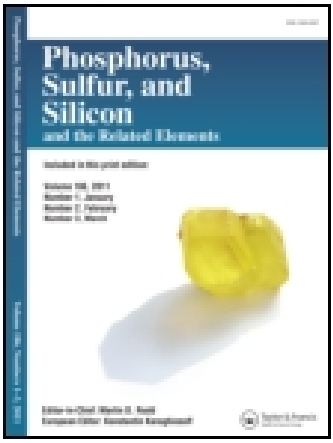

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Site Selectivity in Reactions of Hydrazonoyl Halides With 2-Amino-3-quinoxalinethiol: A New General Access to Functionalized 4H-1,3,4-Thiadiazino-[5,6-b]quinoxalines

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Site Selectivity in Reactions of Hydrazonoyl Halides With 2-Amino-3-quinoxalinethiol: A New General Access to Functionalized 4H-1,3,4-Thiadiazino-[5,6-b]quinoxalines

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The synthesis of various 2,4-disubstituted 4H-1,3,4-thiadiazino-[5,6-b]quinoxalines via reaction of hydrazonoyl halides with 2-amino-3-quinoxalinethiol in ethanol in the presence of sodium ethoxide is described. The structures of the reaction products were elucidated by chemical evidence and by their IR, ^{1}H, ^{13}C-NMR, and MS spectra. The mechanism of the formation of the products is also discussed.

Keywords Heterocycles; hydrazonoyl halides; site selectivity; thiadiazinoquinoxalines

INTRODUCTION

Within the framework of our interest in regioselectivity in the reactions of hydrazonoyl halides **1** with 1,2-aminothiols[1–7] and in continuation of our program aimed at developing new convenient approaches for synthesis of fused heterocycles via utility of **1** as starting materials,[8] we wish to report the results of our study of the reactions of 2-amino-3-quinoxalinethiol **2** with five series of **1** (Scheme 1). Our objective of such a study is to shed some light on the site selectivity in such reactions as they can in principle lead to the formation of 2,4-disubstituted 4H-1,3,4-thiadiazino[5,6-b]quinoxalines **3**, 1,3-disubstituted 4H-1,2,4-triazino[5,6-b]quinoxalines **4** and/or 2,3-disubstituted 4H-1,4-thiazino[5,6-b]quinoxalines **5**(**6**) (Scheme 1). The studied reactions were found to be site selective and provide new general access to various 2,4-disubstituted 4H-1,3,4-thiadiazino[5,6-b]quinoxalines **3**. These latter heterocycles are expected to be of biological and technical interest since they are related to thiazolo[4,5-b]quinoxalines whose 2-styryl derivatives were reported to be useful

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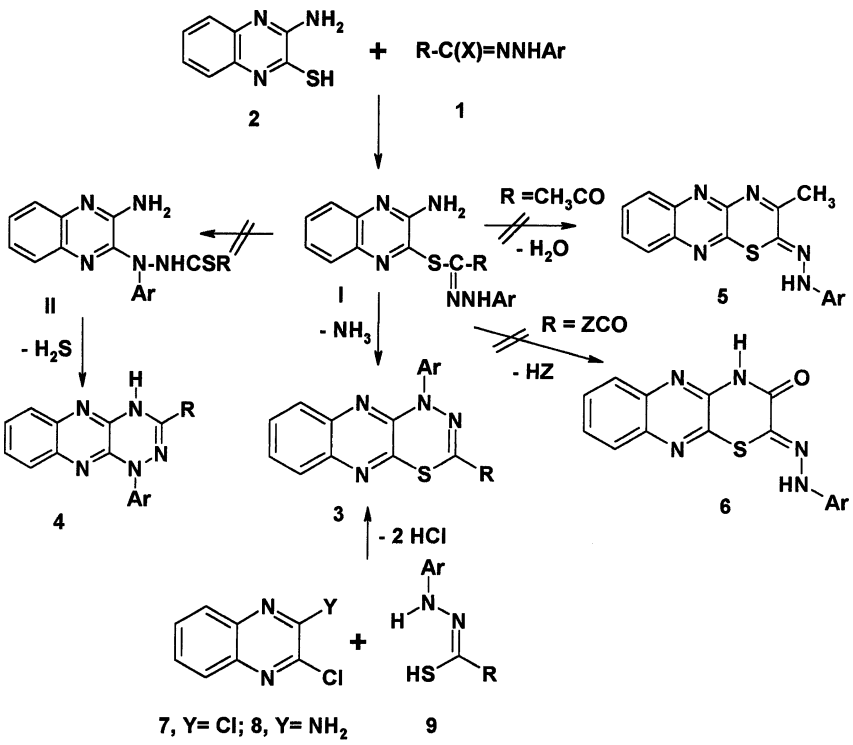


R : A, Ph; B, EtOCO; C,PhNHCO; D, CH_3CO; E, Ar-N=N-
Ar = XC_6H_4: X: a, H, b, 4-NO_2; c, 4-Me; d, 4-Cl;e, 3- Me;
f, 3-Cl; g, 3-NO_2; h, 4-MeO

SCHEME 1

as fluorescent dyes.[9] Other fused quinoxalines were also reported to be commercially important as agrochemicals, herbicides, fungicides, antagonists, and anticiotics.[9] Furthermore, our interest in developing new access to functionalized 4H-1,3,4-thiadiazino[5,6-b]quinoxalines results from the methods that we have reported that are either multisteps or appear to be of limited appilicability. For example, a literature search revealed that some of the 4H-1,3,4-thiadiazino[5,6-b]quinoxalines **10A** have been synthesized by the reaction of 2,3-dichloroquinoxaline with benzoic thiohydrazide (Chart 1).[10,11] Others, such as 2-acylamino-4H-1,3,4-thiadiazino[5,6-b]quinoxalines **10B**, were prepared from 2-thiocarbamoylhydrazinoquinoxaline-4-oxides **11** via a N_4-O-acylated intermediates **12** (Chart 1).[12,13] The third method was based on the reaction of 8-chloro-4-methyl-2-trifluromethyl-4H-1,3,4-oxadiazino[5,6-b]quinoxaline **13** with phosphorus pentasulfide

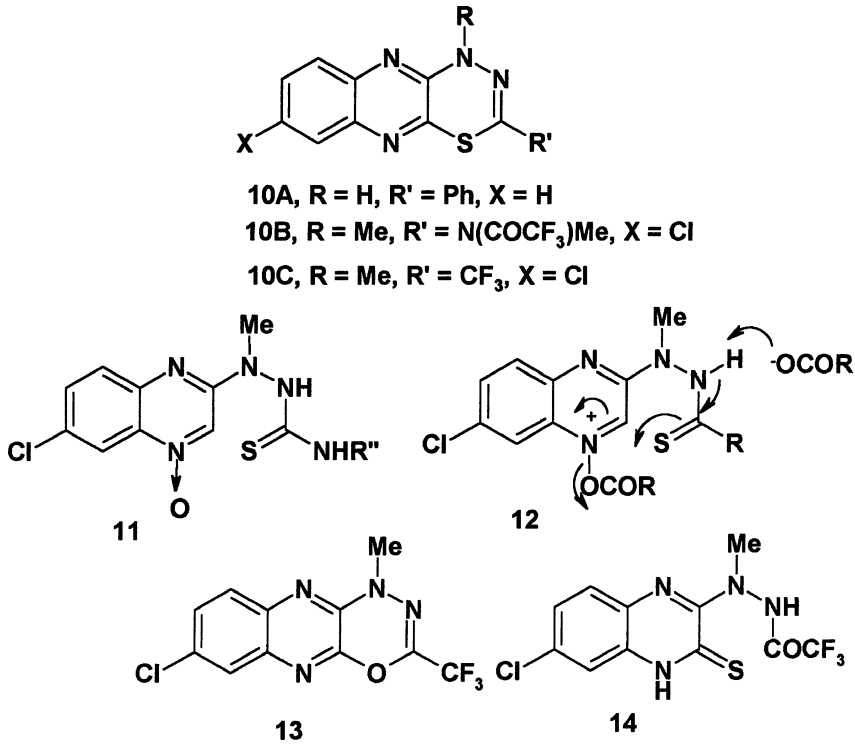
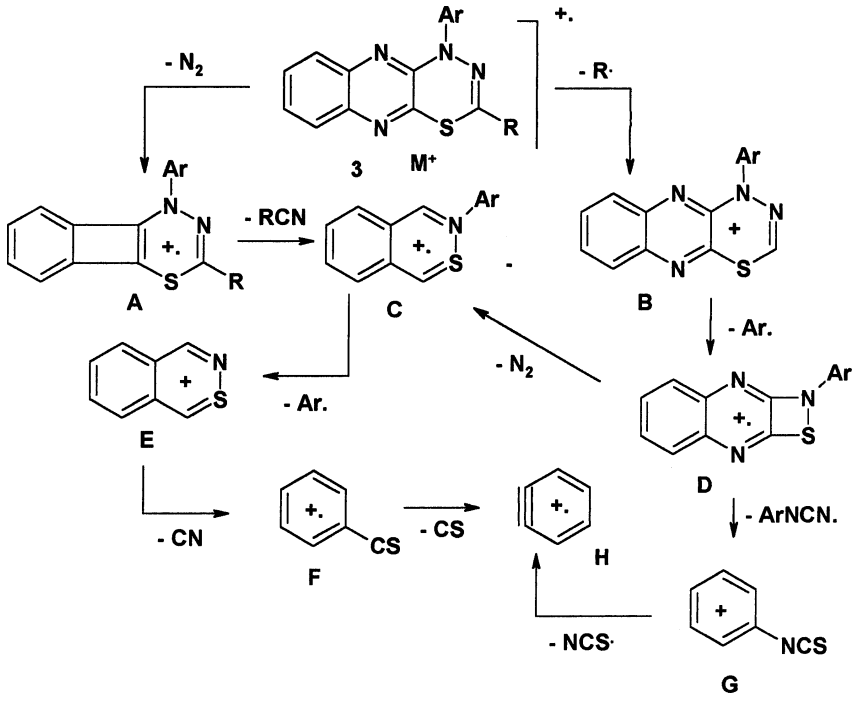


CHART 1

to give 7-chloro-(1-methyl-2-trifluoro-acetylhydrazino)-2-thioxo-1,2-dihydroquinoxaline **14**, whose dehydration with sulfuric acid in acetic acid afforded 8-chloro-4-methyl-2-triflurомethyl-4H-1,3,4-thiadiazino[5,6-b]quinoxaline **10C** (Chart 1).[14]

RESULTS AND DISCUSSION

The starting hydrazonoyl halides **1**[15] and 2-amino-3-quinoxalinethiol **2**[16] were prepared by literature methods. The reaction of **2** with each of the hydrazonoyl halides **1A** and **1E** in ethanol in the presence of sodium ethoxide gave, in each case, a single product whose mass spectrum and elemental analysis proved it to contain sulfur. This finding excludes the possible formation of the triazinoquinoxalines **4** (Scheme 1). Similarly, the reactions of **2** with each of **1B–D** yielded in each case a single product. The IR spectra of the isolated products **3B–D** revealed



SCHEME 2

the presence of ester, amide, and acetyl carbonyl bands, respectively. Their mass spectra displayed the molecular ion peaks in most cases as the base peaks. In addition, the spectra revealed common peaks at m/z values corresponding to the ion fragments A–G shown in Scheme 2. This finding suggests that the fragmentation pattern of the molecular ions of compounds prepared is as depicted in Scheme 2. On the basis of such data, structures of type **5** and **6** were discarded (Scheme 1). The ^{1}H and ^{13}C NMR of the isolated products and their elemental analyses (see experimental section) were also found to be consistent with structure **3**. Further evidence for the assigned structure **3** and in turn the proposed reaction pathway leading to it (Scheme 1) is supported by an alternate synthesis of **3Ea**. Thus, reaction of 1,5-diphenyl-3-mercaptoformazan **9Ea**, commonly known as dithiazone, with either 2,3-dichloroquinoxaline **7**[17] or 2-amino-3-chloroquinoxaline **8**[18] in ethanol in the presence of triethylamine afforded in each case a product that proved identical in all respect with **3Ea** obtained from reaction of **2** with 1,5-diphenyl-3-chloroformazan **1Ea**.

To account for the formation of **3** via the reaction of **1** with **2**, it is suggested, as depicted in Scheme 1, that the reactions started with the formation of the respective thiohydrazonate esters **I** as intermediates which in turn undergo in situ deaminative cyclization to give the respective **3**. The first step is analogous to the formation of thiohydrazonates by reaction of hydrazonoyl halides with thiols.[19] The second cyclization step is reminiscent of the formation of 1H-1,2,4-triazolo[3,4-c]-1,2,4-triazoles via cyclization of *ω*-(3-amino-1,2,4-triazol-4-yl)-*ω*-(phenylhydrazono)acetophenone[20a] and the displacement of the amino group with the hydroxyl group during hydrolysis of 2-aminoquinoxalines.[20b]

In conclusion, compounds **3A–E** represent important extensions in the chemistry of ring-fused 1,3,4-thiadiazines. The availability of the functional groups for further reactions offers the potential for novel biologically active material or dyestuffs.

EXPERIMENTAL

All melting points were determined on an electrothermal Gallenkamp apparatus and are uncorrected. Solvents were generally distilled and dried by standard literature procedures prior to use. The IR spectra were measured on a Pye-Unicam SP300 instrument in potassium bromide discs. The ^{1}H- and ^{13}C-NMR spectra were recorded on a Varian Mercury VXR-300 spectrometer (300 MHz for ^{1}H and 75 MHz for ^{13}C) in $CDCl_3$ or DMSO-d_6 and the chemical shifts were related to that of the solvent. The mass spectra were recorded on a GCMS-Q1000-EX spectrometer; the ionizing voltage was 70 eV. Elemental analyses were carried out by the Microanalytical Center of Cairo University, Giza, Egypt. Dithiazone **9** was purchased from Fluka Chemical Company. Hydrazonoyl halides **1** were prepared as previously described.[15] The reagents, 2-Amino-3-quinoxalinethiol **2**[16], 2,3-dichloroquinoxaline **7**[17] and 2-amino-3-chloroquinoxaline **8**[18] were prepared by the literature methods. The identification of compounds from different experiments were secured by mixed m.p.s and superimposable IR spectra.

2,4-Disubstituted-4H-1,3,4-thiadiazino[5,6-b]quinoxalines (3A–E)

General Procedure

A stirred sodium ethoxide solution, prepared from sodium metal (0.06 g, 2.5 mmol) and absolute ethanol (15 cm^3), was added to 2-amino-3-quinoxalinethiol **2** (0.44 g, 2.5 mmol). After 10 min, the appropriate hydrazonoyl halide **1** (2.5 mmol) was added and the reaction

mixture was left overnight at room temperature while being stirred. The solid that precipitated was filtered off, washed with H_2O, dried, and finally crystallized from the appropriate solvent to give the respective 2,4-disubstituted-4H-1,3,4-thiadiazino[5,6-b]quinoxaline **3**. The compounds **3A–E** that were prepared are listed below with their physical constants.

2,4-Diphenyl-4H-1,3,4-thiadiazino[5,6-b]quinoxaline (3Aa)

Yellow needles, (0.66 g, 75%); m.p. 206°C (EtOH-Dioxane) (Lit. m.p. 196°C)[21]; ^{1}H NMR (DMSO-d_6) δ 7.36–7.81 (m, ArH); ^{13}C NMR (DMSO-d_6) δ 126.0, 126.39, 127.38, 127.72, 127.79, 128.03, 129.42, 129.68, 130.80, 131.66, 134.38, 138.86, 140.68, 143.02; MS m/z (%) 356 (M^++ 2, 6), 355 (M^++ 1, 22), 354 (M^+, 100), 326 (1), 277 (2), 250 (25), 223 (1), 218 (18), 148 (1), 134 (1), 122 (3), 118 (1), 103 (5), 90 (24), 77 (21), 76 (4); Anal. Calcd. for $C_{21}H_{14}N_4S$ (354.44): C, 71.16; H, 3.73; N, 15.85; Found: C, 71.02; H, 3.45; N, 15.58%.

2-Phenyl-4-(4-nitrophenyl)-4H-1,3,4-thiadiazino-[5,6-b]quinoxaline (3Ab)

Orange solid (0.80 g, 80%), m.p. 232°C (EtOH-Dioxane); ^{1}H NMR (DMSO-d_6) δ 8.32 (d, J = 9 Hz, 2H, ArH), 8.01 (d, J = 9 Hz, 2H, ArH), 7.5–7.9 (m, 9H, ArH); MS m/z (%) 401 (M^++ 2, 7), 400 (M^++ 1, 25), 399 (M^+, 100), 371 (1), 352 (14), 322 (1), 269 (5), 250 (29), 219 (2), 206 (17), 191 (8), 176 (8), 164 (2), 160 (8), 152 (2), 146 (1), 134 (8), 129 (5), 122 (17), 90 (65), 77 (25), 76 (30); Anal. Calcd. for $C_{21}H_{13}N_5O_2S$ (399.43): C, 63.15; H, 3.28; N, 17.53; Found: C, 63.02; H, 3.20; N, 17.25%.

Ethyl 4-Phenyl-4H-1,3,4-thiadiazino[5,6-b]quinoxaline-2-carboxylate (3Ba)

Yellow needles (0.74 g, 85%), m.p. 204°C (EtOH-Dioxane); IR (KBr) ν 1707 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 1.26 (t, J = 7 Hz, 3H, CH_3), 4.29 (q, J = 7 Hz, 2H, CH_2), 7.28–7.63 (m, 9H, ArH); ^{13}C NMR (DMSO-d_6) δ 13.83, 62.65, 126.25, 126.72, 127.09, 127.66, 127.92, 128.86, 129.17, 129.99, 139.65, 139.92, 141.50, 142.30, 143.07, 159.94; MS m/z (%) 352 (M^++ 2, 8), 351 (M^++ 1, 12), 350 (M^+, 100), 349 (14), 322 (4), 277 (27), 251 (21), 225 (6), 218 (66), 207 (14), 166 (10), 148 (3), 134 (3), 121 (2), 117 (3), 91 (51), 77 (100), 76 (8); Anal. Cacld. for $C_{18}H_{14}N_4O_2S$ (350.40): C, 61.71; H, 4.03; N, 15.99; Found: C, 61.70; H, 4.00; N, 16.09%.

Ethyl 4-(4-Nitrophenyl)-4H-1,3,4-thiadiazino-[5,6-b]quinoxaline-2-carboxylate (3Bb)

Yellow solid (0.82 g, 82%), m.p. 270°C (EtOH-Dioxane); IR (KBr) ν 1751 cm^{-1}; ^1H NMR (DMSO-d_6) δ 1.29 (t, J = 7 Hz, 3H, CH_3), 4.33 (q, J = 7 Hz, 3H, CH_2), 7.42–7.70 (m, 4H, ArH), 7.85 (d, J = 8 Hz, 2H, ArH), 8.35 (d, J = 9 Hz, 2H, ArH); MS m/z (%) 397 (M^+, + 2, 10), 396 (M^++ 1, 28), 395 (M^+, 100), 394 (17), 367 (9), 322 (16), 296 (5), 266 (4), 250 (19), 218 (10), 164 (93), 149 (2), 134 (4), 122 (4), 102 (7), 90 (23), 76 (6); Anal. Calcd. for $C_{18}H_{14}N_5O_4S$ (395.40): C, 54.63; H, 3.31; N, 17.71; Found: C, 54.50; H, 3.05; N, 17.92%.

Ethyl 4-(4-Methylphenyl)-4H-1,3,4-thiadiazino-[5,6-b]quinoxaline-2-carboxylate (3Bc)

Yellow needles (0.78 g, 86%), m.p. 200°C (EtOH); IR (KBr) 1712 cm^{-1}; ^1H NMR (DMSO-d_6) δ 1.39 (t, J = 7 Hz, 3H), 1.54 (s, 3H, CH_3), 4.38 (q, J = 7 Hz, 2H, CH_2), 7.26–7.46 (m, 4H, ArH); 7.49 (d, J = 8 Hz, 2H, ArH), 7.52 (d, J = 8 Hz, 2H, ArH); MS m/z (%) 366 (M^++ 2, 7), 365 (M^++ 1, 19), 364 (M^+, 71), 291 (23), 264 (25), 234 (4), 232 (100), 134 (7), 129 (10), 122(10), 105 (13), 104 (29), 102 (27), 91 (87), 77 (48); Anal. Calcd. for $C_{19}H_{16}N_4O_2S$ (364.43): C, 62.62; H, 4.43; N, 15.37; Found: C, 62.41; H, 4.15; N, 15.32%.

Ethyl 4-(4-Chlorophenyl)-4H-1,3,4-thiadiazino-[5,6-b]quinoxaline-2-carboxylate (3Bd)

Orange crystals (0.77 g, 80%), m.p. 198°C (EtOH); IR (KBr) ν 1710 cm^{-1}; ^1H NMR (DMSO-d_6) δ 1.26 (t, J = 7 Hz, 2H, CH_3), 4.32 (q, J = 7 Hz, 2H, CH_2), 7.09 (d, J = 7 Hz, 2H, ArH), 7.45 (d, J = 8 Hz, 2H, ArH), 7.57–7,64 (m, 4H, ArH); MS m/z (%) 386 (M^++ 2, 55), 385 (M^++ 1, 29), 384 (M^+, 100), 311 (37), 254 (17), 252 (50), 250 (93), 218 (40), 161 (22), 147 (7), 133 (16), 122 (7), 111 (23), 105 (12), 102 (29), 91 (10), 90 (57), 77 (11), 76 (15); Anal. Calcd. for $C_{18}H_{13}ClN_4O_2S$ (384.85): C, 56.18; H, 3.40; N, 14.56; Found: C, 56.57; H, 3.39; N, 14.32%.

N-Phenyl 4-Phenyl-4H-1,3,4-thiadiazino[5,6-b]quinoxaline-2-carboxamide (3Ca)

Yellow solid, (0.79 g, 80%), m.p. 220°C (EtOH-Dioxane); IR (KBr) ν 3379, 1681 cm^{-1}; ^1H NMR (DMSO-d_6) δ 11.6 (s, 1H, NH), 7.34–7.83 (m, 14H, ArH); MS m/z (%) 400 (M^++ 2, 9), 398 (M^++ 1, 27), 397 (M^+, 100), 277 (37), 259 (27), 251 (16), 233 (8), 225 (2), 218 (45), 148 (2), 134 (2), 117 (2),

120 (10), 104 (4), 91 (14), 77 (68), 76 (6); Anal. Calcd. for $C_{22}H_{15}N_5OS$ (397.46): C, 66.50; H, 3.78; N, 17.63; Found: C, 66.21; H, 4.08; N, 17.30%.

N-Phenyl 4-(4-Nitrophenyl)-4H-1,3,4-thiadiazino-[5,6-b]quinoxaline-2-carboxamide (3Cb)

Orange solid, (0.90 g, 81%), m.p. 180°C, IR (KBr) ν 3432, 1668 cm^{-1}; ^1H NMR (DMSO-d_6) δ 7.70–7.15 (m, 4H, ArH), 7.27 (d, J = 8 Hz, 2H, ArH), 7.29 (d, J = 8 Hz, 2H, ArH), 12.08 (s, 1H, NH); MS m/z (%) 444 (M^+, + 2, 6), 443 (M^++ 1, 6), 442 (M^+, 79), 413 (1), 322 (21), 296 (8), 276 (27), 267 (1), 210 (22), 206 (11), 164 (5), 146 (4), 134 (5), 122 (7), 120 (34), 119 (14), 102 (23), 90 (50), 77 (100), 76 (17); Anal. Calcd. for $C_{22}H_{16}N_6O_3S$ (442.46): C, 59.72; H, 3.19; N, 18.99; Found: C, 59.31; H, 3.45; N, 18.78%.

N-Phenyl 4-(4-Chlorophenyl)-4H-1,3,4-thiadiazino-[5,6-b]quinoxaline-2-carboxamide (3Cd)

Yellow solid (0.88 g, 82%), m.p. 274°C (Dioxane); IR (KBr) ν 3379, 1681 cm^{-1}; ^1H NMR (DMSO-d_6) δ 7.35 (d, J = 8 Hz, 2H, ArH), 7.48–7.67 (m, 4H, ArH), 7.75 (d, J = 8 Hz, 2H, ArH), 10.12 (s, 1H, NH); ^{13}C NMR (DMSO-d_6) δ 121.09, 124.59, 126.76, 127.10, 127.73, 127.95, 128.45, 128.55, 130.00, 131.21, 135.22, 137.07, 139.56, 139.99, 140.05, 142.29, 143.55, 158.13; MS m/z (%) 434 (M^+, + 2, 23), 433 (M^++ 1, 41), 432 (M^+, 30), 431 (100), 430 (12), 311 (37), 285 (17), 255 (5), 250 (53), 218 (26), 151 (2), 147 (3), 137 (6), 120 (21), 111 (13), 102 (13), 90 (45), 77 (70), 76 (6); Anal. Calcd. for $C_{22}H_{14}ClN_5OS$ (431.91): C, 61.18; H, 3.27; N, 16.21; Found: C, 61.63; H, 3.44; N, 16.20%.

2-Acetyl-4-phenyl-4H-1,3,4-thiadiazino[5,6-b]quinoxaline (3Da)

Orange crystals (0.72 g, 90%), m.p. 230°C (EtOH-Dioxane); IR (KBr) ν 1681 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.34 (s, 3H, $COCH_3$), 7.45–7.63 (m, 9H, ArH); MS m/z (%) 322 (M^++ 2, 7), 321 (M^++ 1, 22), 320 (M^+, 100), 305 (11), 277 (65), 251 (22), 225 (2), 218 (46), 160 (2), 148 (2), 134 (2), 129 (3), 120 (1), 118 (3), 102 (20), 90 (34), 77 (78), 76 (15); Anal. Calcd. for $C_{17}H_{12}N_4OS$ (320.38): C, 63.73; H, 3.78; N, 17.43; Found: C, 63.50; H, 3.43; N, 17.34%.

2-Acetyl-4-(4-nitrophenyl)-4H-1,3,4-thiadiazino-[5,6-b]quinoxaline (3Db)

Yellow solid (0.78 g, 85%), m.p. >300°C (Dioxane); IR (KBr) ν 1665 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.40 (s, 3H, $COCH_3$), 7.14–7.84 (m, 4H, ArH), 7.81 (d, J = 9 Hz, 2H, ArH), 8.13 (d, J = 9 Hz, 2H, ArH), MS

m/z (%) 367 (M^+, + 2, 7), 366 (M^+ + 1, 25), 365 (M^+, 9), 236 (9), 206 (9), 196 (91), 174 (9), 162 (9), 160 (100), 148 (9), 134 (23), 122 (6), 120 (9), 105 (22), 102 (9), 91 (9), 78 (10), 76 (3); Anal. Calcd. for $C_{17}H_{11}N_5O_3S$ (365.39): C, 55.89; H, 3.01; N, 19.18; Found: C, 55.71; H, 2.89; N, 19.00%.

2-Acetyl-4-(4-methylphenyl)-4H-1,3,4-thiadiazino-[5,6-b]quinoxaline (3Dc)

Yellow solid, 0.71 g, 85%; m.p. 190°C (Ethanol); IR (KBr) ν 1689 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.00 (s, 3H, $ArCH_3$), 2.35 (s, 3H, $COCH_3$), 6.89–7.13 (m, 4H, ArH), 7.21 (d, J = 8 Hz, 2H, ArH), 7.41 (d, J = 8 Hz, 2H, ArH); MS m/z (%) 336 (M^+ + 2, 7), 335 (M^+ + 1, 23), 334 (M^+, 87), 320 (27), 305 (4), 291 (47), 277 (25), 265 (19), 239 (3), 205 (12), 161 (22), 149 (8), 134 (4), 121 (13), 132 (28), 118 (19), 106 (87), 105 (40), 104 (27), 91 (100), 77 (92), 76 (21); Anal. Calcd. for $C_{18}H_{14}N_4OS$ (334.40): C, 64.65; H, 4.22; N, 16.75; Found: C, 64.41; H, 4.27; N, 16.75%.

2-Acetyl-4-(4-chlorophenyl)-4H-1,3,4-thiadiazino-[5,6-b]quinoxaline (3Dd)

Brown solid (0.80 g, 90%; m.p. 208°C (Ethanol-dioxane); IR (KBr) ν 1689 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.36 (s, 3H, $COCH_3$), 7.39–7.50 (m, 4H, ArH), 7.56 (d, J = 7 Hz, 2H, ArH), 7.66 (d, J = 7 Hz, 2H, ArH); MS m/z (%) 357 (M^+ + 3, 7), 356 (M^+ + 2, 29), 355 (M^+ + 1, 20), 354 (M^+, 84), 339 (14), 311 (38), 285 (16), 277 (16), 255 (5), 250 (71), 218 (27), 152 (96), 148 (5), 137 (10), 111 (32), 125 (20), 102 (38), 90 (100), 77 (12), 76 (32); Anal. Calcd. for $C_{17}H_{11}ClN_4OS$ (354.82): C, 57.55; H, 3.12; N, 15.79; Found: C, 57.10; H, 3.41; N, 15.52%.

2-Acetyl-4-(3-methylphenyl)-4H-1,3,4-thiadiazino[5,6-b]quinoxaline (3De)

Red solid (0.65 g, 78%), m.p. 218°C (Ethanol-dioxane); IR (KBr) ν 1672 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.32 (s, 3H, $ArCH_3$), 2.38 (s, 3H, $COCH_3$), 7.32–7.63 (m, 8H, ArH); MS m/z (%) 336 (M^+, + 2, 7), 335 (M^+ + 1, 22), 334 (M^+, 100), 319 (8), 291 (35), 277 (8), 265 (7), 235 (1), 232 (21), 134 (91), 122 (1), 104 (3), 91 (7), 77 (3), 76 (2); Anal. Calcd. for $C_{18}H_{14}N_4OS$ (334.40): C, 64.65; H, 4.22; N, 16.75; Found: C, 64.23; H, 4.00; N, 16.34%.

2-Acetyl-4-(3-chlorophenyl)-4H-1,3,4-thiadiazino-[5,6-b]quinoxaline (3Df)

Yellow solid (0.71 g, 80%); m.p. 210°C (Ethanol-dioxane); IR (KBr) ν 1681 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.36 (s, 3H, $COCH_3$), 7.39–7.73 (m,

8H, ArH); MS m/z (%) 358 (M^++ 4, 2), 357 (M^++ 3, 7), 356 (M^++ 2, 27), 355 (M^++ 1, 15), 354 (M^+, 64), 339 (12), 311 (39), 285 (9), 259 (2), 277 (12), 250 (36), 218 (25), 148 (5), 134 (5), 122 (9), 111 (32), 102 (41), 90 (83), 75 (100); Anal. Calcd. for $C_{17}H_{11}ClN_4OS$ (354.82): C, 57.55; H, 3.12; N, 15.79; Found: C, 57.30; H, 3.00; N, 15.30%.

2-Acetyl-4-(3-nitrophenyl)-4H-1,3,4-thiadiazino-[5,6-b]quinoxaline (3Dg)

Orange crystals (0.69 g, 75%); m.p. 220°C (Ethanol-dioxane); IR (KBr) ν 1687 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.39 (s, 3H, $COCH_3$), 7.38–8.55 (m, 8H, ArH); ^{13}C NMR (DMSO-d_6) δ 23.96, 120.5, 122.03, 126.76, 127.20, 128.45, 130.11, 132.07, 138.56, 139.14, 140.08, 142.12, 147.79, 192.37; MS m/z (%) 367 (M^+, + 2, 7), 366 (M^++ 1, 21), 365 (M^+, 100), 322 (18), 276 (19), 231 (2), 218 (12), 206 (14), 175 (3), 162 (9), 147 (9), 134 (230), 122 (8), 102 (45), 90 (77), 76 (3); Anal. Calcd. for $C_{17}H_{11}N_5O_3S$ (365.39): C, 55.89; H, 3.01; N, 19.18; Found: C, 55.92; H, 3.33; N, 18.78%.

2-Acetyl-4-(4-methoxyphenyl)-4H-1,3,4-thiadiazino-[5,6-b]quinoxaline (3Dh)

Orange crystals (0.70 g, 80%); m.p. 190°C (Ethanol); IR (KBr) ν 1681 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.49 (s, 3H, $COCH_3$), 3.73 (s, 3H, OCH_3), 7.04 (d, J = 7 Hz, 2H, ArH), 7.33–7.59 (m, 4H, ArH), 7.46 (d, J = 7 Hz, 2H, ArH); MS m/z (%) 352 (M^+, + 2, 20), 351 (M^++ 1, 24), 350 (M^+, 83), 307 (22), 281 (37), 266 (100), 250 (31), 148 (13), 134 (17), 122 (36), 107 (8), 90 (28), 78 (41), 77 (21), 76 (17); Anal. Calcd. for $C_{18}H_{14}N_4O_2S$ (350.40): C, 61.74; H, 4.03; N, 15.99; Found: C, 61.90; H, 3.70; N, 15.78%.

2-Phenylazo-4-(phenyl)-4H-1,3,4-thiadiazino[5,6-b]quinoxaline (3Ea)

Red crystals (0.76 g, 80%), m.p. > 300°C (EtOH-Dioxane) (Lit. m.p. 313°C)[21]; ^1H NMR (DMSO-d_6) δ 7.38–7.87 (m, ArH); MS m/z (%) 384 (M^+, + 2, 2), 383 (M^++ 1, 8), 382 (M^+, 30), 354 (4), 277 (8), 251 (2), 223 (2), 218 (12), 105 (16), 102 (4), 77 (100) 76 (4); Anal. Calcd. for $C_{21}H_{14}N_6S$ (382.45): C, 65.95; H, 3.69; N, 21.97; Found: C, 65.96; H, 3.87; N, 21.35%.

Alternate Synthesis of 3Ea

A stirred sodium ethoxide solution prepared from sodium metal (0.06 g, 2.5 mmol) and absolute ethanol (15 cm^3) was added to dithiazone **9Ea**

(0.64 g, 2.5 mmol) and after 5 min was added 2,4-dichloroquinoxaline **7** (0.50 g, 2.5 mmol) and the reaction mixture was refluxed for 5 h and cooled. The solid that precipitated was filtered off, washed with water, dried, and finally crystallized from ethanol-dioxane mixture to give the respective 2-phenylazo-3-phenyl-4H-1,3,4-thiadiazino[5,6-b]quinoxaline **3Ea**[21], which was found identical in all respects with the product **3Ea** prepared above from **1Ea** and **2**.

Repetition of the above procedure using 2-chloro-3-aminoquinoxaline **8** in place of **7** and work up the reaction mixture also yielded **3Ea**.

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