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Synthesis of a few cyclothiadiazanones and aminosulfonyl benzamides from saccharin

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Saccharin is hydrolyzed with two different acids to yield 1,2-di-acid. The di-acid, on chlorination with phosphorous pentachloride, gave 2-chlorosulfonylbenzoyl chloride. The 2-chlorosulfonylbenzoyl chloride on hydrazinolysis gave benzothiadiazinetrione, while with phenyl hydrazine it selectively yielded 2-phenylbenzothiadiazinetrione. 2-chlorosulfonoylbenzoyl chloride with different aromatic 1,2-diamines resulted in dibenzothiadiazocine derivatives. Electron-donating groups in the diamine facilitate while the electron-withdrawing groups retard the cyclization. However, aliphatic diamines, aniline and substituted anilines readily gave acyclic aminosulfonyl carboxybenzamides on condensation with 2-chlorosulfonylbenzoyl chloride. The di-acid and anhydride did not react with either hydrazine/phenyl hydrazine or amines to give the above products. However, when its ester derivative, isopropyl-2-chlorosulfonylbenzoate, condensed with hydrazine, it gave benzothiadiazinetrione. But the ester failed to react with phenyl hydrazine. All the condensation reactions were carried out at room temperature.

Keywords: hydrazine; 2-chlorosulfonylbenzoyl chloride; phenylenediamine; benzothiadiazepinone; dibenzothiadiazocine

1. Introduction

Chemiluminiscence of cyclic hydrazides continue to raise wide interest as they are considered as effective alternatives to fluorophore and isotopic assays. A considerable body of synthetic work has been carried out with the object of identifying various factors that control light production. Two important generalizations are given with respect to the structure–efficiency relationship. The substituents in a heterocyclic moiety completely inhibit chemiluminiscence, while the steric factors in a non-heterocyclic ring, *i.e*. adjacent to carbonyl carbons, C_1 and C_4, in luminol, are not favorable to the light-emitting process. However, electron-donating groups in the non-heterocyclic part with unimpeded resonance enhance the light output. The synthesis of pyridazine moiety of cyclic hydrazides mostly involved the hydragenolysis of the corresponding anhydrides (*1*), esters (*1b, 2*), alkylated imides (*1b, 1c, 2d, 2e, 3*) and acid chlorides (*4*). Lenev *et al*. (*5*) reported the synthesis of the chiral cyclic monohydrazide of diphenic acid. Pawar *et al*. (*6*) reported the synthesis of dibenzodiazocinediones by Beckmann rearrangement

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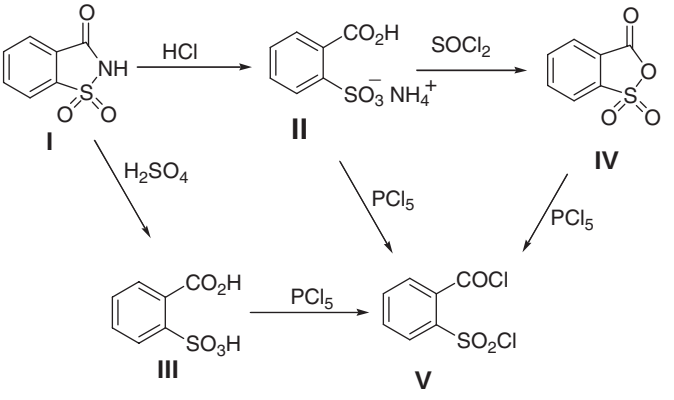
of the oximes of dioxomorphanthridines. Mogilaiah *et al*. (*7*) reported the synthesis of substituted phthalazine-1,4-diones by grinding *para*-toulenesulfonic acid and acid hydrazides in the solid state. Pyridazine-1,4-diones are important molecules that impart various sizes, shapes and colors to cucurbits of the Cucurbutaceae family (*8*). From perusal of the literature, it has been found that the cyclic hydrazides prepared were mostly di-carbonic acid hydrazides, and there is no report on the synthesis of thiadiazanones. Therefore, it was considered worthwhile to prepare a few thiadiazanones, and in this paper, we report the synthesis of a few cyclothiadiazanones and aminosulfonyl benzamides, starting from saccharin.

2. Results and discussion

The present investigation focuses on the development of a few benzothiadiazanones starting from saccharin. Saccharin (**I**) is a readily available stable molecule and is a thio analog of phthalimide. The latter reaction with hydrazine readily gives phthalizine-1,4-dione, a useful luminescent probe. A similar reaction is envisaged with saccharin. When saccharin was charged with hydrazine and refluxed, no hydrazide was obtained. Then it was hydrolyzed with dilute hydrochloric acid to give 2-sulfobenzoate ammonium salt (**II**) (*9*). The product was identified by comparison with an authentic sample and by its melting point. The structure of the salt **II** was confirmed by the disappearance of a saccharin NH signal at δ 12.1 and the appearance of a broad singlet signal at δ 7.26 for ammonium protons and a δ 14.12 singlet signal for a carboxylic acid proton in ^{1}H NMR. In the IR spectrum, the new bands obtained at 2805, 2667 and 2536 cm^{-1} indicate the formation of salt **II**. The molecular ion peak at m/z 219 in the electron impact mass spectrum of **II** indicates the presence of one nitrogen. Compound **II** on reaction with hydrazine did not yield the expected hydrazide. On the other hand, when saccharin was hydrolyzed with dilute H_2SO_4, it yielded 2-sulfobenzoic acid (**III**) (*10*). The negative mode mass spectrum of **III** showed a molecular ion peak at m/z 201. A new peak at 3354 cm^{-1} in the IR spectrum indicates the formation of an acid. The two acidic protons in **III** appeared at δ 11.5 in ^{1}H NMR. The obtained compound **II** is in good yield over compound **III**. Compound **III** is also a derivative of saccharin, which also resisted the formation of hydrazide. When **II** was treated with $SOCl_2$, 2-sulfobenzoic anhydride (**IV**) was accessed quantitatively (*11*). The reaction of **II** with $SOCl_2$ to **IV** was proved by the disappearance of the downfield signal at δ 14.12 of the carboxylic acid proton ^{1}H NMR and with the appearance of a molecular ion peak at m/z 184 in the mass spectrum. The anhydride **IV** also failed to produce hydrazide on reaction with hydrazine. When 25 mmol of either **II**, **III** or **IV** was mixed with 72 mmol of PCl_5, the reaction mixture gave 2-chlorosulfonylbenzoyl chloride (**V**) (*12*) along with a by-product, a gem dichloro compound (2–5%). The by-product was removed by silica gel column employing petroleum ether/ethyl acetate (9:1) eluent. The formation of **V** was confirmed by ^{1}H NMR and mass spectra. The ^{1}H NMR spectrum of **V** showed three signals for four aromatic protons. The downfield doublet signal at δ 7.98 was assigned to the aromatic proton adjacent to the C=O group, the doublet signal at δ 7.78 to that of the proton adjacent to the SO_2 group while the multiplet signal at δ 7.51 to the remaining two aromatic protons. The mass spectrum of **V** showed a pseudo-molecular ion $[M + H]^+$ peak at m/z 239. It has been found that saccharin was not directly transformed to **V** even under extreme conditions such as a longer reaction time and high concentration of PCl_5. Conversion of **I** to **V** involving **II** as an intermediate is more efficient than the remaining two paths, *i.e.* via **III** and **IV**. Scheme 1 depicts the conversion of saccharin to **V**.

Compound **V** on condensation with hydrazines and *ortho*-phenylenediamines (OPDAs) yielded cyclic hydrazides, while with amines it gave the corresponding aminosulfonyl carboxy benzamides. When 2 mmol of **V** was mixed either with 2 mmol of hydrazine hydrate or with phenyl hydrazine, the reaction mixture gave cyclic six membered benzothiadiazintriones, **VIa** and



Scheme 1. Synthesis of 2-chlorosulfonyl benzoylchloride from saccharin.

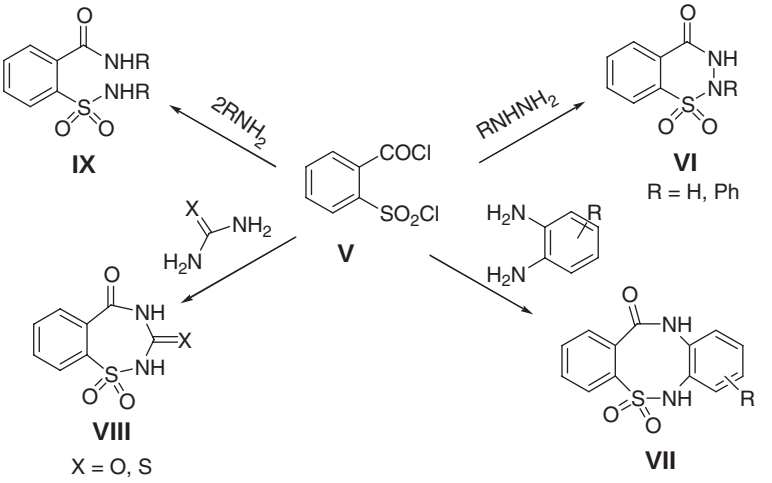
VIb, respectively. ^{1}H NMR spectrum of 1,2,3,4-tetrahydro-1λ^6,2,3-benzothiadiazine-1,1,4-trione (**VIa**) exhibited two singlet signals, one at δ 10.11 characteristic of a sulfoxamide proton and the other at δ 10.65, characteristic of a carboxamide proton, respectively. The four aromatic protons have given only two signals. The down field multiplet signal at δ 8.05 is assigned to the aromatic proton adjacent to the carboxamide, while the multiplet signal at δ 7.93 is assigned to the remaining three aromatic protons. The ^{13}C NMR spectrum of **VIa** has shown seven signals for seven carbons. The carbonyl quaternary carbon gave a signal at 161.7 ppm, while the two aromatic ipso carbons resonated at 138.8 and 126.6 ppm. Similarly, the remaining four aromatic methine carbons gave signals at 133.9, 133.6, 129.5 and 122.1 ppm, confirming the structure of **VIa**. The EI mass spectrum of **VIa** has shown a molecular ion peak at m/z 198, confirming its structure. On the other hand, the regioselective cyclo-condensation of **V** with phenyl hydrazine is demonstrated by its two different types of acid chlorides. The reactive carboxylic acidchloride readily condensed with the more electron-dense terminal amino group, while the less reactive sulfonylchloride condensed less readily with the less reactive aniline nitrogen and gave 2-phenyl-1,2,3,4-tetrahydro-1λ^6,2,3-benzothiadiazine-1,1,4-trione (**VIb**) but not its regioisomer 3-phenyl-1,2,3,4-tetrahydro-1λ^6,2,3-benzothiadiazine-1,1,4-trione. The proton NMR spectrum of **VIb** showed seven signals at δ 7.26 (m, 2H), 7.69 (m, 2H), 7.87 (t, 2H), 7.97 (m, 1H), 8.07 (t, 1H), 8.47 (t, 1H) and 8.84 (br s, 1H), thus ruling out the possibility of 3-phenyl-1,2,3,4-tetrahydro-1λ^6,2,3-benzothiadiazine-1,1,4-trione. The broad signal at the extreme downfield δ 8.84 is due to NH of carboxamide, and all the remaining signals are assigned to the aromatic protons. The ES mass spectrum of **VIb** showed a molecular ion peak at m/z 274, while that of its pseudomolecular ion $[M + Na]^+$ peak at 297 mass units. Similarly, when **V** reacted with OPDA or substituted OPDA in 1:1 molar ratio in methanol at room temperature, it yielded dibenzothiadiazocinones **VIIa**–**VIIg**. Electron-donating groups in OPDA facilitated the formation of **VII** while electron-withdrawing groups retarded it. The proton NMR spectrum of 5,6,11,12-tetrahydro-5,λ^6-dibenzo[*c*,*g*][1,2,5]thiadiazocine-5,5,12-trione (**VIIa**) showed six signals at δ 7.52 (s, 2H), 7.69 (m, 2H), 7.84 (s, 2H), 7.94 (d, 1H), 8.03 (d, 1H) and 14.62 (br. s, 2H). 2,3-Diamino-9,10-acridindione did not give its respective derivative of **VII** even under drastic conditions such as high temperature and in the presence of an acid catalyst.

Compound **V** on treatment with urea and thiourea gave 2,3,4,5-tetrahydro-1*H*-1λ^6,2,4-benzothiadiazepine-1,1,3,5-tetraone (**VIIIa**) and 3-thioxo-2,3,4,5-tetrahydro-1*H*-1λ^6,2,4-benzothiadiazepine-1,1,5-trione (**VIIIb**), respectively. Interestingly, when 2 mmol of **V** was treated with 1–4 mmol equivalents of aniline/substituted anilines or aliphatic diamines, no cyclic imides are obtained, even at higher temperatures; instead, acyclic aminosulfonyl

carboxybenzamides **IXa**–**IXf** were obtained. Similar results were reported by Blernat and Bochenska (*12b*). The reason for **V** not forming cyclic imides on reaction with simple primary amines may be that the initially formed carboxamide nitrogen becomes the less reactive amide nitrogen, which is incapable of undergoing second nucleophillic substitution at the less reactive sulphonyl chloride to give a cyclic product. On the other hand, more reactive primary amine nitrogen can add at the less reactive sulphonyl sulphur. This is further supported by the greater reactivity of aliphatic amines than aromatic amines. It has been always noticed that formation of **IX** occurs immediately after mixing with aliphatic amines, while the aromatic amines take time to give the corresponding **IX**.

Ethylenediamine resembles OPDA. On reaction with 2-chlorosulfonyl benzoylchloride, it is expected to give a product akin to that of OPDA even more readily, since it has reactive aliphatic amino groups. Interestingly, it did not give the expected cyclothiadiazocine derivative. Similarly, 1,3-propylenediamine did not give its respective cyclothiadiazonine derivative. This may be due to the steric effect of the initially formed carboxamide. The free amino group at the end of the initially formed carboxamide has moved away from the proximity of the SO_2Cl group at the *ortho* position preventing the intra-molecular cyclization. This led to the formation of compounds **IXa** and **IXb** by consuming one more ethylenediamine/propylenediamine molecule, respectively. However, OPDA possessing a less reactive aniline group undergoes intra-molecular cyclization due to the rigid geometry of the initially formed carboxamide in which the *ortho* amino group comes closer to the SO_2Cl. Similar results are obtained with the less reactive urea and thiourea due to the rigid geometry of the initially formed carboxamide, as found in OPDA.

However, saccharin did not give **V** directly on reaction with PCl_5. The synthesis of compounds **VI**–**IX** starting from **V** is shown in Scheme 2, and the results are summarized in Table 1.



Scheme 2. Synthesis of benzothiadiazinone, dibenzothiadiazocinone, aminosulfonyl benzamide, benzothiadiazapinone and their derivatives from 2-chlorosulfonyl benzoylchloride.

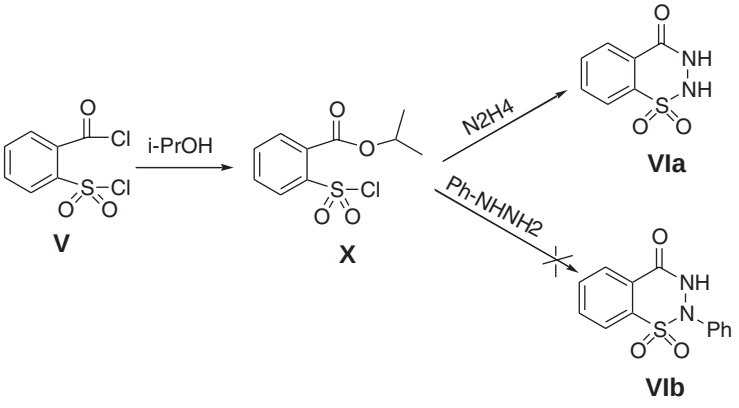
Compound **IV** is an anhydride but did not react with hydrazine and phenyl hydrazine even at reflux temperature. However, on treatment with 2-propanol, it formed 2-chlorosulfonylbenzoic acid isopropyl ester (**X**) as shown in Scheme 3. Subsequently, this ester further reacted with hydrazine (*13*) and gave **VIa**. But attempted condensation of **X** in place of **V** with phenyl hydrazine and other amines under various conditions was not successful.

Compound **V** is unstable at room temperature. It readily hydrolyzes to di-acid even in the presence of traces of water in K_2CO_3. But it is stable at $<10\,^{\circ}C$ in a sealed tube.

Table 1. List of compounds obtained by the reaction of 2-chlorosulfonyl benzoylchloride with various hydrzines/amines.

Entry	Reagent	Product	Yield[a] (%)	M.p. (°C)	Reaction time (min)
1	Hydrazine hydrate	**VIa**	42	211–214	15
2	Phenyl hydrazine	**VIb**	20	190–193	65
3	OPDA	**VIIa**	82	>300	110
4	4-Methyl-OPDA	**VIIb**	65	>300	132
5	4, 5-Dimethyl OPDA	**VIIc**	73	291–294	95
6	4-Chloro-OPDA	**VIId**	78	90–93	76
7	4-Nitro-OPDA	**VIIe**	82	200–202	102
8	Phenylmethanone OPDA	**VIIf**	89	>300	140
9	Naphthalene-2,3-diamine	**VIIg**	74	>300	125
10	Ethylene diamine	**IXa**	88	>300	7
11	1,3-Propylenediamine	**IXb**	90	>300	5
12	Aniline	**IXc**	80	177–179	75
13	*p*-Amino phenol	**IXd**	92	265–269	90
14	*p*-Chloro aniline	**IXe**	81	110–112	67
15	*p*-Anisidine	**IXf**	78	119–121	110
16	Urea	**VIIIa**	77	184–186[b]	72
17	Thiourea	**VIIIb**	53	250–255	98

Notes: [a]Isolated yield. [b]Boiling point.



Scheme 3. Synthesis of 1,2,3,4-tetrahydro-1λ^6,2,3-benzothiadiazine-1,1,4-trione (**VIa**) from 2-chlorosulfonylbenzoic acid isopropylester (**X**).

Entries 4 and 6–8 in Table 1 reveal the regioselective cyclization of substituted OPDA. Substituted OPDAs gave selectively only one of the two possible regioisomers. Condensation of 4-methyl OPDA, 4-chloro OPDA, 4-nitro OPDA and phenylmethanone OPDA with **V** resulted in 9-methyl-5,6,11,12-tetrahydro-5λ^6-dibenzo[c,g][1,2,5]thiadiazocine-5,5,12-trione (**VIIb**), 9-chloro-5,6,11,12-tetrahydro-5λ^6-dibenzo[c,g][1,2,5]thiadiazocine-5,5,12-trione (**VIId**), 9-nitro-5,6,11,12-tetrahydro-5λ^6-dibenzo[c,g][1,2,5] thiadiazocine-5,5,12-trione (**VIIe**) and 9-benzoyl-5,6,11,12-tetrahydro-5λ^6-dibenzo[c,g] [1,2,5] thiadiazocine-5,5,12-trione (**VIIf**), respectively. There is a possibility of obtaining the other regioisomers, *i.e.* 8-methyl-5,6,11,12-tetrahydro-5λ^6-dibenzo[c,g][1,2,5]thiadiazocine-5,5,12-trione, 8-chloro-5,6,11,12-tetrahydro -5λ^6-dibenzo[c,g] [1,2,5]thiadiazocine-5,5,12-trione, 8-nitro-5,6,11,12-tetrahydro-5λ^6-dibenzo [c,g][1,2,5]thiadiazocine-5,5,12-trione and 8-benzoyl-5,6,11,12-tetrahydro-5λ^6-dibenzo[c,g] [1,2,5] thiadiazocine-5,5,12-trione, respectively, under the given experimental conditions; however, these regioisomers were not obtained. The reason for not obtaining the above C-8-substituted regioisomers is not immediately known. All the compounds except the diazepinone formed from

urea were solids, and their melting points are higher than that of the respective starting material. Compounds **VIb**, **VIIIa**, **VIIIb**, **IXa** and **IXb** are hygroscopic.

3. Conclusion

In summary, an effective method for the synthesis of benzothiadiazinones, dibenzothiadiazocinones, aminosulfonyl benzamides and benzothiadiazapinones from 2-chlorosulfonyl benzoylchloride is described. 2-Sulfobenzoic anhydride and saccharin are structural analogs of phthalic anhydride and phthalimides, respectively. 2-Sulfobenzoic anhydride and saccharin are not directly converted to cyclic hydrazides following the Ing–Manske method (*14*). However, when saccharin converted to either 2-sulfonyl bonzoylchloride or 2-chlorosulfonylbenzoic acid ester, these derivatives undergo hydrazenolysis to give 1,2,3,4-tetrahydro-1λ^6,2,3-benzothiadiazine-1,1,4-trione. Structurally dissimilar acid chlorides impart regioselective cyclization.

4. Experimental

The reagents and solvents were of analytical grade and were used without further purification unless otherwise mentioned. Thin layer chromatography (TLC) was carried out on aluminum sheets coated with silica gel 60 F_{254} (Merck). TLC plates were inspected under UV light or developed by charring after spraying with 5% H_2SO_4 in ethanol. Micro-analytical data were obtained by employing a Perkin-Elmer 240c analyzer. IR spectra (KBr pellets) were recorded with a Perkin-Elmer-1700 spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were measured on a Varian INOVA-500 spectrometer. The following abbreviations have been used to explain the observed multiplicities: s, singlet; d, doublet; t, triplet; m, multiplet; br. s, broad singlet. Coupling constants have been assigned and listed without duplication in the ^{1}H NMR description of the synthesized compounds. GCMS was recorded on a Varian 300-MS and electron spray-mass spectra were recorded on an LCQ system (Finngan MAT, USA) using methanol as the mobile phase. Melting points were recorded on a Polmon MP 96.

4.1. *Synthesis of 2-sulfobenzoate ammonium salt (II)*

Saccharin (5 g, 27 mmol) was heated with 20 ml of 10% HCl for 6 h at 95 °C. In the beginning the reaction mixture was turbid and in the due course of time it slowly converted to a clear solution. After the reaction was completed the solvent water was removed under reduced pressure and a white solid separated out. The solid was washed with chilled water and dried. Yield 5.26 g (88%); m.p.: 264–266 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.26 (m, 4H), 7.52 (m, 2H), 7.73 (d, $J = 8.0$ Hz, 1H), 7.84 (d, $J = 7.8$ Hz, 1H) 14.12 (s, 1H); IR (KBr): υ 3136, 3025, 2805, 2667, 2536, 1724, 1593, 1397, 1281, 1239, 1191, 1142, 1136, 1080 cm^{-1}; mass (EI): m/z 219 $[M]^+$.

4.2. *Synthesis of 2-sulfobezoic acid (III)*

Saccharin (7 g, 38 mmol) was suspended in 20 ml of 33% H_2SO_4 and heated at 90 °C for 2 h. After the reaction was complete, 80% of the water was removed under reduced pressure. The residue was washed with 20 ml of ice cold water. Yield 6.5 g (85%); m.p.: 68–69 C; ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.56 (m, 4H), 11.52 (s, 2H); IR (KBr): υ 3354 (br. s), 2924, 2845, 1705, 1585, 1445, 1232, 1184, 1112 1063 cm^{-1}; mass (ES): m/z 201 $[M–H]^-$.

4.3. *Synthesis of 2-sulfobenzoic anhydride (IV)*

To a solution of **II** (5.08 g, 22 mmol) in 10 ml of toluene was slowly added 3.3 ml of $SOCl_2$ (45 mmol) (drop wise) during 30 min at room temperature. The reaction was refluxed for 6 h. After completion of the reaction, the solvent was removed under reduced pressure to yield a white solid. The solid was washed with water and dried over anhydrous $CaCl_2$. Yield 2.63 g (65%); m.p.:128–29 C; ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.56 (s, 2H), 7.69 (s, 1H), 7.82 (s, 1H); IR (KBr): υ 3099, 2954, 1842, 1821, 1721, 1692, 1460, 1373, 1200 cm^{-1}; Mass (EI): m/z 184 $[M]^+$. ^{13}C NMR (75 MHz, DMSO-d_6): δ 123.8, 125.3, 128.1, 136.6, 138.4, 140.4, 155.5.

4.4. *Synthesis of 2-sulfonyl benzoylchloride (V)*

2-Sulfobenzoic acid (5.05 g, 25 mmol), 2-sulfobenzoic anhydride (4.6 g, 25 mmol) or 2-sulfobenzoate ammonium salt (5.48 g) was heated with PCl_5 (15 g, 72 mmol) at 60 °C for 2 h. After the reaction was complete, it was quenched with ice water, extracted with 30 ml of $CHCl_3$ and dried over anhydrous $CaCl_2$. The solvent was concentrated under reduced pressure to yield 2-chlorosulfonyl benzoylchloride. It is purified by column chromatography using petroleum ether/ethyl acetate (9:1) as an eluent. Yield 68–74%; mp: 37–39 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51 (m, 2H), 7.78 (d, $J = 7.1$ Hz, 1H), 7.98 (d, $J = 8.0$ Hz, 1H); IR ($CHCl_3$): υ 3099, 3024, 2955, 1792, 1739, 1570, 1435, 1379, 1298, 1184 cm^{-1}; mass (EI): m/z 239 $[M]^+$. ^{13}C NMR (75 MHz, DMSO-d_6): δ 129.5, 133.2, 135.4, 136.8, 140.0, 161.7.

4.5. *Reaction of V with hydrazine, phenyl hydrazine, urea, thiourea, aliphatic diamines, aniline and substituted anilines (VI, VIII and IX)*

To a solution of **V** (478 mg, 2 mmol) in methanol l5 ml of each corresponding reactant (2–4 mmol) was added at room temperature and the reaction was stirred at room temperature for the appropriate time (shown in Table 1). When the reaction was complete, the excess solvent was removed under reduced pressure and the product was purified by column chromatography (2–26% methanol in chloroform).

4.6. *Reaction of V with OPDA and substituted OPDA (VII)*

To a stirred solution of **V** (478 mg, 2 mmol) in 5 ml of methanol was added OPDA/substituted OPDA (2 mmol) and the reaction mixture was stirred at room temperature for the appropriate time (shown in Table 1). The excess solvent was removed under reduced pressure. The residue was taken in 5 ml of acetone, stirred for 30 min and filtered and washed with acetone to get dibenzothiadiazocinones.

4.7. *Spectral data of synthesized compounds*

4.7.1. *1,2,3,4-Tetrahydro-1λ^6,2,3-benzothiadiazine-1,1,4-trione* ***(VIa)***

^{1}H NMR (300 MHz, DMSO-d_6): δ 7.88 (s, 3H), 8.05 (s, 1H), 10.11 (s, 1H), 10.65 (s, 1H). IR (KBr): υ 3366, 3231, 3126, 2891, 1663, 1570, 1424, 1373, 1344, 1188 cm^{-1}. Mass (EI): m/z 198 $[M]^+$. ^{13}C NMR (75 MHz, DMSO-d_6): δ 122.1, 126.6, 129.5, 133.6, 133.9, 138.8, 161.7. Anal. Calcd for $C_7H_6N_2O_3S$: C, 42.42; H, 3.05; S, 16.18; N, 14.14%. Found: C, 42.39; H, 3.02; S, 16.09; N, 14.22%.

4.7.2. *2-Phenyl-1,2,3,4-tetrahydro-1λ⁶,2,3-benzothiadiazine-1,1,4-trione* ***(VIb)***

^{1}H NMR (300 MHz, DMSO-d_6): δ 7.26 (m, 2H), 7.69 (m, 2H), 7.87 (t, $J = 7.3$ Hz, 2H), 7.97 (m, 1H), 8.07 (t, $J = 7.1$ Hz, 1H), 8.47 (t, $J = 7.5$ Hz, 1H), 8.84 (br. s, 1H). IR (KBr): υ 3448, 2955, 1716, 1640, 1594, 1299, 1238, 1160, 1081 cm^{-1}. Mass (ES): m/z 275 $[M]^+$, 297 $[M + Na]^+$. Anal. Calcd for $C_{13}H_{10}N_2O_3S$: C, 56.92; H, 3.67; N, 10.21; S, 11.69%. Found: C, 57.03; H, 3.49; N, 10.15; S, 11.76%.

4.7.3. *5,6,11,12-Tetrahydro-5λ⁶-dibenzo[c,g][1,2,5]thiadiazocine-5,5,12-trione* ***(VIIa)***

^{1}H NMR (400 MHz, DMSO-d_6): δ 7.52 (s, 2H), 7.69, (m, 2H), 7.84 (s, 2H), 7.94 (d, J =8.1 Hz, 2H), 8.03 (d, $J = 7.9$ Hz, 1H), 14.62 (br. s, 2H). IR (KBr): υ 3426, 3061, 2931, 1626, 1564, 1454, 1234, 1177, 1082 cm^{-1}. Mass: 275 $[M + H]^+$, 297 $[M + Na]^+$. ^{13}C NMR (75 MHz, DMSO-d_6): δ 113.5, 124.1, 125.8, 126.2, 128.4, 129.9, 130.1, 130.6, 142.8, 163.8. Anal. Calcd for $C_{13}H_{10}N_2O_3S$: C, 56.92; H, 3.67; N, 10.21; S, 11.69%. Found: C, 56.79; H, 3.66; N, 10.19; S, 11.71%.

4.7.4. *9-Methyl-5,6,11,12-tetrahydro-5λ⁶-dibenzo[c,g][1,2,5]thiadiazocine-5,5,12-trione* ***(VIIb)***

^{1}H NMR (300 MHz, DMSO-d_6): δ 2.27 (s, 3H), 7.03 (s, 1H), 7.20 (m, 2H), 7.54 (m, 3H), 7.86 (m, 1H), 10.41 (s, 2H). IR (KBr): υ 3223, 2933, 2652, 1718, 1657, 1505, 1334, 1208, 1083 cm^{-1}. Mass (ES): m/z 327 $[M + K]^+$. Anal. Calcd for $C_{14}H_{12}N_2O_3S$: C, 58.32; H, 4.20; N, 9.72; S, 11.12%. Found: C, 57.98; H, 4.23; N, 9.66; S, 11.28%.

4.7.5. *8,9-Dimethyl-5,6,11,12-tetrahydro-5λ⁶-dibenzo[c,g][1,2,5]thiadiazocine-5,5,12-trione* ***(VIIc)***

^{1}H NMR (400 MHz, DMSO-d_6): δ 2.38 (s, 3H), 3.70 (s, 3H), 7.24 (d, $J = 7.8$ Hz, 1H), 7.38 (m, 3H), 7.51 (s, 1H), 7.71 (d, $J = 8.1$ Hz, 1H), 14.32 (br. s, 2H). IR (KBr): υ 3444, 2948, 2922, 1733, 1654, 1440 1320, 1291, 1256, 1174 cm^{-1}. Mass (ES): m/z 341 $[M + K]^+$. ^{13}C NMR (75 MHz, DMSO-d_6): δ 12.1, 19.7, 113.2, 126.6, 127.4, 128.5, 129.2, 131.4, 134.7, 144.3, 150.0, 169.4. Anal. Calcd for $C_{15}H_{14}N_2O_3S$: C, 59.59; H, 4.67; N, 9.27; S, 10.61%. Found: C, 59.62; H, 4.41; N, 9.19; S, 10.53%.

4.7.6. *9-Chloro-5,6,11,12-tetrahydro-5λ⁶-dibenzo[c,g][1,2,5]thiadiazocine-5,5,12-trione* ***(VIId)***

^{1}H NMR (400 MHz, DMSO-d_6): δ 7.23 (d, $J = 7.2$ Hz, 2H), 7.31, (s, 1H), 7.61 (d, $J = 7.2$ Hz, 2H), 7.66 (s, 2H), 8.34 (s, 2H). IR (KBr): υ 3446, 3041, 2927, 1658, 1623, 1566, 1445, 1271, 1163 cm^{-1}. Mass (ES): m/z 309 $[M + H]^+$. Anal. Calcd for $C_{13}H_9ClN_2O_3S$: C, 50.57; H, 2.94; N, 9.07; S, 10.39%. Found: C, 50.49; H, 2.91; N, 9.14; S, 10.33%.

4.7.7. *9-Nitro-5,6,11,12-tetrahydro-5λ⁶-dibenzo[c,g][1,2,5] thiadiazocine-5,5,12-trione* ***(VIIe)***

^{1}H NMR (300 MHz, DMSO-d_6): δ 7.79 (s, 2H), 8.14 (d, $J = 7.9$ Hz, 2H), 8.34 (s, 3H), 13.11 (s, 2H). IR (KBr): υ 3483, 3102, 1787, 1588, 1460, 1407, 1344 cm^{-1}. Mass (ES): m/z 342

$[M + Na]^+$. Anal. Calcd for $C_{13}H_9N_3O_5S$: C, 48.90; H, 2.84; N, 13.16; S, 10.04%. Found: C, 48.82; H, 2.84; N, 13.01; S, 10.11%.

4.7.8. *9-Benzoyl-5,6,11,12-tetrahydro-5λ^6-dibenzo[c,g] [1,2,5] thiadiazocine-5,5,12-trione **(VIIf)***

^{1}H NMR (400 MHz, DMSO-d_6): δ 7.62 (t, $J = 7.4$ Hz, 2H), 7.73, (m, 3H), 7.80 (d, $J = 7.2$ Hz, 2H), 7.90 (d, $J = 7.2$ Hz, 2H); 8.05 (m, 3H), 8.31 (s, 2H). IR (KBr): υ 3048, 2924, 1657, 1622, 1565, 1445, 1325, 1266, 1163 cm^{-1}. Mass (ES): m/z 379 $[M + H]^+$, 401 $[M + Na]^+$. Anal. Calcd for $C_{20}H_{14}N_2O_4S$: C, 63.48; H, 3.73; N, 7.40; S, 8.47 %. Found: C, 63.40; H, 3.78; N, 7.32; S, 8.39 %.

4.7.9. *5,6,13,14-Tetrahydro-5λ^6-benzo[g]naphtho[2,3-c][1,2,5] thiadiazocine-5,5,14-trione **(VIIg)***

^{1}H NMR (400 MHz, DMSO-d_6): δ 7.57 (m, 2H), 7.73 (m, 3H), 7.95 (d, 1H, $J = 7.8$ Hz), 8.04 (d, $J = 7.8$, 1H), 8.19 (m, 3H), 8.41 (s, 2H). IR (KBr): υ 3175, 3024, 2914, 2706, 1609, 1497, 1448, 1243, 1178, 1081 cm^{-1}. Mass (ES): m/z 325 $[M + H]^+$. Anal. Calcd for $C_{17}H_{12}N_2O_3S$: C, 62.95; H, 3.73; N, 8.64; S, 9.89%. Found: C, 62.78; H, 3.69; N, 8.64; S, 10.07%.

4.7.10. *2,3,4,5-Tetrahydro-1H-1λ^6,2,4-benzothiadiazepine-1,1,3,5-tetraone **(VIIIa)***

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45 (m, 3H), 7.95 (d, $J = 8.3$ Hz, 1H), 9.05 (br. s, 2H). IR ($CHCl_3$): υ 3431, 3023, 2786, 2457, 1727, 1640, 1468, 1299, 1194 cm^{-1}. Mass (ES): m/z 265 $[M + K]^+$. Anal. Calcd for $C_8H_6N_2O_4S$: C, 42.48; H, 2.67; N, 12.38; S, 14.18%. Found: C, 42.12; H, 2.22; N, 12.52; S, 14.38%.

4.7.11. *3-Thioxo-2,3,4,5-tetrahydro-1H-1λ^6,2,4-benzothiadiazepine-1,1,5-trione **(VIIIb)***

^{1}H NMR (300 MHz, DMSO-d_6): δ 7.28 (d, 1H, $J = 7.5$ Hz), 7.42 (m, 2H), 7.74 (d, $J = 7.5$, 1H), 8.74 (br. s, 2H). IR (KBr): υ 3433, 3095, 2778, 1713, 1653, 1436, 1303, 1199, 1083, 1021 cm^{-1}. Mass (ES): m/z 281 $[M + K]^+$. Anal. Calcd for $C_8H_6N_2O_3S_2$: C, 39.66; H, 2.50; N, 11.56; S, 26.47%. Found: C, 39.21; H, 2.27; N, 11.61; S, 26.56%.

4.7.12. *N1-(2-aminoethyl)-2-[(2-aminoethyl)amino]sulfonylbenzamide **(IXa)***

^{1}H NMR (400 MHz, DMSO-d_6): δ 2.85 (m, 4H), 3.01 (m, 4H), 3.48 (t, $J = 7.6$ Hz, 4H), 7.42 (m, 1H), 7.64 (m, 1H), 7.81 (d, $J = 7.8$ Hz, 1H), 7.91 (d, $J = 7.9$ Hz, 1H), 8.81(br. s 2H). IR (KBr): υ 3446, 3224, 2989, 1653, 1636, 1559, 1280, 1164 cm^{-1}. Mass (ES): m/z 287 $[M + H]^+$, 309 $[M + Na]^+$. Anal. Calcd for $C_{11}H_{18}N_4O_3S$: C, 46.14; H, 6.34; N, 19.57; S, 11.20%. Found: C, 46.02; H, 6.31; N, 19.57; S, 11.03%.

4.7.13. *N1-(3-aminopropyl)-2-[(3-aminopropyl)amino]sulfonylbenzamide **(IXb)***

^{1}H NMR (300 MHz, DMSO-d_6): δ 1.85 (m, 4H), 2.86 (m, 8H); 3.33 (br. s, 4H), 7.56 (d, $J = 7.9$ Hz, 1H), 7.69 (m, 1H), 7.86 (d, $J = 7.4$, 2H), 8.95 (br. s, 2H). IR (KBr): υ 3441, 3076, 2934, 1734, 1643, 1560, 1446, 1323, 1163, 1020 cm^{-1}. Mass (ES): m/z 315 $[M + H]^+$, 337 $[M + Na]^+$. Anal.

Calcd for $C_{13}H_{22}N_4O_3S$: C,49.66; H, 7.05; N, 17.82; S, 10.20%. Found: C, 49.34; H, 6.88; N, 17.53; S, 10.31%.

4.7.14. *N1-phenyl-2-(anilinosulfonyl)benzamide (**IXc**)*

^{1}H NMR (400 MHz, DMSO-d_6): δ 7.19 (d, $J = 8.1$, 7H), 7.39 (m, 7H), 7.72 (s, 2H). IR (KBr): υ 3456, 2941, 2644, 1716, 1639, 1595, 1304, 1242, 1080, 1014 cm^{-1}. Mass (ES): m/z 353 $[M + H]^+$. ^{13}C NMR (75 MHz, DMSO-d_6): δ 122.3, 126.5, 127.1, 127.3, 128.5, 129.1, 129.6, 130.6, 130.8, 131.3, 132.8, 144.7, 169.2. Anal. Calcd for $C_{19}H_{16}N_2O_3S$: C, 64.76; H, 4.58; N, 7.95; S, 9.10%. Found: C, 64.39; H, 4.56; N, 7.81; S, 9.22%.

4.7.15. *N1-(4-hydroxyphenyl)-2-[(4-hydroxyanilino)sulfonyl]benzamide (**IXd**)*

^{1}H NMR (300 MHz, DMSO-d_6): δ 6.03(s, 1H), 6.49 (s, 1H), 6.75 (m, 3H), 6.89 (t, $J = 7.8$ Hz, 1H), 6.96 (d, $J = 7.2$ Hz, 1H), 7.09 (s, 1H), 7.12 (d, $J = 8.1$ Hz, 1H), 7.40 (s, 1H), 7.51 (t, $J = 8.0$ Hz, 1H), 7.86 (d, $J = 7.7$ Hz, 1H), 9.51 (s, 1H), 9.83 (s, 1H), 11.15 (br. s, 2H). IR (KBr): υ 3457, 3182, 2910, 1642, 1597, 1464, 1280, 1192 cm^{-1}. Mass (ES): 385 $[M + H]^+$, 407 $[M + Na]^+$. Anal. Calcd for $C_{19}H_{16}N_2O_5S$: C, 59.37; H, 4.20; N, 7.29; S, 8.34%. Found: C, 59.27; H, 4.34; N, 7.34; S, 8.28%.

4.7.16. *N1-(4-chlorophenyl)-2-[(4-chloroanilino)sulfonyl]benzamide (**IXe**)*

^{1}H NMR (300 MHz, DMSO-d_6): δ 7.33 (m, 8H), 7.71 (m, 4H), 7.94 (br. s, 2H). IR (KBr): υ 3433, 2928, 1728, 1657, 1595, 1493, 1238, 1024, 619 cm^{-1}. Mass (ES): m/z 444 $[M + Na]^+$. Anal. Calcd for $C_{19}H_{14}Cl_2N_2O_3S$: C, 54.17; H, 3.35; N, 6.65; S, 7.61%. Found: C, 54.11; H, 3.48; N, 6.65; S, 7.73%.

4.7.17. *N1-(4-methoxyphenyl)-2-[(4-methoxyanilino)sulfonyl] benzamide (**IXf**)*

^{1}H NMR (300 MHz, $CDCl_3$): δ 3.56 (s, 6H), 6.53 (s, 4H), 7.14 (m, 8H), 7.83 (br. s, 2H). IR (KBr): υ 3443, 2924, 2843, 1633, 1510, 1452, 1383, 1249, 1170, 1020 cm^{-1}. Mass (ES): m/z 413 $[M + H]^+$, 435 $[M + Na]^+$. Anal. Calcd for $C_{21}H_{20}N_2O_5S$: C, 61.15; H, 4.89; N, 6.79; S, 7.77%. Found: C, 61.02; H, 4.67; N, 7.01; S, 7.91%.

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