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TETRAHEDRON

SYNTHESIS OF NEW 5-ALKYLIDENE-4-CHLORO-5*H*-1,2,3-DITHIAZOLES AND THEIR STEREOCHEMISTRY

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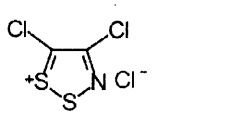
Abstract: A variety of 5-alkylidene-4-chloro-5*H*-1,2,3-dithiazoles (**9-25**) have been prepared from 4-chloro-5*H*-1,2,3-dithiazolium chloride, active methylene compounds, and pyridine. The reactions with ethyl nitroacetate ((*Z*) > (*E*)), ethyl 3-nitrobenzoylacetate ((*E*) > (*Z*)), ethyl 2-fluorobenzoylacetate ((*E*) > (*Z*)), and tetronic acid ((*Z*) > (*E*)) gave a mixture of (*E*)- and (*Z*)-isomers, whereas those of benzoylnitromethane (*Z*), 5,6-dihydro-4-hydroxy-6-methyl-2*H*-pyran-2-one (*E*), 4-hydroxy-6-methyl-2-pyrone (*E*), 4-hydroxycoumarin (*E*), 6-chloro-4-hydroxycoumarin (*E*), and 6-bromo-4-hydroxycoumarin (*E*) afforded only single stereoisomers. The reactions with 4-hydroxy-1-methyl-2(1*H*)-quinolone, 2-hydroxy-1,4-naphthoquinone and homophthalic anhydride gave only single stereoisomers whose stereochemistry is uncertain. It appears that geometrically more rigid cyclic 1,3-dicarbonyl compounds give better yields of dithiazol-5-ylidenes than the corresponding acyclic compounds.

A great deal of work has been done on exploring the synthetic utility of 4,5-dichloro-5*H*-1,2,3-dithiazolium chloride (Appel's salt) (**1**)[1] since Appel and co-workers[2] reported the first synthesis of methyl (R = Me) (**2a**) and ethyl (R = Et) 2-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)cyanoacetate (**2b**) from **1** and the corresponding alkyl cyanoacetates. The stereochemistry around the carbon-carbon double bonds of **2a-2b** has been suggested to be *cis*, presumably due to the strong interaction between the carbonyl oxygen and electron-



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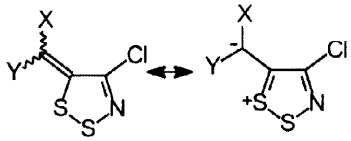

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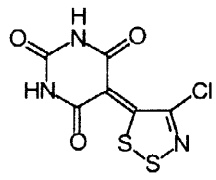
Compd.	X	Y	Yield (%)	Compd.	X	Y	Yield (%)
2a	CN	CO_2Me	68[2]	**2g**	Ph	Ph	83[3]
2b	CN	CO_2Et	76[2]	**2h**	CO_2Et	CO_2Et	37[3]
2c	CN	CN	40[4], 60[4], 72[7]	**2i**	H	CO_2Et	63[3]
2d	COPh	COPh	13[4]	**2j**	CN	COPh	78[5]
2e	CN	COMe	5[5], 62[5]	**2k**	CN	COBu^t	80[5]
2f	CN	Cl	8[5]				



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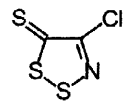

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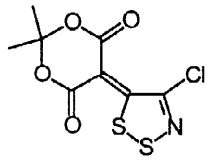

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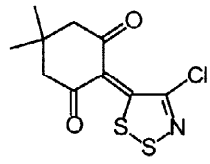

6

deficient S-1 atom.[3] Compounds **2c-e** were obtained from **1** and malononitrile, dibenzoylmethane, and 3-aminocrotononitrile, respectively under the same conditions as for **2a-b**. Compound **2f** was also isolated from

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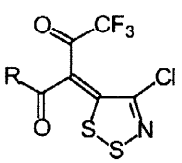
the reaction with the latter. Alternatively compound **2c** was obtained by treatment of **1**[4] or **3**[7] with tetracyanoethylene oxide in toluene at reflux in 60 % and 72 % yields, respectively. Recently Rees and co-workers successfully prepared compounds **2g-i** from 4-chloro-5*H*-1,2,3-dithiazole-5-thione (**4**) and diazo compounds such as diphenyldiazomethane, diethyl diazomalonate, and ethyl diazoacetate, respectively. The reactions of **1** with unsymmetrical nitriles such as enolate ion of 3-oxobutyronitrile, benzonitrile and pivaloylacetonitrile afforded **2h** (62%), **2i**, and **2j**, respectively. Symmetrical active methylene compounds such as barbituric acid, meldrum's acid, and dimedone reacted with **1** under the same conditions as for **2a-b** gave **3** (35%),[4] **5** (26%),[4] and **6** (27%)[4] respectively. Besides, active methylene compounds such as 2,4-pentanedione,[6] ethyl acetoacetate,[6] ethyl phenylacetate,[6] 1-(2-fluorophenyl)-1,3-butanedione,[6] phenylacetonitrile,[6] and diphenylmethane[3] gave essentially no corresponding dithiazol-5-ylidene derivatives. We have shown that the stereochemistry around the unsymmetrically substituted carbon-carbon double bond of dithiazol-5-ylidene derivatives **7** and **8** is governed by the steric and electronic repulsions between the chlorine atom at C-4 and the fluorine atoms of the CF_3 group,[8] which exerts a strong electron-withdrawing effect, in addition to the interaction between S-1 and the carbonyl oxygen by forming a five-membered cycle. Compounds **7b-c** are stereoisomers of **8a-b**, respectively. Their stereochemistry as well as that of **8c-d** was able to be clearly determined based on the ^{19}F NMR spectroscopic data and the relative intensities of ^{1}H and ^{13}C NMR absorptions of the isomers. It is envisaged that the spectroscopic (IR, ^{1}H and ^{13}C NMR) data of **7** and **8** would be



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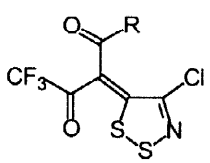
7a, R = CF_3
7b, R = Me
7c, R = EtO



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8a, R = Me
8b, R = EtO
8c, R = Ph
8d, R = 2-Naphthyl

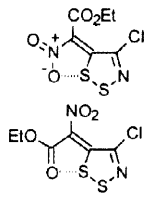
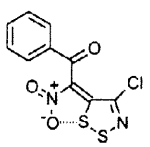
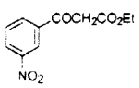
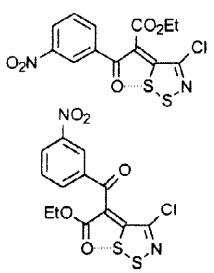
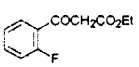
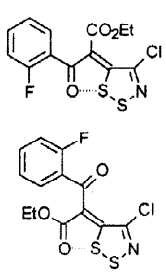
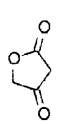
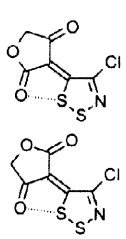
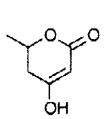
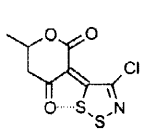
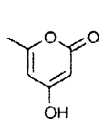
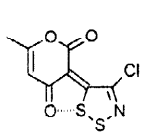
utilized for determining the stereochemistry of unsymmetrically substituted 5-alkyli-dene dithiazoles. To prove this premise we have prepared new symmetrical and unsymmetrical dithiazol-5-ylidenes using **1** and symmetrical and unsymmetrical active methylene compounds and determined the stereochemistry. The results are described herein.

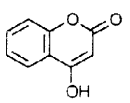
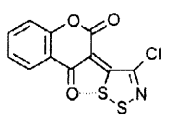
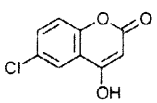
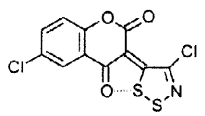
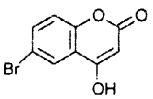
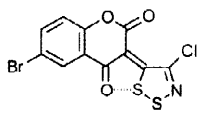
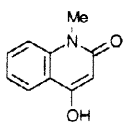
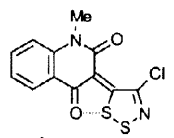
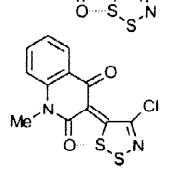
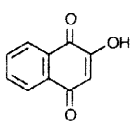
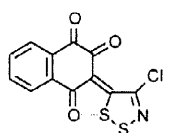
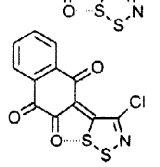
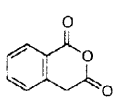
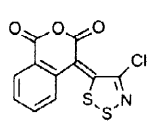
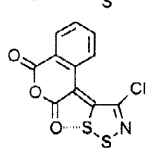
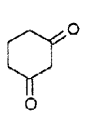
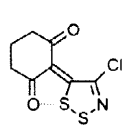
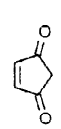
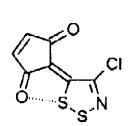
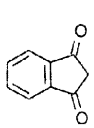
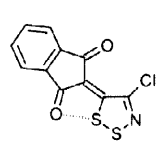
RESULTS AND DISCUSSION

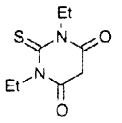
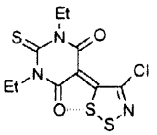
The reactions of **1** (2.50 mmol) with symmetrical and unsymmetrical active methylene compounds (2.50-2.55 mmol) in the presence of pyridine (5.07 mmol) in CH_2Cl_2 at room temperature gave the corresponding 5-alkylidene-5*H*-4-chloro-1,2,3-dithiazoles **9-25** and **4** in 5 to 87% yields and 1 to 19% yields, respectively. Yields of **9-25** and **4** and physical data of **9-25** are summarized in Table 1 and their analytical and spectroscopic data in Table 2.

Most of the dithiazol-5-ylidene derivatives prepared were orange to red solids having a decomposition temperature except for **9** (entry 1) and **24** (entry 16). The ^{13}C NMR spectra of **16-20** were unable to be recorded because of the solubility problem. Compound **4** was isolated in 1 to 19% yields except for the reactions

Table 1. Yields and Physical Data of Compounds **9-25**

Entry	CH_2XY	Yield (%)				mp	color
		4	Dithiazole			°C	
1[a]	$O_2NCH_2CO_2Et$	3	**9a** and **9b**		6 (**9a** : **9b** = 95 : 5)	73-74 (*n*-hexane)	orange
2[b]	O_2NCH_2COPh	1	**10a**		5	169-171 (dec.) (*n*-hexane / CH_2Cl_2)	orange
3		13	**11a** and **11b**		6 (**11a** : **11b** = 53 : 47)	154-158 (dec.) (*n*-hexane / CH_2Cl_2)	orange
4		13	**12a** and **12b**		23 (**12a** : **12b** = 72 : 28)	liq.	orange
5		19	**13a** and **13b**		28 (**13a** : **13b** = 67 : 33)	198-210 (dec.) (CH_2Cl_2)	orange
6		11	**14a**		25	155-160 (dec.) (CH_2Cl_2)	red
7		11	**15a**		57	173 (dec.) (CH_2Cl_2)	red

8		10	**16a**		87	232-235 (dec.) (THF)	orange
9		-	**17a**		39	245-246 (dec.) (THF)	red
10		-	**18a**		43	241-243 (dec.) (THF)	orange
11		10	**19a** or **19b**	 	52	192-194 (dec.) (CH_2Cl_2)	red
12		3	**20a** or **20b**	 	29	245-247 (dec.) (CH_2Cl_2)	red
13		11	**21a** or **21b**	 	47	198-200 (dec.) (CH_2Cl_2)	violet
14		24	**22**		13	131-133 (dec.) (*n*-hexane / CH_2Cl_2)	red
15		16	**23**		4	170 (dec.) (CH_2Cl_2)	orange
16		17	**24**		33	248-250 (CH_2Cl_2)	red

17		15	**25**		74	170-172 (dec.) (CH_2Cl_2)	brownish red

[a] From the reaction was isolated 4-chloro-1,2,3-dithiazol-5-one (21%). [b] From the reaction were isolated 4-chloro-1,2,3-dithiazol-5-one (18%) and an unknown.

of 6-chloro- (entry 9) and 6-bromo-4-hydroxy-2*H*-1-benzopyran-2-ones (entry 10). The mechanism for the formation of **4** has not been elucidated. It appeared that the amount of **4** produced depended markedly on the structures of the active methylene compounds. In fact, **4** was a major product when no dithiazol-5-ylidene derivatives were isolated as exemplified by the reactions of **1** with compounds such as ethyl acetoacetate (2 days, 39%), triethyl phosphonoacetate (30 h, 12%), (2-fluorophenyl)acetone (1 day, 11%), ethyl (methylthio)acetate (1 day, 12%), benzyl cyanide (1 day, 7%), ethyl phenylacetate (30 h, 20%), diethyl cyanomethylphosphonate (1 day, 11%), 2*H*-1,4-benzothiazin-3(4*H*)-one (6 days, 50%), acetoacetanilide (2 days, 12%) and bis(phenylsulfonyl)methane (1 day, 14%) under the same conditions. Most of the reactions (entries 3-17) were completed in 5 h except for the reactions with ethyl nitroacetate (entry 1, 20 h) and with benzoylnitromethane (entry 2, 40 h).

The stereochemistry around the carbon-carbon double bond of dithiazol-5-ylidene derivatives **9-18a** (entries 1-10) was determined based on the previously reported spectroscopic (IR, ^{1}H NMR, ^{13}C NMR) data of **7** and **8**[6] (*vide infra*). The IR data recorded in KBr shows that the carbonyl stretching absorptions of the trifluoroacetyl group possessed by **7a** and **8b-c**, which have the carbonyl groups syn to S-1 of 1,2,3-dithiazole moiety appeared at 1573 to 1586 cm^{-1}, whereas **7a** and **7b** having the carbonyl group anti to S-1 showed absorptions at 1718 to 1731 cm^{-1} (Figure 1). That is, the carbonyl group anti to S-1 needs more energy than that of syn analogs to be a vibrationally excited state. This is in good agreement with the data in the literature.[5] That is, 1,2,3-dithiazoles **2e** and **2j-k**, which were suggested to have a carbonyl group syn to S-1 of the dithiazole moiety exhibited a carbonyl absorption at 1620, 1600, and 1580 cm^{-1}, respectively. Although the IR spectra of **2e** and **2j-k** were recorded in CCl_4 and nujol respectively, the IR data are closer to the values of 1573 to 1586 cm^{-1} than to the values of 1718 to 1731 cm^{-1}. Consequently, of the two carbonyl absorption bands exhibited by **2h** (1662, 1737 cm^{-1}) and **2d** (1552, 1672 cm^{-1}) the former are assigned to the carbonyl group syn to S-1 and the latter assigned to that anti to S-1 of the dithiazoles, respectively. The ^{1}H NMR signals of the methyl groups of **7b** and **7c**, which are syn to S-1 of 1,2,3-dithiazole moiety appeared upfield compared with those having the opposite stereochemistry (cf. **8a** and **8b**, respectively). A similar propensity of the chemical shifts of the methylene protons was observed from **7c** and **8b**. The ^{13}C NMR spectrum of **8c** whose stereochemistry was clearly determined by *X*-ray crystallography exhibited absorptions corresponding to CF_3CO and C_6H_5CO carbonyl carbons at 173.3 and 191.1 ppm, respectively. Based on the absorption of **8c** at 173.3 ppm, the absorption at 172.4 ppm exhibited by **7a** can be assigned to the carbonyl carbon syn to S-1 and the other absorption that appeared downfield (182.2 ppm) can be assigned to the carbonyl carbon anti to S-1 of **7a**. Similarly the ^{13}C NMR absorptions at 171.9 and 186.2 ppm exhibited by a mixture of **7b** and **8a** were assigned to CF_3CO carbonyl carbons syn (**8a**) and anti (**7b**) to S-1, respectively. By the same token, the ^{13}C NMR absorptions at 172.8 and 183.7 pm exhibited by a mixture of **7c** and **8b** were assigned to CF_3CO carbonyl carbons syn (**8b**) and anti (**7c**) to S-1, respectively. The same propensity of the ^{13}C NMR chemical shifts was observed for the carbonyl carbons of the acetyl groups of **7b** and **8a**. That is, **7b** having an acetyl

Table 2. Spectroscopic and Analytical Data of **9-25**

Compound	IR cm^{-1}	^1H NMR (300 MHz) δ, ppm	^{13}C NMR (75 MHz) δ, ppm	MS (EI)[b] m/z	Elemental Analysis
9a and **9b**	(neat) 2968 m, 1722 s (C=O for **9a**), 1515 s, 1432 m, 1237 s, 1184, 1078, 1005, 946, 878, 800, 739, 674	($CDCl_3$) 1.43 (t, 3H, *J* = 7.2 Hz), 4.48 (q, 2H, *J* = 7.2 Hz) for **9a** and 1.35 (t, 3H, *J* = 7.2 Hz), 4.40 (q, 2H, *J* = 7.2 Hz) for **9b**	($CDCl_3$) 14.1, 64.2, 134.9, 141.7, 152.9, 159.9 for **9a**	268 (M^+, 100.0), 270 (M^+ + 2, 42.1), 233 (41.1), 205 (30.5), 179 (95.8), 165 (25.6), 118 (23.5), 86 (27.1), 64 (41.6)	Calcd for $C_6H_5ClN_2O_4S_2$: C, 26.82; H, 1.88; N, 10.43; S, 23.87. Found: C, 26.75; H, 1.93; N, 10.40; S, 23.90.
10a	(neat) 1676 m (C=O), 1596 w, 1515 s, 1451 w, 1417 w, 1314 w, 1272 m, 1226 s, 1199 s, 1175 w, 1125 w, 1099 w, 983 w, 849 w, 819 m, 788 w, 690 w, 670 w	($CDCl_3$) 7.50-7.59 (m, 2H), 7.63-7.72 (m, 1H), 7.91-7.97 (m, 2H)	($CDCl_3$) 110.0, 129.6, 129.7, 135.1, 136.9, 142.2, 153.9, 185.5	300 (M^+, 76.1), 302 (M^+ + 2, 44.6), 265 (42.8), 207 (71.1), 179 (81.2), 121 (27.2), 105 (100.0), 77 (89.5)	Calcd for $C_{10}H_5ClN_2O_3S_2$: C, 39.93; H, 1.68; N, 9.31; S, 22.32. Found: C, 39.90; H, 1.71; N, 9.35; S, 22.40.
11a and **11b**	(KBr) 1715 s, 1574 w, 1542 m, 1515 m, 1456 w, 1405 m, 1339 s, 1318 s, 1251 s, 1174 s, 1131, 1019	($CDCl_3$) 1.31 (t, 3H, *J* = 7.2 Hz), 4.32 (q, 2H, *J* = 7.2 Hz), 7.68 (t, 1H, *J* = 8.0 Hz), 8.04 (d, 1H, *J* = 8.0 Hz), 8.39 (d, 1H, *J* = 8.0 Hz), 8.57 (s, 1H) for **11a** and 1.10 (t, 3H, *J* = 7.2 Hz), 4.23 (q, 2H, *J* = 7.2 Hz), 7.74 (t, 1H, *J* = 8.0 Hz), 8.27 (d, 1H, *J* = 8.0 Hz), 8.44 (d, 1H, *J* = 8.0 Hz), 8.73 (s, 1H) for **11b**	($CDCl_3$) 14.1, 63.23, 117.2, 123.1, 126.3, 130.2, 134.3, 138.7, 145.3, 148.3, 157.9, 166.6 (OC=O), 183.3 (C=O) for **11a** and 14.4, 63.15, 121.6, 124.2, 128.2, 130.5, 134.9, 139.8, 143,0, 149.0, 156.1, 167.4 (OC=O), 190.3 (C=O) for **11b**	372 (M^+, 29.1), 374 (M^+ + 2, 12.5), 337 (100.0), 309 (40.6), 150 (42.8), 104 (22.1)	Calcd for $C_{13}H_9ClN_2O_5S_2$: C, 41.88; H, 2.43; N, 7.51; S, 17.20. Found: C, 41.89; H, 2.45; N, 7.47; S, 17.24.
12a and **12b**	(neat) 1714 s, 1648 m, 1603 m, 1571 m, 1558 m, 1413 m, 1309 s, 1261 s	($CDCl_3$) 1.13 (t, 3H, *J* = 7.1 Hz), 4.17 (q, 2H, *J* = 7.1 Hz), 7.07-7.17 (m, 1H), 7.20 (t, 1H, *J* = 7.3 Hz), 7.38-7.47 (m, 2H) for **12a** and 1.09 (t, 3H, *J* = 7.1 Hz), 4.23 (q, 2H, *J* = 7.1 Hz), 7.07-7.17 (m, 1H), 7.27 (t, 1H, *J* = 7.5 Hz), 7.52-7.59 (m, 1H), 8.06 (t, 1H, *J* = 7.7 Hz) for **12b**	($CDCl_3$) 13.5, 62.1, 116.0 (d, *J* = 21.1 Hz), 122.5, 123.9 (d, *J* = 3.5 Hz), 125.3 (d, *J* = 16.1 Hz), 129.0 (d, *J* = 2.8 Hz), 132.3 (d, *J* = 8.2 Hz), 144.8, 156.8, 159.0 (d, *J* = 251.2 Hz), 165.5 (OC=O), 183.0 (C=O) for **12a** and 13.9, 62.4, 116.8 (d, *J* = 22.9 Hz), 120.8, 124.5 (d, *J* = 3.8 Hz), 126.3 (d, *J* = 8.5 Hz), 130.9, 135.5 (d, *J* = 9.2 Hz), 142.7, 153.0, 161.9 (d, *J* = 257.4 Hz), 167.0 (OC=O), 187.9 (C=O) for **12b**	345 (M^+, 66.1), 347 (M^+ + 2, 41.0), 310 (82.1), 282 (69.2), 186 (45.1), 123 (100.0), 95 (69.1), 75 (51.4)	Calcd for $C_{13}H_9ClFNO_3S_2$: C, 45.15; H, 2.62; N, 4.05; S, 18.55. Found: C, 45.12; H, 2.66; N, 4.11; S, 18.57.
13a and **13b**	(KBr) 2928 w, 1739 m, 1710 s, 1607 s, 1464 s, 1397 s, 1272 m, 1218 w, 1102 m, 1048 m, 856 m, 702 m	(DMSO-d_6) 4.82 (s, 2H) for **13a** and 4.64 (s, 2H) for **13b**	(DMSO-d_6) 71.2, 106.5, 147.6, 164.6, 164.8, 196.2 (C=O) for **13a** and 74.0, 104.2, 147.6, 166.0, 175.4, 187.5 (C=O) for **13b**	235 (M^+, 40.6), 237 (M^+ + 2, 16.9), 205 (21.5), 177 (100.0), 116 (20.6)	Calcd for $C_6H_2ClNO_3S_2$: C, 30.58; H, 0.86; N, 5.94; S, 27.21. Found: C, 30.62; H, 0.89; N, 5.90; S, 27.27.
14a	(KBr) 2968 w, 2920 w, 1670 s (C=O), 1586 s (C=O), 1430 s, 1378 s, 1298 s, 1243 s, 1194 w, 1163 s, 1122 m, 1037 m, 952 w, 850 m, 814 m, 752 m, 618 m	(DMSO-d_6) 1.40 (d, 3H, *J* = 6.6 Hz), 2.78 (d, 2H, *J* = 6.6 Hz), 4.72 (sextet, 1H, *J* = 6.6 Hz)	(DMSO-d_6) 20.6, 41.8, 72.0, 114.0, 147.6, 161.8, 163.3, 190.7	263 (M^+, 58.9), 265 (M^+ + 2, 24.4), 228 (100.0), 222 (20.8), 186 (80.8), 177 (44.8), 116 (21.9), 78 (22.5)	Calcd for $C_8H_6ClNO_3S_2$: C, 36.44; H, 2.29; N, 5.31; S, 24.32. Found: C, 36.42; H, 2.32; N, 5.36; S, 24.35.
15a	(KBr) 3072 w, 1677 s, 1634 m, 1555 s, 1426 m, 1379 s, 1352 m, 1272 w, 1248 w, 1157	(DMSO-d_6) 2.23 (s, 3H), 6.14 (s, 1H)	(DMSO-d_6) 20.4, 104.3, 110.2, 148.4, 157.2, 165.9, 166.2, 178.7	261 (M^+, 52.5), 263 (M^+ + 2, 21.8), 226 (100.0), 219 (53.8), 183 (35.2), 177 (52.1),	Calcd for $C_8H_4ClNO_3S_2$: C, 36.72; H, 1.54; N, 5.35; S, 24.51. Found: C, 36.75; H, 1.58; N, 5.32; S, 24.55.

	w, 1120 w, 1050 m, 989 m, 856 m, 830 m					69 (26.0)	
16a	(KBr) 2040 w, 1683 s, 1592 m, 1544 m, 1459 m, 1416 m, 1360 s, 1259 w, 1218 w, 1149 w, 1114 w, 1022 w, 957 w, 858 w, 790 w, 755 w	(DMSO-d_6) 7.37-7.44 (m, 2H), 7.76 (dt, 1H, J = 7.8, 1.6 Hz), 8.06 (dd, 1H, J = 7.8, 1.6 Hz)	*a*			297 (M^+, 16.7), 299 (M^+ + 2, 7.0), 262 (100.0), 198 (27.6), 120 (21.7), 92 (24.2)	Calcd for $C_{11}H_4ClNO_3S_2$: C, 44.37; H, 1.35; N, 4.70; S, 21.54. Found: C, 44.35; H, 1.39; N, 4.74; S, 21.57.
17a	(KBr) 3072 w, 1682 s, 1594 m, 1555 m, 1437 s, 1370 s, 1294 w, 1253 w, 1211 w, 1118 w, 1062 w, 971 w, 869 w, 826 w, 813 w, 774 w, 717 w	(DMSO-d_6) 7.48 (d, 1H, J = 8.8 Hz), 7.80 (dd, 1H, J = 8.8, 2.6 Hz), 8.00 (d, 1H, J = 2.6 Hz)	*a*			331 (M^+, 20.8), 333 (M^+ + 2, 15.3), 335 (M^+ + 4, 3.5), 296 (100.0), 232 (56.5), 154 (32.3), 126 (22.9)	Calcd for $C_{11}H_3Cl_2NO_3S_2$: C, 39.77; H, 0.91; N, 4.22; S, 19.31. Found: C, 39.81; H, 0.96; N, 4.20; S, 19.38.
18a	(KBr) 3064 w, 1686 s, 1587 m, 1544 m, 1435 s, 1357 s, 1251 w, 1213 w, 1149 w, 1109 w, 962 w, 866 w	(DMSO-d_6) 7.41 (d, 1H, J = 8.8 Hz), 7.91 (dd, 1H, J = 8.8, 2.5 Hz), 8.11 (d, 1H, J = 2.5 Hz)	*a*			375 (M^+, 20.5), 377 (M^+ + 2, 28.9), 379 (M^+ + 4, 9.2), 342 (100.0), 340 (93.8), 276 (41.5), 198 (20.4), 63 (21.7)	Calcd for $C_{11}H_3BrClNO_3S_2$: C, 35.08; H, 0.81; N, 3.72; S, 17.03. Found: C, 35.05; H, 0.86; N, 3.74; S, 17.07.
19a or **19b**	(KBr) 3056 w, 2928 w, 1639 s, 1582 s, 1531 s, 1469 s, 1429 m, 1374 s, 1349 s, 1298 m, 1248 w, 1218 w, 1154 w, 1107 w, 1034 w, 952 w, 894 w, 850 w, 789 w, 766 m, 747 m	(DMSO-d_6) 3.59 (s, 3H), 7.27 (t, 1H, J = 7.8 Hz), 7.49 (d, 1H, J = 7.8 Hz), 7.72 (t, 1H, J = 7.8 Hz), 8.10 (d, 1H, J = 7.8 Hz)	*a*			310 (M^+, 13.5), 312 (M^+ + 2, 5.7), 275 (100.0)	Calcd for $C_{12}H_7ClN_2O_2S_2$: C, 46.38; H, 2.27; N, 9.01; S, 20.64. Found: C, 46.42; H, 2.29; N, 8.98; S,20.68.
20a or **20b**	(KBr) 3064 w, 1688 m, 1614 m, 1581 m, 1544 s, 1414 m, 1360 s, 1330 m, 1282 m, 1251 w, 1147 w, 1112 w, 978 w, 912 w, 861 w, 821 w, 786 w, 768 w, 722 w, 694 w	(DMSO-d_6) 7.85 (t, 1H, J = 7.5 Hz), 7.94 (t, 1H, J = 7.5 Hz), 8.07(d, 1H, J = 7.5 Hz), 8.17 (d, 1H, J = 7.5 Hz)	*a*			309 (M^+, 39.7), 311 (M^+ + 2, 16.8), 281 (96.8), 246 (100.0), 182 (79.6), 126 (34.9), 104 (21.6), 76 (48.9)	Calcd for $C_{12}H_4ClNO_3S_2$: C, 46.53; H, 1.30; N, 4.52; S, 20.70. Found: C, 46.51; H, 1.33; N, 4.50; S,20.75.
21a or **21b**	(KBr) 1750 s, 1646 m, 1582 m, 1562 w, 1480 m, 1414 m, 1328 w, 1301 w, 1259 m, 1238 w, 1186 m, 1133 w, 1098 w, 1019 s, 843 m, 776 w, 760 m	(DMSO-d_6) 7.51 (t, 1H, J = 7.8 Hz), 7.61 (d, 1H, J = 7.8 Hz), 7.72 (t, 1H, J = 7.8 Hz), 8.03 (d, 1H, J = 7.8 Hz)	(DMSO-d_6) 120.0, 128.5, 130.6, 133.7, 145.6, 158.1, 164.3	106.9, 129.8, 133.8, 161.6,		297 (M^+, 81.3), 299 (M^+ + 2, 58.1), 262 (100.0), 225 (39.0), 190 (37.0), 186 (21.3), 154 (87.1), 126 (69.2)	Calcd for $C_{11}H_4ClNO_3S_2$: C, 44.37; H, 1.35; N, 4.70; S, 21.54. Found: C, 44.34; H, 1.36; N, 4.75; S,21.57.
22	(KBr) 2928 w, 1624 m, 1568 s, 1443 m, 1376 s, 1314 w, 1275 w, 1144 m, 858 m, 776 m, 603 m	($CDCl_3$) 2.08-2.21 (m, 2H), 2.71-2.84 (m, 4H)	($CDCl_3$) 19.4, 39.2, 126.0, 162.2, 193.1,	35.5, 149.3, 193.9		247 (M^+, 50.2), 249 (M^+ + 2, 20.8), 212 (100.0), 177 (31.0), 116 (184.1), 78 (26.6)	Calcd for $C_8H_6ClNO_2S_2$: C, 38.79; H, 2.44; N, 5.65; S, 25.89. Found: C, 38.84; H, 2.47; N, 5.61; S, 25.94.
23	(KBr) 3056 w, 1690 m, 1624 s, 1482 s, 1422 m, 1237 m, 1123 w, 1058 w, 1006 m, 837 m, 811 w, 685 w, 626 w, 488 w, 450 w	(DMSO-d_6) 7.09 (d, 1H, J = 6.1 Hz), 7.39 (d, 1H, J = 6.1 Hz)	(DMSO-d_6) 143.4, 146.3, 157.1, 187.8,	115.4, 146.5, 195.7		231 (M^+, 73.2), 233 (M^+ + 2, 31.3), 196 (100.0), 177 (31.4), 132 (21.1), 78 (25.9)	Calcd for $C_7H_2ClNO_2S_2$: C, 36.29; H, 0.87; N, 6.05; S, 27.68. Found: C, 36.30; H, 0.89; N, 6.08; S, 27.74.
24	(KBr) 1685 m, 1635 s, 1582 m, 1458 s, 1411 s, 1339 m, 1322 m, 1237 m, 1117 w, 1027 w, 843 w, 770 w, 728 w, 661 w	(DMSO-d_6) 7.79 (s, 4H)	(DMSO-d_6) 122.8, 123.7, 135.9, 138.8, 147.4, 160.4, 191.0	100.1, 135.3, 141.4, 183.7,		281 (M^+, 41.1), 283 (M^+ + 2, 18.0), 246 (100.0), 182 (30.1)	Calcd for $C_{11}H_4ClNO_3S_2$: C, 46.89; H, 1.43; N, 4.97; S, 22.76. Found: C, 46.87; H, 1.47; N, 4.96; S, 22.82.
25	(KBr) 2968 w, 1646 s, 1595 s, 1448 s, 1374 s, 1286 m, 1238 m, 1102 m, 1058 w, 998 w, 890 w, 851 w, 782 m, 739 w, 490 w	($CDCl_3$) 1.31 (t, 6H, J = 7.0 Hz), 4.57 (q, 4H, J = 7.0 Hz)	($CDCl_3$) 12.9, 44.6, 155.8, 177.6	44.3, 107.7, 162.3,	149.3, 166.4,	335 (M^+, 100.0), 337 (M^+ + 2, 46.5), 302 (86.2), 247 (27.7), 236 (39.5), 177 (37.2), 149 (21.8), 86 (22.8), 69 (31.7), 60 (22.2)	Calcd for $C_{10}H_{10}ClN_3O_2S_3$: C, 35.76; H, 3.00; N, 12.51; S, 28.64. Found: C, 35.79; H, 3.04; N, 12.50; S, 28.67.

[a] Solubility and decomposition problems. [b] DIP-MS except for **9**, **13**, **23**, and **24** which are GC-MS.

group syn to S-1 exhibited an absorption of the CH_3CO carbonyl carbon at 188.0 ppm, whereas **8a** having the corresponding group anti to S-1 showed the corresponding absorption at 197.8 ppm. On the other hand, the ^{13}C NMR absorption of the ester carbonyl carbon of **8b** which is a major isomer appeared at 163.7 ppm, whereas the corresponding absorption of **7c**, which is a minor isomer appeared at 166.0 ppm. The ^{13}C NMR data on the ester carbonyl carbons suggest that the ester carbonyl carbon exhibiting an absorption downfield of that of the other isomer has the group syn to S-1. The assignment of the ^{13}C NMR data of the ester carbonyl carbons was confirmed by the HMBC spectrum of a mixture of stereoisomers, **7c** and **8b**.

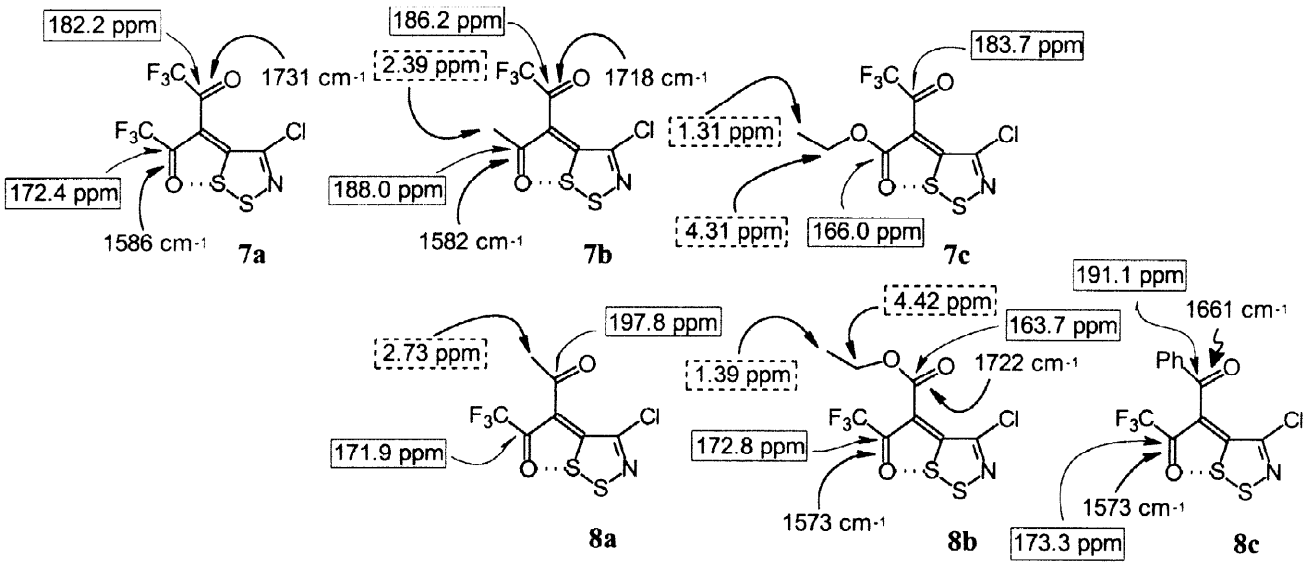


Figure 1. Selected IR, ^1H and ^{13}C NMR Data of Compounds **7a-c** and **8a-c**

Based on the foregoing observations, the stereochemistry of compounds **9-18a** was determined. The mixture of stereoisomers **9a** and **9b** (entry 1) was recrystallized from *n*-hexane to give crystals. The ^1H NMR spectrum of which showed two sets of triplets at 1.35 (minor) and 1.43 (major) ppm and two sets of quartets at 4.40 (minor) and 4.48 (major) ppm due to ethoxy groups. The ratios of the intensities of two sets of peaks were determined to be 95:5. The same ratios were determined from the solution of the crystals in the NMR tube in 24 h at room temperature as well as from the residue after removal of the solvent from the filtrate. The two sets of NMR data clearly indicate that **9a** is a major stereoisomer and the same ratio of 95:5 is maintained at room temperature for a prolonged time. The mixture of stereoisomers **9a** and **9b** exhibited a strong carbonyl absorption at 1722 cm^{-1}, presumably due to a major stereoisomer **9a**, which also suggests that the ester carbonyl group is anti to S-1. The formation of **9a** in preference to **9b** may be attributable to the strong interaction between the negative charge on the oxygen of the nitro group and the electron-deficient S-1 of 1,2,3-dithiazole moiety.

The structure of compound **10a** (entry 2) was assigned based on a carbonyl absorption at 1676 cm^{-1} which is closer to the values shown by the carbonyl groups anti to S-1. The ^{13}C NMR spectrum showed a band assignable to the carbonyl carbon at 185.5 ppm, which is close to the corresponding value of the benzoyl group of **8c**. The assignment based on IR and ^{13}C NMR data was supported by *X*-ray crystallography of **10a**. The molecular structure of **10a** is shown in Figure 2. The dithiazole ring and O-N bond extending to C(2) is nearly planar, there being only a 3 to -7 ° torsional angle between the dithiazole and a O-N bond of the nitro

group as shown by the selected torsional angles (°): S(1)-C(2)-C(3)-N(2) 3.2; C(2)-C(3)-N(2)-O(3) 4.6; C(3)-N(2)-O(3)···S(1) −7.2; N(2)-O(3)···S(1)-C(2) 6.9; O(3)···S(1)-C(2)-C(3) −5.2. In addition there is a short non-bonded O···S contact of 2.451 Å between O(3) and S(1) which is significantly shorter than not only the sum (3.25 Å) of the van der Waals radii[9] but also the intramolecular S···O distance (2.62 Å) of 4-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)-2-cyanothiazolidin-5-one which makes a complex with DMSO.[10] It is interesting to note that a nearly linear relationship exists between O(3), S(1), and S(2) (angle 169.18°). The angle is similar to 164.7(1) ° and 167.1(5) ° which are N-S-N bond angles for sulfuranes, 2,4,8,10-tetramethyl-6λ⁴-pyrimido[1",2":2',3'][1,2,4]thiadiazolo[1',5':1,5][1,2,4]-thiadiazolo[2,3-a]pyrimidine and 2,4,8,10,12,13-hexamethyl-6λ⁴-pyrimido[1",2":2',3'][1,2,4]thiadiazolo[1',5':1,5][1,2,4]-thiadiazolo[2,3-a]pyrimidinium di(triiodide), respectively.[11] The strong interaction between the nitro group and the S-1 through the formation of hypervalent bond may be responsible for the formation of a single stereoisomer **10a** albeit in low yield.

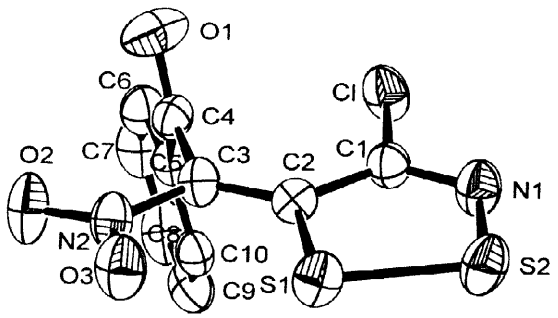
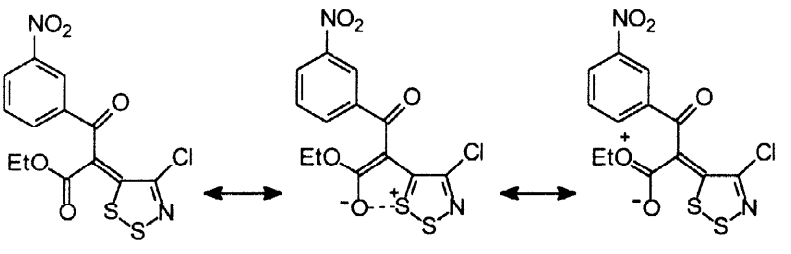


Figure 2. ORTEP Drawing of **10a**

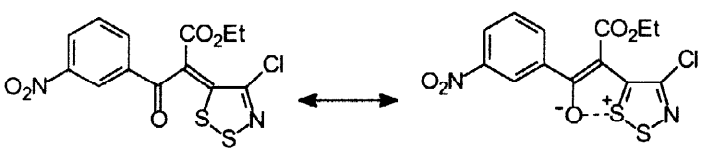
Selected bond lengths (Å): S(1)-S(2) 2.086(2), S(1)-C(2) 1.738(4), C(2)-C(3) 1.371(5), C(3)-N(2) 1.398(5), C(3)-C(4) 1.534(5), N(2)-O(3) 1.242(4), N(2)-O(2) 1.244(4), O(1)-C(4) 1.203(5). Selected bond angles (deg): S(2)-S(1)-C(2) 93.27(13), S(1)-C(2)-C(3) 123.1(3), C(2)-C(3)-N(2) 118.0(3), C(3)-N(2)-O(3) 119.0(3), C(3)-C(2)-C(1) 126.0(3), C(2)-C(3)-C(4) 128.5(3), O(1)-C(4)-C(3) 118.1(3), C(2)-C(1)-Cl 121.1(3).

The mixture of stereoisomers **11a** and **11b** (entry 3) was recrystallized from a mixture of *n*-hexane and CH_2Cl_2 to give crystals. The ^1H NMR spectrum of which exhibited two triplets at 1.10 (minor) and 1.31 (major) ppm and two quartets at 4.23 (minor) and 4.32 (major) ppm due to ethoxy groups. The ratio of each set of peaks was measured to be 53:47, which did not change in 24 h at room temperature. However, the ^1H NMR spectrum of the residue after removal of the solvent from the filtrate exhibited a 66:34 ratio of the corresponding sets of peaks. Interestingly the ratio changed to 53:47 in 24 h. The result suggests that the equilibrium between two stereoisomers **11a** and **11b** may be relatively slowly achieved to give the equilibrium ratio of 53:47 at room temperature. The ^1H NMR data of the carbethoxy group suggests that **11a** having the group anti to S-1 is a major compound. The ^{13}C NMR absorptions of the keto carbonyl carbons and ester carbonyl carbons of a mixture of **11a** and **11b** were assigned to be 183.3 and 190.3 ppm, and 166.6 and 167.4 ppm, respectively based on the intensities of each set of peaks together with the HMBC spectrum of a mixture of **11a** and **11b**. The ^{13}C NMR data of the keto carbonyl carbons suggests **11a** being a major stereoisomer because the absorption of the keto carbonyl carbon would be expected to appear upfield of that of **11b** (cf. **7a**, **7b**, and **8a**). The same conclusion can be drawn from the ^{13}C NMR data of the ester carbonyl carbons. That is, it would be expected that the absorption upfield (166.6 ppm) is due to the isomer **11a** anti to

S-1 (cf. **7c** and **8b**). The reason why **11a** is formed in slight favor of **11b** may be attributable to the greater contribution of the resonance form **11b"** which would give rise to a weak interaction between S-1 and the polarized carbonyl oxygen of the ethoxy carbonyl group compared to the resonance form **11b'**, from which a strong interaction between the electron deficient S-1 and a negative charge on the carbonyl oxygen would be expected. In contrast, there is no direct resonance interaction between the nitro group and the keto carbonyl group of **11a**. Therefore a strong interaction between two opposite charges would be expected from **11a'**.



11b **11b'** **11b"**



11a **11a'**

Apart from the foregoing reactions (entries 1-3), the reaction of **1** with ethyl 2-fluorobenzoylacetate (entry 4) gave a mixture of (*E*)- (**12a**) and (*Z*)-dithiazol-5-ylidenes (**12b**) containing the keto and enol forms of ethyl 2-fluorobenzoylacetate. The latter two isomers were removed from the mixture of **12a** and **12b** by repeated column chromatography using a mixture of *n*-hexane and CH_2Cl_2 (1:1) as an eluent. Recrystallization of the mixture of **12a** and **12b** from *n*-hexane gave a sticky liquid, which was solidified at -10 °C. The solids were rapidly filtered. The ^{1}H NMR spectrum of which exhibited two triplets at 1.09 and 1.13 ppm and two quartets at 4.23 and 4.17 ppm assignable to methyl and methylene protons of the ester functionality of a mixture of **12a** and **12b**. Based on the analogy of the relation between **7c** and **8b**, and **11a** and **11b**, the triplet upfield (1.09 ppm) was assigned to the methyl protons of **12b** in which the ester carbonyl group is syn to S-1. However, **12b** exhibited methylene proton signals downfield (4.23 ppm) and **12a** exhibited the corresponding proton signals upfield (4.17 ppm) which was in contrast with the propensity of the chemical shifts between two stereoisomers **7c** and **8b**, and **11a** and **11b**. Therefore, one should be cautious about assigning the stereochemistry of alkylidene-5-dithiazoles with an ester functionality based simply on the ^{1}H NMR chemical shift of the methylene protons of the ester group. The ^{13}C NMR spectrum showed two absorptions assignable to the keto carbonyl carbons at 183.0 and 187.9 ppm the ratio of the intensities of which was 72:28. Consequently the absorption upfield can be assigned to the carbonyl carbon of the major product **12a** and the absorption with weak intensity downfield can be assigned to **12b**. The propensity of the ^{13}C NMR chemical shifts shown by the stereoisomers **12a** and **12b** is in accord with those shown by a pair of isomers **7b** and **8a**, **7c** and **8b**, and **11a** and **11b**. As shown in the mixture of stereoisomers **9a** and **9b**, the same ratios of 72:28 were measured from the ^{1}H NMR spectrum of the mixture of **12a** and **12b** in 24 h at room temperature and from the ^{1}H NMR spectrum of the residue after removal of the solvent from the filtrate.

The reaction with tetronic acid gave a mixture of (*E*)- and (*Z*)-dithiazol-5-ylidenes **13b** and **13a** (entry 5)

which was recrystallized from CH_2Cl_2. The ratios of the stereoisomers in a recrystallized mixture, in a recrystallized mixture in 24 h at room temperature, and in a residue after removal of the solvent from the filtrate were found to be all 33:67 by comparison of the intensities of ^1H NMR signals of the methylene protons at 4.68 (minor) and 4.86 (major) ppm. However, there is no obvious basis for deciding which of (*E*)-isomer and (*Z*)-isomer is major at the present moment. In addition, it proved impossible to obtain a clean HMBC spectrum of the mixture owing to decomposition in the process of sampling. The IR spectrum of the mixture exhibited three bands at 1739 (m), 1710 (s), and 1607 (s) cm^{-1}, but did not provide a basis for its structural elucidation. Based on an analogy with the foregoing discussion on ^{13}C NMR, the ^{13}C NMR absorption exhibited downfield (196.2 ppm) was assigned to the keto carbonyl carbon of **13a** which is a major isomer and the absorption upfield (187.5 ppm) was assigned to the corresponding carbon of the minor isomer, **13b**. In order to understand a constant ratio of isomers in mixtures of **9a** and **9b**, **12a** and **12b**, and **13a** and **13b**, respectively regardless of physical states, i.e., crystal and solution, a further study on the effect of temperature is needed.

The reaction with 5,6-dihydro-4-hydroxy-6-methyl-2*H*-pyran-2-one (entry 6) gave only single stereoisomer **14a**, which exhibited two IR bands at 1670 (s) and 1586 (s) cm^{-1}. The *X*-ray crystallographic analysis clearly shows that the keto carbonyl group is syn to S-1 of **14a**. The molecular structure of **14a** is shown in Figure 3. There is an increase in the C(3)-O(3) (1.231(3) Å) bond compared with the O(2)-C(1) (1.208(3) Å) bond. The dithiazole ring and O-C bond extending to C(7) is nearly planar, there being a 8 to -11 ° torsional angle between the dithiazole and a O-C bond of the keto carbonyl group as shown by the selected torsional angles (°): S(1)-C(7)-C(2)-C(3) –11.4; C(7)-C(2)-C(3)-O(3) 8.6; C(2)-C(3)-O(3)···S(1) –2.5; C(3)-O(3)···S(1)-C(7) –2.7; O(3)···S(1)-C(7)-C(2) 7.4. In addition there is a short non-bonded O···S contact of 2.395 Å between O(3) and S(1) which is significantly shorter than the sum of the van der Waals radii.[9] A nearly linear relationship exists between O(3), S(1), and S(2) (angle 169.68 °). As mentioned for **10a**, all the data support the formation of hypervalent bond between O(3) and S(1).

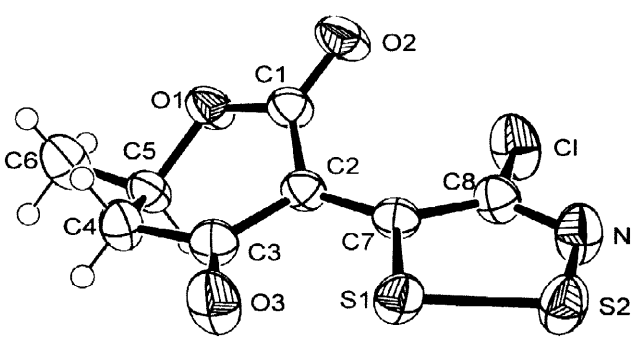
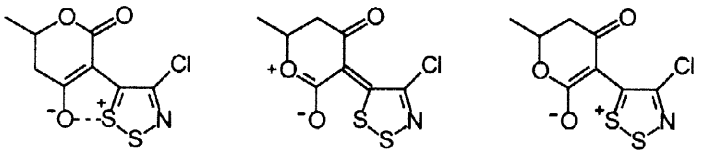


Figure 3. ORTEP Drawing of **14a**

Selected bond lengths (Å): S(1)-S(2) 2.061(10), S(1)-C(7) 1.727(2), C(7)-C(2) 1.395(3), C(2)-C(3) 1.437(3), C(3)-O(3) 1.231(3), C(2)-C(1) 1.459(3), O(2)-C(1) 1.208(3), C(4)-C(3) 1.429(3). Selected bond angles (deg): S(2)-S(1)-C(7) 93.61(8), S(1)-C(7)-C(2) 119.08(8), C(7)-C(2)-C(3) 116.7(2), C(2)-C(3)-O(3) 121.2(2), C(7)-C(8)-Cl 122.80(18), C(2)-C(7)-C(8) 129.9(2), C(7)-C(2)-C(1) 124.9(2), O(2)-C(1)-C(2) 126.1(2).

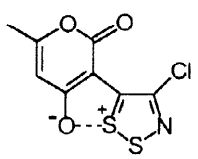
The formation of a single isomer **14a** may be attributable to the formation of hypervalent bond between the negative charge on the keto carbonyl oxygen and the electron deficient S-1, as depicted by **14a'** in

preference to the ester carbonyl group. It is envisaged that the interaction between the ester carbonyl oxygen and the electron deficient S-1, as depicted by **14b**, may be weakened by a resonance contribution such as **14b'**.



14a' **14b'** **14b**

The reaction with 4-hydroxy-6-methyl-2-pyrone gave also a single isomer **15a** in 57 % yield (entry 7). The stereochemistry of **15a** was determined by *X*-ray crystallography. The molecular structure of **15a** is shown in Figure 4. The dithiazole ring and O-C bond extending to C(7) is nearly planar, there being a 8 to -10° torsional angle between the dithiazole and a O-C bond of the keto carbonyl group as shown by the selected torsional angles (°): S(1)-C(7)-C(2)-C(3) −10.3; C(7)-C(2)-C(3)-O(3) 4.3; C(2)-C(3)-O(3)···S(1) 1.9; C(3)-O(3)···S(1)-C(7) −5.7; O(3)···S(1)-C(7)-C(2) 8.5. In addition there is a short non-bonded O···S contact of 2.319 Å between O(3) and S(1) which is shorter than that of **14a**. An essentially linear relationship exists between O(3), S(1), and S(2) (angle 172.93 °), which suggests the formation of hypervalent bond between O(3) and S(1). It would be expected that the dipolar form **15a'** is more stabilized by the presence of a double bond inside the pyrone ring than the analog **14a'**. This might be reflected in the higher yield of **15a** compared with that of **14a**.



15a'

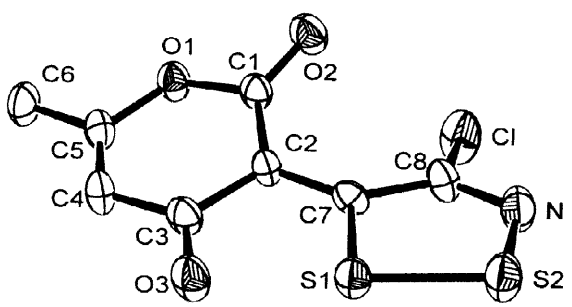


Figure 4. ORTEP Drawing of **15a**

Selected bond lengths (Å): S(1)-S(2) 2.068(2), S(1)-C(7) 1.731(5), C(7)-C(2) 1.390(8), C(2)-C(3) 1.455(8), C(3)-O(3) 1.240(7), C(2)-C(1) 1.436(7), O(2)-C(1) 1.206(7), C(4)-C(5) 1.336(9). Selected bond angles (deg): S(2)-S(1)-C(7) 93.4(2), S(1)-C(7)-C(2) 118.8(4), C(7)-C(2)-C(3) 116.0(5), C(2)-C(3)-O(3) 119.5(5), C(7)-C(8)-Cl 123.3(4), C(2)-C(7)-C(8) 130.3(5), C(7)-C(2)-C(1) 124.7(5), O(2)-C(1)-C(2) 127.5(5).

The reactions of 4-hydroxy- (entry 8), 6-chloro-4-hydroxy- (entry 9), and 6-bromo-4-hydroxycoumarins (entry 10) gave a single stereoisomer **16a**, **17a**, and **18a**, in 87, 39, and 43 % yields, respectively. Compounds **16a** [1683 (s), 1592 (m), 1544 (m) cm^{-1}], **17a** [1682 (s), 1594 (m), 1555 (m) cm^{-1}], and **18a** [1686 (s), 1587 (m), 1544 (m) cm^{-1}] showed three IR bands in the almost the same regions. The stereochemistry of each compound was gauged in the light of the structural similarity with the coumarin skeleton possessed by **16a**,

17a, and **18a** and the pyrone moiety of **15a**, coupled with the similar IR data foregoing.

The reactions of 4-hydroxy-1-methyl-2(1*H*)-quinolone (entry 11), 2-hydroxy-1,4-naphthoquinone (entry 12), and homophthalic anhydride (entry 13) gave single stereoisomers, **19**, **20**, and **21** respectively. Each isomer was solid. Compound **19** exhibited three bands [1639 (s), 1582 (s), 1531 (s) cm^{-1}] in the region where the absorptions of the carbonyl groups appear. Similarly, **20** exhibited four bands [1688 (m), 1614 (m), 1581 (m), 1544 (s) cm^{-1}] and **21** exhibited four bands [1750 (s), 1646 (m), 1582 (m), 1562 (w) cm^{-1}] in the almost same region as for **19**. Attempts for the preparation of a single crystal for *X*-ray crystallography have been unsuccessful. More work has to be done to delineate the stereochemistry of compounds **19**, **20**, and **21**.

The reaction with cyclohexane-1,3-dione gave the corresponding 1,2,3-dithaizol-5-ylidene **21** (entry 14), which is in contrast with no formation of the corresponding 1,2,3-dithiazol-5-ylidene from 2,4-pentanedione. Similarly, the reaction with 1,3-indanedione gave the corresponding 1,2,3-dithiazol-5-ylidene **24** (entry 16) whereas the reaction with open-chain analog, 1-benzoylacetone, did not give a dithiazol-5-ylidene derivative at all. The reaction with 4-cyclopentene-1,3-dione (entry 15) gave 1,2,3-dithiazol-5-ylidene **23** albeit in low yield. It is hard to explain why the yield of **23** is much lower than that of **24** in spite of having similar structure as far as the reaction site is concerned. The reaction with 1,3-diethyl-2-thiobarbituric acid (entry 17) gave 1,2,3-dithiazol-5-ylidene **25** (74 %), which is a much higher yield than that of **5**[4] (*vide supra*). More work is needed to explain the difference.

The formation of 1,2,3-dithiazoles **22** and **24** from 1,3-cyclohexanedione and 1,3-indandione, respectively coupled with the results shown by dithiazol-5-ylidenes prepared from various types of cyclic 1,3-diones (entries 5-13) suggest that the proper geometry for the interaction between the carbonyl oxygen and the S-1 of dithiazole moiety as well as the resonance stabilization gained from each stereoisomer through a five-membered cyclic form formed by the interaction between the carbonyl oxygen and the S-1 of dithiazole moiety play an important role in the success of the reaction and the selective formation of the stereoisomers.

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were recorded at 300 MHz and 75 MHz in $CDCl_3$ or DMSO-d_6 solution containing Me_4Si as an internal standard and the HMBC spectra were recorded at 500 MHz under the same conditions. IR spectra were recorded in KBr or thin films on KBr plates. HPLC was performed with C-18 column (μ Bondapak C18, 10 μm, 7.8 × 300 mm i.d.) and a differential refractomer, using CH_3CN as eluent. Mass spectra were obtained by a VG 12-250 mass spectrometer or HP 6890 GC-HP 5973 MSD using an electron-impact ionization technique at 70 eV. Elemental analyses were determined by the Korea Basic Science Center. Column chromatography was performed using silica gel (70-230 mesh, Merck). Melting points are uncorrected.

4-Chloro-5*H*-1,2,3-dithiazolium chloride (**1**) was prepared according to the documented procedures.[2]

Compounds **7a-c** and **8a-c** were prepared according to the general procedures described below.[6]

7a: mp 77-79 °C (*n*-hexane + CH_2Cl_2); IR (KBr) 1731, 1586, 1398, 1285, 1211, 1179, 1152, 1048, 850 cm^{-1}; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 114.8, 115.8 (q, J = 292.1 Hz), 117.6 (q, J = 286.6 Hz), 146.2, 164.3, 172.4 (q, J = 37.5 Hz), 182.2 (q, J = 38.5 Hz); ^{19}F NMR ($CDCl_3$, 188 MHz) δ -69.2 (q, J = 5.5 Hz), -76.2 (q, J = 5.5 Hz); MS (m/z) 343 (M^+, 32), 274 (100), 224 (60); Anal. Calcd for $C_7ClF_6NO_2S_2$: C, 24.47; N, 4.08; S, 18.66. Found: C, 24.40; N, 4.11; S, 18.59.

7b and **8a**: mp 116-118 °C (*n*-hexane + $CHCl_3$); IR (KBr) 1718, 1582, 1430, 1360, 1302, 1253, 1197,

1142, 1088, 933, 861, 803 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.39 (s, 3H) for **7b** and 2.73 (s, 3H) for **8a**; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 24.6, 115.9 (q, J = 291.6 Hz), 120.5, 143.7, 158.8, 186.2 (q, J = 37.4 Hz), 188.0 for **7b** and 35.4, 117.8 (q, J = 286.3 Hz), 125.1, 145.3, 159.9, 171.9 (q, J = 37.3 Hz), 197.8 for **8a**; ^{19}F NMR ($CDCl_3$, 188 MHz) δ -76.6 for **7b** and –69.2 for **8a**; MS (m/z) 289 (M^+, 74), 254 (73), 220 (100), 178 (74); Anal. Calcd for $C_7H_3ClF_3NO_2S_2$: C, 29.02; H, 1.04; N, 4.84; S, 22.14. Found: C, 29.09; H, 1.08; N, 4.91; S, 22.05.

7c and **8b**: mp 78-80 °C (*n*-hexane + CH_2Cl_2); IR (KBr) 2976, 1722, 1573, 1445, 1402, 1262, 1230, 1146, 1013, 987, 891, 851, 794 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.31 (t, 3H, J = 7.2 Hz), 4.31 (q, 2H, J = 7.2 Hz) for **7c** and 1.39 (t, 3H, J = 7.2 Hz), 4.42 (q, 2H, J = 7.2 Hz) for **8b**; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.9, 63.3, one carbon not detected, 115.3 (q, J = 291.5 Hz), 142.2, 158.2, 166.0, 183.7 (q, J = 37.4 Hz) for **7c** and 13.7, 63.1, 116.9, 117.7 (q, J = 286.6 Hz), 146.0, 160.4, 163.7, 172.8 (q, J = 37.3 Hz) for **8b**; ^{19}F NMR ($CDCl_3$, 188 MHz) δ -75.1 for **7c** and –70.6 for **8b**; MS (m/z) 319 (M^+, 36), 274 (36), 250 (100), 222 (46), 178 (32); Anal. Calcd for $C_8H_5ClF_3NO_3S_2$: C, 30.06; H, 1.58; N, 4.38; S, 20.06. Found: C, 30.09; H, 1.64; N, 4.61; S, 20.09.

8c: mp 155-156 °C (*n*-hexane + $CHCl_3$); IR (KBr) 1661, 1573, 1433, 1398, 1350, 1304, 1206, 1146, 1032, 1019, 845, 803 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.46-7.67 (m, 3H), 7.83-7.94 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 118.1 (q, J = 285.0 Hz), 122.3, 129.4, 129.8, 134.7, 139.3, 146.4, 161.1, 173.3 (q, J = 36.9 Hz), 191.1; ^{19}F NMR ($CDCl_3$, 188 MHz) δ -68.7; MS (m/z) 351 (M^+, 11), 316 (37), 292 (39), 193 (100), 168 (67), 105 (79); Anal. Calcd for $C_{12}H_5ClF_3NO_2S_2$: C, 40.98; H, 1.43; N, 3.98; S, 18.23. Found: C, 41.06; H, 1.38; N, 3.93; S, 18.32.

General Procedure for the Reactions of 4,5-Dichloro-5*H*-1,2,3-dithiazolium Chloride (1) with Active Methylene Compouds. To a solution (entries 1-4, 13, 14, 16 and 17) and to a suspension (entries 5-12, and 15) of active methylene compound (2.50 - 2.55 mmol) in CH_2Cl_2 (30 mL) at room temperature was added **1** (2.50 mmol), followed by dropwise addition of pyridine (5.07 mmol). The mixture was stirred for 5 h in the cases of most reactions (entries 3-17). However, the reactions with ethyl nitroacetate (entry 1) and benzoylnitromethane (entry 2) were stirred for 20 and 40 h, respectively. After removal of the solvent *in vacuo*, the residue was chromatographed on a silica gel (2.5 × 15 cm) (entries 1-8, and 11-17). Elution with *n*-hexane gave sulfur (1-7 %). Subsequent elution with a mixture of *n*-hexane and CH_2Cl_2 (2:1) gave 4-chloro-5*H*-1,2,3-dithiazole-5-thione (**4**) (1-19%). 4-Chloro-5*H*-1,2,3-dithiazol-5-one was eluted in certain cases (21 % for entry 1 and 18 % for entry 2). In addition, an unknown compound (57 mg) was isolated from the reaction with benzoylnitromethane (entry 2). In the case of the reaction with 2-fluorobenzoylacetate (entry 4), elution with a mixture of *n*-hexane and CH_2Cl_2 (1:2) gave an orangish mixture of (*E*)- (**12a**) and (*Z*)-ethyl 2-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)-2'-fluorobenzoylacetate (**12b**) and keto and enol forms of ethyl 2-fluorobenzoylacetate. Elution with a mixture of *n*-hexane and CH_2Cl_2 (1:1 for **9**, 2:1 for **10**, and 1:2 for **11**) gave (*E*)- (**9b**) and (*Z*)-ethyl 2-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)nitroacetate (**9a**) (entry 1), (*Z*)-benzoyl(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)nitromethane (**10a**) (entry 2), (*E*)- (**11a**) and (*Z*)-ethyl 2-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)-3'-nitrobenzoylacetate (**11b**) (entry 3). On the other hand, (*E*)- (**13b**) and (*Z*)-3-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)tetrahydrofuran-2,4-dione (**13a**) (entry 5), (*E*)-3-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)-6-methyl-2*H*-pyran-2,4-dione (**15a**) (entry 7), and (*E*)-3-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)-3,4-dihydro-2*H*-1-benzopyran-2,4-dione (**16a**) (entry 8) were eluted with a mixture of CH_2Cl_2 and acetone (20:1). Elution with the same solvent mixture (50:1) gave (*E*)-3-(4-chloro-5*H*-1,2,3-

dithiazol-5-ylidene)-5,6-dihydro-6-methyl-2*H*-pyran-2,4-dione (**14a**) (entry 6), 3-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)-3,4-dihydro-1-methyl-4-oxo-2(1*H*)-quinolone (**19a** or **19b**) (entry 11), 3-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)-2,3-dihydro-2-oxo-1,4-naphthoquinone (**20a** or **20b**) (entry 12), 2-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)-1,3-cyclohexanedione (**22**) (entry 14), 5-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)-1,3-diethyl-2-thiobarbituric acid (**25**) (entry 17). 4-(4-Chloro-5*H*-1,2,3-dithiazol-5-ylidene)-1*H*-2-benzopyran-1,3-dione (**21a** or **21b**) (entry 13), 2-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)-4-cyclopentene-1,3-dione (**23**) (entry 15), and 2-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)-1,3-indandione (**24**) (entry 16) were eluted with CH_2Cl_2. However, the reactions involving 6-chloro- (entry 9) and 6-bromo-4-hydroxy-2*H*-1-benzopyran-2-ones (entry 10) gave directly solid products, i.e., (*E*)-6-chloro-3-(4-choro-5*H*-1,2,3-dithiazol-5-ylidene)-3,4-dihydro-2*H*-1-benzopyran-2,4-dione (**17a**) (entry 9), and (*E*)-6-bromo-3-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)-3,4-dihydro-2*H*-1-benzopyran-2,4-dione (**18a**) (entry 10), which were filtered, washed with CH_2Cl_2 and then recrystallized from THF. Consult Table 1 for physical properties of dithiazol-5-ylidenes **9-25** and yields of **6** and **9-25** and Table 2 for the spectroscopic (IR, ^1H and ^{13}C NMR, MS) and analytical data of **9-25**.

***X*-Ray Structure Analysis of Compounds 10a, 14a, and 15a.** Crystal data and structure refinement for **10a**, **14a**, and **15a** are summarized in Table 3. Single crystals of **10a**, **14a**, and **15a** were obtained from the concentrated solutions in CH_2Cl_2 (**10a** and **14a**) or a mixture of CH_2Cl_2 and acetone (**15a**). The data were collected on an Enraf-Nomius CAD 4 diffractometer using graphite-monochromated Mo-K_α radiation. The structures were infered by direct methods and subsequent Fourier maps. Refinements were carried out by full-matrix least-squares techniques. Non-hydrogen atoms were anisotropically refined. Atomic scattering factors were taken from International Tables for *X*-ray Crystallography, Vol IV, 1974. All calculations and drawings were performed using a Micro VAX II Computer with an SDP system. Atomic coordinates, bond lengths, angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

Table 3. Crystal Data and Structure Refinement for **10a, 14a,** and **15a**

	10a	**14a**	**15a**
Empirical formula	$C_{10}H_5ClN_2O_3S_2$	$C_8H_6ClNO_3S_2$	$C_8H_4ClNO_3S_2$
Formula weight	300.73	263.71	261.69
Temperature	293(2) K	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	monoclinic	monoclinic	monoclinic
Space group	P2(1)/c	P2(1)/n	Cc(No.9)
Unit cell dimensions	a = 8.546(3) Å	a = 11.718(2) Å	a = 3.8780(4) Å
	α = 90.00(3) deg.	α = 90 deg.	α = 90 deg.
	b = 13.099(5) Å	b = 7.4999(15) Å	b = 14.585(3) Å
	β = 101.37(3) deg.	β = 101.32(3) deg.	β = 92.129(11) deg.
	c = 10.620(4) Å	c = 11.781(2) Å	c = 16.722(3) Å
	γ = 90.00(3) deg.	γ = 90 deg.	γ = 90 deg.
Volume	1165.5(7) $Å^3$	1015.2(4) $Å^3$	945.1(3) $Å^3$
Z	4	4	4
Density (calculated)	1.714 mg/m^3	1.725 mg/m^3	1.839 mg/m^3
Absorption coefficient	0.685 mm^{-1}	0.770 mm^{-1}	0.827 mm^{-1}

F(000)	608	536	528
Theta range for data collection	2.43 to 24.97 deg.	2.24 to 24.89 deg.	2.44 to 25.97 deg.
Index ranges	0<=h<=10, 0<=k<=15, -12<=l<=12	-13<=h<=13, -8<=k<=8, -8<=l<=13	0<=h<=4, 0<=k<=17, -20<=l<=20
Reflections collected	2186	5055	1018
Independent reflections	2048 [R(int) = 0.0198]	1762 [R(int) = 0.0683]	985 [R(int) = 0.0395]
Data/restraints/parameters	2048 / 0 / 179	1762 / 0 / 161	985 / 2 / 136
Goodness-of-fit on F^2	1.219	1.060	1.045
Final R indices [I>2sigma(I)]	R_1 = 0.0504, wR_2 = 0.1150	R_1 = 0.0431, wR_2 = 0.1148	R_1 = 0.0458, wR_2 = 0.1144
R indices (all data)	R_1 = 0.0626, wR_2 = 0.1262	R_1 = 0.0484, wR_2 = 0.1187	R_1 = 0.0461, wR_2 = 0.1149
Extinction coefficient	0.0062(10)	0.014(3)	-0.07(14)
Largest diff. peak and hole	0.373 and -0.324 $e.A^{-3}$	0.425 and -0.419 $e.A^{-3}$	0.559 and -0.363 $e.A^{-3}$

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