Elimination of Dithiocarboxyl Group from I and VI.—Compound I (2 g) was refluxed with 8 ml of morpholine for several minutes. After being cooled, the separated crystals were collected, washed with ether, and dried to yield 1.9 g (73%). Recrystallization from morpholine gave colorless needles (1.2 g) which were identified with IX by mixture melting point and infrared spectrum.

Compound VI was treated in the same way as above to give IX in 65% yield. It seemed that the reaction of VI was somewhat slow. Further, I, on treatment with piperidine, gave only an oily product.

Reaction of 3,4-Dihydro-4,4,6-trimethyl-2H-1,3-thiazine-2-thione (VII) and 4,4,6-Trimethyldihydro-2H-3,1-thiazine-2-thione (VIII) with Morpholine.—Compound VII which was prepared by the method of Jansen and Mathes,[3] on the same treatment as above, yielded an oily product, which was not studied further.

Compound VIII (2 g) was refluxed with 8 ml of morpholine for 15 min; upon heating the solution turned in the sequence of yellow, yellowish green, yellow, and finally red. After being cooled, the whole was poured in 30 ml of ice–water and stirred thoroughly. The solid product was collected, washed with water and ether, and dried: yield 0.4 g. Recrystallization from ethanol gave colorless plates (*ca.* 0.2 g), mp 175–176°.

Anal. Found: C, 41.14; H, 6.29; N, 19.02; S, 22.19.

The compound was not investigated further.

2-Ethyldihydro-2,5,6-trimethyl-4H-3,1-thiazine-4-thione (X).—A mixture of methyl ethyl ketone (50 g, 0.69 mol), carbon disulfide (53 g, 0.63 mol), and 145 ml of aqueous ammonia (28%) was reacted as mentioned already below 0°. When the crude product was recrystallized from methanol, *ca.* 12 g of yellow plates (X) was obtained: mp 145–146°; Grote test, yellow ochre; color reaction toward cupric ion, deep red; uv max (99% EtOH) 334 mμ (log ε 3.65), 406 (ε 3.35); ir (KBr) 3165 (s), 1548 (s), 1516 (vs), 1452 cm^{-1} (m); ir ($CHCl_3$) 3396 (s), 1525 (s), 1455 cm^{-1} (m).

Anal. Calcd for $C_9H_{15}NS_2$: C, 53.72; H, 7.51; N, 6.96; S, 31.81; mol wt (vapor pressure osmometer), 201.22. Found: C, 53.87; H, 7.44; N, 6.82; S, 31.88; mol wt, 200 (in acetone).

In this case, XI (mentioned below) could not be isolated, and XII (also mentioned below) was isolated in poor yield (0.5 g).

4-Ethyl-3,4-dihydro-4,5,6-trimethyl-2(1H)-pyrimidinethione (XI).—The proceding reaction was carried out at 25–30° for *ca.* 70 hr and then kept overnight. The reaction mixture was concentrated, and the yellow pasty mass which separated from the solution was collected and washed with water and ether. The crude product, which weighed *ca.* 16 g, was washed with methanol and recrystallized from ethanol to give *ca.* 12 g of colorless short prisms (XI): mp 246–247°; Grote test, light yellowish green tinged with ochre; uv max (99% EtOH) 265 mμ (log ε 4.08); ir (KBr) 3210 (s), 1702 (m), 1575 cm^{-1} (s).

Anal. Calcd for $C_9H_{16}N_2S$: C, 58.67; H, 8.75; N, 15.21; S, 17.37; mol wt (vapor pressure osmometer), 184.23. Found: C, 58.64; H, 8.48; N, 15.14; S, 17.33; mol wt, 189 (in chloroform).

An additional amount (*ca.* 0.5 g) of X was isolated by concentrating the above methanol washings.

4,5-Dimethyl-1,2-dithiole-3-thione (XII).—To a mixture of methyl ethyl ketone (50 g, 0.69 mol), carbon disulfide (53 g, 0.63 mol), and 300 ml of aqueous ammonia (28%) was gently passed hydrogen sulfide for *ca.* 8 hr with stirring at 25–33° and then kept overnight. When the reaction mixture was concentrated, an yellow-orange pasty mass was obtained, washed with water, and dried; yield *ca.* 2 g. The crude product was shaken with carbon tetrachloride and filtered. The filtrate was concentrated to give *ca.* 1 g of yellow needles (XII): mp 96°; Grote test, dark green; uv max (99% EtOH) 225 mμ (log ε 4.00), 243 (sh) (3.77), 275 (3.81), 310 (3.73), 409 (4.01).

Anal. Calcd for $C_5H_6S_3$: C, 37.05; H, 3.73; S, 59.22; mol wt (vapor pressure osmometer), 162.10. Found: C, 37.05; H, 3.78; S, 59.27; mol wt, 161.2 (in chloroform).

The above crude product from which XII was removed was recrystallized from methanol to give *ca.* 1 g of X.

Registry No.—I, 16504-29-3; II, 16504-30-6; III, 16504-31-7; IV, 16504-32-8; V, 5778-17-6; VI, 16504-34-0; X, 16504-35-1; XI, 16504-36-2; XII, 3354-39-0; carbon disulfide, 75-15-0; ammonia, 7664-41-7; acetone, 67-64-1; methyl ethyl ketone, 78-93-3.

Acknowledgment.—The authors are grateful to Dr. Hiroshi Midorikawa (The Institute of Physical and Chemical Research) for his generous aid in many respects. Heartfelt thanks are also owed to Dr. Heinosuke Yasuda and Miss Hiroe Asaba for their useful advice and help.

The Rearrangement of Methoxylated Phenylanthranils

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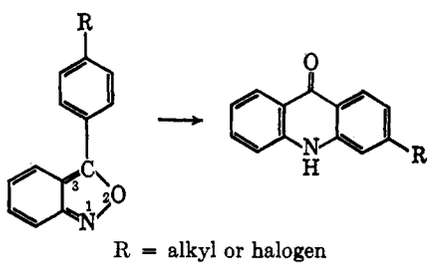
Received February 26, 1968

Methoxylated phenylanthranils rearrange under pyrolytic conditions to acridones in which the nitrogen is *para* instead of *meta* to the methoxyl function. In the presence of nitrous acid, these methoxylated anthranils yield substituted azoxybenzoic acids instead of the anticipated acridones. This new rearrangement and reaction of methoxylated phenylanthranils may be explained by the activating effect of the methoxyl function on the position *para* to it. A nitrene has been proposed as the intermediate in the rearrangement. The application of these new reactions to the synthesis of compounds related to the anticancer alkaloid, acronycine, is reported.

Acridones are often synthesized by the rearrangement of phenylanthranil and *para*-substituted phenylanthranils[1-6] catalyzed by nitrous acid or heat. The yields are generally high and the *para* relationship of the substituent R of the phenyl ring to the carbon 3 of the anthranil ring system has been shown to remain after the rearrangement.[5] The lack of information concerning the rearrangement of alkoxyphenylanthranils and the need for methoxyacridones prompted us to investigate this rearrangement. These methoxyacridones were necessary as starting materials for our work



R = alkyl or halogen

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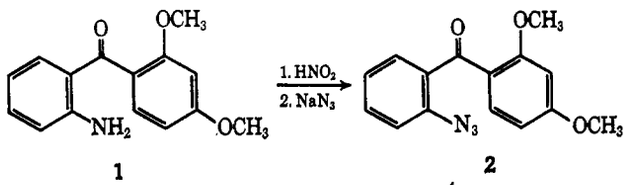
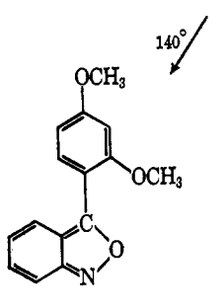
(2) E. Bamberger, *ibid.*, **42**, 1707 (1909).
(3) I. Tanasescu and M. Suciu, *Bull. Soc. Chim. Fr.*, **4**, 245 (1937).
(4) R. B. Davis and L. C. Pizzini, *J. Org. Chem.*, **25**, 1884 (1960).
(5) I. Tanasescu, C. Anghel, and A. Popescu, *Studia Univ. Babes-Bolyai, Ser. 1*, **8**, 141 (1963); *Chem. Abstr.*, **61**, 13279*d* (1964).
(6) P. L. Coe, A. E. Jukes, and J. C. Tatlow, *J. Chem. Soc., Sect. C*, 2020 (1966).

in the synthesis of acronycine.[7,8] The study of the rearrangement of 3-(2,4-dimethoxyphenyl)anthranil (**3**) was therefore undertaken.

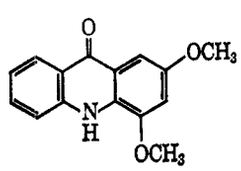


1 **2**



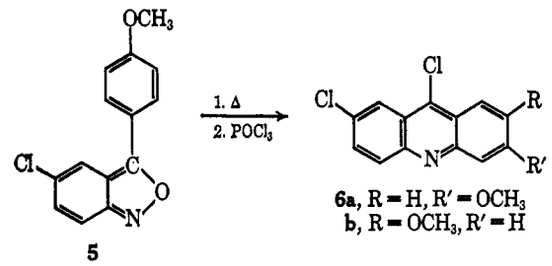
3

Phenylanthranil has been reported as the product from the pyrolysis of 2-azidobenzophenone.[9] Accordingly, conversion of 2,4-dimethoxy-2′-aminobenzophenone[10] (**1**) into 2,4-dimethoxy-2′-azidobenzophenone (**2**) followed by pyrolysis at 140° gave **3**. Pyrolysis of **3** at 260° gave a dimethoxyacridone in 50% yield which was not the expected 1,3-dimethoxyacridone.[11] There was no evidence of any of the expected product. Based on nmr data the product was assigned the structure 2,4-dimethoxyacridone (**4**). H-2 and H-4 of 1,3-dimethoxyacridone in DMSO-d_6 appear as two doublets at 6.26 and 6.51 ppm (J = 2 cps). H-3 of **4** in $CDCl_3$ can be observed as a doublet at 6.67 ppm (J = 2.5 cps). H-1 is deshielded by the carbonyl function and can not be distinguished from the rest of the aromatic protons.



4

The formation of this unexpected product indicated that the methoxy groups may have a strong directing effect on the rearrangement. 3-(*p*-Methoxyphenyl)-5-chloroanthranil[4] (**5**) was pyrolyzed in the same manner in order to assess the influence of the methoxy function on this novel rearrangement. The crude product was very insoluble and was converted into the corresponding 9-chloroacridine by treatment with phosphorous oxychloride.[5] Purification by column chromatography led to the separation of two isomeric 9-chloroacridines in the ratio of 3:1. The major component, mp 192–195°, was assigned the 3-methoxy-7,9-di-



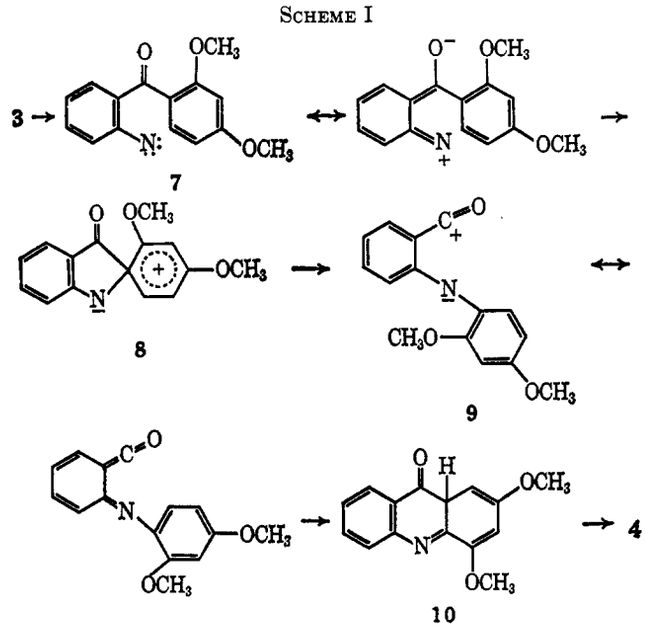
5

6a, R = H, R′ = OCH_3
b, R = OCH_3, R′ = H

chloroacridine (**6a**) structure (lit.[12] mp 194–195°) and the minor component, mp 200–203, was assigned the 2-methoxy-7,9-dichloroacridine (**6b**) structure (lit.[13] mp 204–205°).

The above observations clearly indicate that the methoxy function is changing the course of the rearrangement by activating the position *ortho* and *para* to it. The probable mechanism is outlined in Scheme I. Presumably, a nitrene **7** is initially formed, followed by the formation of a five-membered intermediate **8**. This intermediate **8** is a result of the attack of the positively charged nitrogen at the activated position. In the absence of an activating group, a six-membered intermediate will be formed, leading to the normal rearrangement product, without breaking any C–C bond. Cleavage of the C–C bond of the five-membered ring gives **9**, followed by ring closure to give **10**, which gives the product **4** by a proton shift.

SCHEME I



7 **8** **9** **10**

The nitrous acid catalyzed rearrangement of these substituted phenylanthranils was also investigated. When **5** was treated with sodium nitrite in 5% sulfuric acid in acetic acid, instead of an acridone, a yellow crystalline product was obtained in good yield. Physical and spectral informations pointed to an azoxy function. Even though no satisfactory elemental analysis was obtained, the product, which was probably contaminated with some azo compound was assigned structure **11**. Further support for this structural assignment came

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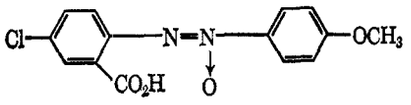


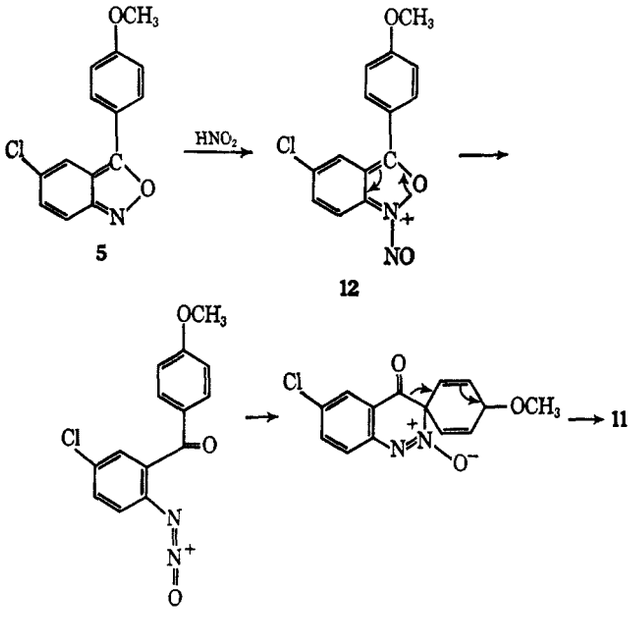
11

from the cleavage of **11** with sodium hydrosulfite to give 5-chloroanthranolic acid and *p*-anisidine.

Similarily, **3** was treated successively with nitrous acid and sodium hydrosulfite. The expected product, 2,4-dimethoxyaniline was isolated and identified by thin-layer chromatography. The position of the azoxy oxygen has not been definitely determined. The assignment is based on mechanistic grounds only.

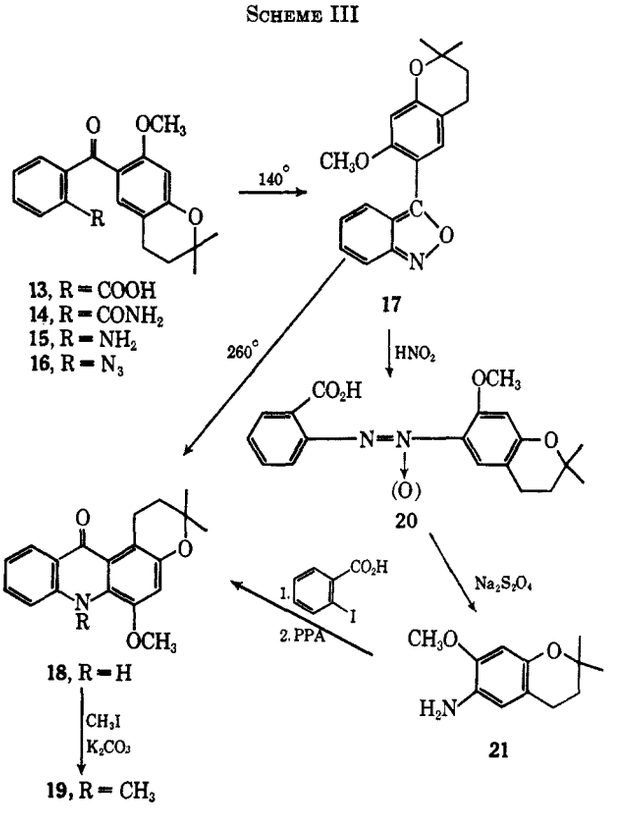
As in the case of the thermal rearrangement, the position *para* to the methoxy function is activated leading to the attack by the nitroso intermediate as shown in the reaction mechanism outlined in Scheme II.

SCHEME II



The utility of this novel rearrangement was applied to the synthesis of compounds related to acronycin.[7] The reaction sequence is shown in Scheme III. Friedel–Crafts reaction between phthalic anhydride and 7-methoxy-2,2-dimethylchroman[8] gave the keto acid **13**, which was converted into the amide **14**. Hofmann rearrangement of **14** gave the amine **15**. Conversion of the amine **15** into the azide **16** followed by pyrolysis gave the anthranil **17**. Heating the anthranil **17** at 260° gave the acridone **18** which was methylated with methyl iodide and potassium carbonate to give **19**. Compound **19** is isomeric to dihydroacronycine.[7] The anthranil **17** reacted with nitrous acid to give a mixture of azo and azoxy compounds **20** which were cleaved with sodium hydrosulfite to give 6-amino-7-methoxy-2,2-dimethylchroman (**21**). Compound **21** was treated with *o*-iodobenzoic acid followed by cyclization in polyphosphoric acid to give **18** (Scheme III).

SCHEME III



Experimental Section

Melting points were determined on a Thomas–Hoover apparatus and are corrected. Nuclear magnetic resonance spectra were recorded using a Varian HA-60 spectrometer. Tetramethylsilane was used as internal reference.

2-Azido-2′,4′-dimethoxybenzophenone (**2**).—A solution of 3 g of 2,4-dimethoxy-2′-aminobenzophenone[11] (**1**) in 30 ml of acetic acid and 15 ml of 1 *M* sulfuric acid was cooled to −20° (Dry Ice, acetone) with stirring. To this solution was added 0.7 g of sodium nitrite in 6 ml of water. After 5 min 1.3 g of sodium azide in 6 ml of water was added as fast as the evolution of nitrogen would allow. The mixture was stirred for another 30 min, and temperature was allowed to go up slowly. It was diluted with 100 ml of water and extracted with ether. The ether solution was washed with water, dilute sodium bicarbonate, and water, and was dried. Removal of solvent under reduced pressure gave an oily residue which crystallized when washed with ether. The product was recrystallized from ether to give 2 g of colorless crystals, mp 96–98°.

Anal. Calcd for $C_{15}H_{13}N_3O_3$: N, 14.83. Found: N, 14.88.

3-(2,4-Dimethoxyphenyl)anthranil (**3**).—The azide **2** (2 g) in a 50-ml round-bottom flask was heated in an oil bath at 140° for 5 min. (Large runs led to uncontrollable exothermic reaction.) The products from seven such runs were combined and recrystallized from hexane to give 13 g of greenish yellow needles, mp 93–95°. Further recrystallization from the same solvent gave the analytical sample, mp 94–95°.

Anal. Calcd for $C_{15}H_{13}NO_3$: C, 70.58; H, 5.13; N, 5.49. Found: C, 70.87; H, 5.22; N, 5.28.

2,4-Dimethoxyacridone (**4**).—A 100-ml, round-bottom flask containing 5 g of 3-(2,4-dimethoxyphenyl)anthranil (**3**) was heated at 255–260° in a Wood's metal bath for 10 min. The crude product was chromatographed on 700 g of Woelm silica gel and was eluted with benzene–ethyl acetate mixture (4:1). The product isolated was recrystallized from benzene–hexane, to give 2.5 g of yellow crystals, mp 185–187°.

Anal. Calcd for $C_{15}H_{13}NO_3$: C, 70.58; H, 5.13; N, 5.49. Found: C, 70.34; H, 5.01; N, 5.29.

Pyrolysis of 3-(*p*-Methoxyphenyl)-5-chloroanthranil[4] (**5**).—A 50-ml round-bottom flask containing 7 g of **5** was heated at 260° for 10 min. The crude product was refluxed in 50 ml of phosphorous oxychloride for 1 hr. The excess phosphorous oxychloride was removed under reduced pressure. The residue was poured into ice-cold ammonium hydroxide. After 2 hr at room temperature the mixture was extracted with chloroform and dried. After removal of solvent, the residue was chromatographed on 1 kg of Woelm silica gel and eluted with 2% ethyl acetate in benzene. The first compound to come out was **6b**. It was recrystallized from hexane to give 0.53 g, mp 200–203°.

Compound **6a** was recrystallized from chloroform–hexane to give 1.5 g, mp 194–195°.

5-Chloro-2-(4-methoxyphenylazoxy)benzoic Acid (11).—A solution of 12 g of the anthranil **5** in 500 ml of 5% sulfuric acid in acetic acid was cooled slightly on ice. To it was added 24 g of finely powdered sodium nitrite in small portions in about 15 min. It was removed from the ice, kept at room temperature for 10 min, and then poured into 1200 ml of water. The precipitate was filtered and recrystallized from acetonitrile to give 10 g of yellow needles, mp 195–197°. The product was cleaved with sodium hydrosulfite in a manner similar to that used in the preparation of **21** to give 5-chloroanthranilic acid and *p*-anisidine, both of which were identical with authentic samples.

Reaction of 3-(2,4-Dimethoxyphenyl)anthranil (3) with Nitrous Acid.—In a manner similar to that of the preparation of **11**, 2 g of **3** was treated with 4 g of sodium nitrite. The crude product (0.5 g) could not be recrystallized. It was treated with sodium hydrosulfite as described in the preparation of **21**. The basic material was extracted with ether, and the product, 2,4-dimethoxyaniline, was identified by thin layer chromatography.

6-(2-Carboxybenzoyl)-7-methoxy-2,2-dimethylchroman (13).—A mixture of 15 g (0.078 *M*) of 7-methoxy-2,2-dimethylchroman[8] and 11.6 g (0.078 *M*) of phthalic anhydride in 100 ml of tetrachloroethane and 20 ml of nitrobenzene was stirred in ice bath until temperature was below 5°. To the mixture was added 21 g (0.156 *M*) of aluminum chloride in small portions. The mixture was kept in the refrigerator for 2 days. It was poured into ice and treated with excess dilute HCl. The organic solvent was removed by steam distillation. The gummy residue from the aqueous layer was cooled and triturated with acetonitrile to give a light brown solid which was recrystallized once from acetonitrile to give 10 g of colorless crystals, mp 180–182°. A further recrystallization from the same solvent gave the analytical sample, mp 181–182°.

Anal. Calcd for $C_{20}H_{20}O_5$: C, 70.57; H, 5.92. Found: C, 70.49; H, 6.01.

6-(2-Carboxyamidobenzoyl)-7-methoxy-2,2-dimethylchroman (14).—To a solution of 8 g of the acid **13** in 60 ml of pyridine cooled in ice bath was added 10 ml of thionyl chloride in small portions. The solution was kept at room temperature for another 2 hr and was then added to ice-cold ammonium hydroxide slowly with stirring. Excess ammonia was removed under reduced pressure. The mixture was further diluted with water, and the precipitate was filtered and washed with water. Recrystallization from acetonitrile gave 5.6 g of colorless crystals, mp 185–188°. The analytical sample from the same solvent had mp 193–195°.

Anal. Calcd for $C_{20}H_{21}NO_4$: C, 70.78; H, 6.24; N, 4.13. Found: C, 71.04; H, 6.45; N, 4.16.

6-(2-Aminobenzoyl)-7-methoxy-2,2-dimethylchroman (15).—To a suspension of 10 g of amide **14** in 30 ml of water containing 2.8 g of sodium hydroxide was added 60 ml of 5% sodium hypochlorite solution. The mixture was stirred at room temperature for 45 min and filtered, and the clear filtrate was heated on a steam bath for 40 min. It was diluted with 150 ml of water and kept in the refrigerator overnight. The yellow precipitate was collected and washed with water and recrystallized once from chloroform–hexane to give 6.6 g of yellow crystals, mp 75–77°. Further recrystallization from hexane gave the analytical sample, mp 77–79°.

Anal. Calcd for $C_{19}H_{21}NO_3$: N, 4.50. Found: N, 4.58.

6-(2-Azidobenzoyl)-7-methoxy-2,2-dimethylchroman (16).—Similar to the preparation of **2**, 6 g of the amine **15** was treated with 2 g of sodium azide. The crude product was recrystallized from hexane to give 4.3 g of colorless crystals, mp 80–83°. The analytical sample from the same solvent had mp 82–83°.

Anal. Calcd for $C_{19}H_{19}N_3O_3$: N, 12.45. Found: N, 12.30.

3-(7-Methoxy-2,2-dimethyl-6-chromanyl)anthranil (17).—The azide **16** (4.5 g) was placed in a test tube and heated to 140° in an oil bath for about 6 min until evolution of nitrogen stopped. The dark brown crude product was chromatographed on 200 g of Woelm silica gel and was eluted with 1% ethyl acetate in benzene. The product failed to crystallize and had uv bands at λ_{max} 260 and 362 mμ.

6-Methoxy-3,3-dimethyl-2,3-dihydro-12(7H)-1H-pyrano[3,2-*a*]-acridone (18).—The anthranil **17** (4 g) was heated to 250–260° for 10 min in a Wood's metal bath. The dark brown crude product was chromatographed on 200 g of Woelm silica gel and was eluted with 10% ethyl acetate in benzene. The isolated product was recrystallized from acetone–hexane to give 2.25 g of yellow crystals, mp 200–202°. Further recrystallizations from the same solvents gave the analytical sample, mp 205–207°.

Anal. Calcd for $C_{19}H_{19}NO_3$: C, 73.76; H, 6.16; N, 4.53. Found: C, 73.65; H, 6.37; N, 4.30.

6-Methoxy-3,3,7-trimethyl-2,3-dihydro-12(7H)-1H-pyrano-[3,2-*a*]acridone (19).—A mixture of 2 g of the acridone **18**, 40 g of anhydrous potassium carbonate, and 50 ml of methyl iodide in 250 ml of acetone was refluxed for 3 days. Solvent was removed under reduced pressure and the residue, diluted with water, was extracted with chloroform, and the chloroform layer was dried. Removal of solvent gave a yellow residue which was chromatographed on 100 g of Woelm silica gel eluted with 1% ethyl acetate in benzene. The product was isolated and recrystallized from hexane to give 1.25 g of yellow crystals, mp 119–121°.

Anal. Calcd for $C_{20}H_{21}NO_3$: C, 74.28; H, 6.54; N, 4.33. Found: C, 73.99; H, 6.57; N, 4.42.

2-(7-Methoxy-2,2-dimethyl-2-chromanylazoxy)benzoic Acid (20).—A solution of 4 g of anthranil **17** in 120 ml of 5% sulfuric acid in acetic acid was treated with 12 g of sodium nitrite in a manner similar to that of the preparation of **11**. The orange-colored product was recrystallized from methanol, mp 170–171°.

6-Amino-7-methoxy-2,2-dimethylchroman[8] (21).—A suspension of 0.9 g of the azoxy compound **20** in 20 ml of water was treated with dilute sodium hydroxide solution until a clear solution was obtained. It was warmed to 45–50° in a water bath with stirring. To this solution was added 1.5 g of sodium hydrosulfite. Stirring was continued for 20 min. After heating on a steam bath for 10 min, the solution became cloudy, and upon cooling a white precipitate was formed. The precipitate was filtered, washed with water, and dried to give 300 mg of material which was recrystallized from hexane twice to give small crystals, mp 89–90°.

6-Methoxy-3,3-dimethyl-2,3-dihydro-12(7H)-1H-pyrano[3,2-*a*]-acridone (18) from 21.—A mixture of 0.4 g of *o*-iodobenzoic acid, 0.11 g of copper, 0.35 g of cupric carbonate and 0.14 g of potassium carbonate in 20 ml of *n*-amyl alcohol was refluxed with stirring for 52 hr. The alcohol was removed by steam distillation. The aqueous portion was filtered and extracted with chloroform to remove unreacted starting material. The aqueous solution was acidified with concentrated HCl, extracted with chloroform, and dried. Solvent was removed under reduced pressure, and the residue was heated on a steam bath with 40 ml of polyphosphoric acid for 2 hr. It was diluted with ice water. The brownish precipitate was extracted with chloroform, washed with sodium bicarbonate solution and water, and dried. After removing the solvent under reduced pressure, the residue was chromatographed on 50 g of Woelm silica gel eluted with 2% ethyl acetate in benzene to give 40 mg of **18**, mp 200–202°.

Registry No.—**2**, 16710-28-4; **3**, 16710-29-5; **4**, 16710-30-8; **6a**, 16710-31-9; **6b**, 16710-32-0; **13**, 16710-33-1; **14**, 16710-34-2; **15**, 16710-35-3; **16**, 16710-36-4; **18**, 16710-38-6; **19**, 16710-37-5; **20**, 16720-15-3.

Acknowledgment.—The authors wish to thank Drs. Jack Baldwin, Nelson Leonard, and Ernest Wenkert for helpful discussions.