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Synthesis and Reactions of 3-(1,2,4-Triazol-5-yl)methylene-2-oxo-1,2,3,4-tetrahydroquinoxalines[1)]

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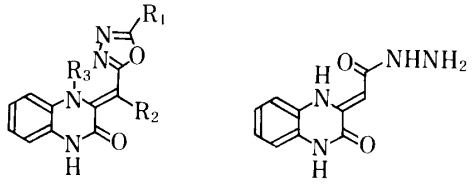
Various 3-(1,2,4-triazol-5-yl)methylene-2-oxo-1,2,3,4-tetrahydroquinoxalines (**4**—**7**, **10**, **11**) and related compounds (**8**, **9**) were synthesized using 3-hydrazinocarbonylmethylene-2-oxo-1,2,3,4-tetrahydroquinoxaline (**2**) as a starting material.

Keywords——methyl isothiocyanate; allyl isothiocyanate; methyl iodide; nitrous acid; *m*-chloroperbenzoic acid; thiosemicarbazide; sulfur extrusion; polyphosphoric acid; benzoyl chloride

Many 1,3,4-oxadiazole derivatives possess fungicidal, herbicidal, and bactericidal activities,[2)] and we have previously synthesized a novel type of 1,3,4-oxadiazoles, 3-(1,3,4-oxadiazol-5-yl)methylene-2-oxo-1,2,3,4-tetrahydroquinoxalines (**1**), from 3-hydrazinocarbonylmethylene-2-oxo-1,2,3,4-tetrahydroquinoxaline (**2**)[3)] (Chart 1) in order to evaluate their activities. In addition, various 1,2,4-triazoles have been reported to possess bactericidal,[4)] fungicidal,[5)] antihistaminic,[6)] and plant growth regulatory[7)] activities, but there have been few reports on the synthesis and biological evaluation of 1,2,4-triazoles having a quinoxalinylmethylene moiety in the 3- or 5-position. This paper describes the synthesis and reactions of the above novel type of 1,2,4-triazoles as a part of our search for new agents having interesting biological activities.



1 2

Chart 1

The reactions of **2** with allyl and methyl isothiocyanates in dioxane gave the thiosemicarbazides (**3a** and **3b**, respectively), which were refluxed with potassium hydroxide in water to effect dehydration,[8)] producing 3-(4-allyl-3,4-dihydro-3-thioxo-2*H*-1,2,4-triazol-5-yl)-methylene-2-oxo-1,2,3,4-tetrahydroquinoxaline (**4a**) and 3-(4-methyl-3,4-dihydro-3-thioxo-2*H*-1,2,4-triazol-5-yl)methylene-2-oxo-1,2,3,4-tetrahydroquinoxaline (**4b**), respectively. Refluxing of **3a** and **3b** with 1,8-diazabicyclo[5.4.0]-7-undecene (DBU) in butanol also afforded **4a** and **4b**, respectively, in improved yields. Moreover, the reactions of **2** with allyl and methyl isothiocyanates in DBU and butanol directly provided **4a** and **4b**, respectively. The infrared (IR) spectra of **4a** and **4b** exhibited the C=S absorption bands near 1460 cm^{-1}, but showed no SH absorption band in the range of 2600—2550 cm^{-1}.[9)] These data are con-

sistent with the structures of **4a** and **4b** shown in Chart 2.

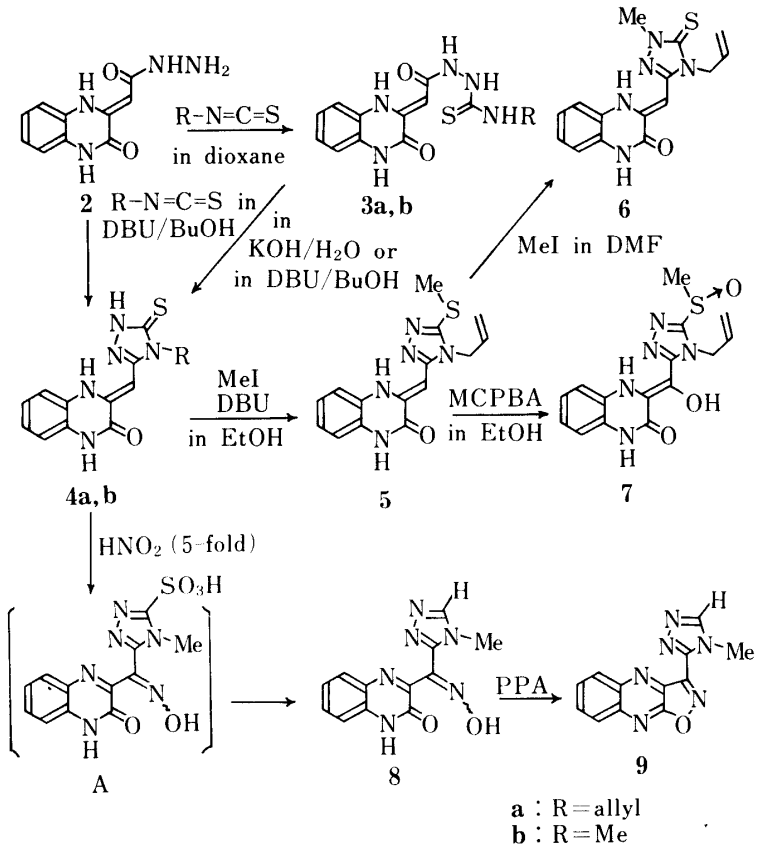


Chart 2

The reaction of **4a** with methyl iodide resulted in S-methylation to give 3-(4-allyl-3-methylthio-4*H*-1,2,4-triazol-5-yl)methylene-2-oxo-1,2,3,4-tetrahydroquinoxaline (**5**). Further refluxing of **5** with methyl iodide in *N*, *N*-dimethylformamide (DMF) afforded 3-(4-allyl-3,4-dihydro-2-methyl-3-thioxo-2*H*-1,2,4-triazol-5-yl)methylene-2-oxo-1,2,3,4-tetrahydroquinoxaline (**6**), presumably *via* an $N^{2'}$-methylated intermediate.[10] Moreover, the reaction of **5** with 2 equivalents of *m*-chloroperbenzoic acid (MCPBA) resulted in methylenic C-hydroxylation[11] and N- or S-oxidation to furnish a yellow product. In the previous paper,[1] the N-oxide structure was proposed for this product on the basis of the mass spectral (MS) data, which showed the $[M-O\ (16)]^+$ and $[M-OH\ (17)]^+$ fragment ion peaks (Table I) ordinarily observed in *ortho*-alkyl N-oxide compounds,[12] but lacked the $[M-CO\ (28)]^+$ ion peak (characteristic of alkyl aryl and diaryl sulfoxides).[13] However, preferential S-oxidations have been reported in the reactions of di-2-pyridylmethyl sulfide[14] and 3-substituted 5-alkylthio-1,2,4-triazoles[15] with MCPBA and hydrogen peroxide–acetic acid, respectively. Therefore, the structure of the above product should be revised to 3-[1-(4-allyl-3-methylsulfinyl-4*H*-1,2,4-triazol-5-yl)-1-hydroxy]methylene-2-oxo-1,2,3,4-tetrahydroquinoxaline (**7**).

The reaction of **4b** with an excess of nitrous acid resulted in hydroxyimination[16] and sulfur extrusion[15,17] to produce 3-[1-hydroxyimino-1-(4-methyl-4*H*-1,2,4-triazol-3-yl)]-methylene-2-oxo-1,2-dihydroquinoxaline (**8**), presumably *via* intermediate A. Namely, it was assumed that the thiol group would be oxidized with nitrous acid to give intermediate A, whose $C^{3'}$-sulfonic acid group was eliminated in the hot acidic medium.[15,17] Heating of **8** in polyphosphoric acid (PPA) resulted in dehydration[16] to afford 3-(4-methyl-4*H*-1,2,4-triazol-

TABLE I. Mass Spectral Data for **7**

m/z	Ion species	Formula	Calcd	Found	Relat. intensity
345	$[M]^{+\cdot}$	$C_{15}H_{15}N_5O_3S$	345.090	345.091	100
329	$[M-O]^{+\cdot}$	$C_{15}H_{15}N_5O_2S$	329.092	329.090	23.6
328	$[M-OH]^+$	$C_{15}H_{14}N_5O_2S$	328.087	328.085	40.0
304	$[M-C_3H_5]^+$	$C_{12}H_{10}N_5O_3S$	304.050	304.049	49.4
289	$[M-C_3H_5-CH_3]^{+\cdot}$	$C_{11}H_7N_5O_3S$	289.027	289.029	70.2
288	$[M-O-C_3H_5]^+$ or $[M-C_3H_5-O]^+$	$C_{12}H_{10}N_5O_2S$	288.055	288.053	34.5

3-yl)isoxazolo[4,5-*b*]quinoxaline (**9**). The nuclear magnetic resonance (NMR) spectra of **8** and **9** showed the $C^{3'}$–H proton signals at δ 8.57 and 9.91 ppm, respectively, supporting the structural assignments of **8** and **9**.

The reactions of **3a** and **3b** in an excess of benzoyl chloride and dioxane also induced cyclization to the 1,2,4-triazole ring to produce 3-(4-allyl-3-benzoylthio-4*H*-1,2,4-triazol-5-yl)methylene-2-oxo-1,2,3,4-tetrahydroquinoxaline (**10a**) and 3-(3-benzoylthio-4-methyl-4*H*-1,2,4-triazol-5-yl)methylene-2-oxo-1,2,3,4-tetrahydroquinoxaline (**10b**), respectively. This type of cyclization with benzoyl chloride into a 1,2,4-triazole ring has already been reported by Marckwald *et al.*[18] The reactions of **2** with allyl and methyl isothiocyanates in an excess of benzoyl chloride and dioxane similarly afforded **10a** and **10b**, respectively. The $C^{3'}$-benzoylthio structures of **10a** and **10b** were elucidated by means of the following reactions. The reaction of **10b** with potassium hydroxide in ethanol caused debenzoylation to give **4b**, whose reaction with an excess of benzoyl chloride in dry pyridine and dioxane resulted in $N^{2'}$-benzoylation to furnish 3-(2-benzoyl-3,4-dihydro-4-methyl-3-thioxo-2*H*-1,2,4-triazol-5-yl)methylene-2-oxo-1,2,3,4-tetrahydroquinoxaline (**11**). The $N^{2'}$-benzoylation under such conditions has already been reported by Tsitsika *et al.*[19] The above results are shown in Chart 3. The NMR spectral data provided additional evidence for the structures of the benzoylated

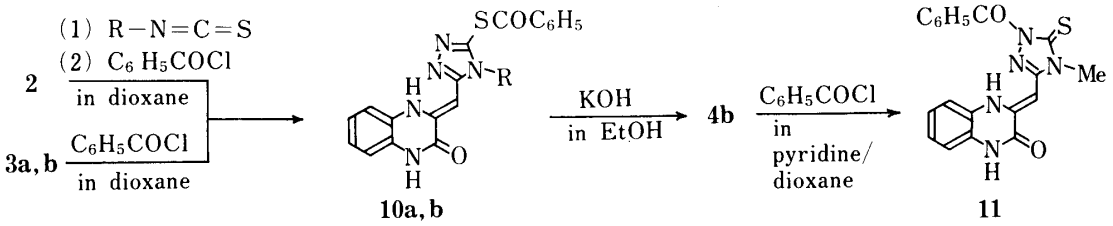
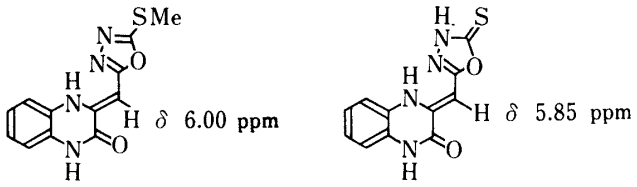


Chart 3

compounds **10a**, **10b**, and **11**. The vinyl proton signals of the dihydrotriazole compounds [$N^{2'}$–H (**4a**) and $N^{2'}$–NMe (**6**)] were observed at δ 5.88 and 5.87 ppm, respectively, but the vinyl proton signal of the aromatized triazole compound (**5**) was observed at a lower magnetic field (δ 5.97 ppm) than those of **4a** and **6**. This tendency was also found in the 3-(1,3,4-oxadiazol-2-yl)methylene-2-oxo-1,2,3,4-tetrahydroquinoxalines (**12a** and **12b** Chart 4);[20] the vinyl proton signal of the aromatized oxadiazole compound **12a** was observed at a lower magnetic field (δ 6.00 ppm) than that of the dihydrooxadiazole compound **12b** (δ 5.85 ppm). On the other hand, no difference was found in the chemical shifts of the vinyl proton signals between the $N^{2'}$–H (**4b**) and $N^{2'}$–benzoyl (**11**) compounds of the dihydrotriazole form (both δ 5.93 ppm). Furthermore, the NMR spectra of **10a** and **10b** exhibited the vinyl proton signals at a lower magnetic field (both δ 6.42 ppm) than those of **5** and **12a**, supporting the conclusion

that **10a** and **10b** possessed the aromatized 1,2,4-triazole ring with the benzoylthio group at the 3′-position.

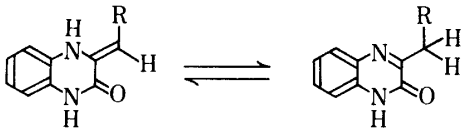


12a **12b**

Chart 4

NMR Spectral Features of the Products

The NMR spectra of 3-alkoxycarbonylmethylene-2-oxo-1,2,3,4-tetrahydroquinoxalines in dimethylsulfoxide-d_6 (DMSO-d_6) have been reported to reveal the presence of two tautomers, I and II,[21] as shown in Chart 5. Compounds **3**—**6**, **10**, and **11** also displayed this tautomerism in DMSO-d_6, and hence the signals due to these two tautomers are observed. The integral ratios of the vinyl (I) and methylene (II) proton signals in the NMR spectra of **3b**, **4b**, **10a**, **10b**, and **11** at 30 °C were 1 : 1, 1 : 0.7, 4.5 : 1, 4 : 1, and 1 : 1.5, respectively, while the integral ratios of the other compounds could not be calculated, since either the vinyl or the methylene proton signal overlapped with other signals.



I II

Chart 5

Experimental

All melting points are uncorrected. IR spectra were recorded from KBr discs on a JASCO IRA-1 spectrophotometer. NMR spectra were measured in DMSO-d_6 (except for **9**) with an EM-390 spectrometer at 90 MHz using tetramethylsilane as an internal standard. Chemical shifts are given in the δ scale, relative to the internal standard. MS were determined with a JMS-O1S spectrometer (Japan Electron Optics Laboratory Co., Ltd.).

Thiosemicarbazides 3a and 3b——A suspension of **2** (10 g, 45.9 mmol) and the appropriate isothiocyanate (equimolar amount) in dioxane (200 ml) was refluxed for 1 h in an oil bath to precipitate a colorless powder, **3a** or **3b**, which was collected by suction filtration.

Compound 3a——Yield, 13.73 g (94.4%). Trituration with hot EtOH gave an analytically pure sample, mp 230—232 °C. MS *m/z*: 317 (M^+). IR ν_{max}: 3300, 1690, 1640 cm^{-1}. NMR: 12.43 (s), 11.43 (s), 10.13 (s), 9.63 (s), 9.40 (s), and 9.15 (s) (4H, NH),[21] 8.10 (t, J=4.5 Hz, 1H, CSNHCH$_2$CH=CH$_2$), 8.00—6.70 (m, 4H, aromatic), 5.83 (m, 1H, –CH$_2$–CH=CH$_2$), 5.68 (s, C^3=CH–),[21] 5.30—4.87 (m, 2H, –CH$_2$–CH=CH$_2$), 4.10 (m, 2H, –CH$_2$–CH=CH$_2$), 3.72 (s, C^3–CH$_2$–).[21] *Anal.* Calcd for $C_{14}H_{15}N_5O_2S$: C, 52.98; H, 4.76; N, 22.07. Found: C, 53.09; H, 4.76; N, 21.85.

Compound 3b——Yield, 12.91 g (96.7%). Trituration with hot EtOH afforded an analytically pure sample, mp 256—258 °C. MS *m/z*: 291 (M^+). IR ν_{max}: 3300, 3160, 3010, 1670, 1630 cm^{-1}. NMR: 11.50 (s), 10.00 (s), 9.33 (s), and 9.10 (s) (4H, NH),[21] 7.90 (q, J=4.5 Hz, 1H, CSNHMe), 7.83—6.67 (m, 4H, aromatic), 5.68 (s, C^3=CH–),[21] 3.73 (C^3–CH$_2$–),[21] 2.94 (d, J=4.5 Hz) and 2.88 (d, J=4.5 Hz) (3H, CSNHMe).[21] The Me proton signals split into two on addition of D_2O. *Anal.* Calcd for $C_{12}H_{13}N_5O_2S$: C, 49.47; H, 4.50; N, 24.04. Found: C, 49.27; H, 4.44; N, 23.76.

3-(4-Allyl-3,4-dihydro-3-thioxo-2*H*-1,2,4-triazol-5-yl)methylene-2-oxo-1,2,3,4-tetrahydroquinoxaline (4a) and 3-(4-Methyl-3,4-dihydro-3-thioxo-2*H*-1,2,4-triazol-5-yl)methylene-2-oxo-1,2,3,4-tetrahydroquinoxaline (4b)——From the Thiosemicarbazides **3a** and **3b** (Method A): A suspension of the appropriate thiosemicarbazide (1 g) and KOH (1.5 eq) in H_2O (30 ml) was refluxed in an oil bath for 1 h to precipitate the product **4a** or **4b** as a yellow powder, which

was collected by suction filtration. Trituration with hot EtOH–H_2O gave an analytically pure sample.

From the Thiosemicarbazide **3a** and **3b** (Method B): A suspension of the appropriate thiosemicarbazide (10 g) and DBU (2 ml) in BuOH (400 ml) was refluxed in an oil bath for 2 h to precipitate the product **4a** or **4b** as a yellow powder, which was collected by filtration. Trituration with hot EtOH afforded an analytically pure sample.

One-Pot Synthesis from the Hydrazide **2** (Method C): A suspension of the hydrazide **2** (5 g), the appropriate isothiocyanate (equimolar amount), and DBU (1 ml) in BuOH (200 ml) was refluxed in an oil bath for 5 h to precipitate the product **4a** or **4b** as a yellow powder, which was collected by suction filtration. Trituration with hot EtOH gave an analytically pure sample.

Compound 4a——Yield, 0.76 g (81%) in method A, 8.02 g (85.5%) in method B, 4.74 g (69.1%) in method C, mp 334—336 °C. MS *m/z*: 299 (M^+). IR ν_{max}: 3120, 3060, 3010, 1680, 1640, 1610, 1260 cm^{-1}. NMR: 13.81 (s), 13.57 (s), 12.40 (s), and 11.46 (s) (2H, N^1– and N^4–H),[21] 10.03 (s, 1H, $N^{2'}$–H), 7.77—6.67 (m, 4H, aromatic), 5.88 (s, C^3=C<u>H</u>–),[21] 5.86 (m, 1H, $-CH_2-C\underline{H}=CH_2$), 5.30—4.83 (m, 2H, $-CH_2-CH=C\underline{H}_2$), 4.68 (dd, J=4.5 Hz, 2H, $-C\underline{H}_2-CH=CH_2$), 4.18 (s, $C^3-C\underline{H}_2-$).[21] *Anal.* Calcd for $C_{14}H_{13}N_5OS$: C, 56.17; H, 4.38; N, 23.40. Found: C, 56.05; H, 4.39; N, 23.22.

Compound 4b——Yield, 0.28 g (29.9%) in method A, 8.74 g (93.2%) in method B, 5.1 g (81.5%) in method C, mp above 340 °C. MS *m/z*: 273 (M^+). IR ν_{max}: 3120, 3060, 3010, 1680, 1640, 1610, 1270, 1260 cm^{-1}. NMR: 13.78 (s), 13.47 (s), 12.40 (s), and 11.43 (s) (2H, N^1– and N^4–H),[21] 10.00 (s, 1H, $N^{2'}$–H), 7.77—6.77 (m, 4H, aromatic), 5.93 (s, C^3=C<u>H</u>–),[21] 4.27 (s, $C^3-C\underline{H}_2-$),[21] 3.53 (s) and 3.50 (s) (3H, $N^{4'}$–Me).[21] *Anal.* Calcd for $C_{12}H_{11}N_5OS$: C, 52.73; H, 4.06; N, 25.63. Found: C, 52.90; H, 4.10; N, 25.75.

3-(4-Allyl-3-methylthio-4*H*-1,2,4-triazol-5-yl)methylene-2-oxo-1,2,3,4-tetrahydroquinoxaline (5)——A solution of **4a** (4.22 g, 16.7 mmol), MeI (2.61 g, 18.4 mmol), and DBU (2.80 g, 18.4 mmol) in EtOH (250 ml) was refluxed on a boiling water bath for 3 h. Removal of the solvent by evaporation gave yellow crystals **5** (3.37 g, 76.2%). Recrystallization from EtOH afforded yellow needles, mp 213—214 °C. MS *m/z*: 313 (M^+). IR ν_{max}: 1675, 1635, 1615 cm^{-1}. NMR: 11.33 (s, 1H, N^1–H), 11.13 (s, 1H, N^4–H), 7.23—6.73 (m, 4H, aromatic), 5.97 (s, C^3=C<u>H</u>–),[21] 5.92 (m, 1H, $-CH_2-C\underline{H}=CH_2$), 5.30—4.53 (m, 4H, $-C\underline{H}_2-CH=C\underline{H}_2$), 4.23 (s, $C^3-C\underline{H}_2-$),[21] 2.63 (s) and 2.58 (s) (3H, SMe).[21] *Anal.* Calcd for $C_{15}H_{15}N_5OS$: C, 57.49; H, 4.82; N, 22.35. Found: C, 57.49; H, 4.74; N, 22.18.

3-(4-Allyl-3,4-dihydro-2-methyl-3-thioxo-2*H*-1,2,4-triazol-5-yl)methylene-2-oxo-1,2,3,4-tetrahydroquinoxaline (6)——A solution of **5** (2 g, 6.39 mmol) and MeI (1.36 g, 9.60 mmol) in DMF (50 ml) was refluxed in an oil bath for 1 h. Removal of the solvent by evaporation provided yellow needles **6** (0.91 g, 45.5%). Trituration with hot EtOH gave analytically pure yellow needles, mp 285—287 °C. MS *m/z*: 313 (M^+). IR ν_{max}: 1680, 1640, 1610, 1270, 1255 cm^{-1}. NMR: 12.37 (s), 11.40 (s), and 10.08 (s), (2H, N^1– and N^4–H),[21] 7.60—6.70 (m, 4H, aromatic), 5.90 (m, 1H, $-CH_2C\underline{H}=CH_2$), 5.87 (s, C^3=C<u>H</u>–),[21] 5.27—4.57 (m, 4H, $-C\underline{H}_2-CH=C\underline{H}_2$), 4.18 (s, $C^3-C\underline{H}_2-$),[21] 3.79 (s) and 3.76 (s) (3H, $N^{2'}$–Me).[21] *Anal.* Calcd for $C_{15}H_{15}N_5OS$: C, 57.49; H, 4.82; N, 22.35. Found: C, 57.29; H, 4.62; N, 22.64.

3-[1-(4-Allyl-3-methylsulfinyl-4*H*-1,2,4-triazol-5-yl)-1-hydroxy]methylene-2-oxo-1,2,3,4-tetrahydroquinoxaline (7)——A solution of **5** (5 g, 16.0 mmol) and MCPBA (6.90 g, 2 eq) in EtOH (200 ml) was refluxed on a boiling water bath for 5 h. The solution was filtered while hot, and yellow needles precipitated. They were collected by filtration (0.94 g, 18%). Recrystallization from EtOH provided analytically pure yellow needles, mp 229—231 °C. MS *m/z*: 345 (M^+). IR ν_{max}: 3220, 1650, 1610 cm^{-1}. NMR: 12.03 (s, 1H, N^1–H), 11.22 (s, 1H, N^4–H), 9.85 (s, 1H, OH), 7.30—6.53 (m, 4H, aromatic), 6.00 (m, 1H, $-CH_2-C\underline{H}=CH_2$), 5.40—4.92 (m, 4H, $-C\underline{H}_2-CH=C\underline{H}_2$), 3.20 (s, 3H, SMe). *Anal.* Calcd for $C_{15}H_{15}N_5O_3S$: C, 52.16; H, 4.38; N, 20.28. Found: C, 52.32; H, 4.41; N, 20.28.

3-[1-Hydroxyimino-1-(4-methyl-4*H*-1,2,4-triazol-3-yl)]methylene-2-oxo-1,2-dihydroquinoxaline (8)——A solution of $NaNO_2$ (6.32 g, 91.6 mmol) in H_2O (60 ml) was added dropwise to a suspension of **4b** (5 g, 18.3 mmol) in H_2O (40 ml) and AcOH (200 ml) with stirring in an ice-water bath. The suspension was heated on a boiling water bath for 2 h. Removal of the solvent by evaporation provided colorless needles (3.89 g, 78.6%). Trituration with hot AcOH afforded analytically pure colorless needles, mp 295—297 °C. MS *m/z*: 270 (M^+). IR ν_{max}: 3140, 1690, 1610 cm^{-1}. NMR: 12.53 (s) and 12.18 (s) (2H, N^1–H and OH), 8.57 (s, 1H, $C^{3'}$–H), 7.90—7.20 (m, 4H, aromatic), 3.87 (s, 3H, Me). *Anal.* Calcd for $C_{12}H_{10}N_6O_2$: C, 53.33; H, 3.73; N, 31.10. Found: C, 53.13; H, 3.66; N, 31.00.

3-(4-Methyl-4*H*-1,2,4-triazol-3-yl)isoxazolo[4,5-*b*]quinoxaline (9)——A solution of **8** (5 g) in polyphosphoric acid [H_3PO_4 (20 ml) and P_2O_5 (10 g)] was heated in an oil bath at 100—110 °C (bath temperature) with stirring for 4 h. The solution was cooled in an ice-water bath and then poured onto crushed ice. Yellow crystals precipitated, and were collected by suction filtration (1.86 g, 39.8%). Recrystallization from EtOH gave yellow needles, mp 303—305 °C. MS *m/z*: 252 (M^+). IR ν_{max}: 1590, 1555, 1515, 1500 cm^{-1}. NMR (CF_3COOH): 9.91 (s, 1H, $C^{3'}$–H), 8.70—8.00 (m, 4H, aromatic), 4.62 (s, 3H, Me). *Anal.* Calcd for $C_{12}H_8N_6O$: C, 57.14; H, 3.20; N, 33.32. Found: C, 57.33; H, 3.07; 33.34.

3-(4-Allyl-3-benzoylthio-4*H*-1,2,4-triazol-5-yl)methylene-2-oxo-1,2,3,4-tetrahydroquinoxaline (10a) and 3-(3-Benzoylthio-4-methyl-4*H*-1,2,4-triazol-5-yl)methylene-2-oxo-1,2,3,4-tetrahydroquinoxaline (10b)——From the Thiosemicarbazides **3a** and **3b** (Method A): A suspension of the appropriate thiosemicarbazide (5 g) in benzoyl chloride (20 ml) and dioxane (100 ml) was refluxed in an oil bath for 4 h to give a clear solution. Removal of the solvent and excess benzoyl chloride by evaporation left an oily mixture, which was triturated with EtOH–H_2O (2 : 1, v/v) (300 ml) on a boiling water bath to precipitate yellow crystals **10a** or **10b**. The yellow crystals **10a** or **10b** were

immediately collected by suction filtration. Further trituration with hot EtOH afforded an analytically pure yellow powder, **10a** or **10b**.

One-Pot Synthesis from the Hydrazide **2** (Method B): A suspension of **2** (10 g, 45.9 mmol) and the appropriate isothiocyanate (equimolar amount) in dioxane (200 ml) was refluxed in an oil bath for 1 h to precipitate colorless crystals, **3a** and **3b**. Benzoyl chloride (40 ml) was added to this suspension, and refluxing was continued for an additional 8 h or 14 h in the case of **3a** or **3b**, respectively. Removal of the solvent and excess benzoyl chloride gave an oily mixture, which was triturated with EtOH–H_2O (2:1, v/v) (600 ml) on a boiling water bath to precipitate the product, **10a** or **10b**. The subsequent procedure is similar to that described in method A.

Compound 10a——Yield, 2.04 g (32.1%) in method A, 5.72 g (30.9%) in method B, mp 213—215 °C. MS *m/z*: 403 (M^+). IR ν_{max}: 1680, 1645, 1625, 1610 cm^{-1}. NMR: 12.43 (s), 11.36 (s), and 11.22 (s) (2H, N^1– and N^4–H),[21] 8.00—6.77 (m, 9H, aromatic), 6.42 (s, C^3=C<u>H</u>–),[21] 5.93 (m, 1H, $-CH_2-C\underline{H}=CH_2$), 5.18—4.87 (m, 2H, $-CH_2-CH=C\underline{H}_2$), 4.70 (m, $-C\underline{H}_2-CH=CH_2$), 4.56 (s, $C^3-C\underline{H}_2-$).[21] *Anal.* Calcd for $C_{21}H_{17}N_5O_2S$: C, 62.52; H, 4.25; N, 17.36. Found: C, 62.70; H, 4.25; N, 17.10.

Compound 10b——Yield, 2.10 g (32.1%) in method A, 6.93 g (40.1%) in method B, mp 301—303 °C. MS *m/z*: 377 (M^+). IR ν_{max}: 1680, 1655, 1635, 1610 cm^{-1}. NMR: 12.43 (s), 11.40 (s), and 11.32 (s) (2H, N^1– and N^4–H),[21] 8.00—6.80 (m, 9H, aromatic), 6.42 (s, C^3=C<u>H</u>–),[21] 4.56 (s, $C^3-C\underline{H}_2-$),[21] 3.60 (s) and 3.56 (s) (3H, NMe).[21] *Anal.* Calcd for $C_{19}H_{15}N_5O_2S$: C, 60.47; H, 4.01; N, 18.56. Found: C, 60.31; H, 3.90; N, 18.41.

3-(2-Benzoyl-3,4-dihydro-4-methyl-3-thioxo-2*H*-1,2,4-triazol-5-yl)methylene-2-oxo-1,2,3,4-tetrahydroquinoxaline (11)——A solution of **4b** (2 g, 7.3 mmol) and benzoyl chloride (1.23 g, 8.76 mmol) in pyridine (10 ml) and dioxane (40 ml) was refluxed in an oil bath for 6 h to yield a clear solution. The solution was filtered while hot. An analytically pure sample precipitated as yellow needles (mp 271—273 °C), which were collected by filtration (1.2 g, 43.5%). MS *m/z*: 377 (M^+). IR ν_{max}: 1720, 1680, 1640, 1620, 1600 cm^{-1}. NMR: 12.43 (s), 11.55 (s), and 9.93 (s) (N^1– and N^4–H),[21] 8.00—6.70 (m, 9H, aromatic), 5.93 (s, C^3=C<u>H</u>–),[21] 4.35 (s, $C^3-C\underline{H}_2-$),[21] 3.53 (s) and 3.49 (s) (3H, NMe).[21] *Anal.* Calcd for $C_{19}H_{15}N_5O_2S$: C, 60.47; H, 4.01; N, 18.56. Found: C, 60.24; H, 3.97; N, 18.63.

References and Notes

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