Preparation of New Nitrogen-Bridged Heterocycles. 38.[1] Synthesis and Reaction of Dimethyl 6-Thia-3-azatricyclo[5.3.1.$0^{3,8}$]undeca-4,9-diene-7,11-dicarboxylates

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The title compounds, dimethyl 6-thia-3-azatricyclo[5.3.1.$0^{3,8}$]undeca-4,9-diene-7,11-dicarboxylates, were smoothly prepared in variable yields by the reactions of some (1-pyridinio)thiocarbonylmethylides with dimethyl acetylenedicarboxylate (DMAD) in chloroform, including various alcohols at room temperature. The mechanistic consideration for these reactions clarified the intervention of primary 1 : 1 zwitterionic intermediates between the ylides and DMAD, which were previously proposed by us, and their traps by alcohol molecules. Some of these dimethyl 6-thia-3-azatricyclo[5.3.1.$0^{3,8}$]undeca-4,9-diene-7,11-dicarboxylates were hydrolyzed by hydrochloric acid to afford dimethyl 7-formyl-4a,5,8,8a-tetrahydro-4*H*-benzo-1,4-thiazine-8,8a-dicarboxylates or tetramethyl 2,2′-oxydi(6-thia-3-azatricyclo[5.3.1.$0^{3,8}$]undeca-4,9-dien-7,11-dicarboxylate)s.

In our previous papers[2] we reported on a simple and convenient preparative method for dimethyl 10a*H*-pyrido[1,2-*d*][1,4]thiazepine-1,2-dicarboxylate derivatives from the reactions of various (1-pyridinio)thiocarbonylmethylides with DMAD. From a mechanistic consideration for this reaction, we described at the same time that the concerted process ($\pi 6a+\pi 2s$) between the ylide and DMAD should be energetically unfavorable because of the presence of a geometrically unreasonable antara mode[3] in the ylide component, and, hence, an alternative stepwise process including the primary 1 : 1 zwitterionic intermediates, such as **A**, between them should be considered (see Fig. 1).

All of our initial attempts to trap such an intermediate **A** by various electrophilic and nucleophilic agents were unsuccessful because of the readiness of an energetically more favorable intramolecular process to 10a*H*-pyrido[1,2-*d*][1,4]thiazepine derivatives[2] and of the high reactivities of the ylides[4] and DMAD[5] toward electrophiles and nucleophiles, respectively. However, we noticed a solvent effect during these reactions. The reactions of (1-pyridinio)thiocarbonylmethylides and DMAD in such solvents as benzene, chloroform, tetrahydrofuran, and dichloromethane at room temperature, or at an elevated temperature, gave the corresponding 10a*H*-pyrido[1,2-*d*][1,4]thiazepines and/or their intramolecular Diels–Alder adducts,[6] while those in alcoholic solvents, such as ethanol and methanol, did not give such types of products at all, but afforded quite different types of compounds. Since both reagents did not react with these alcohols under the reaction conditions employed here, this finding strongly suggests the possibility of a trapping of this ionic intermediate **A** by alcohol molecules. We thus examined in detail these reactions in alcohols, and found the formation of new heterocyclic compounds. In this paper we describe the formations of dimethyl 6-thia-3-azatricyclo[5.3.1.$0^{3,8}$]undeca-4,9-diene-7,11-dicarboxylates due to the reaction of some (1-pyridinio)thiocarbonylmethylides, DMAD, and various primary and secondary alcohols and their hydrolyses in acidic media.

Results and Discussion

Reactions of (1-Pyridinio)(thiocarbonyl)methylides with DMAD and Alcohols. Since the reactions of (1-pyridinio)cyano(thiocarbonyl)methylides (**1**) and DMAD (**2**) in the presence of various electrophilic and nucleophilic agents did not give any significant products, and only those in alcoholic solvents provided a quite different type of adducts as described above, we carefully examined these reactions in alcohols as well as the other reaction conditions used. After much elaboration we found that these reactions successfully proceed in chloroform including excess alcohol (10—30 times), rather than in only alcohol at a temperature above 10 °C. For example, the reaction of (1-pyridinio)cyano(methylthio)- (**1a**) or (1-pyridinio)cyano(ethylthio)thiocarbonylmethylide (**1b**) with DMAD (**2**) and excess methanol (**3a**) in chloroform at room temperature gave the corresponding colorless crystalline product **4a** or **4j** in 80 or 82% yield, respectively. A similar treatment of ylides **1a**,**b** with DMAD (**2**) and some primary and secondary alcohols, such as ethanol (**3b**), 1-propanol (**3c**), 2-propanol

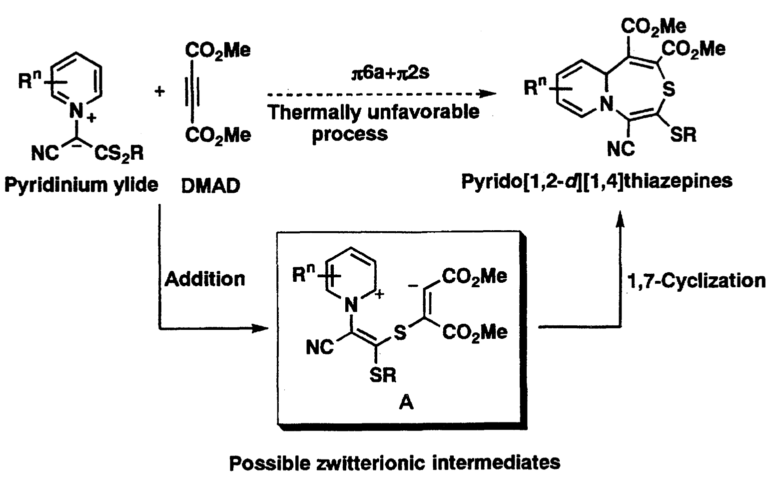
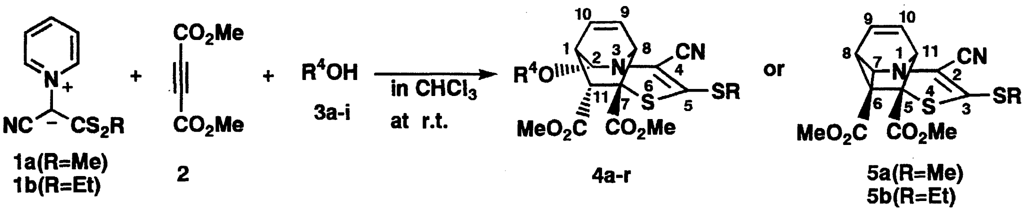


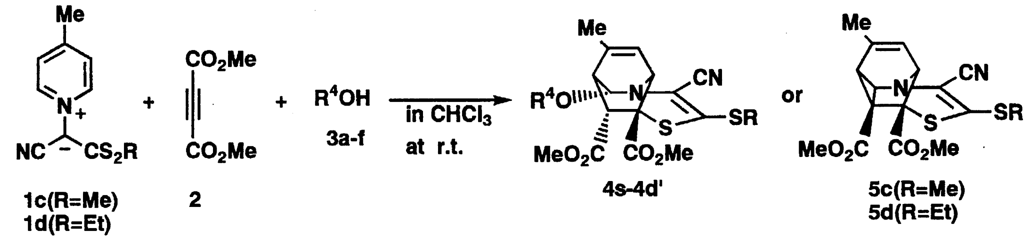
Fig. 1.



3	R^4	Reactants	Product (Yield/%)	R	R^4
a	Me	**1a**+**2**+**3a**	**4a** (80)	Me	Me
b	Et	**1a**+**2**+**3b**	**4b** (84)	Me	Et
c	*n*-Pr	**1a**+**2**+**3c**	**4c** (71)	Me	*n*-Pr
d	*iso*-Pr	**1a**+**2**+**3d**	**4d** (70)	Me	*iso*-Pr
e	*n*-Bu	**1a**+**2**+**3e**	**4e** (82)	Me	*n*-Bu
f	*iso*-Bu	**1a**+**2**+**3f**	**4f** (86)	Me	*iso*-Bu
g	$PhCH_2$	**1a**+**2**+**3g**	**4g** (79)	Me	$PhCH_2$
h	Allyl	**1a**+**2**+**3h**	**4h** (69)	Me	Allyl
i	*t*-Bu	**1a**+**2**+**3i**	**4i** (0), **5a** (6)	Me	*t*-Bu
		1b+**2**+**3a**	**4j** (82)	Et	Me
		1b+**2**+**3b**	**4k** (78)	Et	Et
		1b+**2**+**3c**	**4l** (65)	Et	*n*-Pr
		1b+**2**+**3d**	**4m** (62)	Et	*iso*-Pr
		1b+**2**+**3e**	**4n** (82)	Et	*n*-Bu
		1b+**2**+**3f**	**4o** (72)	Et	*iso*-Bu
		1b+**2**+**3g**	**4p** (76)	Et	$PhCH_2$
		1b+**2**+**3h**	**4q** (51)	Et	Allyl
		1b+**2**+**3i**	**4r** (0), **5b** (5)	Et	*t*-Bu

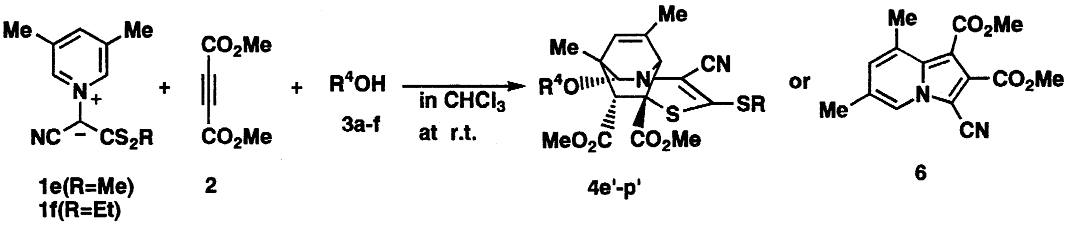
Scheme 1.

(**3d**), butanol (**3e**), isobutyl alcohol (**3f**), benzyl alcohol (**3g**), and allyl alcohol (**3h**), afforded the corresponding adducts **4b**—**h** and **4k**—**q** in comparatively good yields (51—84%) (see Scheme 1). On the other hand, the reaction of ylides **1a**,**b** with DMAD (**2**) and tertially alcohol, such as *t*-butyl alcohol (**3i**), did not give the expected products **4i**,**r** at all, but provided only dimethyl 4-thia-1-azatetracyclo$[5.4.0.0^{5,11}.0^{6,8}]$undeca-2,9-diene-5,6-dicarboxylates (**5a**,**b**) in very low yields (6 and 5%). The latter compounds **5a**,**b** are products which are independent of the alcohol **3i** used. The reactions of (4-methyl-1-pyridinio)cyano(methylthio)-(**1c**) or (4-methyl-1-pyridinio)cyano(ethylthio)thiocarbonylmethylide (**1d**) with DMAD (**2**) and alcohols **3a**—**f** gave the corresponding adducts **4s**—**u**,**y**—**d′** or 9-methyl-4-thia-1-azatetracyclo$[5.4.0.0^{5,11}.0^{6,8}]$undeca-2,9-diene derivative (**5c**), though their yields were low to moderate (4—44%) (Scheme 2). Interestingly, although similar reactions of (3,5-dimethyl-1-pyridinio)(thiocarbonyl)methylides (**1e**,**f**) with **2** and alcohols **3b**—**f** afforded the expected products **4f′**—**j′**,**l′**—**p′** in moderately yields, the same type of adducts **4e′**,**k′** could not be obtained in the reactions of **1e**,**f** with **2**, and methanol (**3a**). The only product isolated from them was dimethyl 3-cyano-6,8-dimethylindolizine-1,2-dicarboxylate (**6**) (see Scheme 3). In the reactions of ylides **1c**—**f** with **2** and alcohols **3g**—**i** no products such as type **4** could be obtained.



Reactants	Product (Yield/%)	R	R^4
1c+**2**+**3a**	**4s** (4)	Me	Me
1c+**2**+**3b**	**4t** (10)	Me	Et
1c+**2**+**3c**	**4u** (28)	Me	*n*-Pr
1c+**2**+**3d**	**4v** (0), **5c** (5)	Me	*iso*-Pr
1c+**2**+**3e**	**4w** (0), **5c** (6)	Me	*n*-Bu
1c+**2**+**3f**	**4x** (0), **5c** (7)	Me	*iso*-Bu
1d+**2**+**3a**	**4y** (6)	Et	Me
1d+**2**+**3b**	**4z** (36)	Et	Et
1d+**2**+**3c**	**4a′** (44)	Et	*n*-Pr
1d+**2**+**3d**	**4b′** (11)	Et	*iso*-Pr
1d+**2**+**3e**	**4c′** (32)	Et	*n*-Bu
1d+**2**+**3f**	**4d′** (16)	Et	*iso*-Bu

Scheme 2.



Reactants	Product (Yield/%)	R	R^4
1e+**2**+**3a**	**4e′** (0), **6** (8)	Me	Me
1e+**2**+**3b**	**4f′** (32)	Me	Et
1e+**2**+**3c**	**4g′** (30)	Me	*n*-Pr
1e+**2**+**3d**	**4h′** (28)	Me	*iso*-Pr
1e+**2**+**3e**	**4i′** (23)	Me	*n*-Bu
1e+**2**+**3f**	**4j′** (39)	Me	*iso*-Bu
1f+**2**+**3a**	**4k′** (0), **6** (10)	Et	Me
1f+**2**+**3b**	**4l′** (39)	Et	Et
1f+**2**+**3c**	**4m′** (32)	Et	*n*-Pr
1f+**2**+**3d**	**4n′** (21)	Et	*iso*-Pr
1f+**2**+**3e**	**4o′** (29)	Et	*n*-Bu
1f+**2**+**3f**	**4p′** (34)	Et	*iso*-Bu

Scheme 3.

The structures of products **4a**—**h**,**j**—**q**,**s**—**u**,**y**—**d′**, **f′**—**j′**,**l′**—**p′** were presumed based on elemental analyses and the IR and ^{1}H NMR spectral inspections, and were finally determined by a single-crystal X-ray analysis of one compound **4b**. Their elemental analyses were in good accord with the compositions of the 1 : 1 : 1 adducts of ylides **1a**—**f**, DMAD (**2**), and the alcohols **3a**—**h** employed here. The IR spectra clearly showed an α,β-unsaturated cyano absorption band at 2206—2216 cm^{-1} and one or two saturated ester carbonyl absorption bands at 1728—1740 cm^{-1}. The ^{1}H NMR spectra (Table 1) distinctly exhibited the presence of a tetrahydropyridine and alkoxyl moieties in the molecule; for example, the ^{1}H NMR spectrum of compound **4a** derived from parent (1-pyridinio)methylide (**1a**) showed signals at δ=2.44 (3H, s, SMe), 3.09 (1H, m, 1-H), 3.51 (3H, s, OMe), 3.70 and 3.80 (each 3H, s, 2×CO$_2$Me), 3.78 (1H, d, J=3.0 Hz, 11-H), 5.18 (1H, d, J=3.0 Hz, 2-H), and 6.2—6.5 (2H, m, 9-H and 10-H)$^{7)}$ and that of **4s** derived from (4-methyl-1-pyridinio)methylide (**1c**) exhibited signals at, *inter alia*, δ=1.88 (3H, d, J=2.0 Hz, 10-Me), 2.84 (1H, m, 1-H), 3.51 (3H, s, OMe), 5.17 (1H, d, J=3.0 Hz, 2-H), and 5.91 (1H, br d, J=6.5 Hz, 9-H).$^{7)}$ In particular, the presences of only two olefinic signals (δ=6.2—6.5) for **4a**—**h**,**j**—**q** and of an olefinic (δ near 5.90) and a methyl signal (δ near 1.85) attached to the sp^2 carbon for **4s**—**u**,**y**—**d′** disclosed that they possess a 1,2,5,6-tetrahydropyridine moiety

Table 1. ^{1}H NMR spectral Data for 4-Thia-1-azatetracyclo[5.4.0.0^{5,11}.0^{6,8}]undeca-2,9-dienes

Compd	δ ($CDCl_3$)												
No.[a]	C-1	C-2	C-8	C-9	C-10	C-11	CO_2Me		SR		OR^4		
4a	3.09	5.18	b)	-6.2—6.5-		3.78	3.70	3.80	2.44		3.51		
	m	d		m		d	s	s	s[c]		s[c]		
4b	3.09	5.30	b)	-6.2—6.5-		3.78	3.71	3.81	2.47		1.20	3.3—4.5	
	m	d		m		d	s	s	s[c]		t[c]	m[d]	
4c	3.10	5.28	b)	-6.2—6.5-		3.77	3.70	3.80	2.44		0.91	1.2—1.9	3.3—4.3
	m	d		m		d	s	s	s[c]		t[c]	m[d]	m[d]
4d	3.02	5.37	b)	-6.2—6.5-		b)	3.71	3.81	2.45		1.19	1.21	3.7—4.4
	m	d		m			s	s	s[c]		d[c]	d[c]	m[e]
4e	3.10	5.28	b)	-6.2—6.5-		3.79	3.71	3.81	2.46		0.91	1.1—1.9	3.3—4.2
	m	d		m		d	s	s	s[c]		t[c]	m[f]	m[d]
4f	3.10	5.27	b)	-6.2—6.5-		3.78	3.71	3.81	2.46		0.91	1.6—2.3	3.2—4.0
	m	d		m		d	s	s	s[c]		d[g]	m[e]	m[d]
4g	3.08	5.45	b)	-6.2—6.5-		3.79	3.69	3.80	2.43		4.61	5.00	7.32
	m	d		m		d	s	s	s[c]		d[e]	d[e]	s[h]
4h	3.10	5.10	b)	-6.2—6.5-		3.78	3.71	3.80	2.45		4.27	5.2—6.4	
	m	d		m		d	s	s	s[c]		br t[d]	m[c]	
4j	3.14	5.21	b)	-6.2—6.5-		3.76	3.71	3.81	1.38	2.90	3.54		
	m	d		m		d	s	s	t[c]	q[d]	s[c]		
4k	3.10	5.28	b)	-6.2—6.5-		3.76	3.71	3.80	1.36	2.89	1.20	3.3—4.5	
	m	d		m		d	s	s	t[c]	q[d]	t[c]	m[d]	
4l	3.09	5.26	b)	-6.2—6.5-		3.77	3.71	3.80	1.36	2.88	0.91	1.2—1.9	3.3—4.3
	m	d		m		d	s	s	t[c]	q[d]	t[c]	m[d]	m[d]
4m	3.05	5.40	b)	-6.2—6.5-		b)	3.72	3.82	1.38	2.90	1.20	1.23	3.6—4.4
	m	d		m		d	s	s	t[c]	q[d]	d[c]	d[c]	m[e]
4n	3.10	5.28	b)	-6.2—6.5-		3.76	3.70	3.80	1.36	2.89	0.91	1.1—1.9	3.3—4.2
	m	d		m		d	s	s	t[c]	q[d]	t[c]	m[f]	m[d]
4o	3.10	5.28	b)	-6.2—6.5-		3.77	3.71	3.81	1.37	2.90	0.91	1.6—2.3	3.2—4.0
	m	d		m		d	s	s	t[c]	q[d]	d[g]	m[e]	m[d]
4p	3.11	5.47	b)	-6.2—6.5-		3.77	3.70	3.81	1.37	2.90	4.61	5.00	7.37
	m	d		m		d	s	s	t[c]	q[d]	d[e]	d[e]	s[h]
4q	3.12	5.13	b)	-6.2—6.5-		3.76	3.71	3.81	1.37	2.90	4.29	5.2—6.4	
	m	d		m		d	s	s	t[c]	q[d]	br t[d]	m[c]	
4s	2.84	5.17	b)	5.91	1.88	b)	3.70	3.80	2.44		3.51		
	m	d		br d	d		s	s	s[c]		s[c]		
4t	2.79	5.23	b)	5.90	1.87	3.64	3.70	3.80	2.43		1.19	3.3—4.5	
	m	d		br d	d		s	s	s[c]		t[c]	m[d]	
4u	2.82	5.24	b)	5.90	1.87	b)	3.70	3.80	2.43		0.91	1.2—1.9	3.3—4.2
	m	d		br d	d		s	s	s[c]		t[c]	m[d]	m[d]
4y	2.82	5.16	b)	5.91	1.88	b)	3.70	3.80	1.35	2.89	3.52		
	m	d		br d	d		s	s	t[c]	q[d]	s[c]		
4z	2.80	5.26	b)	5.90	1.88	b)	3.70	3.80	1.34	2.88	1.19	3.3—4.5	
	m	d		br d	d		s	s	t[c]	q[d]	t[c]	m[d]	
4a′	2.82	5.24	b)	5.90	1.88	b)	3.70	3.80	1.34	2.88	0.91	1.2—1.9	3.3—4.2
	m	d		br d	d		s	s	t[c]	q	t[c]	m[d]	m[d]
4b′	2.80	5.33	b)	5.94	1.87	b)	3.70	3.80	1.35	2.88	1.19	1.21	3.8—4.5
	m	d		br d	d		s	s	t[c]	q[d]	d[c]	d[c]	m[e]
4c′	2.81	5.24	b)	5.90	1.86	b)	3.69	3.79	1.33	2.89	0.90	1.1—1.9	3.4—4.2
	m	d		br d	d		s	s	t[c]	q[d]	t[c]	m[f]	m[d]
4d′	2.80	5.22	b)	5.90	1.87	b)	3.69	3.79	1.34	2.89	0.89	1.6—2.3	3.1—4.0
	m	d		br d	d		s	s	t[c]	q[d]	d[g]	m[e]	m[d]
4f′	1.30	5.06	3.59	1.84	5.63	3.59	3.69	3.80	2.42		1.17	3.3—4.5	
	s	s	s	d	br s	s	s	s	s[c]		t[c]	m[d]	
4g′	1.31	5.05	3.59	1.82	5.64	3.59	3.69	3.81	2.43		0.90	1.1—1.9	3.3—4.5
	s	s	s	d	br s	s	s	s	s[c]		t[c]	m[d]	m[d]
4h′	1.29	5.16	3.59	1.84	5.60	3.59	3.68	3.80	2.44		1.15	3.8—4.5	
	s	s	s	d	br s	s	s	s	s[c]		d[g]	m[e]	

Table 1. (Continued)

Compd	δ ($CDCl_3$)												
No.[a]	C-1	C-2	C-8	C-9	C-10	C-11	CO_2Me		SR		OR^4		
4i′	1.31	5.05	3.59	1.83	5.63	3.59	3.69	3.81	2.43		0.90	1.1—1.9	3.2—4.0
	s	s	s	d	br s	s	s	s	s[c]		t[c]	m[f]	m[d]
4j′	1.33	5.04	3.60	1.84	5.64	3.60	3.70	3.82	2.44		0.90	1.6—2.3	3.2—4.0
	s	s	s	d	br s	s	s	s	s[c]		d[g]	m[e]	m[d]
4l′	1.31	5.08	3.58	1.86	5.63	3.58	3.69	3.80	1.38	2.88	1.18	3.3—4.5	
	s	s	s	d	br s	s	s	s	t[c]	q[d]	t[c]	m[d]	
4m′	1.32	5.08	3.58	1.83	5.62	3.58	3.68	3.80	1.38	2.88	0.90	1.2—1.9	3.3—4.3
	s	s	s	d	br s	s	s	s	t[c]	q[d]	t[c]	m[d]	m[d]
4n′	1.29	5.19	3.58	1.83	5.60	3.58	3.68	3.80	1.37	2.88	1.14	3.8—4.5	
	s	s	s	d	br s	s	s	s	t[c]	q[d]	d[g]	m[e]	
4o′	1.32	5.08	3.58	1.84	5.64	3.58	3.70	3.81	1.39	2.89	0.91	1.1—1.9	3.4—4.2
	s	s	s	d	br s	s	s	s	t[c]	q[d]	t[c]	m[f]	m[d]
4p′	1.33	5.06	3.58	1.84	5.61	3.58	3.69	3.81	1.38	2.89	0.90	1.6—2.3	3.1—4.0
	s	s	s	d	br s	s	s	s	t[c]	q[d]	d[g]	m[e]	m[d]

a) The main coupling constants are as follows: $J_{1,2}=3.5$, $J_{1,10}=6.0$, $J_{1,11}=2.5$, $J_{8,9}=6.5$, $J_{9,10}=8.0$, $J_{8,10}=2.0$, $J_{1,9}=1.5$, and $J_{Et}=7.0$ Hz for **4a**—**q**, $J_{1,2}=3.5$, $J_{1,11}=2.5$, $J_{8,9}=6.5$, $J_{9,10}=2.0$, $J_{1,9}=1.5$, and $J_{Et}=7.0$ Hz for **4s**—**d′**, and $J_{9,10}=2.0$, $J_{8,10}=2.0$, and $J_{Et}=7.0$ Hz for **4f′**—**p′**. b) Overlapped with the proton signals of the two methoxycarbonyl groups. c) 3H. d) 2H. e) 1H. f) 4H. g) 6H. h) 5H.

in the molecule. Furthermore, the presence of a proton signal shifted at low magnetic field (δ=5.05—5.45) in products **4a**—**h**,**j**—**q**,**s**—**u**,**y**—**d′**,**f′**—**j′**,**l′**—**p′** clearly suggested that the alkoxyl group is attached at the 6-position of the tetrahydropyridine moiety. In addition to these facts, the appearance of a doublet signal (δ near 3.80) for a methine proton signal coupled with the 3-proton on the pyridine ring supported our proposed structure, dimethyl 2-alkoxy-4-cyano-5-methylthio- or 2-alkoxy-4-cyano-5-ethylthio-6-thia-3-azatricyclo[5.3.1.0^{3,8}]undeca-4,9-diene-7,11-dicarboxylate (**4**). However, we could not determine the stereochemistry of the 2- and 11-positions for compounds **4a**—**h**,**j**—**q**,**s**—**u**,**y**—**d′**,**f′**—**j′**,**l′**—**p′** from only these data. A final structural assignment for these compounds was carried out by a single-crystal X-ray analysis of one compound **4b**.

The crystal and structure analysis data for dimethyl 4-cyano-2-ethoxy-5-methylthio-6-thia-3-azatricyclo-[5.3.1.0^{3,8}]undeca-4,9-diene-7,11-dicarboxylate (**4b**) are listed in Table 2.[8] An ORTEP drawing[9] for **4b** is shown in Fig. 2. From this figure we could determine the trans configuration of the two methoxycarbonyl groups at the 7- and 11-positions as well as the direction of the alkoxyl group at the 2-position in these molecules **4a**—**h**,**j**—**q**,**s**—**u**,**y**—**d′**,**f′**—**j′**,**l′**—**p′**.

At a glance, products **4** thus obtained have the structures of adding alcohols **3** on the C_6—C_7 single bond of the cyclopropane ring in dimethyl 4-thia-1-azatetracyclo[5.4.0.0^{5,11}.0^{6,8}]undeca-2,9-diene-5,6-dicarboxylates (**5**). It is well established that compounds **5** were formed via a thermal intramolecular Diels–Alder reaction of 10a*H*-pyrido[1,2-*d*][1,4]thiazepine derivatives generated from the reactions of ylides **1** with DMAD (**2**) in the absence of alcohols **3**.[2,6] However, compounds **5a**—**d** did not react at all with alcohols, such as methanol (**3a**) and ethanol (**3b**), even under more vigorous conditions (see mechanism). This fact clearly indicated that these 4-thia-1-azatetracyclo[5.4.0.0^{5,11}.0^{6,8}]undeca-2,9-diene derivatives **5** can not be precursors for 6-thia-3-azatricyclo[5.3.1.0^{3,8}]undeca-4,9-diene derivatives **4**.

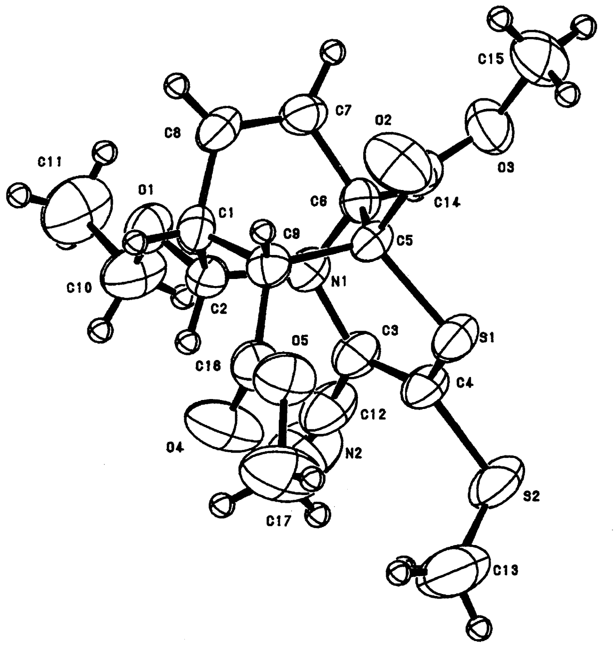


Fig. 2. ORTEP drawing of dimethyl 4-cyano-2-ethoxy-5-methylthio-6-thia-3-azatricyclo[5.3.1.0^{3,8}]undeca-4,9-diene-7,11-dicarboxylate (**4b**) showing the atom labeling scheme and 50% probability thermal ellipsoids.

Acid Hydrolyses of 6-Thia-3-azatricyclo-[5.3.1.0^{3,8}]undeca-4,9-diene Derivatives. Since the reactions of pyridinium ylides **1a**—**f** with DMAD (**2**) and alcohols **3a**—**h** each gave sole products **4a**—**h**,**j**—**q**,**s**—**u**,**y**—**d′**,**f′**—**j′**,**l′**—**p′** with a definite

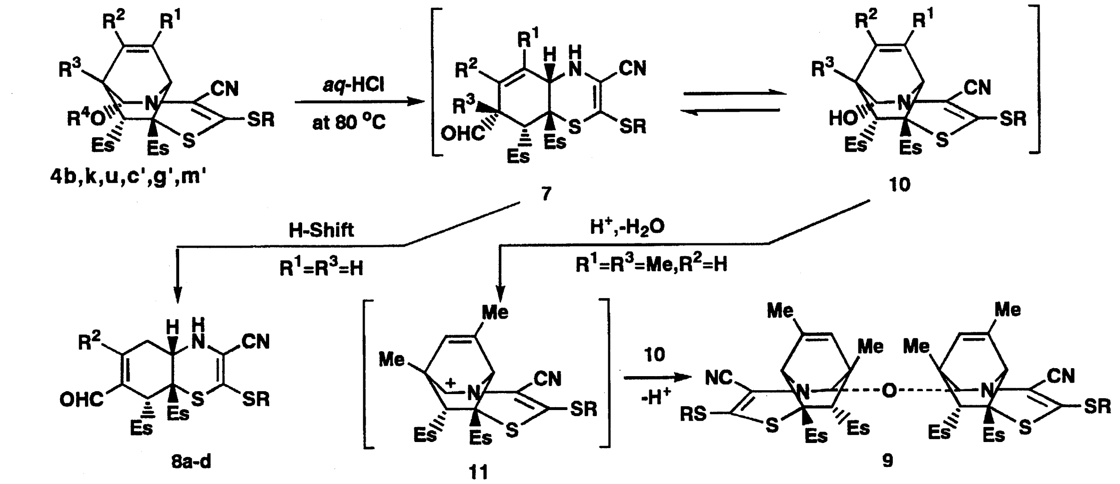
Table 2. Crystal and Structure Analysis Data of Compounds **4b** and **8b**

	4b	**8b**
Formula	$C_{17}H_{20}N_2O_5S_2$	$C_{16}H_{18}N_2O_5S_2$
Formula weight	396.48	382.45
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$; Z=8	$P2_1/n$; Z=4
Lattice parameter		
a/Å	15.420(7)	14.883(4)
b/Å	11.419(3)	8.057(2)
c/Å	22.020(4)	16.404(3)
α/°	90	90
β/°	95.40(2)	108.68(1)
γ/°	90	90
V/Å^3	3860(2)	1863.5(7)
D_{calcd}/g cm^{-3}	1.364	1.363
Crystal size/mm^3	0.20×0.62×0.80	0.26×0.34×0.88
Diffractometer	Rigaku AFC5S	Rigaku AFC5S
Radiation	Mo $K\alpha$ (λ=0.71069 Å)	Mo $K\alpha$ (λ=0.71069 Å)
Monochrometer	Graphite	Graphite
Scan type	ω–2θ	ω–2θ
2θ Max	55.0°	55.0°
Computer program	TEXSAN system[a)]	TEXSAN system[a)]
Structure solution	MITHRIL[b)]	MITHRIL[b)]
Hydrogen atom treatment	Observed, isotropic	Observed, isotropic
Refinement	Full-matrix, anisotropic	Full-matrix, anisotropic
Least-squares weight	$4F_o^2/\sigma^2(F_o^2)$	$4F_o^2/\sigma^2(F_o^2)$
No. of measurement ref.	Total: 4838 Unique: 4658	Total: 4752 Unique: 4581
No. of observations[c)]	2168	2067
No. of variables	316	299
Residuals R ; R_w	0.045; 0.048	0.047; 0.051
Max Shift/Error	0.39	0.18
$\Delta\rho_{\max}$/e$^-$ Å^3	0.21	0.29

a) See Ref. 10. b) Direct method, see Ref. 11. c) $I>3.00\sigma(I)$.

configuration, and these molecules have an *O,N*-acetal structure in the skeleton, we expected that the hydrolyses of compounds **4** would proceed with the retention of the configuration at the remaining positions to provide cyclohexene derivatives, such as **7** in Scheme 4. The treatment of 1-unsubstituted **4b,k,u,c′** with 1 M hydrochloric acid in a water bath, (1 M = 1 mol dm^{-3}), however, did not give the corresponding products **7**. The products actually isolated from these reactions were the 1,3-hydrogen transfer isomers, dimethyl 2-alkylthio-3-cyano-7-formyl-4a,5,8,8a-tetrahydro-4*H*-benzo[1,4]thiazine-8,8a-dicarboxylates (**8a**—**d**). On the other hand, similar treatment of 1,9-dimethyl derivatives **4g′**, **m′** with 1 M HCl resulted in only the recovery of the starting materials; however, under more drastic conditions in which concd HCl was used directly, they were slowly hydrolyzed to afford tetramethyl 2,2′-oxydi(6-thia-3-azatricyclo[5.3.1.0^{3,8}]undeca-4,9-dien-7,11-dicarboxylate)s (**9a,b**) in low yields.

The rough structures of benzo[1,4]thiazine derivatives **8a**—**d** could be decided with ease by IR and ^{1}H NMR spectral inspections. For example, the IR spectra of **8a**—**d** showed the characteristic absorption bands for an α,β-unsaturated aldehyde group, a saturated ester carbonyl group, an α,β-unsaturated cyano group, and an amino group at 1669—1680, 1730—1740, 2220—2222, and 3326—3360 cm^{-1}, respectively. The ^{1}H NMR spectrum of **8a** exhibited proton signals at δ=2.40 (3H, s, SMe), 2.4—2.8 (2H, m, 5-H), 3.74 and 3.81 (each 3H, s, 2×CO$_2$Me), 3.9—4.6 (3H, m, 4a-H, 8-H, and NH), 6.85 (1H, br s, 6-H), and 9.44 (1H, s, CHO). In particular, the presences of 5-methylene protons (δ=2.4—2.8) and the 6-methine proton (δ=6.85) in the ^{1}H NMR spectra and the indication of an α,β-unsaturated aldehyde group (1669—1680 cm^{-1}) in the IR spectra ensured this structure **8**. Furthermore, the X-ray analysis of **8b** finally confirmed their structures including the stereochemistry. The crystal and structure analysis data for dimethyl 3-cyano-2-ethylthio-7-formyl-4a,5,8,8a-tetrahydro-4*H*-benzo[1,4]thiazine-8,8a-dicarboxylate (**8b**) are listed in Table 2.[8)] An ORTEP drawing[9)] for **8b** is shown in Fig. 3. As might be expected, the configurations at the 4a-, 8-, and 8a-positions in products **8a**—**d** were retained. On the other hand, the structures of ethers **9a,b** were determined based on the elemental and spectral analyses and its mechanistic consideration. The chemical shifts and signal patterns in the ^{1}H NMR spectra of compounds **9a,b** were similar to those for the starting materials **4g′,m′**, expect for the absence



Reactant	Product(Yield/%)	R	R^2
4b	8a(96)	Me	H
4k	8b(76)	Et	H
4u	8c(79)	Me	Me
4c'	8d(72)	Et	Me

Reactant	Product(Yield/%)	R
4g'	9a(16)	Me
4m'	9b(19)	Et

Scheme 4.

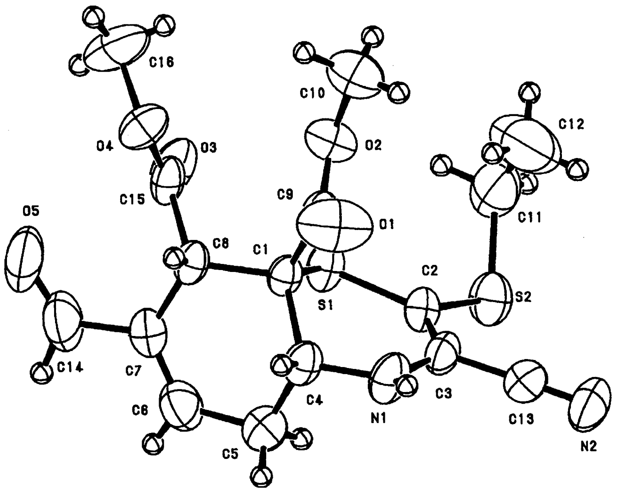
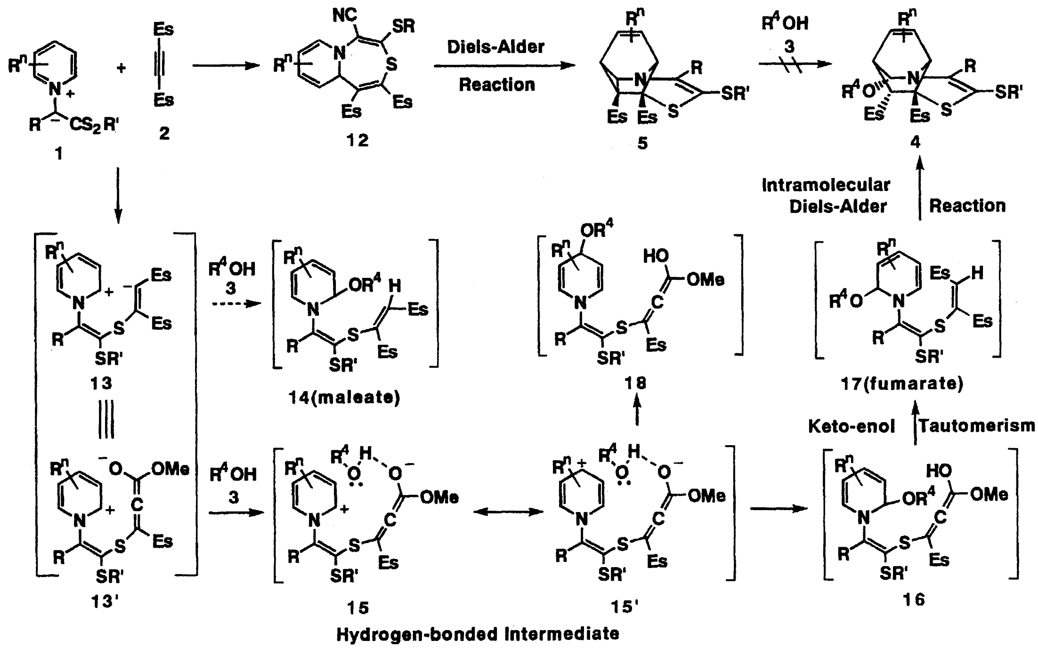


Fig. 3. ORTEP drawing of dimethyl 3-cyano-2-ethylthio-7-formyl-4a,5,8,8a-tetrahydro-4*H*-benzo[1,4]-thiazine-8,8a-dicarboxylate (**8b**) showing the atom labeling scheme and 50% probability thermal ellipsoids.

of the 2-alkoxy proton signals and the low-field shift of the 2-proton. The IR spectra were also very similar to those of **4g′**,**m′**. This fact strongly indicated the possibility that compounds **9a**,**b** have the same skeleton as **4** in these molecules. The elementary analyses for **9a**,**b** were consistent with the compositions in which a molecule of water was removed from two molecules of hydrolyzed products, such as **7**. Furthermore, the formation of ethers **9a**,**b** can be skillfully explained by considering the equilibrium between the initial hydrolyzed product **7** and its cyclic amino alcohol **10**. Although the reason why the amino alcohol **10** could not be isolated is still unclear, the strong acidic condition (concd HCl) employed here may lead them to ethers **9a**,**b** via dehydration from the protonated **10** followed by the addition of another molecule of **10** to the resulting carbonium ion **11** and deprotonation. From these data we concluded that compounds **9a**,**b** were tetramethyl 2,2′-oxydi(6-thia-3-azatricyclo[5.3.1.0^{3,8}]undeca-4,9-dien-7,11-dicarboxylate)s.

Mechanisms. The possible mechanisms for the formation reactions of 6-thia-3-aza-tricyclo[5.3.1.0^{3,8}]-undeca-4,9-diene derivatives **4** are summarized in Scheme 5. Since products **4** could not be obtained by the addition of alcohols **3** onto 4-thia-1-azatetracyclo[5.4.0.0^{5,11}.0^{6,8}]undeca-2,9-diene derivatives **5**, as described above, other routes to provide **4** were considered. According to the retro-synthesis procedure, the trans configuration of the two ester group at the 7- and 11-positions in **4** indicated that the precursor for **4** must be a 2-alkoxy-1,2-dihydropyridine derivative **17** having a fumarate moiety and not **14** bearing a maleate moiety. This intermediate **17** was also supported by a consideration of the configuration of the 2-alkoxyl group, because the observed configuration was completely consistent with that expected by the attack of the fumarate moiety (2π) to the less-hindered plane (4π) of the 2-alkoxy-1,2-dihydropyridine ring in **17** in its intramolecular Diels–Alder reaction. Furthermore, the intervention of the fumarate type of intermediate **17** means that an allenyl alcoholate type of intermediate **13′** is a plausible precursor for it, since the addition of alcohols **3** on the



Scheme 5.

vinyl anion type of species **13** should lead to maleate **14**,[12] which can not lead to actual products **4**; that of alcohols **3** on **13′** gives an allenyl alcohol **16**, and, in turn, it can be converted to fumarate **17** through the keto–enol tautomerism. However, the very weak nucleophilicity of the alcohol molecule and no precedent for the direct addition of alcohol onto pyridinium ylides forced us to consider some participation in order to enhance the addition. In view of the high ability for forming hydrogen bonding of the hydroxyl group in alcohol and of the enhanced nucleophilicity of the alkoxyl oxygen in intramolecular mode, we tentatively propose the intervention of hydrogen-bonded intermediates **15** and/or **15′** in reaction sequence. The comparatively high yields of adducts **4a**—**h**,**j**—**q** in reactions using (1-pyridinio)thiocarbonylmethylides (**1a**, **b**) and the decrease in the yields of adducts **4s**—**u**,**y**—**d′** in those using (4-methyl-1-pyridinio)thiocarbonylmethylides (**1c**,**d**), can be successfully explained by considering the stabilities of these intermediate ions **15** and **15′**. A nucleophilic attack of the alkoxyl group to **15′** stabilized by the 4-methyl group may provide 4-alkoxy-4-methyl-1,4-dihydropyridine derivatives, such as **18** or significant products, though we could not isolate them during these reactions. The presence of this route would naturally decrease the yields of products **4s**—**u**,**y**—**d′**. Furthermore, the decreased electrophilicity of the pyridine ring due to the inductive effect of the 4-methyl group may be considered to be a reason for it. On the other hand, the decrease in the yields of adducts **4f′**—**j′**,**l′**—**p′** in reactions using 1-(3,5-dimethyl-1-pyridinio)thiocarbonymethylides **1e**,**f** may be due to a retardation of the reactions because of the steric hindrance of the two methyl groups. The formation of indolizine **6** apparently results in 1,3-dipolar cycloadditions between ylides **1e**,**f** and DMAD (**2**) with the elimination of dithioformate.

In conclusion, we could demonstrate the intervention the 1 : 1 zwitterionic intermediates in the reactions of the (1-pyridinio)thiocarbonylmethylides (**1**) with DMAD (**2**). In the near future reactions between certain dipolar species and DMAD (**2**) in the presence of alcohol may be used as a criterion as to whether their process is concerted or not.

Experimental

The melting points were measured with 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 Hitachi R-600 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.

Preparations of Dimethyl 6-Thia-3-azatricyclo[5.3.1.0^{3,8}]undeca-4,9-diene-7,11-dicarboxylates. General Method. A chloroform solution (20 ml) of (1-pyridinio)thiocarbonylmethylide (**1**)[13] (5 mmol), DMAD (**2**) (1 g, 7 mmol), and alcohol **3** (2 ml) was allowed to react at room temperature for 5—7 h; the reaction mixture was then concentrated at reduced pressure. The residue was separated by column chromatography on alumina using chloroform as an eluent. The chloroform layers including the title compound **4** were combined and concentrated at reduced pressure. The crude product thus obtained was recrystallized from chloroform–hexane to give colorless crystals of 6-thia-3-azatricyclo[5.3.1.0^{3,8}]undeca-4,9-diene derivatives **4**.

When the reactions of ylide **1**, DMAD (**2**), and alcohol **3** were carried out at a temperature of below 10 °C, the yields of title compounds **4** were dramatically decreased, and the formation of considerable amounts of 10a*H*-pyrido-

Table 3. Some Data for Heterocage Compounds **4**

Compd[a)]	Reactants	Yield	Mp	ν (KBr)			Formula	Calcd (%)			Found (%)		
No.		%	°C	$\mathrm{cm^{-1}}$				C	H	N	C	H	N
4a	**1a+2+3a**	80	150—152	2214	1734		$C_{16}H_{18}N_2O_5S_2$	50.25	4.74	7.32	50.21	4.71	7.32
4b	**1a+2+3b**	84	140—142	2214	1736		$C_{17}H_{20}N_2O_5S_2$	51.50	5.08	7.07	51.75	5.09	7.06
4c	**1a+2+3c**	71	135—137	2207	1730		$C_{18}H_{22}N_2O_5S_2$	52.67	5.40	6.82	52.70	5.45	6.78
4d	**1a+2+3d**	70	155—157	2214	1734		$C_{18}H_{22}N_2O_5S_2$	52.67	5.40	6.82	52.52	5.28	7.10
4e	**1a+2+3e**	82	141—143	2207	1736		$C_{19}H_{24}N_2O_5S_2$	53.75	5.70	6.60	53.46	5.71	6.55
4f	**1a+2+3f**	86	109—111	2214	1738		$C_{19}H_{24}N_2O_5S_2$	53.75	5.70	6.60	53.73	5.54	6.65
4g	**1a+2+3g**	79	173—175	2214	1728		$C_{22}H_{22}N_2O_5S_2$	57.62	4.84	6.11	57.49	4.81	6.05
4h	**1a+2+3h**	69	129—131	2213	1738		$C_{18}H_{20}N_2O_5S_2$	52.93	4.94	6.86	52.93	4.97	7.02
4i	**1b+2+3a**	82	150—152	2213	1730		$C_{17}H_{20}N_2O_5S_2$	51.50	5.08	7.07	51.38	5.11	7.07
4k	**1b+2+3b**	78	122—124	2214	1736		$C_{18}H_{22}N_2O_5S_2$	52.67	5.40	6.82	52.54	5.38	6.97
4l	**1b+2+3c**	65	108—110	2211	1732		$C_{19}H_{24}N_2O_5S_2$	53.75	5.70	6.60	53.85	5.73	6.67
4m	**1b+2+3d**	62	117—119	2213	1738		$C_{19}H_{24}N_2O_5S_2$	53.75	5.70	6.60	53.80	5.76	6.65
4n	**1b+2+3e**	82	100—102	2212	1736		$C_{20}H_{26}N_2O_5S_2$	54.77	5.98	6.39	54.80	6.10	6.37
4o	**1b+2+3f**	72	88—90	2213	1738		$C_{20}H_{26}N_2O_5S_2$	54.77	5.98	6.39	54.56	5.95	6.31
4p	**1b+2+3g**	76	111—113	2211	1736		$C_{23}H_{24}N_2O_5S_2$	58.46	5.12	5.97	58.46	5.10	5.84
4q	**1b+2+3h**	51	117—119	2209	1738		$C_{19}H_{22}N_2O_5S_2$	54.01	5.25	6.63	54.21	5.33	6.78
4s	**1c+2+3a**	4	147—149	2211	1738		$C_{17}H_{20}N_2O_5S_2$	51.50	5.08	7.07	51.70	5.07	7.17
4t	**1c+2+3b**	10	131—133	2211	1732		$C_{18}H_{22}N_2O_5S_2$	52.67	5.40	6.82	52.41	5.21	7.08
4u	**1c+2+3c**	28	110—112	2213	1734		$C_{19}H_{24}N_2O_5S_2$	53.75	5.70	6.60	53.69	5.73	6.63
4y	**1d+2+3a**	6	138—140	2213	1740		$C_{18}H_{22}N_2O_5S_2$	52.67	5.40	6.82	52.68	5.64	6.57
4z	**1d+2+3b**	36	124—126	2213	1730		$C_{19}H_{24}N_2O_5S_2$	53.75	5.70	6.60	53.52	5.49	6.89
4a′	**1d+2+3c**	44	96—98	2214	1736		$C_{20}H_{26}N_2O_5S_2$	54.77	5.98	6.39	54.62	5.81	6.71
4b′	**1d+2+3d**	11	126—128	2209	1736		$C_{20}H_{26}N_2O_5S_2$	54.77	5.98	6.39	54.90	5.96	6.40
4c′	**1d+2+3e**	32	91—93	2213	1736		$C_{21}H_{28}N_2O_5S_2$	55.73	6.24	6.19	55.66	6.27	6.22
4d′	**1d+2+3f**	16	86—88	2216	1736		$C_{21}H_{28}N_2O_5S_2$	55.73	6.24	6.19	55.67	6.29	6.21
4f′	**1e+2+3b**	32	144—146	2209	1734		$C_{19}H_{24}N_2O_5S_2$	53.75	5.70	6.60	53.77	5.65	6.62
4g′	**1e+2+3c**	30	137—139	2209	1740		$C_{20}H_{26}N_2O_5S_2$	54.77	5.98	6.39	54.81	5.95	6.41
4h′	**1e+2+3d**	28	181—183	2209	1734		$C_{20}H_{26}N_2O_5S_2$	54.77	5.98	6.39	54.77	6.01	6.45
4i′	**1e+2+3e**	23	119—121	2207	1740		$C_{21}H_{28}N_2O_5S_2$	55.73	6.24	6.19	55.44	6.05	6.18
4j′	**1e+2+3f**	39	142—144	2209	1734		$C_{21}H_{28}N_2O_5S_2$	55.73	6.24	6.19	55.61	6.04	6.17
4l′	**1f+2+3b**	39	91—94	2216	1730		$C_{20}H_{26}N_2O_5S_2$	54.77	5.98	6.39	54.88	6.04	6.43
4m′	**1f+2+3c**	32	93—95	2213	1738		$C_{21}H_{28}N_2O_5S_2$	55.73	6.24	6.19	55.77	6.15	6.16
4n′	**1f+2+3d**	21	129—131	2207	1746	1728	$C_{21}H_{28}N_2O_5S_2$	55.73	6.24	6.19	55.81	6.14	6.21
4o′	**1f+2+3e**	29	109—111	2216	1736		$C_{22}H_{30}N_2O_5S_2$	56.63	6.48	6.00	56.41	6.30	5.99
4p′	**1f+2+3f**	34	138—140	2213	1738		$C_{22}H_{30}N_2O_5S_2$	56.63	6.48	6.00	56.69	6.42	6.00

a) All new compounds **4a**—**p′** were obtained as colorless prisms.

[1,2-*d*][1,4]thiazepines (**12**) and/or their Diels–Alder adducts **5**, which were formed from the reactions of only ylides **1** and DMAD (**2**), were observed. Although the yields of the reactions of ylides **1a**—**d** with DMAD (**2**) and alcohols **3a**,**b** in chloroform were slightly higher than those in only alcohol, the isolations of **4a**,**b**,**j**,**k**,**s**,**t**,**y**,**z** from the reaction mixtures under the former conditions were also easier than in the latter.

In the reactions of **1a**,**b** with **2** and **3i**, **1c** with **2** and **3d**—**i**, and **1d** with **2** and **3g**—**i** the corresponding 2-alkoxy derivatives, such as **4i**,**r**,**v**—**x**, could not be isolated; instead of them, small amounts of dimethyl 4-thia-1-azatetracyclo-$[5.4.0.0^{5,11}.0^{6,8}]$undeca-2,9-diene-5,6-dicarboxylate derivatives **5a**—**d**[14] were formed. The reactions of ylides **1e**,**f** with **2** and methanol (**3a**) did not provide the corresponding 2-methoxy compounds **4e**′,**k**′, pyridothiazepines (**12**), and tetracycloundecadiene derivatives **5** at all, but afforded dimethyl 3-cyano-6,8-dimethylindolizine-1,2-dicarboxylate (**6**), mp 159—161 °C, IR (KBr) 1732 (CO) and 2216 $\mathrm{cm^{-1}}$ (CN); ^{1}H NMR ($CDCl_3$) δ=2.33 (3H, s, 8-Me), 2.44 (3H, s, 6-Me), 3.97 (6H, s, $2\times CO_2Me$), 4.88 (1H, br s, 7-H), and 8.04 (1H, br s, 5-H). Found: C, 63.20; H, 4.90; N, 10.00%. Calcd for $C_{15}H_{14}N_2O_4$: C, 62.95; H, 4.93; N, 9.79%, as an only isolable product. ^{1}H NMR spectra and some physical and IR spectral data for title compounds **4** are listed in Tables 1 and 3, respectively.

Hydrolyses of Dimethyl 6-Thia-3-azatricyclo $[5.3.1.0^{3,8}]$undeca-4,9-diene-7,11-dicarboxylates. General Method A. A suspension of 6-thia-3-azatricyclo-$[5.3.1.0^{3,8}]$undeca-4,9-diene derivative **4** (1 mmol) and 1 M HCl (20 ml) was heated in a water bath (80 °C) for about 3 h. The resulting transparent solution was abstracted twice with a 30 ml portion of chloroform, and the combined chloroform layer was concentrated at reduced pressure. The residue was separated by column chromatography on alumina using chloroform as an eluent. The chloroform layers including benzothiazine were combined, and the solvent was removed at reduced pressure. The crude crystals of product was recrystallized from ether to give pure **8** as colorless prisms.

These results and some other data for new compounds are as follows;

8a (from **4b**): 96%, mp 140—142 °C, IR (KBr) 1674 and 1740 (CO), 2222 (CN), 3360 $\mathrm{cm^{-1}}$ (NH); ^{1}H NMR ($CDCl_3$) δ=2.40 (3H, s, SMe), 2.4—2.8 (2H, m, 5-H), 3.74 and 3.81 (each 3H, s, $2\times CO_2Me$), 3.9—4.6 (3H, m, 4a-H, 8-H, and NH), 6.85 (1H, br s, 6-H), and 9.44 (1H, s, CHO). Found: C, 49.10; H, 4.36; N, 7.42%. Calcd for $C_{15}H_{16}N_2O_5S_2$: C, 48.90; H, 4.38; N, 7.60%.

8b (from **4k**): 76%, mp 135—138 °C, IR (KBr) 1680 and 1734 (CO), 2220 (CN), 3337 $\mathrm{cm^{-1}}$ (NH); ^{1}H NMR ($CDCl_3$) δ=1.30 (3H, t, J=7.0 Hz, $SCH_2\underline{CH_3}$), 2.4—2.8 (2H, m, 5-H), 2.90 (2H, q, J=7.0 Hz, $S\underline{CH_2}CH_3$), 3.74 and 3.81 (each 3H, s, $2\times CO_2Me$), 3.9—4.6 (3H, m, 4a-H, 8-H, and NH), 6.83 (1H, br s, 6-H), and 9.43 (1H, s, CHO). Found: C, 50.23; H, 4.73; N, 7.36%. Calcd for $C_{16}H_{18}N_2O_5S_2$: C, 50.25; H, 4.74; N, 7.32%.

8c (from **4u**): 79%, mp 164—166 °C, IR (KBr) 1671 and 1730 (CO), 2222 (CN), 3349 $\mathrm{cm^{-1}}$ (NH); ^{1}H NMR ($CDCl_3$) δ=2.26 (3H, s, 6-Me), 2.41 (3H, s, SMe), 2.4—2.9 (2H, m, 5-H), 3.73 and 3.81 (each 3H, s, $2\times CO_2Me$), 3.9—4.4 (3H, m, 4a-H, 8-H, and NH), and 10.04 (1H, s, CHO). Found: C, 50.19; H, 4.80; N, 7.23%. Calcd for $C_{16}H_{18}N_2O_5S_2$: C, 50.25; H, 4.74; N, 7.32%.

8d (from **4c**′): 72%, mp 154—156 °C, IR (KBr) 1669 and 1736 (CO), 2222 (CN), 3326 $\mathrm{cm^{-1}}$ (NH); ^{1}H NMR ($CDCl_3$) δ=1.29 (3H, t, J=7.0 Hz, $SCH_2\underline{CH_3}$), 2.25 (3H, s, 6-Me), 2.4—2.8 (2H, m, 5-H), 2.91 (2H, q, J=7.0 Hz, $S\underline{CH_2}CH_3$), 3.71 and 3.79 (each 3H, s, $2\times CO_2Me$), 3.9—4.6 (3H, m, 4a-H, 8-H, and NH), and 10.02 (1H, s, CHO). Found: C, 51.78; H, 5.07; N, 6.83%. Calcd for $C_{17}H_{20}N_2O_5S_2$: C, 51.50; H, 5.08; N, 7.07%.

General Method B. A suspension of 1,9-dimethyl-6-thia-3-azatricyclo$[5.3.1.0^{3,8}]$undeca-4,9-diene derivative **4g**′ or **4m**′ (1 mmol) and concd HCl (20 ml) was heated in a water bath (80 °C) for about 10 h. The resulting solution was then neutralized with aqueous sodium hydroxide. After the solution was abstracted twice with a 30 ml portion of chloroform, the combined chloroform layers were dried over sodium sulfate and then filtrated. The usual work-ups for the filtrate gave the corresponding tetramethyl 1,1′,9,9′-tetramethyl-2,2′-oxydi(6-thia-3-azatricyclo$[5.3.1.0^{3,8}]$undeca-4,9-dien-7,11-dicarboxylate)s (**9a**,**b**) as colorless crystals.

The reactions (Method A) of **4g**′,**m**′ with 1 M HCl did not give any significant products, and only the starting materials were recovered.

These results and some other data for new compounds are as follows; **9a** (from **4g**′), 16%, mp 165—167 °C, IR (KBr) 1738 (CO), 2216 $\mathrm{cm^{-1}}$ (CN); ^{1}H NMR ($CDCl_3$) δ= 1.24 (3H, s, 1-Me), 1.83 (3H, d, J=2.0 Hz, 9-Me), 2.47 (3H, s, SMe), 3.4—3.6 (2H, br s, 8- and 11-H), 3.72 and 3.79 (each 3H, s, $2\times CO_2Me$), 5.47 (1H, br s, 2-H), and 5.56 (1H, br s, 10-H). Found: C, 52.76; H, 5.18; N, 6.94%. Calcd for $C_{34}H_{38}N_4O_9S_4$: C, 52.70; H, 4.94; N, 7.23%.

9b (from **4m**′): 19%, mp 209—211 °C, IR (KBr) 1741 (CO), 2214 $\mathrm{cm^{-1}}$ (CN); ^{1}H NMR ($CDCl_3$) δ=1.25 (3H, s, 1-Me), 1.36 (3H, t, J=7.0 Hz, $SCH_2\underline{CH_3}$), 1.84 (3H, d, J=2.0 Hz, 9-Me), 2.93 (2H, q, J=7.0 Hz, $S\underline{CH_2}CH_3$), 3.4—3.6 (2H, br s, 8- and 11-H), 3.71 and 3.79 (each 3H, s, $2\times CO_2Me$), 5.48 (1H, br s, 2H), and 5.59 (1H, br s, 10-H). Found: C, 53.94; H, 5.36; N, 6.80%. Calcd for $C_{36}H_{42}N_4O_9S_4$: C, 53.85; H, 5.27; N, 6.98%.

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14) Compounds **5a**—**d** were completely in accord with those reported earlier by us (see Ref. 6) in all respects.