Notes

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Studies on Herbicides and Plant Growth Regulators. I. Synthesis and Herbicidal Activity of 6-Phenyl-2,4-dinitrophenol Derivatives.[*1]

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2,4-Dinitro-*o*-cresol,[1] 6-*sec*-butyl-2,4-dinitrophenol[2] and their derivatives[3] are well known herbicides. 6-Cyclohexyl-2,4-dinitrophenol was disclosed as a herbicide in some patents,[4] but few investigations have been reported about the structurally related compound, 6-phenyl-2,4-dinitrophenol (I)[*3] and its derivatives, on the evaluation as herbicides. These situations led the author to prepare the derivatives of 6-phenyl-2,4-dinitrophenol (I) for possible herbicides.

Synthesis of 6-Phenyl-2,4-dinitrophenol Derivatives

6-Phenyl-2,4-dinitrophenol (I) was prepared by the method of Borsche[5] or by adding 2-phenylphenol to warm nitric acid. Various derivatives of this compound were synthesized, involving the acetyl-,[6] propionyl-,[7] and benzoyl[8] derivatives, which had been prepared for other purposes.

As initial efforts to obtain 6-phenyl-2,4-dinitrophenyl acetate (II, $R=CH_3$) by the action of acetyl chloride on an aqueous solution of the sodium salt of I or on I in pyridine were proved to be unsuccessful, 6-phenyl-2,4-dinitrophenyl alkanoates (II, $R=CH_3$, C_2H_5, C_3H_7, C_4H_9) were prepared from I by the action of corresponding acid anhydrides. Ethyl 6-phenyl-2,4-dinitrophenyl carbonate (III) was obtained by the reaction of I with ethyl chloroformate in aqueous acetone in the presence of sodium hydroxide, but phosgene and thiophosgene did not give the carbonates (IV, X=O, S) in this reaction condition. Bis(6-phenyl-2,4-dinitrophenyl)carbonate and thiocarbonate (IV, X=O, S) were successfully prepared from I by conversion to the sodium salt (V), followed by the action of phosgene and thiophosgene respectively in acetone. Equimolar action of phosgene on the sodium salt (V) gave 6-phenyl-2,4-dinitrophenyl chloroformate (VI). Treatment of VI with methyl alcohol, 2,4-dichlorophenol and 3,4-dichloroaniline afforded corresponding carbonates (VII) and carbamate (VIII).

Also Esters (IX) of 6-phenyl-2,4-dinitrophenol with the acids available as hormone-like herbicides, such as (2,4-dichlorophenoxy)- and (2-methyl-4-chlorophenoxy)-acetic

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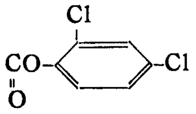
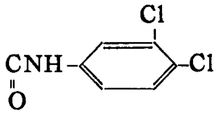
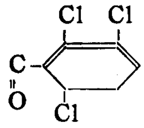
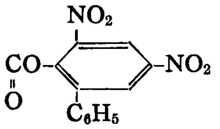
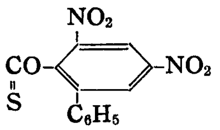
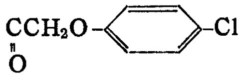
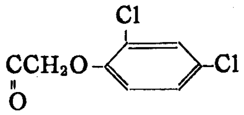
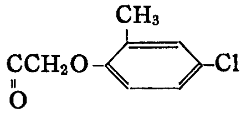
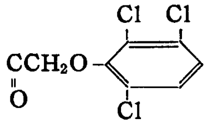
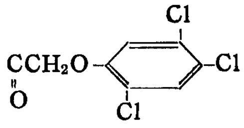
[*1] This paper was presented at the Kinki Branch Meeting of Pharmaceutical Society of Japan, Kyoto, March, 1964.

[*2] Juso-nishino-cho, Higashiyodogawa-ku, Osaka (落合道彦).

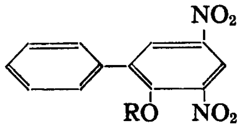
[*3] Dinitrophenol having aromatic substituent had been referred to in the literature[2] without detailed description.

1) G. Truffaut, I. Pastac : Brit. Pat., 425,295.
2) A.S. Craft : Science, **101**, 417 (1945).
3) K. Reichner, H. Habicht, K. Härtel, L. Emmel : Angew. Chem., **74**, 994 (1962); Hoechst : Ger. Pat., 1,088,757, 1,103,072; Belg. Pat., 596,057. etc.
4) C.M. Keyworth : Brit. Pat., 573,241; Dow : Japan. Pat., 899 (1956).
5) W. Borsche : Ann., **312**, 211 (1900).
6) G.T. Bottger, A.P. Yerington, S.I. Gertler : U.S. Bur. Entomol. and Plant Quarantine E-859, 31 (1953); C.A., **47**, 7724 (1953).
7) G.T. Bottger, A.P. Yerington, S.I. Gertler : U.S. Dept. Agr., Bur. Entomol. Plant Quarantine E-862, 31 (1953); C.A., **48**, 936 (1954).
8) V.J. Mikeska, M.T. Bogert : J. Am. Chem. Soc., **57**, 2121 (1935).

Table I. 6-Phenyl-2,4-dinitrophenol

R	m.p. (°C)	Yield (%)	Recrystallization solvent	Appearance
$COCH_3$	134～134.5	87	Me_2CO-MeOH	colorless crystals
COC_2H_5	123～124.5	85	〃	〃
COC_3H_7	89～90	83	〃	yellow crystals
COC_4H_9	70～71	83	〃	〃
$COOCH_3$	126～127.5	85	MeOH	yellowish crystals
$COOC_2H_5$	112～113	75	〃	yellow prisms
	95～96	72	ligroin	colorless crystals
	195～197	72	Me_2CO	yellow crystals
	139	80	benzene-ligroin	colorless cryst.
	187～200	72	DMF-H_2O	yellowish crystals
	141	75	Me_2CO	yellow crystals
	90～91.5	82	benzene-ligroin	colorless prisms
	117～119	85	Me_2CO-EtOH	yellowish crystals
	105～107	80	benzene-ligroin	colorless prisms
	141～142	81	〃	〃
	99～101	75	〃	〃

Derivatives



Formula	Analysis					
	Calcd.			Found		
	C	H	N	C	H	N
$C_{14}H_{10}O_6N_2$	55.63	3.34	9.27	55.81	3.27	9.14
$C_{15}H_{12}O_6N_2$	56.96	3.82	8.86	56.78	3.85	8.92
$C_{16}H_{14}O_6N_2$	58.18	4.27	8.48	58.34	4.25	8.52
$C_{17}H_{16}O_6N_2$	59.30	4.68	8.14	59.67	4.95	7.70
$C_{14}H_{10}O_7N_2$	52.83	3.17	8.80	52.78	3.41	8.79
$C_{15}H_{12}O_7N_2$	54.22	3.64	8.43	54.25	3.92	8.73
$C_{19}H_{10}O_7N_2Cl_2$	50.75	2.24	6.23	50.95	2.38	5.98
$C_{19}H_{11}O_6N_3Cl_2$	50.91	2.47	9.37	50.79	2.92	9.54
$C_{19}H_9O_6N_2Cl_3$	—	—	5.59	—	—	6.06
$C_{25}H_{14}O_{11}N_4$	54.96	2.58	10.25	55.05	2.99	10.02
$C_{25}H_{14}O_{10}N_4S$	—	—	9.96	—	—	9.57
$C_{20}H_{13}O_7N_2Cl$	56.03	3.05	6.53	56.05	3.13	6.45
$C_{20}H_{12}O_7N_2Cl_2$	51.85	2.61	6.04	51.93	2.63	5.99
$C_{21}H_{15}O_7N_2Cl$	56.95	3.64	—	57.14	3.49	—
$C_{20}H_{11}O_7N_2Cl_3$	48.27	2.20	5.63	48.47	2.60	5.50
〃	48.27	2.20	5.63	48.42	2.50	5.81

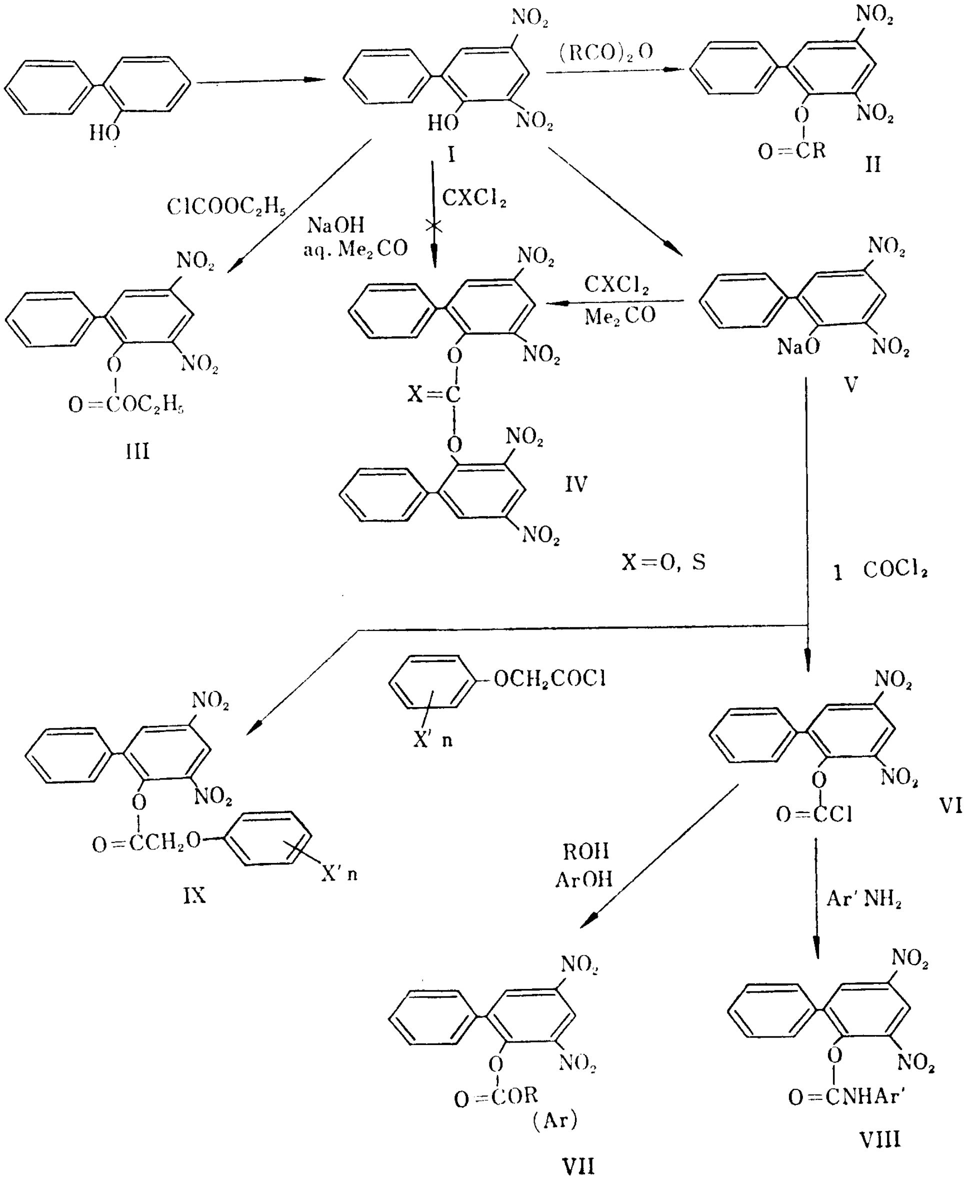


Chart 1.

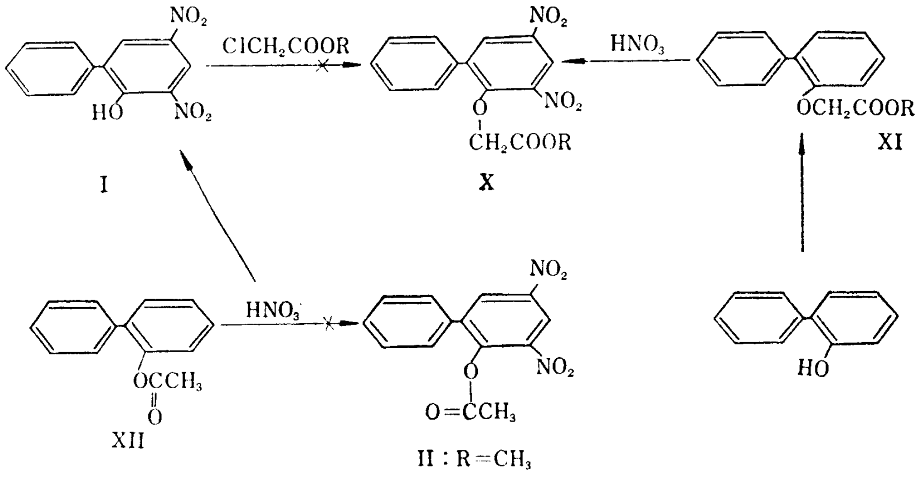


Chart 2.

acids, were obtained by the action of the acid chlorides on the sodium salt (V).

6-Phenyl-2,4-dinitrophenol derivatives thus obtained were listed in Table I.

Several salts of 6-phenyl-2,4-dinitrophenol were also prepared. Attempts to obtain a phenoxyacetic acid-type compound (X) of 6-phenyl-2,4-dinitrophenol were made by acting chloroacetic acid and its ethyl ester on I and V, or by nitrating 2-phenylphenoxy acetic acid and its ethyl ester (XI) in several conditions.

The former trial resulted in the recovery of I and the latter gave compounds, which were not in agreement with X in elemental analysis. Alternative attempt to obtain 6-phenyl-2,4-dinitrophenyl acetate (II, R$=CH_3$) by nitrating 2-phenylphenyl acetate (XII) in glacial acetic acid resulted in the formation of 6-phenyl-2,4-dinitrophenol (I) unexpectedly. Treatment of I or V with chlorosulfonic acid also did not afford 6-phenyl-2,4-dinitrophenylsulfuric acid.

Herbicidal Activity

Herbicidal activity of 6-phenyl-2,4-dinitrophenol and its derivatives was evaluated by the following methods.

(1) Growth inhibition test of young plant (Petri-dish test).

(2) Growth inhibition and withering test by foliar application at post-emergence (Pot test).

(3) Growth inhibition and withering test by soil treatment at pre-emergence (Pot test).

The results are summarized in Table II, III and IV respectively.

Table II shows that 6-phenyl-2,4-dinitrophenol and its salts have highly growth-inhibitory activity against *Oryza sativa* L., *Panicum crusgalli* L. and *Cucumis sativus* L. Although simple esters of I such as alkanoates and benzoate were almost ineffective, the phenoxyacetates (IX) showed excellent activity.

Table III shows that almost all the compounds have high activity, among which, 6-phenyl-2,4-dinitrophenyl (2-methyl-4-chlorophenoxy)acetate was most effective, thus indicating a possibility of these compounds as post-emergent herbicides. And also some selectivity in the post-emergent herbicidal activity is expected from the data shown in Table III (dicotyledonous or broadleaf plants were more susceptible to these compounds than monocotyledonous plant).

Table IV shows that 6-phenyl-2,4-dinitrophenol (I), its salts and simple esters such as alkanoates and benzoate are almost ineffective, and so their practical use as pre-emergent herbicide may not be promising. Contrary to these, phenoxyacetates of I showed excellent activity also in this test.

Experimental[*4]

6-Phenyl-2,4-dinitrophenol (I)——This compound was produced quantitatively by the method of Borsche[5)] or by adding dropwise 8.6 g. of 2-phenylphenol to 30 ml. of warm (60~70°) HNO_3 ($d=1.38$) over a period of 30 min. and stirring the mixture for 30 min. Yellow prisms (from aq. Me_2CO) m.p. 204°; Yield, 11.5 g.

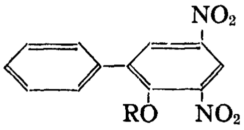
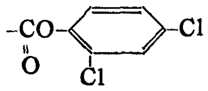
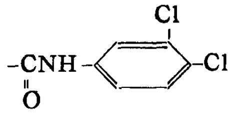
6-Phenyl-2,4-dinitrophenyl Chloroformate (VI)——To a solution of 5 g. of sodium 6-phenyl-2,4-dinitrophenolate in 40 ml. of Me_2CO, 23.5 g. of 9% solution of phosgene in toluene was added over a period of 15 min. at 10~12°. After being stirred for 15 min. (12~10°), the separated solid was filtered off and the filtrate was condensed under reduced pressure. The residue which solidified on cooling was recrystallized from benzene-ligroin to yield colorless crystals, m.p. 104~105°; Yield, 2.5 g. *Anal.* Calcd. for $C_{13}H_7O_6N_2Cl$: C, 48.39; H, 2.18; N, 8.68. Found: C, 48.63; H, 2.33; N, 8.69.

Methyl 6-Phenyl-2,4-dinitrophenyl Carbonate (VII, R$=CH_3$)——6-Phenyl-2,4-dinitrophenyl chloroformate (120 mg.) was refluxed for 30 min. witn MeOH (3 ml.). After cooling, 10 ml. of H_2O was added to the mixture and the separated solid was recrystallized from aq. MeOH to yield yellowish crystals; Yield, 100 mg. Analytical data are listed in Table I.

[*4] All melting points are uncorrected.

TABLE II. Growth Inhibition of Young Plants

$$\text{Inhibition Rate} = \left(1 - \frac{\text{Root Length of Treated Seed}}{\text{Root Length of Untreated Seed}}\right) \times 100 (\%)$$

Compound  R =	Plant Conc. (p.p.m.)	Rice (*Oryza sativa* L.)	Cocks Foot (*Panicum crusgalli* L.)	Cucumber (*Cucumis sativus* L.)
H	1	22	54	5
	10	73	65	31
	100	100	100	100
Na salt	1	19	0	0
	10	86	86	27
	100	100	100	100
NH_4 salt	1	0	54	0
	10	79	73	32
	100	100	100	98
Ca salt	1	44	38	0
	10	76	66	35
	100	100	100	100
$(CH_3)_2NH_2$ salt	1	0	36	0
	10	72	85	40
	100	100	100	100
$(HOCH_2CH_2)_2NH_2$ salt	1	6	45	0
	10	40	74	6
	100	100	100	100
 $-NH_3$ salt	1	3	57	0
	10	52	77	23
	100	100	100	100
$-COCH_3$	1	16	8	0
	10	11	0	0
	100	52	36	0
$-COC_2H_5$	1	18	6	0
	10	15	17	42
	100	72	25	46
$-COC_3H_7$	1	16	25	0
	10	19	0	0
	100	70	68	24
$-COC_4H_9$	1	25	11	0
	10	64	0	0
	100	100	100	50
$-COOCH_3$	1	13	0	0
	10	31	0	0
	100	81	87	54
$-COOC_2H_5$	1	20	0	17
	10	64	97	36
	100	100	86	82
	1	0	0	0
	10	74	10	28
	100	94	31	81
	1	6	0	14
	10	57	66	42
	100	99	99	85

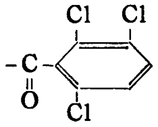
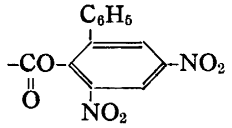
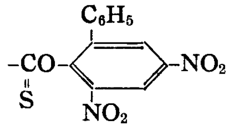
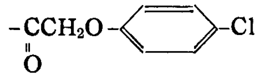
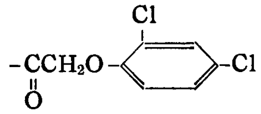
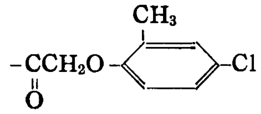
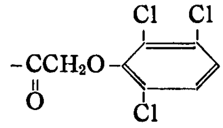
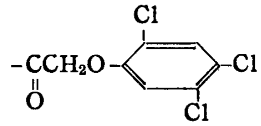
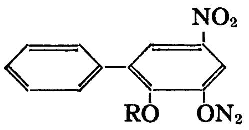
$-COC_6H_5$	1 10 100	0 9 58	0 0 40	0 0 0
	1 10 100	0 23 100	10 7 100	0 26 82
	1 10 100	11 76 100	69 68 95	0 24 83
	1 10 100	22 25 66	0 8 74	−1 0 12
	1 10 100	51 85 100	52 75 100	71 90 100
	1 10 100	78 96 100	31 85 100	62 86 96
	1 10 100	94 100 100	84 100 100	80 90 100
	1 10 100	53 94 100	0 66 100	45 78 78
	1 10 100	30 10 55	4 28 82	0 16 23

Table III. Growth Inhibition and Withering by Foliar Application at Post-emergence

$$\text{I : Inhibition Rate} = \left(1 - \frac{\text{Fresh Weight of Treated Plant}}{\text{Fresh Weight of Untreated Plant}}\right) \times 100\,(\%)$$

$$\text{W : Withering Rate} = \frac{\text{Number of Completely Withered Plant}}{\text{Number of Treated Plant}} \times 100\,(\%)$$

Compound  R =	Plant / Conc. (%)	Rice (*Oryza sativa* L.) W	Rice (*Oryza sativa* L.) I	Soy Bean (*Glycine max* M.) W	Soy Bean (*Glycine max* M.) I	Tomato (*Lycopersicon esculentum* M.) W	Tomato (*Lycopersicon esculentum* M.) I
H	0.5 2	0 50	28 82	35 100	71 100	100 100	100 100

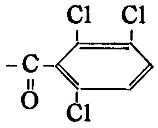
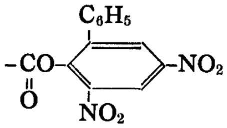
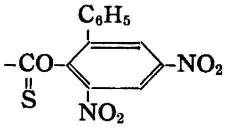
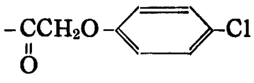
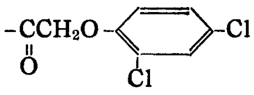
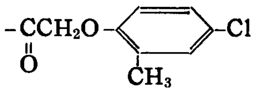
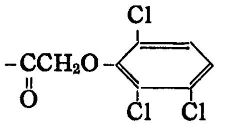
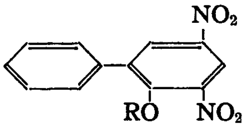
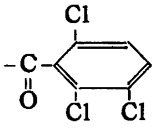
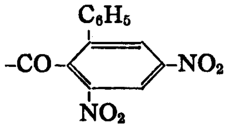
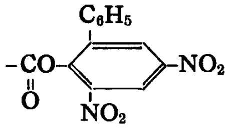
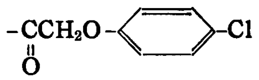
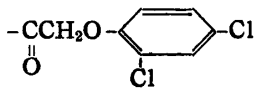
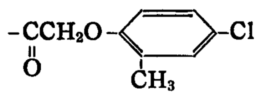
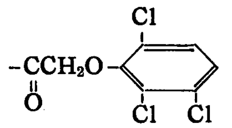
Na salt	0.5	25	50	60	81	100	100
	2	100	100	100	100	100	100
NH_4 salt	0.5	25	50	100	100	100	100
	2	50	50	100	100	100	100
Ca salt	0.5	0	0	0	18	15	66
	2	25	0	100	100	100	100
$(CH_3)_2NH_2$ salt	0.5	25	50	50	59	100	100
	2	100	100	100	100	100	100
$(HOCH_2CH_2)_2NH_2$ salt	0.5	0	50	100	100	100	100
	5	50	50	100	100	100	100
$-COCH_3$	0.5	0	−9	40	29	65	99
	2	0	32	15	23	100	100
$-COC_2H_5$	0.5	—	—	—	—	—	—
	2	0	29	0	21	0	40
$-COC_3H_7$	0.5	—	—	—	—	—	—
	2	60	78	0	42	100	100
$-COC_4H_9$	0.5	—	—	—	—	—	—
	2	0	10	0	42	100	100
$-COOC_2H_5$	0.5	5	6	0	9	100	100
	2	100	100	100	100	100	100
$-COC_6H_5$	0.5	0	10	15	34	100	100
	2	0	5	0	15	100	100
	0.5	0	17	0	0	100	100
	2	0	29	85	84	100	100
	0.5	0	28	35	36	100	100
	2	35	69	50	72	100	100
	0.5	—	—	—	—	—	—
	2	10	37	65	81	100	100
	0.5	0	28	0	6	100	100
	2	60	92	100	100	100	100
	0.5	15	35	0	56	100	100
	2	15	42	85	84	100	100
	0.5	40	70	100	100	100	100
	2	100	100	100	100	100	100
	0.5	0	0	35	42	55	73
	2	55	70	100	100	100	100

Table IV. Growth Inhibition and Withering by Soil Treatment at Pre-emergence

$$\text{I : Inhibition Rate} = \left(1 - \frac{\text{Fresh Weight of Treated Plant}}{\text{Fresh Weight of Control Plant}}\right) \times 100 (\%)$$

$$\text{W : Withering Rate} = \frac{\text{Number of Completely Withered Plant}}{\text{Number of Control Plant}} \times 100 (\%)$$

Compound 	Plant	Rice (*Oryza sativa.* L.)		Soy Bean (*Glycine max* M.)		Tomato (*Lycopersicon esculentum* M.)	
R =	Conc. (%)	W	I	W	I	W	I
H	0.5	40	33	0	0	50	65
	2	30	55	15	0	65	81
Na salt	0.5	15	0	50	70	35	9
	2	55	44	50	47	55	48
$-COCH_3$	0.5	5	0	35	47	15	18
	2	30	0	65	65	2	2
$-COC_2H_5$	0.5	—	—	—	—	—	—
	2	5	0	—	—	5	2
$-COC_3H_7$	0.5	—	—	—	—	—	—
	2	5	0	0	0	35	16
$-COC_4H_9$	0.5	—	—	—	—	—	—
	2	70	77	0	−4	50	67
$-COC_6H_5$	0.5	30	16	0	0	50	41
	2	45	44	0	7	30	32
	0.5	40	37	90	91	65	50
	2	95	75	90	93	100	100
	0.5	15	0	0	−5	15	18
	2	25	0	65	64	30	28
	0.5	—	—	—	—	—	—
	2	60	55	0	0	0	−2
	0.5	20	50	50	96	40	33
	2	100	100	100	100	100	100
	0.5	40	60	100	100	90	93
	2	100	100	60	84	100	100
	0.5	100	100	100	100	100	100
	2	100	100	100	100	100	100
	0.5	100	100	90	62	100	100
	2	100	100	100	100	100	100

Ethyl 6-Phenyl-2,4-dinitrophenyl Carbonate (III)——To a solution of 0.4 g. of NaOH and 2.4 g. of 6-phenyl-2,4-dinitrophenol in a mixture of 10 ml. of Me_2CO and 30 ml. of H_2O was added dropwise, with stirring, 2 g. of ethyl chloroformate over a period of 5 min. at $15\sim19°$. After being stirring for 30 min. $(19\sim15°)$, the separated solid was collected and recrystallized from MeOH (Table I).

2,4-Dichlorophenyl 6-Phenyl-2,4-dinitrophenyl Carbonate (VII, Ar=2,4-dichlorophenyl)——To a solution of 0.1 g. of NaOH and 0.3 g. of 2,4-dichlorophenol in 15 ml. of H_2O was added a solution of 0.3 g of 6-phenyl-2,4-dinitrophenyl chloroformate in 10 ml. of Me_2CO at $20\sim21°$. After being stirred for 30 min., 30 ml. of H_2O was added to the mixture and the separated solid was recrystallized from ligroin (Table I).

6-Phenyl-2,4-dinitrophenyl (3,4-dichlorophenyl)carbamate (VIII, Ar'=3,4-dichlorophenyl)——To 0.2 g. of 3,4-dichloroaniline in 4 ml. of Me_2CO was added 0.1 g. of 6-phenyl-2,4-dinitrophenyl chloroformate and the mixture was stirred for 1 hr. Then 4 ml. of H_2O was added to the mixture and the separated solid was recrystallized from Me_2CO (Table I).

Other Esters of 6-Phenyl-2,4-dinitrophenol

Typical runs are described.

6-Phenyl-2,4-dinitrophenyl Acetate (II, R=CH_3)——A mixture of 4 g. of 6-phenyl-2,4-dinitrophenol (I) and 40 ml. of Ac_2O was refluxed for 2 hr., during which I dissolved completely. Then the mixture was condensed under reduced pressure and the residue, which solidified on cooling, was recrystallized from Me_2CO-MeOH (Table I).

6-Phenyl-2,4-dinitrophenyl (2,4-dichlorophenoxy)acetate (IX, X'n=2,4-di-Cl)——To a solution of 4 g. of sodium 6-phenyl-2,4-dinitrophenolate in 20 ml. of Me_2CO was added with stirring a solution of 3.7 g. of (2,4-dichlorophenoxy)acetyl chloride in 20 ml. of Me_2CO, then the mixture was refluxed for 30 min. After cooling, 200 ml. of H_2O was added to the mixture and the separated oil was worked up with benzene. The solid which was obtained from the benzene layer in the usual way was recrystallized from Me_2CO-EtOH (Table I).

Biological Tests

Test solutions were prepared by dissolving the compounds in an appropriate solvent (DMF or Me_2CO), followed by dispersion in H_2O to desired concentration with aid of an emulsifier.

Testing of blank formulations showed no phytotoxicity in any treatment.

1) **Growth Inhibition Test of Young Plant (Petri-dish Test)**——5 ml. of the test solution was poured on filter-paper in a 9 cm. Petridish, 10 seeds of the test plant which previously germinated were then placed on the filter-paper. After being kept 4 days in the dark at 25°, the lengths of main roots were measured and compared with the lengths of roots from the control seeds. Three dishes were used for each compound at each concentration. Inhibition rate was expressed by the fraction

$$\left(1-\frac{\text{Root length of treated seed}}{\text{Root length of untreated seed}}\right)\times 100(\%).$$

Figures given in Table II express the average value of each run.

2) **Growth Inhibition and Withering Test by Foliar Application at Post-emergence (Pot Test)**——Ten plants of each test species which had been planted in soil in a Wagner pot (1/5000 are) were sprayed with 10 ml. of the test solution at the $2\sim3$ leaf stage. The vegetative growth was assessed 14 days after the treatment. Two replicates at each concentration were run on each compound. Inhibition- and withering rates were defined as follows.

$$\text{Inhibition rate}=\left(1-\frac{\text{Fresh weight of treated plant}}{\text{Fresh weight of untreated plant}}\right)\times 100(\%)$$

$$\text{Withering rate}=\frac{\text{Number of completely withered plant}}{\text{Number of treated plant}}\times 100(\%)$$

Figures given in Table III express the average value of each run.

3) **Growth Inhibition and Withering Test by Soil Treatment at Pre-emergence (Pot Test)**——Ten seeds of each test plant were sown in soil in a Wagner pot (1/5000 are), then 10 ml. of the test solution was applied evenly over the soil surface. The vegetative growth was evaluated 30 days after the treatment. Two replicates at each concentration were run on each compound. Inhibition- and withering rates were defined as follows.

$$\text{Inhibition rate}=\left(1-\frac{\text{Fresh weight of treated plant}}{\text{Fresh weight of control plant}}\right)\times 100(\%)$$

$$\text{Withering rate}=\left(\frac{\text{Number of completely withered plant}}{\text{Number of control plant}}\right)\times 100(\%)$$

Figures given in Table IV express the average value of each run.

The author wishes to express his deep gratitude to Dr. S. Tatsuoka, Director of these Laboratories, for his permission to publish this work and to Dr. T. Harukawa for his encouragement and helpful advice throughout the course of this work. Grateful acknowledgment is made to Mr. T. Toyosato and his co-workers of Kyoto Herbal Garden of these Laboratories for their biological tests.

Thanks are also due to Mr. M. Kan for elemental analyses, and to Mr. K. Maki for his assistance in the experimental work.

Summary

6-Phenyl-2,4-dinitrophenol derivatives were prepared for their evaluation as herbicides.

Some of these compounds were found to be promising.

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Eisaku Hayashi and Takeo Higashino:

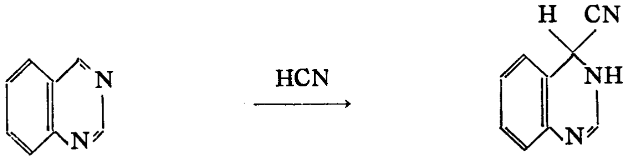
On the Reaction of Quinazoline with Acetophenone

(*Shizuoka College of Pharmacy*[*1])

In the previous paper of this series we have reported that the 4-position in quinazoline (I), owing to the overlapping of -M and -E effects of the nitrogen atoms of the ring and the effect of the fused benzene-ring, is very reactive to nucleophilic reagents.[1)]

Especially we attended to the formation of 3,4-dihydro-4-quinazolinecarbonitrile (II) on the reaction of I with hydrogen cyanide which is thought to be weaker of nucleophilic reagents at the activity.

In the present series of our work, the interests are focussed to attempting the reaction of I with carbanion as nucleophilic reagents.



I II

When I is made to react with acetophenone in the presence of sodium hydroxide solution at room temperature, an addition product agreed with $C_{16}H_{14}ON_2$ (III) in analytical values is obtained. In the ultraviolet spectrum of this compound, the two absorption peaks are located at 285 and 245 mμ. The former approximates to that of 3,4-dihydroquinazoline (IV) (290 mμ), and the latter does to that of acetophenone (242 mμ).[2)] Moreover, III shows the marked absorption bands at 3090 cm^{-1} for secondary amine and at 1665 cm^{-1} for carbonyl group in its infrared spectrum.

[*1] Oshika, Shizuoka (林 英作, 東野武郎).

1) T. Higashino: Yakugaku Zasshi, **80**, 245 (1960).

2) J. Tanaka, S, Nagakura, M. Kobayashi: J. Chem. Phys., **24**, 311 (1956).