A Facile Synthesis of Enol Type Acyl Cyanides *via* a 1,3-Dipolar Cycloaddition Reaction and a Cyano Group Migration

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The reaction of 7-chlorotetrazolo[1,5-*a*]quinoxaline 5-oxide **4a** or 7-chloro-1,2,4-triazolo[4,3-*a*]quinoxaline 5-oxide **4b** with 2-chloroacrylonitrile gave 7-chloro-4-(2-cyano-2-hydroxyvinyl)tetrazolo[1,5-*a*]quinoxaline **5a** or 7-chloro-4-(2-cyano-2-hydroxyvinyl)-1,2,4-triazolo[4,3-*a*]quinoxaline **5b**, respectively. Alcoholysis of compound **5a** or **5b** afforded 7-chloro-4-ethoxycarbonylmethylene-4,5-dihydrotetrazolo[1,5-*a*]quinoxaline **6a** or 7-chloro-4-ethoxycarbonylmethylene-4,5-dihydro-1,2,4-triazolo[4,3-*a*]quinoxaline **6b**, respectively. Compounds **5a,b** were found to exist as a *syn* and *anti* mixture of the enol form, while compounds **6a,b** occurred as the enamine and methylene imine forms. The tautomeric character and/or D-H exchange of the vinyl protons are described for compounds **5a,b** and **6a,b**.

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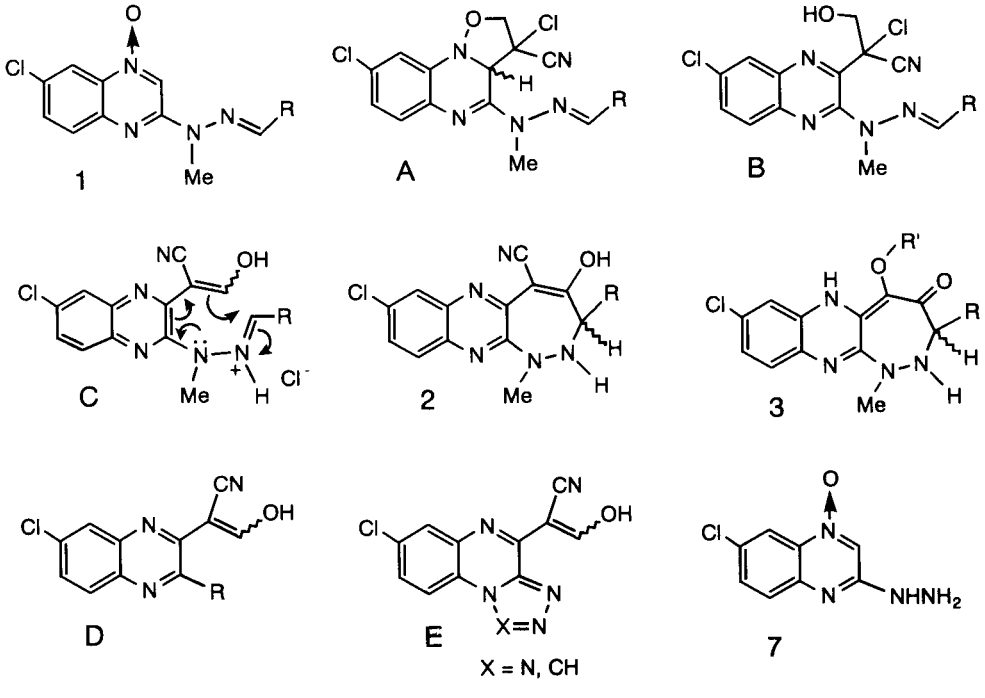
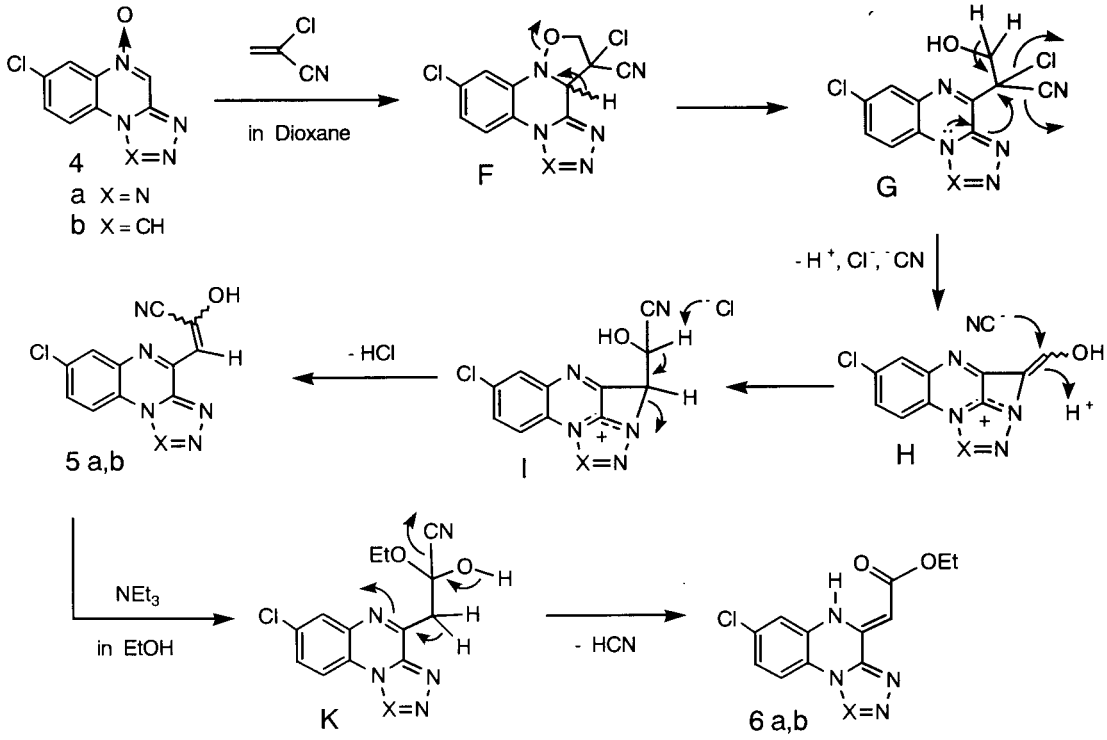
In previous papers [1,2], we reported that the 1,3-dipolar cycloaddition reaction of the quinoxaline 4-oxides **1** with 2-chloroacrylonitrile gave the 1,2-diazepino[3,4-*b*]quinoxalines **2** presumably *via* intermediates **A**, **B** and **C**, wherein an intermediate **C** was not isolable (Chart 1) [1-4]. Moreover, the alcoholysis of compounds **2** provided the 5-alkoxy-1,2-diazepino[3,4-*b*]quinoxalines **3**. If there is not a hydrazone function in compound **1** or an intermediate **C**, the C_3-enolnitrile moiety would be preserved, providing a species **D**. Since the enolnitrile moiety was expected to be converted into various functional groups [1-5], we planned the preparation of some enolnitrile compounds in the pre-

Chart 1



Scheme 1



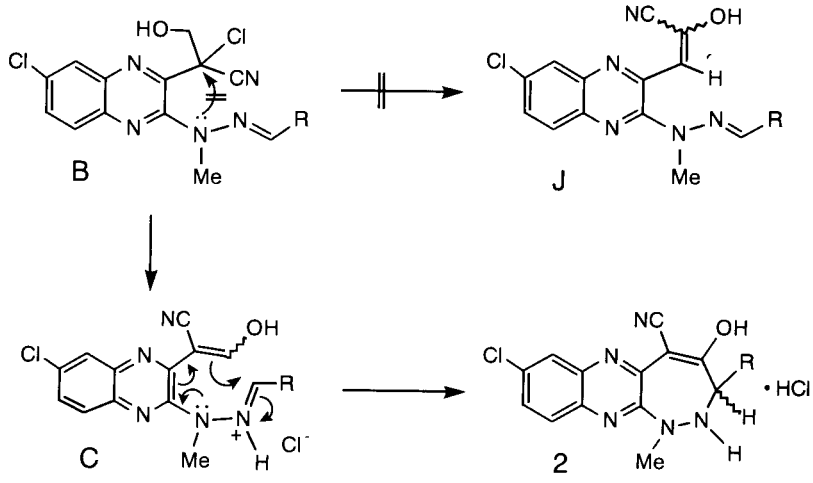
sent investigation. Accordingly, we chose quinoxaline *N*-oxides **4a** and **4b** (Scheme 1) as starting materials in place of compound **1** and tried the 1,3-dipolar cycloaddition reaction of the quinoxaline *N*-oxides **4a,b** with 2-chloroacrylonitrile in order to obtain the enolnitrile compounds **E**. However, this reaction was found to result in the cyano group migration affording the enol type acyl cyanides **5a,b**, but not the enolnitrile **E**. Furthermore, compounds **5a,b** also underwent alcoholysis to change into compounds **6a,b**, which showed interesting behavior in a solution. This paper describes the synthesis of the enol type acyl cyanides **5a,b** *via* a 1,3-dipolar cycloaddition reaction accompanied with a cyano group migration and the transformation of compounds **5a,b** into compounds **6a,b** together with the isomeric structure of compounds **5a,b** and **6a,b**.

The reaction of 2-hydrazinoquinoxaline 4-oxide **7** (Chart 1) with nitrous acid gave 7-chlorotetrazolo[1,5-*a*]-quinoxaline 5-oxide **4a**, while the synthesis of 7-chloro-1,2,4-triazolo[4,3-*a*]quinoxaline 5-oxide **4b** was reported in a previous paper [6]. The reaction of compound **4a** or **4b** with 2-chloroacrylonitrile afforded 7-chloro-4-(2-cyano-2-hydroxyvinyl)tetrazolo[1,5-*a*]quinoxaline **5a** or 7-chloro-4-(2-cyano-2-hydroxyvinyl)-1,2,4-triazolo[4,3-*a*]quinoxaline **5b**, respectively, presumably *via* intermediates **F-I**. The nucleophilic attack of the azole ring nitrogen atom to the C_4-side chain carbon would initiate the cyano group migration in an intermediate **G**. The subsequent production of a cyanohydrin intermediate **I** *via* an intermediate **H** followed by deprotonation of an intermediate **I** led to the formation of compounds **5a,b**. In contrast, intermediate **B** has no nucleophilic nitrogen atom in the C_2-side chain, and hence species **J** is not produced, but compounds **2** were formed *via* an intermediate **C**, as shown in Scheme 2. The nucleophilicity of the $N_{1'}$ atom in an intermediate **B** would be reduced by the electron withdrawing C_6-chlorine atom [7], while the $N_{2'}$ atom trapped hydrogen chloride. Thus, the above nitrile group migration seems to depend on whether the nucleophilic tertiary nitrogen atom is present or not in a proximal position to the 1-chloro-1-cyano-2-hydroxyethyl group.

Refluxing of compound **5a** or **5b** in triethylamine/ethanol resulted in alcoholysis to furnish 7-chloro-4-ethoxycarbonylmethylene-4,5-dihydrotetrazolo[1,5-*a*]quinoxaline **6a** or 7-chloro-4-ethoxycarbonylmethylene-4,5-dihydro-1,2,4-triazolo[4,3-*a*]quinoxaline **6b**, respectively, presumably *via* an intermediate **K**.

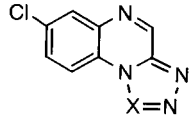
The structural assignment of new compounds **4a**, **5a,b** and **6a,b** was based on the analytical and spectral data. In order to ascertain the chemical shifts of the C_{3a} and C_4 carbon signals in compounds **5a,b**, all the carbon signals of known compounds **8a,b** (Chart 2) [8] were assigned from the ^{13}C-^1H COSY, long range ^{13}C-^1H COSY and LSPD spectral data (Table 1), indicating that the C_{3a} and C_4 carbon signals of compounds **8a,b** were observed at a lower magnetic field than δ 140 ppm. The C_{3a} carbon signal of

Scheme 2



compound **5a** was observed at δ 143.50 ppm, showing the ^3J coupling with the vinyl ($C_{1'}$-H) proton (Table 2). Moreover,

Chart 2



8a X = N
8b X = CH

Table 1

NMR Spectral Data for Compounds **8a,b**

Carbon	Chemical Shift [a] Compound **8a**	Compound **8b**
C_1	-----	137.22
C_{3a}	141.88	142.99
C_4	141.83	144.93
C_{5a}	135.41	136.17
C_6	127.85	129.01
C_7	138.45	131.71
C_8	134.07	130.01
C_9	117.63	118.69
C_{9a}	123.60	123.97

[a] Shown in δ ppm, and assigned from the ^{13}C-^1H COSY, long range ^{13}C–^1H COSY and LSPD spectral data.

the C_{3a} carbon signal of compound **5b** was observed at δ 141.66 ppm, exhibiting the ^3J coupling with the vinyl and C_1-H protons. These ^3J coupling data definitely excluded the structure **E**. The C_4 and $C_{2'}$ carbon signal and the ^2J coupling data are also shown in Table 2. The selective ^{13}C-{^1H} NOE spectral data of compound **5a** (Chart 3) represented the enhancements of $C_{2'}$, C_4 and C_{3a} carbon signals by radiation of the vinyl proton signal [9]. The NOE of the ^2J carbon signal is twice the intensity of that of

Table 2

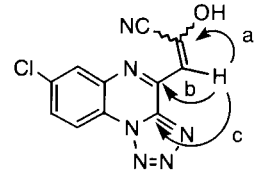
NMR Spectral Data for Compounds **5a,b**

Carbon	Chemical Shift (δ) [Coupling Constant (Hz)] Compound **5a**	Compound **5b**
C_1	-----	139.64 [$^1J(C_1$-C_1-H) = 213.5]
C_{3a}	143.50 [$^3J(C_{3a}$-$C_{1'}$-H) = 4.5]	141.66 [$^3J(C_{3a}$-$C_{1'}$-H) = 4.5] [$^3J(C_{3a}$-C_1-H) = 4.0]
C_4	141.50 [$^2J(C_4$-$C_{1'}$-H) = 2.0]	143.14 [a]
$C_{1'}$	94.34 [$^1J(C_{1'}$-$C_{1'}$-H) = 168.0]	92.54 [$^1J(C_{1'}$-$C_{1'}$-H) = 168.5]
$C_{2'}$	160.70 [$^2J(C_{2'}$-$C_{1'}$-H) = 2.1]	160.08 [$^2J(C_{2'}$-$C_{1'}$-H) = 2.5]

[a] Observed as a singlet.

the ^3J carbon signal, also excluding the structure **E**. On the other hand, the one dimensional NOE difference spectral data of compounds **5a,b** (Chart 4) indicated that compounds **5a,b** are a *syn* and *anti* mixture of the enol type acyl cyanide. This enol structure is similar to that of the 2-(α-cyano-β-keto)pyridine derivatives **9** (Chart 5) reported by Gutsche and Voges [10].

Chart 3



	NOE
a H - $C_{2'}$	25.7%
b H - C_4	23.1%
c H - C_{3a}	12.5%

C-H NOE Data for Compound 5a

Compounds **6a,b** were found to exist as the enamine **A** and methylene imine **B** forms (Schemes 3 and 4) in a dimethyl sulfoxide or trifluoroacetic acid solution from the

Table 3

^{1}H-NMR Spectral Data (δ) for Compounds **6a,b**

Compound	Solvent	Tautomer Ratio A	Tautomer Ratio B	Tautomer A Vinyl	Tautomer A Methylene	Tautomer A C_1-H	Tautomer A C_6-H	Tautomer A C_8-H	Tautomer A C_9-H	Tautomer A OCH_2	Tautomer A CH_3	Tautomer B C_1-H	Tautomer B C_6-H	Tautomer B C_8-H	Tautomer B C_9-H	Tautomer B OCH_2	Tautomer B CH_3
6a	DMSO-d_6	10	1	5.73	4.47	---	8.03	7.29	8.06	4.20	1.27	---	8.36	[a]	8.61	4.18	1.21
	DMSO-d_6/TFA (1:4)	2	1	5.58	4.27	---	7.07	6.82	7.61	3.89	0.97	---	7.92	7.57	8.19	3.89	0.89
	TFA-d_1	1	1	[b]	[b]	---	7.27	7.03	7.85	4.11	1.15	---	8.13	7.75	8.40	4.08	1.06
6b	DMSO-d_6	8	1	5.75	4.33	9.78	7.92	7.27	8.05	4.19	1.27	10.14	8.14	7.91	8.47	4.15	1.19
	DMSO-d_6/TFA (1:4)	4	1	5.71	4.20	9.87	7.20	6.89	7.56	3.94	0.99	10.09	7.92	7.56	8.04	3.94	0.99
	TFA-d_1	2	1	[b]	[b]	9.97	7.22	6.95	7.54	4.01	1.07	10.29	8.10	7.63	8.60	4.06	1.01

[a] Overlapped with other signal. [b] Deuterized.

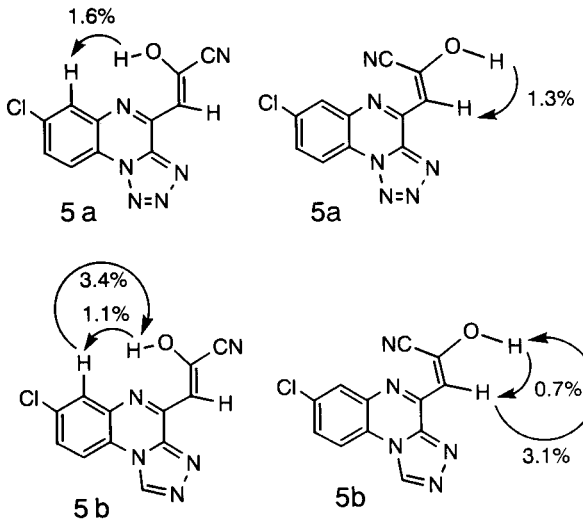
Table 4

^{13}C-NMR Spectral Data (δ) for Compounds **6a,b**

Compound	Solvent	Tautomer A C_1	Tautomer A C_{3a}	Tautomer A C_4	Tautomer A Vinyl	Tautomer A C=O	Tautomer A OCH_2	Tautomer A CH_3	Tautomer B C_{3a}	Tautomer B C_4	Tautomer B Methylene	Tautomer B C=O	Tautomer B OCH_2	Tautomer B CH_3
6a	DMSO-d_6	---	144.91 [a]	137.09 [b]	85.24 [c]	167.87 [d]	59.71	14.36	149.02	---	40.08	167.96	61.25	14.05
	DMSO-d_6/TFA (1:4)	---	147.90	140.81	90.82	174.63	65.70	16.39	151.37	140.09	43.77	174.42	67.37	16.39
	TFA-d_1	---	144.15	138.00	87.00	171.38	62.17	12.09	147.24	142.04	39.00	170.96	64.18	11.90
6b	DMSO-d_6	139.18 [e]	142.66 [f]	138.51 [g]	82.19 [h]	168.55 [i]	59.38	14.44	---	---	---	---	61.02	14.06
	DMSO-d_6/TFA (1:4)	140.87	147.04	138.85	91.02	173.04	65.26	16.32	---	---	43.55	---	66.80	16.32
	TFA-d_1	138.66	143.43	136.47	---	171.04	62.18	11.90	146.91	138.27	---	170.80	64.06	11.78

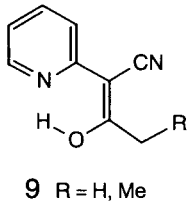
[a] $^3J(C_{3a}\text{-}C_{1'}\text{-}H) = 5.5$ Hz, $^3J(C_{3a}\text{-}N_5\text{-}H) = 3.5$ Hz. [b] $^2J(C_4\text{-}C_{1'}\text{-}H) = 1.5$ Hz. [c] $^1J(C_{1'}\text{-}C_{1'}\text{-}H) = 167.5$ Hz. [d] $^2J(C_{2'}\text{-}CH_2) = 3.5$ Hz. [e] $^1J(C_1\text{-}C_1\text{-}H) = 207.0$ Hz. [f] $^3J(C_{3a}\text{-}C_1\text{-}H) = 4.2$ Hz, $^3J(C_{3a}\text{-}C_{1'}\text{-}H) = 4.5$ Hz, $^3J(C_{3a}\text{-}N_5\text{-}H) = 1.0$ Hz. [g] $^2J(C_4\text{-}C_{1'}\text{-}H) = 1.5$ Hz, [h] $^1J(C_{1'}\text{-}C_{1'}\text{-}H) = 168.0$ Hz. [i] $^3J(C_{2'}\text{-}CH_2) = 3.5$ Hz.

Chart 4

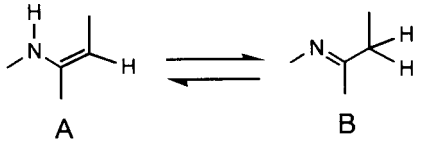


NOE Spectral Data (%) for Compounds 5a,b

Chart 5



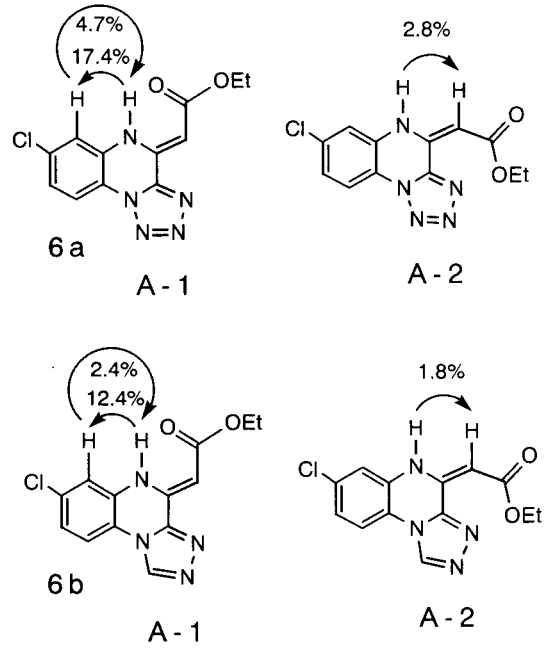
Scheme 3



Enamine Form Methylene Imine Form

^{1}H-nmr spectral data (Table 3) [11], which further showed that the enamine species **A** was predominant. The ^{13}C-nmr and LSPD spectral data of compounds **6a,b** also supported their tautomeric equilibria (Table 4). Especially, the vinyl and methylene carbon signals were observed at δ 91-85 and 44-39 ppm, respectively. The one dimensional NOE difference spectral data of compounds **6a,b** (Chart 6) showed the enhancements of the C_6-H and vinyl proton signals by radiation of the N_5-H proton signal, proving that the enamine form **A** of compounds **6a,b** occurred as two geometrical isomers **A-1** and **A-2** in a dimethyl sulfoxide solution.

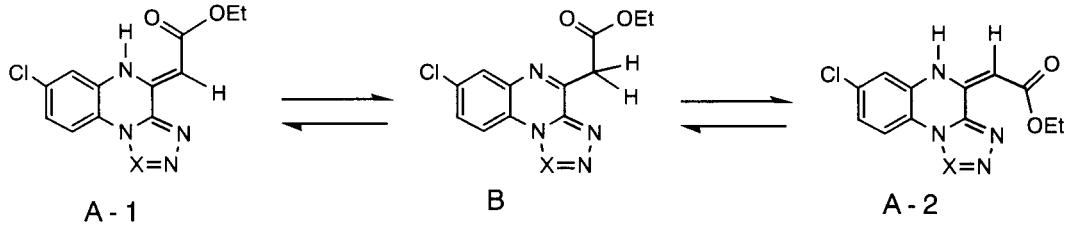
Chart 6



NOE Spectral Data (%) for Compounds 6a,b

The D-H exchange was observed for the OH and vinyl protons of compounds **5a,b** in a deuteriodimethyl sulfoxide/deuterium oxide solution (Chart 7), and for the NH, vinyl and methylene protons of compounds **6a,b** in a deuteriodimethyl sulfoxide/deuterium oxide solution (Scheme 5). On the other hand, the D-H exchange was not observed for the vinyl and methylene protons of known compounds **10** and **11** [11-13] (Scheme 6) in a deuteriodimethyl sulfoxide/deuterium oxide solution. These results suggested that the equilibration rates between the enamine **A** and

Scheme 4

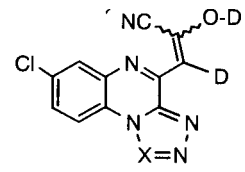


Tautomeric Equilibria of Compounds 6a,b

methylene imine **B** forms were faster in compounds **6a,b** than in compounds **10,11**.

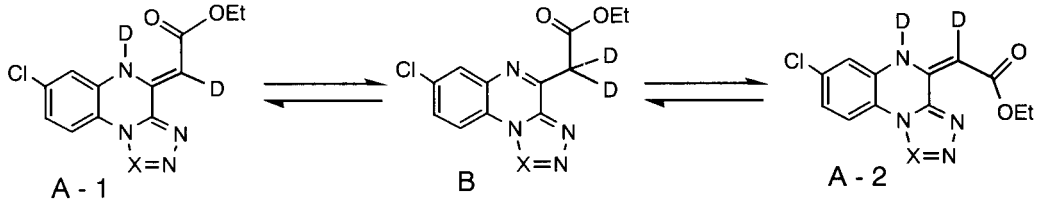
The study on the transformation of compounds **5a,b** into various heterocyclic compounds is now in progress in our laboratory.

Chart 7



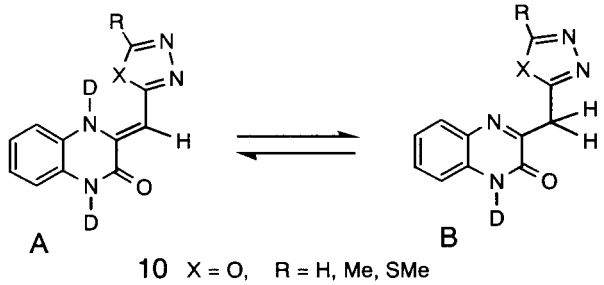
Deuterized Species of Compounds 5a,b in DMSO-d_6/D_2O

Scheme 5



Tautomeric Equilibria of Compounds 6a,b in DMSO-d_6 / D_2O

Scheme 6



10 X = O, R = H, Me, SMe
11 X = N - R', R = SMe

Tautomeric Equilibria of Compounds 10 and 11 in DMSO-d_6 / D_2O

EXPERIMENTAL

All melting points were determined on a Yazawa micro melting point BY-2 apparatus and are uncorrected. The ir spectra (potassium bromide) were recorded with a JASCO IRA-1 spectrophotometer. The nmr spectra were measured with a VXR-300 spectrometer at 300 MHz. Chemical shifts are given in the δ scale. The mass spectra (ms) were determined with a JEOL JMS-01S spectrometer. Elemental analyses were performed on a Perkin-Elmer 240B instrument.

7-Chlorotetrazolo[1,5-*a*]quinoxaline 5-Oxide **4a**.

A solution of sodium nitrite (7.21 g, 104.5 mmoles) in water (100 ml) was added dropwise to a suspension of compound **7** (20 g, 95.0 mmoles) in acetic acid (100 ml)/water (200 ml) with stirring in an ice-water bath for 30 minutes. Then, the mixture was heated with stirring on a boiling water bath for 30 minutes to precipitate colorless needles **4a**, which were collected by suction filtration (20.34 g, 97%). Recrystallization from dioxane gave colorless needles, mp 226-227°; ir: ν cm^{-1} 3080, 3040, 1610, 1600, 1540, 1505; ms: m/z 221 (M^+), 223 ($M^+ + 2$); pmr (deuteriodimethyl sulfoxide): 9.70 (s, 1H, C_4-H), 8.67 (d, J = 8.9 Hz, 1H, C_9-H), 8.55 (d, J = 2.1 Hz, 1H, C_6-H), 8.17 (dd, J = 8.9 Hz, J = 2.1 Hz, 1H, C_8-H).

Anal. Calcd. for $C_8H_4ClN_5O$: C, 43.36; H, 1.82; Cl, 16.00; N, 31.61. Found: C, 43.19; H, 1.73; Cl, 16.20; N, 31.46.

7-Chloro-4-(2-cyano-2-hydroxyvinyl)tetrazolo[1,5-*a*]quinoxaline **5a**.

A solution of compound **4a** (10 g, 45.2 mmoles) and 2-chloroacrylonitrile (5.93 g, 67.7 mmoles) in dioxane (300 ml) was refluxed in an oil bath for 1 hour. Evaporation of the solvent *in vacuo* gave yellow crystals **5a**, which were triturated with ethanol/*n*-hexane and then collected by suction filtration (11.49 g, 93%). Recrystallization from dioxane afforded yellow needles,

mp 205-206°; ir ν cm^{-1} 3060, 2220, 1615, 1560, 1525; ms: m/z 272 (M^+), 274 ($M^+ + 2$); pmr (deuteriodimethyl sulfoxide): 12.82 (brs, 1H, OH), 8.45 (d, J = 2.0 Hz, 1H, C_6-H), 8.33 (d, J = 8.5 Hz, 1H, C_9-H), 7.64 (dd, J = 2.0 Hz, J = 8.5 Hz, 1H, C_8-H), 6.61 (s, 1H, vinylic H).

Anal. Calcd. for $C_{11}H_5ClN_6O$: C, 48.46; H, 1.85; Cl, 13.00; N, 30.82. Found: C, 48.34; H, 1.82; Cl, 13.05; N, 30.92.

7-Chloro-4-(2-cyano-2-hydroxyvinyl)-1,2,4-triazolo[4,3-*a*]quinoxaline **5b**.

A solution of compound **4b** (10 g, 45.4 mmoles) and 2-chloroacrylonitrile (5.96 g, 68.1 mmoles) in dioxane (300 ml) was refluxed in an oil bath for 1 hour to precipitate yellow crystals **5b**. After the reaction mixture was cooled to room temperature, the yellow crystals were collected by suction filtration and then washed with ethanol (10.48 g). The filtrate was evaporated *in vacuo* to afford yellow crystals **5b**, which were triturated with ethanol and then collected by suction filtration (1.82 g), total yield, 10.48 g (85%). Recrystallization from *N,N*-dimethylformamide/ethanol provided yellow needles, mp 259-260°; ir: ν cm^{-1} 3110, 2220, 1615, 1570; ms: m/z 271 (M^+), 273 ($M^+ + 2$); pmr (deuteriodimethyl sulfoxide): 12.71 (brs, 1H, OH), 10.04 (s, 1H, C_1-H), 8.30 (d, J = 2.0 Hz, 1H, C_6-H), 8.26 (d, J = 8.5 Hz, 1H, C_9-H), 7.60 (dd, J = 2.0 Hz, J = 8.5 Hz, 1H, C_8-H), 6.52 (s, 1H, vinylic H).

Anal. Calcd. for $C_{12}H_6ClN_5O$: C, 53.05; H, 2.23; Cl, 13.05; N, 25.78. Found: C, 53.28; H, 2.45; Cl, 12.83; N, 25.65.

7-Chloro-4-ethoxycarbonylmethylene-4,5-dihydrotetrazolo[1,5-*a*]quinoxaline **6a**.

A solution of compound **5a** (3 g, 11.0 mmoles) in triethylamine (0.3 ml)/ethanol (50 ml)/dioxane (50 ml) was refluxed on a boiling water bath for 2 hours. Evaporation of the solvent *in vacuo* gave yellow crystals **5a**, which were triturated with ethanol/*n*-hexane and then collected by suction filtration (3.03 g, 94%). Recrystallization from dioxane/ethanol/*n*-hexane afforded yellow needles, mp 135-136°; ir: ν cm^{-1} 3080, 2990, 1650, 1630, 1610, 1585, 1520; ms: m/z 291 (M^+), 293 ($M^+ + 2$); pmr for the tautomer **A** (deuteriodimethyl sulfoxide): 11.16 (brs, 1H, NH), 8.06 (d, J = 8.5 Hz, 1H, C_9-H), 8.03 (d, J = 2.0 Hz, 1H, C_6-H), 7.29 (dd, J = 8.5 Hz, J = 2.0 Hz, 1H, C_8-H), 5.73 (s, 1H, vinylic H), 4.20 (q, J = 7.0 Hz, OCH_2), 1.27 (t, J = 7.0 Hz, CH_3).

Anal. Calcd. for $C_{12}H_{10}ClN_5O_2$: C, 49.41; H, 3.46; Cl, 12.15; N, 24.01. Found: C, 49.37; H, 3.39; Cl, 12.14; N, 24.30.

7-Chloro-4-ethoxycarbonylmethylene-4,5-dihydro-1,2,4-triazolo-[4,3-*a*]quinoxaline **6b**.

A solution of compound **5b** (3 g, 11.1 mmoles) in triethylamine (0.3 ml)/ethanol (30 ml)/*N,N*-dimethylformamide (70 ml) was heated on a boiling water bath for 3 hours. Subsequently, the solution was filtered, and ethanol (300 ml) was added to the filtrate to precipitate yellow needles **6b**, which were collected by suction filtration and then washed with ethanol/*n*-hexane to give an analytically pure sample (2.14 g). Evaporation of the filtrate *in vacuo* afforded yellow crystals, which were triturated with ethanol/*n*-hexane and then collected by suction filtration (0.58 g), total yield, 2.72 g (85%).

Compound **6b** had mp 236-237°; ir: ν cm^{-1} 3270, 3200, 3120, 3100, 2970, 2930, 2900, 1660, 1640, 1630; ms: m/z 290 (M^+), 292 ($M^+ + 2$); pmr for the tautomer **A** (deuteriodimethyl sulfoxide): 11.12 (s, 1H, NH), 9.87 (s, 1H, C_1-H), 8.05 (d, J = 8.5 Hz, 1H, C_9-H), 7.92 (d, J = 2.1 Hz, 1H, C_6-H), 7.27 (dd, J = 8.5 Hz, J = 2.1 Hz, 1H, C_8-H), 5.75 (s, 1H, vinylic H), 4.19 (q, J = 7.0 Hz, OCH_2), 1.27 (t, 7.0 Hz, CH_3).

Anal. Calcd. for $C_{13}H_{11}ClN_4O_2$: C, 53.71; H, 3.81; Cl, 12.19; N, 19.27. Found: C, 53.85; H, 3.63; Cl, 12.28; N, 19.38.

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