Preparation of New Nitrogen-Bridged Heterocycles. 35.[1] Smooth Synthesis of 10a*H*-Pyrido[1,2-*d*][1,4]thiazepine Derivatives

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Various 1-pyridinio(thiocarbonyl)methylides and 2-isoquinolinio(thiocarbonyl)methylides react smoothly with dimethyl acetylenedicarboxylate at room temperature or at the reflux temperature in chloroform to give new heterocycles, dimethyl 10a*H*-pyrido[1,2-*d*][1,4]thiazepine-1,2-dicarboxylate derivatives, in moderate yields. Similarly, the reactions of some 3-(1-pyridinio)thiophene-2-thiolates with the same reagent afforded the corresponding dimethyl 6a*H*-pyrido[1,2-*d*]thieno[2′,3′-*b*][1,4]thiazepine-5,6-dicarboxylates. The structures of these 1,4-thiazepine derivatives were mainly assigned based on physical and spectral inspections, and were finally confirmed by X-ray analyses of three compounds.

In recent years we have developed two novel synthetic methods for polyfunctionalized indolizine and pyrazolo[1,5-*a*]pyridine derivatives using various 1-pyridinio(thiocarbonyl)methylides or 1-pyridinio(thiocarbonyl)amides as a starting meterial.[2,3] In both routes the most important step of the reactions is the exclusive attack of an alkylating agent on the thiolate anion in the betaine structure **B** (See Fig. 1) of these pyridinium ylides; this means that the nucleophilicity of the sulfur atom in the betaine structure **B** is higher than that of the cabanion in the ylide structure **A**. On the other hand, it is also well known that a variety of pyridinium ylides have a remarkable character as a 1,3-dipole, and that their reactions with various olefinic and acetylenic dipolarophiles give the corresponding 1,3-dipolar cycloadducts.[4] The large contribution of the betaine structure **B** in pyridinium ylides bearing a thiocarbonyl group at the ylidic anion prompted us to examine their reactions with some electron-poor unsaturated substrates. We found a new constructive method for a 1,4-thiazepine skeleton in their reactions with dimethyl acetylenedicarboxylate (DMAD).[5] In this paper we report on details concerning the syntheses of 10a*H*-pyrido[1,2-*d*][1,4]thiazepines, 6a*H*-pyrido[1,2-*d*]thieno[2′,3′-*b*]-[1,4]thiazepines, and 12b*H*-1,4-thiazepino[5,4-*a*]isoquinolines from the reactions of DMAD with 1-pyridinio(thiocarbonyl)methylides, 3-(1-pyridinio)thiophene-2-thiolates, and 2-isoquinolinio(thiocarbonyl)methylides, respectively.

Results and Discussion

Preparations of Pyridothiazepine Derivatives. Although the reactions of 1-pyridinio[cyano[(methylthio)thiocarbonyl]]methylide (**1a**) with electron-poor olefins, such as diethyl fumarate, were examined while expecting the participation of the betaine structure **B**, no significant product could be obtained. On the other hand, the same ylide **1a** reacted smoothly with an acetylenic reagent (DMAD, **2**) in chloroform at room temperature to give a red crystalline product **3a** in 34% yield. Similar reactions of the other 1-pyridiniomethylides **1b**—**l** with **2** afforded the corresponding adducts **3b**—**l** in 13—49% yields (Scheme 1).

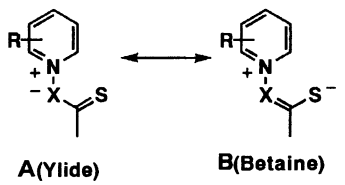
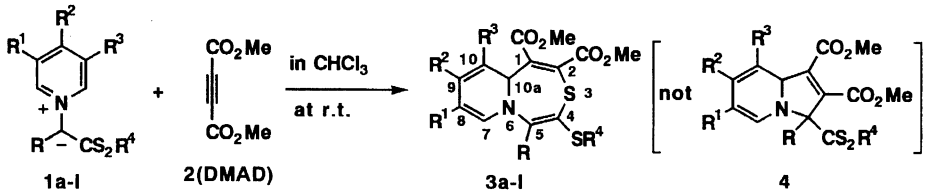


Fig. 1.

Similarly, 3-(1-pyridinio)thiophene-2-thiolates (**5a**—**i**) were reacted with **2** in chloroform at room temperature to yield the corresponding crystalline products **6a**—**i** in 16—70% yields, respectively (Scheme 2). On the other hand, isoquinolinium ylides **7a**—**c** did not react with **2** at room temperature, but reacted in chloroform at the reflux temperature to give the expected compounds **8a**—**c** in 33—50% yields, respectively (Scheme 3). In the above-mentioned reactions no other product, except for **3a**—**l**, **6a**—**i**, and **8a**—**c**, could be detected.

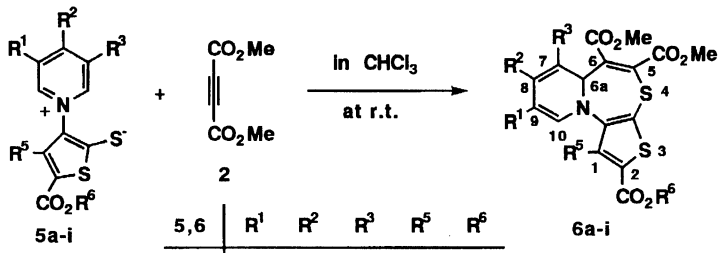
Elemental analyses clearly showed that products **3a**—**g**, **i**—**l**, **6a**—**i**, and **8a**—**c** are 1:1 adducts of pyridinium ylides **1a**—**g**, **i**—**l**, **5a**—**i**, and **7a**—**c** and DMAD (**2**). The IR spectra of compounds **3a**—**f** each exhibited one α,β-unsaturated cyano absorption band at 2205—2218 cm^{-1}, indicating that they are not primary 1,3-dipolar adducts, the 3,8a-dihydroindolizine derivative, such as **4** (see Scheme 1). Furthermore, the ^1H NMR spectra (Table 1) of products **3a**—**l**, **6a**—**i**, and **8a**—**c** distinctly showed the presence of a nonaromatic dihydropyridine moiety in these molecules based on signals appearing at δ=4.58—6.99 (ring proton) and δ=1.26—1.95 (ring methyl protons). From these results, we concluded that compounds **3a**—**l**, **6a**—**i**, and **8a**—**c** are dimethyl 10a*H*-pyrido[1,2-*d*][1,4]thiazepine-1,2-dicarboxylates, dimethyl 6a*H*-pyrido[1,2-*d*]thieno-[2′,3′-*b*][1,4]thiazepine-5,6-dicarboxylates, and dimethyl 12b*H*-1,4-thiazepino[5,4-*a*]isoquinoline-1,2-dicarboxylates, respectively. However, because the ambiguity for these structural assignments still remained to some extent, we carried out X-ray analyses for three new skeletal compounds, and finally confirmed our proposed



1a-l 2(DMAD) 3a-l 4

1,3	R	R^1	R^2	R^3	R^4	1,3	R	R^1	R^2	R^3	R^4
a	CN	H	H	H	Me	g	COPh	H	H	H	Me
b	CN	H	Me	H	Me	h	COPh	H	Me	H	Me
c	CN	Me	H	Me	Me	i	COPh	Me	H	Me	Me
d	CN	H	H	H	Et	j	COPh	H	H	H	Et
e	CN	H	Me	H	Et	k	COPh	H	Me	H	Et
f	CN	Me	H	Me	Et	l	COPh	Me	H	Me	Et

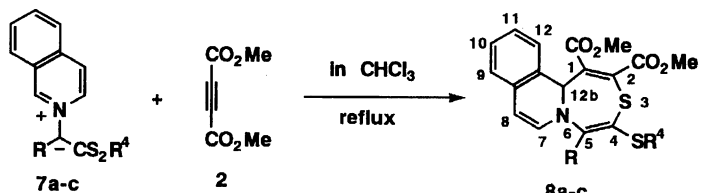
Scheme 1.



5a-i 2 6a-i

5,6	R^1	R^2	R^3	R^5	R^6
a	H	H	H	Me	Me
b	H	Me	H	Me	Me
c	Me	H	Me	Me	Me
d	H	H	H	Me	Et
e	H	Me	H	Me	Et
f	Me	H	Me	Me	Et
g	H	H	H	Ph	Et
h	H	Me	H	Ph	Et
i	Me	H	Me	Ph	Et

Scheme 2.



7a-c 2 8a-c

7,8	R	R^4
a	CO_2Et	Me
b	CO_2Et	Et
c	COPh	Me

Scheme 3.

Table 1. ^{1}H NMR Spectral Data of Pyrido[1,2-*d*][1,4]thiazepines

Compd[a,b] No.	δ ($CDCl_3$)									
	C-7	C-8	C-9	C-10	C-10a	R^4 (or R^6)		R (or R^5)	Esters	
3a	6.65	5.26	6.20	5.46	5.87	2.52		—	3.71	3.78
	br d	br t	m	m	d	s			s	s
3b	6.54	5.11	1.77	5.11	5.79	2.49		—	3.68	3.75
	d	dd	s	br d	d	s			s	s
3c	6.23	1.71	5.75	1.88	5.75	2.48		—	3.69	3.77
	br s	s	br s	s	s	s			s	s
3d	6.62	5.27	6.23	5.46	5.85	1.37	2.92	—	3.75	3.81
	d	br t	m	m	d	t	q		s	s
3e	6.59	5.17	1.78	5.17	5.80	1.37	2.91	—	3.76	3.82
	d	br d	s	br d	d	t	q		s	s
3f	6.25	1.68	5.72	1.83	5.72	1.31	2.92	—	3.72	3.78
	br s	s	br s	s	s	t	q		s	s
3g	c)	4.90	c)	5.44	c)	2.14		7.3—8.3	3.71	3.79
		br t		br q		s		m	s	s
3h	6.41	4.82	1.82	5.21	5.95	2.13		7.3—8.3	3.72	3.79
	d	br d	s	br d	d	s		m	s	s
3i	6.03	1.50	5.63	1.88	5.70	2.03		7.3—8.3	3.67	3.76
	br s	s	br s	s	s	s		m	s	s
3j	d)	4.98	d)	5.51	d)	1.12	2.70	7.3—8.3	3.73	3.79
		t		q		t	q	m	s	s
3k	6.00	4.75	1.67	5.16	6.00	1.08	2.62	7.3—8.3	3.66	3.74
	d	dd	s	br d	d	t	q	m	s	s
3l	6.05	1.55	5.71	1.95	5.71	1.11	2.68	7.3—8.3	3.73	3.82
	br s	s	br s	s	s	t	q	m	s	s
6a	6.28	e)	6.13	5.1—5.6		3.81		2.41	3.75	3.87
	d		m	m		s		s	s	s
6b	6.20	f)	1.84	4.9—5.5		3.84		2.41	3.72	3.77
	d		s	m		s		s	s	s
6c	5.88	1.72	5.80	1.92	5.33	3.78		2.30	3.67	3.76
	br s	s	br s	s	s	s		s	s	s
6d	6.28	e)	6.13	5.1—5.6		1.37	4.33	2.38	3.73	3.80
	d		m	m		t	q	s	s	s
6e	6.17	g)	1.81	4.8—5.4		1.35	4.31	2.39	3.70	3.77
	d		s	m		t	q	s	s	s
6f	5.93	1.74	5.83	1.94	5.35	1.34	4.29	2.33	3.72	3.78
	br s	s	br s	s	s	t	q	s	s	s
6g	5.55	4.74	6.01	5.23	5.82	1.17	4.16	7.36	3.70	3.79
	br d	br t	q	br t	d	t	q	br s	s	s
6h	5.44	4.58	1.66	4.91	5.71	1.15	4.10	7.30	3.64	3.74
	d	dd	s	br d	d	t	q	br s	s	s
6i	5.30	1.26	5.69	1.92	5.74	1.16	4.16	7.32	3.69	3.83
	br s	s	br s	s	s	t	q	br s	s	s
8a	6.11	5.61	6.8—7.4[h]		6.62	2.35		1.28 4.20	3.20	3.68
	d	d	m		s	s		t q	s	s
8b	6.13	5.56	6.8—7.4[h]		6.60	1.26	2.82	1.28 4.17	3.23	3.66
	d	d	m		s	t	q	t q	s	s
8c	6.06	5.40	6.8—8.2[h]		6.99	2.09		6.8—8.2	3.27	3.76
	d	d	m		s	s		m	s	s

a) For the dihydropyridine moiety in compounds **6a**—**i** and **8a**—**c**, the same numberings with that in non-fused compounds **3a**—**l** were used. b) The coupling constants are as follows: $J_{7,8}=8.0$, $J_{8,9}=7.0$, $J_{9,10}=6.0$, and $J_{10,10a}=6.5$. c) Overlapped with the signals appeared at $\delta=5.8$—6.3. d) Overlapped with the signals appeared at $\delta=5.9$—6.3. e) Overlapped with the signals appeared at $\delta=5.1$—5.6. f) Overlapped with the signals appeared at $\delta=4.9$—5.5. g) Overlapped with the signals appeared at $\delta=4.8$—5.4. h) Four proton signals of the fused benzene ring.

structures (see below).

Crystallography of Pyridothiazepine Derivatives. The crystal and structure analysis data as well as selected bond lengths and angles for dimethyl 5-cyano-4-methylthio-10a*H*-pyrido[1,2-*d*][1,4]thiazepine-1,2-dicarboxylate (**3a**), 2-ethyl 5,6-dimethyl 1-phenyl-

Table 2. Crystal and Structure Analysis Data of Compounds **3a**, **6g**, and **8a**

	3a	**6g**	**8a**
Formula	$C_{15}H_{14}N_2O_4S_2$	$C_{24}H_{21}NO_6S_2$	$C_{21}H_{21}NO_6S_2$
Formula weight	350.41	483.55	447.52
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$; Z=8	$C2/c$; Z=16	$P2_1/n$; Z=2
Lattice parameters			
a/Å	23.975(4)	52.683(4)	7.690(3)
b/Å	7.593(5)	7.450(8)	13.810(4)
c/Å	19.635(4)	24.201(5)	21.074(3)
α/°	90	90	90
β/°	112.38(1)	98.67(1)	96.95(2)
γ/°	90	90	90
V/Å^3	3305(2)	9390(1)	2222(1)
D_{calcd}/g cm^{-3}	1.408	1.368	1.338
Crystal size/mm^3	0.12×0.24×0.46	0.20×0.38×0.60	0.50×0.58×0.80
Diffractometer	Rigaku AFC5S	Rigaku AFC5S	Rigaku AFC5S
Radiation	Mo $K\alpha$ (λ=0.71069 Å)	Mo $K\alpha$ (λ=0.71069 Å)	Mo $K\alpha$ (λ=0.71069 Å)
Monochrometer	Graphite	Graphite	Graphite
Scan type	ω–2θ	ω	ω–2θ
2θ	55.0°	54.9°	55.0°
Computer program	TEXSAN System[a)]	TEXSAN System[a)]	TEXSAN System[a)]
Structure solution	MITHRIL[b)]	MITHRIL[b)]	MITHRIL[b)]
Hydrogen atom treatment	Observed, isotropic	Calculated, not refined	Calculated, not refined
Refinement	Full-matrix, anisotropic	Full-matrix, anisotropic	Full-matrix, anisotropic
Least-squares weight	$4F_o^2/\sigma^2$ (F_o^2)	$4F_o^2/\sigma^2$ (F_o^2)	$4F_o^2/\sigma^2$ (F_o^2)
No. of measurement ref.	Total: 4185 Unique: 4087	Total: 9647 Unique: 9517	Total: 5683 Unique: 5296
No. of observations[c)]	1308	3194	2973
No. of variables	301	595	271
Residuals R; R_w	0.044; 0.045	0.051; 0.054	0.057; 0.077
Max Shift/Error	0.27	0.03	0.14
$\Delta\rho_{max}$/e$^-$ Å^3	0.25	0.31	0.47

a) See Ref. 6. b) Direct method, see Ref. 7. c) $I>3.00\sigma(I)$.

6a*H*-pyrido[1,2-*d*]thieno[2′,3′-*b*][1,4]-thiazepine-2,5,6-tricarboxylate (**6g**), and 5-ethyl 1,2-dimethyl 12b*H*-1,4-thiazepino[5,4-*a*]isoquinoline-1,2,5-tricarboxylate (**8a**) are summarized in Tables 2 and 3. Tables of the coordinates, bond lengths, bond and torsion angles, and F_o-F_c tables are deposited as Document No. 66050 at the Office of the Editor of Bull. Chem. Soc. Jpn. ORTEP drawings[8)] for **3a**, **6g** and **8a** are shown in Figs. 3, 4, and 5. Interestingly, a racemic compound was observed in an X-ray analysis of compound **6g** (see Fig. 4). The crystal data of the pyridothiazepine moiety in compound **3a** were very similar to those in compounds **6g**, and **8a**, expect for those at the fused position of the hetero ring.

Mechanistic Consideration. The possible reaction routes are given in Scheme 4. From the construction of a 1,4-thiazepine skeleton and the absence of a normal 1,3-dipolar cycloadduct, such as **4** or a significant secondary product derived from **4**, it is clear that their reactions occurred via an interaction between the betaine strcuture **9** of pyridinium ylides **1a**—**l**, **5a**—**i**, and **7a**—**c** and DMAD **2**. In the routes leading to final products **3a**—**l**, **6a**—**i**, and **8a**—**c**, however, there is a problem as to whether this reaction proceed via a concerted 1,5-dipolar cycloaddition between **9** and **2** or via an electrophilic addition of acetylenic compound **2** onto the thiolate anion in **9** followed by a 1,7-cyclization of the resulting 1,7-dipole, such as **10**. According to the Woodward–Hoffmann rule,[9)] the former route must be a π6a+π2s process. In general, it is known that an antara process is energetically less favorable in many cycloaddition reactions, and that some special steric or electronic demand is necessary to cause it.[9)] Although the latter stepwise path seems to be mechanistically more favorable, no evidence for it could be obtained in an examination of other reaction conditions, in which another solvent, such as benzene or ethanol, was used in these reaction.

In conclusion, we found that 1-pyridinio(thiocarbonyl)methylides act as extended dipoles having a 6π electron system and react smoothly with an electron-poor acetylenic substrate (DMAD) to afford dimethyl 10a*H*-pyrido[1,2-*d*][1,4]thiazepine-1,2-dicarboxylates (**3a**—**l**), (**6a**—**i**) and (**8a**—**c**), which are not available with ease

Table 3. Selected Bond Lengths and Bond Angles for Compounds **3a**, **6g**, and **8a** (esd's, where given, are in parentheses)

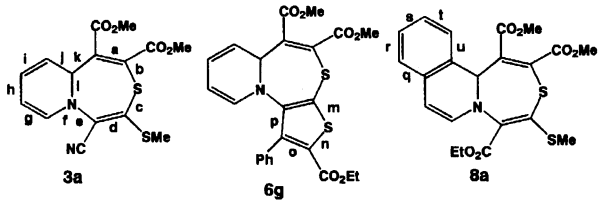


Fig. 2.

	3a	6g[a)]	8a		3a	6g[a)]	8a
Bond lengths[b)]							
a	1.320(8)	1.329(8)	1.334(5)	l	1.474(6)	1.459(7)	1.464(5)
b	1.766(5)	1.772(6)	1.769(4)	m	—	1.722(6)	—
c	1.759(5)	1.759(6)	1.773(4)	n	—	1.726(6)	—
d	1.351(8)	1.380(8)	1.342(5)	o	—	1.369(8)	—
e	1.383(7)	1.407(7)	1.388(5)	p	—	1.429(7)	—
f	1.392(7)	1.387(8)	1.402(5)	q	—	—	1.384(6)
g	1.325(9)	1.336(9)	1.316(6)	r	—	—	1.368(7)
h	1.436(8)	1.442(13)	1.453(6)	s	—	—	1.385(7)
i	1.319(8)	1.310(11)	1.406(5)	t	—	—	1.382(6)
j	1.500(8)	1.504(9)	1.519(5)	u	—	—	1.385(5)
k	1.542(6)	1.532(8)	1.539(5)				
Bond angles[b)]							
ab	124.6(3)	125.0(5)	123.3(3)	cm	—	113.7(3)	—
ak	120.2(4)	120.3(6)	120.0(4)	dm	—	111.4(4)	—
bc	108.1(3)	105.8(3)	106.4(2)	dp	—	112.5(6)	—
cd	131.5(4)	134.7(5)	131.7(3)	mn	—	91.8(3)	—
de	128.1(4)	124.9(5)	127.7(3)	no	—	111.9(4)	—
ef	122.0(4)	121.6(6)	121.4(3)	op	—	112.3(6)	—
el	118.4(4)	118.1(5)	119.0(3)	hq	—	—	123.8(4)
fl	119.2(4)	118.1(5)	118.5(3)	iq	—	—	118.6(4)
fg	121.6(4)	120.2(8)	122.3(4)	iu	—	—	120.0(4)
gh	118.8(6)	118.5(8)	121.4(4)	ju	—	—	119.9(3)
hi	121.2(6)	120.2(8)	117.4(4)	qr	—	—	121.4(4)
ij	121.0(4)	120.9(8)	120.0(3)	rs	—	—	119.8(4)
jk	114.0(4)	113.8(5)	112.5(3)	st	—	—	120.3(4)
jl	109.6(4)	107.5(6)	110.9(3)	tu	—	—	119.9(4)
kl	111.8(3)	112.1(5)	111.2(3)				

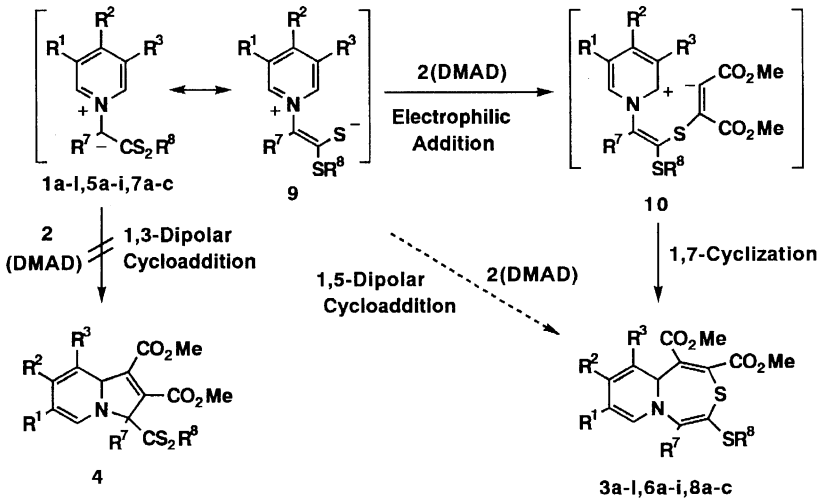
a) The values for only one isomer of the *dl*-mixture were used. b) For the alphabetical symbols of the bond lengths and angles, see Fig. 2.

by other methods.

Experimental

The melting points were measured using a Yanagimoto micromelting point apparatus and were not corrected. Microanalyses were carried out on a Perkin-Elmer 2400 elemental analyzer. The ^{1}H NMR spectra were determined with a Varian EM360A spectrometer in deuteriochloroform with tetramethylsilane used as an internal standard; the chemical shifts are expressed in δ values. The IR spectra were taken with a JASCO FT/IR-5300 infrared spectrophotometer.

Material. 1- Pyridinio(thiocarbonyl)methylides (**1a**—**l**), 3-(1-pyridinio)thiophene-2-thiolates (**5a**—**i**), and 2-isoquinolinio(thiocarbonyl)methylides (**7a**—**c**) were prepared according to the procedures described by us[3b—d,g] and other investigators.[10] The yields and some properties of new ylides are as follows: **1c**, 69%, orange needles (chloroform–ether), mp 147—148 °C, ν (KBr) 2180 cm^{-1} (CN), Anal. ($C_{11}H_{12}N_2S_2$) C,H,N. **1d**, 42%, orange needles (chloroform–ether), mp 122—123 °C, ν (KBr) 2170 cm^{-1} (CN), Anal. ($C_{10}H_{10}N_2S_2$) C,H,N. **1e**, 58%, orange needles (chloroform–ether), mp 141—143 °C, ν (KBr) 2164 cm^{-1} (CN), Anal. ($C_{11}H_{12}N_2S_2$) C,H,N. **1f**, 67%, orange needles (chloroform–ether), mp 138—139 °C, ν (KBr) 2182 cm^{-1} (CN), Anal. ($C_{12}H_{14}N_2S_2$) C,H,N. **1i**, yellow needles (chloroform), mp 241—242 °C, ν (KBr) 1547 cm^{-1} (CO), Anal. ($C_{17}H_{17}NOS_2$) C,H,N. **1j**, 67%, yellow needles (chloroform–ether), mp 213—215 °C, ν (KBr) 1622 cm^{-1} (CO), Anal. ($C_{16}H_{15}NOS_2$) C,H,N. **1k**, 74%, yellow flakes (chloroform–ether), mp 194—195 °C, ν (KBr) 1634 cm^{-1} (CO), Anal. ($C_{17}H_{17}NOS_2$) C,H,N. **11**, 79%, yellow needles (chloroform–ether), mp 227—229 °C, ν (KBr) 1549 cm^{-1} (CO), Anal. ($C_{18}H_{19}NOS_2$) C,H,N. **5a**, 77%, red needles (chloroform), mp 203—205 °C, ν (KBr) 1675 cm^{-1} (CO), Anal.



Scheme 4.

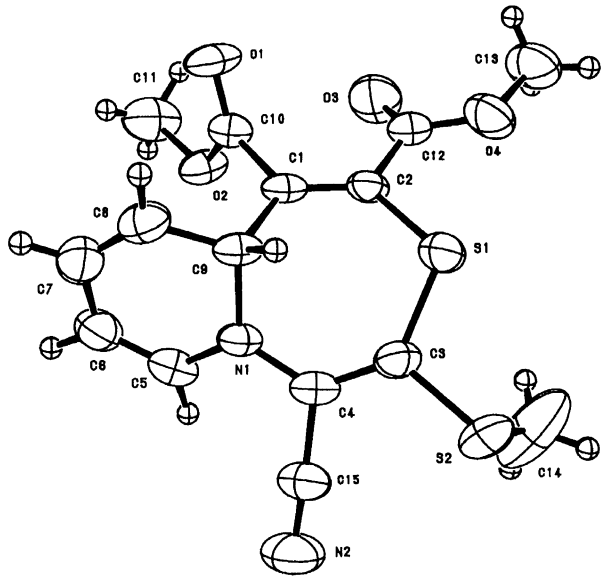


Fig. 3. ORTEP drawing of dimethyl 5-cyano-4-methylthio-10a*H*-pyrido[1,2-*d*][1,4]thiazepine-1,2-dicarboxylate (**3a**) showing the atom labeling scheme and 50% probability thermal ellipsoids.

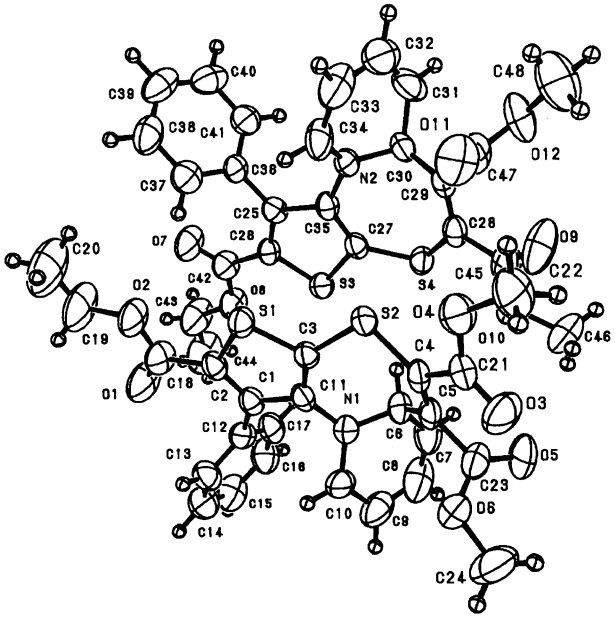


Fig. 4. ORTEP drawing of 2-ethyl 5,6-dimethyl 1-phenyl-6a*H*-pyrido[1,2-*d*]thieno[2′,3′-*b*][1,4]-thiazepine-2,5,6-tricarboxylate (**6g**) showing the atom labeling scheme and 50% probability thermal ellipsoids.

($C_{12}H_{11}NO_2S_2$) C,H,N. **5b**, 88%, dark red flakes (chloroform), mp 202—204 °C, ν (KBr) 1671 cm^{-1} (CO), Anal. ($C_{13}H_{13}NO_2S_2$) C,H,N. **5c**, 74%, dark red prisms (chloroform), mp 192—195 °C, ν (KBr) 1686 cm^{-1} (CO), Anal. ($C_{14}H_{15}NO_2S_2$) C,H,N. **7b**, 57%, orange needles (chloroform), mp 178—180 °C, ν (KBr) 1637 cm^{-1} (CO), Anal. ($C_{16}H_{17}NO_2S_2$) C,H,N. **7c**, 72%, orange needles (chloroform), mp 180—182 °C, Anal. ($C_{19}H_{15}NOS_2$) C,H,N.

Preparation of 10a*H*-Pyrido[1,2-*d*][1,4]thiazepines. General Method A: A chloroform solution (30 ml) of a pyridinium ylide or a 3-(1-pyridinio)thiophene-2-thiolate (**1** or **5**, 3 mmol) and DMAD (**2**, 0.426 g, 3 mmol) was stirred at room temperature for 12 h; the resulting mixture was then concentrated at reduced pressure. The residual oil was separated by column chromatography on silica gel using chloroform as an eluent. The red chloroform layers were then combined and concentrated at reduced pressure. Recrystallizations of the crude products from chloroform–hexane gave the corresponding dimethyl 10a*H*-pyrido[1,2-*d*]-[1,4]thiazepine-1,2-dicarboxylates (**3a**—**l**) or dimethyl 6a*H*-pyrido[1,2-*d*]thieno[2′,3′-*b*][1,4]thiazepine-5,6-dicarboxylates (**6a**—**i**), respectively.

General Method B: Since isoquinolinium ylides **7a**—**c** did not react with DMAD at room temperature, the chloroform solution of this ylide (**7**, 5 mmol) and DMAD (**2**, 1 g, 7 mmol) was allowed to react under the reflux temperature in a water bath for 4 h. The usual work-ups of the resulting reaction mixture gave the corresponding dimethyl 12b*H*-1,4-thiazepino[5,4-*a*]isoquinoline-1,2-dicarboxylates (**8a-c**).

These results as well as some physical and spectral data

Table 4. Some Data for Pyrido[1,2-*d*][1,4]thiazepines

Compd[a]	Ylide	Yield %	Mp °C	ν(KBr)/cm^{-1} CN	and/or	CO	Formula[b]
3a	**1a**	34	127—128	2218	1725		$C_{15}H_{14}N_2O_4S_2$
3b	**1b**	30	128—129	2214	1740		$C_{16}H_{16}N_2O_4S_2$
3c	**1c**	41	129—130	2209	1738		$C_{17}H_{18}N_2O_4S_2$
3d	**1d**	49	108—110	2213	1732		$C_{16}H_{16}N_2O_4S_2$
3e	**1e**	29	126—127	2216	1732		$C_{17}H_{18}N_2O_4S_2$
3f	**1f**	39	143—144	2205	1730		$C_{18}H_{20}N_2O_4S_2$
3g	**1g**	41	132—133	1730	1688		$C_{21}H_{19}NO_5S_2$
3h	**1h**	37	Red oil	1730	1667[c]		d)
3i	**1i**	20	107—109	1734	1665		$C_{23}H_{23}NO_5S_2$
3j	**1j**	49	123—125	1728	1672		$C_{22}H_{21}NO_5S_2$
3k	**1k**	30	107—109	1727	1665		$C_{23}H_{23}NO_5S_2$
3l	**1l**	13	133—134	1734	1661		$C_{24}H_{25}NO_5S_2$
6a	**5a**	16	121—123	1723	1694		$C_{18}H_{17}NO_6S_2$
6b	**5b**	44	110—111	1725			$C_{19}H_{19}NO_6S_2$
6c	**5c**	70	153—154	1721			$C_{20}H_{21}NO_6S_2$
6d	**5d**	49	120—121	1725			$C_{19}H_{19}NO_6S_2$
6e	**5e**	51	88—90	1730			$C_{20}H_{21}NO_6S_2$
6f	**5f**	53	134—135	1717			$C_{21}H_{23}NO_6S_2$
6g	**5g**	57	124—125	1726	1687		$C_{24}H_{21}NO_6S_2$
6h	**5h**	21	127—128	1725			$C_{25}H_{23}NO_6S_2$
6i	**5i**	40	141—144	1728	1680		$C_{26}H_{25}NO_6S_2$
8a	**7a**	50	127—130	1730			$C_{21}H_{21}NO_6S_2$
8b	**7b**	44	114—116	1736	1723	1709	$C_{22}H_{23}NO_6S_2$
8c	**7c**	33	166—167	1728	1668		$C_{25}H_{21}NO_5S_2$

a) Compounds **3a**, **c**, **f**, and **8a** are obtained as red prisms, **3b**, **d**, **g**, **j**, **6c**, **f**—**i**, and **8b** as orange needles, **3e**, **i**, **l** as red needles, **3k** as orange prisms, and **6a**, **b**, **d**, **e** as yellow needles. b) Satisfactory analytical data (within ±0.3% for C, H, and N) were obtained for compounds **3a**—**g**, **i**—**l**, **6a**—**i**, and **8a**—**c**. c) Neat. d) The analytical data was not obtained because of the failure of the crystallization.

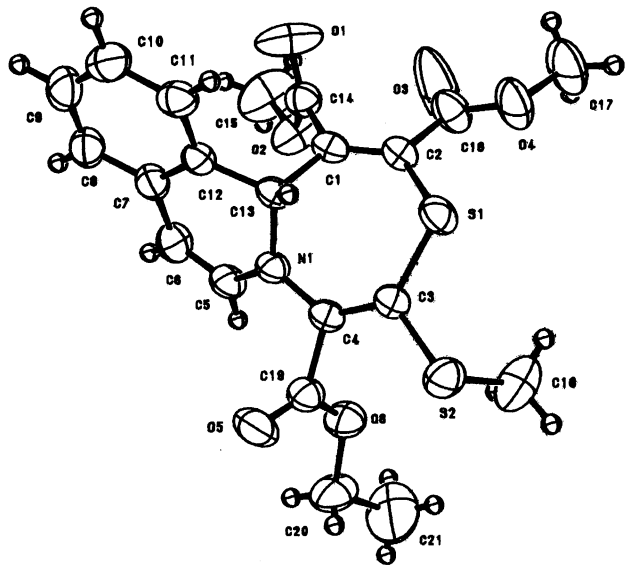


Fig. 5. ORTEP drawing of 5-ethyl 1,2-dimethyl 4-methylthio-12b*H*-1,4-thiazepino[5,4-*a*]isoquinoline-1,2,5-tricarboxylate (**8a**) showing the atom labeling scheme and 50% probability thermal ellipsoids.

are listed in Tables 1 and 4.

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