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Reactions of 4-Hydrazinocarbonylmethylene 3-Arylsydnones and 3-(4-Hydrazinocarbonylphenyl)sydnones

Shaw-Tao Lin*[a] (林孝道), Mein-Lin Yang[b] (楊美玲) and Hsien-Ju Tien*[b] (田憲儒)
[a]*Department of Applied Chemistry, Providence University, Sha-Lu, Taichung 433, Taiwan, R.O.C.*
[b]*Department of Chemistry, National Cheng-Kung University, Tainan 701, Taiwan, R.O.C.*

The phenyl ring of 3-(4-hydrazinocarbonylphenyl)sydnone activates a hydrazinocarbonyl group to undergo a series of reactions for preparing heterocyclic compounds including oxadiazoles, dihydropyrroles, and pyrroles. However, the hydrazinocarbonyl group on the $C(4)$-CH_2 resists a cyclization under the same reaction conditions.

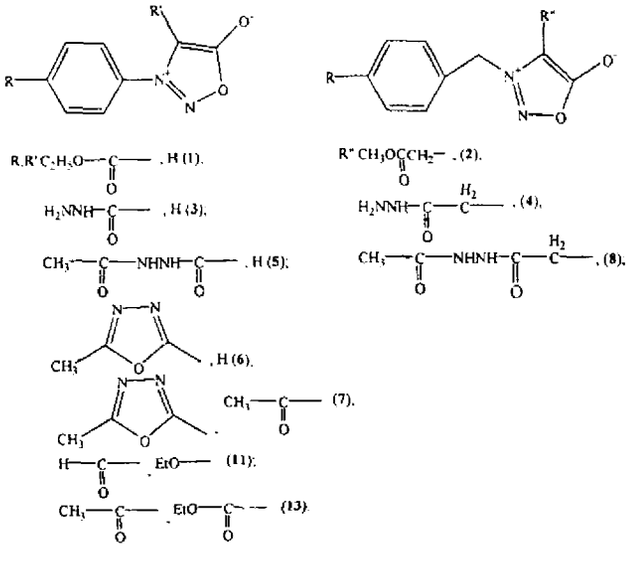
INTRODUCTION

The charge density distribution of the atoms of the sydnone ring has been discussed since this series of sydnone compounds were discovered. The concept of unequal distribution of electron density around the sydnone ring resulting in a mesoionic character is well accepted.[1] The unequal electron densities of the atoms lead to the different natures of N(3) and C(4). The possible distribution for positive charges and negative charges varies depending on the resonance forms of sydnone rings. Chemical characteristics and calculation results suggest that N(3) bears a positive charge and possesses an electron-withdrawing group, while C(4) contains more electrons and behaves as an electron-donor.[2] A typical example is the nitration of 3,4-diphenylsydnone. When it was nitrated using a limited amount of nitronium ion yielding a 4-(4-nitrophenyl)-3-phenylsydnone. 3-Phenyl-4-nitrosydnone was resulted from the nitration of 3-phenylsydnone.[3] This suggests that C(4) is an electron-donor activating the phenyl ring for nitration. At the same time, the activity of the functional group on the phenyl ring or the C(4) position of 3-phenylsydnones is also different. In general, the hydroxyalkyl on the N(3)-phenyl ring is easily oxidized by using various oxidants. However, the hydroxyl group of 1-hydroxyalkyl on the C(4) position is oxidized by using DMSO/acetic anhydride[4] but resists oxidation when chromic acid or manganese dioxide is used.[5]

In this work, we investigated and compared the reactivity of the hydrazinocarbonyl group on the phenyl ring and the C(4) position of 3-phenylsydnones. The reactions included cyclization with acetic anhydride to form 1,3,4-oxadiazoles, and condensation with some carbonyl group or carbon disulfide to form heterocyclic rings. 1,3,4-Oxadiazoles have a number of bioactivities.[6] Formation of these oxadiazoles as a functional group of arylsydnones may possess some bioactivities and shall be worth reporting.

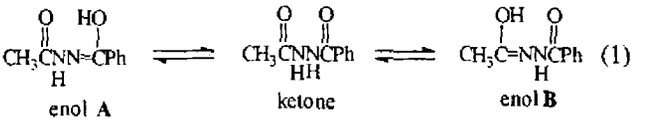
RESULTS AND DISCUSSION

Hydrazinocarbonyl groups, prepared simply from reaction of hydrazine with corresponding ester, can be further acylated to form diacyl hydrazine by using either acid anhydride or acid halides.[7] Hydrazinocarbonyl also undergoes cyclization to form 1,3,4-oxadiazoline in the presence of acetic anhydride as an acetylation reagent as well as a dehydrating reagent.[8] Accordingly, we treated hydrazine with 3-(4-ethoxycarbonylphenyl)sydnone (**1**) and 3-benzyl-4-methoxycarbonylmethylenesydnone (**2**) to give 3-(4-hydrazinocarbonylphenyl)sydnone (**3**) and 3-benzyl-4-hydrazinocarbonylmethylsenesydnone (**4**) in good yields, respectively. When compound **3** was reacted with acetic anhydride, an acylated product **5** was obtained as a product.



Oxadiazole (**7**) was formed *via* a cyclization of compound **5** using one equivalent of acetic anhydride in the presence of perchloric acid as a catalyst, and a further acylation at C(4) position was obtained as a final product by using an excess of acetic anhydride. On the other hand, under the same reaction conditions, mixing compound **4** (a hydrazinocarbonylmethylenesydnone) and excess acetic anhydride in the presence of perchloric acid as a catalyst yielded an acetylated product **8** only. The different resultants obtained is attributed to the different nature of the phenyl ring and the C(4)-CH_2 group. There are two possible tautomers for the further cyclization to form the resultant (Scheme I). In both tautomers, the oxygen of the enol undergoes a nucleophilic reaction by attacking the carbon of the carbonyl group of the acetyl group for cyclization. The electron-donating nature of the C(4)-CH_2 group is less favorable to stabilizing the enol form leading to a simple acetylation product only. This comparison shows that the hydrazinocarbonyl group of compound **3** can be more easily cyclized than that of compound **4**. Hence, compound **3** was used for the following reactions to prepare the additional heterocyclic derivatives (**9**, **10**, **12**, **14**, **15**, and **17**).

A well-known tautomerization in the acetylacetone derivatives can be used to illustrate the possible tautomerization taking place as shown in Eq. 1. The tautomerization of acetylacetone and acetylacetophenone to form the enol forms in the solution are 80%,[9a] 89%,[9b] respectively. We simulated the heat formation of the *N*-acetyl-*N'*-bezoylhydrazine and the two enols by using PM3 method for comparison.[10] Three tautomers were used as the models because their parameters are well evaluated for this semi-empirical calculation. The heats of formation of the most stable conformers of ketone, enol **B**, and enol **A** are -35.74, -29.58, and -16.69 Kcal/mole, respectively.



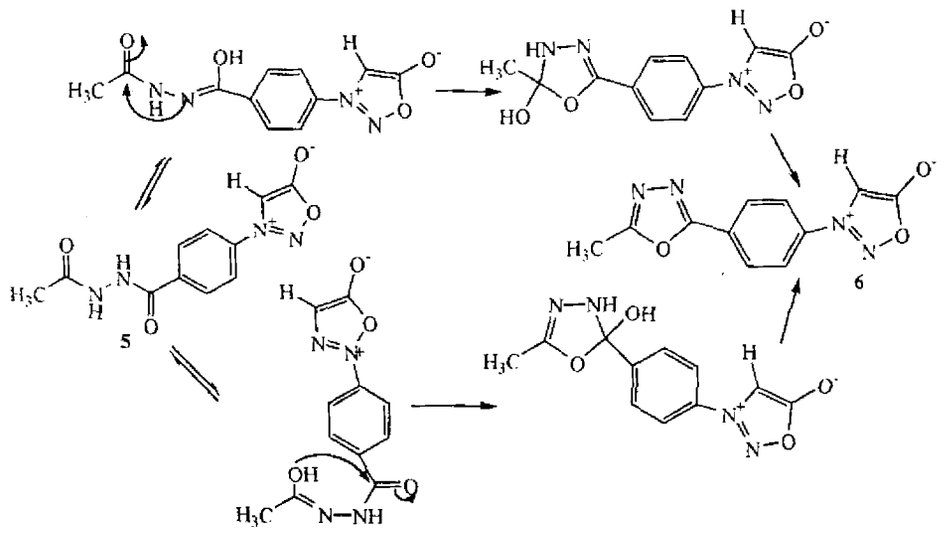
(1)

The simulated results for the compounds containing sydnone ring are less reliable because the parameters for the semi-empirical simulation are not well correlated for the sydnone series. However, the general trend obtained from the non-mesoionic compounds can be applied for this series of compounds. Two carbonyl groups of diacetylhydrazine were not in 2,3-positions, which may be a reason for the increase in the heat during the formation of an enol forms.

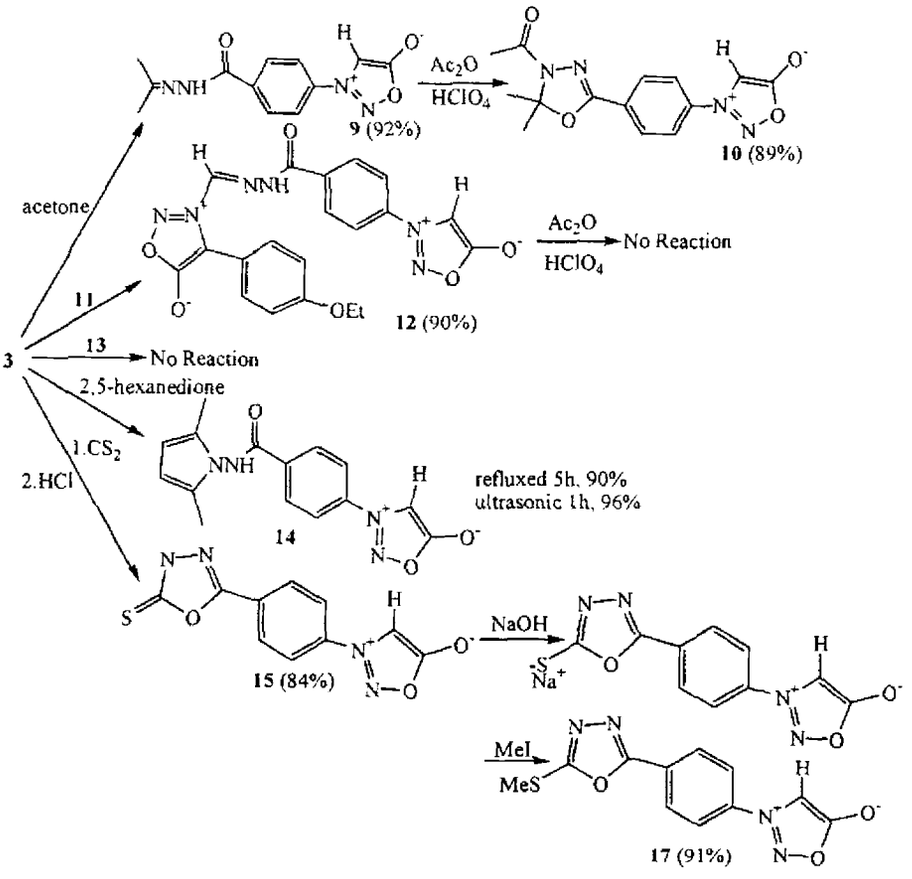
Reaction of compound **3** with an acetone was performed to yield a corresponding imine derivative **9** which was cyclized to form dihydrooxadiazole **10** with acetylation at N(4) of the new heterocyclic ring. The same mechanism as before can be initiated, i.e., formation of an enol whose oxygen attacks at the carbon of imine to give a negative charge of the nitrogen atom which would accept an acetyl cation.

Reaction of compound **3** with 3-(4-ethoxyphenyl)-4-formylsydnone **11** yielded a hydrazone product **12**, which resists cyclization in the presence of acetic anhydride and perchloric acid. This is due to the electron-donating nature of C(4) which enhances the electron density of carbon of the imine group making it unfavorable for the attack by oxygen

Scheme I



Scheme II



of carbonyl (or oxygen of enol). Unexpectedly, compound **3** did not react with 3-(4-methoxyphenyl)-4-acetylsydnone **13**. Reaction of compound **3** with 2,5-hexanedione under refluxing condition for 5 h produced an *N*-substituted pyrrole derivative **14** in 94% yield. The reaction rate was accelerated by ultrasonic irradiation giving a comparable yield after only one hour.

Condensation of compound **3** with a carbon disulfide produced an oxadiazothione **15** with the formation of carbon-sulfur double bond rather than a thiol. Thiol **16** should be an aromatic system. However, poor sulfur-hydrogen bonding enhanced the tautomerization to form a carbon-sulfur double bond. Compound **15** was enthiolized to compound **16** in the presence of sodium hydroxide for methylation by the methyl group.

CONCLUSION

The alkoxycarbonyl group on either the phenyl ring or C(4)-CH_2 of 3-arylsydnone can be converted to corresponding hydrazinocarbonyl derivatives. However, the hydrazinocarbonyl on the phenyl ring will be acetylated followed by cyclization while the same group on C(4)-CH_2 does not undergo a similar reaction. Equation 1 shows that the phenyl ring is able to stabilize the transition-state with an enol form in which the oxygen of enol undergoes a nucleophilic reaction toward another carbon of carbonyl group to initiate the cyclization. For compound **4**, the electron-donating character and lower efficiency in stabilizing the enol form may be the reason for inhibiting the cyclization. A similar mechanism can be applied for the formation of compounds **10**, **15** *via* cyclization.

EXPERIMENTAL

^{1}H NMR spectra were recorded at 250 MHz at an ambient temperature on a Bruker AC-250 NMR spectrometer. Mass spectra were obtained on a JEOL DX-300 double-focusing mass spectrometer. Samples were introduced *via* a direct insertion probe. The ionization energy was 70 eV. Microanalyses were performed on a Heraeus CHN-O-Rapid analyzer. 3-(4-Ethoxycarbonylphenyl)sydnone (**1**), 3-benzyl-4-(methoxycarbonylmethylene)sydnone (**2**), 3-(4-hydrazinocarbonylphenyl)sydnone (**3**), and 3-(4-ethoxyl-

phenyl)-4-formylsydnone (**11**) were prepared according to the literature.[11,12]

Acetylation of 3-(4-Ethoxycarbonylphenyl)sydnone (1) to Prepare 3-(Ethoxycarbonylphenyl)-4-acetylsydnone (13)

To a solution of compound **1** (5.0 g, 0.021 mol) in the acetic anhydride (50 mL) on an ice-bath, perchloric acid (60%, 1.0 mL) was added. After stirring at that temperature for 30 min and at room temperature for an additional 5 h, the mixture was poured onto ice-water (500 mL) giving an oily resultant, which solidified upon stirring and neutralization using $NaHCO_3$. The yellow flake product **13** (4.8 g, 83% yield) was obtained from filtration and recrystallization from 95% ethanol, mp. 134.5-135.0 °C; ^{1}H NMR ($CDCl_3$) δ 1.43 (t, 3H, J = 7.1 Hz, CH_3-CH_2-C(O)-), 2.54 (s, 3H, CH_3-C(O)-), 4.45 (q, 2H, J = 7.1 Hz, -CH_2-), 7.58 (d, 2H, J = 8.7 Hz, Ar-H), 8.27 (d, 2H, J = 8.7 Hz, Ar-H); IR (KBr) 1788 ($\nu_{C=O}$), 1713 ($\nu_{C=O}$), 1674 ($\nu_{C=O}$) cm^{-1}; MS (*m/z*, %) 276 (M$^+$, 14), 176 (100); Anal. Calcd. for $C_{13}H_{12}N_2O_5$: C, 56.52; H, 4.38; N, 10.14. Found: C, 56.31; H, 4.36; N, 10.14.

Preparation of 3-Benzyl-4-hydrazinocarbonylmethylenesydnone 4

A mixture of compound **2** and hydrazine (1.0 mL, 0.02 mol) in ethanol (99.5%, 5.0 mL) was stirred at room temperature for 30 min. After removing the solvent to dry followed by recrystallization from water yielded the white needles of compound **4** (0.55 g, 69% yield); mp 151.0-152.0 °C; ^{1}H NMR (DMSO-d_6) δ 3.36 (s, 2H, -CH_2-C(O)-), 4.25 (s, 2H, -NH_2), 5.69 (s, 2H, Ar-CH_2-), 7.41 (s, 5H, Ar-H), 9.29 (s, 1H, -NH-); IR (KBr) 3298 (ν_{N-H}), 1737 ($\nu_{C=O}$) cm^{-1}; MS (*m/z*, %) 248 (M$^+$, 8), 91 (100); Anal. Calcd. for $C_{11}H_{12}N_4O_3$: C, 53.22; H, 4.87; N, 22.57. Found: C, 53.18; H, 4.89; N, 22.43.

Reactions of Hydrazinocarbonyl Group and Acetic Anhydride

(a) Without addition of perchloric acid: A mixture of 3-(4-hydrazinocarbonylphenyl)sydnone **3** in acetic anhydride (30 mL) was stirred at room temperature for 30 min. After the mixture was poured onto ice-water (300 mL), a solid product was obtained upon stirring and neutralization by using $NaHCO_3$ powder. The white powder (0.98 g, 75% yield) was obtained after filtration and recrystallization from acetic acid and was identified as 3-(4-acetylhydrazinocarbonylphenyl)sydnone (**5**); mp. 233.0-234.0 °C (dec.); ^{1}H NMR (DMSO-d_6) δ 1.93 (s, 3H, CH_3-C(O)-), 7.87 (s, 1H, Ar-H), 8.10 (m, 4H, Ar-H), 10.00 (s, 1H, -NH-), 10.58 (s, 1H, -NH-); IR (KBr) 3286 (ν_{N-H}), 1767 ($\nu_{C=O}$) cm^{-1}; MS (*m/z*, %) 262 (M$^+$, 2), 204 (100); Anal. Calcd. for $C_{11}H_{10}N_4O_4$: C, 50.38; H, 3.84; N, 21.37. Found: C, 50.24; H, 3.93; N, 21.07.

(b) With limited amount of acetic anhydride and perchloric acid: To a mixture of compound **3** (1.1 g, 0.005 mol) in acetic anhydride (10 mL) on an ice-bath, perchloric acid (60%, 0.1 mL, 0.003 mol) was added. After stirring at that temperature for 30 min and at room temperature for 4 h, the mixture was poured onto ice-water (100 mL) giving an oily resultant. The solid was obtained upon stirring and neutralization by using $NaHCO_3$ powder. Yellow powder of compound **6** (0.87 g, 71% yield) was obtained from the filtration and recrystallization from 95% ethanol; mp 241.5-243.0 °C; ^{1}H NMR (DMSO-d_6) δ 2.61 (s, 3H, -CH_3), 7.90 (s, 1H, Ar-H), 8.05 (d, 2H, J = 8.8 Hz, Ar-H); IR (KBr) 1755 ($\nu_{C=O}$) cm^{-1}; MS (*m/z*, %) 244 (M$^+$, 2), 186 (100); Anal. Calcd. for $C_{11}H_8N_4O_3$: C, 54.10; H, 3.30; N, 22.94. Found: 53.87; H, 3.30; N, 22.85.

(c) Same procedure was used except for the amount of acetic anhydride (50 mL) and perchloric acid (0.2 mL). The product was identified as compound **7** (0.86 g, 60% yield); mp 248.0-249.0 °C; ^{1}H NMR (DMSO-d_6) δ 2.38 (s, 3H, CH_3-C(O)-), 2.61 (s, 3H, -CH_3), 7.91 (d, 2H, J = 8.6 Hz, Ar-H), 8.22 (d, 2H, J = 8.6 Hz, Ar-H); IR (KBr) 1767 ($\nu_{C=O}$), 1677 ($\nu_{C=O}$) cm^{-1}; MS (*m/z*, %) 286 (M$^+$, 21), 186 (98), 43 (100); Anal. Calcd. for $C_{13}H_{10}N_4O_4$: C, 54.55; H, 3.52; N, 19.57. Found: C, 54.31, H, 3.51; N, 19.45.

(d) Reaction of compound **4** and acetic anhydride was carried out using Method (a) to give a white cotton-like solid from water, which was identified as an acetylated compound **8** (0.3 g, 52% yield); mp 216.0-217.0 °C; ^{1}H NMR (DMSO-d_6) δ 1.86 (s, 3H, CH_3-C(O)-), 3.46 (s, 2H, -CH_2-C(O)-), 5.68 (Ar-CH_2-), 7.42 (s, 5H, Ar-H), 9.92 (s, 1H, -NH-), 10.14 (s, 1H, -NH-); IR (KBr) 3220 (ν_{N-H}), 1731 ($\nu_{C=O}$) cm^{-1}; MS (*m/z*, %) 290 (M$^+$, 1), 91 (100); Anal. Calcd. for $C_{13}H_{14}N_4O_4$: C, 53.79; H, 4.86; N, 19.30. Found: C, 53.69; H, 4.92; N, 19.21.

(e) Reaction of compound **8** in a solution of acetic anhydride and perchloric acid: A mixture of compound **8** and perchloric acid in acetic anhydride was stirred at room temperature for 24 h. Method (d) was applied to give compound **8** (80% recovery).

Condensation of Compound 3 and Acetone

A solution of compound **3** in acetone (30 mL) was stirred at room temperature for an hour to give a yellow solid. Filtration and recrystallization from ethanol yielded yellow needles of compound **9** (1.2 g, 92% yield); mp 215.0-

216.0 °C; ^{1}H NMR (DMSO-d_6) δ 1.96 (s, 3H, -CH_3), 2.02 (s, 3H, -CH_3), 7.87 (s, 1H, Ar-H), 8.08 (s, 4H, Ar-H), 10.71 (s, 1H, -NH-); IR (KBr) 3286 (ν_{N-H}), 1773 ($\nu_{C=O}$), 1659 ($\nu_{C=O}$) cm^{-1}; MS (*m/z*, %) 260 (M^+, 2), 202 (100); Anal. Calcd. for $C_{12}H_{12}N_4O_3$: C, 55.38; H, 4.65; N, 21.53. Found: C, 55.09; H, 4.58; N, 21.43.

Reaction of Hydrazone 9 with Acetic Anhydride

A solution of compound **9** (1.3 g, 0.005 mol) in acetic anhydride (30 mL) was refluxed for an hour. After removing acetic acid and excess acetic anhydride, a yellow residue was obtained which was recrystallized from ethanol to give a yellow granule solid of compound **10** (1.34 g, 89% yield), mp 265.0-266.0 °C; ^{1}H NMR (DMSO-d_6) δ 1.82 (s, 6H, 2 × CH_3), 2.24 (s, 3H, CH_3-C(O)-), 7.90 (s, 1H, syd-H), 8.07 (m, 4H, Ar-H); IR (KBr) 1755 ($\nu_{C=O}$), 1662 ($\nu_{C=O}$) cm^{-1}; MS (*m/z*, %) 302 (M^+, 3), 244 (100); Anal. Calcd. for $C_{14}H_{14}N_4O_4$: C, 55.63; H, 4.67; N, 18.53. Found: C, 55.47; H, 4.68; N, 18.53.

Condensation of Compound 3 with 3-(4-Ethoxycarbonylphenyl)-4-formylsydnone (11)

A solution of compound **3** (1.1 g, 0.005 mole) and compound **11** (1.2 g, 0.005 mol) in ethanol (99.5%, 50 mL) was refluxed for 5 h. A product of yellow powder, obtained upon filteration from ice-cooled solution and then recrystallization from methanol, was identified as compound **12** (1.96 g, 90% yield), mp 178.0-179.0 °C (dec.); ^{1}H NMR (DMSO-d_6) δ 1.37 (t, 3H, J = 6.9 Hz, CH_3-CH_2-C(O)-), 4.16 (q, 2H, J = 6.9 Hz, CH_3-CH_2-C(O)-), 7.05 (s, 1H, -N=CH-), 7.27 (d, 2H, J = 8.9 Hz, Ar-H), 7.73 (d, 2H, J = 8.9 Hz, Ar-H), 7.89 (s, 1H, syd-H), 8.17 (s, 4H, Ar-H), 12.57 (s, 1H, -NH-); IR (KBr) 1749 ($\nu_{C=O}$), 1725 ($\nu_{C=O}$), 1677 ($\nu_{C=O}$) cm^{-1}; FABMS (*m/z*, %) 437 ([M+1]$^+$, 100); Anal. Calcd. for $C_{20}H_{16}N_6O_6$: C, 55.05; H, 3.70; N, 19.26. Found: C, 54.80; H, 3.70; N, 19.23.

Attempt Condensation of Compound 3 with 3-(4-Ethoxycarbonylphenyl)-4-acetylsydnone (13)

A mixture of compound **3** (1.1 g, 0.005 mol) and compound **13** (1.3 g, 0.005 mol) in ethanol (99.5%, 50 mL) was refluxed for 5 h. After removing the solvent, the residue was identified as a mixture of compounds **3** and **13** (1.0 g, 90% recovery) by comparing ^{1}H NMR with an authentic sample.

Condensation of Compound 3 with 2,5-Hexanedione

(a) A solution of compound **3** (1.1 g, 0.005 mol) and 2,5-hexadione (2.95 mL, 0.025 mol) in ethanol (99.5%, 20 mL) was refluxed for 5 h. After removing the solvent, ice-cooled aqueous $NaHCO_3$ (saturated, 50 mL) was added. A yellow pyrrol derivative **14** (1.34 g, 90% yield) was collected by filtration and then recrystallization from ethanol, mp 217.0-218.0 °C, (lit.[12] 215 °C).

(b) Same reaction was carried out under ultrasonic irradiation for an hour at room temperature to give compound **14** in 96% yield. The product was confirmed by comparing the mp and ^{1}H NMR with an authentic sample.

Condensation of Compound 3 with Carbon Disulfide

A solution of compound **3** (2.2 g, 0.01 mol), KOH (0.56 g, 0.01 mol), and CS_2 (1.2 mL, 0.02 mol) in ethanol (99.5%, 100 mL) was refluxed for 6 h. After removing the solvent, the residue was mixed with water (300 mL) and then was acidified with dil. HCl to give a yellow solid. Filtration and recrystallization from ethanol afforded yellow 5-thia-1,3,4-dioxadiazole derivative **15** (2.3 g, 84% yield), mp 225.0-226.0 °C (dec.); ^{1}H NMR (DMSO-d_6) δ 1.90 (s, 3H, -CH_3-), 8.03 (s, 1H, syd-H), 8.19 (s, 4H, Ar-H); IR (KBr) 1719 ($\nu_{C=O}$) cm^{-1}; MS (*m/z*, %) 262 (M^+, 1), 90 (100); Anal. Calcd. for $C_{10}H_6N_4O_3S$: C, 45.80; H, 2.31; N, 21.36; S, 12.23. Found: C, 45.72; H, 2.32; N, 21.28; S, 12.11.

Methylation of Compound 15

To an aqueous solution (50 mL) of compound **15** (1.1 g, 0.004 mol) and NaOH (0.16 g, 0.004 mol), CH_3I (0.3 mL, 0.005 mol) was added. After stirring that solution at room temperature for 6 h, the yellow solid was harvested and recrystallized from ethanol to give 5-methylthio-1,3,4-dioxadiazole derivative **17** (1.0 g, 91% yield); mp 249.0-250.0 °C; ^{1}H NMR (DMSO-d_6) δ 2.79 (s, 3H, -CH_3), 7.90 (s, 1H, syd-H), 8.04 (d, 2H, J = 8.9 Hz), 8.25 (d, 2H, J = 8.9 Hz); IR (KBr) 1755 ($\nu_{C=O}$) cm^{-1}; MS (*m/z*, %) 276 (M^+, 2), 218 (100); Anal. Calcd. for $C_{11}H_8N_4O_3S$: C, 47.82; H, 2.92; N, 20.28; S, 11.61. Found: C, 47.77; H, 2.91; N, 20.22; S, 11.66.

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Key Words

Hydrazinocarbonylphenylsydnones; Cyclization; Oxadiazoles; Dihydropyrroles; Pyrroles;

Tautomerization.

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