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Synthesis of Sydnone Compounds Having Heterocyclic Groups at the 4-Positions from 4-(Bromoacetyl)sydnones

Toshio Fuchigami,* Takushi Goto, Mou-Yung Yeh,†
Tsutomu Nonaka,* and Hsien-Ju Tien†
Department of Electronic Chemistry, Graduate School at Nagatsuta
Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 227
†*Department of Chemistry, National Cheng Kung University,*
Tainan, Taiwan, Republic of China
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New sydnone derivatives having heterocyclic substituents such as 4-thiazolyl, 3-thienyl, 2H-1,4-benzothiazin-3-yl, 2H-1,4-benzoxazin-3-yl, and 1,2-dihydro-3-quinoxalinyl groups at the 4-positions were prepared from 4-bromoacetyl-3-arylsydnones (**1**). Sydnone compounds substituted by a 1,2,3-triazol-4-yl group were prepared *via* new type phosphonium ylids derived from **1**. Electroreduction of **1** was also attempted in order to prepare a syndnone derivatives having a furyl group.

Although sydnone compounds are interesting in their chemical, physical, and biological properties,[1] their syntheses are limited[2] because a sydnone ring is unstable to acid, alkali, and heat.

As a part of a broad program to study on the synthesis of sydnone compounds and their properties,[3] we have investigated possible synthetic methods for sydnones having heterocyclic groups at their 4-positions: In earlier works, sydnone derivatives substituted directly by 4-thiazolyl,[4,5] 4-sydnonyl,[6,7] 1,2,4-thiadiazol-5-yl,[8] 1,2,4-oxadiazol-5-yl,[9] 3,4-dihydro-1,2,4-oxadiazol-3-yl,[9] 1,2,4-oxadiazol-5-yl,[8] and 1,2,4-triazol-3-yl[8] groups were successfully synthesized. In most of the above synthesis,[8,9] derivatives of sydnone-4-carboxylic acids were used as the starting materials and they were converted into the desired sydnone compounds having heterocyclic groups *via* acyclic intermediates.

Haloacetyl groups are known as good precursors to heterocyclic groups.[10] We have found that 4-bromoacetyl-3-arylsydnones (**1**) could be easily prepared *via* 4-acetyl-3-arylsydnones from the corresponding 4-unsubstituted 3-arylsydnones.[4,11] In this paper, we wish to report the synthesis of new sydnone compounds substituted directly by heterocyclic groups at the 4-positions from **1**.

Results and Discussion

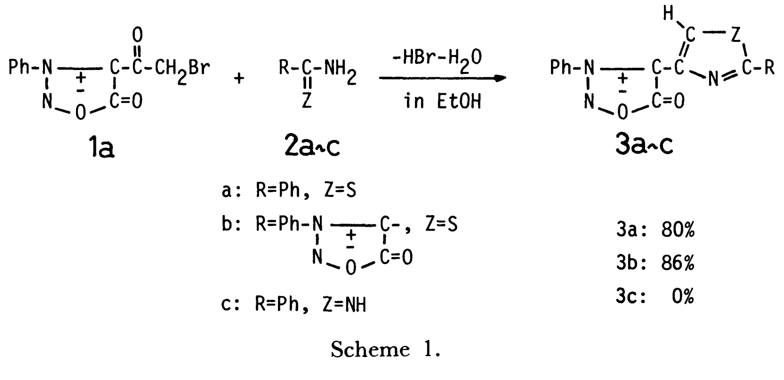
*Reaction of 4-Bromoacetyl-3-phenylsydnone (**1a**) with Thioamides (**2a,b**) and Amidine (**2c**).* Only one synthetic reaction using **1** has been reported by us: It was found that **1a** reacted with thiourea to give 4-(2-amino-4-thiazolyl)-3-phenylsydnone.[4,5] This is the first synthesis of a sydnone having a heterocyclic group at the 4-position, except for 4,4′-bisydnone.[7]

At the first stage of investigation, an analogous reaction (Scheme 1) to the above was examined by using thioamides (**2a,b**) and benzamidine (**2c**) instead of thiourea.

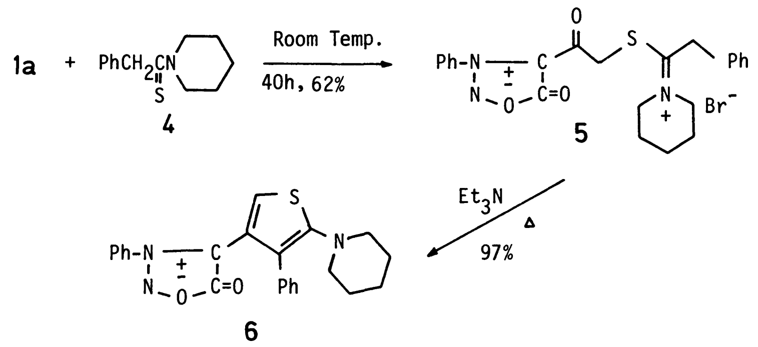
Thiobenzamide (**2a**) reacted readily with **1a** suspended in ethanol at room temperature to form 3-phenyl-4-(2-phenyl-4-thiazolyl)sydnone (**3a**) in a good yield. 3-Phenyl-4-thiocarbamoylsydnone (**2b**) did not react with **1a** under the same conditions. When the reaction was carried out under reflux for a short time, 2,4-bis(3-phenyl-4-sydnonyl)thiazole (**3b**) was obtained in a good yield.

4-(2-Phenyl-4-imidazolyl)-3-phenylsydnone (**3c**) was expected to be formed from **1a** and benzamidine (**2c**), since it is known that α-bromoacetophenone reacts with **2c** to give the corresponding imidazole compound.[12] However, **3c** could not be obtained in ethanol at either room temperature or higher one and decomposition of **1a** and/or **3c** seemed to occur. The reaction in DMF instead of ethanol also gave a similar result. These unsuccessful results may be due to the decomposition of sydnone rings by a strong base of **2c**.

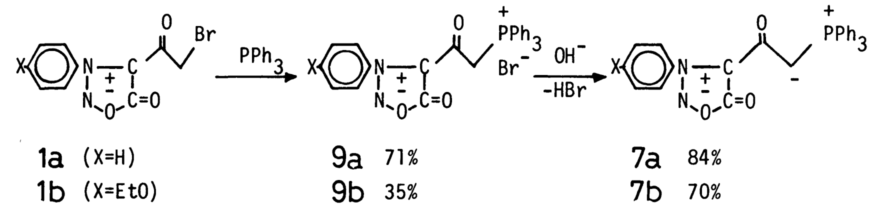
*Reaction of 4-Bromoacetyl-3-phenylsydnone (**1a**) with* N,N*-Disubstituted Thioamide (**4**).* It is known that the reaction of α-bromoacetophenone with *N,N*-disubstituted thioamides gives the corresponding thiophene



Scheme 1.



Scheme 2.



Scheme 3.

compounds.[13)]

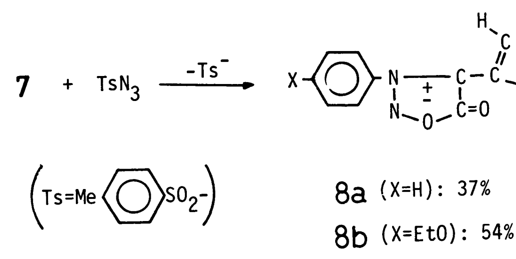
4-(Bromoacetyl)sydnone **1a** reacted with *N*-[benzyl(thiocarbonyl)]piperidine (**4**) in dichloromethane at room temperature to form a salt (**5**) (Scheme 2). The structure of **5** was confirmed by IR and mass spectra and elemental analysis. A peak at *m/z* 403 ($M^+-HBr-H_2O$) was observed in the mass spectrum. The salt **5** decomposes gradually in the air.

The conversion of **5** into 3-phenyl-4-(4-phenyl-5-piperidino-3-thienyl)sydnone (**6**) was successfully carried out by heating **5** with triethylamine in ethanol. In the IR spectrum of **6**, absorption of the carbonyl group of the original **5** disappeared and the molecular ion peak at *m/z* 403 was observed in the mass spectrum.

*Synthesis of Phosphonium Ylids (7) from 1 and Triphenylphosphine and their Conversion to 4-(1*H*-1,2,3-Triazol-4-yl)sydnones (8).* It is known that phenacylidentriphenylphosphorane reacts with *p*-toluenesulfonyl azide to give 3-tosyl-4-phenyl-1,2,3-triazole.[14)] Since the reaction proceeds under mild conditions, this method seems to be applicable to the synthesis of sydnone derivatives having a 1,2,3-triazol-4-yl group.

First, the synthesis of phosphonium ylid was attempted. Phosphonium bromide (**9**) was obtained by the reaction of **1** with triphenylphosphine in acetonitrile at room temperature. Treatment of **9** with aqueous sodium hydroxide provided phosphonium ylid **7** in a good yield. The structure of **7** was confirmed by comparison of IR spectra of **7** with those of **9**: The C=O stretching vibration band of **9** was at 1660—1670 cm^{-1}, while that of **7** was at 1530—1540 cm^{-1}. The shift was analogous to that of observed in the case of phenacylidenetriphenylphosphorane. The ylid **7** thus obtained melts around 200 °C and was found to be stable.

Next, the synthesis of 4-(1,2,3-triazol-4-yl)sydnone (**8**) from **7** was carried out. The reaction of **7** with



Scheme 4.

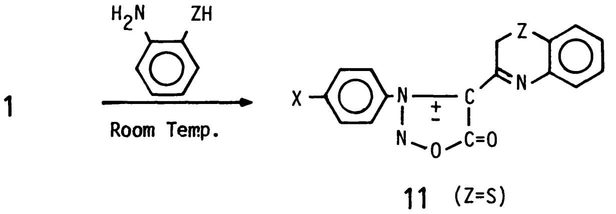
p-toluenesulfonyl azide took place in dichloromethane at room temperature, however **8** could not be obtained. The desired product **8** was obtained by the reaction in benzene under reflux for a long time. It is known that a tosyl group is easily eliminated from 4-aryl-3-tosyl-1,2,3-triazole under reflux in ethanol.[14)] In a similar manner, **8** seems to be formed by hydrolysis of 3-aryl-4-[3-(*p*-tolylsulfonyl)-1*H*-1,2,3-triazol-4-yl]sydnone formed initially under the reaction conditions used.

*Electroreduction of 4-Bromoacetyl-3-phenylsydnone (**1a**).* Barba *et al.*[15)] have recently reported an interesting electroreduction of α-bromoacetophenone to 2,4-diphenylfuran. Using the electrochemical method, the synthesis of a sydnone having a furyl group from 4-(bromoacetyl)sydnone (**1a**) was attempted.

The electroreduction of **1a** was carried out by means of controlled potential electrolysis at a mercury pool cathode in a DMF solution containing lithium perchlorate as a supporting electrolyte in a divided cell. One Faraday (96480 C)/mol of charge was coulometrically passed at −0.15 V *vs.* Ag/$AgNO_3$ (saturated in DMF). Products separated by a column chromatograph were not the expected furan compound but 4-acetyl-3-phenylsydnone (22% yield and 44% current efficiency) and the corresponding reduction dimer, 1,4-bis(3-phenyl-4-sydnonyl)-1,4-butanedi-

Table 1. Synthesis of sydnone derivatives (**11**—**13**)

X	Z	Solvent	Molar ratio (amine/**2**)	Reaction time (Temp)	Product (Yield/%)
H	S	EtOH	1	5 min (rt)	**11a**(85)
EtO	S	EtOH	1	1 h (rt)	**11b**(83)
H	O	DMF	1	30 h (rt)	**12** (15)
H	NH_2	EtOH	1	1 h (rt)	**13a**(0)
H	NH_2	EtOH	1	5 min (reflux)	**13a**(0)
H	NH_2	EtOH	2	5 min (reflux)	**13a**(80)
H	NH_2	DMF	1	75 min (rt)	**13a**(43)
H	NH_2	DMF	2	75 min (rt)	**13a**(82)
EtO	NH_2	EtOH	2	10 min (60 °C)	**13b**(72)



11 (Z=S)
12 (Z=O)
13 (Z=NH)

Scheme 5.

one (**10**) (7% yield and 7% current efficiency) whose structure was assigned from IR and mass spectra and analytical data.

Although a few papers deal with electrooxidation[16—18] and polarography[2b] of sydnones, no report of the electroreduction of sydnone compounds by means of preparative electrolysis has been published.[19] In this situation, it is interesting to note that the electroreduction of **1a** proceeded without any decomposition of the sydnone ring.

Synthesis of Sydnone Compounds Having Six-membered Heterocyclic Groups (11, 12, 13). The synthesis of sydnones substituted by six-membered heterocyclic groups at the 4-position has not been reported. In this work, the synthesis of such sydnone compounds was attempted using the reaction of **1** with *o*-aminophenol, *o*-aminobenzenethiol, and *o*-phenylenediamine.

o-Aminobenzenethiol reacted readily with **1** in ethanol at room temperature to give 4-(2*H*-1,4-benzothiazin-3-yl)sydnone (**11**) in a good yield, while *o*-aminophenol did not give the corresponding 4-(2*H*-1,4-benzoxazin-3-yl)sydnone (**12**) under the same conditions. Recently, Schrider *et al.*[20] prepared 2*H*-1,4-benzoxazines by heating α-bromoacetophenones and *o*-aminophenol in acetone in the presence of excess potassium carbonate. Using their procedure the reaction of **1a** with *o*-aminophenol was attempted. However, only decomposition took place even when the reaction was carried out at room temperature and no desired **12** was formed. After several trials, **12** could be synthesyzed by changing the solvent and base to DMF and 1 equiv. of sodium hydroxide, respectively. The compound **12** was very sensitive to base and the use of excess amount of the base caused the decomposition of **12**.

In the reaction with *o*-phenylenediamine, as shown in Table 1, the yield of 4-(3,4-dihydro-2-quinoxalinyl)-sydnone (**13**) strongly depended on the reaction conditions. When 2 equiv. of the diamine was used, the expected product **13** was obtained in satisfactory yields.

The new types of sydnone compounds thus prepared are expected to be pharmacologically active and screening tests of several biological activities of these sydnones are currently under investigation.

Experimental

^1H NMR spectra were recorded at 60 MHz on a Varian EM360 NMR spectrometer using DMSO-d_6 and Me_4Si as solvent and an internal standard, respectively. IR spectra were obtained on a Hitachi 295 infrared spectrometer. Electron impact mass spectra were determined at 30 eV on a JEOL JMS-D100 mass spectrometer by direct introduction *via* probe.

*4-Bromoacetyl-3-(*p*-ethoxyphenyl)sydnone (**1b**).* Using the procedure similar to preparation of **1a**,[4] the crude product was obtained. Recrystallization from ethanol provided pure **1b** as a yellow solid. Yield, 71%. Mp 133—134 °C. IR (KBr) 3000, 2950, 2900 ($\nu_{C\text{-}H}$), 1770, and 1690 cm^{-1} ($\nu_{C=O}$). MS: *m/z* (rel intensity) 298 (M^++2—NO, 2), 296 (M^+—NO, 2), 270 (M^++2—NO—CO, 24), 268 (M^+—NO—CO, 24), and 148 (100). Found: C, 44.00; H, 3.20; N, 8.41; Br, 24.24%. Calcd for $C_{12}H_{11}N_2O_3Br$: C, 44.06; H, 3.39; N, 8.56; Br, 24.43%.

*3-Phenyl-4-(2-phenyl-4-thiazolyl)sydnone (**3a**).* To a stirred solution of 0.39 g (2.84 mmol) of thiobenzamide in 10 ml of ethanol was added 0.80 g (2.83 mmol) of **1a** and the mixture was stirred at room temperature for 10 min. The yellow precipitates were collected by filtration and washed with ethanol; 0.73 g, 80%. Recrystallization from ethanol provided 0.68 g (75%) of pure **2a** as pale yellow needles. Mp 183—183.5 °C. IR (KBr) 1770 cm^{-1} ($\nu_{C=O}$). ^1H NMR δ=7.47 (s, 5H, $C_6\underline{H}_5$), 7.80 (s, 5H, $C_6\underline{H}_5$), and 8.15 (s, 1H, thiazol C-$\underline{H}$). MS: *m/z* (rel intensity) 321 (M^+, 30) and 263 (M^+—NO—CO, 100). Found: C, 63.50; H, 3.23; N, 13.12; S, 10.26%. Calcd for $C_{17}H_{11}N_3O_2S$: C, 63.54; H, 3.45; N, 13.08; S, 9.98%.

*2,4-Bis(3-phenyl-4-sydnonyl)thiazole (**3b**).* After a mixture of 0.39 g (1.39 mmol) of **1a** and 0.30 g (1.36 mmol) of 3-phenyl-4-thiocarbamoylsydnone in 2 ml of ethanol was refluxed for 15 min, yellow precipitates appeared. After cooling, the precipitates were collected by filtration and washed with ethanol; 0.47 g, 86%. Mp 241—242.5 °C (decomp). Recrystallization from dichloromethane-hexane provided pure 0.37 g (66%) of **2b** as yellow needles. Mp 242—243 °C (decomp). IR (KBr) 1775 and 1765 cm^{-1} ($\nu_{C=O}$). ^{1}H NMR δ=7.45—7.83 (m, 10H, $C_6\underline{H}_5$), 8.21 (s, 1H, thiazol C-$\underline{H}$). MS: *m/z* (rel intensity) 405 (M^+, 5), 347 (M^+—NO—CO, 10), 289 (M^+—2NO—2CO, 5), and 147 (100). Found: C, 56.26; H, 2.63; N, 17.24; S, 8.04%. Calcd for $C_{19}H_{11}N_5O_4S$: C, 56.29; H, 2.74; N, 17.28; S, 7.91%.

*1-[2-Phenyl-1-[(3-phenyl-4-sydnonyl)carbonylmethylthio]ethylidene]piperidinium Bromide (**5**).* A mixture of 0.78 g (3.56 mmol) of *N*-[benzyl(thiocarbonyl)]piperidine (**4**)[21] and 1.00 g (3.53 mmol) of **1a** in 15 ml of dichloromethane was allowed to stand for 40 h at room temperature. The resulting precipitates were collected by filtration and pale pink prisms (0.95 g, 54%) were obtained. The filtrate was concentrated under reduced pressure and 0.14 g (8%) of a precipitating solid was obtained. Recrystallization from dichloromethane-ether provided 0.72 g (41%) of pure **5** as a pale pink solid. Mp 183—185 °C (decomp). IR (KBr) 1780 and 1720 cm^{-1} ($\nu_{C=O}$). MS: *m/z* (rel intensity) 403 (M^+—HBr—H_2O, 45) and 345 (M^+—HBr—H_2O—NO—CO, 100). Found: C, 55.20; H, 4.86; N, 8.21; S, 6.32; Br, 16.09%. Calcd for $C_{23}H_{24}N_3O_3SBr$: C, 54.98; H, 4.82; N, 8.46; S, 6.38; Br, 15.90%.

*3-Phenyl-4-(4-phenyl-5-piperidino-3-thienyl)sydnone (**6**).* A mixture of 0.60 g (1.19 mmol) of **5** and 0.13 g (1.29 mmol) of triethylamine in 20 ml of ethanol was refluxed for 30 min. After concentration, the residue was mixed with *ca.* 50 ml of water. A precipitating solid was collected by filtration, washed with water, and 0.47 g (97%) of a yellow solid was obtained. Mp 129.5—133 °C (decomp). Recrystallization from aq ethanol provided 0.29 g (59%) of pure **6** as a yellow solid. Mp 131—133 °C (decomp). IR (KBr) 1760 cm^{-1} ($\nu_{C=O}$). ^{1}H NMR δ=1.43 (br. S, 8H, $C\underline{H}_2$), 4.55 (s, 2H, $C\underline{H}_2$), 6.39 (s, 1H, thiophene C–$\underline{H}$), 7.23 (s, 5H, $C_6\underline{H}_5$), and 7.64 (s, 5H, $C_6\underline{H}_5$). MS: *m/z* (rel intensity) 403 (M^+, 7), 345 (M^+—NO—CO, 13), and 64 (100). Found: C, 68.51; H, 5.50; N, 10.04%. Calcd for $C_{23}H_{21}N_3O_2S$: C, 68.46; H, 5.25; N, 10.41%.

*(3-Phenyl-4-sydnonylcarbonylmethyl)triphenylphosphonium Bromide (**9a**).* To a stirred solution of 4.00 g (14.9 mmol) of triphenylphosphine in 60 ml of acetonitrile was added a solution of 4.00 g (14.1 mmol) of **1a** in 20 ml of acetonitrile and the mixture was stirred for 2 h. After concentration of the solution, ether was added and 5.45 g of insoluble material was collected by filtration. Mp 208—210 °C (decomp). Recrystallization from dichloromethane-hexane provided 2.70 g (50%) of pure **9a** as pale yellow crystals. Mp 209—211 °C (decomp). IR (KBr) 1775 and 1670 cm^{-1} ($\nu_{C=O}$). ^{1}H NMR δ=5.65 (s, 1H, $C\underline{H}$), 5.85 (s, 1H, $C\underline{H}$), 7.63, 7.75, and 7.88 (s, 20H, $C_6\underline{H}_5$). Found: C, 61.96; H, 4.10; N, 5.38%. Calcd for $C_{28}H_{22}N_2O_3BrP$: C, 61.67; H, 4.07; N, 5.14%.

*(3-Phenyl-4-sydnonylcarbonylmethylene)triphenylphosphorane (**7a**).* To a stirred solution of 1.96 g (9.94 mmol) of **9a** in 40 ml of dichloromethane was added 10 ml of 10% sodium hydroxide at room temperature. After the dichloromethane layer had been separated and dried over sodium sulfate, concentration of the solution provided 1.40 g (84%) of **7a**. Mp 222—224 °C (decomp). IR (KBr) 1760 and 1530 cm^{-1} ($\nu_{C=O}$). ^{1}H NMR δ=4.56, 4.96 (s, 1H, $C\underline{H}$), 7.60, 7.62, and 7.71 (s, 20H, C_6H_5). Found: C, 72.61; H, 4.49; N, 5.97%. Calcd for $C_{28}H_{21}N_2O_3P$: C, 72.41; H, 4.56; N, 6.03%.

*[3-(p-Ethoxyphenyl)-4-sydnonylcarbonylmethylene]triphenylphosphorane (**7b**).* Phosphonium bromide (**9b**) was prepared from **1b** and triphenylphosphine. IR (KBr) 1780 and 1660 cm^{-1} ($\nu_{C=O}$). Without purification, crude **9b** was used for the preparation of **7b**. By the procedure similar to the preparation of **7a**, crude **7b** was obtained from **9b**. Mp 196—197 °C. Recrystallization from dichloromethane-hexane provided pure **7b** as yellow crystals. Mp 196—197 °C. IR (KBr) 1750 and 1540 cm^{-1} ($\nu_{C=O}$). MS: *m/z* (rel intensity) 508 (M^+, 3) and 262 (PPh_3, 100). Found: C, 70.67; H, 4.89; N, 5.37%. Calcd for $C_{30}H_{25}N_2O_4P$: C, 70.86; H, 4.96; N, 5.51%.

*3-Phenyl-4-(1H-1,2,3-triazol-4-yl)sydnone (**8a**).* A mixture of 1.00 g (2.15 mmol) of **7a** and 0.50 g (2.54 mmol) of *p*-toluenesulfonyl azide in 80 ml of benzene was refluxed for 44 h. Black oily material was obtained after concentration of the solution. A solution of the oil in a small amount of ethyl acetate was allowed to stand for one week and crystals precipitated. Colorless needles were collected by filtration and washed with ethyl acetate, 0.18 g (37%). Mp 215—217 °C. Recrystallization from dichloromethane-hexane provided pure 0.12 g (24%) of **8a** as colorless needles. Mp 215—217 °C. IR (KBr) 3160 (ν_{NH}), 1715 ($\nu_{C=O}$), and 1605 cm^{-1} ($\nu_{C=N}$). ^{1}H NMR δ=7.79 (s, 5H, $C_6\underline{H}_5$), 8.13 (br. s, 1H, triazole C–$\underline{H}$), and 15.49 (br. s, 1H, N$\underline{H}$). MS: *m/z* (rel intensity) 229 (M^+, 12), 171 (M^+—NO—CO, 87), and 77 (C_6H_5, 100). Found: C, 52.20; H, 2.87; N, 30.58%. Calcd for $C_{10}H_7N_5O_2$: C, 52.40; H, 3.08; N, 30.56%.

*3-(p-Ethoxyphenyl)-4-(1H-1,2,3-triazol-4-yl)sydnone (**8b**).* In a similar manner, the reaction of **7b** with *p*-toluenesulfonyl azide was carried out. After the reaction, benzene was removed by evaporation and black oily material remained. The oil was dissolved in dichloromethane and the solution was treated with active charcoal. Concentration of the solution to dryness provided a solid. Recrystallization from dichloromethane-hexane (4:1) provided pure **8b** as colorless needles (54%). Mp 241—242 °C. IR (KBr) 3130 (ν_{NH}), 3000, 2920, 2860 (ν_{C-H}), and 1740 cm^{-1} ($\nu_{C=O}$). ^{1}H NMR δ=1.38 (t, 3H, $C\underline{H}_3$), 4.14 (q, 2H, $C\underline{H}_2$), 7.16 (d, 2H, *p*-EtO$C_6\underline{H}_4$), 7.70 (d, 2H, *p*-EtO$C_6\underline{H}_4$), 8.04 (s, 1H, triazole C–$\underline{H}$), 15.30 (br. s, 1H, N$\underline{H}$). MS: *m/z* (rel intensity) 273 (M^+, 18) and 215 (M^+—NO—CO, 100). Found: C, 52.70; H, 3.85; N, 25.28%. Calcd for $C_{12}H_{11}N_5O_3$: C, 52.75; H, 4.06; N, 25.63%.

*Electroreduction of 4-Bromoacetyl-3-phenylsydnone (**1a**).* An H-type cell divided with a sintered glass diaphragm was used. The cathode and anode were a mercury pool (7.07 cm^2) and a platinum plate (2.5×2.5 cm^2), respectively. 50 ml and 30 ml of 0.2 M $LiClO_4$/MeCN solution were used as catholyte and anolyte, respectively. To the catholyte was added 1.42 g (5 mmol) of **1a** and electricity was supplied. The cathode potential and temperature were maintained at −0.15 V *vs.* Ag/$AgNO_3$ (sat. in DMF) (an initial cathodic current density, 1.13 A/dm^2) and at 20 °C, respectively, during electrolysis. When 495 C (1.03F/mol) was passed, the cathodic current decreased to the background level. After electrolysis, the brown catholyte was concentrated under reduced pressure below 60 °C and 50 ml of water was added. The mixture was extracted respeatedly with dichloromethane and the extracts were washed with water, and then dried over anhydrous sodium sulfate. After the extract solution had been concentrated, the remaining reddish oily material was subjected to TLC (silica gel). Elution with dichloromethane provided 0.22 g (22%) of 4-acetyl-3-phenylsydnone (first elution component) and 0.15 g (7%) of 1,4-bis(3-phenyl-4-sydnonyl)-1,4-butandione (**10**) (second component). Product **10**: mp 237—238 °C (decomp). IR (KBr) 3080 (ν_{CH}), 2930 (ν_{CH_2}), 1780 ($\nu_{C=O}$ of sydnone ring), and 1660 cm^{-1} ($\nu_{C=O}$). *m/z* 406 (M^+). Found: C, 58.87; H, 3.20; N, 13.71%. Calcd for $C_{20}H_{14}N_4O_6$: C, 59.12; H, 3.47; N, 13.79%.

*4-(2H-1,4-Benzothiazin-3-yl)-3-phenylsydnone (**11a**).* To a stirred solution of 0.30 g (1.06 mmol) of **1a** in 2 ml of ethanol was added a solution of 0.14 g (1.08 mmol) of *o*-

aminobenzenethiol in 2 ml of ethanol at room temperature. After stirring for 5 min, *ca.* 10 ml of water was added to the reaction mixture and a resulting solid was collected by filtration. Washing with ethanol provided 0.28 g (85%) of an orange yellow solid. Mp 166—168 °C (decomp). Recrystallization from ethanol provided 0.25 g (76%) of pure **11a** as orange yellow needles. Mp 166—168 °C (decomp). IR (KBr) 3060, 2990 (ν_{C-H}), 1770 ($\nu_{C=O}$), and 1590 cm^{-1} ($\nu_{C=N}$). ^{1}H NMR δ=3.84 (s, 2H, $C\underline{H}_2$), 6.56—7.26 (m, 4H, aromatic C-$\underline{H}$), and 7.93 (s, 5H, $C_6\underline{H}_5$). MS: *m/z* (rel intensity) 309 (M$^+$, 53) and 251 (M$^+$—NO—CO, 100). Found: C, 62.35; H, 3.89; N, 13.49; S, 10.36%. Calcd for $C_{16}H_{11}N_3O_2S$: C, 62.12; H, 3.58; N, 13.58; S, 10.37%.

4-(2H-1,4-Benzothiazin-3-yl)-3-(p-ethoxyphenyl)sydnone (11b). By the same procedure, the pure product **11b** was directly obtained without purification. Mp 132—134 °C. IR (KBr) 3000, 2950, 2900 (ν_{C-H}), 1775 ($\nu_{C=O}$), and 1600 cm^{-1} ($\nu_{C=N}$). ^{1}H NMR δ=1.38 (t, 3H, $C\underline{H}_3CH_2O$), 3.80 (s, 2H, $C\underline{H}_2$), 4.17 (q, 2H, $CH_3C\underline{H}_2O$), 6.56—7.30 (m, 4H, aromatic C-$\underline{H}$), 7.12 (d, 2H, *p*-$EtOC_6\underline{H}_4$), and 7.68 (d, 2H, *p*-$EtOC_6\underline{H}_4$). MS: *m/z* (rel intensity) 353 (M$^+$, 11), 295 (M$^+$—NO—CO, 17), and 44 (100). Found: C, 61.33; H, 4.21; N, 11.80; S, 8.91%. Calcd for $C_{18}H_{15}N_3O_3S$: C, 61.15; H, 4.28; N, 11.89; S, 9.07%.

4-(2H-1,4-Benzoxazin-3-yl)-3-phenylsydnone (12). To a mixture of 0.40 g (3.67 mmol) of *o*-aminophenol, 3.9 ml of 1 M[†] sodium hydroxide and 20 ml of DMF was added a solution of 1.00 g (3.53 mmol) of **1a** in 5 ml of DMF. The mixture was allowed to stand for 30 h. To the brown reaction mixture was added *ca.* 100 ml of water and a precipitating solid was collected, and then washed with water. The solid was chromatographed on silica gel (70—230 mesh). Elution with benzene provided 0.15 g (15%) of almost pure **12**. Mp 162.5—163.5 °C (decomp). Recrystallization from dichloromethane-hexane provided **12** as yellow needles. Mp 162.5—163.5 °C (decomp). IR (KBr) 3070 (ν_{C-H}), 1770 ($\nu_{C=O}$), and 1605 cm^{-1} ($\nu_{C=N}$). ^{1}H NMR δ= 5.05 (s, 2H, $C\underline{H}_2$), 6.70—7.10 (m, 4$\underline{H}$, aromatic C-$\underline{H}$), and 7.93 (s, 5H, $C_6\underline{H}_5$). MS: *m/z* (rel intensity) 293 (M$^+$, 57) and 235 (M$^+$—NO-CO, 100). Found: C, 65.60; H, 3.61; N, 14.24%. Calcd for $C_{16}H_{11}N_3O_3$: C, 65.53; H, 3.78; N, 14.33%.

4-(3,4-Dihydro-2-quinoxalinyl)-3-phenylsydnone (13a). To a hot solution of 0.16 g (1.45 mmol) of *o*-phenylenediamine in 2 ml of ethanol was added 0.20 g of **1a** and the mixture was refluxed for *ca.* 5 min. After cooling, 0.17 g (80%) of resulting reddish precipitate were collected by filtration. Recrystallization from dichloromethane-hexane provided pure **13a** as reddish crystals. Mp 143—146 °C (decomp). IR (KBr) 3430 (ν_{NH}), 1775 ($\nu_{C=O}$), and 1610 cm^{-1} ($\nu_{C=N}$). ^{1}H NMR δ=4.23 (d, 2H, *J*=1.8 Hz, $C\underline{H}_2$), 6.08 (d, 1H, *J*= 1.8 Hz, N$\underline{H}$), 6.31—7.01 (m, 4H, aromatic C-$\underline{H}$), and 7.69 (s, 5H, $C_6\underline{H}_5$). MS: *m/z* (rel intensity) 292 (M$^+$, 18), 248 (M$^+$—CO_2, 27), 234 (M$^+$—NO—CO, 45), and 44 (100). Found: C, 65.62; H, 4.21; N, 19.14%. Calcd for $C_{16}H_{12}N_4O$: C, 65.75; H, 4.14; N, 19.17%.

When DMF was used as a solvent, the reaction was carried out at room temperature. After the reaction, addition of water to the reaction mixture provided the crude product of **13a**.

4-(3,4-Dihydro-2-quinoxalinyl)-3-(p-ethoxyphenyl)sydnone (13b). By the same procedure, pure **13b** was obtained without purification by the reaction of **1b** in ethanol. Mp 162.5—163 °C. IR (KBr) 3380 (ν_{NH}), 3000, 2950, 2900 (ν_{C-H}), 1780, 1760 ($\nu_{C=O}$), and 1610 cm^{-1} ($\nu_{C=N}$). ^{1}H NMR δ=1.40 (t, 3H, $C\underline{H}_3$), 4.00—4.36 (m, 4H, $CH_3C\underline{H}_2$, and $C\underline{H}_2NH$), 6.12 (s, 1H, N$\underline{H}$), 6.40—7.18 (m, 4H, aromatic C-$\underline{H}$), 7.22 (d, 2H, *p*-$EtOC_6\underline{H}_4$), and 7.73 (d, 2H, *p*-$EtOC_6\underline{H}_4$). MS: *m/z* (rel intensity), 336 (M$^+$, 26), 278 (M$^+$—NO—CO, 81), and 276 (100). Found: C, 64.07; H, 4.60; N, 16.54%. Calcd for $C_{18}H_{16}N_4O_3$: C, 64.28; H, 4.79; N, 16.66%.

[†] 1 M=1 mol dm^{-3}.

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