Reactions of 5-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione with primary and secondary alkylamines †

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Received (in Cambridge, UK) 18th April 2000, Accepted 24th July 2000
Published on the Web 4th September 2000

The reactions of 5-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione with primary alkylamines (2 equiv.) in CH_2Cl_2 at rt gave 5-[(alkylamino)(cyano)methylidene]-2,2-dimethyl-1,3-dioxane-4,6-diones (**2**) in excellent yields. Similarly, the reactions with ethylenediamine, *trans*-1,2-diaminocyclohexane, 2-aminobenzylamine, and 2-aminoethanol under the same conditions afforded 5-(imidazolidin-2-ylidene)- (**3a**), 5-(octahydro-2*H*-benzimidazol-2-ylidene)- (**3b**), 5-[3,4-dihydroquinazolin-2(1*H*)-ylidene]- (**3c**), and 5-(1,3-oxazolidin-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-diones (**3d**) in moderate to excellent yields. Interestingly, the reactions with secondary acyclic dialkylamines under the same conditions yielded 5-(4-dialkylamino-5*H*-1,2,3-dithiazol-5-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-diones (**7**) (0–60%), 6-carbamoyl-5-oxo-5*H*-furo[2,3-*d*][1,2,3]-dithiazoles (**8**) (0–28%), sulfur, and bis(dialkylamino) sulfides ($R_2N–S_x–NR_2$), whereas the reactions with cyclic amines, *i.e.*, pyrrolidine and piperidine, gave the corresponding methylidene-Meldrums acid derivatives **9**, analogous to **2**, as major products. Mechanisms are proposed for the formation of these products.

Introduction

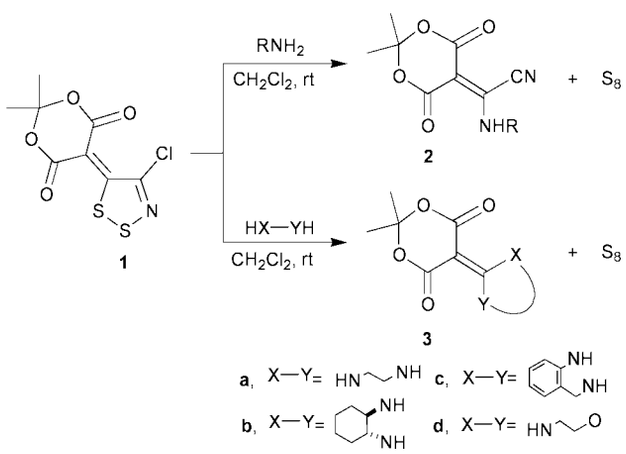
In recent years, flash vacuum thermolysis of (alkylamino)- and (arylamino)methylidene derivatives of Meldrum's acid has been an important topic owing to its potential synthetic utility, and much theoretical and mechanistic interest has been shown in the formation of its products.[1] The compounds have been mostly prepared by treatment of Meldrum's acid with a variety of electrophiles such as orthoformates,[2] dimethylamino orthoformates,[3] dicyclohexylcarbodiimide,[4] isocyanates,[5] isothiocyanates,[6] imidates,[7] α-chloro- and α-methylthio-immonium salts[8] in the presence of triethylamine at rt or reflux temperature. 5-[Bis(methylthio)methylidene]-2,2-dimethyl-1,3-dioxane-4,6-dione, prepared by treatment of Meldrum's acid with CS_2 in the presence of Et_3N in DMSO at rt, followed by addition of iodomethane,[2a–b,9] was reported as an important precursor for the preparation of various Meldrum's acid-aminomethylidene products,[2b,10] depending on the nucleophiles which replace either or both methylthio groups.

In the course of exploration of the synthetic utility of 5-alkylidene-4-chloro-5*H*-1,2,3-dithiazoles,[11] 5-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (**1**), prepared by the reaction of 4,5-dichloro-5*H*-1,2,3-dithiazolium chloride (Appel's salt) with Meldrum's acid in the presence of pyridine in CH_2Cl_2 at rt,[12] was envisaged to be a good precursor for (alkylamino)- and (arylamino)methylene derivatives of Meldrum's acid in view of the formation of *N′*-aryl-*N*-alkylcyanoformamidines by treatment of 5-arylimino-4-chloro-5*H*-1,2,3-dithiazoles with alkylamines.[13] We have studied this possibility by treatment of **1** with primary and secondary alkylamines. The results are described herein.

Results and discussion

Reactions with primary alkylamines

Treatment of **1** with primary alkylamines (2 equiv.) in CH_2Cl_2 at rt afforded 5-[(alkylamino)(cyano)methylidene]-2,2-dimethyl-1,3-dioxane-4,6-diones (**2**) in excellent yields along with sulfur (Scheme 1). Similarly, the reactions with ethylenediamine, *trans*-1,2-diaminocyclohexane, 2-aminobenzylamine, and 2-aminoethanol under the same conditions gave 5-(imidazolidin-2-ylidene)- (**3a**), 5-(octahydro-2*H*-benzimidazol-2-ylidene)- (**3b**), 5-[3,4-dihydroquinazolin-2(1*H*)-ylidene]- (**3c**), and 5-(1,3-oxazolidin-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-diones (**3d**), respectively, in moderate to excellent yields together with sulfur. Quantities of reactants, reaction times, yields, and mps of compounds **2** and **3** are summarized in Table 1.



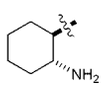
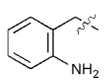
Scheme 1

Table 1 shows that the reactions of **1** with primary alkylamines are completed within 5 min, whereas the reaction with *t*-$BuNH_2$ (entry 4) needs more time presumably due to the steric bulkiness. The longer reaction time observed for the reaction with 2-aminobenzylamine (entry 7) may be due to a weak nucleophilicity of the arylamine compared with alkylamines. Yields of **2** and **3**, except for **2d**, are excellent and it is a promising method for the preparation of (alkylamino)- and (arylamino)(cyano)methylidene derivatives of Meldrum's acid,

† Analytical and spectroscopic data for compounds **2a–d**, **3a–d** and **7–9** are available as supplementary data. For direct electronic access see http://www.rsc.org/suppdata/p1/b0/b003109g/

DOI: 10.1039/b003109g

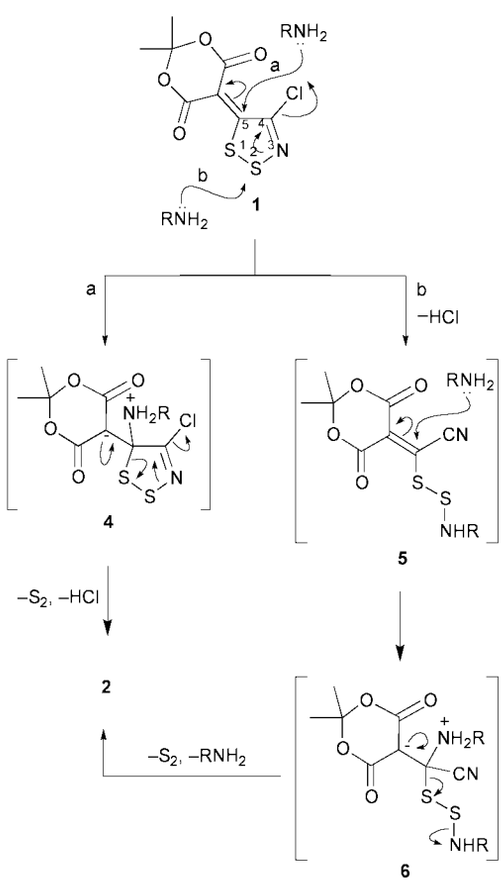
Table 1 Quantities of reactants, reaction times, yields, and mps of **2** and **3**

Entry	**1**/mmol	RNH_2/mmol	Time	Yield[a] (%) Compd.		S_8	Mp[b] (*T*/°C)
1	0.765	R = *n*-Pr 1.58	5 min	**2a**	95	82	127–128
2	1.85	R = *n*-Hexyl 3.78	5 min	**2b**	83	93	59–60
3	1.47	R = *i*-Pr 3.40	5 min	**2c**	94	93	166–167 (decomp.)
4	1.64	R = *t*-Bu 3.81	19 h	**2d**	55	59	119–121
5	0.751	R = $CH_2CH_2NH_2$ 1.62	5 min	**3a**	89	50	194–195
6	0.740	R =  1.50	5 min	**3b**	86	80	234–235
7	0.761	R =  1.53	3 h	**3c**	96	100	183–184[c]
8	0.708	R = CH_2CH_2OH 1.49	5 min	**3d**	93	77	197–198 (decomp.)

[a] Isolated yields. [b] Melting points of **2** and **3**. Recrystallized from a mixture of *n*-hexane and CH_2Cl_2 except for **2b** (*n*-hexane). [c] White solids except for **3c** (pale yellow).

which, to the best of our knowledge, have never been reported in the literature.

The mechanism for the formation of **2** may be explained by nucleophilic attack of amines on C(5) to give an intermediate **4** (path a, Scheme 2). Subsequent loss of S_2 and HCl would give **2**. Alternatively, the amine could attack S(2), yielding amino disulfides **5** (path b), which subsequently react with another molecule of amine to give an intermediate **6**. Migration of electrons concomitant with loss of S_2 and amine would give **2**.



Scheme 2

Analogous mechanisms involving both path a and path b have been proposed for the formation of *N′*-(*p*-tolylsulfonyl)-*N*-alkyl- and *N*,*N*-dialkylcyanoformamidine from the reactions of 4-chloro-5-(*p*-tolylsulfonylimino)-5*H*-1,2,3-dithiazole with primary and secondary alkylamines in CH_2Cl_2 at rt,[14] whereas the reactions of 5-arylimino-4-chloro-5*H*-1,2,3-dithiazoles with alkylamines under the same conditions proceed to give *N′*-aryl-*N*-alkylcyanoformamidines *via* amino disulfides analogous to the intermediate **5**.[13] Since not only has the amino disulfide **5** not been detected, but also the negative charge at C(5) of the Meldrum's acid moiety of **4** can be efficiently stabilized by two ester carbonyl groups, path a is more likely to be involved than path b. This view is supported by the fact that when more bulky amines such as secondary dialkylamines are employed, the reactions follow path b to avoid the steric interaction arising from nucleophilic attack on C(5) of the dithiazole moiety (*vide infra*).

Reactions with secondary alkylamines

The reactions of **1** with secondary alkylamines under the same conditions as for primary alkylamines afforded 5-(4-dialkylamino-5*H*-1,2,3-dithiazol-5-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-diones (**7**), 6-carbamoyl-5-oxo-5*H*-furo[2,3-*d*][1,2,3]-dithiazoles (**8**), and 5-[(dialkylamino)(cyano)methylidene]-2,2-dimethyl-1,3-dioxane-4,6-diones (**9**) together with sulfur and bisamino sulfides ($R_2NS_xNR_2$) (Scheme 3). Quantities of reactants, reaction times, and yields of compounds **7**, **8**, **9**, sulfur, and bisamino sulfides are summarized in Table 2.

Interestingly, the reactions with acyclic dialkylamines (entries 1–7) did not give compounds **9**, which are analogous to compounds **2**, obtained from the reactions with primary alkylamines. However, cyclic amines such as pyrrolidine (entry 8) and piperidine (entry 9) gave the expected compounds **9a** and **9b**, respectively as major products. This result may be rationalized in terms of the steric effect by which pyrrolidine and piperidine are sterically less hindered amines compared with the corresponding acyclic dialkylamines such as diethylamine and dipropylamine. Therefore, **9a** and **9b** may be formed *via* path a in Scheme 2. Compounds **7a**–**e**, **8a**–**g**, and **9a**–**b** are all unknown. Attempts to obtain ^{13}C NMR spectra of compounds **7a**–**c** and **7e** were unsuccessful owing to their low solubility. The assignment of the structures of compounds **7** was supported by

Table 2 Quantities of reactants, reaction times, yields of compounds **7**, **8**, **9**, sulfur, and bisamino sulfides [$(R_2N)_2S_x$]

				Yield[a] (%)							
Entry	**1**/mmol	R_2NH/mmol	Time		**7**		**8**		**9**	S_8	$(R_2N)_2S_x$/mg
1	0.776	R = Et 1.64	1 h	**a**	1	**a**	22		0	10	7
2	0.826	R = *n*-Pr 1.68	1 h	**b**	3	**b**	22		0	8	10
3[b]	0.808	R = *i*-Pr 1.64	5 days		0	**c**	19		0	10	0
4	0.694	R = *n*-Bu 1.42	80 min	**c**	4	**d**	24		0	11	9
5[c]	0.740	R = *i*-Bu 1.55	5 h	**d**	60	**e**	2		0	6	5
6	0.794	R = *n*-Pentyl 1.63	1 h		0	**f**	28		0	6	8
7	0.747	R = Allyl 1.54	22 h	**e**	4	**g**	20		0	17	11
8	3.74	R_2 = –$(CH_2)_4$– 7.68	5 min		0		0	**a**	53	73	0
9	0.797	R_2 = –$(CH_2)_5$– 1.62	5 min		0		0	**b**	18	74	0

[a] Isolated yields. [b] Compound **1** (10%) was recovered. [c] Compound **1** (22%) was recovered.

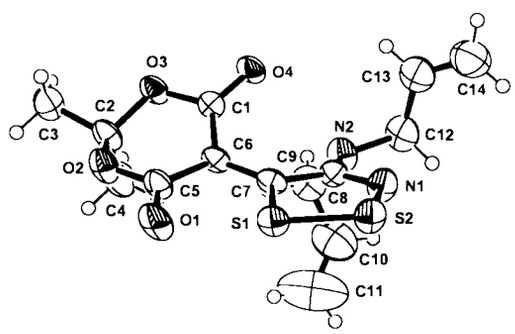
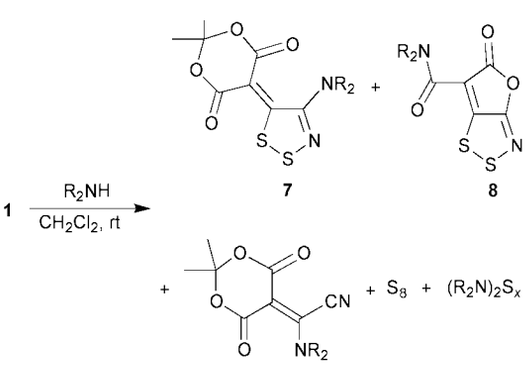


Fig. 1 ORTEP plot of **7e**. Selected bond lengths (Å): S(1)–S(2) 2.0433(19), S(1)–C(7) 1.715(4), C(7)–C(6) 1.400(6), C(6)–C(5) 1.451(6), C(6)–C(1) 1.441(6), C(5)–O(1) 1.215(5), C(1)–O(4) 1.206(5), C(5)–O(2) 1.339(6), C(1)–O(3) 1.368(6), O(2)–C(2) 1.443(5), O(3)–C(2) 1.434(6), O(1)···S(1) 2.528. Selected bond angles (°): S(2)–S(1)–C(7) 93.57(17), S(1)–C(7)–C(6) 119.7(3), C(7)–C(6)–C(5) 117.5(4), C(6)–C(5)–O(1) 123.4(5), C(5)–O(1)···S(1) 97.86, O(1)···S(1)–C(7) 79.16, O(1)···S(1)–S(2) 172.61.



Scheme 3

the X-ray crystal structure of **7e** (Fig. 1). Several resonance structures of **7e** can be envisaged (Fig. 2). Among them, the polar forms **7e-I** and **7e-III**, and a sulfurane structure **7e-II**[15] are considered to be important in view of the X-ray crystallographic data: that is, the bond length C(6)–C(5) of 1.451(6) Å is slightly longer than that of C(6)–C(1) (1.441(6) Å). In addition, the bond length C(5)–O(1) of 1.215(5) Å is slightly greater than that of C(1)–O(4) (1.206(5) Å), which is indicative of some double bond character between the C(5)–C(6) bond and some

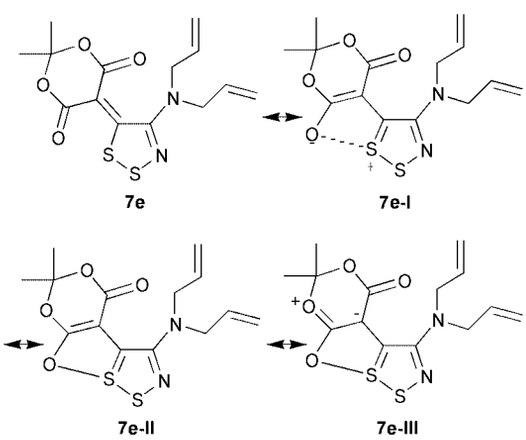


Fig. 2 Resonance structures of **7e**.

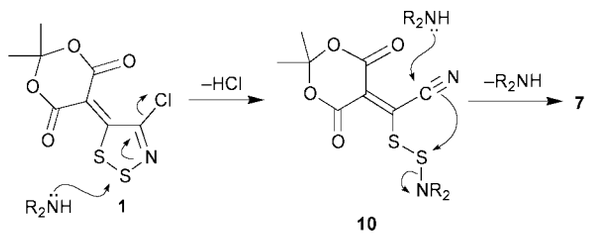
single bond character between the C(5)–O(1) bond, consistent with the structures of **7e-I** and **7e-II**. Moreover, the C(5)–O(2) bond length of 1.339(6) Å is considerably less than that for C(1)–O(3) (1.368(6) Å), which may be indicative of the double bond character of the C(5)–O(2) bond as shown in the structure **7e-III**. The dithiazole ring and the C(5)–O(1) bond extending to S(1) are nearly planar, there being only a 14 to −16° torsional angle shown by the selected torsional angles (°): S(1)–C(7)–C(6)–C(5) −15.5; C(7)–C(6)–C(5)–O(1) 1.7; C(6)–C(5)–O(1)···S(1) 7.3; C(5)–O(1)···S(1)–C(7) −11.9; O(1)···S(1)–C(7)–C(6) 14.0. In addition, there is a short non-bonded O(1)···S(1) contact of 2.528 Å, which is significantly shorter than not only the sum (3.25 Å)[16] of the van der Waals radii 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.[17] A nearly linear relationship between O(1), S(1), and S(2) (angle 172.61 °) may be responsible for the formation of either a polar form or a sulfurane structure.

The formation of **7** with a dialkylamino group instead of a chlorine atom at C(4) of **1** can be explained by a nucleophilic attack of dialkylamine on S(2), with concomitant loss of hydrogen chloride to give an intermediate **10**. This is followed by recyclization of the imino anion formed by addition of dialkylamine to the nitrile carbon atom of **10** (Scheme 4) on the basis of the proposed mechanism for the reaction of 4-dialkylamino-5-arylimino-5*H*-1,2,3-dithiazoles and some dialkylamines.[18] The reactions were repeated at low temper-

Table 3 Reactions of **1** with diethylamine under different conditions

Entry	**1**/mmol	Et_2NH/mmol	Solvent	Temp.	Time (*t*/h)	Yields[a] (%) **7**	**8**	S_8	$(Et_2N)_2S_x$[b]	[d]
1	0.776	1.64	CH_2Cl_2	rt	1	1	22	10	7	27
2	0.774	1.55	THF	rt	1	0	4	21	29	26
3	0.772	1.45	CH_2Cl_2	−78 °C	1	0	0	43	11	54
4	0.794	1.64	CH_2Cl_2	Reflux	0.5	1	16	6	9	58
5[c]	0.751	1.55	CH_2Cl_2	rt	1	3	19	2	2	32

[a] Isolated yields. [b] A mixture of diverse bis(diethylamino) sulfides (mg). [c] Et_2NH was added dropwise to **1** in CH_2Cl_2 for 40 min. [d] Unknown mixtures (mg).

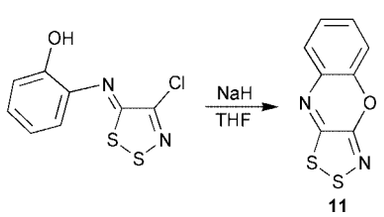


Scheme 4

atures in order to confirm the involvement of the intermediate **10**. For example, the reaction with diisobutylamine did not proceed at −78 °C. As the temperature increased, only the spot corresponding to **7d** was observed on TLC ($R_f = 0.25$, *n*-hexane–ethyl acetate = 5 : 1). The result indicates that the intermediate **10**, once formed (apart from in the case of compounds **2** and **9**), undergoes very rapid reaction with the amine to give **7**.

To the best of our knowledge, compounds **7** are the first examples of 1,2,3-dithiazoles bearing Meldrum's acid moiety at C(5) and an amino group at C(4) albeit in low yields. The reaction with diisobutylamine afforded **7d** in 60% yield, whereas essentially no formation of **7** was observed from the reactions with diisopropylamine (entry 6). It is hard to explain the differences of reactivity of **1** toward such relatively bulky amines. However, the result shows that the reaction site to be attacked by nucleophiles in compound **1** varies with the steric effect of the nucleophiles.

Compounds **8** are products formed by an intramolecular nucleophilic displacement of a chlorine atom at C(4) of **1** by a carboxylate ion. Although yields of **8** are not satisfactory from a synthetic point of view, the formation of **8** is interesting since there has been only one report relating to an intramolecular displacement of the chlorine atom, *i.e.*, formation of dithiazolobenzoxazine (**11**) from 4-chloro-5-[(*o*-hydroxyphenyl)imino]-5*H*-1,2,3-dithiazole and NaH in THF[12] (Scheme 5).



Scheme 5

To find better conditions leading to compound **8a**, the reactions were carried out at different temperatures in different solvents. The results are summarized in Table 3. Table 3 shows that CH_2Cl_2 is a better solvent than THF as far as compound **8** is concerned (entries 1, 3–5, *cf.* 2). At low temperature in CH_2Cl_2 (entry 3), compound **1** decomposed to give sulfur and unknown mixtures, whereas at reflux temperature in CH_2Cl_2 (entry 4), the reaction was completed in a short time. However, the yield of **8** decreased somewhat along with a yield of unknown mixtures twice as high as that obtained at rt (entry 1). Dropwise addition of Et_2NH for 40 min has little effect on the ratio of products (entry 5).

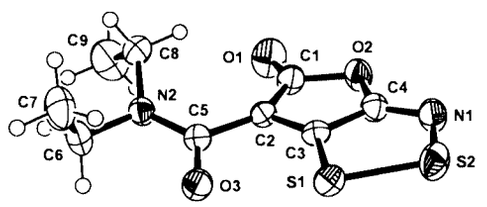


Fig. 3 ORTEP plot of **8a**. Selected bond lengths (Å): S(1)–S(2) 2.1114(13), S(1)–C(3) 1.690(3), C(3)–C(2) 1.363(4), C(2)–C(5) 1.484(4), C(2)–C(1) 1.465(4), C(5)–O(3) 1.235(3), C(1)–O(1) 1.189(4), O(3)···S(1) 2.782. Selected bond angles (°): S(2)–S(1)–C(3) 90.83(11), S(1)–C(3)–C(2) 136.0(2), C(2)–C(5)–O(3) 115.0(3), C(5)–O(3)···S(1) 101.41, O(3)···S(1)–C(3) 67.75, O(3)···S(1)–S(2) 157.83.

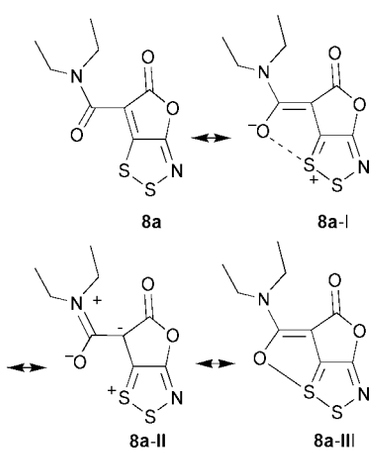


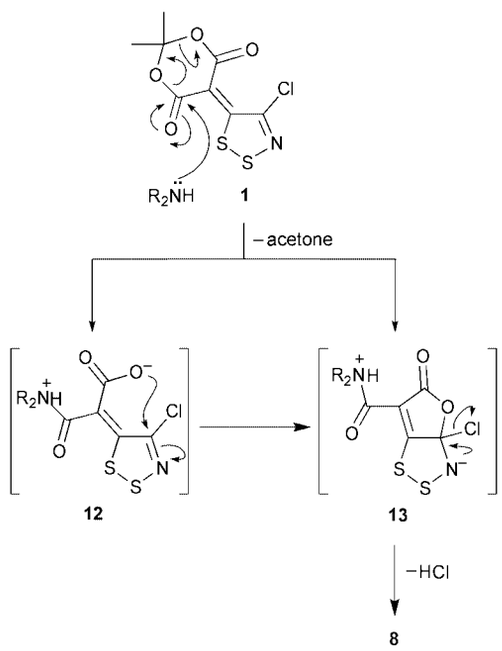
Fig. 4 Resonance structures of **8a**.

The structures of compounds **8** were determined based on the spectroscopic (IR, ^1H and ^{13}C NMR) and analytical data, as well as the X-ray crystal structure of **8a** (Fig. 3). Compound **8a** may be represented by several resonance structures (Fig. 4), of which one can envisage the polar structures **8a-I** and **8a-II** and a sulfurane structure **8a-III**.

Fig. 3 clearly shows that the amide carbonyl group is *syn* to S(1) of **8a**. There is a decrease in the S(1)–C(3) (1.690(3) Å) bond length compared with the S(1)–C(7) (1.715(4) Å) bond length of **7e**, whereas the C(2)–C(5) (1.484(4) Å) bond of **8a** is slightly longer than the C(5)–C(6) (1.451(6) Å) bond of **7e**, which may reflect the contribution of the resonance form **8a-II**. However, the dithiazole ring and the O(3)–C(5) bond extending to S(1) are nearly coplanar, as shown by the selected torsional angles (°): S(1)–C(3)–C(2)–C(5) −0.7; C(3)–C(2)–C(5)–O(3) −15.3; C(2)–C(5)–O(3)···S(1) 16.2; C(5)–O(3)···S(1)–C(3) −13.4, O(3)···S(1)–C(3)–C(2) 7.2. In addition, there is a short nonbonded O···S contact of 2.782 Å between O(3) and S(1) which is significantly shorter than the sum of the van der Waals radii. Nevertheless, in view of the angle, O(3)···S(1)–S(2) of

157.83°, which deviates considerably from 180°, the polar structures **8a-I** and **8a-II** may be more important than the sulfurane **8a-III**.

The formation of **8** may be explained by nucleophilic attack of the dialkylamine on the carbonyl carbon of **1**, which is *cis* to S(1) (Scheme 6). Subsequent extrusion of acetone would gener-



Scheme 6

ate a carboxylate anion **12**, which engages in an intramolecular nucleophilic attack on C(4) of the dithiazole ring to displace a chlorine atom *via* intermediate **13**. Elimination of HCl would give **8**. Alternatively, the intermediate **13** can be formed by a concerted mechanism without the intermediacy of **12**. At this moment, it is uncertain whether the reaction proceeds by a concerted or a stepwise mechanism.

It is notable that the spectroscopic data for compounds **9a** and **9b** show very great polarization of the C=C double bond [**9a**: δ_C 89.1 ppm (=*C*$(CO)_2$) and 139.1 ppm (=*C*(N)(CN)). **9b**: δ_C 88.7 ppm (=*C*$(CO)_2$) and 142.0 ppm (=*C*(N)(CN))] and 2 carbonyl carbons as apparently equivalent (**9a**: δ_C 161.0 ppm. **9b**: δ_C 161.2 ppm) but these are noted as being broad. This may indicate a significant contribution from a fully charge-separated form in which there is a single bond and thus free rotation of the C(CN)(NR_2) group.[19]

The reactions of **1** with dialkylamines gave mixtures corresponding to bis(dialkylamino) sulfides, R_2N-S_x-NR_2 (x = 1, 2, 3, *etc.*), which was confirmed by ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry. Separation of the mixtures either by column chromatography or HPLC was unsuccessful.

In summary, the reactions of 5-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione with primary alkylamines in CH_2Cl_2 at rt afforded 5-[(alkylamino)(cyano)-methylidene]-2,2-dimethyl-1,3-dioxane-4,6-diones (**2**) in excellent yields, whereas the same reactions with secondary alkylamines under the same conditions yielded 5-(4-dialkylamino-5*H*-1,2,3-dithiazol-5-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-diones (**7**), 6-carbamoyl-5-oxo-5*H*-furo[2,3-*d*][1,2,3]dithiazoles (**8**), and 5-[(dialkylamino)(cyano)methylidene]-2,2-dimethyl-1,3-dioxane-4,6-diones (**9**) whose yields are variable, depending on the bulkiness of dialkylamines. A noteworthy result is that the reaction with diisobutylamine gave **7** with a diisobutylamino group at C(4) of the dithiazole ring as a major product. Products **8** are new compounds formed by an intramolecular displacement of a chlorine atom at C(4) of the dithiazole ring, which is seldom reported.

Experimental

The ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75 MHz in $CDCl_3$ solution containing Me_4Si as an internal standard; *J*-values are given in Hz. IR spectra were recorded in KBr or for thin-film samples on KBr plates. Elemental analyses were determined by the Inter-University Center for Natural Science Research facilities, Seoul National University. Column chromatography was performed using silica gel (70–230 and 230–400 mesh, Merck). Mps were determined on a Fisher-Johns melting point apparatus and are uncorrected.

4,5-Dichloro-5*H*-1,2,3-dithiazolium chloride[20] and 5-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (**1**)[12] were prepared according to the documented procedures.

General procedure for the reactions of 1 with primary alkylamines

To a solution of **1** (0.71–1.9 mmol) in CH_2Cl_2 (30 mL) was added the alkylamine (1.5–3.8 mmol) in one portion. The mixture was stirred for an appropriate time at rt. After removal of the solvent *in vacuo*, the residue was chromatographed on a silica gel column (70–230 mesh, 2.5 × 10 cm for **2a** and **3c**; 70–230 mesh, 2.5 × 5 cm for **3a**, **3b**, and **3d**; 230–400 mesh, 2.5 × 12 cm for **2b**; 230–400 mesh, 2.5 × 7 cm for **2c**; 230–400 mesh, 2.5 × 15 cm for **2d**). Elution with *n*-hexane gave sulfur. Subsequent elution with a mixture of *n*-hexane and EtOAc (3 : 1 for **2a**; 4 : 1 for **2b** and **2d**; 2 : 1 for **2c** and **3b**–**c**; 1 : 5 for **3a**) or EtOAc (**3d**) afforded compounds **2** and **3**. Consult Table 1 for quantities of reactants, reaction times, yields and mps of **2a**–**d** and **3a**–**d**. Analytical and spectroscopic data for compounds **2a**–**d** and **3a**–**d** are available as supplementary information.

General procedure for the reactions of 1 with secondary alkylamines

To a solution of **1** (0.69–7.7 mmol) in CH_2Cl_2 (30 mL) was added the dialkylamine (1.6–7.7 mmol) in one portion. The mixture was stirred for an appropriate time at rt and worked up as described in the general procedure for the reaction with primary alkylamines. Chromatography (70–230 mesh, 2.5 × 15 cm in the cases of R_2NH = $(i\text{-Pr})_2NH$, $(i\text{-Bu})_2NH$, $(n\text{-pentyl})_2NH$, pyrrolidine; 230–400 mesh, 2.5 × 12 cm in the cases of R_2NH = Et_2NH, $n\text{-Pr}_2NH$, $n\text{-Bu}_2NH$, $(allyl)_2NH$, piperidine) of the reaction mixture with *n*-hexane gave sulfur and bis(dialkylamino) sulfides. Subsequent elution with a mixture of *n*-hexane and EtOAc (3 : 1 for 5-(4-diethylamino-5*H*-1,2,3-dithiazol-5-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (**7a**) and 6-diethylcarbamoyl-5-oxo-5*H*-furo[2,3-*d*][1,2,3]dithiazole (**8a**); 5 : 1 for 2,2-dimethyl-5-(4-di-*n*-propylamino-5*H*-1,2,3-dithiazol-5-ylidene)-1,3-dioxane-4,6-dione (**7b**), 6-di-*n*-propylcarbamoyl-5-oxo-5*H*-furo[2,3-*d*][1,2,3]dithiazole (**8b**), 6-diisopropylcarbamoyl-5-oxo-5*H*-furo[2,3-*d*][1,2,3]dithiazole (**8c**), 5-(4-diisobutylamino-5*H*-1,2,3-dithiazol-5-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (**7d**), and 6-diisobutylcarbamoyl-5-oxo-5*H*-furo[2,3-*d*][1,2,3]dithiazole (**8e**); 7 : 1 for 5-(4-diallylamino-5*H*-1,2,3-dithiazol-5-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (**7e**), 6-diallylcarbamoyl-5-oxo-5*H*-furo[2,3-*d*]-[1,2,3]dithiazole (**8g**), and 6-di-*n*-pentylcarbamoyl-5-oxo-5*H*-furo[2,3-*d*][1,2,3]dithiazole (**8f**); 10 : 1 for 5-(4-di-*n*-butylamino-5*H*-1,2,3-dithiazol-5-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (**7c**) and 6-di-*n*-butylcarbamoyl-5-oxo-5*H*-furo[2,3-*d*]-[1,2,3]dithiazole (**8d**)) gave compounds **7** and **8**. In the cases of R_2NH = $(i\text{-Pr})_2NH$ and $(i\text{-Bu})_2NH$, continuous elution with a mixture of *n*-hexane and EtOAc (3 : 1) and the same solvent mixture (5 : 1) gave unreacted **1** in 10 and 22% yields, respectively. In the cases of R_2NH = pyrrolidine and piperidine, 5-[(cyano)(pyrrolidino)methylidene]-2,2-dimethyl-1,3-dioxane-4,6-dione (**9a**) and 5-[(cyano)(piperidino)methylidene]-2,2-

Table 4 Crystal data and structure refinement for **7e** and **8a**

	7e	**8a**
Chemical formula	$C_{14}H_{16}N_2O_4S_2$	$C_9H_{10}N_2O_3S_2$
Formula weight, M	340.41	258.31
Crystal system	Triclinic	Monoclinic
Unit cell dimensions	a = 7.389(2) Å	a = 7.517(2) Å
	α = 109.600(10)°	α = 90.000(10)°
	b = 10.165(2) Å	b = 19.328(2) Å
	β = 107.55(2)°	β = 107.39(2)°
	c = 12.128(3) Å	c = 7.9740(10) Å
	γ = 94.24(2)°	γ = 90.000(10)°
Volume, U/Å^3	802.5(3)	1105.6(3)
Temperature, T/K	293(2)	293(2)
Space group	$P\bar{1}$ (No. 2)	$P2(1)/n$ (No. 14)
Z	2	4
Linear absorption coefficient, μ/mm^{-1}	0.350	0.474
Reflections collected	1890	1506
Independent reflections	1767 [R(int) = 0.0391]	1388 [R(int) = 0.0158]
Final R indices	R_1 = 0.0550	R_1 = 0.0391
[$I > 2\sigma(I)$]	wR_2 = 0.1496	wR_2 = 0.0907
R indices (all data)	R_1 = 0.0587	R_1 = 0.0413
	wR_2 = 0.1528	wR_2 = 0.0926

dimethyl-1,3-dioxane-4,6-dione (**9b**) were obtained by elution with 1 : 2 and 1 : 5 mixtures of *n*-hexane and EtOAc, respectively. Consult Table 2 for quantities of reactants, reaction times, yields of compounds **7**, **8**, **9**, and bis(dialkylamino) sulfides $[(R_2N)]_2S_x$. Mps and analytical and spectroscopic data of **7**, **8** and **9** are available as supplementary information.

Crystal structure determination of compounds 7e and 8a

Crystal data and structure refinement for **7e** and **8a** are summarized in Table 4. Single crystals of **7e** and **8a** were obtained from concentrated solutions in a mixture of *n*-hexane and CH_2Cl_2. The data were collected on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo-Kα radiation. CCDC reference number 207/460. See http://www.rsc.org/suppdata/p1/b0/b003109g for crystallographic files in .cif format.

Acknowledgements

The authors are grateful for the financial support of the Korea Research Foundation made in the program of 1999.

References

1 (*a*) C. Wentrup, V. V. R. Rao, W. Frank, B. E. Fulloon, D. W. J. Moloney and T. Mosandl, *J. Org. Chem.*, 1999, **64**, 3608; (*b*) D. W. J. Moloney, M. W. Wong, R. Flammang and C. Wentrup, *J. Org. Chem.*, 1997, **62**, 4240; (*c*) D. Clarke, R. W. Mares and H. McNab, *J. Chem. Soc.*, *Perkin Trans. 1*, 1997, 1799; (*d*) B. E. Fulloon and C. Wentrup, *J. Org. Chem.*, 1996, **61**, 1363; (*e*) F. Jourdain and J. C. Pommelet, *Tetrahedron Lett.*, 1994, **35**, 1545; (*f*) H. McNab and K. Withell, *Tetrahedron*, 1996, **52**, 3163; (*g*) C. O. Kappe, G. Kollenz, R. Leung-Toung and C. Wentrup, *J. Chem. Soc.*, *Chem. Commun.*, 1992, 487; (*h*) C. Wentrup, H. Briehl, P. Lorencak, U. J. Vogelbacher, H.-W. Winter, A. Maquestiau and R. Flammang, *J. Am. Chem. Soc.*, 1988, **110**, 1337; (*i*) A. Gómez-Sánchez, M. de G. G. Martin and P. Borrachero, *J. Chem. Soc.*, *Perkin Trans. 2*, 1987, 301.

2 (*a*) A. B. Ben Cheikh, J. Chuche, N. Manisse, J. C. Pommelet, K.-P. Netsch, P. Lorencak and C. Wentrup, *J Org. Chem.*, 1991, **56**, 970; (*b*) H. Briehl, A. Lukosch and C. Wentrup, *J. Org. Chem.*, 1984, **49**, 2772; (*c*) G. A. Bihlmayer, G. Derflinger, J. Derkosch and O. E. Polansky, *Monatsh. Chem.*, 1967, **98**, 564; (*d*) O. S. Wolfbeis, *Monatsh. Chem.*, 1981, **112**, 369; (*e*) H. J. Gordon, J. C. Martin and H. McNab, *J. Chem. Soc.*, *Perkin Trans. 1*, 1984, 2129; (*f*) R. Cassis, R. Tapia and J. A. Valderrama, *Synth. Commun.*, 1985, **15**, 125.

3 F. E. Ziegler, T. Guenther and R. V. Nelson, *Synth. Commun.*, 1980, **10**, 661.

4 (*a*) A. Stephen, *Monatsh. Chem.*, 1966, **97**, 695; (*b*) M. Augustin and E. Guenther, *Z. Chem.*, 1990, **30**, 169.

5 H. K. Lee, J. P. Lee, G. H. Lee and C. S. Pak, *Synlett*, 1996, 1209.

6 M. Augustin and E. Guenther, *Z. Chem.*, 1987, **27**, 68.

7 (*a*) Y. Yamamoto, Y. Morita and K. Minami, *Chem. Pharm. Bull.*, 1986, **34**, 1980; (*b*) J.-P. Célérier, E. Deloisy, P. Kapron, G. Lhommet and P. Maitte, *Synthesis*, 1981, 130; (*c*) P. Kapron, G. Lhommet and P. Maitte, *Tetrahedron Lett.*, 1981, **22**, 2255.

8 (*a*) J.-P. Célérier, M. G. Richaud and G. Lhommet, *Synthesis*, 1983, 195; (*b*) M. Huché and G. Lhommet, *J. Heterocycl. Chem.*, 1986, **23**, 701.

9 X. Huang and B.-C. Chen, *Synthesis*, 1986, 967.

10 (*a*) F.-C. Ye, B.-C. Chen and X. Huang, *Synthesis*, 1989, 317; (*b*) X. Huang and B.-C. Chen, *Synthesis*, 1987, 480; (*c*) B.-C. Chen. X. Huang and J. Wang, *Synthesis*, 1987, 482.

11 M.-K. Jeon and K. Kim, *Tetrahedron*, 1999, **55**, 9651.

12 K. Emayan, R. F. English, P. A. Koutentis and C. W. Rees, *J. Chem. Soc.*, *Perkin Trans. 1*, 1997, 3345.

13 H. Lee and K. Kim, *J. Org. Chem.*, 1993, **58**, 7001.

14 K. C. Oh, H. Lee and K. Kim, *Tetrahedron Lett.*, 1992, **33**, 4963.

15 K. Ohkata, M. Ohsugi, K. Yamamoto, M. Ohsawa and K.-y. Akiba, *J. Am. Chem. Soc.*, 1996, **118**, 6355.

16 A. Kucsman and I. Kapovits, in *Organic Sulfur Chemistry*: *Theoretical and Experimental Advances*, ed. I. G. Csizmadia, A. Mangini and F. Bernardi, Elsevier, Amsterdam, 1985, p. 191.

17 R. F. Hudson, J. D. Wallis and D. P. Hansell, *Heterocycles*, 1994, **37**, 1933.

18 H. Lee, K. Kim, D. Whang and K. Kim, *J. Org. Chem.*, 1994, **59**, 6179.

19 The authors gratefully acknowledge the comments of one of the referees.

20 R. Appel, H. Janssen, M. Siray and F. Knoch, *Chem. Ber.*, 1985, **118**, 1632.