Synthesis Using Pyridinium *N*-Ylides. I. Synthesis and Some Reactions of Substituted 1-(Acetylimino)pyridinium Ylides

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Pyridinium *N*-imines reacted smoothly with diethyl malonate and ethyl cyanoacetate in ethanol at room temperature to give the corresponding 1-(ethoxycarbonylacetylimino)- and 1-(cyanoacetylimino)pyridinium ylides in 59—87% yields. These ylides were converted to 1-(acetylimino)pyridinium ylide derivatives by the treatment with acetic anhydride. The alkaline treatment of the pyridinium salts which were prepared by the alkylation of the *N*-ylides with alkyl halides, gave the corresponding 3-ethoxycarbonyl- and 3-cyano-1,2-dihydropyrazolo-[1,5-*a*]pyridin-2-one derivatives in 8—51% yields.

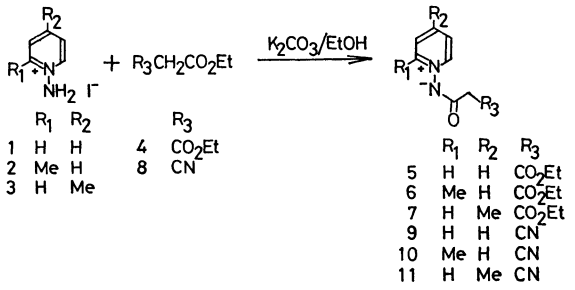
In connection with our work in the chemistry of pyridinium *N*-ylides, we became especially interested in the reactions of pyridinium *N*-imines and *N*-methylides with various unsaturated bonds substituted with a leaving group.[1-4] Recently, we found that a certain ester group reacted smoothly with pyridinium *N*-imines to give the corresponding 1-(acetylimino)pyridinium ylides. Since the use of ester compounds such as diethyl malonate and ethyl cyanoacetate in this reaction can lead to the formation of pyridinium *N*-ylides bearing an active methylene group in the substituent at 1-position, we examined the possibility of a new intramolecular coupling reaction between the cationic center of the pyridinium moiety and the anionic center generated at the methylene group.

Kato and Masuda reported recently the preparation of 1-(acetoacetylimino)pyridinium ylide and its conversion to 1,2-dihydropyrazolo[1,5-*a*]pyridin-2-one.[5] In the pyrazolone formation step, a similar coupling reaction of the cationic center with the carbanion was proposed. In this paper we wish to report the new preparations of some 1-(ethoxycarbonylacetylimino)- and 1-(cyanoacetylimino)pyridinium ylides and their reactions which lead to 1-(acetylimino)pyridinium ylide and 1-alkyl-1,2-dihydropyrazolo[1,5-*a*]pyridin-2-one derivatives.

Results and Discussion

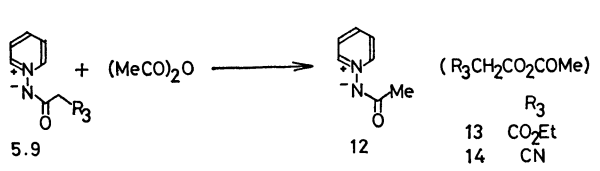
*Preparation of 1-(Ethoxycarbonylacetylimino)- **5**—**7** and 1-(Cyanoacetylimino)pyridinium Ylides **9**—**11**.* Syntheses of pyridinium *N*-ylides possessing an active methylene group were achieved by using nucleophilic reactions of pyridinium *N*-imines onto the ester carbonyl carbon of sufficiently active methylene compounds. When 1-aminopyridinium iodides **1**—**3** were treated with diethyl malonate **4** or ethyl cyanoacetate **8** in ethanol in the presence of potassium carbonate at room temperature for 3 days, the expected 1-(ethoxycarbonylacetylimino)-**5**—**7** or 1-(cyanoacetylimino)pyridinium ylides **9**—**11** were obtained in 59—87% yilds (Scheme 1). These *N*-ylides were very stable, colorless hygroscopic substances which solidified gradually on standing, and were not decomposedeven at the refluxing temperature of xylene.

Structural assignments of *N*-ylides **5**—**7** and **9**—**11** were generally accomplished by comparison of their spectra with those of other 1-(acylimino)pyridinium ylides.[6-9] In particular, the IR spectra exhibited a widely shifted absorption band of the carbonyl group conjugated with the imino nitrogen (near 1600 cm^{-1}), and the NMR chemical shifts and their signal patterns due to protons except the methylene protons (δ=3.3—3.5, singlet) are quite similar to those of 1-(ethoxycarbonylimino)-[6-8] and 1-(acetylimino)pyridinium ylides[9] which have already been reported.



Scheme 1.

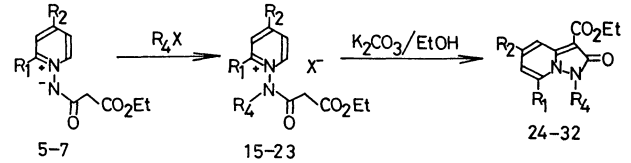
Reactions of N-*Ylides **5** and **9** with Acetic Anhydride.* In order to examine the reactivity of the active methylene group of the *N*-ylides prepared above, the reaction with acetic anhydride was first carried out. When *N*-ylide **5** was heated with a large excess of acetic anhydride at ca. 80 °C for 3 h, 1-(acetylimino)pyridinium ylide **12** was obtained in 96% yield as the only isolated product. Similarly, the same *N*-ylide **12** was formed in 65% yield by the reaction of *N*-ylide **9** with acetic anhydride under the same conditions. However, the attempted isolation of the anhydride derivatives **13** and **14** which might be formed in these reactions was unsuccessful. These results are shown in Scheme 2. The structure of *N*-ylide **12** was determined by comparison with the authentic specimen described by Okamoto *et al.*[10]



Scheme 2.

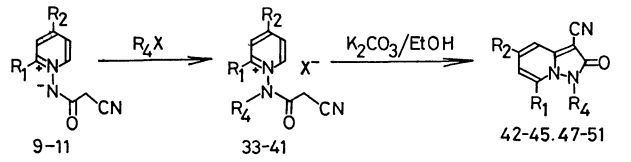
*Alkaline Treatment of Pyridinium Salts **15**—**23** and **33**—**41**.* Since the proceeding of transacylation in the above reactions might suggest that the generation of carbanion at the methylene group is unfavorable, we next attempted the formation of a carbanion

by the alkaline treatments of the corresponding 1-(*N*-alkylated imino)pyridinium salts. When pyridinium salts **15**—**23**, readily obtainable from the reactions of *N*-ylides **5**—**7** with methyl iodide, allyl bromide, and benzyl bromide, were treated with excess potassium carbonate in ethanol at room temperature, crystalline products **24**—**32** were formed in 16—51% yields (calculated from *N*-ylide). Similarly, the salts **33**—**41** obtained from *N*-ylides **9**—**11** and the same alkylating agents gave the corresponding products **42**—**45** and **47**—**51** in 8—40% yields. Furthermore, the reaction of the salt **36** also gave the colorless crystalline product **46** in only 4% yield, together with the compound **45** (21%). In the cases of the reactions of pyridinium salts **16**, **19**, **22**, **34**, **37**, and **40** which have a methyl group at 2-position, the yields of products **25**, **28**, **31**, **43**, **47**, and **50** always diminished. These results are shown in Schemes 3 and 4.

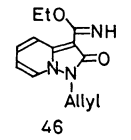


Ylide	R_4X	Salt	Pyrazole	R_1	R_2	R_4	Yield(%, Ylide→Pyrazole)
5	MeI	15	24	H	H	Me	25
6	〃	16	25	Me	H	〃	16
7	〃	17	26	H	Me	〃	22
5	AllylBr	18	27	H	H	Allyl	51
6	〃	19	28	Me	H	〃	19
7	〃	20	29	H	Me	〃	49
5	$PhCH_2Br$	21	30	H	H	$PhCH_2$	34
6	〃	22	31	Me	H	〃	16
7	〃	23	32	H	Me	〃	40

Scheme 3.



Ylide	R_4X	Salt	Pyrazole	R_1	R_2	R_4	Yield(%, Ylide→Pyrazole)
9	MeI	33	42	H	H	Me	13
10	〃	34	43	Me	H	〃	11
11	〃	35	44	H	Me	〃	40
9	AllylBr	36	45	H	H	Allyl	21
〃	〃	〃	46	H	H	〃	4
10	〃	37	47	Me	H	〃	15
11	〃	38	48	H	Me	〃	37
9	$PhCH_2Br$	39	49	H	H	$PhCH_2$	11
10	〃	40	50	Me	H	〃	8
11	〃	41	51	H	Me	〃	20

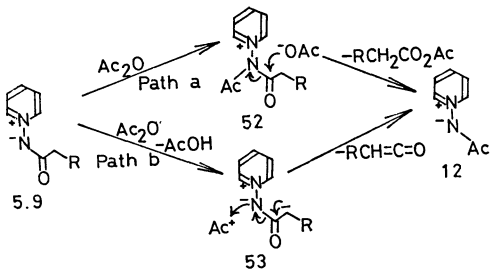


Scheme 4.

These products **24**—**32**, **42**—**45**, and **47**—**51** are colorless or pale yellow crystals which are well characterized by their strong fluorescences, their high melting points, and their comparatively low solubilities in common organic solvents. Each IR spectrum showed a characteristic absorption band at 1621—1676 cm^{-1} due to an amide carbonyl group and at 1694—1729 cm^{-1} due to an ester carbonyl group (**24**—**32**) or at 2215—2225 cm^{-1} due to a cyano group (**42**—**45** and **47**—**51**). The NMR spectrum of compound **24**, for example, showed signals at δ=6.89 (1H, br t, J=7.5, 7.0 and 2.0 Hz), 7.45 (1H, br t, J=9.0, 7.5 and 1.0 Hz), 7.93 (1H, dd, J=7.0 and 1.0 Hz), and 8.08 (1H, dd, J=9.0 and 2.0 Hz) due to the protons on the pyridine ring and at δ=3.65 (3H, s) due to the methyl protons, together with proton signals at δ=1.37 (3H, t, J=7.0 Hz) and 4.33 (2H, q, J=7.0 Hz) attributable to the ethoxycarbonyl group (see Table 4). The chemical shifts of the protons of the pyridine ring are intermediate between those in 1-(vinylimino)pyridinium ylides[11] and those in 3,3a-dihydropyrazolo[1,5-*a*]pyridines[11] and are rather similar to those in 1-alkyl-2-allylidene-1,2-dihydropyridines.[12,13] The methyl signals appeared at δ=3.65 indicated that this methyl group is a substituent on a nitrogen atom rather than an oxygen atom. The other chemical shifts of the *N'*-alkyl group derived from alkylating agents were, of course, in good accord with those of known *N*-alkylated compounds,[12-14] and this fact excluded the possibility of the *O*-alkylated compounds, that is, 2-alkoxypyrazolo[1,5-*a*]pyridines, for these products: **24**—**32**, **45**, **47**, **48**, **50**, and **51**. From the above spectral data and an analogous reaction given by Kato and Masuda,[5] these products were assigned to be 1-alkyl-3-ethoxycarbonyl- **24**—**32** and 1-alkyl-3-cyano-1,2-dihydropyrazolo[1,5-*a*]pyridin-2-one derivatives **42**—**45** and **47**—**51**.

On the other hand, the structure of compound **46** was determined to be a 1 : 1 adduct of 1-allyl-3-cyano-1,2-dihydropyrazolopyridine **45** and ethanol by its microanalysis and its NMR spectral inspection. Furthermore, the IR spectrum exhibited absorption bands at 1668 and 3340 cm^{-1} due to an amide carbonyl and a secondary amino group, respectively, but no cyano absorption band was observed. These results suggested clearly that compound **46** is 1-allyl-3-ethoxycarbonimidoyl-1,2-dihydropyrazolo[1,5-*a*]pyridin-2-one.

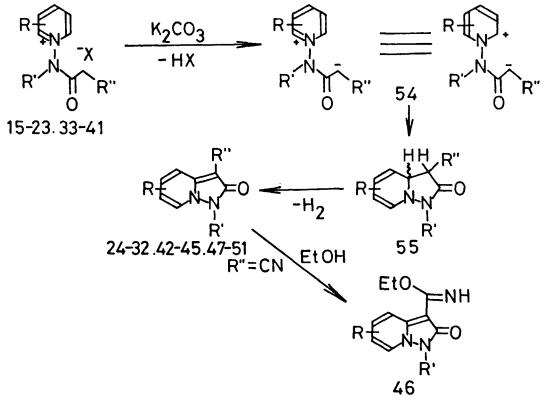
Mechanism. The transacylations of *N*-ylides **5** and **9** with acetic anhydride may proceed via the formation of *N'*-acetylated intermediate **52**, followed by its decomposition to 1-(acetylimino)pyridinium ylide **12** and anhydride **13** or **14** (Path a). An alternate route (Path b) in which the formation of dehydrogenated compound **53** followed by its decomposition to *N*-ylide **12** and ketene takes place is negligible because the collapse of the intermediate such as **53** should lead to the formation of 2-hydoxypyrazolo[1,5-*a*]pyridine derivative rather than *N*-ylide, as suggested in the alkaline treatment[5] of 1-(acetoacetylimino)pyridinium ylide (Scheme 5).



Scheme 5.

On the other hand, the formation of 1,2-dihydropyrazolo[1,5-*a*]pyridin-2-ones **24**—**32**, **42**—**45**, and **47**—**51** seems to proceed via the intramolecular coupling reaction of intermediate **54** formed initially by dehydro-

halogenation of 1-(*N*-alkylated imino)pyridinium salts **15**—**23** and **33**—**41**, followed by the oxidation of the resulting 1,2,3,3a-tetrahydropyrazolopyridine **55** (Scheme 6). This mechanism is the same as that proposed for the alkaline treatment of 1-[*N*-(acetoacetyl)methylamino]pyridinium iodide by Kato and Masuda.[5] Furthermore, imidate **46** must be formed by a base-catalyzed addition of ethanol on the 3-cyano group in 1-allyl-3-cyano-1,2-dihydropyrazolo[1,5-*a*]pyridin-2-one **45**, since the reaction of compound **45** with ethanol did not give the imidate **46** in the absence of alkali even under more drastic conditions, but gave it in the presence of alkali. Similar additions[15] of alcohol to a cyano group have been found often.



Scheme 6.

Experimental

Melting points were measured with a Yanagimoto micro-melting point apparatus and are uncorrected. Microanalyses were carried out on a Perkin-Elmer 240 Elemental Analyzer. The NMR spectra were determined with a JEOL JNM-100 spectrometer in deuteriochloroform with tetramethylsilane as an internal standard, The chemical shifts are expressed in δ values. The IR spectra were taken with a JASCO DS-301 spectrophotometer.

Preparations of Pyridinium N-*Ylides* ***5***—***7*** *and* ***9***—***11***. *General Method*: A solution of 1-aminopyridinium iodide (3 mmol) and diethyl malonate (4 g, 25 mmol) or ethyl cyanoacetate (4 g, 35 mmol) in 50 ml of ethanol was stirred with potassium carbonate (5 g) at room temperature for 3 days. The reaction mixture was then filtered to remove insoluble inorganic substances and the filtrate was concentrated under reduced pressure. The residue was separated by column chromatography (alumina) using ether and then chloroform as eluents. The pyridinium *N*-ylides **5**—**7** and **9**—**11** thus obtained are colorless substances which solidified gradually on standing. Except for *N*-ylide **11**, recrystallizations of the other *N*-ylides, **5**—**7**, **9**, and **10**, were unsuccessful because of their high hygroscopic properties. Some physical and spectral data of *N*-ylides **5**—**7** and **9**—**11** are summarized in Tables 1 and 2.

Reactions of N-*Ylides* ***5*** *and* ***9*** *with Acetic Anhydride*. A solution of *N*-ylide **5** (208 mg, 1 mmol) in 10 ml of acetic anhydride was heated at *ca.* 80 °C in a water bath for 3 h, and then the reaction mixture was concentrated under reduced pressure. The usual work-up of the residual oil gave 1-(acetylimino)pyridinium ylide **12** (130 mg, 96%) as colorless hygroscopic needless, mp (its picrate) 169—170 °C (lit,[10] 168 °C). The same *N*-ylide **12** was also obtained in 65% yield from the reaction of *N*-ylide **9** and acetic anhydride. However, our attempts to isolate the anhydride **13** or **14** were unsuccessful.

Alkaline Treatments of Pyridinium Salts ***15***—***23*** *and* ***33***—***41***. *General Method*: Pyridinium *N*-ylide (2 mmol) was treated with an alkylating agent (5 ml) without solvent at room temperature for 3—7 days, and then the reaction mixture was concentrated to remove the excess alkylating agent under reduced pressure. The ethanolic solution (50 ml) of the crude pyridinium salt was stirred with potassium carbonate (5 g) at room temperature for 3—5 days. The reaction mixture was filtered and the filtrate was concentrated under reduced pressure. The usual separations of the residues using column chromatography (alumina) gave the corresponding 1-alkyl-3-

Table 1. Some data of pyridinium *N*-ylides

Compd No.	Materials No.	Yield (%)	Mp (°C)	IR (Neat, cm^{-1}) C=O	CN
5	**1** **4**	86	125—126[a]	1730	1585
6	**2** **4**	64	130—132[a]	1732	1585
7	**3** **4**	59	137—138[a]	1728	1585
9	**1** **8**	87	154—156[a]		1588 2269
10	**2** **8**	69	184—186[a]		1590 2275
11	**3** **8**	74	138—140		1593[b] 2269[b]

Compd No.	Formula	Calcd % C	H	N	Found % C	H	N
5[a]	$C_{16}H_{15}N_5O_{10}$	43.94	3.46	16.02	43.80	3.42	16.13
6[a]	$C_{17}H_{17}N_5O_{10}$	45.24	3.80	15.52	45.17	3.81	15.41
7[a]	$C_{17}H_{17}N_5O_{10}$	45.24	3.80	15.52	45.28	3.76	15.55
9[a]	$C_{14}H_{10}N_6O_8$	43.08	2.58	21.54	42.88	2.46	21.46
10[a]	$C_{15}H_{12}N_6O_8$	44.56	2.99	20.79	44.63	3.04	20.92
11	$C_9H_9N_3O$	61.70	5.18	23.99	61.69	5.17	24.11

a) Its picrate. b) KBr.

Table 2. NMR data of pyridinium *N*-ylides

Compd No	C-2	C-3	C-4	C-5	C-6	CH_2	R_3	
5	8.67	7.64	7.92	7.64	8.67	3.34	4.17	1.28
	br d	br t	br t	br t	br d	s	q	t
	$J_{2,3}=J_{5,6}=7.0$, $J_{3,4}=J_{4,5}=7.5$, $J_{Et}=7.0$ Hz							
6	2.69	7.56	7.92	7.56	8.47	3.40	4.21	1.31
	s	m	br t	m	br d	s	q	t
	$J_{3,4}=J_{4,5}=7.5$, $J_{5,6}=7.0$, $J_{Et}=7.0$ Hz							
7	8.45	7.46	2.52	7.46	8.45	3.33	4.17	1.28
	d	d	s	d	d	s	q	t
	$J_{2,3}=J_{5,6}=7.0$, $J_{Et}=7.0$ Hz							
9	8.65	7.69	7.99	7.69	8.65	3.37		
	br d	br t	br t	br t	br d	s		
	$J_{2,3}=J_{5,6}=7.0$, $J_{3,4}=J_{4,5}=7.5$ Hz							
10	2.61	7.68	8.02	7.68	8.41	3.43		
	s	m	br t	m	br d	s		
	$J_{3,4}=J_{4,5}=7.5$, $J_{5,6}=7.5$ Hz							
11	8.43	7.46	2.53	7.46	8.43	3.32		
	d	d	s	d	d	s		
	$J_{2,3}=J_{5,6}=7.0$ Hz							

TABLE 3. SOME DATA OF 1,2-DIHYDROPYRAZOLO[1,5-a]PYRIDIN-2-ONES

Compd No.	Materials			Yield (%)	Mp (°C)	IR (KBr, cm^{-1})		Appearance	Formula	Calcd %			Found %		
	N-Ylide	Halide	Salt			C=O	CN(NH)			C	H	N	C	H	N
24	**5**	MeI	**15**	25	177—178	1694	1650	Colorless Needles	$C_{11}H_{12}N_2O_3$	59.99	5.49	12.72	59.91	5.53	12.63
25	**6**	MeI	**16**	16	150—151	1680	1656	Colorless Needles	a)	57.13	6.39	11.11	57.28	6.20	10.82
26	**7**	MeI	**17**	22	185—186	1694	1633	Pale Yellow Needles	$C_{12}H_{14}N_2O_3$	61.52	6.02	11.96	61.49	6.00	12.00
27	**5**	AllylBr	**18**	51	138—139	1704	1623	Pale Yellow Needles	$C_{13}H_{14}N_2O_3$	63.40	5.73	11.38	63.21	5.77	11.13
28	**6**	AllylBr	**19**	19	139—140	1709	1621	Pale Yellow Needles	$C_{14}H_{16}N_2O_3$	64.60	6.20	10.76	64.53	6.21	10.78
29	**7**	AllylBr	**20**	49	172—173	1703	1630	Pale Yellow Needles	$C_{14}H_{16}N_2O_3$	64.60	6.20	10.76	64.60	6.21	10.67
30	**5**	$PhCH_2Br$	**21**	34	173—174	1699	1627	Pale Yellow Needles	$C_{17}H_{16}N_2O_3$	68.90	5.44	9.45	68.79	5.49	9.30
31	**6**	$PhCH_2Br$	**22**	16	144—146	1729	1621	Pale Yellow Needles	b)	65.84	6.14	8.53	65.80	5.87	8.83
32	**7**	$PhCH_2Br$	**23**	40	171—172	1698	1630	Pale Yellow Needles	$C_{18}H_{18}N_2O_3$	69.66	5.85	9.03	69.62	5.90	8.97
42	**9**	MeI	**33**	13	271—273	1676	2218	Colorless Needles	$C_9H_7N_3O$	62.42	4.07	24.27	62.14	4.16	24.49
43	**10**	MeI	**34**	11	241—243	1657	2215	Colorless Needles	$C_{10}H_9N_3O$	64.16	4.85	22.45	63.87	4.93	22.59
44	**11**	MeI	**35**	40	277—279	1639	2220	Colorless Needles	$C_{10}H_9N_3O$	64.16	4.85	22.45	64.09	4.89	22.24
45	**9**	AllylBr	**36**	21	143—144	1658	2215	Pale Yellow Needles	$C_{11}H_9N_3O$	66.32	4.55	21.10	66.27	4.54	20.86
46	**9**	AllylBr	**36**	4	96—97	1668	(3340)	Colorless Needles	$C_{13}H_{15}N_3O_2$	63.66	6.16	17.13	63.66	6.17	17.33
47	**10**	AllylBr	**37**	15	158—159	1673	2225	Pale Yellow Needles	$C_{12}H_{11}N_3O$	67.59	5.20	19.71	67.29	5.22	19.42
48	**11**	AllylBr	**38**	37	152—153	1664	2220	Pale Yellow Needles	$C_{12}H_{11}N_3O$	67.59	5.20	19.71	67.60	5.14	19.83
49	**9**	$PhCH_2Br$	**39**	11	206—209	1666	2223	Pale Yellow Needles	$C_{15}H_{11}N_3O$	72.27	4.45	16.86	72.23	4.47	16.88
50	**10**	$PhCH_2Br$	**40**	8	185—186	1671	2220	Yellow Needles	$C_{16}H_{13}N_3O$	72.98	4.98	15.96	72.68	5.01	15.95
51	**11**	$PhCH_2Br$	**41**	20	165—167	1634	2220	Pale Yellow Needles	$C_{16}H_{13}N_3O$	72.98	4.98	15.96	72.04	4.99	16.18

a) $C_{12}H_{14}N_2O_3 \cdot H_2O$. b) $C_{18}H_{18}N_2O_3 \cdot H_2O$.

Table 4. NMR data of 1,2-dihydropyrazolo[1,5-*a*]pyridin-2-ones[a]

Compd No.	C-4	C-5	C-6	C-7	R_4				R_3[b]	
24	8.08	7.45	6.89	7.93	3.65				4.33	1.37
	dd	br t	br t	dd	s				q	t
	$J_{4,5}=9.0$, $J_{5,6}=7.5$, $J_{6,7}=7.0$, $J_{4,6}=2.0$, $J_{5,7}=1.0$ Hz									
25	8.03	7.34	6.53	2.72	3.68				4.34	1.38
	dd	q	d	s	s				q	t
	$J_{4,5}=9.0$, $J_{5,6}=7.5$, $J_{4,6}=2.0$ Hz									
26	7.88	2.36	6.67	7.71	3.56				4.33	1.37
	br s	s	dd	d	s				q	t
	$J_{6,7}=7.0$, $J_{4,6}=2.0$ Hz									
27[c]	8.15	7.47	6.85	7.93	4.86	5.24	5.34	5.80	4.38	1.42
	dd	br t	br t	dd	d	br d	br d	m	q	t
	$J_{4,5}=9.0$, $J_{5,6}=7.5$, $J_{6,7}=7.0$, $J_{4,6}=2.0$, $J_{5,7}=1.0$ Hz									
28	8.07	7.40	6.58	2.68	4.77	4.94	5.02	5.40	4.27	1.41
	dd	q	d	s	d	br d	br d	m	q	t
	$J_{4,5}=9.0$, $J_{5,6}=7.5$, $J_{4,6}=1.5$, $J_{allyl}=5.0$, 10.0, 17.0 Hz									
29	7.93	2.40	6.64	7.78	4.78	5.20	5.28	5.77	4.35	1.40
	br s	s	dd	d	d	br d	br d	m	q	t
	$J_{6,7}=7.0$, $J_{4,6}=2.0$, $J_{allyl}=5.0$, 10.0, 17.0 Hz									
30	8.12	7.40	6.70	7.79	5.40	7.18[d]			4.38	1.42
	dd	br t	br t	d	s	s			q	t
	$J_{4,5}=9.0$, $J_{5,6}=7.5$, $J_{6,7}=7.0$, $J_{4,6}=1.5$ Hz									
31	7.98	e)	6.39	2.56	5.41	6.8—7.4[d]			4.35	1.39
	dd		d	s	s	m			q	t
	$J_{4,5}=9.0$, $J_{5,6}=7.5$, $J_{4,6}=2.0$ Hz									
32	7.93	2.35	6.53	7.68	5.37	7.28[d]			4.39	1.42
	br s	s	dd	d	s	s			q	t
	$J_{6,7}=7.0$, $J_{4,6}=2.0$ Hz									
45	7.3—7.6		6.85	7.93	4.81	5.21	5.33	5.75		
	m		br t	d	d	br d	br d	m		
	$J_{5,6}=7.0$, $J_{6,7}=7.0$, $J_{allyl}=5.0$, 10.0, 17.0 Hz									
46	7.68	7.19	6.65	8.18	4.06	5.12	5.25	6.10	f)	
	dd	br t	br t	d	br t	br d	br d	m		
	$J_{4,5}=9.0$, $J_{5,6}=7.5$, $J_{6,7}=7.0$, $J_{4,6}=1.5$, $J_{allyl}=5.0$, 10.0, 17.0 Hz									
47	7.2—7.5		6.55	2.70	4.86	5.02	5.15	5.50		
	m		br d	s	d	br d	br d	m		
	$J_{5,6}=7.0$, $J_{allyl}=5.0$, 10.0, 17.0 Hz									
48	7.18	2.41	6.66	7.79	4.78	5.20	5.33	5.75		
	br s	s	dd	d	d	br d	br d	m		
	$J_{6,7}=7.0$, $J_{4,6}=1.5$, $J_{allyl}=5.0$, 10.0, 17.0 Hz									
50	e)	e)	6.45	2.63	5.43	6.8—7.5[d]				
			br d	s	s	m				
	$J_{5,6}=7.0$ Hz									
51	e)	2.36	6.53	7.60	5.33	7.0—7.3[d]				
		s	dd	d	s	m				
	$J_{6,7}=7.0$, $J_{4,6}=1.5$ Hz									

a) The NMR spectra of compounds **42**—**44** and **49** could not be measured because of their low sulubilities in deuteriochloroform. b) $J_{ethyl}=7.0$ Hz. c) $J_{allyl}=5.0$, 10.0, and 17.0 Hz. d) Phenyl protons. e) Overlapped with the phenyl proton signals. f) The signals due to the ethoxycarbonimidoyl group appeared at $\delta=1.39$ (3H, t, $J=7.0$ Hz), 4.34 (2H, q, $J=7.0$ Hz), and 6.10 (1H, m, NH).

ethoxycarbonyl- **24**—**32** and 1-alkyl-3-cyano-1,2-dihydropyrazolo[1,5-*a*]pyridin-2-one derivatives **42**—**45** and **47**—**51**. In the reaction of salt **36**, imidate **46** was also obtained in only 4% yield, together with compound **45** (21%). These results and some data are shown in Tables 3 and 4.

Furthermore, pyrazolopyridine **45** was converted slowly to the imidate **46** by the reaction with ethanol in the presence of alkali, but not at all in its absence.

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