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Pyridazines. I. Novel Intramolecular Cycloaddition of 3-Chloro-6-(2-allylphenoxy)pyridazines[1]

Teruomi Jojima, Hideo Takeshiba, and Takuo Konotsune

Agricultural Chemicals Research Laboratory, Sankyo Co., Ltd.[2]

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Heating 3-chloro-6-(2-allylphenoxy)pyridazine (IIIa) with or without a solvent afforded xanthene (Va) by a novel intramolecular cycloaddition reaction followed by elimination of nitrogen and hydrogen chloride. Formation of a fully aromatized product indicated that elimination of both N_2 and HCl has occurred from the initially formed $\pi^4+\pi^2$ cycloadduct (IV). Variously substituted xanthenes were prepared by heating the corresponding 3-chloro-6-(2-allylphenoxy)pyridazines in diethylaniline (DEA). The compound having an allylic group at the *para*-position of the benzene ring did not give any cyclized product, because the allylic double bond was too far from the pyridazine ring. Similar treatment of 3-chloro-6-(2-propenylphenoxy)pyridazine (XXVI) gave rise to 1-methyldibenzofuran (XXVIII) in a low yield.

Recently, application of tetrazine, *asym*-triazine or pyridazine components as dienes in $\pi^4+\pi^2$ cycloaddition reactions has been amply reported. Sauer and Lang synthesized pyridazine derivatives by reacting *sym*-tetrazine with styrene or with its morpholine enamine,[3] and this reaction was developed by Poffey and Verge,[4] and Heinrichs, *et al.*[5] Similarly, Dittmer and his co-workers obtained azanorcaladiene derivatives from *asym*-triazines and cyclopropene.[6] Further, Dittmar, *et al.* reported on the Diels-Alder addition between pyridazine ring systems and dienophiles such as cyclopropene, norbornen, *etc.*[7] All of these reactions are intermolecular, and there has been no report on an intramolecular cycloaddition reaction of cyclic azine systems.

During our studies on the nucleophilic substitution reaction of several halo-pyridazines with various nucleophiles to produce substituted pyridazines as pesticides,[8] we have taken our notice in 3-chloro-6-(2-allylphenoxy)pyridazine[9] (IIIa) and the related compounds. Molecular model of IIIa shows that its allylic double bond can closely locate over the pyridazine nucleus and an intramolecular $\pi^4+\pi^2$ cycloaddition reaction may occur.

Heating the phenoxypyridazine (IIIa) without a solvent at 180° for 2 hr afforded the cyclized product (Va), mp 99°, in 54% yield under vigorous evolution of nitrogen and hydrogen chloride gas. The infrared (IR) spectrum and the nuclear magnetic resonance (NMR) spectrum of Va agreed in all respects with those of authentic xanthene.[10] Formation of the fully aromatized product from IIIa indicates that elimination of both nitrogen and hydrogen chloride from the initially formed adduct (IV) has occurred during this reaction (Chart 1).

1) Part of this paper was presented at "The Third International Congress of Heterocyclic Chemistry," Sendai, August 26, 1971.
2) Location: *2-58, 1-chome, Hiromachi, Shinagawa-ku, Tokyo.*
3) J. Sauer and L. Lang, *Angew. Chem.*, **76**, 603 (1964).
4) D. Poffey and J.P. Verge, *J. Heterocyclic Chem.*, **6**, 497 (1969).
5) G. Heinrichs, H. Krapf, B. Schröder, A. Steigel, T. Troll, and J. Sauer, *Tetrahedron Letters*, **1970**, 1617.
6) W. Dittmar, J. Sauer, and A. Steigel, *Tetrahedron Letters*, **1969**, 5171.
7) W. Dittmar, G. Heinrichs, A. Steigel, T. Troll, and J. Sauer, *Tetrahedron Letters*, **1970**, 1623.
8) T. Jojima, K. Oyamada, and S. Tamura, *Agr. Biol. Chem.*, **32**, 1376 (1968).
9) T. Jojima, K. Kawakubo, and T. Honma, Abstract of Papers, Annual Meeting of the Agricultural Chemical Society of Japan, Tokyo, April, 1971, p. 397.
10) Purchased from Tokyo Kasei Kogyo Co., Ltd., Tokyo.

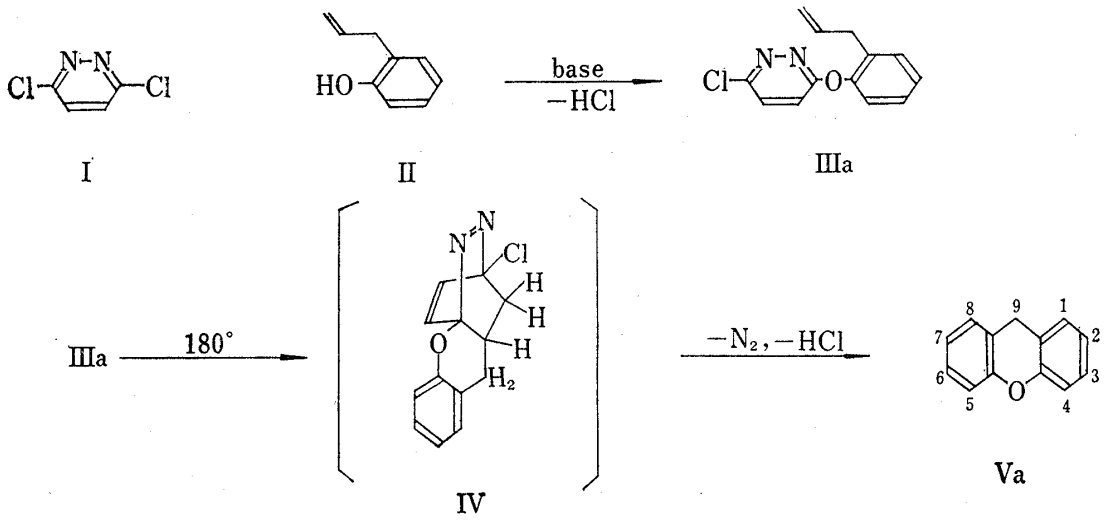
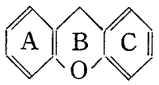


Chart 1



Usually, xanthenes have been prepared by the reaction of phenols with aldehydes or ketones under the presence of acid or alkali, heating *ortho*-hydroxy-triarylcarbinols, reduction of the corresponding xanthones with alkaline reducing agents, or heating xanthylium salts with alcohols.[11] In the present method, both A and B rings of xanthene systems are constructed in one step syntheses, and this is a novel route to variously substituted xanthene derivatives.

At first, preparation of Va under a variety of conditions was investigated. When the reaction was carried out without a solvent, maximum yield of Va was 60% (at 240°). However, it was formed in better yield by refluxing IIIa either in diethylaniline (DEA) or in tetralin. The reaction was neither accelerated nor depressed in the presence of trace acid (Table I).

Table I. Preparation of Xanthene (Va) from 3-Chloro-6-(2-allylphenoxy)pyridazine (IIIa) under Various Conditions[a]

Solvent	Temperature (°C)	Yield[b] (%)	Recovered IIIa (%)
—	100	0	98
—	150	11	80
—	180	54	20
—	200	54	0
—	240	60	0
Tetralin	reflux	80	0
Tetralin+trace conc. HCl	reflux	80	0
Xylene	reflux	7	83
Nitrobenzene	reflux	76	6
Dimethylformamide	reflux	16	80
Diethylaniline	reflux	80	0

a) The reaction was ceased after 2 hr in each run.
b) Yields were based on the pure material separated by a silica gel chromatography followed by distillation.

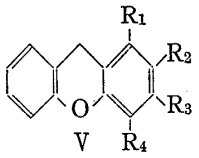
Next, a series of xanthenes have been synthesized by refluxing 3-chloro-6-(2-allyl-substituted-phenoxy)pyridazines (IIIb—n) in DEA. The progress of the cyclization reaction was checked by the gas evolution and thin-layer chromatography (TLC). Usually, the starting phenoxypyridazines (III) completely disappeared within 2 hr. These xanthene derivatives exhibited the IR absorptions assignable to a diphenyl ether group at 1250—1270

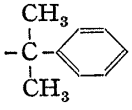
11) S. Wawzonek, "Heterocyclic Compounds," Vol. 2, ed. by R.C. Elderfield John Willey & Sons, New York, N.Y., 1951, p. 444.

cm^{-1}, and UV absorptions characteristic of a diphenylmethane system. Their NMR spectra also exhibited typical two-proton singlets at *ca.* 4 ppm ascribable to the diphenyl methylene protons. Sometimes, formation of small amounts of by-products was inferred from the NMR spectra of the crude products. The structure of these by-products will be discussed in the forthcoming paper.

Thus, various xanthenes which were prepared by the present method are shown in Table II. Among them, 2-methyl-,[12] 4-methyl-,[12] 1,3-di-methyl-,[13] and 2-methoxy[12]-xanthenes have been reported in the literature.

Table II. Xanthenes (V) from 3-Chloro-6-(2-allylphenoxy)pyridazine (III)



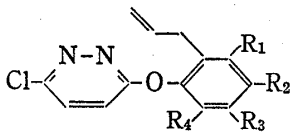
Compound (V)	R_1	R_2	R_3	R_4	mp (°C), or bp °C(mm Hg)	Yield (%)	Formula	Analyses (%) Calcd. C	Calcd. H	Found C	Found H
b	H	CH_3	H	H	96[a,b]	79	$C_{14}H_{12}O$	85.68	6.16	85.40	6.17
c	H	H	H	CH_3	113—115(0.5)[c]	64	$C_{14}H_{12}O$	85.68	6.16	85.69	6.29
d	CH_3	H	CH_3	H	44—45[a,d]	76	$C_{15}H_{14}O$	85.68	6.71	85.26	6.77
e	H	CH_3	H	CH_3	125—130 (0.1)	72	$C_{15}H_{14}O$	85.68	6.71	85.38	6.63
f	H	H	H	iso-C_3H_7	120—123 (0.1)	45	$C_{16}H_{16}O$	85.68	7.19	85.29	7.65
g	H	*t*-C_4H_9	H	H	70—71[e]	70	$C_{17}H_{18}O$	85.67	7.61	85.32	7.44
h	H	H	H	CH_2–CH=CH_2	119—121 (0.2)	59	$C_{16}H_{14}O$	86.45	6.35	86.42	5.79
i	H		H	H	96—97[e]	69	$C_{22}H_{20}O$	87.96	6.71	87.90	6.69
j	H	H	H		183—185 (0.4)	91	$C_{19}H_{14}O$	88.34	5.46	87.76	5.46
k	H	CH_3O	H	H	68—70[a,f]	87	$C_{14}H_{12}O_2$	79.22	5.60	78.77	5.82
l	H	H	H	CH_3O	120—130 (0.2)	78	$C_{14}H_{12}O_2$	79.22	5.60	79.16	5.63
m	H	Cl	H	H	109[a]	58	$C_{13}H_9OCl$	72.07	4.18	71.63	4.08[g]
n	H	H	H	Cl	135—143 (0.2)	75	$C_{13}H_9OCl$	72.07	4.18	71.52	4.24[h]

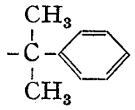
a) recrystallized from hexane; *b*) lit.[12] mp 98°; *c*) lit.[12] mp 40°; *d*) lit.[13] mp 45—46°; *e*) recrystallized from MeOH; *f*) lit.[12] mp 70°; *g*) Cl (%): Calcd: 16.36 Found: 16.45; *h*) Cl (%): Calcd.: 16.36, Found: 16.59

The phenoxypyridazines (III) employed as starting materials were prepared by heating 3,6-dichloropyridazine (I) with the corresponding 2-allylphenols (II) in the presence of anhydrous potassium carbonate at 150—180° for 2—5 hr (Method A), or by the reaction of I with sodium salts of the corresponding 2-allylphenols (II) in hot toluene (Method B). In the former method, minor amounts of the corresponding xanthenes were usually produced along with the products (III). Obviously, these xanthenes were formed from the corresponding allyl-phenoxypyridazines during the reaction. In the case of IIIf and IIIj having a bulky substituent at the *ortho*-position of the benzene ring, the yields of the pyridazines were rather low (14% and 9%, respectively) and the major reaction products were the xanthene derivatives (Vf and Vj). Presumably, I reacts very slowly with 2-allyl-6-isopropyl-, or with 2-allyl-6-phenyl-phenols so that the resulted phenoxypyridazines have been converted into the corresponding xanthenes during the progress of the reaction (Table III).

12) R.J. McConnel, *J. Chem. Soc.*, **1956**, 812.
13) H.L. Bender and A.G. Farnham, U.S. Patent, 2744882 (1956) [*C.A.*, **51**, 479i (1957)].

TABLE III. 3-Chloro-6-(2-allylphenoxy)pyridazines (III)



Compound (III)	R_1	R_2	R_3	R_4	Method	mp (°C)[a]
a	H	H	H	H	B	—[b]
b	H	CH_3	H	H	A	54
c	H	H	H	CH_3	A	46—48
d	CH_3	H	CH_3	H	B	64—65
e	H	CH_3	H	CH_3	A	63—65
f	H	H	H	iso-C_3H_7	A	93—95
g	H	t-C_4H_9	H	H	A	—[d]
h	H	H	H	CH_2-CH=CH_2	B	63—64
i	H		H	H	A	64—65
j	H	H	H		A	93—94
k	H	CH_3O	H	H	A	76
l	H	H	H	CH_3O	A	76
m	H	Cl	H	H	B	78—79
n	H	H	H	Cl	A	59

Compound (III)	Yield (%)	Formula	Analyses (%) Calcd. C	H	N	Found C	H	N	Xanthenes Produced (%)
a	42	$C_{13}H_{11}ON_2Cl$	63.29	4.49	11.36	62.75	4.19	12.02	—
b	56	$C_{14}H_{13}ON_2Cl$	64.49	5.03	10.74	64.23	5.02	10.61	Vb (25)
c	73	$C_{14}H_{13}ON_2Cl$	64.49	5.03	10.74	64.62	5.06	10.96	Vc (10)
d	90	$C_{15}H_{15}ON_2Cl$	65.57	5.50	10.20	65.52	5.43	10.29	—
e	43	$C_{15}H_{15}ON_2Cl$	65.57	5.50	10.20	64.53	5.56	9.72	Ve (25)
f	14	$C_{16}H_{17}ON_2Cl$	66.55	5.93	9.70	66.50	5.67	9.78	Vf (25)[e]
g	55	$C_{17}H_{19}ON_2Cl$	67.43	6.32	9.25	67.51	6.31	8.87	Vg (25)
h	68	$C_{16}H_{15}ON_2Cl$	67.03	5.17	9.77	67.05	5.31	10.06	—
i	45	$C_{22}H_{21}ON_2Cl$	72.42	5.80	7.68	72.27	5.82	7.85	Vi (23)
j	9	$C_{19}H_{15}ON_2Cl$	70.70	4.68	8.68	70.52	4.62	8.66	Vj (51)[e]
k	75	$C_{14}H_{13}ON_2Cl$	60.76	4.74	10.12	60.74	4.86	9.88	Vk (18)
l	40	$C_{14}H_{13}ON_2Cl$	60.76	4.74	10.12	60.69	4.45	10.25	VI (17)
m	61	$C_{13}H_{10}ON_2Cl_2$	55.54	3.59	9.96	55.40	3.65	10.06	—
n	65	$C_{13}H_{10}ON_2Cl_2$	55.54	3.59	9.96	55.45	3.62	9.96	Vn (14)

a) All the solid materials were recrystallized from hexane. *b*) n_D^{23}: 1.5823; *c*) Recovered I was 55 % after 2.5 hr. *d*) n_D^{22}: 1.5572; *e*) Recovered I was 35% after 5.5 hr.

Reaction of 3,6-dichloro-4-methylpyridazine[14] (VIa) with sodium salt of 2-allylphenol in hot toluene afforded a mixture of 3-chloro-4-methyl-6-(2-allylphenoxy)pyridazine (VIIa) and the 5-methyl analogue (VIIIa). Because the two compounds could not be separated by column chromatography, the mixture was treated with potassium acetate in hot acetic acid to give a mixture of 4-methyl-6-(2-allylphenoxy)-3(2H)pyridazinone (XIII) and 5-methyl-6-(2-allylphenoxy)-3(2H)pyridazinone (XIV) which could be easily separated by a silica

14) J. Druey, Kd. Meier, and K. Eichenberger, *Helv. Chim. Acta*, **37**, 121 (1954).

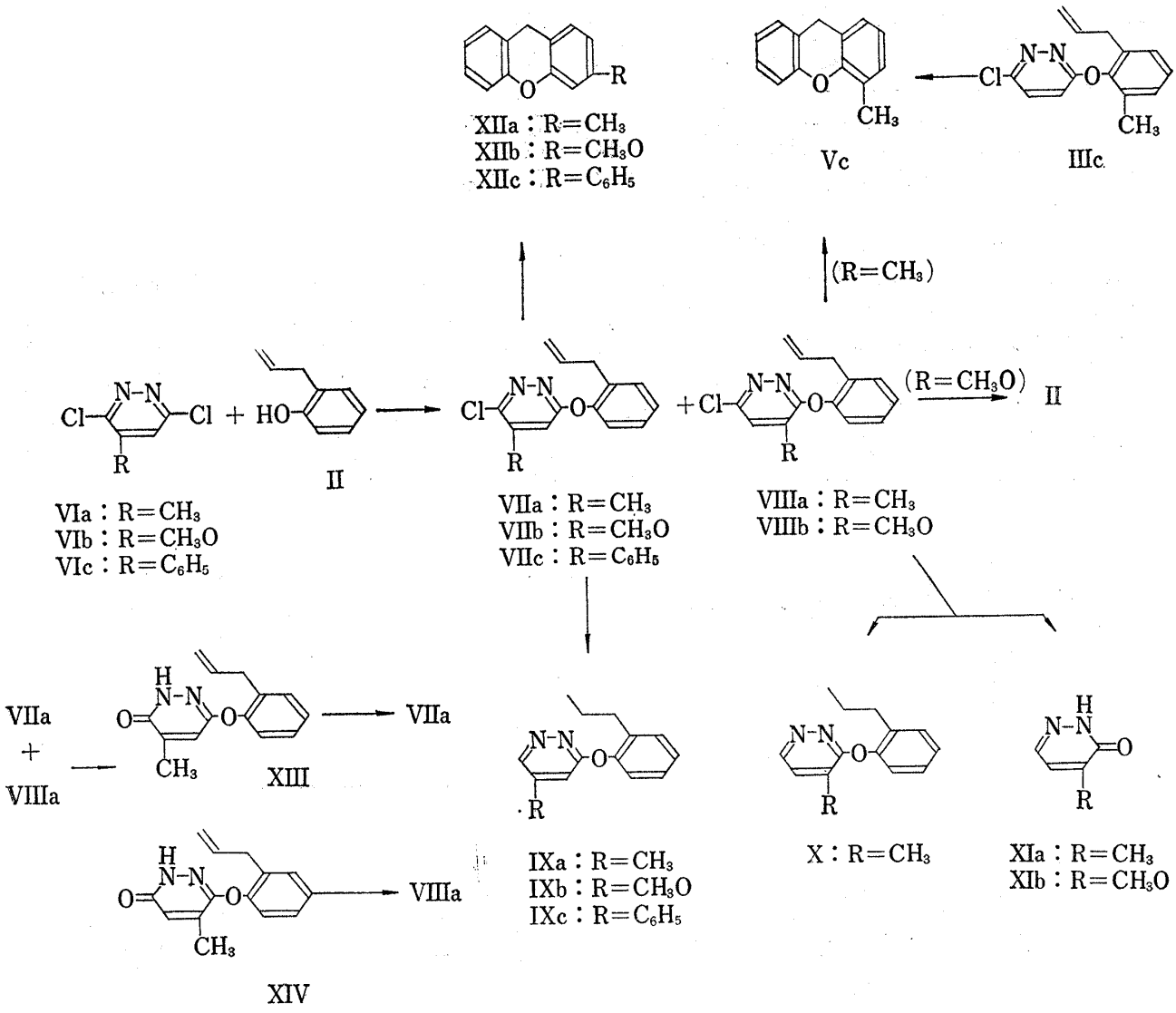


Chart 2

gel column. These pyridazinone derivatives were re-chlorinated with phosphoryl chloride into VIIa and VIIIa, respectively.

3,6-Dichloro-4-methoxypyridazine[15] (VIb) with sodium 2-allyl phenolate under the same reaction condition gave 3-chloro-4-methoxy-6-(2-allylphenoxy)pyridazine (VIIb) and 3-chloro-5-methoxy-6-(2-allylphenoxy)pyridazine (VIIIb), which could be easily separated by chromatography on silica gel. Similarly, 3,6-dichloro-4-phenylpyridazine[16] (VIc) afforded a single product, 3-chloro-4-phenyl-6-(2-allylphenoxy)pyridazine (VIIc).

In order to clarify the structure of these chloro-pyridazines, the compounds were catalytically hydrogenated over palladium on charcoal. Compounds VIIa—c gave the 3-(2-propylphenoxy)-5-substituted-pyridazines (IXa—e), whereas VIIIa produced 3-(2-propylphenoxy)-4-methylpyridazine (X) along with 4-methyl-3(2H)pyridazinone[17] (XIa), and VIIIb gave 4-methoxy-3(2H)pyridazinone (XIb) alone. The hydrogenolysis of the ether linkage as well as the chlorine atom has occurred in the 5-substituted series (VIIIa and VIIIb).

15) K. Eichenberger, R. Romefsch, and J. Druey, *Helv. Chim. Acta*, **39**, 1755 (1956).
16) J. Levisalles, *Bull. Soc. Chim. France*, **1957**, 1004.
17) S. Linholter, A.B. Kristensen, R. Rosenø rn, S.E. Nielsen, and H. Kaaber, *Acta Chem. Scand.*, **15**, 1660 (1961).

The NMR spectra showed *meta* coupling constants in compounds IXa—c (J=2 cps), and *ortho* coupling constants in X, XIa, and XIb (J=4 cps).[18]

Heating the compounds VIIa—c in DEA gave the corresponding 3-substituted-xanthenes (XIIa—c) in 65%, 18%, and 98% yields, respectively. Among the compounds thus prepared, 3-methylxanthene (XIIa) was reported in the literature,[19] and 3-metnoxyxanthene (XIIb) and 3-phenylxanthene (XIIc) are hitherto unknown. All of these compounds gave UV and NMR spectra characteristic of a xanthene ring system. As a typical example, a UV spectrum of XIIa is included in Fig. 1. Similarly, the 5-methyl analogue VIIIa afforded 4-methylxanthene (Vc) in 89% yield, which was spectroscopically identical with the material prepared from 3-chloro-6-(2-allyl-6-methylphenoxy)pyridazine (IIIc). Thus, it has been confirmed that the same cyclized xanthene (Vc) could be prepared from the two different pyridazines, IIIc and VIIIa. On the other hand, the 5-methoxy derivative (VIIIb) failed to give any cyclized product under the same condition, the only identifiable material being a small amount of 2-allylphenol (II). Presumably, the phenyl-pyridazyl ether linkage has cleaved before the intramolecular cyclization (Chart 2).

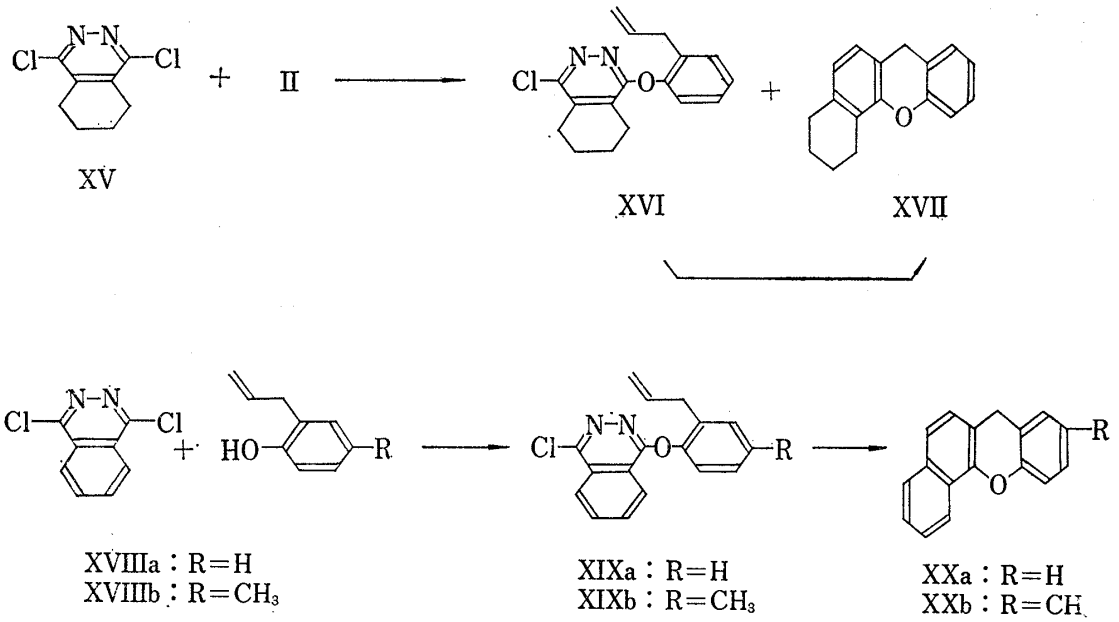


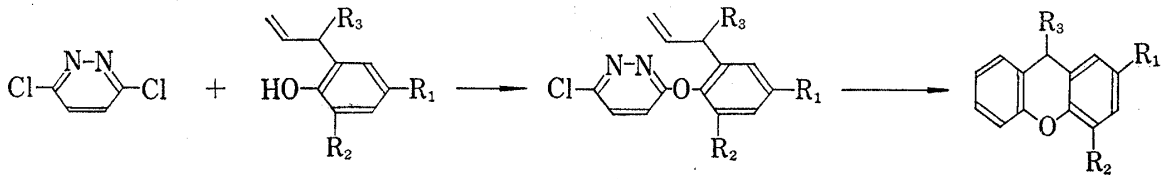
Chart 3

Next, the cyclization of the chloro-allylphenoxypyridazines having fused cyclohexane or benzene rings on the heterocyclic ring was investigated. Reaction of 1,4-dichloro-5,6,7,8-tetrahydrophthalazine[20] (XV) with 2-allylphenol (II) in the presence of anhydrous potassium carbonate afforded 1-chloro-4-(2-allylphenoxy)-5,6,7,8-tetrahydrophthalazine (XVI), and the unknown 1,2,3,4-tetrahydro-7H-benzo(c)xanthene (XVII) in 58% and 11% yield, respectively. The former compound (XVI) was converted into XVII in refluxing DEA in 90% yield. Its NMR spectrum exhibited signals at 3.93 ppm (2H, singlet) assignable to diphenyl methylene protons in addition to cyclohexane hydrogen and aromatic hydrogen peaks.

1-Chloro-4-(2-allylphenoxy)phthalazine (XIXa) and its *para*-methyl analogue (XIXb) which were obtained by the reaction of 1,4-dichlorophthalazine (XVIII) with sodium salt of 2-allylphenol or 2-allyl-4-methylphenol in hot toluene cyclized to the knwon 7H-benzo-

18) M. Yanai, T. Kinoshita, H. Watanabe, and S. Iwasaki, *Chem. Pharm. Bull.* (Tokyo), **19**, 1849 (1971).
19) W. Borsche and A. Geyer, *Chem. Ber.*, **47**, 1154 (1914).
20) *a*) R.H. Harning and E.D. Amstutz, *J. Org. Chem.*, **20**, 707 (1955); *b*) I. Satoda, F. Kusuda, and K. Mori, *Yakugaku Zasshi*, **82**, 233 (1962).

(c)xanthene[21] (XXa) and 9-methyl-7H-benzo(c)xanthene[22] (XXb) in refluxing DEA in 64% and 88% yield, respectively. The physical constants of the two benzo(c)xanthenes agreed with those of the reported compounds. The NMR spectra of the compounds, XXa and XXb gave peaks due to diphenyl methylene protons at 4.15 ppm and 4.07 ppm, respectively (2H, singlet). The foregoing results clearly indicate that xanthene ring systems can be successfully constructed from 3-chloro-6-(2-allylphenoxy)pyridazines substituted on the benzene ring as well as from the pyridazines substituted on the heterocyclic ring.



I XXI XXII XXIII

XXI a: $R_1=R_2=H$, $R_3=CH_3$ XXII a: $R_1=R_2=H$, $R_3=CH_3$ XXIII a: $R_1=R_2=H$, $R_3=CH_3$
XXI b: $R_2=H$, $R_1=R_3=CH_3$ XXII b: $R_2=H$, $R_1=R_3=CH_3$ XXIII b: $R_2=H$, $R_1=R_3=CH_3$
XXI c: $R_1=H$, $R_2=R_3=CH_3$ XXII c: $R_1=H$, $R_2=R_3=CH_3$ XXIII c: $R_1=H$, $R_2=R_3=CH_3$
XXI d: $R_1=Cl$, $R_2=H$, $R_3=CH_3$ XXII d: $R_1=Cl$, $R_2=H$, $R_3=CH_3$ XXIII d: $R_1=Cl$, $R_2=H$, $R_3=CH_3$
XXI e: $R_1=CH_3$, $R_2=H$, $R_3=$ XXII e: $R_1=CH_3$, $R_2=H$, $R_3=$ XXIII e: $R_1=CH_3$, $R_2=H$, $R_3=$

Chart 4

9-Methylxanthene (XXIIIa) which is unknwon, was likely obtained from 3-chloro-6-[2-(1-methylallyl)phenoxy]pyridazine (XXIIa) in almost quantitative yield (Chart 4). The characterization of XXIIIa was made from the following physical data. Its elemental analysis was equivalent to $C_{14}H_{12}O$, its UV spectrum showed a maximum absorption peak at 243 mμ characteristic of a xanthene ring system (Fig. 1), and the NMR spectrum gave the signals at 4.00 ppm (1H, quartet) assignable to a methine proton and at 1.45 ppm (3H, doublet) due to a methyl group coupled to the methine proton.

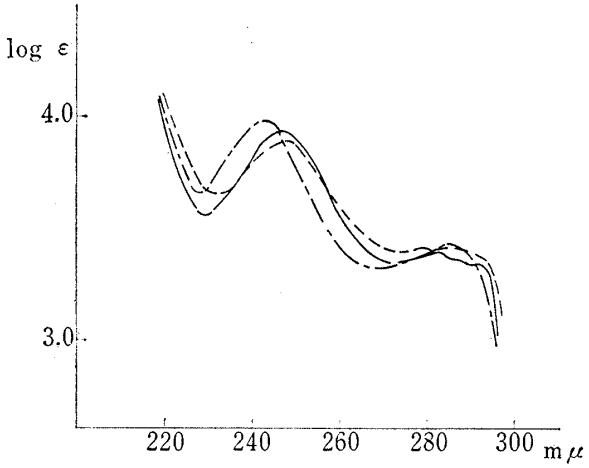


Fig. 1. UV Spectra of Va (——), XIIa (------), and XXIIIa (·····) in EtOH

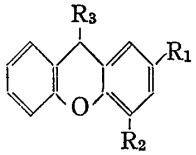
Similarly, the unknown 2,9-dimethyl- (XXIIIb), 4,9-dimethyl- (XXIIIc), and 2-chloro-9-methyl- (XXIIId)-xanthenes were obtained in good yields from the corresponding 3-chloro-6-[2-(1-methylallyl)phenoxy]-pyridazines (XXIIb—d), respectively. Treatment of 3-chloro-6-[2-(1-phenylallyl)-4-methylphenoxy]pyridazine (XXIIe) in hot DEA gave the known 2-methyl-9-phenylxanthene[23] (XXIIIe). The results are summarized in Table IV and the NMR data of the xanthenes, XXIIIa—e, are shown in Table V. The physical constants of the phenoxypyridazines (XXIIa—e) employed as starting materials are shown in Table VI.

In contrast to the facile intramolecular cycloaddition of the 3-chloro-6-(2-allylphenoxy)-pyridazine derivatives mentioned above, the compound such as 3-chloro-6-(2-methoxy-4-

21) A. Mustafa and M.K. Hilny, *J. Chem. Soc.*, **1952**, 1343.
22) M. Gindy and I.M. Dwidar, *J. Chem. Soc.*, **1953**, 893.
23) A. Berlitzer, *Monatsch. Chem.*, **36**, 207 (1915).

allylphenoxy)pyridazine (XXIV) with an allylic group at the *para*-position of the benzene ring did not produce any cyclized product. Although XXIV was heated in hot DEA for a long time, any cyclized product could not be detected from TLC, and only the starting material was recovered unchanged. Clearly, the interaction between the allylic group and pyri-

Table IV. 9-Substituted-xanthenes (XXIII)



Compound (XXIII)	R_1	R_2	R_3	bp °C (mmHg), or mp (°C)	Yield (%)	Formula	Analyses (%) Calcd. C	Calcd. H	Found C	Found H
a	H	H	CH_3	95—97 (0.3)	98	$C_{14}H_{12}O$	85.68	6.16	85.45	6.18
b	CH_3	H	CH_3	118—122 (0.2)	66	$C_{15}H_{14}O$	85.68	6.71	85.42	6.78
c	H	CH_3	CH_3	100—105 (0.1)	61	$C_{15}H_{14}O$	85.68	6.71	85.57	6.57
d	Cl	H	CH_3	120—124 (0.1)	60	$C_{14}H_{11}OCl$	72.89	4.81	72.82	4.84[a]
e	CH_3	H		148—150[b]	65	$C_{20}H_{16}O$	88.20	5.92	87.75	5.89

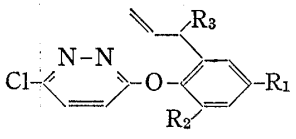
a) Cl (%): Calcd.: 15.37, Found: 15.97, *b*) lit.[24] 145°

Table V. NMR Spectral Data[a] of XXIIIa—e

Compound (XXIII)	9-CH_3	9-H	Phenyl	Aromatic CH_3
a	1.45[d]	4.00[q]	6.9—7.3[m] (8H)	—
b	1.43[d]	3.95[q]	6.7—7.3[m] (7H)	2.27[s] (2-CH_3)
c	1.44[d]	4.00[q]	6.7—7.3[m] (7H)	2.37[s] (4-CH_3)
d	1.48[d]	4.00[q]	6.9—7.5[m] (7H)	—
e	—	5.10[s]	6.7—7.2[m] (12H)	2.19[s] (2-CH_3)

a) δ ppm (CCl_4), s=singlet. d=doublet, q=quartet, m=multiplet

Table VI. 3-Chloro-6-[2-(1-substituted-allyl)phenoxy]pyridazines (XXII)



Compound (XXII)	R_1	R_2	R_3	Method[a]	mp (°C)	Yield (%)	Formula	Analyses (%) Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
a	H	H	CH_3	A	52[b]	62	$C_{14}H_{13}ON_2Cl$	64.49	5.03	10.74	64.37	5.12	10.64
b	CH_3	H	CH_3	A	104—105[b]	46	$C_{15}H_{15}ON_2Cl$	65.57	5.50	10.20	65.53	5.56	10.42
c	H	CH_3	CH_3	A	98—99[b]	38	$C_{15}H_{15}ON_2Cl$	65.57	5.50	10.20	65.62	5.32	10.11
d	Cl	H	CH_3	A	93[b]	70	$C_{14}H_{12}ON_2Cl_2$	56.97	4.10	9.50	57.07	4.00	9.54
e	CH_3	H		B	92—94[c]	62	$C_{20}H_{17}ON_2Cl$	71.32	5.09	8.32	71.14	4.90	8.52

a) See Table III. *b*) recrystallized from hexane *c*) recrystallized from petroleum ether-benzene

dazine ring as depicted in Chart 5 could not occur, because both functional groups were so removed from each other in XXV.

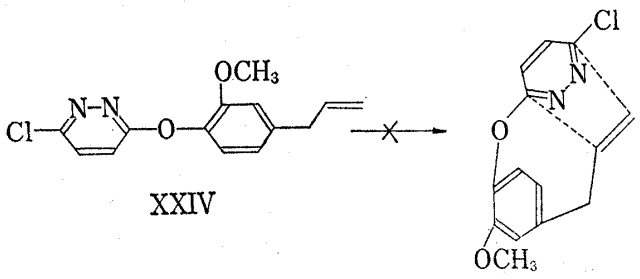


Chart 5

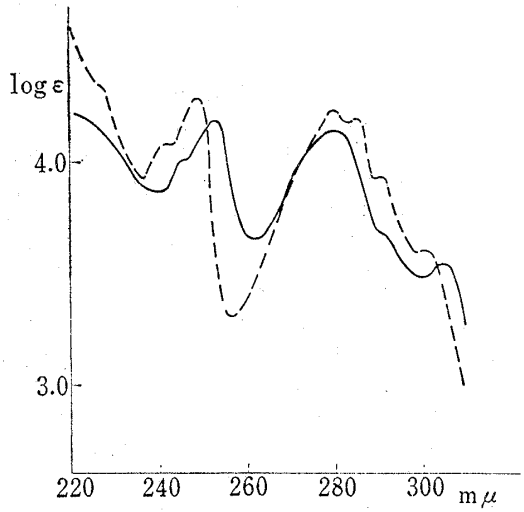
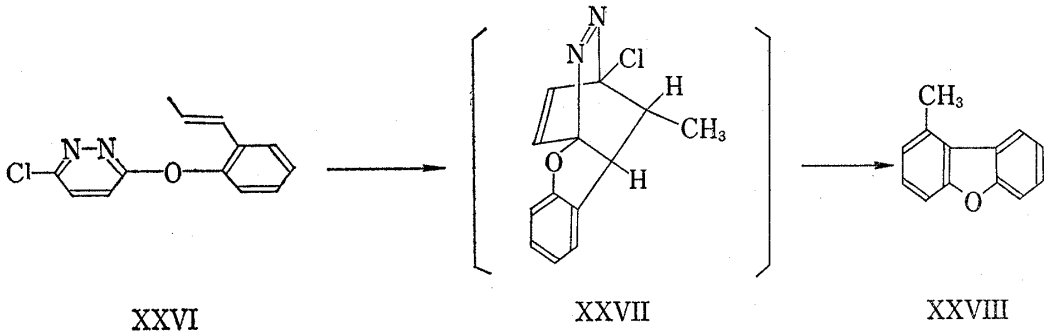


Fig. 2. UC Spectra of XXIV (——) and Dibenzofuran (-----) in EtOH

Finally, intramolecular cycloaddition of 3-chloro-6-(2-propenylphenoxy)pyridazine (XXVI) was attempted. Treatment of XXVI in refluxing DEA for 12 hr gave the dibenzofuran (XXVIII) as a yellow oil in a low yield. The molecular formula of XXVIII was approximately equivalent to $C_{13}H_{10}O$. Its UV spectrum was very similar to that of authentic dibenzofuran (Fig. 2), and its NMR spectrum exhibited strong signals at 2.77 ppm (3H, singlet) assignable to an aromatic methyl in addition to aromatic hydrogen peaks. From the above data, and in analogy to the formation of xanthene ring systems from 3-chloro-6-(2-allylphenoxy)pyridazines, XXVIII was identified with 1-methyl-dibenzofuran which is not reported in the literature. It seems very difficult to form the intermediate XXVII, because the side chain double bond cannot locate so closely over the pyridazine ring in XXVI as in the 2-allylphenoxy compounds (III) (Chart 6).

We are now continuing further experiments to clarify the synthetic scope along with mechanisms of this intramolecular cycloaddition reaction.



XXVI XXVII XXVIII

Chart 6

Experimental

All melting points were uncorrected. NMR spectra were taken using Varian A-60 spectrometer with tetramethylsilane as an internal standard. 2-Allylphenols (II), 2-(1-methylallyl)phenols, and 2-(1-phenylallyl)phenol (XXI) were prepared as reported in the literature.[24]

24) D.S. Tarbell, "Organic Reactions," Vol. II, ed. by R. Adams, John Wiley, and Sons, Inc., New York, N.Y., 1960, p. 1.

3-Chloro-6-(2-allylphenoxy)pyridazines (IIIa—n)——Method A: Generally, an equimolar mixture (0.067 mole) of 3,6-dichloropyridazine (I), 2-allylphenols (II), and K_2CO_3 was heated at 150—180° for 2—4 hr. After cooling, dilute aqueous NaOH was added to the reaction mixture, and the alkaline solution was repeatedly extracted with ether. The ether extracts were dried over Na_2SO_4, and the solvent was evaporated, and the residue was chromatographed on silica gel (300 g). The column was successively eluted with benzene–hexane (1:1), benzene, and benzene–ethyl acetate (40:1). The substance eluted first with benzene–hexane (1:1) was the corresponding xanthene derivatives (V), and the second one eluted with benzene was trace amount of the 2-allylphenol (II), and the third substance eluted with benzene–ethyl acetate (40:1) was the desired compounds, III. The crude products were recrystallized from appropriate solvents, or, if liquid, the solvents were completely evaporated under high vacuum.

Method B: Generally, sodium (0.0067 mole) was added to a mixture of II (0.01 mole) and dry toluene (50 ml), and the mixture was refluxed for 2—3 hr. After cooling, I (0.0067 mole) dissolved in dry toluene (10 ml) was added, and the toluene solution was refluxed for further 2—3 hr. The reaction mixture was poured into dil. NaOH, and the aqeous layer was extracted with toluene. The combined toluene extracts were washed with H_2O, dried over Na_2SO_4, and the solvent was evaporated *in vacuo*. The crude products were purified as Method A. The physical constants are shown in Table III.

Preparation of Xanthene (Va) from 3-Chloro-6-(2-allylphenoxy)pyridazine (IIIa) under Various Conditions (Table I)——a) Without Solvent: IIIa (1.0 g) was heated on an oil bath kept at an appropriate temperature for 2 hr. After cooling, the reaction mixture was repeatedly extracted with ether. The ether extracts were washed with H_2O, dried over Na_2SO_4, and the ether was evaporated. The crude products were passed through a column of silica gel (100 g). Elution with benzene–hexane (1:1) and successively with benzene gave Va and the recovered IIIa, respectively. Recrystallization of Va from hexane gave pure product as colorless leaflets, mp 99°. This compound was identical in all respects with the authentic material.[10]

b) In DEA: A mixture of IIIa (1.0 g) and DEA (5 ml) was refluxed for 2 hr. Ether (15 ml) was added to the cooled reaction mixture, and the solution was repeatedly extracted with cold 6N HCl. The ether layer was once washed with H_2O and dried over Na_2SO_4, and the ether was evaporated *in vacuo*. The crude product was purified as described above.

c) In the Other Solvent: A mixture of IIIa (1.0 g) and an appropriate solvent (*ca.* 5 ml) was refluxed for 2 hr. After cooling, the solvent was evaporated *in vacuo*, and the residue was purified as described in a).

Xanthenes (Vb—n)——As a general method, a mixture of 3-chloro-6-(2-allylphenoxy)pyridazines (III, 0.005—0.01 mole) and DEA (5—15 ml) was refluxed for 2 hr. Ether (50 ml) was added to the cooled reaction mixture, and the solution was repeatedly extracted with cold 6N HCl. The ether solution was once washed with H_2O, dried over Na_2SO_4, and the solvent was evaporated *in vacuo*. The crude product was recrystallized from appropriate solvents or fractionally distilled *in vacuo*. Their physical constants are given in Table II.

3-Chloro-4-methyl-6-(2-allylphenoxy)pyridazine (VIIa) and 3-Chloro-5-methyl-6-(2-allylphenoxy)pyridazine (VIIIa)——a) Preparation of 4-Methyl-6-(2-allylphenoxy)-3(2H)pyridazinone (XIII) and 5-Methyl-6-(2-allylphenoxy)-3(2H)pyridazinone (XIV): From sodium (4.6 g), 2-allylphenol (26.8 g), and 3,6-dichloro-4-methylpyridazine[14] (VIa, 32.6 g), an oily mixture of VIIa and VIIIa (48.6 g, 94%) was obtained by the same procedure as described for the allyl-phenoxypyridazines (IIIa—n) (Method B).

The above mixture (48.4 g) and AcOK (39.2 g) was refluxed in acetic acid (160 ml) for 2 hr. After the excess solvent was evaporated *in vacuo*, the residue was repeatedly extracted with hot benzene. The benzene extraxts was washed with 2N NaOH, and then with H_2O, and the solvent was dried over Na_2SO_4 and evaporated *in vacuo* to give 44.2 g (98%) of a mixture of XIII and XIV. This mixture was dissolved in benzene and chromatographed over silica gel (1 kg). Elution with benzene–ethyl acetate (10:1) afforded 28.7 g (64%) of XIII in the earlier eluate, mp 144—147° (from benzene–hexane, colorless needles). IR ν_{max}^{Nujol} cm^{-1}: 1650 (C=O). *Anal.* Calcd. for $C_{14}H_{14}O_2N_2$: C, 69.40; H, 5.83; N, 11.56. Found: C, 69.96; H, 5.69; N, 11.61. Compound XIV (8.3 g, 19%) was obtained from the following eluate, mp 195—198° (from benzene–hexane, colorless needles). IR ν_{max}^{Nujol} cm^{-1}: 1680 (C=O). *Anal.* Calcd. for $C_{14}H_{14}O_2N_2$: C, 69.40; H, 5.83; N, 11.56. Found: C, 69.78; H, 5.66; N, 11.62.

b) Preparation of VIIa: A mixture of XIII (9.95 g) and $POCl_3$ (200 ml) was refluxed for 1.5 hr, the excess solvent was evaporated *in vacuo*, and the residue was poured into ice-H_2O. The aqeous solution was neutralized with 2N NaOH, and repeatedly extracted with ether. Evaporation of the ether gave a crude oil which was passed through a column of silica gel. Elution with benzene–ethyl acetate (10:1) afforded 10.7 g (100%) of 3-chloro-4-methyl-6-(2-allylphenoxy)pyridazine (VIIa) as a yellow oil, n_D^{21}: 1.5765. NMR δ ppm (CCl_4): 7.0—7.3 (5 H, m, phenyl+5-H), 5.6—6.2 (1 H, m, =CH), 5.10, 4.90 (2 H, m, $=CH_2$), 3.28 (2 H, d, $-CH_2-$), 2.33 (3 H, s, $-CH_3$). *Anal.* Calcd. for $C_{14}H_{13}ON_2Cl$: C, 64.49; H, 4.99; N, 10.75; Cl, 13.63. Found: C, 64.14; H, 5.07; N, 10.99; Cl, 13.83.

c) Preparation of VIIIa: A mixture of XIV (3.9 g) and $POCl_3$ (50 ml) was treated as above to give 4.15 g (99%) of 3-chloro-5-methyl-6-(2-allylphenoxy)pyridazine (VIIIa), n_D^{19}: 1.5764. NMR δ ppm (CCl_4): 7.0—7.4 (5H, m, phenyl+4-H), 5.6—6.2 (1H, m, =CH), 5.10, 4.90 (2H, m, $=CH_2$), 3.29 (2H, d, $-CH_2-$), 2.33

(3H, s, -CH_3). *Anal.* Calcd. for $C_{14}H_{13}ON_2Cl$: C, 64.49; H, 4.99; N, 10.75; Cl, 13.63. Found: C, 64.68; H, 5.26; N, 11,01; Cl, 13.42.

3-Chloro-4-methoxy-6-(2-allylphenoxy)pyridazine (VIIb) and 3-Chloro-5-methoxy-6-(2-allylphenoxy)-pyridazine (VIIIb)——Sodium (1 g) was added to a mixture of 2-allylphenol (6.7 g) and dry toluene (200 ml). The toluene suspension was heated on steam bath for 2 hr. After cooling, 3,6-dichloro-4-methoxypyridazine[15] (7.7 g) dissolved in dry toluene (30 ml) was added dropwise, and the solution was stirred at 50° for 2 hr, then refluxed for 1 hr. The reaction mixture was poured into 2N NaOH (22 ml). The toluene layer was once washed with H_2O, dried over Na_2SO_4, and the solvent was evaporated *in vacuo*. The oily residue (10 g) was dissolved in benzene and chromatographed on silica gel (400 g). Elution with benzene–ethyl acetate (4:1) gave 5.5 g (46%) of 3-chloro-4-methoxy-6-(2-allylphenoxy)pyridazine (VIIb) in the first eluate, mp 113° (from ligroin–EtOH, colorless leaflets). NMR δ ppm (CCl_4): 7.0—7.6 (4H, m, phenyl), 6.48 (1H, s, the proton at 5-position), 5.5—6.1 (1H, m, =CH), 4.83, 5.07 (2H, m, $=CH_2$), 3.90 (3H, s, OCH_3), 3.30 (2H, d, -CH_2-). *Anal.* Calcd. for $C_{14}H_{13}O_2N_2Cl$: C, 60.76; H, 4.74; N, 10.12; Cl, 12.81. Found: C, 60.61; H, 4.91; N, 9.81; Cl, 12.89. 3-Chloro-5-methoxy-6-(2-allylphenoxy)pyridazine (VIIIb) (2.2 g, 19%) was obtained from the following eluate, mp 74—76° (from ligroin–EtOH, colorless needles). NMR δ ppm (CCl_4): 7.0—7.3 (4H, m, phenyl), 6.82 (1H, s, the proton at 4-position), 5.7—6.3 (1H, m, -CH=), 5.10, 4.87 (2H, m, $=CH_2$), 3.92 (3H, s, OCH_3), 3.30 (2H, d, -CH_2-). *Anal.* Calcd. for $C_{14}H_{13}O_2N_2Cl$: C, 60.76; H, 4.74; N, 10.12; Cl, 12.81. Found: C, 60.37; H, 4.65; N, 10.11; Cl, 12.67.

3-Chloro-4-phenyl-6-(2-allylphenoxy)pyridazine (VIIc)——Sodium (0.48 g), 2-allylphenol (4.02 g), and 3,6-dichloro-4-phenylpyridazine[16] (VIc, 4.5 g) were treated in dry toluene (100 ml) as above. The crude crystalline solid which was obtained from the toluene extracts were recrystallized from hexane to give 4.7 g (72%) of colorless plates, mp 82—83°. NMR δ ppm (CCl_4) 7.0—7.5 (10H, m, phenyl+5H), 5.5—6.2 (1H, m, =CH), 5.08, 4.85 (2H, m, $=CH_2$), 3.32 (2H, d, -CH_2-). *Anal.* Calcd for $C_{19}H_{15}ON_2Cl$: C, 70.70; H, 4.68; N, 8.68. Found: C, 71.17; H, 4.67; N, 8.84.

Hydrogenation of 3-Chloro-4-methyl-6-(2-allylphenoxy)pyridazine (VIIa)——VIIa (2 g) in a mixture of 100 ml of MeOH and 3 ml of 28% aqeous ammonia was hydrogenated over 0.3 g of 5% Pd-C. The catalyst was filtered off, the filtrate was evaporated *in vacuo*, and the residue was extracted with ether. The ether extracts were dried over Na_2SO_4, and the solvent was evaporated *in vacuo*, and the residue was distilled to give 1.7 g (98%) of 3-(2-propylphenoxy)-5-methylpyridazine (IXa) as a yellow oil, bp 141—143° (0.3 mmHg). NMR δ ppm (CCl_4): 8.63 (1H, d, the proton at 6-position, J=2 cps), 7.0—7.3 (4H, m, phenyl), 6.83 (1H, d, the proton at 4-position, J=2 cps), 2.53 (2H, t, -C$\underline{H}_2$-CH_2-CH_3), 2.27 (3H, s, 5-CH_3), 1.57 (2H, m, -CH_2-C$\underline{H}_2$-CH_3), 0.90 (3H, t, -CH_2-CH_2-C$\underline{H}_3$). *Anal.* Calcd. for $C_{14}H_{16}ON_2$: C, 73.65; H, 7.06; N, 12.27. Found: C, 73.45; H, 6.82; N, 11.90.

Hydrogenation of 3-Chloro-5-methyl-6-(2-allylphenoxy)pyridazine (VIIIa)——VIIIa in a mixture of 50 ml of MeOH and 3 ml of 28% aqueous ammonia was hydrogenated over 0.2 g of 5% Pd-C, and worked up as above. The crude crystalline solid was recrystallized from hexane to give 0.05 g (13%) of 4-methyl-3(2H)pyridazinone as colorless prisms, mp 159°, NMR δ ppm (CCl_4): 12.80 (1H, broad, exchangeable with D_2O), 7.83 (1H, d, 6-H, J=4 cps), 7.17 (1H, d, 5-H, J=4 cps), 2.23 (3H, s, CH_3). The IR and NMR spectra of this substance was identical with those of the compound reported by Linholter[17] (reported mp: 156°). The filtrate was kept in an ice-box to separate crystals, which were filtered to give 0.24 g (30%) of 3-(2-propylphenoxy)-4-methylpyridazine as colorless prisms, mp 65—66°. NMR δ ppm (CCl_4): 8.83 (1H, d, 6-H, J=5 cps), 7.2—7.4 (5-H, m, phenyl+5H), 2.57 (2H, t, -C$\underline{H}_2$-C_2H_5), 2.40 (3H, s, 4-CH_3), 1.63 (2H, m, -CH_2-C$\underline{H}_2$-CH_3), 0.90 (3H, t, -CH_2-CH_2-C$\underline{H}_3$). *Anal.* Calcd. for $C_{14}H_{16}ON_2$: C, 73.65; H, 7.06; N, 12.27. Found: C, 73.43; H, 7.12; N, 12.33.

Hydrogenation of 3-Chloro-4-methoxy-6-(2-allylphenoxy)pyridazine (VIIb)——VIIb (1.55 g) in a mixture of 100 ml of MeOH and 3 ml of 28% aqeous ammonia was hydrogenated over 0.3 g of 5% Pd-C, and worked up as above. The residue after evaporation of the ether, was distilled to give 0.8 g (60%) of 3-(2-propylphenoxy)-5-methoxypyridazine (IXb) as a yellow oil, bp 171—173° (0.4 mmHg). NMR δ ppm (CCl_4): 8.53 (1H, d, the proton at 3-position, J=2 cps), 7.0—7.3 (4H, m, phenyl), 6.45 (1H, d, the proton at 5-position, J=2 cps), 3.83 (3H, s, OCH_3), 2.52 (2H, t, -C$\underline{H}_2C_2H_5$), 1.62 (2H, m, -CH_2-C$\underline{H}_2$-CH_3), 0.90 (3H, t, -CH_2-CH_2-C$\underline{H}_3$). *Anal.* Calcd. for $C_{14}H_{16}O_2N_2$: C, 68.83; H, 6.60; N, 11.47. Found: C, 69.19; H, 6.92; N, 10.92.

Hydrogenation of 3-Chloro-5-methoxy-6-(2-allylphenoxy)pyridazine (VIIIb)——VIIIb (0.5 g) in a mixture of 50 ml of MeOH and 2 ml of 28% aqueous ammonia was hydrogenated over 0.2 g ov 5% Pd-C. The catalyst was filtered off, the filtrate was evaporated to dryness *in vacuo*, and the residue was recrystallized from ethyl acetate to give 4-methoxy-3(2H)pyridazinone (XIb) in 90% yield, mp 226°. NMR δ ppm (CCl_4): 7.77 (1H, d, 6-H, J=4 cps), 6.72 (1H, d, 5-H, J=4 cps), 3.80 (3H, s, OCH_3). *Anal.* Calcd. for $C_5H_6O_2N_2$: C, 47.62; H, 4.80; N, 22.21. Found: C, 47.64; H, 4.81; N, 21.97.

Hydrogenation of 3-Chloro-4-phenyl-6-(2-allylphenoxy)pyridazine (VIIc)——VIIc (1.05 g) in a mixture of 100 ml of MeOH and 3 ml of 28% aqueous ammonia was hydrogenated over 2.3 g of 5% Pd-C to give 0.6 g (63%) of 3-(2-propylphenoxy)-5-phenylpyridazine (IXc) as a yellow oil, bp 182—185° (0.15 mmHg). NMR δ ppm (CCl_4): 9.33 (1H, d, the proton on 6-position, J=2 cps), 7.2—7.8 (10H, m, phenyl+4-H), 2.60 (2H, t, -C$\underline{H}_2$-C_2H_5), 1.35—1.98 (2H, m, -CH_2C$\underline{H}_2$-CH_3), 0.90 (3H, t, -CH_2-CH_2-C$\underline{H}_3$). *Anal.* Calcd. for $C_{19}H_{18}ON_2$: C, 78.59; H, 6.25; N, 9.65. Found: C, 78.55; H, 6.25; N, 9.85.

3-Methylxanthene (XIIa)——A mixture of 3-chloro-4-methyl-6-(2-allylphenoxy)pyridazine (VIIa, 2.6 g) and DEA (10 ml) was heated at 200° for 2 hr, and worked up as the general procedure for preparation of xanthenes (V). Recrystallization of the crude crystalline solid from hexane gave 1.3 g (65%) of 3-methylxanthene as colorless leaflets, mp 120—122°. UV λ_{max}^{EtOH} mμ (ε): 248 (7800). NMR δ ppm (CCl_4): 6.7—7.1 (7H, m, phenyl), 3.94 (2H, s, $-CH_2-$), 2.29 (3H, s, $-CH_3$). This substance was identical with the compound reported by Borsche and Geyer[19] (reported mp: 121°).

3-Methoxyxanthene (XIIb)——A mixture of 3-chloro-4-methoxy-6-(2-allylphenoxy)pyridazine (VIIb, 2 g) and DEA (3 ml) was refluxed for 1 hr. Ether (15 ml) was added to the cooled reaction mixture, and the solution was repeatedly extracted with cold 6N HCl. A large amount of tarry substance insoluble in ether was formed. The ether layer was once washed with H_2O, and dried over Na_2SO_4, and the ether was evaporated *in vacuo*. The oily residue was dissolved in benzene and put on a column of silica gel (100 g). Elution with benzene–hexane (1:1) afforded a crystalline solid which was recrystallized from hexane to give 0.28 g (18%) of colorless leaflets, mp 79—80°. UV λ_{max}^{EtOH} mμ (ε): 248 (6600), 276 (5000). *Anal.* Calcd. for $C_{14}H_{12}O_2$: C, 79.22; H, 5.60. Found: C, 78.74; H, 5.57.

3-Phenylxanthene (XIIc)——A mixture of 3-chloro-4-phenyl-6-(2-allylphenoxy)pyridazine (VIIc, 1.8 g) and DEA (5 ml) was refluxed for 1.5 hr, and worked up as described for XIIa to give 1.4 g (98%) of 3-phenylxanthene (XIIc) as colorless leaflets, mp 107° (from hexane). NMR δ ppm (CCl_4): 6.9—7.6 (12H, m, phenyl), 3.97 (2H, s, $-CH_2-$). *Anal.* Calcd. for $C_{19}H_{14}O$: C, 88.34; H, 5.46. Found: C, 88.21; H, 5.35.

4-Methylxanthene (Vc) from 3-Chloro-5-methyl-6-(2-allylphenoxy)pyridazine (VIIIa)——A mixture of VIIIa (1.3 g) and DEA (5 ml) was heated at 210—220° for 2 hr, and worked up as described for XIIa to give 0.9 g (89%) of 4-methylxanthene (Vc) as a yellow oil, bp 103° (0.15 mmHg) (mp 39—40°). NMR δ ppm (CCl_4): 6.8—7.3 (7H, m, phenyl), 3.93 (2H, s, $-CH_2-$), 2.32 (3H, s, $-CH_3$). This substance proved to be identical with the compound obtained from 3-chloro-6-(2-allyl-6-methylphenoxy)pyridazine (IIIc) under the same condition.

Reaction of 1,4-Dichloro-5,6,7,8-tetrahydrophthalazine (XV) with 2-Allylphenol——An equimolar (0.005 mole) mixture of XV, 2-allylphenol, and K_2CO_3 was heated at 150—160° for 3 hr. After cooling, dilute NaOH was added to the reaction mixture, and the alkaline solution was repeatedly extracted with ether. The ether extracts were dried over Na_2SO_4, and the ether was evaporated, and the residue was chromatographed on silica gel (100 g). Elution with benzene–ethyl acetate (40:1) afforded 0.11 g (11%) of 1,2,3,4-tetrahydro-7H-benzo(c)xanthene (XVII) in the earlier eluate, mp 57—58° (from hexane, colorless leaflets). NMR δ ppm (CCl_4): 6.7—7.2 (6H, m, phenyl), 3.93 (2H, s, Ar-CH_2-Ar), 2.5—3.0 (4H, m, Ar-CH_2-, Ar-CH_2-), 1.6—2.0 (4H, m, $-CH_2-C\underline{H}_2-C\underline{H}_2-CH_2-$). *Anal.* Calcd. for $C_{15}H_{16}O$: C, 84.87; H, 7.60. Found: C, 84.84; H, 6.85. From the following eluate, 0.86 g (58%) of 1-chloro-4-(2-allylphenoxy)-5,6,7,8-tetrahydrophthalazine (XVI) was obtained, mp 88° (from hexane, colorless prisms). NMR δ ppm (CCl_4): 7.0—7.6 (4H, m, phenyl), 5.6—6.4 (1H, m, =CH), 5.10, 4.87 (2H, m, $=CH_2$), 3.27 (2H, d, $C\underline{H}_2$-CH=), 2.5—2.9 (4H, Ar-CH_2-, Ar-CH_2-), 1.7—2.0 (4H, m, $-CH_2-C\underline{H}_2-C\underline{H}_2-CH_2-$). *Anal.* Calcd. for $C_{17}H_{17}ON_2Cl$: C, 67.88; H, 5.70; N, 9.31. Found: C, 67.90; H, 5.45; N, 9.75.

1,2,3,4-Tetrahydro-7H-benzo(c)xanthene (XVII)——Refluxing 3-chloro-4-(2-allylphenoxy)-5,6,7,8-tetrahydrophthalazine (XVI, 12.5 g) in DEA (5 ml) for 2 hr gave the compound (XVII) in 90% yield, mp 57—58°. This product was identical with the substance obtained by the reaction of XV with 2-allylphenol as above.

1-Chloro-4-(2-allylphenoxy)phthalazine (XIXa)——1,4-Dichlorophthalazine (XVIII, 2 g) was reacted with sodium 2-allylphenolate (0.01 mole) in hot toluene and worked up as described for VIIb, VIIIb, and VIIc. The crude crystalline solid thus obtained was recrystallized from hexane to give 1.60 g (54%) of 1-chloro-4-(2-allylphenoxy)phthalazine (XIXa) as colorless needles, mp 122—123°. *Anal.* Calcd. for $C_{17}H_{13}ON_2Cl$: C, 68.92; H, 4.42; N, 9.47. Found: C, 68.65; H, 4.39; N, 9.33.

1-Chloro-4-(2-allyl-4-methylphenoxy)phthalazine (XIXb)——XVIII (2 g) was reacted with sodium 2-allyl-4-methylphenolate (0.01 mole) and worked up as above. The crude crystalline solid thus obtained was recrystallized from hexane to give 2.69 g (87%) of 1-chloro-4-(2-allyl-4-methylphenoxy)phthalazine (XIXb) as colorless needles, mp 138—139°. *Anal.* Calcd. for $C_{18}H_{15}ON_2Cl$: C, 69.67; H, 4.83; N, 9.03. Found: C, 69.42; H, 4.75; N, 8.85.

7H-Benzo(c)xanthene (XXa)——By refluxing 1-chloro-4-(2-allylphenoxy)phthalazine (XIXa, 1.5 g) in DEA (5 ml) for 2 hr, XXa was obtained in 64% yield, mp 92° (from hexane, colorless leaflets). UV λ_{max}^{EtOH} mμ (ε): 236 (32000), 286 (6000), 300 (6300), 312 (4900), 327 (2700). NMR δ ppm (CCl_4): 8.30 (1H, m, probably, the proton at 1-position), 6.9—7.8 (9H, m, phenyl), 4.15 (1H, s, $-CH_2-$). This substance was identical with the compound reported by Mustafa and Hilny[21] (reported mp: 95—96°).

9-Methyl-7H-benzo(c)xanthene (XXb)——By refluxing 1-chloro-4-(2-allyl-4-methylphenoxy)phthalazine (XIXb, 1.55 g) in DEA (5 ml) for 2 hr, XXb was obtained in 88% yield, mp 99—100° (from hexane, colorless leaflets). UV λ_{max}^{EtOH} mμ (ε): 238 (29000), 289 (6900), 301 (6600), 315 (5400), 328 (3200). NMR δ ppm (CCl_4): 8.27 (1H, m, probably, the proton at 1-position), 6.8—7.3 (8H, m, phenyl), 4.07 (2H, s, $-CH_2-$), 2.28 (3H, s, $-CH_3$). This substance was identical with the compound reported by Gindy and Dwidar[22] (reported mp: 99—100°).

3-Chloro-6-[2-(1-methylallyl)phenoxy]pyridazines (XXIIa—d)——By heating equimolar (0.04 mole) mixture of 3,6-dichloropyridazine (I), 2-(1-methylallyl)phenols (XXI), and K_2CO_3 at 160° for 1—2 hr, XXIIa—d were obtained by the same procedure as described for the compounds IIIa—n (Method A). Their physical constants are listed in Table VI.

3-Chloro-6-[2-(1-phenylallyl)phenoxy]pyridazine (XXIIe)——A mixture of sodium (1.15 g), 2-(1-phenylallyl)-4-methylphenol (11.2 g), and 3,6-dichloropyridazine (I, 7.9 g) was treated in dry touene (100 ml) as described for the compounds VIIb, VIIIb, and VIIc. The crude crystalline solid thus obtained was recrystallized from petroleum ether–benzene to give 10.5 g (62%) of XXIIe as colorless needles, mp 92—94°. NMR δ ppm (CCl_4): 6.6—7.3 (10H, m, phenyl+4-H+5-H), 5.9—6.5 (1H, m, =CH), 5.23, 4.90 (2H, m, $=CH_2$), 4.70 (1H, d, =CH-CH-phenyl), 2.33 (3H, s, $-CH_3$). The analytical data are included in Table VI.

9-Substituted-xanthenes (XXIIIa—e)——By refluxing the compounds XXIIa—e (0.008 mole) obtained as above in DEA (6 ml) for 2 hr, XXIIIa—e was obtained by the same procedure as described for xanthenes (Vb—n). Their physical constants are listed in Table IV, and the NMR data are tabulated in Table V.

3-Chloro-6-(2-methoxy-4-allylphenoxy)pyridazine (XXIV)——By heating equimolar (0.01 mole) mixture of 3,6-dichloropyridazine (I), 2-allylphenol, and K_2CO_3 at 170° for 2.5 hr and working up by the same procedure for the compounds IIIa—n (Method A), XXIV was obtained as colorless prisms in 70% yield, mp 90° (from hexane). NMR δ ppm (CCl_4): 6.6—7.4 (5H, m, phenyl), 5.6—6.3 (1H, m, -CH=), 5.15, 4.93 (2H, m, $-CH_2$), 3.67 (3H, s, OCH_3), 3.33 (2H, d, $-CH_2$-). *Anal.* Calcd. for $C_{14}H_{13}O_2N_2Cl$: C, 60.77; H, 4.74; N, 10.12. Found: C, 60.77; H, 4.72; N, 10.04.

3-Chloro-6-[2-(1-propenyl)pyridazine (XXVI)——By heating an equimolar (0.034 mole) mixture of 3,6-dichloropyridazine (I), 2-(1-propenyl)phenol, and K_2CO_3 at 180° for 3 hr (Method A), XXVI was obtained as colorless needles in 90% yield, mp 77° (from hexane). *Anal.* Calcd. for $C_{13}H_{11}ON_2Cl$: C, 63.29; H, 4.49; N, 11.36. Found: C, 63.01; H, 4.50; N, 11.26.

1-Methyl-dibenzofuran (XXVIII)——A mixture of the compound XXVI (2 g) prepared as above and DEA (5 ml) was refluxed for 12 hr. The solvent was evaporated *in vacuo*, and 20 ml of 3N HCl was added to the residue, and the solution was repeatedly extracted with ether. The fraction was once washed with H_2O, and dried over Na_2SO_4 and the solvent was evaporated to give an oily residue (1.8 g). The oil was dissolved in benzene, and passed through a column of silica gel (100 g). Elution with benzene–hexane (2:1) afforded crude 1-methyl-dibenzofuran (XXVIII) which was purified by distillation to give a yellow oil (0.3 g), bp 123—128° (bath temperature) (0.25 mmHg). NMR δ ppm (CCl_4): 6.9—7.5 (7H, m, phenyl), 2.77 (3H, s, 1-CH_3). The UV spectrum was shown in Fig. 2. Although this oil was re-distilled twice, the analytically pure substance could not be obtained. *Anal.* Calcd. for $C_{13}H_{10}O$: C, 85.69; H, 5.53; N, 0. Found: C, 87.84; H, 5.45; N, 0. The second product eluted with benzene–ethyl acetate (40:1) was the starting compound (XXVI, 1 g).

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