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90. Michihiko Ochiai and Toshiya Kamikado : Studies on Herbicides and Plant Growth Regulators. II.*1 Synthesis and Some Reactions of 1-Aryloxyacylpyrazoles.*2

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Since Zimmerman1) first recorded (2,4-dichlorophenoxy)acetic acid as a potent synthetic plant growth regulator, a number of its derivatives have been prepared and considerable differences in activities were disclosed. Nevertheless, there dose not appear to be agreement among workers in this field as to whether the amides of (2,4-dichlorophenoxy)acetic acid and the related acids are active as such or the hydrolysis of the amide to the parent acid is a pre-requisite for the activity.2) Sudi and his co-workers3) recently stated that these amides would be converted to the acids. Contrary to this, Johnston4) concluded on the basis of the comparison between plant growth activities and the rate of alkaline hydrolysis of the amides that the activity is revealed by the amide itself.

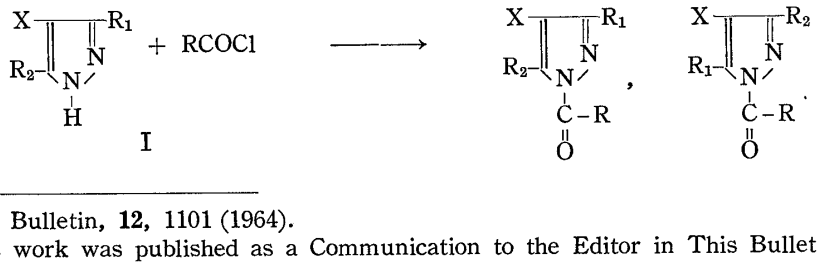
In view of recently reported chemical properties of the azolides,*4,5,6) we attempted the synthesis of a number of 1-aryloxyacylpyrazoles for the evaluation as plant growth regulator.

The present paper deals with the synthesis, structure, some nuclear magnetic resonance spectroscopic aspects and some reactions of 1-aryloxyacylpyrazoles.

Synthesis of 1-Aryloxyacylpyrazoles

1-Aryloxyacylpyrazoles were prepared by either of the following methods; the action of the 1-aryloxyacyl chlorides on pyrazoles in pyridine or without solvent (Method A), the condensation of aryloxyacetic acid hydrazides with acetylacetone in ethanol (Method B), and the action of ethyl chloroformate on aryloxyacetic acids followed by the treatment of mixed anhydrides thus obtained with pyrazoles (Method C). The results are summarized in Table I.

Structure



I

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*1 Part I : This Bulletin, **12**, 1101 (1964).

*2 A part of this work was published as a Communication to the Editor in This Bulletin, **12**, 1515 (1964).

*3 Juso-nishino-cho, Higashiyodogawa-ku, Osaka (落合道彦, 上門敏也).

*4 Azolide : N-acyl derivatives of five-membered heterocyclic compounds containing two or more nitrogen atoms in the ring.

1) P.W. Zimmerman, A.E. Hitchcock : Contribs. Boyce Thompson Inst., **12**, 321 (1942).

2) *a*) C.H. Fawcett, H.F. Taylor, R.L. Wains, F. Wightman: "In the Chemistry and Mode of Action of Plant Growth Substances," p. 187 (London), Ed. by R.L. Wain, F. Wightman (1956). *b*) R.C. Seely, C.H. Fawcett, R.L. Wain, F. Wightman : *Ibid.*, p. 234 (1956), etc.

3) J. Sudi, Gy. Josepovits, Gy. Matolcsy : Novenyved. Ind. Tanacskozas Kozlemen, Budapest, **2**, 401 (1960); C.A., **57**, 14224c (1962).

4) A.M. Johnston : J. Chem. Soc., **1961**, 2335; Biochem. J., **82**, 425 (1962).

5) H.A. Staab : Angew. Chem., **74**, 407 (1962).

6) W. Ried, K. Marquard : Ann., **642**, 141 (1961), etc.

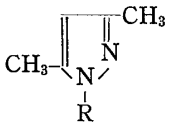
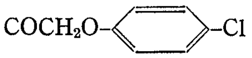
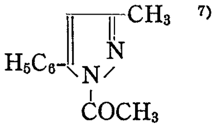
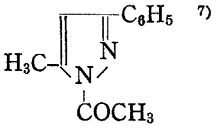
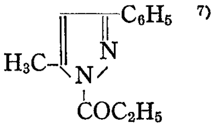
When unsymmetrically substituted pyrazoles (I) are acylated two isomeric N-acyl compounds should theoretically be formed.

Investigations by Auwers[7] and Wahlberg[8] on this problem demonstrated that the acylation actually led to a single product. However, these authors did not make clear the structural assignment of the compound obtained.

We used the nuclear magnetic resonance spectra[*5] for determining the structure of the compound obtained by the acylation of I. Reddy, *et al.*[9] observed in the nuclear magnetic resonance spectra of imidazoles and purines that a proton adjacent to the acetyl position showed a down-field shift of about 19 c.p.s. (40 Mc. in $CDCl_3$) and that also methyl proton at the same position showed down-field shift of about one-third the magnitude. This may be explained partly by the electron-withdrawing effect and partly by anisotropy effects of the carbonyl group.

We observed in the nuclear magnetic resonance spectra of the N-acylated 3,5-dimethylpyrazoles (II~VII) that the chemical shifts of the methyl groups in the 3- and 5-positions differed appreciably from each other, and that the lower signals were assigned to the methyl groups adjacent to the acyl group as shown with the authentic compounds (VIII~X).[7] (Table II, nuclear magnetic resonance spectra of all the pyrazole derivatives reported here were measured in carbon tetrachloride containing tetramethylsilane as an internal referenec at 60 Mc. with a Varian A-60 spectrometer).

TABLE II. Nuclear Magnetic Resonance Spectra of Some 1-Acylpyrazoles

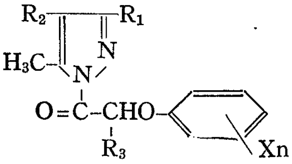
		Chemical shift (τ) of the methyl group		
	R=	3-CH_3	5-CH_3	Δ_τ 3~5
II	COC_6H_5	7.79	7.37	0.42
III	$CONH_2$	7.79	7.45	0.34
IV	$COCH_3$	7.82	7.52	0.30
V	COC_2H_5	7.82	7.50	0.32
VI	$COCH_2OC_6H_5$	7.81	7.48	0.33
VII	 [10]	7.80	7.47	0.33
VIII	 [7]	7.75	—	
IX	 [7]	—	7.41	
X	 [7]	—	7.41	

[*5] After this work was completed, a paper[11] entitled " Proton Nuclear Magnetic Resonance Spectra of 1-Acyl Pyrazoles " was published, in which the structures of N-acetylated pyrazoles were discussed on the basis of the nuclear magnetic resonance spectra of the annular protons.

7) K. v. Auwers, K. Dietrich : J. prakt. Chem., **139**, 65 (1934).
8) H. E. Wahlberg : Arkiv Kemi., **20**, 153 (1962).
9) G .S. Reddy, L. Mandell, J. H. Goldstein : J. Chem. Soc., **1963**, 1414.
10) W. Ried, B. Schleimer : Ann., **626**, 98 (1959).
11) J. K. Williams : J. Org. Chem., **29**, 1377 (1964).

Table I. 1-Aryloxyacylpyrazoles

No.	R_1	R_2	R_3	Xn	m.p. (°C)	Method	Yield (%)	Solvent of recrystaln.
1	CH_3	H	H	2-Cl	124~126	A	55	acetone
2	〃	NO_2	〃	〃	192~193	〃	53	〃
3	〃	Cl	〃	〃	154.5~155.5	〃	71	〃
4	〃	Br	〃	〃	157~158	〃	74	〃
5	OC_2H_5	H	〃	〃	98~100	〃	47	〃
6	〃	Cl	〃	〃	141~142	〃	32	〃
7	〃	Br	〃	〃	133~134	〃	46	〃
8	C_6H_5	H	〃	〃	138~138.5	〃	85	〃
9	〃	Cl	〃	〃	185~186	〃	71	DMF
10	〃	Br	〃	〃	190~191	〃	80	〃
11	CH_3	H	〃	3-Cl	100~101	〃	62	acetone
12	〃	NO_2	〃	〃	164~166	〃	57	acetone-DMF
13	〃	Cl	〃	〃	108~109	〃	74	acetone
14	〃	Br	〃	〃	120~121	〃	77	〃
15	OC_2H_5	H	〃	〃	101	〃	40	〃
16	〃	Cl	〃	〃	77	〃	39	〃
17	〃	Br	〃	〃	78~80	〃	31	ligroin
18	C_6H_5	H	〃	〃	114~115	〃	83	acetone
19	〃	Cl	〃	〃	108~109	〃	74	〃
20	〃	Br	〃	〃	97~99	〃	63	〃
21	CH_3	H	〃	4-Cl	112~113	〃	72	〃
22	〃	NO_2	〃	〃	184~186	〃	66	acetone-DMF
23	〃	Cl	〃	〃	151~153	〃	48	acetone
24	OC_2H_5	H	〃	〃	101~103	〃	76	〃
25	〃	Cl	〃	〃	85~87	〃	69	〃
26	〃	Br	〃	〃	111~113	〃	86	〃
27	C_6H_5	H	〃	〃	121~122	〃	88	〃
28	〃	Cl	〃	〃	109~110	〃	79	〃
29	〃	Br	〃	〃	102~104	〃	75	〃
30	CH_3	H	〃	2-CH_3-4-Cl	137.5~138.5	〃	72	〃
31	〃	NO_2	〃	〃	172~173	〃	50	〃
32	〃	Cl	〃	〃	113~114	〃	75	〃
33	〃	Br	〃	〃	121~122	〃	77	〃
34	OC_2H_5	H	〃	〃	105	〃	83	〃
35	〃	Cl	〃	〃	130~131.5	〃	20	〃
36	〃	Br	〃	〃	137~137.5	〃	18	〃



Appearance	Formula	Analysis (%)					
		Calcd.			Found		
		C	H	N	C	H	N
colorless prisms	$C_{13}H_{13}O_2N_2Cl$	58.98	4.95	10.58	59.05	4.99	10.48
〃 〃	$C_{13}H_{12}O_4N_3Cl$	50.41	3.90	13.57	50.40	4.22	13.55
〃 needles	$C_{13}H_{12}O_2N_2Cl_2$	52.19	4.04	9.36	51.96	3.85	9.17
〃 〃	$C_{13}H_{12}O_2N_2BrCl$	45.44	3.53	8.15	45.38	3.37	8.14
〃 prisms	$C_{14}H_{15}O_3N_2Cl$	57.06	5.14	9.51	56.95	5.07	9.19
〃 〃	$C_{14}H_{14}O_3N_2Cl_2$	51.08	4.29	—	51.21	4.19	—
〃 〃	$C_{14}H_{14}O_3N_2BrCl$	45.01	3.77	7.50	45.28	3.83	7.45
〃 〃	$C_{18}H_{15}O_2N_3Cl$	66.17	4.63	8.58	65.94	4.58	8.79
〃 〃	$C_{18}H_{14}O_2N_2Cl_2$	59.86	3.90	7.75	59.69	3.90	7.83
〃 〃	$C_{18}H_{14}O_2N_2BrCl$	53.29	3.48	6.91	53.01	3.46	6.89
〃 〃	$C_{13}H_{13}O_2N_2Cl$	58.98	4.95	10.58	58.86	4.73	10.24
〃 〃	$C_{13}H_{12}O_4N_3Cl$	50.41	3.90	13.57	50.19	3.75	13.01
〃 〃	$C_{13}H_{12}O_2N_2Cl_2$	52.19	4.04	9.36	52.05	3.73	9.30
〃 〃	$C_{13}H_{12}O_2N_2BrCl$	45.44	3.53	8.15	45.65	3.51	8.07
〃 crystals	$C_{14}H_{15}O_3N_2Cl$	57.06	5.14	—	56.92	5.10	—
〃 prisms	$C_{14}H_{14}O_3N_2Cl_2$	51.08	4.29	8.52	51.07	4.27	8.40
〃 〃	$C_{14}H_{14}O_3N_2BrCl$	45.01	3.77	7.50	45.13	3.58	7.18
〃 〃	$C_{18}H_{15}O_2N_2Cl$	66.17	4.63	8.58	66.00	4.47	8.49
〃 〃	$C_{18}H_{14}O_2N_2Cl_2$	59.86	3.90	7.75	59.94	3.88	7.61
〃 〃	$C_{18}H_{14}O_2N_2BrCl$	53.29	3.48	6.91	53.55	3.43	6.66
〃 scales	$C_{13}H_{13}O_2N_2Cl$	58.98	4.95	10.58	59.14	4.82	10.32
〃 needles	$C_{13}H_{12}O_4N_3Cl$	50.41	3.90	13.57	50.65	4.03	14.03
〃 plates	$C_{13}H_{12}O_2N_2Cl_2$	52.19	4.04	9.36	51.69	3.85	8.84
〃 needles	$C_{14}H_{15}O_3N_2Cl$	57.06	5.14	9.51	57.22	5.05	9.26
〃 〃	$C_{14}H_{14}O_3N_2Cl_2$	51.08	4.29	8.52	51.36	4.07	8.40
〃 〃	$C_{14}H_{14}O_3N_2BrCl$	45.01	3.77	7.50	44.86	3.87	7.30
〃 prisms	$C_{18}H_{15}O_2N_2Cl$	66.17	4.63	8.58	65.90	4.55	8.32
〃 〃	$C_{18}H_{14}O_2N_2Cl_2$	59.86	3.90	7.75	59.86	4.12	7.30
〃 〃	$C_{18}H_{14}O_2N_2BrCl$	53.29	3.48	6.91	53.10	3.76	6.81
〃 〃	$C_{14}H_{15}O_2N_2Cl$	60.32	5.42	10.05	60.33	5.53	10.32
〃 〃	$C_{14}H_{14}O_4N_3Cl$	51.94	4.35	12.97	51.70	4.28	12.69
〃 〃	$C_{14}H_{14}O_2N_2Cl_2$	53.69	4.50	8.94	53.49	4.37	8.60
〃 〃	$C_{14}H_{14}O_2N_2BrCl$	47.01	3.94	7.83	46.89	3.85	7.63
〃 〃	$C_{15}H_{17}O_3N_2Cl$	58.34	5.44	9.07	58.68	5.27	8.47
〃 〃	$C_{15}H_{16}O_3N_2Cl_2$	52.49	4.69	8.16	52.58	4.48	7.96
〃 〃	$C_{15}H_{16}O_3N_2BrCl$	46.47	4.16	7.22	46.62	4.02	6.99

37	C_6H_5	H	H	2-CH_3-4-Cl	125～125.5	A	50	acetone
38	〃	Cl	〃	〃	126～128	〃	74	〃
39	〃	Br	〃	〃	140～142	〃	85	〃
40	CH_3	H	〃	2,4-di-Cl	134～136	A B C	80 90.5 12	〃
41	〃	NO_2	〃	〃	161～162	A C	47.5 20	〃
42	〃	Cl	〃	〃	127～128	A C	64 15	〃
43	〃	Br	〃	〃	135～137	A C	85 30	〃
44	OC_2H_5	H	〃	〃	107～109	A C	85 12	〃
45	〃	Cl	〃	〃	132～134	A C	82 19	〃
46	〃	Br	〃	〃	131～132	A C	87 18	〃
47	C_6H_5	H	〃	〃	118～119	A C	60 25	〃
48	〃	Cl	〃	〃	109～110	A C	89 14	〃
49	〃	Br	〃	〃	122.5～124	A C	79 15	〃
50	CH_3	H	〃	2-CH_2OH-4-Cl	133	B	82	DMF
51	〃	〃	CH_3	2,4-di-Cl	108	A	77	acetone
52	〃	NO_2	〃	〃	97～98	〃	11.7	*n*-hexane
53	〃	Cl	〃	〃	100～101	〃	73	acetone
54	〃	Br	〃	〃	110	〃	78	〃
55	OC_2H_5	H	〃	〃	73～74	〃	52	*n*-hexane
56	〃	Cl	〃	〃	63	〃	16.8	acetone
57	〃	Br	〃	〃	80～82	〃	78	〃
58	C_6H_5	H	〃	〃	109～110	〃	79	〃
59	〃	Cl	〃	〃	129～130	〃	75	〃
60	〃	Br	〃	〃	132～132.5	〃	74	〃
61	CH_3	H	H	2,5-di-Cl	112～113	〃	65	〃
62	〃	NO_2	〃	〃	160～161	〃	71	〃
63	〃	Cl	〃	〃	150～151	〃	67	〃
64	〃	Br	〃	〃	157～158	〃	48	〃
65	OC_2H_5	H	〃	〃	121～122	〃	55	acetone-MeOH
66	〃	Cl	〃	〃	115～116	〃	56	acetone
67	〃	Br	〃	〃	91～92	〃	70	〃
68	C_6H_5	H	〃	〃	120～121	〃	72	〃
69	〃	Cl	〃	〃	116～117	〃	59	〃
70	〃	Br	〃	〃	113～115	〃	54	〃
71	CH_3	H	〃	2,6-di-Cl	145	〃	64	〃
72	〃	NO_2	〃	〃	177～179	〃	70	DMF-acetone
73	〃	Cl	〃	〃	148～149	〃	68	〃
74	〃	Br	〃	〃	145～146	〃	74	〃
75	OC_2H_5	H	〃	〃	81～83	〃	53	acetone

colorless	prisms	$C_{19}H_{17}O_2N_2Cl$	66.95	5.02	8.22	66.96	5.07	8.05
〃	〃	$C_{19}H_{16}O_2N_2Cl_2$	60.81	4.29	7.46	60.98	4.25	7.34
〃	〃	$C_{19}H_{16}O_2N_2BrCl$	54.36	3.84	6.67	54.46	3.89	6.43
〃	needles	$C_{13}H_{12}O_2N_2Cl_2$	52.19	4.04	9.36	52.06	4.01	9.63
〃	prisms	$C_{13}H_{11}O_4N_3Cl_2$	45.37	3.22	12.21	45.54	3.32	12.26
〃	needles	$C_{13}H_{11}O_2N_2Cl_3$	46.76	3.32	8.39	46.88	3.37	8.16
〃	prisms	$C_{13}H_{11}O_2N_2BrCl_2$	41.30	2.93	7.41	41.22	2.71	7.13
〃	crystals	$C_{14}H_{14}O_3N_2Cl_2$	51.08	4.29	8.52	51.21	4.39	8.42
〃	prisms	$C_{14}H_{13}O_3N_2Cl_3$	46.24	3.60	7.71	46.50	3.50	7.66
〃	〃	$C_{14}H_{13}O_3N_2BrCl_2$	41.20	3.21	6.87	41.21	3.44	6.75
〃	needles	$C_{18}H_{14}O_2N_2Cl_2$	59.86	3.90	7.75	60.01	3.77	7.26
〃	〃	$C_{18}H_{13}O_2N_2Cl_3$	54.69	3.32	7.08	54.45	3.25	6.92
〃	〃	$C_{18}H_{13}O_2N_2BrCl_2$	49.12	2.98	6.37	49.05	2.98	6.16
〃	〃	$C_{14}H_{15}O_3N_2Cl$	57.06	5.14	9.51	56.89	4.96	9.43
〃	prisms	$C_{14}H_{14}O_2N_2Cl_2$	53.71	4.51	8.95	53.92	4.36	8.67
〃	crystals	$C_{14}H_{13}O_4N_3Cl_2$	46.96	3.66	11.74	46.90	3.75	11.70
〃	needles	$C_{14}H_{13}O_2N_2Cl_3$	48.42	3.78	8.06	48.71	3.71	7.96
〃	prisms	$C_{14}H_{13}O_2N_2BrCl_2$	42.88	3.34	7.15	42.99	3.23	6.85
〃	needles	$C_{15}H_{16}O_3N_2Cl_2$	52.49	4.70	8.17	52.70	4.83	8.49
〃	prisms	$C_{15}H_{15}O_3N_2Cl_3$	47.71	4.01	7.42	47.91	4.04	7.92
〃	〃	$C_{15}H_{15}O_2N_2BrCl_2$	42.68	3.58	6.41	42.91	3.60	6.70
〃	needles	$C_{19}H_{16}O_2N_2Cl_2$	60.82	4.28	7.47	60.54	4.47	7.22
〃	〃	$C_{19}H_{15}O_2N_2Cl_3$	55.70	3.70	6.84	55.41	3.58	6.65
〃	〃	$C_{19}H_{15}O_2N_2BrCl_2$	50.25	3.33	6.17	49.79	3.35	5.94
〃	prisms	$C_{13}H_{12}O_2N_2Cl_2$	52.19	4.04	9.36	52.32	3.98	9.01
〃	〃	$C_{13}H_{11}O_4N_3Cl_2$	45.37	3.22	12.21	45.58	3.42	11.75
〃	〃	$C_{13}H_{11}O_2N_2Cl_3$	46.76	3.32	8.39	46.81	3.31	8.03
〃	〃	$C_{13}H_{11}O_2N_2BrCl_2$	41.30	2.93	7.41	41.50	2.82	7.07
〃	〃	$C_{14}H_{14}O_3N_2Cl_2$	51.08	4.29	8.52	50.78	4.21	8.14
〃	〃	$C_{14}H_{13}O_3N_2Cl_3$	46.24	3.60	7.71	46.62	3.65	7.28
〃	〃	$C_{14}H_{13}O_3N_2BrCl_2$	41.20	3.21	6.87	41.43	3.31	7.12
〃	〃	$C_{18}H_{14}O_2N_2Cl_2$	59.86	3.90	7.75	60.17	3.93	7.41
〃	〃	$C_{18}H_{13}O_2N_2Cl_3$	54.69	3.32	7.08	54.96	3.30	6.91
〃	〃	$C_{18}H_{13}O_2N_2BrCl_2$	49.12	2.98	6.37	49.12	3.01	6.20
〃	〃	$C_{13}H_{12}O_2N_2Cl_2$	52.19	4.04	9.36	51.99	3.97	9.18
〃	〃	$C_{13}H_{11}O_4N_3Cl_2$	45.37	3.22	—	45.63	3.31	—
〃	〃	$C_{13}H_{11}O_2N_2Cl_3$	46.76	3.32	8.39	46.81	3.08	7.97
〃	〃	$C_{13}H_{11}O_2N_2BrCl_2$	41.30	2.93	7.41	41.45	3.12	7.42
〃	〃	$C_{14}H_{14}O_3N_2Cl_2$	51.08	4.29	8.52	51.21	4.28	8.14

76	OC_2H_5	Cl	H	2,6-di-Cl	122～124	A	64	acetone
77	〃	Br	〃	〃	147～148	〃	62	〃
78	C_6H_5	H	〃	〃	133～134	〃	73	〃
79	〃	Cl	〃	〃	160～161	〃	56	〃
80	〃	Br	〃	〃	162～163	〃	49	〃
81	CH_3	H	〃	2,4,5-tri-Cl	177～178	〃	61	〃
82	〃	NO_2	〃	〃	160	〃	57	〃
83	〃	Cl	〃	〃	136.5～138	〃	79	〃
84	〃	Br	〃	〃	154～154.5	〃	66	〃
85	OC_2H_5	H	〃	〃	123～124	〃	79	〃
86	〃	Cl	〃	〃	107～108	〃	74	〃
87	〃	Br	〃	〃	120	〃	82	〃
88	C_6H_5	H	〃	〃	131～133	〃	81	〃
89	〃	Cl	〃	〃	159.5～160.5	〃	82	〃
90	〃	Br	〃	〃	157～158	〃	72	〃
91	CH_3	H	〃	2-NO_2	130～131	〃	66	〃
92	〃	NO_2	〃	〃	184～185	〃	80	DMF-acetone
93	〃	Cl	〃	〃	139～140	〃	65	acetone
94	〃	Br	〃	〃	153～154	〃	75	〃
95	C_6H_5	H	〃	〃	147～148	〃	80	DMF-acetone
96	〃	Cl	〃	〃	169～170	〃	62	〃
97	〃	Br	〃	〃	176～177	〃	63	〃
98	OC_2H_5	H	〃	〃	109～111	〃	66	acetone
99	CH_3	〃	〃	3-NO_2	137～137.5	〃	76	〃
100	〃	NO_2	〃	〃	148～149	〃	62	〃
101	〃	Cl	〃	〃	155～156	〃	60	DMF-acetone
102	〃	Br	〃	〃	167～168	〃	74	〃
103	OC_2H_5	H	〃	〃	109～110	〃	73	acetone
104	C_6H_5	〃	〃	〃	139～140	〃	72	DMF-acetone
105	〃	Cl	〃	〃	131～132	〃	66	acetone
106	〃	Br	〃	〃	117～118	〃	65	〃
107	CH_3	H	〃	4-NO_2	168～169	〃	67	〃
108	〃	NO_2	〃	〃	160	〃	27	〃
109	〃	Cl	〃	〃	176～178	〃	50	〃
110	〃	Br	〃	〃	190～191	〃	29	〃
111	C_6H_5	H	〃	〃	220～222	〃	46	〃
112	〃	Cl	〃	〃	164～165	〃	48	〃
113	〃	Br	〃	〃	149～151	〃	36	〃
114	CH_3	H	〃	2,4-di-NO_2	161～162	〃	70	〃
115	〃	〃	〃	2,3,4,6-tetra-Cl	159～160	〃	73	DMF-acetone
116	〃	Cl	〃	〃	178～179	〃	50	〃
117	C_6H_5	H	〃	〃	146～147	〃	53	〃
118	CH_3	〃	〃	2,3,4,5,6-penta-Cl	180～181	〃	71	DMF
119	〃	Cl	〃	〃	195	〃	66	〃

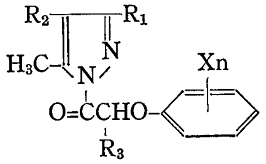
colorless	prisms	$C_{14}H_{13}O_3N_2Cl_3$	46.24	3.60	7.71	46.16	3.59	7.50
〃	needles	$C_{14}H_{13}O_3N_2BrCl_2$	41.20	3.21	6.87	41.33	3.05	6.66
〃	crystals	$C_{18}H_{14}O_2N_2Cl_2$	59.86	3.90	7.75	60.09	3.85	7.34
〃	needles	$C_{18}H_{13}O_2N_2Cl_3$	54.69	3.32	7.08	54.64	3.31	7.33
〃	〃	$C_{18}H_{13}O_2N_2BrCl_2$	49.12	2.98	6.37	49.12	2.93	6.10
〃	〃	$C_{13}H_{11}O_2N_2Cl_3$	46.76	3.32	8.39	46.74	3.35	8.37
〃	〃	$C_{13}H_{10}O_4N_3Cl_3$	41.24	2.67	11.10	41.22	2.66	10.61
〃	scales	$C_{13}H_{10}O_2N_2Cl_4$	42.42	2.74	7.61	42.28	2.84	7.64
〃	needles	$C_{13}H_{10}O_2N_2BrCl_3$	37.85	2.44	6.79	37.80	2.19	6.72
〃	crystals	$C_{14}H_{13}O_3N_2Cl_3$	46.24	3.60	7.71	45.84	3.71	7.39
〃	〃	$C_{14}H_{12}O_3N_2Cl_4$	42.25	3.04	7.04	42.45	3.10	6.72
〃	prisms	$C_{14}H_{12}O_3N_2BrCl_3$	38.00	2.74	6.33	38.12	2.98	6.40
〃	needles	$C_{18}H_{13}O_2N_2Cl_3$	54.69	3.32	7.08	54.64	3.38	6.96
〃	prisms	$C_{18}H_{12}O_2N_2Cl_4$	50.26	2.81	6.52	50.32	2.56	6.37
〃	〃	$C_{18}H_{12}O_2N_2BrCl_3$	45.56	2.55	5.91	45.72	2.62	5.81
〃	〃	$C_{13}H_{13}O_4N_3$	56.72	4.77	15.27	56.92	4.71	14.96
〃	needles	$C_{13}H_{12}O_6N_4$	48.75	3.78	17.50	48.90	3.79	17.27
〃	prisms	$C_{13}H_{12}O_4N_3Cl$	50.41	3.91	13.57	50.48	3.80	13.45
〃	〃	$C_{13}H_{12}O_4N_3Br$	44.08	3.42	11.87	44.05	3.46	11.54
〃	needles	$C_{18}H_{15}O_4N_3$	64.09	4.48	12.46	64.08	4.72	12.45
〃	〃	$C_{18}H_{14}O_4N_3Cl$	58 15	3.80	11.31	58.32	3.76	11.28
〃	〃	$C_{18}H_{14}O_4N_3Br$	51.94	3.39	10.10	52.26	3.45	10.18
〃	crystals	$C_{14}H_{15}O_5N_3$	55.08	4.95	13.77	55.07	4.94	13.59
〃	prisms	$C_{13}H_{13}O_4N_3$	56.72	4.77	15.27	56.76	4.79	15.27
〃	〃	$C_{13}H_{12}O_6N_4$	48.75	3.78	17.50	48.89	3.86	17.44
〃	〃	$C_{13}H_{12}O_4N_3Cl$	50.41	3.91	13.57	50.02	3.87	13.34
〃	crystals	$C_{13}H_{12}O_4N_3Br$	44.08	3.42	11.87	44.41	3.35	12.17
〃	prisms	$C_{14}H_{15}O_5N_3$	55.08	4.95	13.77	55.15	4.95	13.52
〃	〃	$C_{18}H_{15}O_4N_3$	64.09	4.48	12.46	64.13	4.50	12.56
〃	〃	$C_{18}H_{14}O_4N_3Cl$	58.15	3.80	11.31	58.41	3.84	11.24
〃	crystals	$C_{18}H_{14}O_4N_3Br$	51.94	3.39	10.10	52.13	3.53	9.98
〃	scales	$C_{13}H_{13}O_4N_3$	56.72	4.76	15.27	57.15	4.76	14.99
〃	crystals	$C_{13}H_{12}O_6N_4$	48.75	3.78	17.50	48.91	3.84	17.24
〃	prisms	$C_{13}H_{12}O_4N_3Cl$	50.41	3.96	13.57	50.43	3.86	13.01
〃	〃	$C_{13}H_{12}O_4N_3Br$	44.08	3.42	11.87	44.41	3.44	11.63
〃	plates	$C_{18}H_{15}O_4N_3$	64.09	4.48	12.46	64.42	4.47	12.35
〃	needles	$C_{18}H_{14}O_4N_3Cl$	58.15	3.80	—	58.56	3.77	—
〃	〃	$C_{18}H_{14}O_4N_3Br$	51.94	3.39	10.10	52.51	3.35	9.94
〃	〃	$C_{13}H_{12}O_6N_4$	48.75	3.78	17.50	48.91	3.94	17.57
〃	crystals	$C_{13}H_{10}O_2N_2Cl_4$	42.42	2.74	7.61	42.15	2.64	7.48
〃	prisms	$C_{13}H_9O_2N_2Cl_5$	38.79	2.26	6.96	38.57	2.00	6.73
〃	〃	$C_{18}H_{12}O_2N_2Cl_4$	50.26	2.81	6.52	50.24	3.09	6.27
〃	crystals	$C_{13}H_9O_2N_2Cl_5$	38.79	2.26	6.96	39.01	2.30	6.62
〃	〃	$C_{13}H_8O_2N_2Cl_6$	35.74	1.85	6.41	36.12	1.91	6.32

Table II also shows that structural modifications of the acyl group of N-acylpyrazoles have little effect on the chemical shift either of the methyl groups.

Chemical shifts (τ) of the methyl group of N-aryloxyacylpyrazoles derived from unsymmetric methylpyrazoles (I) were found at about 7.41 which indicated the existence of the methyl group adjacent to the acyl group.

These nuclear magnetic resonance data, therefore, strongly suggest that N-aryloxyacylpyrazoles derived from I should be 1-aryloxyacyl-3-phenyl(or ethoxy)-5-methylpyrazoles (Table III).

TABLE III. Nuclear Magnetic Resonance Spectra of 1-Aryloxyacylpyrazoles



R_1	R_2	R_3	Xn	Chemical shift (τ) of the methyl group	
				τ	τ −7.41
C_6H_5	H	H	4-Cl	7.37	−0.04
〃	Cl	〃	〃	7.35	−0.06
〃	Br	〃	〃	7.37	−0.04
OC_2H_5	H	〃	〃	7.46	0.05
〃	Cl	〃	〃	7.45	0.04
〃	Br	〃	〃	7.45	0.04
C_6H_5	Cl	〃	2,4-di-Cl	7.37	−0.04
〃	Br	〃	〃	7.34	−0.07
OC_2H_5	H	〃	〃	7.47	0.06
〃	Cl	〃	〃	7.44	0.03
〃	Br	〃	〃	7.45	0.04
C_6H_5	H	CH_3	〃	7.37	−0.04
〃	Cl	〃	〃	7.36	−0.05
〃	Br	〃	〃	7.33	−0.08
OC_2H_5	H	〃	〃	7.45	0.04
〃	Cl	〃	〃	7.46	0.05
〃	Br	〃	〃	7.45	0.04
C_6H_5	H	H	2-CH_3-4-Cl	7.38	−0.03
〃	Cl	〃	〃	7.40	−0.01
〃	Br	〃	〃	7.40	−0.01
OC_2H_5	H	〃	〃	7.48	0.07
〃	Cl	〃	〃	7.47	0.06
〃	Br	〃	〃	7.47	0.06
C_6H_5	H	〃	2,4,5-tri-Cl	7.37	−0.04
OC_2H_5	〃	〃	〃	7.48	0.07
〃	Cl	〃	〃	7.46	0.05
〃	Br	〃	〃	7.43	0.02

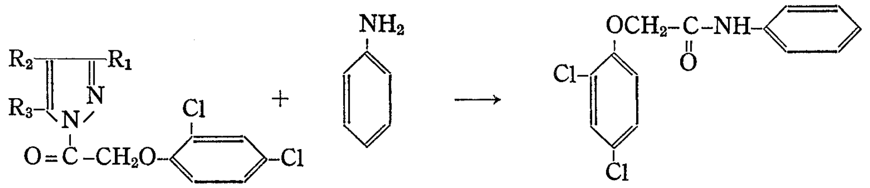
Reaction of 1-Aryloxyacylpyrazoles

In the infrared absorption spectra, stretching vibration bands of the carbonyl group of the azolides appear at the region of relatively higher frequencies (1730~1780 cm^{-1}) owing to increase of the bond order of the carbonyl group.[5] Higher chemical reactivity of the carbonyl group of the azolide has been correlated with higher frequency band of the compound.[5]

The carbonyl band of 1-aryloxyacylpyrazoles occurred at the region of 1720~1770 cm^{-1}, therefore, a high chemical reactivity of the compounds was expected. This was substantiated by the reactions described below. Firstly, 1-(2,4-dichlorophenoxyacetyl)-pyrazoles were allowed to react with aniline in benzene solution at 50° for 2 hr.

The reaction proceeded smoothly and 2-(2,4-dichlorophenoxy)acetanilide was obtained in good yields as shown in Table IV.

Table IV. Infrared Absorption Spectra of 1-(2,4-Dichlorophenoxyacetyl)-pyrazoles and Yield of 2-(2,4-Dichlorophenoxy)acetanilide



R_1	R_2	R_3	ν_{max} C=O cm^{-1} (KBr)	Yield (%)
CH_3	H	CH_3	1740	74
〃	NO_2	〃	1770	87
〃	Cl	〃	1730	84
〃	Br	〃	1730	85
C_6H_5	H	〃	1734	94
〃	Cl	〃	1727	86
〃	Br	〃	1724	83
OC_2H_5	H	〃	1721	89
〃	Cl	〃	1730	81
〃	Br	〃	1733	89

Secondly, the reactions with alcohols and phenol were undertaken. Staab[5] pointed out that the reaction of azolide with alcohols proceeded less smoothly than with amines, but the addition of a catalytic amount of a base enhanced the reactivity.

In our hands the refluxing of an ethanol solution of 1-(2,4-dichlorophenoxyacetyl)-3,5-dimethylpyrazole (XI) for 4 hr. caused no alcoholysis of the material. However, it was found that ethanol, benzyl alcohol and phenol went into smooth reaction with XI in the presence of 0.25 mole equivalent of the sodium alcoholate or phenolate to yield the corresponding esters of (2,4-dichlorophenoxy)acetic acid in yields of 74, 77 and 88%, respectively. Similar results were also obtained when the amount of sodium alcoholate or phenolate was increased to one mole equivalent.

When the reaction was run in tetrahydrofuran using one mole of sodium alcoholate or phenolate, an unexpected result was obtained. With sodium ethylate and benzylate, there were obtained substances which were almost insoluble in water or in usual organic solvent and decomposed after melting at 217° and 220°, respectively. Contrary to this, phenolate gave neither an ester nor a substance of high melting point. From elemental analyses and infrared absorption spectra, the compounds obtained were assigned to the structure (XII). Structure (XIII) was accordingly assigned to the substances which resulted by treatment of XII with hot mixture of dilute hydrochloric acid and acetone. (Chart 1).

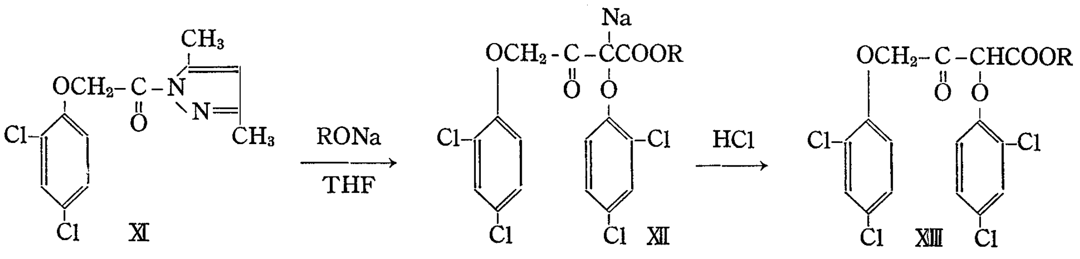


Chart 1.

These conclusions received support from the comparison of infrared absorption spectra and melting points with the samples obtained by base catalyzed selfcondensation[12)] of (2,4-dichlorophenoxy)acetic acid esters.

The mechanism of the formation of esters of 2,4-bis(2,4-dichlorophenoxy)acetoacetic acid (XIII) in tetrahydrofuran can be explained by either a C-acylation reaction[*6] of the azolide or a selfcondensantion reaction.

In case the C-acylation of the azolide is operative, the reaction would then be explicable by the sequence (1)→(2)→(3). (Chart 2).

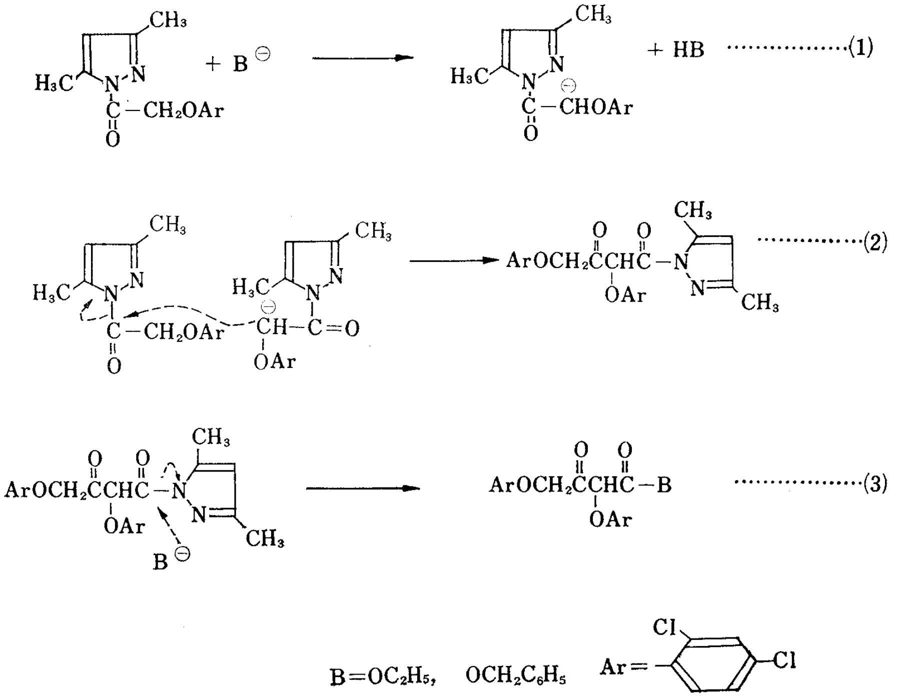


Chart 2.

This, however, looks to be ruled out because there exists no reason for predominance of the C-acylation due to steric hindrance. The evidence is provided by the fact that when the reaction was carried out in HB the corresponding ester was obtained in good yield as mentioned above.

Alternative mechanism of selfcondensation can be formulated by the sequence (4)→(5)→(6). (Chart 3).

This involves an ester formation followed by selfcondensation catalyzed by sodium

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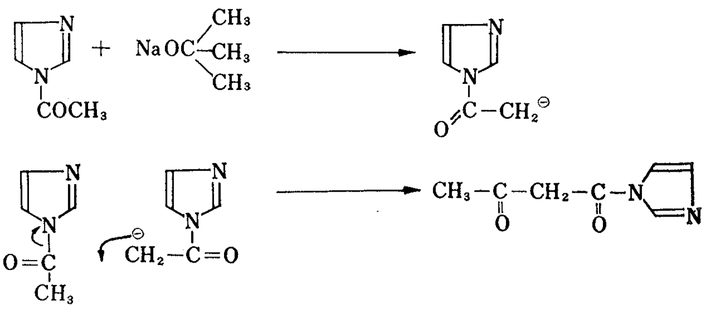
[*6] A C-acylation reaction of azolide has been observed only in the case where the usual O-acylation is hindered sterically, to which the mechanism of the Claisen condensation was given.[5)]



12) J.H. Petersen: Acta Chem. Scand., **5**, 519 (1951); J.M. Petersen, C.R. Hauser: J. Am. Chem. Soc., **71**, 770 (1949); G.W.K. Cavill, D.L. Ford: J. Chem. Soc., **1954**, 1388.

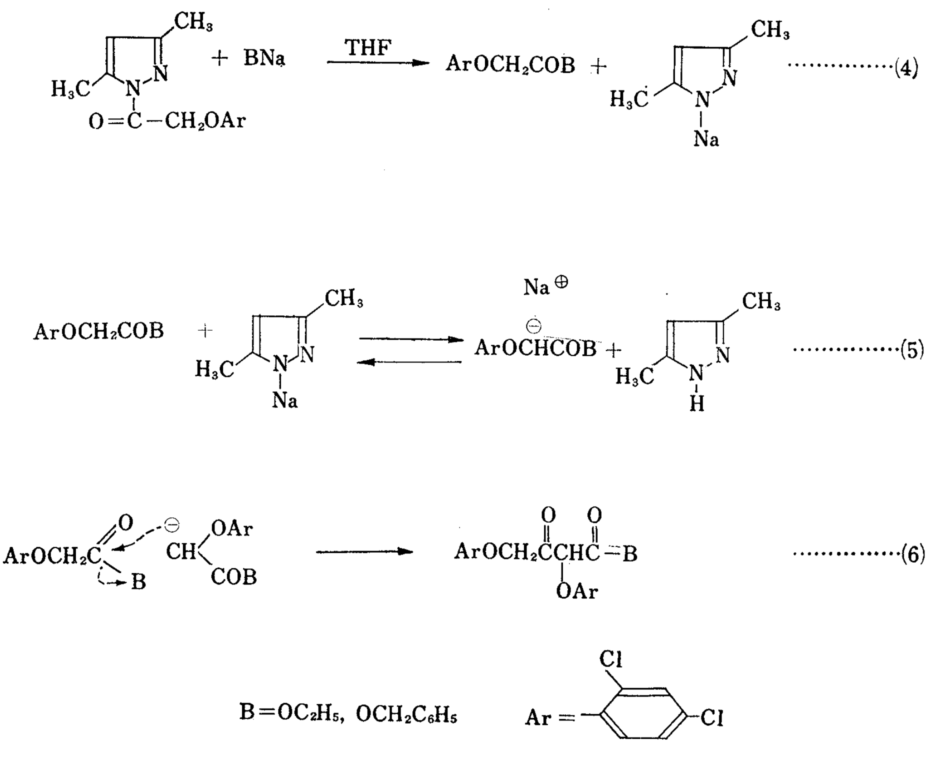


Chart 3.

salt of 3,5-dimethylpyrazole formed. This receives support by the fact that reaction of ethyl (2,4-dichlorophenoxy)acetate with sodium salt of 3,5-dimethylpyrazole, prepared from equimolar sodium and 3,5-dimethylpyrazole, in tetrahydrofuran afforded XII ($R=C_2H_5$) in good yield.

Experimental[7]

3(5)-Methyl-4-chloro-5(3)-ethoxypyrazole——To a solution of 5 g. of 3(5)-methyl-5(3)-ethoxypyrazole in 30 ml. of ether was added dropwise with stirring 6 g. of sulfuryl chloride over a period of 15 min. at 5~7°. After being stirred for 30 min. at room temperature, the separated solid was collected by suction and dissolved in 100 ml. of H_2O. From the aqueous solution separated an oily substance which solidified on cooling and was recrystallized from *n*-hexane to give colorless prisms, m.p. 107~109°; yield, 4 g. *Anal.* Calcd. for $C_6H_9ON_2Cl$: C, 44.88; H, 5.65; N, 17.44. Found : C, 44.81; H, 5.52; N, 17.41.

3(5)-Methyl-4-bromo-5(3)-ethoxypyrazole——To a solution of 5 g. of 3(5)-methyl-5(3)-ethoxypyrazole in 30 ml. of glacial acetic acid was added 6.4 g. of bromine at room temperature. After being stirred for 30 min. the separated solid was collected by suction and dissolved in 100 ml. of H_2O. The separated solid was recrystallized from aq. MeOH to give colorless prisms, m.p. 112°; yield, 6 g. *Anal.* Calcd. for $C_6H_9ON_2Br$: C, 35.15; H, 4.43; N, 13.67. Found : C, 35.12; H, 4.54; N, 13.34.

1-(2,4-Dichlorophenoxyacetyl)-3,5-dimethylpyrazole——a) To a solution of 1.5 g. of 3,5-dimethylpyrazole in 5 ml. of pyridine was added with stirring 3 g. of (2,4-dichlorophenoxy)acetyl chloride at room temperature. After being stirred for 1 hr. 40 ml. of H_2O was added to the reaction mixture and the separated solid was recrystallized from acetone to give colorless needles, m.p. 134~136°; yield, 3 g. Analytical data are shown in Table I.

b) The mixture of 2 g. of 3,5-dimethylpyrazole and 4.8 g. of (2,4-dichlorophenoxy)acetyl chloride was heated at 120° for several hours. After cooling, 100 ml. of H_2O was added to this mixture and the separated solid was purified as described above, colorless needles, m.p. 134~136°; yield, 4.3 g.

c) To a suspension of 2 g. of (2,4-dichlorophenoxy)acetic acid hydrazide in 30 ml. of EtOH were added 0.85 g. of acetylacetone and 0.2 ml. of 10% aq. HCl. The mixture was refluxed for 1 hr. After cooling, the separated solid was recrystallized from acetone to give colorless needles, m.p. 134~136°; yield, 2.3 g.

d) To a solution of 15.5 g. of (2,4-dichlorophenoxy)acetic acid and 7.1 g. of triethylamine in 60 ml. of

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[7] All melting points are uncorrected.

benzene was added dropwise 7.7 g. of ethyl chloroformate over a period of 15 min. at 8~10°. After being stirred for 5 min., a solution of 8.1 g. of 3,5-dimethylpyrazole in 60 ml. of benzene was added over a period of 30 min. at 10° to this reaction mixture. The whole mixture was stirred for 1 hr. and washed with 5% aq. $NaHCO_3$, 10% aq. HCl and H_2O, respectively. The solid which was obtained from the dried benzene layer was purified as described above, colorless needles, m.p. 134~136°; yield, 2.5 g.

Other 1-aryloxyacylpyrazoles shown in Table I were prepared in a similar way.

Reaction of 1-Aryloxyacylpyrazoles with Aniline——Typical run was shown with 1-(2,4-dichlorophenoxyacetyl)-3,5-dimethylpyrazole. 0.5 g. of aniline and 1.5 g. of 1-(2,4-dichlorophenoxyacetyl)-3,5-dimethylpyrazole were warmed at 50° for 2 hr. in absolute benzene. The reaction mixture was condensed under reduced pressure at room temperature and the residue was treated with 10 ml. of 10% aq. HCl. The separated solid was collected and heated in 5% aq. NaOH in boiling water bath. After cooling, undissolved solid was collected and washed with 10% aq. HCl, then with H_2O, and recrystallized from EtOH to give 2-(2,4-dichlorophenoxy)acetanilide as colorless needles, m.p. 110°; yield, 1.1 g. *Anal.* Calcd. for $C_{14}H_{11}O_2NCl_2$: C, 56.77; H, 3.75; N, 4.73. Found: C, 56.83; H, 3.56; N, 4.49.

Reaction of 1-(2,4-Dichlorophenoxyacetyl)-3,5-dimethylpyrazole with Alcohols and Phenol——a) Reaction with boiling ethanol. 3 g. of 1-(2,4-dichlorophenoxyacetyl)-3,5-dimethylpyrazole was refluxed with 30 ml. of EtOH for 4 hr. After cooling, the separated solid was collected (2.9 g), m.p. 134~136°. This was confirmed to be identical with starting material by the mixed melting point determination and comparison of infrared absorption spectrum.

b) Reaction with ethanol in the presence of sodium ethylate. To a solution of 0.1 g. of sodium in 20 ml. of EtOH was added 5 g. of 1-(2,4-dichlorophenoxyacetyl)-3,5-dimethylpyrazole. The mixture was kept standing at room temperature for 30 min. The solvent was removed under reduced pressure and to the residue was added 100 ml. of H_2O and the separated oil was extracted with ether. From the ether layer was obtained ethyl (2,4-dichlorophenoxy)acetate as colorless oil; yield, 3.2 g. (74%). The identity of the compound was confirmed by the comparison of the infrared absorption spectrum with authentic sample.

c) Reaction with benzyl alcohol in the presence of sodium benzylate. Above mentioned reaction was carried out in 20 ml. of benzyl alcohol containing 0.1 g. of sodium. Benzyl (2,4-dichlorophenoxy)acetate was obtained as colorless needles, m.p. 45~46°, in 77% yield. *Anal.* Calcd. for $C_{15}H_{12}O_3Cl_2$: C, 57.90; H, 3.89. Found: C, 57.53; H, 3.55.

d) Reaction with phenol in the presence of sodium phenolate. To a solution of 0.1 g. of sodium in 10 g. of phenol was added 5 g. of 1-(2,4-dichlorophenoxyacetyl)-3,5-dimethylpyrazole. After being stirred for 30 min. at room temperature, 100 ml. of benzene was added. The mixture was washed with 5% aq. NaOH, then with H_2O. The solid obtained from the dried benzene layer was recrystallized from EtOH to give phenyl (2,4-dichlorophenoxy)acetate as colorless needles, m.p. 100°; yield, 4.4 g. (88%). Infrared absorption spectrum confirmed the identity of the compound.

e) Reaction with sodium ethylate in tetrahydrofuran. To a solution of 0.4 g. of sodium and 0.8 g. of EtOH in 20 ml. of tetrahydrofuran was added 5 g. of 1-(2,4-dichlorophenoxyacetyl)-3,5-dimethylpyrazole. After being stirred for 30 min. at room temperature, the mixture was condensed under reduced pressure. To the residue was added 100 ml. of H_2O and the separated solid was collected and recrystallized from DMF to give the sodio-compound of ethyl 2,4-bis(2,4-dichlorophenoxy)acetoacetate as colorless powder, m.p. 217° (decomp.). *Anal.* Calcd. for $C_{18}H_{13}O_5Cl_4Na$: C, 54.60; H, 2.76; O, 16.88; Cl, 29.92. Found: C, 45.43; H, 2.73; O, 17.19; Cl, 29.17.

Acidification by adding 10% aq. HCl to a warm suspension of this sodio-compound afforded ethyl 2,4-bis(2,4-dichlorophenoxy)acetoacetate. Recrystallization from *n*-hexane gave colorless crystals, m.p. 97~98°; yield, 0.9 g. *Anal.* Calcd. for $C_{18}H_{14}O_5Cl_4$: C, 47.71; H, 3.12; Cl, 31.37. Found: C, 47.96; H, 3.12; Cl, 31.53. This and sodio-compound were confirmed to be identical with authentic samples[12] by the comparison of infrared absorption spectra.

f) Reaction with sodium benzylate in tetrahydrofuran. Above mentioned reaction was run in 20 ml. of tetrahydrofuran containing 0.4 g. of sodium and 2 g. of benzyl alcohol. The sodio-compound of benzyl 2,4-bis(2,4-dichlorophenoxy)acetoacetate was obtained as colorless crystals, m.p. 220° (decomp.). *Anal.* Calcd. for $C_{23}H_{15}O_5Cl_4Na$: C, 51.22; H, 2.83; O, 14.93; Cl, 26.45. Found: C, 51.57; H, 2.72; O, 15.07; Cl, 26.02. Benzyl 2,4-bis(2,4-dichlorophenoxy)acetoacetate as colorless needles, m.p. 122~123°, yield, 4 g. *Anal.* Calcd. for $C_{23}H_{16}O_5Cl_4$: C, 53.72; H, 3.13; O, 15.56. Found: C, 54.12; H, 3.13; O, 15.58.

These compounds were confirmed to be identical with the compounds described below by the comparison of infrared absorption spectra.

Benzyl 2,4-Bis(2,4-dichlorophenoxy)acetoacetate——To a solution of 2 g. of benzyl (2,4-dichlorophenoxy)-acetate in 20 ml. of ether was added 0.3 g. of sodium amide. The mixture was refluxed for about 1 hr. until the evolution of NH_3 was ceased. To this was added a solution of 2 g. of benzyl (2,4-dichlorophenoxy)-acetate in 50 ml. of ether and the mixture was refluxed for 4 hr. After cooling, the separated solid was collected (sodio-compound, m.p. 220°) and then suspended in warm acetone. Acidification with 10% aq. HCl gave a substance which afforded colorless needles after recrystallization from EtOH, m.p. 122~123°; yield, 2 g. (60%). *Anal.* Calcd. for $C_{23}H_{16}O_5Cl_4$: C, 53.72; H, 3.13; Cl, 27.58. Found: C, 53.90; H, 3.14; Cl, 27.31.

Ethyl 2,4-Bis(2,4-dichlorophenoxy)acetoacetate——To a solution of 2 g. of 3,5-dimethylpyrazole and 0.4 g. of sodium in 20 ml. of tetrahydrofuran was added 5.6 g. of ethyl (2,4-dichlorophenoxy)acetate. After being stirred for 30 min. at room temperature, 300 ml. of H_2O was added to the mixture and the separated solid was collected (sodio-compound, m.p. 217°) and then suspended in warm acetone. Acidification with 10% aq. HCl and recrystallization from *n*-hexane gave colorless crystals, m.p. 97~98°; yield, 3.8 g.

(2-Hydroxymethyl-4-chlorophenoxy)acetic Acid Hydrazide——A mixture of 4.9 g. of ethyl 2-hydroxymethyl-4-dichlorophenoxy)acetate and 1.5 g. of hydrazine hydrate (80%) was refluxed in 20 ml. of EtOH for 2 hr. After cooling, the separated solid was collected and recrystallized from DMF-H_2O to give colorless needles, m.p. 151.5°; yield, 4 g. (87%). *Anal.* Calcd. for $C_9H_{11}O_3N_2Cl$: C, 46.86; H, 4.81; N, 12.15. Found : C, 46.87; H, 4.79; N, 11.95.

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Summary

In view of recently reported chemical reactivities of the azolides, a number of 1-aryloxyacylpyrazoles were synthesized for their evaluation as plant growth regulator.

The structure of 1-aryloxyacylpyrazoles derived from unsymmetrical pyrazoles was discussed on the basis of nuclear magnetic resonance data.

Some reactions of 1-aryloxyacylpyrazoles were also described.

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91. Kōtaro Takahashi and Toshie Nakagawa : Studies on Constituents of Medicinal Plants. VIII.*1 The Stereochemistry of Paulownin and Isopaulownin.

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Paulownin,1) $C_{20}H_{18}O_7$, m.p. 105~106°, $[\alpha]_D=29.0$, a new lignan, isolated together with *d*-sesamin, from the wood of *Paulownia tomentosa* (kiri) has been established as 1,4-bis(3,4-methylenedioxyphenyl)-tetrahydro-1*H*,3*H*-furo[3,4-*c*]furan-3*a*-ol. The present paper deals with certain nuclear magnetic resonance (NMR) evidence for the assignment of the stereochemistry of *d*-sesamin (Ia) and *d*-asarinin (Ib), and with the stereochemistry of paulownin (IIa) and isopaulownin (IIb), m.p. 132°, $[\alpha]_D=127.0°$, the latter of which was derived from paulownin. Paulownin was refluxed with 20% formic acid or 5% ethanol-hydrochloric acid to give isopaulownin, $C_{20}H_{18}O_7$, which gave a monoacetate $C_{22}H_{20}O_8$, m.p. 105°, $[\alpha]_D=83.1°$. The ultraviolet spectrum of IIb is superimposable with that of IIa.

The NMR spectra of *d*-sesamin and *d*-asarinin has been reported by Jones, *et al.*2)

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*1 A part of this study was presented at the XXVth International Congress of the Pharmaceutical Sciences (F. I. P.), Prague, August 25, 1965. Part VII : Yakugaku Zasshi, **86**, 441 (1966).

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