 35), 441 (M^+, 7), 384 (16), 383 (15), 134 (60), 119 (100), 105 (13), 91 (68), 77 (87). Anal. Calcd. for $C_{23}H_{17}N_6O_4$ (441.43) C: 62.58, H: 3.88, N: 19.04. found C: 62.52, H: 3.88, N: 19.07.

2-(4-Chlorophenyl)-6-[3-(4-methoxyphenyl)sydnon-4-yl]-4-phenyl-3,4-dihydro-3-oxo-1,2,4,5-tetrazin-1(2*H*)-yl radical (9e)

Dark green powder; mp 198.5~198.5 °C, IR (KBr), cm^{-1}: 1767, 1701 (ν C=O), UV λ_{max} (EtOAc) 259, 323, 337, 450, 584 nm. EIMS (70 eV), *m/z* (%): 478 (M^++3, 3), 477 (M^++2, 3), 476 (M^++1, 8), 475 (M^+, 2), 446 (11), 417 (10), 294 (8), 272 (15), 153 (95), 134 (57), 119 (100), 91 (92), 77 (75). Anal. Calcd. for $C_{23}H_{16}N_6O_4Cl$ (475.87) C: 58.05, H: 3.39, N: 17.66. found C: 58.03, H: 3.46, N: 17.63.

2-(4-Methoxyphenyl)-6-[3-(4-methoxyphenyl)sydnon-4-yl]-4-phenyl-3,4-dihydro-3-oxo-1,2,4,5-tetrazin-1(2*H*)-yl radical (9f)

Dark green powder; mp 174.5~175.5 °C, IR (KBr), cm^{-1}: 1764, 1695 (ν C=O), UV λ_{max} (EtOAc) 265, 303, 357, 459, 588 nm. EIMS (70 eV), *m/z* (%): 472 (M^++1, 20), 471 (M^+, 7), 414 (8), 413 (12), 309 (7), 268 (7), 206 (6), 149 (100), 134 (88), 119 (57), 91 (55), 77 (62). Anal. Calcd. for $C_{24}H_{19}N_6O_5$ (417.45) C: 61.14, H: 4.06, N: 17.83. found C: 61.01, H: 4.06, N: 17.86.

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Key Words

2-Arylamino-2*H*-1,2,3-triazole;
3,4-Dihydro-3-oxo-1,2,4,5-tetrazin-1(2*H*)-yl radical.

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