Preparation of New Nitrogen-Bridged Heterocycles. XXIV.[1] Syntheses and Reactions of Pyrazolo[1,5-*a*]pyridine-2-thiols. (2)

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Various 2-(acrylmethylthio)-, 2-(benzylthio)-, and 2-(propargylthio)pyrazolo[1,5-*a*]pyridine derivatives (4a—n′ and 7a—n′) were prepared in moderate to good yields by the reactions of potassium pyrazolo[1,5-*a*]pyridine-2-thiolates (2 and 6), readily available by the treatment of 2-[(2-ethoxycarbonylethyl)thio]- and 2-[(2-cyanoethyl)thio]pyrazolo[1,5-*a*]pyridines (1a—h and 5a—h) with potassium *tert*-butoxide in *N,N*-dimethylformamide (DMF), with alkylating agents such as chloroacetone (3a), phenacyl bromides (3b—d), ethyl bromoacetate (3e), benzyl bromides (3f—k), and propargyl bromide (3l). Of these *S*-functionalized pyrazolo[1,5-*a*]pyridines only 2-(acetonylthio)- and 2-(phenacylthio)pyrazolo[1,5-*a*]pyridine-3-carbonitriles (4a—t) were converted to new heterocycles, thieno[2′,3′:3,4]pyrazolo[1,5-*a*]pyridines (8a—t) by heating them with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU); the other compounds did not provide any tricyclic heterocycles under various alkaline conditions. The structures of thieno[2′,3′:3,4]pyrazolo[1,5-*a*]pyridines (8a—t) were determined mainly by elemental analyses and spectral inspections, and the structural assignment was confirmed by the X-ray analysis of compound 8d.

Keywords pyrazolo[1,5-*a*]pyridine-2-thiol; *S*-alkylation; thieno[2′,3′:3,4]pyrazolo[1,5-*a*]pyridine; X-ray analysis; cyclization; *S*-functionalized pyrazolo[1,5-*a*]pyridine

Although many pyrazolo[1,5-*a*]pyridine derivatives having various substituents have been synthesized by several methods,[2] only a few bearing both an active methylene group and an electron-withdrawing group on the 5-membered ring have been reported.[3] A principal reason for the inaccessibility of these polyfunctionalized pyrazolo[1,5-*a*]pyridines may be the extremely high reactivity of the active methylene group toward electron-withdrawing groups which are present in the reaction system. In order to avoid such undesirable reactions and to obtain authentic compounds, development of some other reaction route including the use of the protecting groups may be necessary. In our preceding paper[1] we described the first preparations of pyrazolo[1,5-*a*]pyridine-2-thiol derivatives by the treatment of 2-[(2-ethoxycarbonylethyl)thio]- and 2-[(cyanoethyl)thio]pyrazolo[1,5-*a*]pyridines with potassium *tert*-butoxide in *N,N*-dimethylformamide (DMF). The smooth accessibility of pyrazolo[1,5-*a*]pyridine-2-thiol derivatives and our previous results on 2-indolizinethiols[4] prompted us to investigate a possible preparative route to polyfunctionalized pyrazolo[1,5-*a*]pyridines *via* *S*-alkylation. In this paper we wish to report the *S*-alkylations of pyrazolo[1,5-*a*]pyridine-2-thiols and the transformations of some of the products into new heterocyclic compounds, thieno[2′,3′:3,4]pyrazolo[1,5-*a*]pyridines.

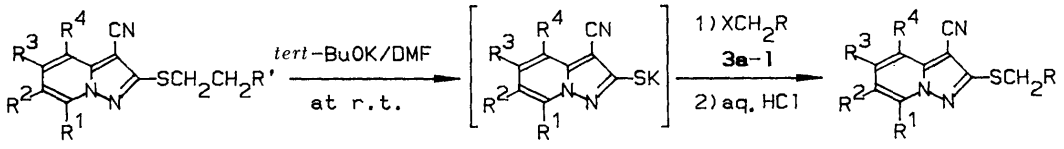
Results and Discussion

S-Alkylations of Pyrazolo[1,5-*a*]pyridine-2-thiols According to the procedure described previously by us,[4] 2-[(2-ethoxycarbonylethyl)thio]pyrazolo[1,5-*a*]-pyridine-3-carbonitriles (**1a—e**) were treated with potassium *tert*-butoxide in DMF at room temperature and the resulting potassium pyrazolo[1,5-*a*]pyridine-2-thiolates (**2**) were then allowed to react with chloroacetone (**3a**) to afford the expected 2-(acetonylthio)pyrazolo[1,5-*a*]pyridine-3-carbonitriles (**4a—e**) in 61—87% yields. The same compounds (**4a—c**) were also obtained in 73, 85, and 79% yields by the reactions of 2-[(2-cyanoethyl)thio]pyrazolo[1,5-*a*]pyridines (**1f—h**) with potassium *tert*-butoxide and **3a**, respectively. Similarly, the reactions of potassium pyrazolo[1,5-*a*]pyridine-2-thiolates (**2**) with phenacyl bromides (**3b—d**), ethyl bromoacetate (**3e**), benzyl bromides (**3f—k**), and propargyl bromide (**3l**) afforded the corresponding *S*-alkylated pyrazolo[1,5-*a*]pyridines **4f—n′** in moderate to good yields (Chart 1). Similar reactions of ethyl 2-[(2-substituted ethyl)thio]pyrazolo[1,5-*a*]pyridine-3-carboxylates (**5a—h**) with potassium *tert*-butoxide and alkylating agents (**3a—l**) provided the corresponding compounds **7a—n′** in 52—98% yields (Chart 2).

The structures of these products **4a—n′** and **7a—n′** could be determined with ease by means of spectroscopic inspections: the appearance of the proton signals of the 2-substituents derived from the alkylating agents in their proton nuclear magnetic resonance (^{1}H-NMR) spectra (Table I) and the change in the absorption bands attributable to the 2-substituents in their infrared (IR) spectra were observed. In particular, the presence of a methylene singlet (**4a—m′** and **7a—m′**) or a methylene doublet (**4n′** and **7n′**) appearing at δ 3.89—4.76 in their ^{1}H-NMR spectra strongly supported the *S*-alkylation at the 2-thiol function. In their IR spectra, the ester carbonyl (1718—1733 cm^{-1}) or the cyano absorption bands (2238—2247 cm^{-1}) due to the 2-substituents in the starting compounds **1a—h** and **5a—h**[1] had completely disappeared, and distinct absorption bands corresponding to the newly introduced 2-substituents were observed at 1701—1720 (**4a—e** and **7a—e**, acetonyl carbonyl), 1672—1690 (**4f—t** and **7f—t**, aroyl carbonyl), 1721—1738 (**4u—y and 7u—y**, ester carbonyl), 1500—1521 and 1332—1366 (**4z—i′** and **7z—i′**, nitro), and 3225 and 2115 or 2120 cm^{-1} (**4n′** and **7n′**, terminal acetylene).

Ethyl 2-(ethoxycarbonylmethylthio)pyrazolo[1,5-*a*]pyridine-3-carboxylates (**7u—w**) were identical with authentic samples.[3]

Reactions of *S*-Functionalized Pyrazolo[1,5-*a*]pyridines (4a—n′ and 7a—n′) in the Presence of Base Since pyrazolo[1,5-*a*]pyridine derivatives having an active methylene group at the 2-position could be synthesized with



1a-h 2 4a-n'

1	R^1	R^2	R^3	R^4	R'
a	H	H	H	H	COOEt
b	Me	H	H	H	COOEt
c	H	H	Me	H	COOEt
d	H	H	Et	H	COOEt
e	H	Me	H	Me	COOEt
f	H	H	H	H	CN
g	Me	H	H	H	CN
h	H	H	Me	H	CN

3	R	X
a	Ac	Cl
b	Bz	Br
c	*p*-ClBz	Br
d	*p*-BrBz	Br
e	COOEt	Br
f	*p*-NO_2Ph	Br
g	*o*-NO_2Ph	Br
h	Ph	Br
i	*p*-MePh	Br
j	*p*-ClPh	Br
k	*p*-BrPh	Br
l	C≡CH	Br

4	R^1	R^2	R^3	R^4	R
a	H	H	H	H	Ac
b	Me	H	H	H	Ac
c	H	H	Me	H	Ac
d	H	H	Et	H	Ac
e	H	Me	H	Me	Ac
f	H	H	H	H	Bz
g	Me	H	H	H	Bz
h	H	H	Me	H	Bz
i	H	H	Et	H	Bz
j	H	Me	H	Me	Bz
k	H	H	H	H	*p*-ClBz
l	Me	H	H	H	*p*-ClBz
m	H	H	Me	H	*p*-ClBz
n	H	H	Et	H	*p*-ClBz
o	H	Me	H	Me	*p*-ClBz
p	H	H	H	H	*p*-BrBz
q	Me	H	H	H	*p*-BrBz
r	H	H	Me	H	*p*-BrBz
s	H	H	Et	H	*p*-BrBz
t	H	Me	H	Me	*p*-BrBz

4	R^1	R^2	R^3	R^4	R
u	H	H	H	H	COOEt
v	Me	H	H	H	COOEt
w	H	H	Me	H	COOEt
x	H	H	Et	H	COOEt
y	H	Me	H	Me	COOEt
z	H	H	H	H	*p*-NO_2Ph
a'	Me	H	H	H	*p*-NO_2Ph
b'	H	H	Me	H	*p*-NO_2Ph
c'	H	H	Et	H	*p*-NO_2Ph
d'	H	Me	H	Me	*p*-NO_2Ph
e'	H	H	H	H	*o*-NO_2Ph
f'	Me	H	H	H	*o*-NO_2Ph
g'	H	H	Me	H	*o*-NO_2Ph
h'	H	H	Et	H	*o*-NO_2Ph
i'	H	Me	H	Me	*o*-NO_2Ph
j'	H	H	H	H	Ph
k'	H	H	H	H	*p*-MePh
l'	H	H	H	H	*p*-ClPh
m'	H	H	H	H	*p*-BrPh
n'	H	H	H	H	C≡CH

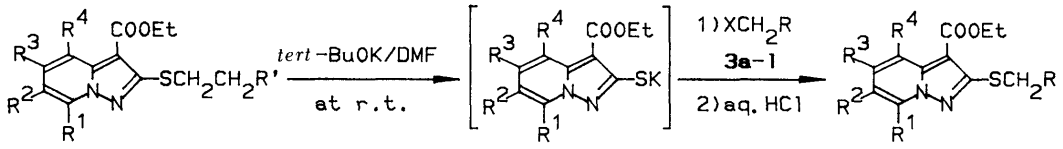
Bz: benzoyl

Chart 1

ease, the interactions between the substituents at the 2- and 3-positions were examined. When the 2-(acetonylthio)pyrazolo[1,5-*a*]pyridine-3-carbonitriles (**4a—e**) in ethanolic solution were heated under reflux in the presence of DBU, the corresponding 2-acetyl-3-aminothieno[2',3' : 3,4]pyrazolo[1,5-*a*]pyridine derivatives (**8a—e**), new thiophene-fused heterocycles, were formed in 41—83% yields, respectively. Similar treatment of 2-(phenacylthio)pyrazolo[1,5-*a*]pyridine-3-carbonitriles (**4f—i, k—m, p—s**) provided the corresponding 3-aminothieno[2',3' : 3,4]pyrazolo[1,5-*a*]pyridines (**8f—i, k—m, p—s**). However, the reactions of 4,6-dimethyl-2-(phenacylthio)pyrazolo[1,5-*a*]-pyridines (**4j, o, t**) with DBU in ethanol gave complex mixtures of **8j, o, t** and unidentified products, and separation was unsuccessful because of their low solubility. Heating of compounds **4j, o, t** with DBU in *tert*-butanol followed by filtration of the hot reaction solutions afforded the expected heterocycles **8j, o, t** in a pure state, respectively, but the yields were very low (Chart 3). On the other hand, the similar treatment of 2-(ethoxycarbonylmethylthio)-(**4u—y**), 2-[(4-nitrobenzyl)thio]-(**4z—d'**), and 2-[(2-nitrobenzyl)thio]pyrazolo[1,5-*a*]pyridine-3-carbonitriles (**4e'—i'**) did not give any significant products at all. Furthermore, all our attempts to obtain the intramolecular cycloadduct **9** from ethyl pyrazolo[1,5-*a*]pyridine-3-carboxylates (**7a—i'**) under various alkaline conditions (DBU/ethanol, potassium *tert*-butoxide/DMF, and so on) were unsuccessful. In the cases of ethyl 2-(ethoxycarbonylmethylthio)pyrazolo[1,5-*a*]pyridine-3-carboxylates (**7u—y**), the reactions with potassium *tert*-butoxide in DMF at 80—90 °C gave only the monohydrolyzed products, ethyl 2-(carboxymethylthio)pyrazolo[1,5-*a*]pyridine-3-carboxylates (**10a—e**), in 44—64% yields, respectively (Chart 4).

The tendency of these pyrazolo[1,5-*a*]pyridines (**4u—i'** and **7a—i'**) not to cyclize is in marked contrast to the case of the polyfunctionalized indolizine derivatives which were recently reported by us.[4,5]

The structural assignments of these thieno[2',3' : 3,4]pyrazolo[1,5-*a*]pyridines (**8a—t**) were accomplished mainly on the basis of spectral data: the absence of the cyano and the presence of the primary amino group absorption bands (3150—3480 cm^{-1}) in their IR spectra, and the desappearance of the methylene signal and the appearance of the broad amino signal (δ 6.91—8.2) in the ^{1}H-NMR spectra of **8a—j** (Table II). Furthermore, the X-ray analysis of compound **8d** strongly supported our proposed structures for **8a—t** (see below). On the other hand, compounds **10a—e** were concluded to be ethyl 2-(carboxymethylthio)pyr-



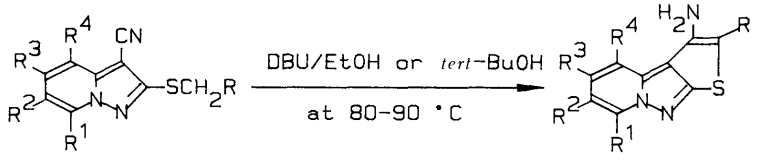
5a-h 6 7a-n'

5	R^1	R^2	R^3	R^4	R'
a	H	H	H	H	COOEt
b	Me	H	H	H	COOEt
c	H	H	Me	H	COOEt
d	H	H	Et	H	COOEt
e	H	Me	H	Me	COOEt
f	H	H	H	H	CN
g	Me	H	H	H	CN
h	H	H	Me	H	CN

7	R^1	R^2	R^3	R^4	R
a	H	H	H	H	Ac
b	Me	H	H	H	Ac
c	H	H	Me	H	Ac
d	H	H	Et	H	Ac
e	H	Me	H	Me	Ac
f	H	H	H	H	Bz
g	Me	H	H	H	Bz
h	H	H	Me	H	Bz
i	H	H	Et	H	Bz
j	H	Me	H	Me	Bz
k	H	H	H	H	*p*-ClBz
l	Me	H	H	H	*p*-ClBz
m	H	H	Me	H	*p*-ClBz
n	H	H	Et	H	*p*-ClBz
o	H	Me	H	Me	*p*-ClBz
p	H	H	H	H	*p*-BrBz
q	Me	H	H	H	*p*-BrBz
r	H	H	Me	H	*p*-BrBz
s	H	H	Et	H	*p*-BrBz
t	H	Me	H	Me	*p*-BrBz

7	R^1	R^2	R^3	R^4	R
u	H	H	H	H	COOEt
v	Me	H	H	H	COOEt
w	H	H	Me	H	COOEt
x	H	H	Et	H	COOEt
y	H	Me	H	Me	COOEt
z	H	H	H	H	*p*-NO_2Ph
a'	Me	H	H	H	*p*-NO_2Ph
b'	H	H	Me	H	*p*-NO_2Ph
c'	H	H	Et	H	*p*-NO_2Ph
d'	H	Me	H	Me	*p*-NO_2Ph
e'	H	H	H	H	*o*-NO_2Ph
f'	Me	H	H	H	*o*-NO_2Ph
g'	H	H	Me	H	*o*-NO_2Ph
h'	H	H	Et	H	*o*-NO_2Ph
i'	H	Me	H	Me	*o*-NO_2Ph
j'	H	H	H	H	Ph
k'	H	H	H	H	*p*-MePh
l'	H	H	H	H	*p*-ClPh
m'	H	H	H	H	*p*-BrPh
n'	H	H	H	H	C≡CH

Chart 2



4a-t 8a-t

8	R^1	R^2	R^3	R^4	R
a	H	H	H	H	Ac
b	Me	H	H	H	Ac
c	H	H	Me	H	Ac
d	H	H	Et	H	Ac
e	H	Me	H	Me	Ac
f	H	H	H	H	Bz
g	Me	H	H	H	Bz
h	H	H	Me	H	Bz
i	H	H	Et	H	Bz
j	H	Me	H	Me	Bz

8	R^1	R^2	R^3	R^4	R
k	H	H	H	H	*p*-ClBz
l	Me	H	H	H	*p*-ClBz
m	H	H	Me	H	*p*-ClBz
n	H	H	Et	H	*p*-ClBz
o	H	Me	H	Me	*p*-ClBz
p	H	H	H	H	*p*-BrBz
q	Me	H	H	H	*p*-BrBz
r	H	H	Me	H	*p*-BrBz
s	H	H	Et	H	*p*-BrBz
t	H	Me	H	Me	*p*-BrBz

Chart 3

azolo[1,5-*a*]pyridine-3-carboxylates on the basis of the absence of ethoxy proton signals (δ 1.24—1.32 (t) and 4.16—4.28 (q)) at higher magnetic field in the ^{1}H-NMR spectra of the starting compounds **7u**—**y**, and the presence of a broad carboxy proton signal at δ 8.63—9.80 in the ^{1}H-NMR spectra of **10a**—**e**.

TABLE I. ^{1}H-NMR Spectral Data for 2-(Substituted Methylthio)pyrazolo[1,5-*a*]pyridines

Compd.	δ (CDCl$_3$)[a] C-4	C-5		C-6	C-7	SCH$_2$	Others
4a	7.2—7.8			6.93	8.49	4.02	2.30
	m			dt	brd	s	s
4b	7.1—7.8			6.84	2.70	4.02	2.38
	m			brd	s	s	s
4c	7.30	2.42		6.72	8.28	4.01	2.33
	brs	s		dd	d	s	s
4d	7.38	1.27	2.72	6.78	8.40	3.98	2.33
	brs	t	q	dd	d	s	s
4e	2.58	7.02		2.26	8.14	3.96	2.31
	s	brs		s	brs	s	s
4f	*b*)	*b*)		6.92	8.42	4.76	7.2—8.3
				dt	brd	s	m
4g	*b*)	*b*)		6.73	2.48	4.69	7.1—8.3
				brd	s	s	m
4h	7.21	2.38		6.63	8.15	4.66	7.1—8.3
	brs	s		dd	d	s	m
4i	7.30	1.28	2.73	6.68	8.31	4.72	7.1—8.3
	brs	t	q	dd	d	s	m
4j	2.58	6.99		2.26	*b*)	4.68	7.2—8.2
	s	brs		s		s	m
4k	*b*)	*b*)		6.94	8.42	4.68	7.3—8.2
				dt	brd	s	m
4l	*b*)	*b*)		6.76	2.53	4.63	7.2—8.3
				brd	s	s	m
4m	7.38	2.43		6.74	8.28	4.67	7.2—8.3
	brs	s		dd	d	s	m
4n	7.34	1.32	2.75	6.78	8.30	4.56	7.3—8.2
	brs	t	q	dd	d	s	m
4o	2.58	6.99		2.26	8.05	4.63	7.2—8.2
	s	brs		s	brs	s	m
4p	*b*)	*b*)		6.93	8.42	4.68	7.3—8.1
				dt	brd	s	m
4q	*b*)	*b*)		6.75	2.56	4.67	7.2—8.2
				brd	s	s	m
4r	7.37	2.38		6.75	8.29	4.64	7.5—8.1
	brs	s		dd	d	s	m
4s	7.39	1.27	2.70	6.77	8.31	4.67	7.5—8.1
	brs	t	q	dd	d	s	m
4t	2.60	6.99		2.26	8.05	4.63	7.2—8.2
	s	brs		s	brs	s	m
4u	7.4—7.8			6.93	8.51	3.99	1.29 4.19
	m			dt	brd	s	t q
4v	7.1—7.7			6.80	2.66	3.97	1.25 4.18
	m			brd	s	s	t q
4w	7.40	2.43		6.76	8.33	3.95	1.22 4.17
	brs	s		dd	d	s	t q
4x	7.39	1.30	2.76	6.81	8.33	3.99	1.32 4.21
	brs	t	q	dd	d	s	t q
4y	2.56	7.00		2.28	8.13	3.93	1.25 4.18
	s	brs		s	brs	s	t q
4z	*b*)	*b*)		6.97	8.56	4.46	7.3—8.5
				dt	brd	s	m
4a′	*b*)	*b*)		6.83	2.74	4.48	7.2—8.5
				brd	s	s	m
4b′	7.40	2.42		6.78	8.38	4.43	7.4—8.5
	brs	s		dd	d	s	m
4c′	7.39	1.31	2.76	6.83	8.36	4.48	7.3—8.4
	brs	t	q	dd	d	s	m
4d′	2.64	7.02		2.32	*b*)	4.47	7.4—8.4
	s	brs		s		s	m
4e′	*b*)	*b*)		6.95	8.51	4.75	7.2—8.2
				dt	brd	s	m
4f′	*b*)	*b*)		6.81	2.69	4.76	7.2—8.2
				brd	s	s	m
4g′	*b*)	2.39		6.75	8.35	4.70	7.2—8.2
		s		dd	d	s	m

TABLE I. (continued)

Compd.	δ (CDCl$_3$)[a] C-4	C-5		C-6	C-7	SCH$_2$	Others
4h′	*b*)	1.32	2.76	6.80	8.35	4.76	7.2—8.2
		t	q	dd	d	s	m
4i′	2.59	6.97		2.33	8.12	4.75	7.3—8.1
	s	brs		s	brs	s	m
4j′	*b*)	*b*)		6.93	8.54	4.42	7.1—7.9
				dt	brd	s	m
4k′	*b*)	*b*)		6.92	8.50	4.39	7.0—7.9 2.27
				dt	brd	s	m s
4l′	*b*)	*b*)		6.97	8.62	4.41	7.1—7.9
				dt	brd	s	m
4m′	*b*)	*b*)		6.94	8.47	4.39	7.1—7.8
				dt	brd	s	m
4n′	7.71	7.45		6.97	8.53	3.97	2.25
	brd	brt		dt	brd	d	t
7a	8.06	7.39		6.86	8.40	3.93	1.38 4.31 2.32
	brd	brt		dt	brd	s	t q s
7b	7.95	7.26		6.67	2.64	3.91	1.41 4.31 2.34
	brd	q		brd	s	s	t q s
7c	7.80	2.38		6.66	8.25	3.92	1.40 4.32 2.32
	brs	s		dd	d	s	t q s
7d	7.84	1.27	2.73	6.71	8.29	3.95	1.42 4.34 2.38
	brs	t	q	dd	d	s	t q s
7e	2.66	6.94		2.24	8.06	3.89	1.39 4.32 2.33
	s	brs		s	brs	s	t q s
7f	*b*)	*b*)		6.80	8.35	4.70	1.38 4.35 7.1—8.3
				dt	brd	s	t q m
7g	7.87	7.17		6.50	2.32	4.56	1.40 4.28 7.3—8.3
	brd	q		brd	s	s	t q m
7h	7.86	2.38		6.66	*b*)	4.68	1.39 4.34 7.3—8.4
	brs	s		dd		s	t q m
7i	7.85	1.28	2.70	6.65	*b*)	4.66	1.43 4.35 7.3—8.4
	brs	t	q	dd		s	t q m
7j	2.65	6.91		2.21	7.94	4.63	1.39 4.33 7.2—8.4
	s	brs		s	brs	s	t q m
7k	*b*)	*b*)		6.80	8.33	4.62	1.41 4.35 7.2—8.2
				dt	brd	s	t q m
7l	7.95	7.27		6.64	2.35	4.54	1.40 4.33 7.3—8.2
	brd	q		brd	s	s	t q m
7m	7.82	2.36		6.67	8.19	4.58	1.39 4.31 7.3—8.3
	brs	s		dd	d	s	t q m
7n	7.85	1.28	2.74	6.69	8.21	4.66	1.43 4.40 7.3—8.2
	brs	t	q	dd	d	s	t q m
7o	2.63	6.90		2.19	7.94	4.54	1.38 4.31 7.3—8.3
	s	brs		s	brs	s	t q m
7p	*b*)	7.31		6.82	8.28	4.60	1.39 4.34 7.5—8.2
		brt		dt	brd	s	t q m
7q	*b*)	7.29		6.65	2.41	4.58	1.40 4.37 7.5—8.2
		q		brd	s	s	t q m
7r	7.81	2.35		6.63	8.17	4.56	1.38 4.31 7.4—8.3
	brs	s		dd	d	s	t q m
7s	7.83	1.26	2.69	6.68	8.19	4.60	1.39 4.35 7.4—8.1
	brs	t	q	dd	d	s	t q m
7t	2.62	6.91		2.17	*b*)	4.54	1.39 4.29 7.4—8.2
	s	brs		s		s	t q m
7u	8.13	7.42		6.91	8.46	4.05	1.30 4.28 1.44 4.43
	brd	brt		dt	brd	s	t q t q
7v	7.98	7.32		6.75	2.72	4.03	1.29 4.26 1.43 4.41
	brd	q		brd	s	s	t q t q
7w	7.80	2.43		6.68	8.25	3.99	1.28 4.23 1.42 4.38
	brs	s		dd	d	s	t q t q
7x	7.84	1.32	2.75	6.72	8.30	4.00	1.32 4.24 1.46 4.39
	brs	t	q	dd	d	s	t q t q
7y	2.64	6.91		2.21	8.06	3.89	1.24 4.16 1.38 4.29
	s	brs		s	brs	s	t q t q
7z	*b*)	7.37		6.88	8.42	4.44	1.37 4.32 7.5—8.3
		brt		dt	brd	s	t q m
7a′	*b*)	7.33		6.70	2.68	4.48	1.39 4.34 7.4—8.4
		q		brd	s	s	t q m

TABLE I. (continued)

Compd.	δ (CDCl$_3$)[a] C-4	C-5		C-6	C-7	SCH_2	Others			
7b′	7.48	2.41		6.70	8.35	4.44	1.40	4.33	7.5—8.5	
	brs	s		dd	d	s	t	q	m	
7c′	7.94	1.34	2.81	6.85	8.47	4.58	1.46	4.45	7.4—8.4	
	brs	t	q	dd	d	s	t	q	m	
7d′	2.66	6.99		2.25	*b*)	4.46	1.40	4.35	7.4—8.4	
	s	brs		s		s	t	q	m	
7e′	*b*)	*b*)		6.83	8.39	4.70	1.37	4.30	7.1—8.2	
				dt	brd	s	t	q	m	
7f′	*b*)	7.30		6.72	2.67	4.80	1.37	4.34	7.2—8.2	
		q		brd	s	s	t	q	m	
7g′	*b*)	2.36		6.64	8.33	4.71	1.35	4.30	7.1—8.1	
		s		dd	d	s	t	q	m	
7h′	*b*)	1.30	2.73	6.71	8.32	4.73	1.43	4.35	7.0—8.3	
		t	q	dd	d	s	t	q	m	
7i′	2.68	6.93		2.31	8.10	4.69	1.42	4.32	7.2—8.1	
	s	brs		s	brs	s	t	q	m	
7j′	8.16	*b*)		6.88	8.56	4.49	1.38	4.38	7.2—7.8	
	brd			dt	brd	s	t	q	m	
7k′	8.12	*b*)		6.85	8.51	4.43	1.37	4.35	7.0—7.7	2.30
	brd			dt	brd	s	t	q	m	s
7l′	8.08	*b*)		6.86	8.46	4.42	1.35	4.35	7.1—7.6	
	brd			dt	brd	s	t	q	m	
7m′	8.07	*b*)		6.86	8.44	4.41	1.42	4.38	7.1—7.6	
	brd			dt	brd	s	t	q	m	
7n′	8.09	7.40		6.89	8.50	4.00	1.47	4.40	2.23	
	brd	brt		dt	brd	d	t	q	t	
10a	8.08	7.42		6.91	8.42	4.01	1.44	4.40	8.63	
	brd	brt		dt	brd	s	t	q	br	
10b	8.10	7.45		6.84	2.72	4.04	1.45	4.47	9.08	
	brd	q		brd	s	s	t	q	br	
10c	7.82	2.44		6.73	8.29	3.99	1.42	4.40	9.42	
	brs	s		dd	d	s	t	q	br	
10d	7.83	1.32	2.75	6.78	8.29	3.98	1.44	4.40	9.67	
	brs	t	q	dd	d	s	t	q	br	
10e	2.67	6.97		2.26	8.03	3.90	1.39	4.34	9.80	
	s	brs		s	brs	s	t	q	br	

a) The coupling constants are as follows: $J_{4,5}=9.0$, $J_{5,6}=J_{6,7}=7.0$, $J_{4,6}=2.0$, $J_{Et}=7.0$, and $J_{propargyl}=3.0$ Hz. *b*) Overlapped with the phenyl proton signals.

X-Ray Crystallography of 2-Acetyl-3-amino-5-ethylthieno-[2′,3′:3,4]pyrazolo[1,5-*a*]pyridine (8d) The X-ray analysis of thieno[2′,3′:3,4]pyrazolo[1,5-*a*]pyridine (**8d**) was carried out on a single crystal grown from ethanol solution. The X-ray diffraction data were collected with a Rigaku AFC-5 four-circle diffractometer with graphite-monochromated MoK_α radiation ($\lambda=0.71073$). The structural analysis was performed with the TEXSAN (Molecular Structure Corporation) system. The space group is $R\bar{3}$, $a=27.118$ (6), $c=9.557$ (5) Å for hexagonal axes, $V=6086$

TABLE II. ^{1}H-NMR Spectral Data for 3-Aminothieno[2′,3′:3,4]pyrazolo[1,5-*a*]pyridines

Compd. **8**	δ (CDCl$_3$)[a,b] C-4	C-5		C-6	C-7	NH_2	R^5
a	7.88	7.48		7.03	8.43	7.01	2.37
	brd	brt		dt	brd	brs	s
b	7.77	7.40		6.92	2.85	6.97	2.36
	brs	q		brd	s	brs	s
c	7.53	2.48		6.85	8.58	6.91	2.34
	brs	s		dd	d	brs	s
d	7.55	1.34	2.79	6.88	8.63	6.96	2.36
	brs	t	q	dd	d	brs	s
e	2.81	7.01		2.36	8.35	7.24	2.36
	s	brs		s	brs	brs	s
f	8.26	*c*)		6.99	8.63	*c*)	7.0—8.0
	brd			dt	brd		m
g	*c*)	*c*)		6.89	2.83	*c*)	7.1—8.1
				brd	s		m
h	*c*)	2.51		6.76	8.59	*c*)	7.0—8.1
		s		dd	d		m
i	*c*)	1.26	2.71	6.88	8.52	*c*)	7.1—8.2
		t	q	dd	d		m
j	2.81	6.96		2.32	8.25	*c*)	7.8—8.0
	s	brs		s	brs	—	m

a) The coupling constants are as follows: $J_{4,5}=9.0$, $J_{5,6}=J_{6,7}=7.0$, $J_{4,6}=2.0$, and $J_{Et}=7.0$ Hz. *b*) The ^{1}H-NMR spectra of other compounds could not be measured because of their low solubility. *c*) Overlapped with the phenyl proton signals.

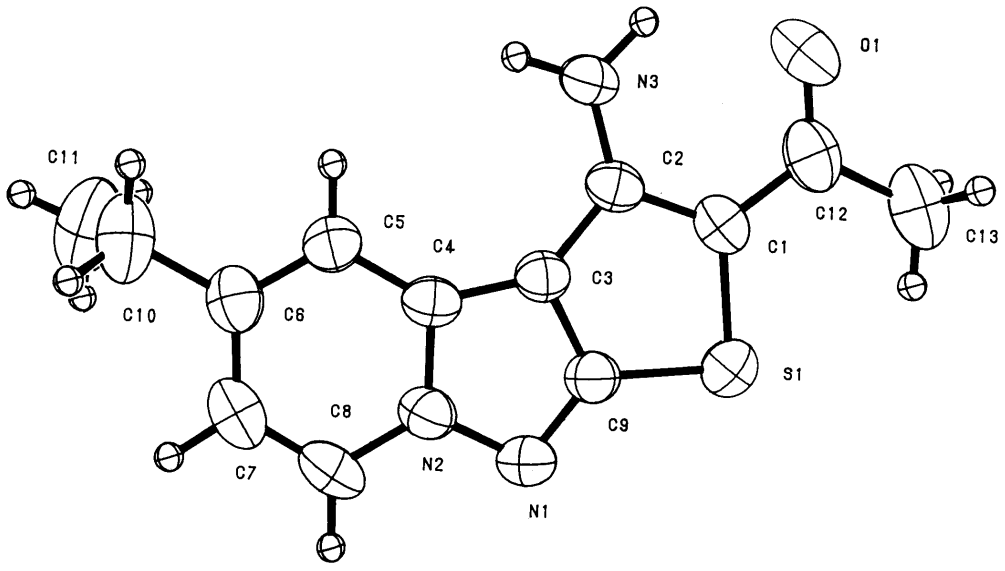
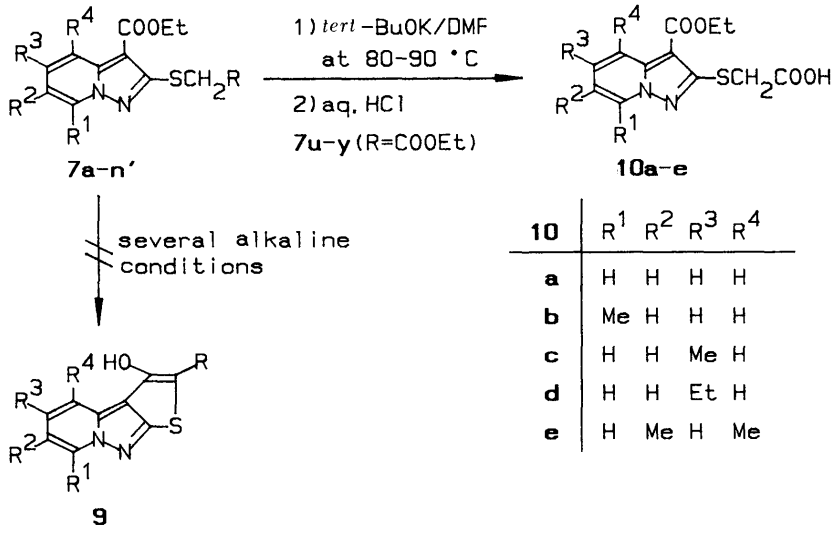


Fig. 1. ORTEP Drawing of **8d**



10	R^1	R^2	R^3	R^4
a	H	H	H	H
b	Me	H	H	H
c	H	H	Me	H
d	H	H	Et	H
e	H	Me	H	Me

Chart 4

TABLE III. Intramolecular Bond Distances (Å) and Angles (°) of **8d**

Atom	Atom	Distance[a]	Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
S1	C1	1.785 (6)	C1	S1	C9	89.2 (2)	C7	C6	C10	120.5 (5)
S1	C9	1.721 (5)	C9	N1	N2	102.0 (4)	C6	C7	C8	122.3 (5)
O1	C12	1.253 (7)	C4	N2	C8	122.0 (5)	C7	C8	N2	118.4 (5)
N1	C9	1.331 (6)	C4	N2	N1	114.2 (4)	C3	C9	N1	114.8 (5)
N1	N2	1.384 (6)	C8	N2	N1	123.8 (5)	N1	C9	S1	131.6 (4)
N2	C4	1.382 (6)	C2	C1	C12	124.2 (5)	C3	C9	S1	113.6 (4)
N2	C8	1.370 (7)	C2	C1	S1	113.5 (4)	C6	C10	C11	113.8 (6)
N3	C2	1.321 (6)	C12	C1	S1	122.2 (5)	C1	C12	O1	121.6 (6)
C1	C2	1.406 (7)	N3	C2	C1	124.0 (5)	C13	C12	O1	119.2 (6)
C1	C12	1.410 (7)	N3	C2	C3	126.0 (5)	C1	C12	C13	119.3 (6)
C2	C3	1.420 (7)	C1	C2	C3	110.0 (5)				
C3	C4	1.413 (7)	C4	C3	C9	104.5 (4)				
C3	C9	1.407 (7)	C2	C3	C4	142.0 (5)				
C4	C5	1.408 (7)	C2	C3	C9	113.5 (5)				
C5	C6	1.366 (7)	N2	C4	C3	104.5 (4)				
C6	C7	1.399 (8)	N2	C4	C5	118.3 (5)				
C6	C10	1.498 (8)	C3	C4	C5	137.2 (5)				
C7	C8	1.362 (8)	C4	C5	C6	120.6 (5)				
C10	C11	1.46 (1)	C5	C6	C7	118.4 (5)				
C12	C13	1.516 (9)	C5	C6	C10	121.6 (6)				

a) See Fig. 1 for the numberings in this molecule (**8d**).

(3) Å^3, $Z=18$. The structure was solved by the direct method MITHRIL, and refined by the full-matrix least squares method. The final *R*-factor was 0.064 for the 1573 observed reflections. The ORTEP drawing is shown in Fig. 1. The molecule is almost planar, except for the terminal carbon atom of the 5-ethyl group, which undergoes large thermal vibration. The intramolecular bond lengths and bond angles are summarized in Table III. There are no marked differences between double and single bond lengths within the ring carbons, which indicates the involvement of aromatic resonance structure.

In conclusion, the utility of 2-[(2-cyanoethyl)thio]- and 2-[(2-ethoxycarbonylethyl)thio]pyrazolo[1,5-*a*]pyridine derivatives (**1a—h** and **5a—h**) as key intermediates for synthesizing polyfunctionalized and thiophene-fused pyrazolo[1,5-*a*]pyridines, which are not easily obtainable by other methods, has been proved.

Experimental

Melting points were measured with a Yanagimoto micromelting point apparatus and are uncorrected. The microanalyses were carried out on a Perkin-Elmer 240 elemental analyzer. The ^{1}H-NMR spectra were determined with a Varian EM360A spectrometer in deuteriochloroform with tetramethylsilane as an internal standard and the chemical shifts are expressed in δ values. The IR spectra were taken with a Hitachi 260-10 infrared spectrophotometer.

Preparations of Polyfunctionalized Pyrazolo[1,5-*a*]pyridines (4a—n' and 7a—n') General Method: A solution of a 2-[(2-ethoxycarbonylethyl)thio]- or 2-[(2-cyanoethyl)thio]pyrazolo[1,5-*a*]pyridine (**1** or **5**, 1 mmol) in 2 ml of DMF was treated with potassium *tert*-butoxide (0.168 g, 1.5 mmol) at room temperature with occasional stirring for 2 h. An alkylating agent (**3**, 1.2 mmol) was added to the mixture and the resulting solution was kept standing with occasional stirring for an additional 4h. Diluted hydrochloric acid and water (30 ml) were added, and the precipitates separated were collected by filtration. The precipitates were dissolved in chloroform (30 ml) and the solution was freed from water by filtration through a phase-separating filter paper. The filtrate was concentrated under reduced pressure and the residue was separated by column chromatography on activated alumina using chloroform as an eluent. Evaporation of the solvent and recrystallization of the crude product from ethanol gave the corresponding *S*-alkylated pyrazolo[1,5-*a*]pyridine derivative (**4a—n'** or **7a—n'**).

These results and some spectral data are summarized in Tables I and IV.

Preparations of Thieno[2',3':3,4]pyrazolo[1,5-*a*]pyridines (8a—t) Gen-

TABLE IV. Some Data for 2-(Substituted Methylthio)pyrazolo[1,5-*a*]pyridines

Compd.[a]	React.	Yield (%)	m.p. (°C)	ν (KBr)	Formula	Analysis (%) Calcd			Found		
						C	H	N	C	H	N
4a	**1a**	**3a**	80	137—139	2200 1705	$C_{11}H_9N_3OS$	57.13	3.92	18.17	56.99	3.70	18.53
	1f	**3a**	73									
4b	**1b**	**3a**	87	138—140	2200 1701	$C_{12}H_{11}N_3OS$	58.76	4.52	17.13	58.68	4.49	16.96
	1g	**3a**	85									
4c	**1c**	**3a**	90	162—164	2200 1715	$C_{12}H_{11}N_3OS$	58.76	4.52	17.13	59.00	4.67	16.84
	1h	**3a**	79									
4d	**1d**	**3a**	72	99—100	2208 1710	$C_{13}H_{13}N_3OS$	60.21	5.05	16.20	60.26	5.19	16.24
4e	**1e**	**3a**	61	125—126	2201 1720	$C_{13}H_{13}N_3OS$	60.21	5.05	16.20	60.08	5.10	16.09
4f	**1a**	**3b**	77	129—131	2207 1673	$C_{16}H_{11}N_3OS$	65.51	3.78	14.32	65.52	3.80	14.27
4g	**1b**	**3b**	98	157—159	2201 1690	$C_{17}H_{13}N_3OS$	66.43	4.26	13.67	66.39	4.35	13.62
	1g	**3b**	90									
4h	**1c**	**3b**	96	138—139	2207 1674	$C_{17}H_{13}N_3OS$	66.43	4.26	13.67	66.71	4.15	13.50
4i	**1d**	**3b**	75	125—127	2202 1679	$C_{18}H_{15}N_3OS$	67.27	4.70	13.07	67.26	4.71	13.07
4j	**1e**	**3b**	60	167—168	2206 1672	$C_{18}H_{15}N_3OS$	67.27	4.70	13.07	67.08	4.73	12.91
4k	**1a**	**3c**	57	150—151	2210 1675	$C_{16}H_{10}ClN_3OS$	58.63	3.08	12.82	58.57	3.11	12.85
4l	**1b**	**3c**	60	166—168	2217 1681	$C_{17}H_{12}ClN_3OS$	59.74	3.54	12.29	59.56	3.65	12.56
	1g	**3c**	60									
4m	**1c**	**3c**	63	130—131	2202 1680	*b*)	59.26	4.14	11.52	59.15	4.13	11.63
4n	**1d**	**3c**	76	151—153	2215 1675	$C_{18}H_{14}ClN_3OS$	60.76	3.97	11.81	60.67	3.95	11.92
4o	**1e**	**3c**	66	193—194	2208 1674	$C_{18}H_{14}ClN_3OS$	60.76	3.97	11.81	60.98	3.98	11.58
4p	**1a**	**3d**	54	149—150	2208 1673	$C_{16}H_{10}BrN_3OS$	51.63	2.71	11.29	51.56	2.75	11.38
4q	**1b**	**3d**	80	166—168	2220 1685	$C_{17}H_{12}BrN_3OS$	52.86	3.13	10.88	53.00	2.97	10.90
4r	**1c**	**3d**	56	167—168	2202 1678	*c*)	52.82	3.69	10.27	52.64	3.69	10.42
4s	**1d**	**3d**	90	147—150	2211 1674	$C_{18}H_{14}BrN_3OS$	54.01	3.53	10.50	54.07	3.49	10.48
4t	**1e**	**3d**	56	196—197	2209 1674	$C_{18}H_{14}BrN_3OS$	54.01	3.53	10.50	54.18	3.61	10.25
4u	**1a**	**3e**	76	107—108	2220 1738	$C_{12}H_{11}N_3O_2S$	55.16	4.24	16.08	55.15	4.39	15.97
4v	**1b**	**3e**	91	107—108	2208 1727	$C_{13}H_{13}N_3O_2S$	56.71	4.76	15.26	56.46	4.58	15.18
	1g	**3e**	69									
4w	**1c**	**3e**	86	122—124	2218 1732	$C_{13}H_{13}N_3O_2S$	56.71	4.76	15.26	56.65	4.72	15.25
4x	**1d**	**3e**	80	93—95	2210 1721	$C_{14}H_{15}N_3O_2S$	58.11	5.23	14.52	58.16	5.22	14.28
4y	**1e**	**3e**	80	137—138	2210 1722	$C_{14}H_{15}N_3O_2S$	58.11	5.23	14.52	58.13	5.09	14.37
4z	**1a**	**3f**	91	179—180	2217 1512 1345	$C_{15}H_{10}N_4O_2S$	58.06	3.25	18.05	58.03	3.34	18.05
4a′	**1b**	**3f**	91	197—199	2218 1512 1343	$C_{16}H_{12}N_4O_2S$	59.25	3.73	17.27	59.11	3.81	17.33
4b′	**1c**	**3f**	91	192—193	2213 1511 1345	$C_{16}H_{12}N_4O_2S$	59.25	3.73	17.27	59.20	3.68	17.21
4c′	**1d**	**3f**	92	105—106	2206 1504 1330	$C_{17}H_{14}N_4O_2S$	60.34	4.17	16.56	60.41	4.26	16.52
4d′	**1e**	**3f**	69	236—237	2202 1507 1349	$C_{17}H_{14}N_4O_2S$	60.34	4.17	16.56	60.35	4.21	16.53
4e′	**1a**	**3g**	74	153—155	2212 1507 1352	$C_{15}H_{10}N_4O_2S$	58.06	3.25	18.05	58.15	3.39	18.08
4f′	**1b**	**3g**	65	166—167	2210 1516 1334	$C_{16}H_{12}N_4O_2S$	59.25	3.73	17.27	59.58	3.73	16.99
4g′	**1c**	**3g**	83	160—161	2208 1510 1332	$C_{16}H_{12}N_4O_2S$	59.25	3.73	17.27	59.19	3.80	17.12
4h′	**1d**	**3g**	87	122—123	2203 1509 1342	$C_{17}H_{14}N_4O_2S$	60.34	4.17	16.56	60.57	4.25	16.25
4i′	**1e**	**3g**	85	175—177	2210 1510 1366	$C_{17}H_{14}N_4O_2S$	60.34	4.17	16.56	60.61	4.10	16.36
4j′	**1a**	**3h**	78	98—100	2208	$C_{15}H_{11}N_3S$	67.90	4.18	15.84	68.16	4.21	15.55
4k′	**1a**	**3i**	74	126—128	2202	$C_{16}H_{13}N_3S$	68.79	4.69	15.04	68.97	4.70	14.85
4l′	**1a**	**3j**	79	110—112	2208	$C_{15}H_{10}ClN_3S$	60.10	3.36	14.02	60.24	3.52	13.72
4m′	**1a**	**3k**	67	118—119	2210	$C_{15}H_{10}BrN_3S$	52.34	2.93	12.21	52.39	3.21	12.17
4n′	**1a**	**3l**	74	136—137	3225 2202 2115	$C_{11}H_7N_3S$	61.95	3.31	19.70	62.11	3.34	19.51
7a	**5a**	**3a**	76	143—146	1705 1676	$C_{13}H_{14}N_2O_3S$	56.10	5.07	10.07	56.39	5.27	9.78
	5f	**3a**	81									
7b	**5b**	**3a**	79	138—139	1718 1681	$C_{14}H_{16}N_2O_3S$	57.52	5.52	9.58	57.61	5.57	9.44
7c	**5c**	**3a**	56	116—118	1716 1688	$C_{14}H_{16}N_2O_3S$	57.52	5.52	9.58	57.52	6.63	9.67
	5h	**3a**	98									
7d	**5d**	**3a**	86	102—104	1716 1681	$C_{15}H_{18}N_2O_3S$	58.80	5.92	9.14	58.50	5.88	9.12
7e	**5e**	**3a**	60	98—99	1717 1690	$C_{15}H_{18}N_2O_3S$	58.80	5.92	9.14	58.85	5.83	9.08
7f	**5a**	**3b**	59	114—116	1690 1675	$C_{18}H_{16}N_2O_3S$	63.51	4.74	8.23	63.26	4.75	8.04
7g	**5b**	**3b**	73	167—169	1676	$C_{19}H_{18}N_2O_3S$	64.39	5.12	7.90	64.38	4.92	7.96
	5g	**3b**	84									
7h	**5c**	**3b**	80	146—147	1680	$C_{19}H_{18}N_2O_3S$	64.39	5.12	7.90	64.29	5.09	8.02
7i	**5d**	**3b**	93	136—138	1689 1677	$C_{20}H_{20}N_2O_3S$	65.20	5.47	7.60	65.25	5.63	7.64
7j	**5e**	**3b**	73	129—130	1687	$C_{20}H_{20}N_2O_3S$	65.20	5.47	7.60	65.33	5.59	7.35
7k	**5a**	**3c**	54	144—147	1688 1680	$C_{18}H_{15}ClN_2O_3S$	57.68	4.03	7.47	57.59	4.08	7.51
7l	**5b**	**3c**	54	168—169	1687 1680	$C_{19}H_{17}ClN_2O_3S$	58.68	4.41	7.20	58.41	4.22	7.25
7m	**5c**	**3c**	62	138—140	1685 1675	$C_{19}H_{17}ClN_2O_3S$	58.68	4.41	7.20	58.54	4.48	7.16
	5h	**3c**	62									
7n	**5d**	**3c**	59	146—148	1685 1680	$C_{20}H_{19}ClN_2O_3S$	59.62	4.75	6.95	59.41	4.66	6.84
7o	**5e**	**3c**	59	147—148	1688 1671	$C_{20}H_{19}ClN_2O_3S$	59.62	4.75	6.95	59.61	4.75	6.91
7p	**5a**	**3d**	71	135—137	1686 1675	$C_{18}H_{15}BrN_2O_3S$	51.56	3.61	6.68	51.46	3.70	6.41

TABLE IV. (continued)

Compd.[a]	React.	Yield (%)	m.p. (°C)	ν (KBr)	Formula	Analysis (%) Calcd C	Calcd H	Calcd N	Found C	Found H	Found N
7q	**5b**	**3d**	69	161—163	1687	$C_{19}H_{17}BrN_2O_3S$	52.66	3.95	6.46	52.73	3.82	6.52
7r	**5h**	**3d**	91	144—145	1685	$C_{19}H_{17}BrN_2O_3S$	52.66	3.95	6.46	52.43	4.24	6.19
7s	**5d**	**3d**	54	140—141	1680 1671	$C_{20}H_{19}BrN_2O_3S$	53.70	4.28	6.26	53.48	4.14	6.03
7t	**5e**	**3d**	59	129—130	1686 1669	$C_{20}H_{19}BrN_2O_3S$	53.70	4.28	6.26	53.86	4.34	6.23
7u	**5a**	**3e**	98	90—91	Known compound[d]							
7v	**5b**	**3e**	85	125—126	Known compound[d]							
7w	**5c**	**3e**	98	110—111	Known compound[d]							
7x	**5d**	**3e**	72	102—103	1731 1670	$C_{16}H_{20}N_2O_4S$	57.13	5.99	8.33	57.11	5.93	8.14
7y	**5e**	**3e**	73	88—90	1736 1694	$C_{16}H_{20}N_2O_4S$	57.13	5.99	8.33	57.21	5.98	8.30
7z	**5a**	**3f**	73	148—150	1676 1509 1341	$C_{17}H_{15}N_3O_4S$	57.13	4.23	11.76	57.20	4.33	11.58
7a′	**5b**	**3f**	50	122—123	1687 1507 1337	$C_{18}H_{17}N_3O_4S$	58.21	4.61	11.31	57.98	4.51	11.15
7b′	**5c**	**3f**	57	130—131	1689 1500 1344	$C_{18}H_{17}N_3O_4S$	58.21	4.61	11.31	58.25	4.59	11.29
7c′	**5d**	**3f**	64	110—112	1680 1507 1341	$C_{19}H_{19}N_3O_4S$	59.21	4.97	10.90	59.45	4.87	10.92
7d′	**5e**	**3f**	70	139—140	1681 1500 1345	$C_{19}H_{19}N_3O_4S$	59.21	4.97	10.90	59.06	4.94	10.66
7e′	**5a**	**3g**	81	118—120	1674 1510 1365	$C_{17}H_{15}N_3O_4S$	57.13	4.23	11.76	57.14	4.14	11.56
7f′	**5b**	**3g**	58	127—128	1684 1510 1337	$C_{18}H_{17}N_3O_4S$	58.21	4.61	11.31	58.44	4.61	11.08
7g′	**5c**	**3g**	52	119—120	1675 1515 1352	$C_{18}H_{17}N_3O_4S$	58.21	4.61	11.31	58.09	4.67	11.21
7h′	**5d**	**3g**	53	115—118	1680 1510 1354	$C_{19}H_{19}N_3O_4S$	59.21	4.97	10.90	59.28	4.98	10.63
7i′	**5e**	**3g**	63	108—109	1666 1521 1358	$C_{19}H_{19}N_3O_4S$	59.21	4.97	10.90	59.46	4.96	10.66
7j′	**5a**	**3h**	71	103—104	1681	$C_{17}H_{16}N_2O_2S$	53.36	5.16	8.97	53.65	5.18	8.68
7k′	**5a**	**3i**	67	124—125	1674	$C_{18}H_{18}N_2O_2S$	66.23	5.56	8.58	66.22	5.52	8.45
7l′	**5a**	**3j**	84	121—122	1688	$C_{17}H_{15}ClN_2O_2S$	58.87	4.36	8.08	58.73	4.30	7.84
7m′	**5a**	**3k**	52	127—129	1684	$C_{17}H_{15}BrN_2O_2S$	52.18	3.86	7.16	52.01	3.83	7.00
7n′	**5a**	**3l**	70	119—120	3225 2120 1680	$C_{13}H_{12}N_2O_2S$	59.98	4.65	10.76	59.81	4.53	10.48

a) Compounds **4a**, **b**, **d**—**j**, **l**—**p**, **s**—**y**, **d′**—**g′**, **i′**—**n′** and **7a**—**c**, **e**—**h**, **j**—**n′** were obtained as colorless needles, **4c** and **7d**, **i** as colorless prisms, and **4k**, **q**, **r**, **z**—**c′**, **h′** as pale yellow needles. *b*) $C_{17}H_{12}ClN_3OS+1/2EtOH$. *c*) $C_{17}H_{12}BrN_3OS+1/2EtOH$. *d*) See ref. 3.

TABLE V. Some Data for 3-Aminothieno[2′,3′:3,4]pyrazolo[1,5-*a*]pyridines

Compd. 8[a]	React. 4	Yield (%)	mp (°C)	ν (KBr)	Formula	Analysis (%) Calcd C	Calcd H	Calcd N	Found C	Found H	Found N
a	**a**	61	255—257	3367 3257 1590	$C_{11}H_9N_3OS$	57.13	3.92	18.17	57.12	4.15	17.95
b	**b**	41	263—264	3400 3280 1558	$C_{12}H_{11}N_3OS$	58.76	4.52	17.13	58.74	4.53	16.89
c	**c**	85	267—270	3340 3260 1576	$C_{12}H_{11}N_3OS$	58.76	4.52	17.13	58.60	4.69	17.02
d	**d**	76	249—250	3320 3150 1570	$C_{13}H_{13}N_3OS$	60.21	5.05	16.20	60.23	5.29	15.93
e	**e**	83	273—275	3400 3250 1595	$C_{13}H_{13}N_3OS$	60.21	5.05	16.20	60.02	5.23	16.17
f	**f**	68	209—212	3320 3230 1581	$C_{16}H_{11}N_3OS$	65.51	3.78	14.32	65.37	3.69	14.41
g	**g**	88	217—220	3340 3250 1540	$C_{17}H_{13}N_3OS$	66.43	4.26	13.67	66.19	4.56	13.47
h	**h**	80	256—258	3360 3250 1587	$C_{17}H_{13}N_3OS$	66.43	4.26	13.64	66.48	4.36	13.52
i	**i**	63	213—215	3300 3150 1545	$C_{18}H_{15}N_3OS$	67.27	4.70	13.07	67.01	4.59	12.96
j	**j**	13	238—241	3440 3280 1580	$C_{18}H_{15}N_3OS$	67.27	4.70	13.07	67.00	4.73	13.31
k	**k**	89	293—296	3360 3232 1577	$C_{16}H_{10}ClN_3OS$	58.63	3.08	12.82	58.52	3.12	12.90
l	**l**	58	186—187	3380 3270 1541	*b*)	56.74	3.92	11.68	56.81	3.89	11.54
m	**m**	65	297—298	3480 3230 1579	$C_{17}H_{12}ClN_3OS$	59.74	3.54	12.29	59.62	3.64	12.30
n	**n**	65	268—270	3320 3220 1576	$C_{18}H_{14}ClN_3OS$	60.76	3.98	11.81	60.67	4.07	11.82
o	**o**	20	252—254	3460 3250 1573	$C_{18}H_{14}ClN_3OS$	60.76	3.98	11.81	60.82	4.12	11.60
p	**p**	74	292—295	3370 3240 1578	$C_{16}H_{10}BrN_3OS$	51.63	2.71	11.29	51.59	2.69	11.35
q	**q**	31	154—155	3390 3260 1543	$C_{17}H_{12}BrN_3OS$	52.86	3.13	10.88	52.81	3.42	10.69
r	**r**	73	296—298	3350 3220 1577	$C_{17}H_{12}BrN_3OS$	52.86	3.13	10.88	52.88	3.12	10.87
s	**s**	86	275—277	3320 3220 1573	$C_{18}H_{14}BrN_3OS$	54.01	3.53	10.50	53.90	3.47	10.67
t	**t**	18	262—264	3460 3250 1567	$C_{18}H_{14}BrN_3OS$	54.01	3.53	10.50	53.96	3.78	10.20

a) Compounds **8a**—**f**, **i**—**t** were obtained as yellow needles, **8g** as yellow prisms, and **8h** as yellow flakes. *b*) $C_{17}H_{12}ClN_3OS+H_2O$.

eral Method A: An ethanolic solution (40 ml) of pyrazolo[1,5-*a*]pyridine-3-carbonitrile (**4**, 0.200 g) and DBU (0.30 g, 2 mmol) was heated under reflux until the starting pyrazolo[1,5-*a*]pyridine (**4**) was no longer detectable by thin layer chromatographic monitoring (6 h—3 d). The reaction solution was cooled to room temperature and kept standing overnight. The precipitates were collected by filtration and the crude product was purified by recrystallization from ethanol or chloroform.

By this method, the thieno[2′,3′:3,4]pyrazolo[1,5-*a*]pyridines **8a**—**i**, **k**—**n**, **p**—**s** were prepared, but its application to **4j**, **o**, **t** gave complex mixtures including **8j**, **o**, **t** and unidentified products, which could not be separated owing to their low solubilities in organic solvents.

Method B: In this method, *tert*-butanol (40 ml) instead of ethanol was used as the solvent, and the reaction was carried out at 80—90 °C. In order to obtain only the corresponding thieno[2′,3′:3,4]pyrazolo[1,5-*a*]pyridine **8**, the hot reaction solution was filtered. The product thus collected was purified by recrystallization from chloroform. By this method, compounds **8j**, **o**, **t** were obtained.

These results and some data are listed in Tables II and V.

Preparations of Ethyl 2-(Carboxymethylthio)pyrazolo[1,5-*a*]-pyridine-3-carboxylates (10a—e) General Method: A solution of a pyrazolopyridine (**7u—y**, 1 mmol) and potassium *tert*-butoxide (0.244 g, 2 mmol) in DMF (2 ml) was heated at 80—90 °C in a water bath for 5 h. Similar work-up afforded the corresponding carboxylic acids (**10a—e**)[6] from the resulting mixture.

The ^{1}H-NMR data for **10a—e** are included in Table I, and the other data are as follows, **10a**, 47% from **7u**, colorless prisms, mp 150—152 °C. IR (KBr): 1679 cm^{-1} (CO). *Anal.* Calcd for $C_{12}H_{12}N_2O_4S$: C, 51.42; H, 4.32; N, 9.99. Found: C, 51.47; H, 4.29; N, 9.96. **10b**, 44% from **7v**, colorless prisms, mp 167—169 °C. IR (KBr): 1678 and 1709 cm^{-1} (CO). *Anal.* Calcd for $C_{13}H_{14}N_2O_4S$: C, 53.05; H, 4.79; N, 9.52. Found: C, 53.28; H, 4.85; N, 9.28. **10c**, 64% from **7w**, colorless prisms, mp 179—180 °C. IR (KBr); 1722 and 1655 cm^{-1} (CO). *Anal.* Calcd for $C_{13}H_{14}N_2O_4S$: C, 53.05; H, 4.79; N, 9.52. Found: C, 52.94; H, 4.87; N, 9.55. **10d**, 47% from **7x**, colorless prisms, mp 139—141 °C. IR (KBr): 1691 cm^{-1} (CO). *Anal.* Calcd for $C_{14}H_{16}N_2O_4S$: C, 54.53; H, 5.23; N, 9.08. Found: C, 54.56; H, 5.42; N, 8.86. **10e**, 58% from **7y**, colorless prisms, mp 146—148 °C. IR (KBr): 1660 and 1709 cm^{-1} (CO). *Anal.* Calcd for $C_{14}H_{16}N_2O_4S$: C, 54.53; H, 5.23; N, 9.08. Found: C, 54.71; H, 5.16; N, 8.97.

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6) These compounds **10a—e** were recrystallized from chloroform–hexane.