dibromo compound as white hexagonal plates, mp 243–247°. Recrystallization of this material from 3:1 ether–chloroform gave pure isomer, mp 250–251°, probably of structure V. This structure, which has a center of symmetry, is probably the higher melting and more insoluble isomer.

Reaction of 4,15-Dibromo[2.2]paracyclophane (V) with Potassium *t*-Butoxide in Dimethyl Sulfoxide.—Pure dibromo compound V (mp 250–251°, 18.7 g) was added rapidly to a well-stirred solution of potassium *t*-butoxide (45.6 g) and *t*-butyl alcohol (29.5 ml) in purified dimethyl sulfoxide (500 ml) at 120°. During the vigorous reaction, the temperature rose to 140°. After 2 min, the mixture (black) was poured into 1.5 l. of water. The mixture was acidified and extracted with first dichloromethane and then chloroform, and the combined organic layers were washed with saturated sodium chloride solution, dried, and evaporated. The residue (gum) was filtered through 200 g of silica gel in 3:1 benzene–ether. The filtrate was evaporated, the residue was dissolved in acetic acid (500 ml), and 350 ml of concentrated hydrochloric acid was added, followed by 1.5 l. of water. The black glass that separated (13.45 g) was dissolved in a mixture of dichloromethane and chloroform, and the solution was washed with saturated sodium bicarbonate solution. The solution was dried, evaporated, and submitted to molecular distillation at temperatures up to 260° (0.4 mm). The distillate (6.61 g) was chromatographed on 400 g of silica gel, and elution with 4:1 pentane–benzene (4.8 l.) gave mixtures of two isomeric bromohydroxymethylthioparacyclophanes, XIIa and XIIb, 3.37 g (19%). Further elution with solvents containing increasing proportions of benzene gave only traces of material until 1:2 pentane–benzene (4.2 l.) eluted 2.09 g (13.5%) of a solid mixture of isomeric bromophenols XIa and XIb. Later fractions gave gums, which could not be crystallized.

Early fractions of the bromohydroxymethylthio[2.2]paracyclophane (XII) crystallized slowly, and, after three recrystallizations from hexane, a single pure isomer was isolated as white needles, mp 118.5–119.5°. The infrared spectrum of this compound in methylene dichloride exhibited an intramolecularly bonded hydroxyl group absorbing at 3358 cm^{-1}. The nmr spectrum in carbon tetrachloride had τ 7.99 (three protons of methylthio group as a singlet), 3.43 (one proton of the hydroxyl group as a singlet which disappeared on addition of deuterium oxide), and complex aromatic and methylene protons. *Anal.* Calcd for $C_{17}H_{17}BrOS$: C, 58.45; H, 3.91; Br, 22.88; S, 9.18. Found: C, 58.44; H, 4.92; Br, 22.76; S, 9.52.

Later noncrystalline fractions of XII were combined and divided into 16 fractions by careful rechromatography on silica gel, and the last nine fractions (0.33 of material involved) were again chromatographed. The last 50% of the material collected from this chromatograph was distilled at 165° (bath) at 0.9 mm to give a second isomer of XII as an oil. The infrared spectrum of this material closely resembled that of the solid isomer, but was sufficiently different in the fingerprint region to show that it contained none of the latter. The nmr spectrum in carbon tetrachloride of the compound had τ 7.99 (three protons of the methylthio group, singlet) and 3.38 (hydroxyl proton as singlet that disappeared on addition of deuterium oxide). The aromatic region (five protons) and methylenic region (eight protons) were very complex. *Anal.* Calcd for $C_{17}H_{17}BrOS$: C, 58.45; H, 4.91; S, 9.18. Found: C, 58.53; H, 4.94; S, 9.37.

The isomeric bromophenols, XIa and XIb, were obtained distributed among seven chromatographic fractions. Recrystallized separately from cyclohexane–benzene mixtures, all of these gave material melting between 170 and 180°. Second crops all gave solids melting about 150°.

Three recrystallizations of the lower melting crops (collected) from 1:2 cyclohexane–benzene gave large hard crystals, mp 154–157°. The infrared spectrum in methylene dichloride exhibited a free hydroxyl band at 3580 cm^{-1}. *Anal.* Calcd for $C_{16}H_{15}BrO$: C, 63.38; H, 4.99; Br, 26.36. Found: C, 63.55; H, 5.02; Br, 26.17.

Four recrystallizations of the higher melting crops (collected) from benzene gave either rods or needles, mp 181.5–184.5°, whose infrared spectrum in methylene dichloride gave a free hydroxyl band at 3584 cm^{-1}. The difference in the infrared spectra of the two isomers was slight, except in the 800–1000-cm^{-1} region, where differences were prominent.

A New General Approach to the Synthesis of Oxygen-Containing Heterocycles by Virtue of Hydroxyl Neighboring Group Participation. The Condensation of Enamines with Salicylaldehydes[1]

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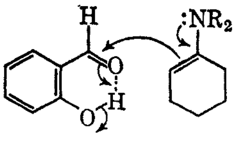
The reaction of cyclic and acyclic enamines with variously substituted salicylaldehydes has been shown to give quantitative yields of cyclic O,N-ketals having a pyran nucleus. Chromium trioxide–pyridine oxidation of such alcohols has provided an efficient, rather general, two-step synthetic route to tetrahydroxanthones, chromones, flavones, and isoflavones. Several other transformations of these products are described.

The present research was undertaken to test the possible utilization of a neighboring hydroxyl group, well known for its ability to function as a catalyst of amide and ester hydrolysis,[4,5] as a building block in the construction of oxygen heterocycles. Specifically, the conception was founded on the rationalization that intermediates of type **1**, believed to result in the reaction of enamines with aldehydes,[6] might be expected to respond to the well-established relative basicity order of alkoxide and phenoxide ions. In other words, despite the fact that **1** represents an unusual alkoxide ion (unusual in that it is zwitterionic and that its existence must, of necessity, be transitory), it appeared likely that **3** would quite possibly result if the R group bore a neighboring *phenolic* hydroxyl function as in **2**.[7] Neutralization of **3** could be readily accomplished by cyclization to a six-membered heterocyclic ring.



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[1] Unsaturated Heterocyclic Systems. XXII. For paper XXI of this series, see L. A. Paquette, *J. Am. Chem. Soc.*, **87**, 5186 (1965).

[2] Alfred P. Sloan Foundation Research Fellow.

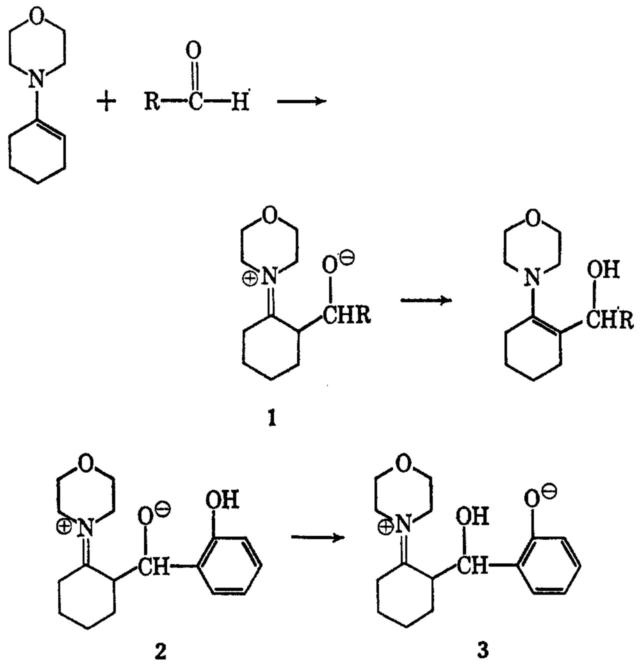
[3] National Science Foundation Undergraduate Research Participant, summer 1965.

[4] M. L. Bender, *Chem. Rev.*, **60**, 53, (1960); M. L. Bender, F. J. Kézdy, and B. Zerner, *J. Am. Chem. Soc.*, **85**, 3017 (1963).

[5] T. C. Bruice and T. H. Fife, *ibid.*, **84**, 1973 (1962); T. C. Bruice and F.-H. Marquardt, *ibid.*, **84**, 365 (1962); T. C. Bruice and D. W. Tanner, *J. Org. Chem.*, **30**, 1668 (1965).

[6] L. Birkhofer, S. M. Kim, and H. D. Engels, *Chem. Ber.*, **95**, 1495 (1962).

[7] Although the mechanistic detail has been pictured in a stepwise fashion, it is, of course, possible that the entire process may be concerted and not mediated by species **3**.



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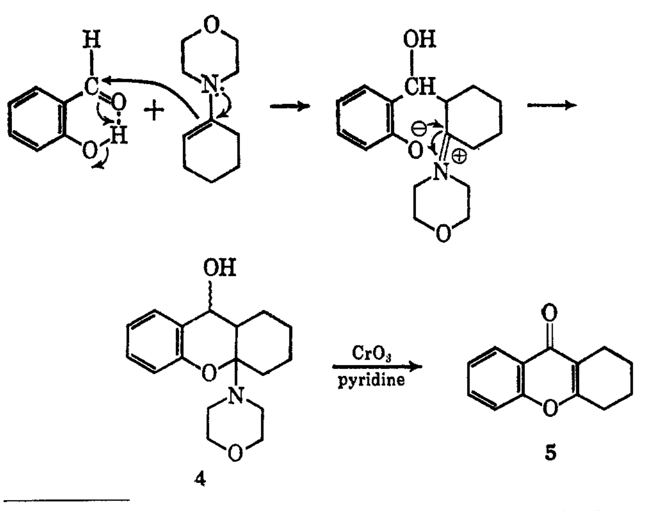
3

In actual fact, the anticipated reaction proceeds smoothly and results in the ready formation of cyclic O,N-ketals having the pyran nucleus. Further simple transformations of such adducts have provided a valuable new approach to the synthesis of tetrahydroxanthones,[8] chromones, flavones, and isoflavones. In addition, the method, which has proven quite general in scope among the cases investigated, possesses the distinct advantages that the starting materials are readily available and that the few required steps are easily carried out.[9]

The system chosen initially for study was the condensation of salicylaldehyde with 1-morpholinocyclohexene. Admixture of equimolar quantities of these two substances in an inert solvent such as benzene or hexane resulted in a mildly exothermic reaction and gave in very high yield a noncrystalline viscous oil formulated as **4**. In agreement with structure **4**, the adduct exhibited a strong infrared peak at 3350 cm^{-1} and lacked significant absorption in the 1630–1700 cm^{-1} region. Chemical confirmation was realized by Sarett oxidation[10] of this complex alcohol to the known tetrahydroxanthone **5** in 55% over-all yield. These results argue for the reaction course anticipated, for no plausible alternative mechanisms are available to explain the ultimate attachment of the phenolic oxygen atom to the cyclohexane ring derived from the enamine.



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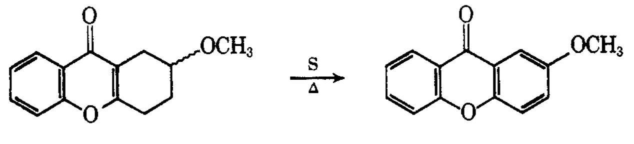
An identical reaction course was observed with the morpholine enamine of 4-methoxycyclohexanone. Dehydrogenation of **6**, obtained in 41% yield, by heating with elemental sulfur at 210–240° gave a good yield of 2-methoxyxanthone (**7**). The advantages of the present xanthone synthesis may be gauged by comparison with another recently reported synthesis of **7**,[11] wherein low yields and difficultly separable mixtures plagued the investigators.



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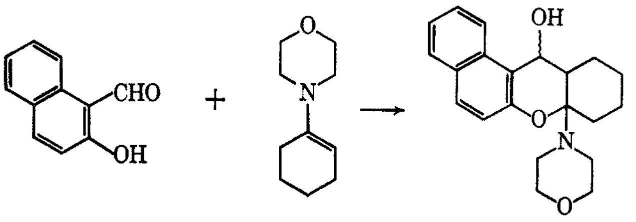
In a number of cases, exemplified by the addition of 1-morpholinocyclohexene to 2-hydroxy-1-naphthaldehyde, crystalline adducts such as **8** were slowly deposited when the benzene solution was allowed to stand overnight at room temperature. Although the rather sharp melting points of this group of solids would strongly suggest the presence of a single stereoisomer in each instance, we have not been able to determine unequivocally the orientation of the hydroxyl group on the basis of the available spectral data.



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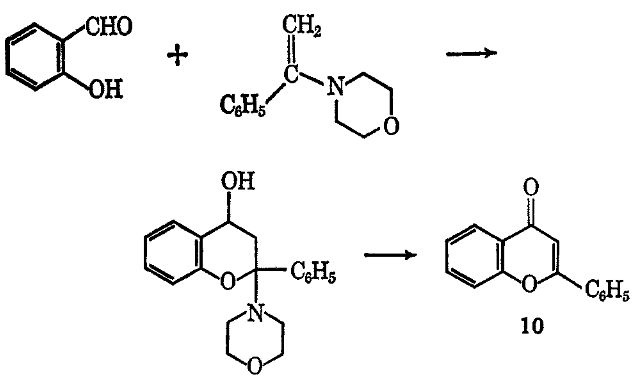
Turning our attention to acyclic enamines, we allowed salicylaldehyde to react with 1-morpholino-1-phenylethylene in benzene solution to form the noncrystalline adduct **9**; this was oxidized to **10** with



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10

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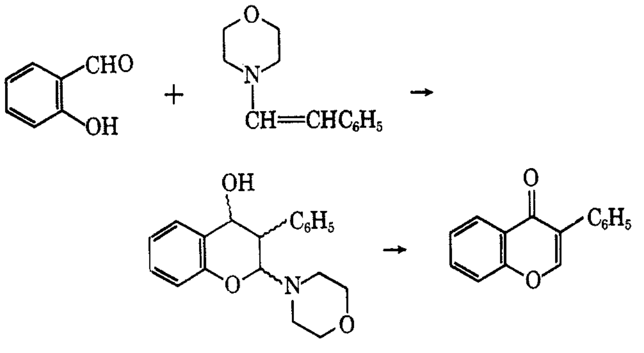
(8) A preliminary account of this work has been published: L. A. Paquette, *Tetrahedron Letters*, 1291 (1965).

(9) For surveys of previous methods employed in the preparation of this group of heterocycles, see S. Wawzonek in "Heterocyclic Compounds," Vol. 2, R. C. Elderfield, Ed., John Wiley and Sons, Inc., New York, N. Y., 1951, Chapters 8 and 12.

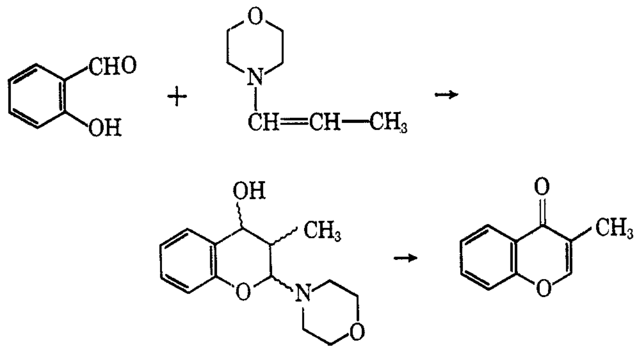
(10) G. I. Poos, G. E. Arth, R. E. Beyler, and L. H. Sarett, *J. Am. Chem. Soc.*, **75**, 422 (1953).

(11) R. A. Finnegan and P. L. Bachmann, *J. Pharm. Sci.*, **54**, 633 (1965).

chromium trioxide–pyridine. Isoflavone (**12**) was likewise readily prepared from N-styrylmorpholine and salicylaldehyde, followed by oxidation of the primary product **11**. When 1-morpholino-1-propene was treated with salicylaldehyde in the absence of solvent, there was formed a crystalline 1:1 adduct, with spectral properties corresponding to **13**. The nmr spectrum of this material indicated it to be a mixture of isomers despite its rather sharp melting point characteristics (albeit with decomposition). Oxidation of **13** to 3-methylchromone (**14**) served further to determine the carbon framework of this cycloadduct.



11 **12**



13 **14**

Several preliminary attempts to employ 2,5-dihydroxybenzaldehyde in such condensation reactions proved unsuccessful. In contrast, high yields were achieved with *o*-vanillin (2-hydroxy-3-methoxybenzaldehyde). Apparently, therefore, the presence of additional phenolic hydroxyl groups served to interfere with the cycloaddition process, as might be expected from the proposed mechanistic pathway.

In conclusion, we wish to call attention to somewhat related phenomena. For example, the reaction of enamines with an excess of diketene has been shown to give tetrahydrochromones.[12] Also, Miyano has recently observed that salicylic acids and 1-morpholinocyclohexene in the presence of dicyclohexylcarbodiimide will give rise to tetrahydroxanthones among several other products.[13] von Strandtmann and coworkers have found it possible to isolate similar cyclic O,N-acetals from the interaction of enamines with Mannich bases.[14]

Experimental Section[15]

General Procedure for the Reaction of Salicylaldehydes with Enamines.—A solution of the salicylaldehyde in anhydrous benzene was treated in one portion with an equimolar quantity of the enamine dissolved usually in the same volume of identical solvent. The resulting solution was allowed to stand in a loosely stoppered flask for a period of 24 hr. If no crystals had formed, the solvent was removed *in vacuo* and the viscous oil was generally used without further purification.[16] If crystals had deposited, the reaction mixture was cooled for a brief period of time and the solid was separated by filtration. The product was subsequently recrystallized to constant melting point.

General Procedure for the Chromium Trioxide–Pyridine Oxidation of the Primary Adducts.—To a stirred suspension of the chromium trioxide–pyridine complex in pyridine[10] cooled in an ice bath was added dropwise a solution of the alcohol in pyridine. Upon completion of the addition, the mixture was stirred with cooling for another 2 hr and was allowed to stand overnight at room temperature. The mixture was poured into ice water and and the dark brown slurry was extracted with ether. The combined ether layers were washed three times with water, dried, filtered, and evaporated. The crystalline product was most easily separated from adhering quantities of pyridine by rapid elution (with ether–hexane, 1:1) through a small column of alumina. The crystalline product was then recrystallized to constant melting point.

1,2,3,4-Tetrahydroxanthone (5).—From 2.5 g (0.02 mole) of salicylaldehyde and 3.3 g (0.02 mole) of 1-morpholinocyclohexene[17] in a total volume of 4 ml of benzene there was obtained 5.8 g (100%) of a pale yellow viscous oil.

Oxidation of this alcohol with 10 g (0.10 mole) of chromium trioxide in 100 ml of pyridine gave 2.1 g (52.5%) of white solid, mp 100–102°. Three recrystallizations from hexane gave pure white prisms of **5**, mp 102–103° (lit.[18] mp 104°). The oxidation product **5** was further characterized by nitration (fuming nitric acid, 0°) to the known 7-nitro derivative, mp 202° (lit.[18] mp 203°).

4-Methoxy-1-morpholino-1-cyclohexene.—A solution of 25 g (0.218 mole) of 4-methoxycyclohexanone,[19] 22 g (0.218 mole) of morpholine, and 0.3 g of *p*-toluenesulfonic acid in 42 ml of toluene was refluxed in a nitrogen atmosphere for 9 hr under a Dean–Stark trap. After cooling the reaction mixture, the solvent was removed and the residue was fractionated to give 30.9 g (75%) of the enamine, bp 99.5° (0.5 mm), ν^{CCl_4} 1650 cm^{-1}.

2-Methoxy-1,2,3,4-tetrahydroxanthone (6).—From 7.1 g (0.058 mole) of salicylaldehyde and 11.0 g (0.058 mole) of 4-methoxy-1-morpholino-1-cyclohexene in 30 ml of dry benzene there was obtained 18.1 g (100%) of a glassy yellow oil. Oxidation of this adduct with 30.5 g (0.305 mole) of chromium trioxide in 240 ml of pyridine gave 10.6 g (41%) of **6** as white crystals, mp 101° (from Skellysolve C), ν^{Nujol} 1650 and 1590 cm^{-1}.

Anal. Calcd for $C_{14}H_{14}O_3$: C, 73.02; H, 6.13. Found: C, 72.84; H, 6.03.

2-Methoxyxanthone (7).—An intimate mixture of 1.16 g (5.43 mmoles) of **6** and 380 mg (12 mmoles) of sulfur flowers was heated at 210–240° for 5 hr. The brown reaction mixture was dissolved in a small amount of chloroform and chromatographed on neutral alumina (elution with hexane–ether, 3:2) to yield 660 mg (59%) of **7** as white crystals, mp 130.0–130.4° (lit. mp 131°,[20] 133–134°[11]), ν^{Nujol} 1660 and 1620 cm^{-1}. This material proved identical in all respects with an authentic sample.[21]

5-Methoxy-1,2,3,4-tetrahydroxanthone.—From 11.4 g (0.08 mole) of *o*-vanillin and 13.4 g (0.08 mole) of 1-morpholinocyclohexene in 32 ml of anhydrous benzene there was obtained 24.7 g (100%) of a dense light brown oil. Oxidation of this crude adduct with 44.5 g (0.445 mole) of chromium trioxide in 330 ml

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[12] B. B. Millward, *J. Chem. Soc.*, 26 (1960); S. Hünig, E. Benzing, and K. Hübner, *Chem. Ber.*, **94**, 486 (1961).

[13] M. Miyano, *J. Am. Chem. Soc.*, **87**, 3958 (1965).

[14] M. von Strandtmann, M. P. Cohen, and J. Shavel, Jr., *Tetrahedron Letters*, 3103 (1965); *J. Org. Chem.*, **30**, 3240 (1965).

[15] Melting points and boiling points are uncorrected. Infrared spectra were determined with a Perkin-Elmer Model 137 Infracord spectrophotometer. Elemental analyses were obtained from the Scandinavian and Huffman Microanalytical Laboratories.

[16] The primary adducts appear to be formed in near quantitative yield.

[17] S. Hünig, E. Lücke, and W. Brenninger, *Org. Syn.*, **41**, 65 (1961).

[18] H. I. Hall and S. G. P. Plant, *J. Chem. Soc.*, 232 (1933).

[19] The authors are indebted to M. S. Duggan of the Upjohn Co. for a generous sample of this material.

[20] F. Ullmann and M. Zlokasoff, *Ber.*, **38**, 2111 (1905).

[21] The authors are indebted to Professor R. A. Finnegan and Dr. P. L. Bachmann for the generous gift of **7**.

of pyridine afforded 10.9 g (42.0%) of white crystals, mp 113° (from Skellysolve C), ν^{Nujol} 1640 and 1590 cm^{-1}.

Anal. Calcd for $C_{14}H_{14}O_3$: C, 73.02; H, 6.13. Found: C, 72.86; H, 6.04.

4-Methoxyxanthone.—The tetrahydroxanthone above (1.6 g, 7.5 mmoles) was dehydrogenated with sulfur as above to give 980 mg (61.2%) of the xanthone, mp 168–169° (from Skellysolve C) (lit.[20] mp 173°).

2,5-Dimethoxy-1,2,3,4-tetrahydroxanthone.—From 11.4 g (0.08 mole) of *o*-vanillin and 15.1 g (0.08 mole) of 4-methoxy-1-cyclohexene in 32 ml of dry benzene there was isolated 24.2 g (91.5%) of pale yellow crystals of 1,2,3,4,4a,9a-hexahydro-2,5-dimethoxy-4a-morpholinoxanthen-9-ol, mp 92.5–93.0° (from benzene), ν^{Nujol} 3320 and 1580 cm^{-1}.

Anal. Calcd for $C_{19}H_{27}NO_5 \cdot C_6H_6$: C, 70.23; H, 7.78; N, 3.28. Found: C, 70.77; H, 7.75; N, 3.45.

Oxidation of 22.3 g (0.064 mole) of this purified adduct with 35 g (0.35 mole) of chromium trioxide in 345 ml of pyridine yielded 7.5 g (46%) of the tetrahydroxanthone, mp 90° (from Skellysolve C), ν^{Nujol} 1660 and 1590 cm^{-1}.

Anal. Calcd for $C_{16}H_{16}O_4$: C, 69.21; H, 6.20. Found: C, 68.56; H, 5.96.

5,7-Dichloro-1,2,3,4-tetrahydroxanthone.—From 8.0 g (0.042 mole) of 3,5-dichloro-2-hydroxybenzaldehyde[22] and 8.0 g (0.042 mole) of 1-morpholinocyclohexene in 16 ml of dry benzene there was isolated 15.5 g (97%) of grayish crystals, mp 131–132°, which began to separate immediately after admixture of the two reactants. This alcohol, which proved to be quite insoluble in certain solvents, was difficult to purify by recrystallization and therefore was not prepared for elemental analysis.

Oxidation of a 5.0-g (0.0134-mole) sample of the crude alcohol with 7.0 g (0.07 mole) of chromium trioxide in 100 ml of pyridine afforded 2.86 g (81.0%) of the tetrahydroxanthone, mp 171–172° (from Skellysolve C–chloroform), ν^{Nujol} 1640 and 1620 cm^{-1}.

Anal. Calcd for $C_{13}H_{10}Cl_2O_2$: C, 58.01; H, 3.72; Cl, 26.93. Found: C, 57.94; H, 3.79; Cl, 25.93.

8,9,10,11-Tetrahydro-12H-benzo[*a*]xanthen-12-one.—From 3.4 g (0.02 mole) of 2-hydroxy-1-naphthaldehyde[23] and 3.3 g (0.02 mole) of 1-morpholino-1-cyclohexene in 10 ml of dry benzene there was obtained 6.7 g (100%) of a viscous oil which crystallized on scratching, mp 85–90°. Recrystallization from acetone raised the melting point to 90–91°. After several months at room temperature, the pure solid was observed to slowly revert to a thick brown oil.

Anal. Calcd for $C_{21}H_{25}NO_3$: C, 74.31; H, 7.42; N, 4.13. Found: C, 74.49; H, 7.60; N, 3.90.

Oxidation of 7.8 g (0.023 mole) of the pure alcohol with 12.5 g (0.125 mole) of chromium trioxide in 170 ml of pyridine afforded 4.3 g (74.8%) of long, fine, white crystals, mp 155.5° (from ether), ν^{Nujol} 1640 and 1605 cm^{-1}.

Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C, 81.63; H, 5.67.

1,2-Benzoxanthone.—A mixture of 1.1 g (4.4 mmoles) of the above tetrahydroxanthone, 1 g of 10% palladium on charcoal, and 3 ml of decalin was refluxed for 24 hr. The cooled mixture was diluted with chloroform, filtered to remove the insoluble materials, and evaporated *in vacuo*. The solid residue was recrystallized from ethanol to give 900 mg (82%) of pale yellow needles, mp 142–142.5° (lit.[24] mp 143°).

1-Morpholino-1-phenylethylene.—A solution of 12 g (0.10 mole) of acetophenone and 13 g (0.15 mole) of morpholine in 40 ml of toluene was refluxed in an atmosphere of nitrogen under a Dean-Stark trap for 6 days. After evaporation of the solvent, the residual oil was distilled to give 12.6 g (89.4%) of colorless liquid, bp 74–75° (0.2 mm) [lit. bp 86–89° (0.1 mm),[25] 72° (0.02 mm),[26] 85–86° (0.2 mm)[27]].

Flavone (12).—From 7.0 g (0.05 mole) of 1-morpholino-1-phenylethylene and 6.1 g (0.05) mole of salicylaldehyde in 20 ml of dry benzene there was obtained 13.1 g of a viscous dark yellow oil (**9**). Oxidation of this quantity of **9** with 24 g (0.24 mole) of chromium trioxide in 175 ml of pyridine produced 3.64 g (38.1%) of colorless crystals, mp 95.3–96.3° (from hexane) (lit.[28] mp 97°).

Isoflavone. (12)—From 7.5 g (0.053 mole) of N-styrylmorpholine[29] and 6.5 g (0.053 mole) of salicylaldehyde in 10 ml of dry benzene (solution was refluxed under nitrogen for 4 hr) there was obtained 14.0 g of a viscous yellowish oil (**11**). Oxidation of this quantity of **11** with 29.6 g (0.296 mole) of chromium trioxide in 175 ml of pyridine gave rise to 4.8 g (46.2%) of white crystals, mp 150° (from hexane) (lit. mp 148°,[30] 131°[31]).

Anal. Calcd for $C_{15}H_{10}O_2$: C, 81.06; H, 4.54. Found: C, 81.03; H, 4.58.

8-Methoxyisoflavone.—From 7.5 g (0.053 mole) of N-styrylmorpholine and 7.5 g (0.053 mole) of *o*-vanillin in 10 ml of dry benzene (solution was refluxed under nitrogen for 4 hr) there was obtained 15 g of a viscous yellow oil. Oxidation of this material with 29 g (0.29 mole) of chromium trioxide in 300 ml of pyridine afforded 5.4 g (42.8%) of white crystals of the isoflavone, mp 138–139°.

Anal. Calcd for $C_{16}H_{12}O_3$: C, 76.18; H, 4.80. Found: C, 76.30; H, 4.86.

3-Methylchromone (14).—1-Morpholino-1-propene (33.3 g, 0.26 mole) and salicylaldehyde (33.0 g, 0.26 mole) were mixed without solvent. A solid (66.0 g, 100%) slowly formed which upon recrystallization from benzene gave white crystals of **13**, mp 124–125° dec, ν^{Nujol} 3250 cm^{-1}.

Anal. Calcd for $C_{14}H_{19}NO_3$: C, 67.44; H, 7.68; N, 5.62. Found: C, 67.14; H, 7.55; N, 5.44.

Oxidation of 22.0 g (0.12 mole) of **13** with 44.5 g (0.45 mole) of chromium trioxide in 350 ml of pyridine yielded 6.0 g (30.5%) of **14**, mp 69.8–70.6° (from hexane) (lit.[32] mp 68°).

Acknowledgment.—The authors acknowledge with gratitude the financial support of the National Institutes of Health, U. S. Public Health Service.

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(22) Obtained from the Gallard-Schlesinger Chemical Mfg. Corp., Long Island, N. Y.

(23) Obtained from the Aldrich Chemical Co., Milwaukee, Wis.

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