[Chem. Pharm. Bull. 34(8)3153—3158(1986)]

An Efficient Synthesis of 4-Acyl-5-hydroxy-3-methylisoxazoles through an Acyl-Transfer Reaction

KAZUO SATO,* TAKASHI UEDA, and SOJI SUGAI

Agricultural Chemicals Research Laboratories, Sankyo Co., Ltd., 1–2–58, Hiromachi, Shinagawa-ku, Tokyo 140, Japan

(Received January 17, 1986)

Acylation of 3-methyl-3-isoxazolin-5-one (**2a**) with acyl chlorides was investigated. 2-Acyl-3-methyl-3-isoxazolin-5-ones **5** and 5-acyloxy-3-methylisoxazoles **6**, which were prepared from **2a** and acyl halides, underwent acyl-transfer reaction in the presence of 4-(*N*,*N*-dimethylamino)-pyridine or potassium carbonate to give 4-acyl-5-hydroxy-3-methylisoxazoles **4**. By using this reaction, 4-(2,4-dichlorobenzoyl)-5-hydroxy-3-methylisoxazole (**4h**), which can be viewed as a bioisostere of the herbicidal compound, 4-(2,4-dichlorobenzoyl)-1,3-dimethyl-5-hydroxypyrazole (**1a**), was synthesized.

Keywords——5-hydroxyisoxazole; 3-methyl-3-isoxazolin-5-one; 4-(2,4-dichlorobenzoyl)-5-hydroxy-3-methylisoxazole; 4-(2,4-dichlorobenzoyl)-1,3-dimethyl-5-hydroxypyrazole; acylation; rearrangement

In our laboratories, pyrazolate, 4-(2,4-dichlorobenzoyl)-1,3-dimethyl-5-pyrazolyl *p*-toluenesulfonate (**1b**), was recently developed as a paddy field herbicide and commercialized under the name Sanbird.[1] The active form of pyrazolate is 4-(2,4-dichlorobenzoyl)-1,3-dimethyl-5-hydroxypyrazole (DTP, **1a**).[1b] From the viewpoint of molecular modification based on the concept of bioisosterism,[2] we were interested in the synthesis of 4-(2,4-dichlorobenzoyl)-5-hydroxy-3-methylisoxazole (**4h**), which can be viewed as a bioisostere of DTP (**1a**), because the isoxazole ring is isosteric with the pyrazole ring.

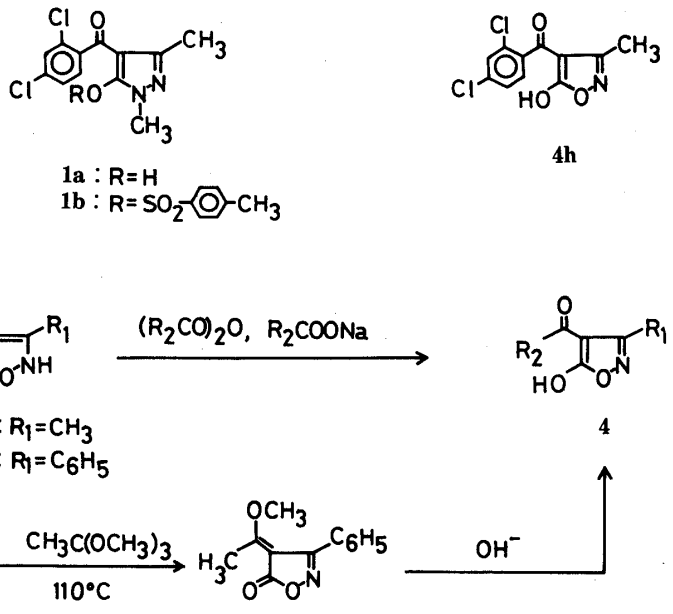


Fig. 1

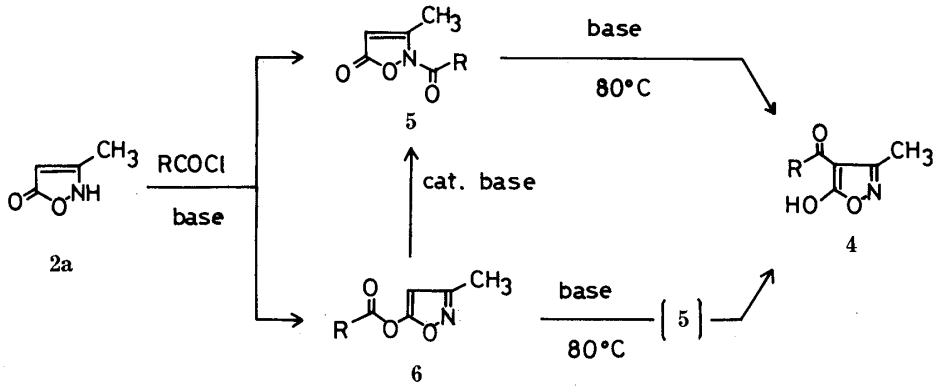
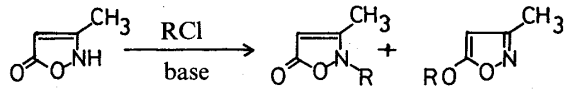


Fig. 2

TABLE I. Acylation of 3-Methyl-3-isoxazolin-5-one (**2a**)



Run	R	Conditions[a]	5	Yield (%)	mp (°C)	6	Yield (%)	mp (°C)
1	C_6H_5CO	α-Picoline/benzene, 10 min	**5a**	28.3	74—76	**6a**	58.5	52—54.5
2	C_6H_5CO	Et_3N/benzene, 3 h	**5a**	87.3		**6a**	9.8	
3	*o*-$CH_3C_6H_4CO$	α-Picoline (excess), 10 min	**5b**	36.1	94—96	**6b**	58.4	57.5—59
4	*m*-$CH_3C_6H_4CO$	α-Picoline (excess), 1.5 h	**5c**	49.8	83—84	**6c**	47.9	51—52
5	*p*-$CH_3C_6H_4CO$	α-Picoline (excess), 0.5 h	**5d**	22.3	92—94.5	**6d**	66.5	130—131.5
6	*o*-ClC_6H_4CO	α-Picoline (excess), 1 h	**5e**	93.3	130—131			
7	*m*-ClC_6H_4CO	α-Picoline (excess), 1.5 h	**5f**	94.8	96—98	**6f**	4.4	78—81
8	*p*-ClC_6H_4CO	α-Picoline (excess), 2 h	**5g**	44.6	137—139	**6g**	21.3	105—107
9	*p*-ClC_6H_4CO	α-Picoline/benzene, 2 h	**5g**	33.3		**6g**	59.0	
10	*p*-ClC_6H_4CO	2,6-Lutidine/benzene, 3 h	**5g**	25.5		**6g**	67.3	
11	*p*-ClC_6H_4CO	Et_3N/benzene, 6 h	**5g**	70.0		**6g**	24.3	
12	*p*-ClC_6H_4CO	$(iso\text{-}Pr)_2EtN$/benzene, 2 h	**5g**	36.7		**6g**	53.4	
13	2,4-$Cl_2C_6H_3CO$	α-Picoline (excess), 1 h	**5h**	72.5	138—140	**6g**	9.1	83—84
14	2,4-$Cl_2C_6H_3CO$	α-Picoline/benzene, 8 h	**5h**	25.2		**6g**	72.1	
15	*o*-$ClC_6H_4SO_2$	α-Picoline/benzene, 8 h	**5i**	28.0	137—139	**6i**	25.1	114—117

a) The reaction was carried out at room temperature, and 1.1 eq of the base was used, except in runs 3—8, and 13.

To our knowledge, there are two methods for the introduction of an acyl group at the 4-position of 5-hydroxyisoxazoles: one is the reaction of 3-isoxazolin-5-one **2a** or **2b** with an acid anhydride and the sodium salt of the acid[3]; the other is the treatment of **2b** with trimethyl orthoformate, followed by alkaline hydrolysis[4a] (Fig. 1). In both methods, the kinds of acyl groups that can be introduced are limited by the availability of the reagents, such as acid anhydrides and orthoformates.

In this paper, we wish to describe the acylation of 3-methyl-3-isoxazolin-5-one (**2a**) and the successive acyl transfer reaction of the acylated products **5** and **6**, as well as a one-pot synthesis of 4-acyl-5-hydroxyisoxazoles **4** from **2a**.

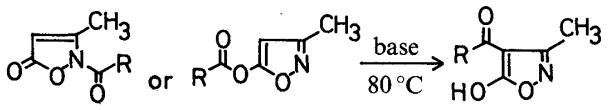
The reaction of **2a**[5] with a variety of acyl chlorides gave 2-acyl compounds **5** and 5-acyloxy compounds **6** (Table I). The product ratio could be varied by changing the reaction conditions, especially the type of base used as an acid scavenger. Triethylamine gave rise to a larger amount of 2-acyl compounds **5** (runs 2 and 11). Similarly, sulfonylation of **2a** took

TABLE II. Acyl-Transfer Reaction of **6g** to Give **5g**

Run	Conditions	Yield (%) of **5g**	Recovery (%) of **6g**
1	Et_3N (0.5 eq) in benzene, r.t., 4 h	75	5
2	α-Picoline (excess), r.t., 8 h	15	72
3	α-Picoline (2 eq) in benzene, r.t., 10 h	No reaction	
4	DMAP[a] (0.3 eq) in benzene, r.t., 3 h	83	0
5	K_2CO_3 (0.1 eq) in *tert*-BuOH, 80 °C, 2 h	90	4

a) DMAP: 4-(*N*,*N*-dimethylamino)pyridine. r.t. = room temperature.

TABLE III. Acyl-Transfer Reaction of **5** and **6** to Give the 4-Acyl Derivatives **4**



5 **6** **4**

Run	Starting material	R	Conditions[a]	**4**	Yield (%)	mp (°C)
1	**6a**	C_6H_5	K_2CO_3 in *tert*-BuOH	**4a**	40.0	160—162[b]
2	**5b**	*o*-$CH_3C_6H_4$	DMAP in benzene	**4b**	38.3	134—135
3	**6c**	*m*-$CH_3C_6H_4$	K_2CO_3 in *tert*-BuOH	**4c**	66.7	159—161
4	**6d**	*p*-$CH_3C_6H_4$	K_2CO_3 in *tert*-BuOH	**4d**	61.4	174—177.5
5	**5e**	*o*-ClC_6H_4	DMAP in benzene	**4e**	50.2	141—142
6	**5f**	*m*-ClC_6H_4	K_2CO_3 in *tert*-BuOH	**4f**	40.2	152—154
7	**6g**	*p*-ClC_6H_4	K_2CO_3 in *tert*-BuOH	**4g**	63.0	157—160
8	**6g**	*p*-ClC_6H_4	DMAP in *tert*-BuOH	**4g**	70.0	
9	**6g**	*p*-ClC_6H_4	DMAP in benzene	**4g**	73.0	
10	**5g**	*p*-ClC_6H_4	DMAP in benzene	**4g**	70.0	
11	**5h**	2,4-$Cl_2C_6H_3$	DMAP in benzene	**4h**	77.2	152—153

a) 2.0 eq of the base was used. *b*) Lit., 158 °C (Beilstein, E III/IV, 27, 0000, p. 3391).

place to give **5i** and **6i** (run 15).

In the literature, acyl groups on pyrazole rings have been reported to be rearranged under both basic and acidic conditions; 1,3-dimethyl-5-pyrazolyl 2,4-dichlorobenzoate was converted into DTP (**1a**) in the presence of potassium carbonate in *tert*-butyl alcohol,[6] and 2-acetyl-3-hydroxy-5-methylpyrazole was rearranged into 1-acetyl-3-hydroxy-5-methylpyrazole and related compounds under acidic conditions.[7] We examined the acyl-transfer reaction of 5-(*p*-chlorobenzoyloxy)-3-methylisoxazole (**6g**) under basic conditions (Table II). The treatment of **6g** with 0.5 eq of triethylamine in benzene for 4 h at room temperature gave rise to the rearranged product **5g** in 75% yield. α-Picoline in large excess was observed to accelerate the rearrangement, but the yield was only 15%. It can therefore be presumed that in the reaction course of runs 2, 6, 7 and 11 in Table I, the initially formed 5-acyloxy compounds **6** were subjected to acyl-transfer with the aid of triethylamine or α-picoline to give the 2-acyl compounds **5**, and larger quantities of **5** were consequently obtained. Both 4-(*N*,*N*-dimethylamino)pyridine (DMAP) and potassium carbonate also catalyzed the rearrangement of **6g** into **5g** in good yields (Table II).

The further transfer of the *p*-chlorobenzoyl group on the nitrogen atom of **5g** to the 4-position was completed by heating **5g** at 80 °C with 1 eq of DMAP[8] to afford 4-(*p*-

TABLE IV. 4-Acyl Derivatives **4** Directly Obtained from **2a**

Run	4	R	Yield (%)	mp (°C)
1	**4g**	*p*-ClC_6H_4	70.2	157—160
2	**4i**	2-NO_2-3-$CH_3C_6H_3$	76.3	144—146
3	**4j**	2-NO_2-4-ClC_6H_3	42.9	168—169 (dec.)
4	**4k**	2-Cl-4-$NO_2C_6H_3$	63.8	156—159 (dec.)
5	**4l**	$(CH_3)_2CHCH_2$	44.3	Oil
6	**4m**	$(CH_3)_2CH$	64.3	Oil
7	**4n**	Cyclohexyl	70.0	99—101.5

TABLE V. Analytical Data for Synthesized Compounds

Compound	Formula	Calcd (%)			Found (%)		
		C	H	N	C	H	N
5a	$C_{11}H_9NO_3$	65.02	4.46	6.89	65.09	4.29	6.81
5b	$C_{12}H_{11}NO_3$	66.35	5.10	6.45	66.46	5.10	6.41
5c	$C_{12}H_{11}NO_3$	66.35	5.10	6.45	66.53	5.13	6.47
5d	$C_{12}H_{11}NO_3$	66.35	5.10	6.45	66.43	5.00	6.32
5e	$C_{11}H_8ClNO_3$	55.60	3.39	5.89	55.37	3.35	5.74
5f	$C_{11}H_8ClNO_3$	55.60	3.39	5.89	55.67	3.32	5.82
5g	$C_{11}H_8ClNO_3$	55.60	3.39	5.89	55.30	3.29	5.75
5h	$C_{11}H_7Cl_2NO_3$	48.56	2.59	5.15	48.31	2.46	4.97
5i	$C_{10}H_8ClNO_4S$	43.88	2.95	5.12	43.84	2.88	5.16
6a	$C_{11}H_9NO_3$	65.02	4.46	6.89	65.19	4.36	6.79
6b	$C_{12}H_{11}NO_3$	66.35	5.10	6.45	66.65	5.14	6.35
6c	$C_{12}H_{11}NO_3$	66.35	5.10	6.45	66.63	5.18	6.16
6d	$C_{12}H_{11}NO_3$	66.35	5.10	6.45	66.65	5.11	6.37
6f	$C_{11}H_8ClNO_3$	55.60	3.39	5.89	55.67	3.32	5.82
6g	$C_{11}H_8ClNO_3$	55.60	3.39	5.89	55.30	3.29	5.75
6h	$C_{11}H_7Cl_2NO_3$	48.56	2.59	5.15	48.72	2.60	4.94
6i	$C_{10}H_8ClNO_4S$	43.88	2.95	5.12	43.59	3.02	4.99
4a	$C_{11}H_9NO_3$	65.02	4.46	6.89	65.32	4.55	6.91
4b	$C_{12}H_{11}NO_3$	66.35	5.10	6.45	66.58	5.19	6.29
4c	$C_{12}H_{11}NO_3$	66.35	5.10	6.45	66.64	5.20	6.33
4d	$C_{12}H_{11}NO_3$	66.35	5.10	6.45	66.63	5.11	6.37
4e	$C_{11}H_8ClNO_3$	55.60	3.39	5.89	55.68	3.44	5.97
4f	$C_{11}H_8ClNO_3$	55.60	3.39	5.89	55.89	3.51	5.82
4g	$C_{11}H_8ClNO_3$	55.60	3.39	5.89	55.34	3.44	5.88
4h	$C_{11}H_7Cl_2NO_3$	48.56	2.59	5.15	48.60	2.58	5.19
4i	$C_{12}H_{10}N_2O_5$	54.96	3.82	10.69	55.25	3.94	10.99
4j	$C_{11}H_7ClN_2O_5$	46.75	2.50	9.91	46.71	2.44	9.83
4k	$C_{11}H_7ClN_2O_5$	46.75	2.50	9.91	46.83	2.41	9.81
4l	$C_9H_{13}NO_3$	59.00	7.15	7.65	58.75	6.99	7.77
4m	$C_8H_{11}NO_3$	56.79	6.55	8.27	56.71	6.63	8.41
4n	$C_{11}H_{15}NO_3$	63.14	7.23	6.69	62.93	7.27	6.71

chlorobenzoyl)-5-hydroxy-3-methylisoxazole (**4g**). Compound **6g** was also transformed into **4g** with the aid of more than 1 eq of DMAP or potassium carbonate, *via* **5g**. In a similar manner, a series of 4-acyl-5-hydroxy-3-methylisoxazoles **4** was obtained from the corresponding **5** or **6** (Table III). On the other hand, no rearrangement of the sulfonyl group of **5i** and **6i** was observed.

This acyl-transfer reaction was extended to the direct acylation of **2a** to the 4-acyl

TABLE VI. IR and ^{1}H-NMR Data for Synthesized Compounds

Compound	IR ν_{max}^{Nujol} cm^{-1} (C=O)	^{1}H-NMR δ ($CDCl_3$)[a] ppm
5a	1760, 1700	2.70 (3H, s), 5.42 (1H, m), 7.45—7.6 (2H, m), 7.85—8.05 (2H, m)
6a	1760	2.32 (3H, s), 6.05 (1H, s), 7.5—7.7 (2H, m), 8.1—8.3 (2H, m)
5b	1760, 1700	2.65 (3H, s), 3.38 (3H, s), 5.37 (1H, m), 7.0—7.6 (4H, m)
6b	1755	2.32 (3H, s), 2.67 (3H, s), 6.03 (1H, s), 7.2—7.7 (3H, m), 8.1—8.25 (1H, m)
5c	1795, 1765, 1745, 1700	2.40 (3H, s), 2.67 (3H, s), 5.38 (1H, m), 7.3—7.4 (4H, m)
6c	1770	2.30 (3H, s), 2.43 (3H, s), 6.03 (1H, s), 7.35—8.0 (4H, m)
5d	1790, 1750, 1690	2.42 (3H, s), 2.67 (3H, s), 5.38 (1H, m), 7.28 (2H, d, J=8), 7.83 (2H, d, J=8)
6d	1750	2.32 (3H, s), 2.45 (3H, s), 6.03 (1H, s), 7.32 (2H, d, J=8), 8.07 (2H, d, J=8)
5e	1775, 1700	2.70 (3H, s), 5.38 (1H, m), 7.40 (4H, m)
5f	1790, 1700	2.68 (3H, s), 5.38 (1H, m), 7.2—7.8 (4H, m)
6f	1760	2.30 (3H, s), 6.00 (1H, s), 7.2—8.1 (4H, m)
5g	1770, 1690	2.67 (3H, s), 5.37 (1H, m), 7.38 (2H, d, J=8), 7.80 (2H, d, J=8)
6g	1755	2.30 (3H, s), 5.98 (1H, s), 7.43 (2H, d, J=8), 8.05 (2H, d, J=8)
5h	1780, 1770, 1700	2.68 (3H, s), 5.38 (1H, m), 7.37 (2H, m), 7.43 (2H, m)
6h	1770	2.33 (3H, s), 6.07 (1H, s), 7.13 (1H, d, J=2), 7.27 (1H, dd, J=2, 9), 7.98 (1H, d, J=9)
4a	1680	2.00 (3H, s), 7.60 (5H, s), 10.58 (1H, br s)
4b	1725	1.72 (3H, s), 2.40 (3H, s), 7.28—7.50 (4H, m), 11.18 (1H, s)
4c	1690	2.02 (3H, s), 2.43 (3H, s), 7.37 (4H, s), 11.20 (1H, s)
4d	1670	2.17 (3H, s), 2.45 (3H, s), 7.32 (2H, d, J=8), 7.53 (2H, d, J=8)
4e	1740	1.79 (3H, s), 7.45—7.6 (4H, m), 10.80 (1H, s)
4f	1660	2.15 (3H, s), 7.45—7.55 (4H, m), 10.47 (1H, s)
4g	1670	2.07 (3H, s), 7.48 (1H, br s), 7.57 (4H, s)
4h	1730	1.84 (3H, s), 7.4—7.7 (3H, m), 9.40 (1H, s)
4i	1700	(DMSO-d_6): 2.24 (3H, s), 2.29 (3H, s), 7.26—7.30 (3H, m), 7.80 (1H, s)
4j	1710	(DMSO-d_6): 2.50 (3H, s), 7.3—8.05 (3H, m), 10.30 (1H, s)
4k	1710	(DMSO-d_6): 2.42 (3H, s), 7.35—7.5 (1H, m), 8.0—8.6 (2H, m), 10.60 (1H, s)
4l	1700	1.05 (3H, m), 2.1—2.65 (3H, m), 2.40 (3H, s), 10.27 (1H, s)
4m	1700	1.26 (6H, d, J=8), 2.47 (3H, s), 3.05—3.5 (1H, m), 9.79 (1H, s)
4n	1705	1.3—2.0 (11H, m), 2.39 (3H, s), 10.78 (1H, s)

a) J refers to a coupling constant in Hz.

compounds **4** without isolation of the intermediates **5** and **6**. Thus, compound **2a** was treated with *p*-chlorobenzoyl chloride in the presence of 2.1 eq of DMAP in benzene at room temperature, followed by heating at 80 °C for 6 h to give the 4-(*p*-chlorobenzoyl) compound **4g** in 70.2% yield (Table IV). In a similar manner, various 4-acylisoxazoles **4** were directly synthesized from **2a**.

Among the synthesized compounds, 4-(2,4-dichlorobenzoyl)-5-hydroxy-3-methylisoxazole (**4h**), which had been predicted to be a bioisostere of the herbicidal compound **1a**, was found to have almost no herbicidal activity, contrary to our expectation.

Experimental

All melting points are uncorrected. The infrared (IR) spectra were determined on a Jasco A-102 spectrometer in Nujol mulls. The proton nuclear magnetic resonance (^{1}H-NMR) spectra were recorded at 60 MHz on a Varian 360A spectrometer, with tetramethylsilane as an internal standard. Analytical, IR and ^{1}H-NMR data for synthesized compounds are summarized in Tables V and VI.

2-(*p*-Chlorobenzoyl)-3-methyl-3-isoxazolin-5-one (5g) and 5-(*p*-Chlorobenzoyloxy)-3-methylisoxazole (6g)——*p*-Chlorobenzoyl chloride (1.96 g, 11.2 mmol) and α-picoline (1.05 g, 11.2 mmol) were added to a solution of **2a** (1.0 g, 10.2 mmol) in dry benzene (20 ml) under ice-cooling. After being stirred at room temperature for 2 h, the reaction mixture was poured into water and extracted with ethyl acetate. The extract was washed with water and brine, dried over $MgSO_4$, and evaporated *in vacuo*. The residue was chromatographed over silica gel to give 0.81 g (33.3%) of **5g** and 1.43 g (59.0%) of **6g** as a less polar fraction.

Other compounds **5** and **6** were synthesized in the same manner (Table I).

Acyl-Transfer Reaction of 6g to Give 5g——Triethylamine (0.27 g, 2.1 mmol) was added to a solution of **6g** (1.0 g, 4.2 mmol) in dry benzene (10 ml) at room temperature. The mixture was stirred for 4 h, then water was added. The whole was extracted with ethyl acetate, and the extract was washed with water and brine, dried over $MgSO_4$, and evaporated *in vacuo*. The residue was chromatographed over silica gel to give 0.75 g (75.0%) of **5g**; 0.05 g (5.0%) of **6g** was recovered.

Runs 2—5 in Table II were performed similarly.

4-Benzoyl-5-hydroxy-3-methylisoxazole (4a)——Potassium carbonate (anhydrous) (0.55 g) was added to a solution of 5-benzoyloxy-3-methylisoxazole (**6a**) (0.40 g) in *tert*-butyl alcohol (15 ml). After heating at 80 °C for 3 h, the reaction was quenched with water. The mixture was washed with benzene, acidified to pH 1 with 2 N hydrochloric acid, and extracted with dichloromethane. The dichloromethane layer was washed with water, and extracted with saturated sodium carbonate. After being washed with dichloromethane, this extract was acidified to pH 1 with 2 N hydrochloric acid, and extracted with dichloromethane. This organic layer was washed with water and brine, and dried over $MgSO_4$. After removal of the solvent, 0.16 g (40.0%) of **4a** was obtained as crystals. If necessary, this product was further purified by recrystallization (*n*-hexane–ethyl acetate).

Compounds **4b—h** were synthesized similarly (Table III).

Direct Acylation of 3-Methyl-3-isoxazolin-5-one (2a)——Synthesis of 4-(*p*-Chlorobenzoyl)-5-hydroxy-3-methylisoxaole (**4g**): *p*-Chlorobenzoyl chloride (0.43 g, 2.5 mmol) and DMAP (0.55 g, 4.5 mmol) were added to a solution of **2a** (0.20 g, 2.0 mmol) in dry benzene (10 ml) under ice-cooling. The mixture was heated at 80 °C for 6 h, and work up as described for the synthesis of **4a** afforded 0.34 g (70.2%) of **4g**.

Compounds **4i—n** were synthesized similarly (Table IV).

References

1) *a*) Review: M. Ishida, T. Matsui, T. Yanai, K. Kawakubo, T. Honma, K. Tanizawa, M. Nakagawa, and H. Okudaira, *Ann. Rep. Sankyo Res. Lab.*, **36**, 44 (1984) (Japanese); *b*) T. Konotsune, K. Kawakubo, and T. Yanai, "Advances in Pesticide Sciences," Zurich 1978, ed. by Geissbuler, Pergamon Press, Oxford, Part 2, 1979, p. 94.
2) *a*) A. Burger, "Medicinal Chemistry," 3rd ed., Wiley-Interscience, New York, 1970, p. 72; *b*) W. O. Foye, "Principles of Medicinal Chemistry," Lea & Febiger, Philadelphia, 1975, p. 92; *c*) C. W. Thornber, *Chem. Soc. Rev.*, **1979**, 563; *d*) M. Yoshimoto, *Ann. Rep. Sankyo Res. Lab.*, **34**, 1 (1982).
3) F. Korte and K. Storike, *Chem. Ber.*, **94**, 1956 (1961).
4) *a*) A. E. Hydorn, F. A. McGinn, J. R. Moetz, and J. Schinartz, *J. Org. Chem.*, **27**, 4305 (1962); *b*) Recently, acylation of 3-phenoxymethyl or 3-phenylthiomethylisoxazol-5(4*H*)-one to the 4-acyl derivative by Korte's method[3] or Hydorn's method[4a] was reported; see G. Deshayers, M. Chabannet, B. Najib, and S. Gelin, *Heterocycles*, **23**, 1651 (1985).
5) M. Fujimoto and M. Sakai, *Chem. Pharm. Bull.*, **13**, 248 (1965).
6) T. Yanai, *Ann. Rep. Sankyo Res. Lab.*, **36**, 174 (1984).
7) K. Arakawa, T. Miyasaka, and H. Ochi, *Chem. Pharm. Bull.*, **22**, 214 (1974).
8) DMAP is an effective acyl-transfer inducing reagent; see E. F. V. Scrinen, *Chem. Soc. Rev.*, **1983**, 129.