over $MgSO_4$. The solution was evaporated to $^1/_4$ volume and diluted with 75 mL of diethyl ether. Bubbling HCl gas into the cold solution yielded a white crystalline solid: mp 185-187 °C; IR (KBr) 1745 cm^{-1}. A solution of penicillamine methyl ester which can be used directly in the thiazoline synthesis was obtained when the basic aqueous phase was extracted 5 times with CH_2Cl_2. Penicillamine ethyl ester **12** was prepared and used in the same manner.

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Registry No. **1**, 55771-38-5; **2**, 89530-15-4; **3**, 55771-72-7; **4**, 89530-16-5; **5**, 89530-17-6; **6**, 62096-93-9; **7**, 2519-89-3; **8**, 3113-46-0; **9**, 89530-18-7; **10**, 89530-19-8; **11**, 34297-27-3; **12**, 63474-91-9; penicillamine, 52-67-5; cysteine ethyl ester hydrochloride, 868-59-7; benzonitrile, 100-47-0; ethyl acetimidate hydrochloride, 2208-07-3; methyl benzimidate hydrochloride, 5873-90-5.

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Structure of a New 1,4-Diphenyl-3*H*-2-benzopyran-3-one Derivative

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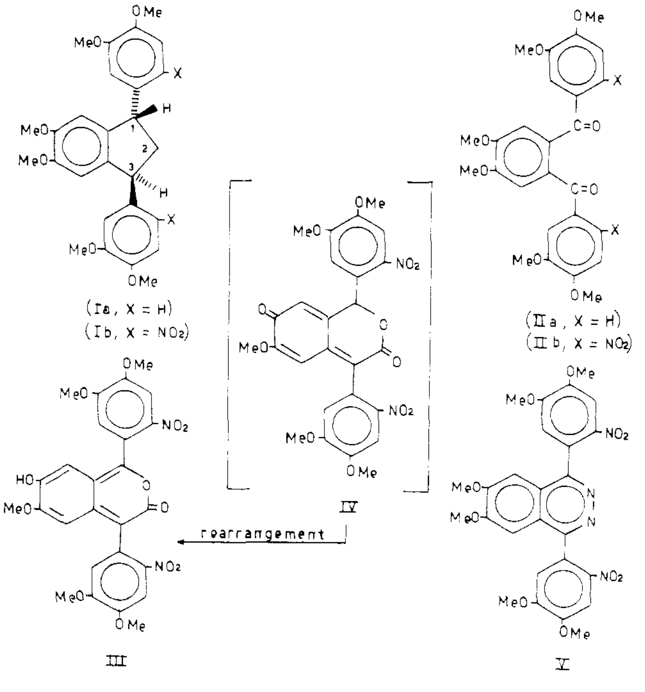
Diketone IIb and small amounts of 1,4-bis(3,4-dimethoxy-2-nitrophenyl)-7-hydroxy-6-methoxy-3*H*-2-benzopyran-3-one (III) were obtained by oxidation of *trans*-1,3-bis(4,5-dimethoxy-2-nitrophenyl)-5,6-dimethoxyindane (Ib) prepared by nitration of Ia. Compound IIb treated with hydrazine hydrate afforded the corresponding 1,4-diarylphthalazine V. The compounds were characterized by microanalysis and NMR, IR, and mass-spectral data.

In the present paper we report on studies of the oxidation of 1,3-bis(4,5-dimethoxy-2-nitrophenyl)-5,6-dimethoxyindane (Ib) obtained by nitration of Ia (*1*). On the basis of NMR spectral evidence, trans configurations must be assigned to both Ia and Ib because the protons of positions 2 are magnetically equivalent.

Compound Ib oxidized similarly to Ia (*1*) gave two products. The first one was identified as (4,5-dimethoxy-1,2-phenylene)-bis[(2-nitro-4,5-dimethoxyphenyl)methanone] (IIb), sparingly soluble in ethanol. For the second product, $C_{26}H_{22}N_2O_{12}$, soluble in ethanol as well as aqueous sodium hydroxide solution, we tentatively assign the structure of 1,4-bis(4,5-dimethoxy-2-nitrophenyl)-7-hydroxy-6-methoxy-3*H*-2-benzopyran-3-one (III). It probably is formed via the quinone intermediate IV (*2*).

By analogy with *o*-diaroylbenzenes which upon treatment with hydrazine hydrate give the corresponding 1,4-diarylphthalazines (*3*), the diketone IIb was transformed readily into 1,4-bis(2-nitro-4,5-dimethoxyphenyl)-6,7-dimethoxyphthalazine (V).



Experimental Section

General Methods. Melting points were determined on Thiele (Ib and IIb) and Kofler (III and V) apparatus and are uncorrected. Infrared spectra were recorded in Nujol mulls with a

Perkin-Elmer 137 IR spectrophotometer. NMR spectra were obtained with a Jeol C-60H spectrometer at 60 MHz (Ib, IIb, and V) and a Perkin-Elmer spectrometer at 90 MHz (III) (Me_4Si as internal reference). Mass spectra were recorded on a Jeol JMS-10SG-2 mass spectrometer. Elemental analyses were carried out by the Kurt Eder service (Genève, Suisse) and satisfactory microanalysis results (C, H, and N) were obtained for all products.

trans-1,3-Bis(4,5-dimethoxy-2-nitrophenyl)-5,6-dimethoxyindane (Ib). To a suspension of 1,3-bis(3,4-dimethoxyphenyl)-5,6-dimethoxyindane (Ia) (5 g, 0.011 mol) in acetic anhydride (100 mL) was added dropwise nitric acid (65%) (2.5 mL), while the mixture was stirred vigorously for 15 min, at 0 °C. The reaction mixture was quenched with crushed ice and the precipitate collected; it was washed with water and dried to give a yellow solid, Ib, 2 g (33.3 %). An analytical sample was recrystallized from ethanol to yield yellow crystals: mp 192 °C; NMR ($CDCl_3$) δ 2.77 (t, J = 7.5 Hz, 2 H, C_2–H), 3.80, 3.85, and 4.00 (3s, 18 H, 6 OCH_3), 5.27 (t, J = 7.5 Hz, 2 H, $C_{1,3}$–H), 6.52, 6.65, and 7.60 (3s, 6 H, aromatic H). This compound had molecular weight by mass spectroscopy *m/e* 540.

(4,5-Dimethoxy-1,2-phenylene)bis[(2-nitro-4,5-dimethoxyphenyl)methanone] (IIb) and 1,4-bis(4,5-dimethoxy-2-nitrophenyl)-7-hydroxy-6-methoxy-3H-2-benzopyran-3-one (III). To a solution of 1,3-bis(4,5-dimethoxy-2-nitrophenyl)-5,6-dimethoxyindane (Ib) (2 g, 0.0037 mol) in acetic acid (10 mL) was added dropwise an aqueous acetic acid solution of $Na_2Cr_2O_7$ (1 g-atom of oxygen/L) (80 mL). The mixture was refluxed for 1 h and then allowed to stand for 2 h at room temperature. Addition of water to the solution gave a precipitate which was filtered, washed until neutral, dried, and chromatographically separated into two products over a column of silica gel (200 g) with 15% of water by using a solvent system consisting of 7 parts ethyl acetate to 3 parts petroleum ether as eluent. The first product was IIb, sparingly soluble in ethanol (0.55 g, 26.7% yield): mp 194–195 °C (recrystallized from acetic acid); IR 1653 cm^{-1} (C=O); NMR ($CDCl_3$) δ 3.90 and 4.00 (2s, 18 H, 6 OCH_3), 7.00, 7.02, and 7.42 (3s, 6 H, aromatic H). Compound IIb had molecular weight by mass spectroscopy *m/e* 556. To the second product (orange solid, sensible to light) is assigned structure III; it is more soluble in ethanol than IIb (0.15 g, 7.3% yield): mp 239–240 °C (recrystallized from ethanol); IR 3440 (OH), 1720 (C=O) cm^{-1}; NMR (pyridine-d_5) δ 3.70, 3.72, 3.76, 3.80, and 3.85 (5s, 15 H, 5 OCH_3), 4.65 (br s, 1 H, exchangeable with deuterium oxide, OH), 6.75, 7.00, 7.18, 7.60, 7.80, and 8.40 (6s, 6 H, aromatic H). The mass spectrum was in agreement with the structure of 1,4-diphenyl-3*H*-2-benzopyran-3-one derivative.

1,4-Bis(2-nitro-4,5-dimethoxyphenyl)-6,7-dimethoxyphthalazine (V). To a suspension of (4,5-dimethoxy-1,2-phenylene)bis[(2-nitro-4,5-dimethoxyphenyl)methanone] (IIb) (0.5 g, 0.000 89 mol) in ethanol (300 mL) was added hydrazine hydrate (85%) (1 mL). The mixture was refluxed for 10 h. After the mixture was cooled, the resulting solid material was filtered, washed, dried, and then recrystallized repeatedly from ethanol yielding 0.32 g (64.4%) of V as yellow crystals: mp 169–170 °C; NMR ($CDCl_3$) δ 3.86, 4.05, and 4.10 (3s, 18 H, 6 OCH_3), 6.77, 7.15, and 7.87 (3s, 6 H, aromatic H). This compound had molecular weight by mass spectroscopy *m/e* 552.

Registry No. Ia, 90047-39-5; Ib, 90047-40-8; IIb, 90047-41-9; III, 90047-42-0; V, 90047-43-1.

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Syntheses of 1,3-Disubstituted 4-Arylidenepyrazolin-5-ones and the Keto and Enol Forms of 4,4′-Arylidenebis(1,3-disubstituted pyrazolin-5-ones)

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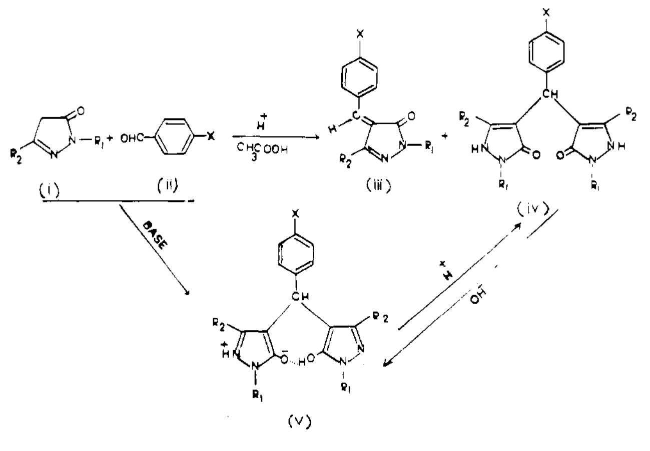
A number of 1,3-disubstituted 4-arylidenepyrazolin-5-ones and keto and enol forms of 4,4′-arylidenebis(1,3-disubstituted pyrazolin-5-ones) have been synthesized as possible antifungal agents by condensing 1,3-disubstituted pyrazolin-5-ones with aromatic aldehydes in acidic and basic media. The compounds were characterized by UV, IR, NMR, and elemental analysis.

The syntheses and therapeutical studies of pyrazolones and their derivatives were undertaken by several groups of workers (*1–5*). We wish to report some important compounds of this class (Scheme I).

Experimental Section

Melting points are uncorrected. All the elemental analyses were carried out on Coleman C, H, and N analyzers; the analytical values for C, H, and N were within ±0.4% of the calculated values. The IR spectra were recorded on Perkin-Elmer (Models 257 and 720) spectrometers in Nujol. Qualitative UV spectra were recorded on a Beckman spectrometer in methanol. The NMR spectra were recorded on a Varian-A-60D spectrometer in $CDCl_3$ and the chemical shifts are reported in

Scheme I



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