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Pyridazines. II.[1] Intramolecular Cycloaddition of 3-Substituted-6-[2-(2-methylallyl)phenoxy]pyridazines[2]

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Heating of 3-phenyl-, 3-methyl-, and 3-chloro-6-[2-(2-methylallyl)phenoxy]pyridazine in diethylaniline or without a solvent afforded 2-substituted-9a-methyl-1,9a-dihydroxanthenes, which are previously unknown group of compounds. The mechanism of this reaction may be explained by an intramolecular cycloaddition between pyridazine nucleus and the allylic side chain to give the $(4+2)\pi$ adduct followed by N_2 elimination. Similarly, cyclization of 1-phenyl-4-[2-(1-methylallyl)-1-naphthyloxy]phthalazine gave 5-phenyl-6a-methyl-6a,12a-dihydro-7*H*-benzo[*c*]xanthene.

In our preceding paper,[1] we showed a novel one-step synthesis of xanthenes (II) involving the thermal cyclization reaction of 3-chloro-6-(2-allylphenoxy)pyridazines (I). As shown in Chart 1, the first step of this reaction is most probably a Diels-Alder type cycloaddition of the allylic side chain toward the pyridazine nucleus to form adducts (III). Then, nitrogen was eliminated from III to form 1,9a-dihydroxanthenes (A) and other compounds such as B–D produced from A by hydrogen transfer, and finally, HCl was removed from C or D to give xanthenes (II).

Considering the above mechanism, substitution of the side chain allyl with 2-methylallyl will stop the reaction in the stage of dihydroxanthenes such as A. Thus, in the present investigation, various 3-substituted-6-[2-(2-methylallyl)phenoxy]pyridazines and related compounds were subjected to intramolecular cycloaddition reaction.

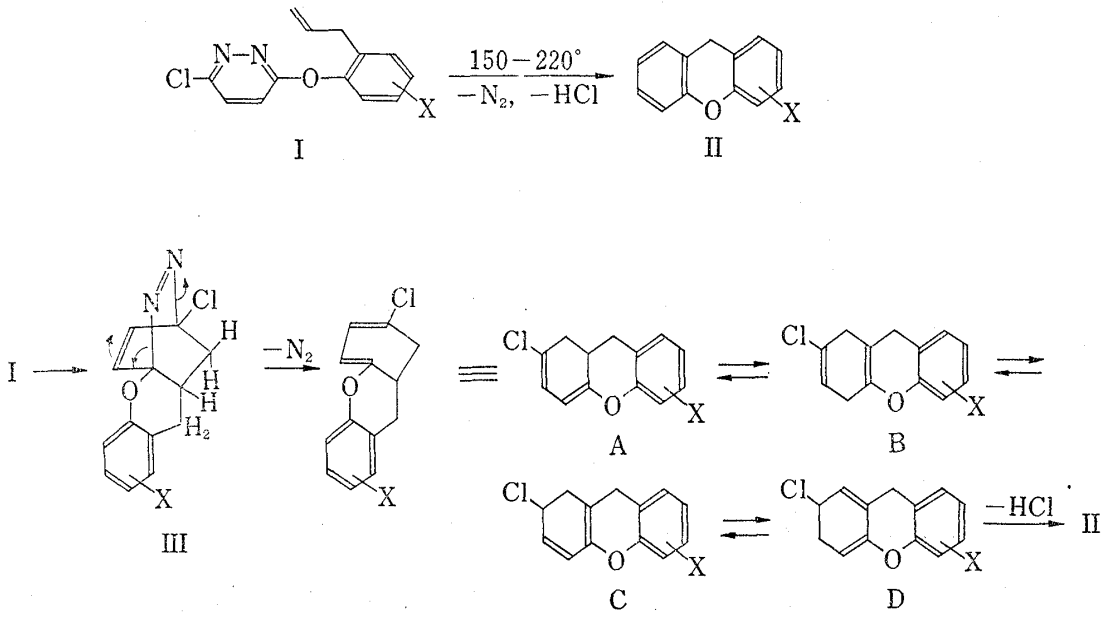


Chart 1

1) Part I: T. Jojima, H. Takeshiba, and T. Konotsune, *Chem. Pharm. Bull.* (Tokyo), **20**, 2191 (1972).
2) A part of this work was presented at the 7th Congress of Heterocyclic Chemistry, Chiba, October 1974.
3) Location: *Hiromachi, Shinagawa-ku, Tokyo.*

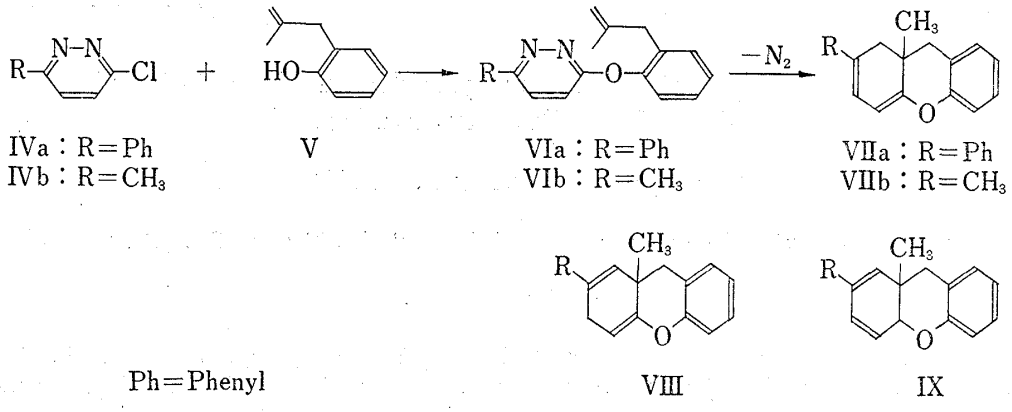


Chart 2

Reaction of 3-phenyl-, and 3-methyl-6-chlorpyridazines (IV) with sodium salt of *o*-(2-methylallyl)phenol (V) in refluxing toluene produced the corresponding 3-substituted-6-[2-(2-methylallyl)phenoxy]pyridazines (VI) in good yields. When 3-phenyl-6-[2-(2-methylallyl)-phenoxy]pyridazine (VIa) was heated in refluxing diethylaniline (DEA), a vigorous evolution of nitrogen gas was observed, and working up as usual gave rise to fine crystalls of a molecular formula, $C_{20}H_{18}O$ in an excellent yield. The structure of this compound was confirmed on the basis of the nuclear magnetic rosonance (NMR) spectrum (Fig. 1). Namely, in its NMR

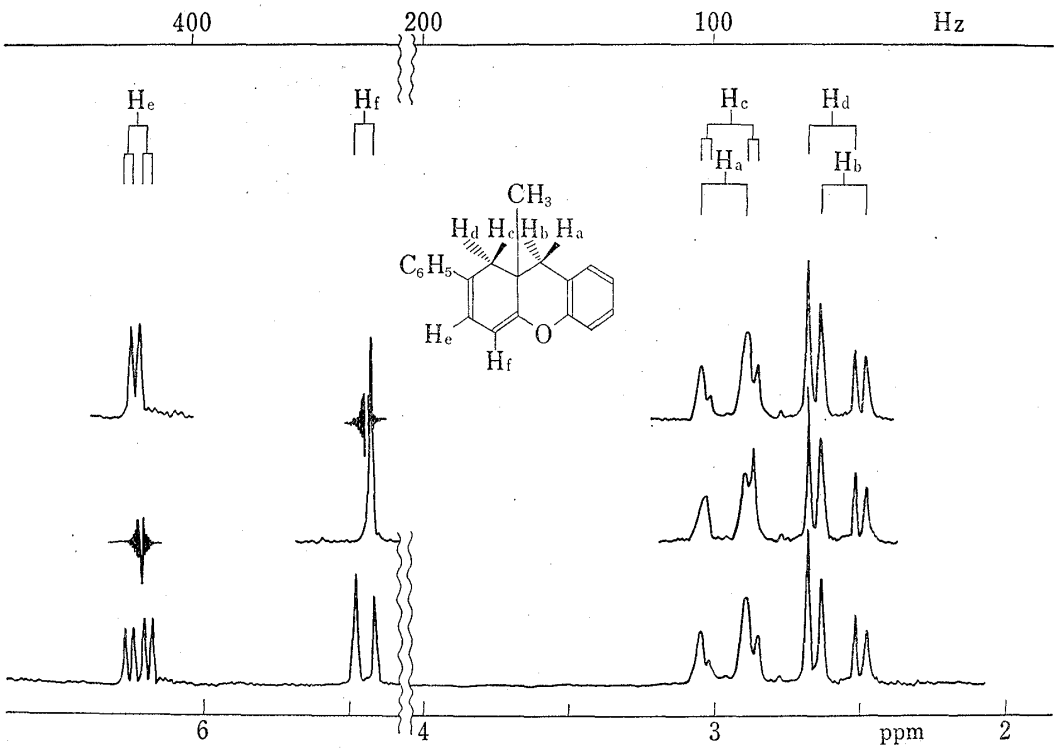


Fig. 1. NMR Spectrum of 2-Phenyl-9a-methyl-1,9a-dihydroxanthene (VIIa)

spectrum, a double-doublet (1H, J=6.0 and 2.5 Hz) centered at δ 6.23, a doublet at δ 5.45 due to H_e and H_f protons in the partial structure, $-CH_2-\dot{C}=CH_e-CH_f=C-$, two sets of broad doublets (2H) at δ 2.8—3.1 due to methylene protons coupling to a β-olefinic proton, two sets of doublets (2H) at δ 2.4—2.7 due to another methylene protons appeared in addition to a methyl and aromatic proton peaks. When the signal at δ 6.23 was irradiated the signal at δ 5.45 changed into a singlet and the doublet at δ 3.05 changed into a broad singlet, and when

the doublet at δ 5.45 was irradiated, the double-doublet at δ 6.23 changed into a doublet. From these results, this compound should be formulated as 2-phenyl-9a-methyl-1,9a-dihydroxanthene (VIIa) as shown in Chart 2, and the alternate structures such as VIII and IX were excluded.

Similarly, heating 3-methyl-6-[2-(2-methylallyl)-phenoxy]pyridazine (VIb) in DEA gave 2,9a-dimethyl-1,9a-dihydroxanthene (VIIb) in 60% yield. The ultraviolet (UV) spectra of VIIa and VIIb are shown in Fig. 2.

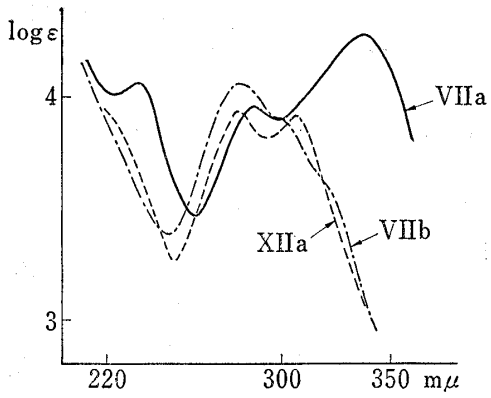


Fig. 2. UV Spectra of 2-Phenyl-9a-methyl-1,9a-dihydroxanthene (VIIa), 2,9a-Dimethyl-1,9a-dihydroxanthene (VIIb), and 2-Chloro-9a-methyl-1,9a-dihydroxanthene (XIIa)

The former compound (VIIa) shows red-shift owing to an extended conjugation of the phenyl ring in the 2-position.

Next, thermal treatment of various 3-chloro-6-[2-(2-methylallyl)phenoxy]pyridazines (XI) with or without substituents on the benzene rings gave 2-chloro-9a-methyl-1,9a-dihydroxanthenes (XII) (Chart 3).

The structure of these compounds were confirmed by microanalyses and NMR spectra. Their UV spectra were similar to that of 2-methyl derivative (VIIb), and, as an example, the spectrum of 2-chloro-9a-methyl-1,9a-dihydroxanthene (XIIa) is shown in Fig. 2. The yields of the dihydroxanthenes (XII) were good to excellent except for *o*-phenyl (XIe) and *p*-ethoxycarbonyl (XIf) derivatives (Table I).

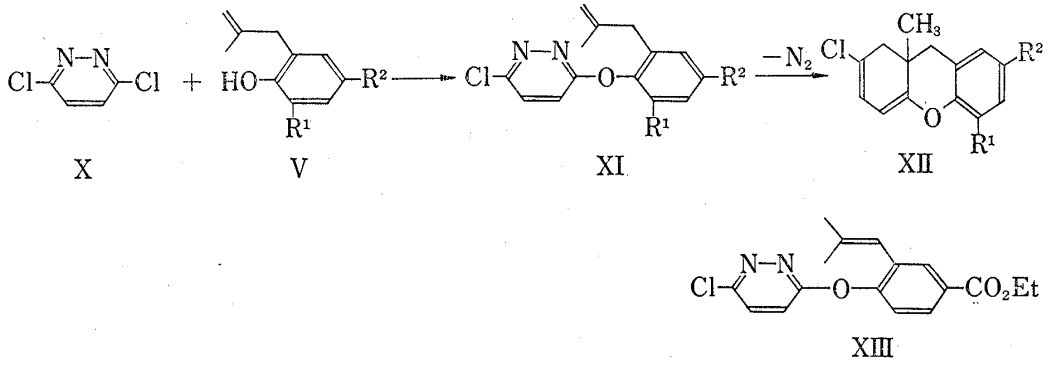


Chart 3

TABLE I. Cyclization of 3-Chloro-6-[2-(2-methylallyl)phenoxy]pyridazines (XI) to give 2-Chloro-9a-methyl-1,9a-dihydroxanthenes (XII)

Pyridazines	R^1	R^2	Solvent	Temperature	Time (hr)	Yield (%) of XII	Others
XIa	H	H	DEA	reflux	2	99	—
XIb	H	CH_3	DEA	reflux	10	79	—
XIc	CH_3	H	DEA	reflux	2	94	—
XId	CH_3O	H	DEA	reflux	2	44	XId (51%)
XIe	C_6H_5	H	DEA	reflux	5	19	XIe (75%)
XIf	H	COOEt	DEA	reflux	2	—	a mixture of XIf and XIII (33 : 67[a], total 46%)
XIf	H	COOEt	—	180—185°	4	11	a mixture of XIf and XIII (65 : 35[a], total 80%)

a) calculated from NMR spectra of the mixture

Table II. 2-Chloro-9a-methyl-1,9a-dihydroxanthenes (XII)

Compounds	R^1	R^2	Physical constant	Formula	Analyses (%) Calcd. (Found) C	H	Cl
XIIa	H	H	bp 115—118° (0.5 mmHg)	$C_{14}H_{13}OCl$	72.26 (71.44)	5.63 (5.68)	15.23 (14.46)
XIIb	H	CH_3	mp 76—79°a)	$C_{15}H_{15}OCl$	73.02 (73.05)	6.13 (6.09)	14.37 (14.27)
XIIc	CH_3	H	bp 119—125° (0.4 mmHg)	$C_{15}H_{15}OCl$	73.02 (72.90)	6.13 (6.23)	14.37 (14.05)
XIId	CH_3O	H	n_D^{27} 1.5993	$C_{15}H_{15}O_2Cl$	68.57 (68.17)	5.75 (5.75)	13.49 (13.07)
XIIe	C_6H_5	H	n_D^{25} 1.6252	$C_{20}H_{17}OCl$	77.80 (77.32)	5.55 (5.61)	11.48 (10.44)
XIIf	H	COOEt	mp 78°a)	$C_{17}H_{17}O_3Cl$	67.06 (67.19)	5.62 (5.72)	11.63 (11.48)

a) recrystallized from hexane

Cyclization of 3-chloro-6-[2-(2-methylallyl)-6-phenylphenoxy]pyridazine (XIe) proceeded very sluggishly, yielding only 19% of the cyclized product (XIIe) after 5 hr's refluxing in DEA, and 75% of the starting material was recovered. This result may be ascribed to a steric hindrance of the phenyl substituent which is located closely to the pryidazine ring.

3-Chloro-6-[4-ethoxycarbonyl-2-(2-methylallyl)phenoxy]pyridazine (XIf) did not yield any cyclized product in refluxing DEA, and a mixture of XIf and 3-chloro-6-[4-ethoxycarbonyl-2-(2-methylpropenyl)phenoxy]pyridazine (XIII) was obtained from the reaction mixture. On the other hand, heating XIf without a solvent at 180—185° for 4 hr gave the cyclized product, 2-chloro-7-ethoxycarbonyl-9a-methyl-1,9a-dihydroxanthene (XIIf, 11%) along with a mixture of XIf and XIII (80%, ratio, 65: 35). By the isomerization of XIf into XIII, strong resonance stabilization may arise between the side chain and the benzene ring. Moreover, as reported earlier,[1] 3-chloro-6-(2-propenylphenoxy)pyridazines like XIII are generally very reluctant to intramolecular cyclization, since the side chain propenyl can not locate so closely over the pyridazine ring during intramolecular cycloaddition as the allyl radical in the 2-allylphenoxy compounds. These will be the reason for the low yield in the cyclization of XIf. The physical constants of these 2-chloro-9a-methyl-1,9a-dihydroxanthenes are shown in Table II.

3-Chloro-6-[2-(2-methylallylphenoxy]pyridazines (XI) used as starting materials were obtained by the reaction of 3,6-dichloropyridazine (X) with the corresponding phenols in the presence of base.

Treatment of X and 1-(2-methylallyl)-2-naphthol (XIV) in the presence of anhyd. potassium carbonate at 165° for 2 hr produced 3-chloro-6-[1-(2-methylallyl)-2-naphthyloxy]pyridazine (XV) as the major product and 10-chloro-11a-methyl-11,11a-dihydro-12*H*-benzo[*a*]-xanthene (XVI) as the minor one. Heating XV without a solvent at 180—185° for 3 hr gave XVI in 22% yield along with a mixture of 3-chloro-6-[1-(2-methylpropenyl)-2-naphthyloxy]-pyridazine (XVII), the isomerized ether and XV (Chart 4). The structure of XVI was supported by microanalysis and spectral data. The low yield of XVI in the cyclization of XV may be ascribed to the ready isomerization of the allylic side chain of XV into propenyl to give XVII.

Finally, intramolecular cyclization of 1-phenyl-4-[2-(2-methylallylphenoxy]phthalazine (XIX) yielded a product having a little different ring system from compounds described above. Namely, refluxing XIX in DEA for 6 hr gave 5-phenyl-6a-methyl-6a,12a-dihydro-7*H*-benzo[*c*]xanthene (XXI) in 60% yield (Chart 5). The microanalysis and mass spectrum of

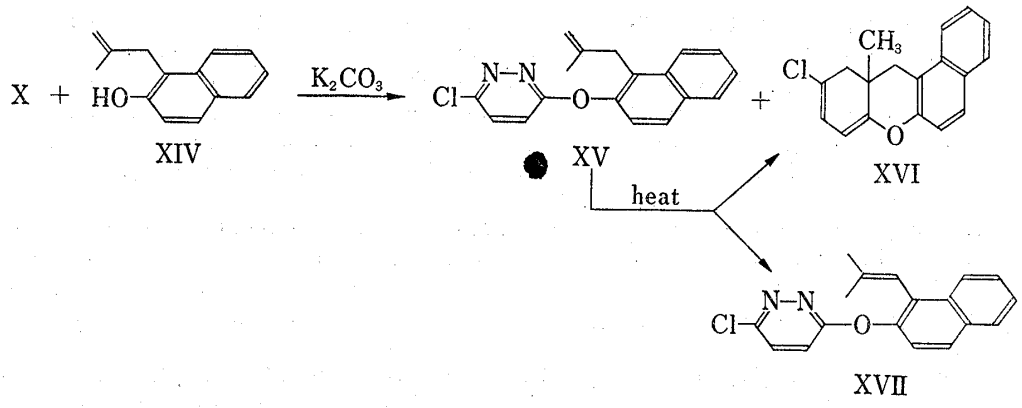
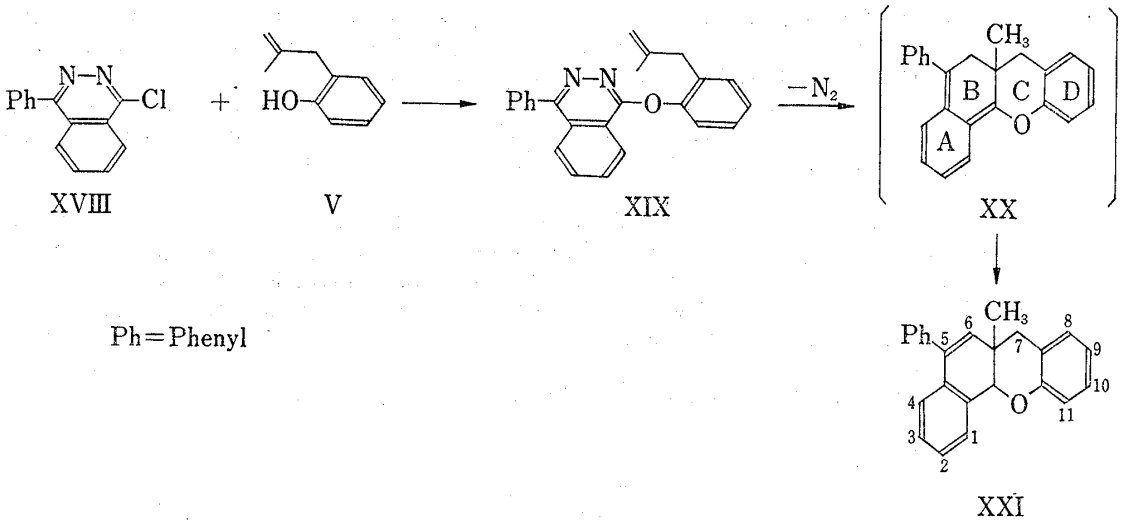


Chart 4



Ph=Phenyl

Chart 5

XXI supported the expected molecular formula $C_{24}H_{20}O$. The NMR spectrum showed a double-doublet (1H) at δ 8.07 due to C_1-proton on the 7*H*-benzo[*c*]xanthene system.[1] It also showed a singlet peak (1H) at δ 5.70 due to an allylic proton, a singlet (1H) at δ 5.30 due to a methine proton, a double-doublet (2H) at δ 2.60 due to methylene protons and a singlet peak (3H) at δ 0.88 due to a methyl in addition to aromatic proton peaks (7H). On the basis of these spectral evidences as well as the ready aromatization of the ring A of XX, the possible intermediate, the structure of XXI should be formulated as shown in Chart 5.

The dihydroxanthene derivatives disclosed in the present report are previosuly unknown type of compounds. Further studies to clarify the synthetic scope of this intramolecular cycloaddition reaction are in progress.

Experimental

All melting points are uncorrected. NMR spectra were taken using Varian A-60 and HA-100 spectrometers with tetramethylsilane as an internal standard.

***o*-(2-Methylallyl)phenols (V) and 1-(2-Methylallyl)-2-naphthol (XIV)**——These phenols were prepared by the Claisen rearrangement of the corresponding phenyl-(2-methylallyl)ethers as reported in the literature.[4] The previously unknown derivatives are as follows: 2-(2-methylallyl)-6-phenylphenol, n_D^{22} 1.5893; 2-(2-methylallyl)-4-ethoxycarbonylphenol, mp 72—74°, IR ν_{max}^{Nujol}: 1670 cm^{-1} (COOEt); 1-(2-methylallyl)-2-naphthol, n_D^{22} 1.6218.

3-Phenyl-6-[2-(2-methylallylphenoxy)]pyridazine (VIa)——Sodium (0.21 g) was added to a mixture of *o*-(2-methylallyl)phenol (3 g) and toluene (10 ml), and the mixture was refluxed for 2 hr. After cooling, 3-

4) Q.R. Bartz, R.F. Miller, and R. Adams, *J. Am. Chem. Soc.*, **57**, 371 (1935).

phenyl-6-chloropyridazine (IVa, 1.5 g)[5] dissolved in toluene (5 ml) was added, and the whole was refluxed further 6 hr. When cool, the reaction mixture was poured into dil. NaOH (20 ml), and the aq. layer was extracted twice with 20-ml portions of toluene. The combined toluene extracts were washed with water, dried over anhyd. Na_2SO_4, and the solvent was evaporated *in vacuo*. The crude product was recrystallized from hexane to give 2 g (85%) of VIa as colorless leaflets, mp 113°. NMR δ ppm ($CDCl_3$): 7.0—8.1 (9H, m, Ar), 4.70 (2H, d, $=CH_2$), 3.32 (2H, s, $-CH_2-$), 1.68 (3H, s, $-CH_3$). *Anal.* Calcd. for $C_{20}H_{18}ON_2$: C, 79.44; H, 6.00; N, 9.27. Found: C, 79.84; H, 6.11; N, 9.34.

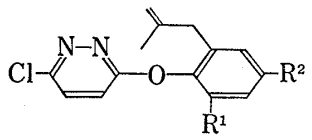
3-Methyl-6-[2-(2-methylallyl)phenoxy]pyridazine (VIb)——This compound was prepared from 3-methyl-6-chloropyridazine (IVb)[6] in the same way as above in 89% yield, mp 47° (from hexane, colorless prisms). NMR δ ppm (CCl_4): 6.8—7.4 (6H, m, Ar), 4.68 (2H, m. $=CH_2$), 3.27 (2H, s, $-CH_2-$), 2.58 (3H, s, 3-CH_3), 1.63 (3H, s, $\underline{CH_3}-\underline{C}=CH_2$). *Anal.* Calcd. for $C_{15}H_{15}ON_2$: C, 74.97; H, 6.71; N, 11.66. Found: C, 74.50; H, 6.65; N, 11.56.

2-Phenyl-9a-methyl-1,9a-dihydroxanthene (VIIa)——A mixture of VIa (1.5 g) and DEA (7 ml) was refluxed for 3 hr. Ether (20 ml) was added to the cooled reaction mixture, and the solution was washed three times with 10-ml portions of cold 6 N HCl, and then cold water. The ether layer was dried over Na_2SO_4, and the ether was evaporated *in vacuo*. The crude product was dissolved in minimum amount of benzene and passed through a column of silica gel. Elution with benzene–ethyl acetate (40: 1, v/v) gave 1.2 g (88%) of VIIa, mp 136—140° (from hexane, colorless prisms). UV λ_{max}^{EtOH} mμ (log ε): 236 (4.06), 288 (3.94), 341 (4.28). *Anal.* Calcd. for $C_{20}H_{18}O$: C, 87.56; H, 6.61. Found: C, 87.58; H, 6.65.

1,9a-Dimethyl-1,9a-dihydroxanthene (VIIb)——This compound was prepared from VIb in the same way as above in 60% yield, colorless oil, bp 117—120°/1.5 mmHg. The oil solidified to prisms after storage, mp 43.5°. UV λ_{max}^{EtOH} mμ (log ε): 280 (4.06), 301 (3.90) (sh). *Anal.* Calcd. for $C_{15}H_{16}O$: C, 84.87; H, 7.60. Found: C, 84.28; H, 7.51.

3-Chloro-6-[2-(2-methylallyl)phenoxy]pyridazines (XIa—f)——Method A): A mixture of 3,6-dichloropyridazine (X), *o*-(2-methylallyl)phenols (V) and sodium were treated in the same way as VIa. Method B): An equimolar mixture (0.04 mole) of X, *o*-(2-methylallyl)phenols and anhyd. K_2CO_3 was heated at 190° for 2.5 hr. When cool, dil. aq. NaOH (20 ml) was added to the reaction mixture, and the alkaline solution was repeatedly extracted with ether. The ether extracts were dried over anhyd. Na_2SO_4 and the solvent was

Table III. 3-Chloro-6-[2-(2-methylallyl)phenoxy]pyridazines (XI)



Compounds	R^1	R^2	Method[a]	Yield (%)	mp or bp (°C)	Formula	Analyses (%) Calcd. (Found) C	H	N
XIa	H	H	A	80	bp 174—175 (1.1 mmHg)	$C_{14}H_{13}ON_2Cl$	64.49 (64.54)	5.03 (5.17)	10.74 (10.33)
XIb	H	CH_3	A	76	54—60	$C_{15}H_{15}ON_2Cl$	65.57 (65.59)	5.50 (5.54)	10.20 (10.31)
XIc	CH_3	H	A	62	64.5	$C_{15}H_{15}ON_2Cl$	65.57 (65.27)	5.50 (5.47)	10.20 (10.14)
XId	CH_3O	H	A	89	64—65	$C_{15}H_{15}O_2N_2Cl$	61.97 (62.04)	5.20 (5.17)	9.64 (9.65)
XIe	C_6H_5	H	B	45	115—116	$C_{20}H_{17}ON_2Cl$	71.32 (71.34)	5.09 (5.14)	8.32 (8.46)
XIf	H	COOEt	A	8[b]	76—78	$C_{17}H_{17}O_3N_2Cl$	61.36 (61.77)	5.15 (5.20)	8.42 (8.52)
			B	28[c]					

a) A: The reaction of 3,6-dichloropyridazine (X) with the corresponding sodium *o*-(2-methylallyl)phenolates (V) in refluxing toluene.
B: The reaction of X with V in the presence of anhyd. K_2CO_3.
b) recovered X: 70%
c) other products: XIII, 28% calculated from NMR and XIIf, 4.9% isolated by a column

5) T. Jojima, N. Yoshimura, T. Takematsu, and S. Tamura, *Agr. Biol. Chem.*, 33, 96 (1969).
6) M. Kumagai, *Nippon Kagaku Zasshi*, **81**, 489 (1960).

evaporated *in vacuo*, and the residue was chromatographed over silica gel by elution with benzene followed by benzene–ethyl acetate (40: 1). Analytical samples were obtained by distillation for XIa and recrystallization from hexane for XIb—f. The physical constants are listed in Table III.

Cyclization of XIa—f——Method A): A mixture of XI (0.01 mole) and DEA (10 ml) was heated for appropriate period of time. Working up as described for VIIa afforded corresponding dihydroxanthenes (XIIa—e). The physical constants are tabulated in Table II.

Method B): Two g of XIf was heated at 180—185° for 4 hr. When cool, the reaction mixture was repeatedly extracted with ether. The ether extracts were dried over anhyd. Na_2SO_4, and the ether was evaporated. The crude products were chromatographed over silica gel. Elution with benzene–ethyl acetate (40: 1, v/v) gave 0.2 g (11%) of XIIf, mp 78° (colorless prisms[7]). IR ν_{max}^{Nujol} cm^{-1}: 1710 (COOEt). UV λ_{max}^{EtOH} mμ (log ε): 232 (3.91), 315 (3.94), 327 (3.90). NMR δ ppm (CCl_4): 7.6—8.0 (2H, m, 6–H+8–H), 6.82 (1H, d, 5–H), 5.90 (1H, dd, J=6.5 and 3.0 Hz, 3–H), 5.28 (1H, d, J=3.0 Hz, 4–H), 4.30 (2H, q, $-\underline{CH_2}-CH_3$), 2.22—3.48 (4H, m, $-CH_2-\dot{C}-CH_2-$), 1.37 (3H, t, $-CH_2-\underline{CH_3}$), 1.25 (3H, s, $-CH_3$). Further elution with the same solvent afforded 5.55 g (56%) of a mixture of XIf and XIII (ratio: *ca.* 50: 50 from NMR).

3-Chloro-6-[4-ethoxycarbonyl-2-(2-methylpropenyl)phenoxy]pyridazine (XIII)——The mixture (5.55 g) of XIf and XIII obtained as above was recrystallized several times from hexane to give 0.55 g of pure XIII, mp 96°, NMR δ ppm ($CDCl_3$): 7.0—8.1 (5H, m, Ar), 6.05 (1H, broad s, $-CH=C\langle$), 4.37 (2H, q, $-\underline{CH_2}-CH_3$), 1.77 [6H, s, $=C(CH_3)_2$], 1.38 (3H, t, $-CH_2-\underline{CH_3}$). *Anal.* Calcd. for $C_{17}H_{17}O_3N_2Cl$: C, 61.36; H, 5.15; N, 8.42; Cl, 10.65. Found: C, 61.67; H, 5.10; N, 8.52; Cl, 10.88.

3-Chloro-6-[1-(2-methylallyl)-2-naphthyloxy]pyridazine (XV) and 10-Chloro-11a-methyl-11,11a-dihydro-12*H*-benzo[*a*]xanthene (XVI)——A mixture of X (5.96 g), 1-(2-methylallyl)-2-naphthol (XIV, 7.93 g) and anhyd. K_2CO_3 (5.52 g) was heated at 160—165° for 2 hr. Working up as described for XIe gave crude products which were chromatographed over silica gel. Elution with hexane gave 1.3 g (12%) of XVI, mp 80—85°. NMR δ ppm (CCl_4): 7.0—7.9 (6H, m, Ar), 5.93 (1H, dd, J=6.5 and 3.0 Hz, 9–H), 5.31 (1H, d, J=6.5 Hz, 8–H), 2.3—3.3 (4H, m, $-CH_2-\dot{C}-CH_2$), 1.33 (3H, s, $-CH_3$). *Anal.* Calcd. for $C_{18}H_{15}OCl$: C, 76.46; H, 5.35; Cl, 12.54. Found: C, 76.31; H, 5.46; Cl, 12.05. Further elution with benzene gave 7.2 g (58%) of XV, mp 113—114° (from hexane). NMR δ ppm ($CDCl_3$): 7.0—8.0 (8H, m, Ar), 4.58 (2H, d, $=CH_2$), 3.70 (2H, s, $-CH_2-\dot{C}=$), 1.71 (3H, s, $-CH_3$). *Anal.* Calcd. for $C_{18}H_{15}ON_2Cl$: C, 69.57; H, 4.87; N, 9.01; Cl, 11.41. Found: C, 69.57; H, 4.77; N, 9.07; Cl, 11.68.

Cyclization of XV——Five grams of XV was heated at 180—185° for 3 hr. Working up as descrived for the cyclization of XIf gave 1 g (22%) of XVI and 3.5 g (70%) of a mixture of XV and 3-chloro-6-[2-(2-methylpropenyl)-1-naphthyloxy]pyridazine (XVII) (ratio: 45: 55 from NMR). NMR δ ppm ($CDCl_3$): 7.1—8.5 (m, Ar), 6.13 (broad s, $-CH=C\langle$), 4.60 (d. $-\dot{C}=CH_2$), 3.70 (broad s, $-CH_2-\dot{C}=$), 1.71 {s, $-CH_2-(\underline{CH_3})C=CH_2$}, 1.85 and 1.47 {d, J=1.5 Hz, $=C(CH_3)_2$}.

1-Phenyl-4-[2-(2-methylallyl)phenoxy]phthalazine (XIX)——A mixture of 1-phenyl-4-chlorophthalazine (XVIII, 1.92 g), *o*-(2-methylallyl)phenol (V, 1.2 g) and sodium (0.18 g) was refluxed in dry toluene for 3 hr. Working up as described for VIa gave 2.7 g (96%) of XIX, mp 145° (from hexane–benzene, colorless prisms). *Anal.* Calcd. for $C_{24}H_{20}ON_2$: C, 81.79; H, 5.72; N, 7.95. Found: C, 81.37; H, 5.68; N, 7.99.

Cyclization of XIX——The procedure described for the cyclization of VIa applied to XIX to give 6a-methyl-5-phenyl-6a,12a-dihydro-7*H*-benzo[*c*]xanthene (XXI) in 60% yield, mp 153—154° (from hexane, colorless prisms). UV λ_{max}^{EtOH} mμ (log ε): 252 (3.32), 258 (3.63), 266 (3.99) (sh), 272 (4.03), 280 (3.97). NMR δ ppm (CCl_4): 8.07 (1H, dd, 1–H), 6.9—7.3 (4H, m, Ar), 5.70 (1H, s, $C_6H_5-\dot{C}=CH-$), 5.03 (1H, s, $-\dot{C}H-O-$), 2.87 (1H, d, J=15 Hz, $\frac{H_A}{H_B}\rangle C-Ar$), 2.28 (1H, d, J=15 Hz, $\frac{H_A}{H_B}\rangle C-Ar$), 0.88 (3H, s, $-CH_3$). Mass Spectrum *m/e*: 325 (M+1), 309 (M–CH_3). *Anal.* Calcd. for $C_{24}H_{20}O$: C, 88.85; H, 6.21. Found: C, 88.21; H, 5.92.

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7) Recrystallization of this product from several kinds of solvents resulted in decomposition.