Anal. Calcd for $C_{12}H_{11}N_3O_3$: C, 58.77; H, 4.52; N, 17.13. Found: C, 58.49; H, 4.54; N, 16.91.

Prolonged heating or an increase in the concentration of HCl diminished the yield of **5b**.

cis-**5-Carboxamido-3-phenyl-2-isoxazoline-4-carboxylic Acid (6a)**.—To concentrated ammonium hydroxide (10 ml) at 10° was added **1** (1.08 g, 0.005 mol) in small portions, keeping the temperature below 10°. The reaction mixture was filtered and acidified with cold concentrated hydrochloric acid in an ice bath. The colorless solid (0.86 g, 73.5%) was collected and dried: mp 165–166°; ir 1650 and 1725 cm^{-1}; pmr δ 4.84 (d, H-4), 5.25 (d, H-5, $J_{4,5}$ = 12 Hz), 6.5–7.18 (m, 5, Ar H); mass spectrum *m/e* (rel intensity) 234 (1), 218 (8), 217 (62), 191 (5), 190 (6), 159 (16), 147 (7), 146 (64), 145 (40), 144 (76), 119 (7), 118 (32), 117 (19), 116 (11), 115 (12), 104 (15), 103 (20), 91 (19), 90 (12), 89 (15), 78 (10), 77 (100), 76 (16), 75 (7), 66 (7), 65 (6), 64 (16), 63 (6), 57 (8), 52 (6), 51 (40), 50 (15), 44 (62), 43 (9), 41 (8), 39 (15), 36 (10), 32 (19), 29 (5).

Anal. Calcd for $C_{11}H_{10}N_2O_4$: N, 11.96. Found: N, 11.82.

3-Phenyl-2-isoxazoline-5-carboxamide (6b).—On heating 5-carboxamido-3-phenyl-2-isoxazoline-4-carboxylic acid (**6a**) (0.75 mg, 0.0032 mol) for 15 min *in vacuo* until the oil bath temperature had risen to 190°, a solid material formed which was triturated with saturated aqueous sodium bicarbonate solution (10 ml), collected, and washed with three portions of cold water (5 ml). The solid was extracted with boiling benzene to afford 0.2 g (33%) of **6b**: mp 200–201° (lit.[6] mp 204°); ir 1650 and 1660 cm^{-1}; pmr δ 3.1–3.6 (m, 2 H at C-4), 4.67–5.13 (m, H-5, the X part of an ABX pattern), 7.1–7.84 (m, C_6H_5); mass spectrum *m/e* (rel intensity) 190 (13), 159 (33), 147 (10), 146 (100), 119 (10), 118 (75), 117 (13), 115 (6), 104 (14), 103 (9), 91 (30), 78 (15), 77 (95), 76 (10), 63 (6), 51 (32), 50 (10), 44 (19), 32 (7).

Anal. Calcd for $C_{10}H_{10}N_2O_2$: N, 14.73. Found: N, 14.45.

3-Phenyl-2-isoxazoline-5-carboxylic Acid.—To concentrated hydrochloric acid (10 ml) was added **6a** (0.468 g, 0.002 mol), and the solution was warmed on a steam bath for 20 min. The reaction mixture was allowed to stand for 12 hr to furnish **6c**: 0.21 g (55%); mp 140–143° (lit.[6] mp 143°); ir 1720 cm^{-1}; pmr, computer-checked spectrum for ABX pattern of ring protons offers this solution:[15] δ 5.203 (H-5), 3.745, 3.613 (H-4, J_{gem} = −17.27, $J_{4,5}$ = 11.83 and 6.77 Hz), 7.20–7.80 (m, C_6H_5); mass spectrum *m/e* (rel intensity) 191 (30), 147 (8), 146 (64), 119 (10), 118 (86), 117 (12), 115 (7), 104 (14), 103 (19), 91 (32), 89 (8), 78 (13), 77 (100), 76 (16), 75 (6), 74 (5), 65 (6), 63 (11), 52 (6), 51 (40), 50 (17), 46 (7), 39 (11).

Anal. Calcd for $C_{10}H_9NO_3$: N, 7.33. Found: N, 7.51.

Methyl *cis* **3-Phenyl-2-isoxazoline-4,5-dicarboxylate**.—This ester was prepared in 44% yield by the literature[6] method: mp 89–92° (lit.[6] mp 91°); pmr ($CDCl_3$) δ 3.73, 3.87 (OCH_3), 4.80 (H-4), 5.43 (H-5, $J_{4,5}$ = 12 Hz); lit.[11] pmr ($CDCl_3$) δ 3.65, 3.80 (OCH_3), 4.81 (H-4), 5.29 (H-5, $J_{4,5}$ = 12 Hz), pmr $(CD_3)_2SO$ δ 3.65, 3.77 (OCH_3), 5.23 (H-4), 5.66 (H-5, $J_{4,5}$ = 12 Hz); mass spectrum *m/e* (rel intensity) 264 (11), 263 (62), 231 (5), 204 (27), 178 (21), 177 (14), 176 (100), 172 (23), 160 (14), 146 (6), 144 (85), 134 (18), 119 (11), 118 (9), 117 (12), 116 (12), 115 (6), 113 (16), 105 (8), 104 (6), 103 (15), 91 (18), 89 (9), 77 (51), 76 (9), 59 (31), 51 (22), 39 (6), 31 (11), 29 (5).

trans-**3-Phenyl-2-isoxazoline-4,5-dicarboxamide**.—A mixture of methyl *cis*-3-phenyl-2-isoxazoline-4,5-dicarboxylate (2.61 g) and concentrated NH_4OH (20 ml) was allowed to react for 8 hr at 25°. The solid (2.1 g, 91%) was collected and dried: mp 250–252°; ir 1660 cm^{-1}; pmr δ 4.73 (d, H-4), 5.07 (d, H-5, $J_{4,5}$ = 6 Hz), 7.33–7.92 (m, C_6H_5); mass spectrum *m/e* (rel intensity) 234 (3), 233 (13), 190 (10), 189 (80), 172 (29), 147 (10), 146 (100), 145 (5), 144 (24), 130 (16), 118 (12), 117 (7), 116 (7), 115 (6), 104 (17), 103 (10), 91 (30), 89 (7), 87 (6), 86 (74), 78 (7), 77 (58), 76 (7), 63 (6), 51 (23), 50 (5), 44 (31), 39 (5) ir (Nujol) 1660 cm^{-1} (C=O).

Anal. Calcd for $C_{11}H_{11}N_3O_3$: N, 18.02. Found: N, 18.20.

Registry No.—**2a**, 35053-65-7; **2b**, 35053-66-8; **2c**, 35053-67-9; **3a**, 35053-68-0; **3b**, 35053-69-1; **3c**, 35053-70-4; **3d**, 35053-71-5; **5a**, 35053-72-6; **5b**, 35053-73-7; **6a**, 35053-74-8; **6b**, 35053-75-9; **6c**, 35053-76-0; 3-phenyl-2-isoxazoline-5-carboxylic acid, 4872-58-6; *trans*-3-phenyl-2-isoxazoline-4,5-dicarboxamide, 35053-78-2.

Acknowledgments.—We thank Professor C. L. Bell for valuable comments and Messrs. Earl A. Dau and Kenneth S. H. Woo for technical help.

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(15) We are grateful to Dr. Richard S. Egan for this spectrum and solution. The ABX spectrum was calculated using LAOCN3 [S. Castellano and A. A. Bothner-by, *J. Chem. Phys.*, **41**, 3853 (1964)], as modified by Mr. W. C. Bass, Abbott Laboratories.

The Synthesis of 2,5- and 4,5-Dihydroxyxanthone[1]

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The photo-Fries rearrangement of *p*-methoxyphenyl 2,3-dimethoxybenzoic acid was advantageously employed in the preparation of 2-hydroxy-2′,3′,5-trimethoxybenzophenone which, after demethylation and cyclodehydration, provided the previously unknown 2,5-dihydroxyxanthone. Similarly, the irradiation of *o*-methoxyphenyl 2,3-dimethoxybenzoate provided the Fries rearrangement products 4-hydroxy- and 2-hydroxy-2′,3,3′-trimethoxybenzophenone. Demethylation and cyclization of the latter yielded 4,5-dihydroxyxanthone, also previously unknown.

We have already described research on the constituents of *Mammea americana* L. which led to the isolation of some simple mono- and dihydroxyxanthones.[4] Among the 16 possible dihydroxyxanthones, we noted that the 1,5, 2,5, and 4,5 isomers were unknown in the literature. The 1,5 isomer was synthesized and shown to be identical to one of the *Mammea* constituents.[4] Here we report the synthesis of the remaining two isomers and describe two new examples of the photo-Fries reaction.

2,5-Dihydroxyxanthone (Ia).—A simple and obvious pathway to Ia would involve treatment of the tetramethoxybenzophenone II with a Lewis acid in order to

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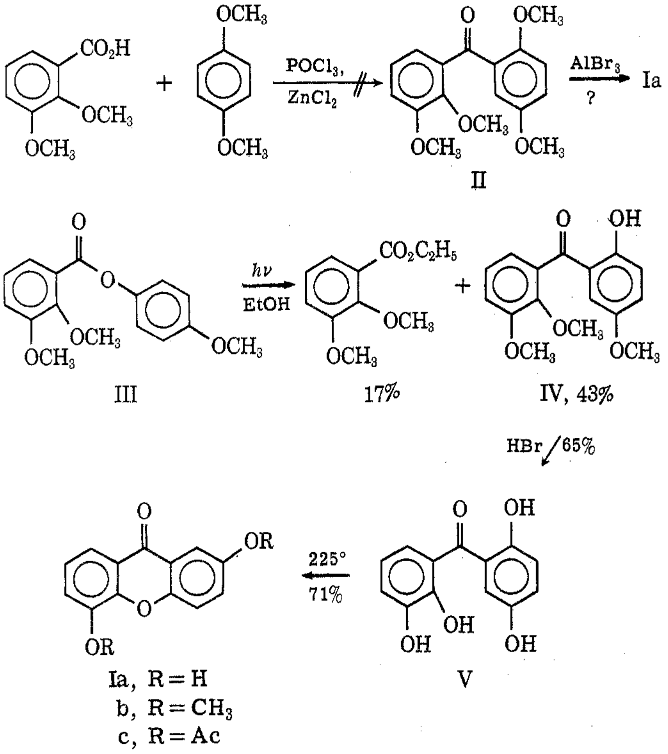
(2) This article was written while the author was a Guest Professor at the Institut für Pharmazeutische Arzneimittellehre der Universität München, and he wishes to thank the Directors of the Institute for their hospitality during this period.

(3) The experiments on which this article is based were taken from the Ph.D. thesis of K. E. M., presented to the Department of Medicinal Chemistry, State University of New York at Buffalo, April 1970.

(4) R. A. Finnegan and J. K. Patel, *J. Chem. Soc., Perkin Trans. 1*, (1972); see also R. A. Finnegan, J. K. Patel, and P. L. Bachman, *Tetrahedron Lett.*, 6087 (1966).

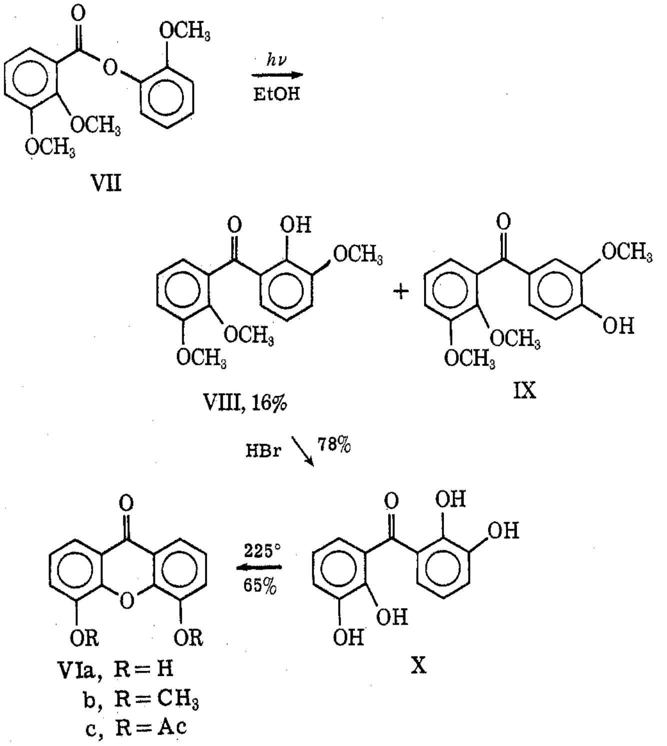
cause demethylation and cyclodehydration in a single operation,[5] as suggested at the top of Scheme I. Furthermore, the preparation of II was thought to be merely a matter of the condensation of 2,3-dimethoxybenzoic acid with *p*-dimethoxybenzene. In the event, however, neither of these reactions were directly realized. When the benzoic acid was condensed with the dimethoxybenzene, using the conditions established by Grover, Shah, and Shah,[6] a multicomponent mixture was produced which showed OH absorption in the infrared. Treatment of this product with dimethyl sulfate and alkali produced the ester III, identified by comparison with an authentic sample prepared separately. This indicates that even under the relatively mild conditions of the condensation reaction, demethylation was a primary reaction. This acid-catalyzed side reaction was avoided and the equally useful benzophenone IV was obtained indirectly by application of the photo-Fries reaction[7] to the ester III, as outlined in Scheme I. In addition to IV, there was formed a 17% yield of solvolysis product, the corresponding ethyl benzoate, which is of interest since this type of photosolvolysis is usually a very minor process except in the case of certain nitrobenzoates.[8] An attempt to convert IV directly to Ia with aluminum bromide[5] gave black tar. Compound IV was therefore demethylated by reaction with hydrogen bromide and the resultant tetrahydroxybenzophenone V was smoothly converted to the desired xanthone Ia, mp 303–305°, by heating it in water in a bomb at 225°.[9] The product Ia was further characterized by formation of its dimethyl ether Ib, mp 178–179°, and its diacetate derivative Ic, mp 159–160°.

Scheme I



4,5-Dihydroxyxanthone (VIa).—Following the precedent set above for the preparation of Ia, the synthesis of VIa began with the preparation and irradiation of an ethanol solution of *o*-methoxyphenyl 2,3-dimethoxybenzoate (VII). In this case the photo-Fries rearrangement can and does lead to both the *o*- and *p*-hydroxy ketones VIII and IX, as shown in Scheme II. (Curiously, less than 2% of the photosolvolysis product, ethyl 2,3-dimethoxybenzoate, was formed in this reaction.) Treatment of VIII with aluminum bromide did not give the desired xanthone Va as expected, but only a low yield of 2,2′,3,3′-tetrahydroxybenzophenone (X). When VIII was refluxed with hydrobromic acid, however, compound X was produced in 78% yield. Cyclodehydration of X then afforded the xanthone VIa which was derivatized by preparation of the dimethyl ether VIb, mp 273–274°, and the diacetate VIc, mp 270–272°.

Scheme II



Experimental Section[10]

Methylation Procedure.—A mixture of the hydroxyxanthone (0.20–0.25 g), anhydrous potassium carbonate (3 g), acetone (50 ml), and dimethyl sulfate (4 ml) was refluxed for 15–20 hr. The potassium carbonate was filtered and the filtrate was evaporated nearly to dryness. Excess dimethyl sulfate was decomposed by addition of aqueous 2 *N* NaOH solution (5 ml) and by heating the resulting mixture on the steam bath. The

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(5) G. V. Rao and T. R. Seshadri, *Proc. Indian Acad. Sci. Sect. A*, **37**, 710 (1953).

(6) P. K. Grover, G. D. Shah, and R. C. Shah, *J. Chem. Soc.*, 3982 (1955).

(7) For an excellent review, see D. Bellus, *Advan. Photochem.*, **8**, 109 (1971).

(8) R. A. Finnegan and D. Knutson, *J. Amer. Chem. Soc.*, **90**, 1670 (1968).

(9) J. M. Dutta, and E. R. Watson, *J. Chem. Soc. Ind.* **30**, 196 (1911).

(10) Melting points are uncorrected and were determined on a Fisher-Johns block for melting points below 300° and with a Mel-Temp apparatus for those above 300°. Infrared spectra were determined with a Perkin-Elmer Model 237 spectrophotometer. Only characteristic and/or strong absorptions (75% of the strongest) are reported. Ultraviolet and visible spectra were obtained with a Beckman DB-G grating spectrophotometer. Nmr spectra were determined with a Varian A-60 instrument using tetramethylsilane (TMS) as internal standard. Photolyses were carried out using a 450-W Hanovia medium pressure mercury arc lamp housed in a double-walled quartz immersion well. Additional details may be found in ref 3.

products were collected by filtration of the reaction mixture through a sintered glass funnel, washed extensively with water, dried, and purified by recrystallization or sublimation.

Acetylation Procedure.—A mixture of hydroxyxanthone (0.20–0.25 g), pyridine (4 ml), and acetic anhydride (4 ml) was allowed to stand for 24 hr at room temperature. The mixture was then poured into ice water and the resulting precipitate was collected on a filter. The solid was washed extensively with water, dried, and purified by recrystallization or sublimation.

***p*-Methoxyphenyl 2,3-Dimethoxybenzoate (III).**—A solution of 2,3-dimethoxybenzoyl chloride, bp 146–147° at 13 mm (lit.[11] bp 142–143° at 13 mm) (10.41 g), in pyridine (20 ml) was added to a solution of *p*-methoxyphenol (5.97 g) in pyridine (30 ml). The reaction mixture was refluxed for 4.5 hr, allowed to cool to room temperature, and poured into 200 ml of ice water. The aqueous mixture was extracted with ether (5 × 40 ml) and the combined ether extracts were washed with 10% aqueous HCl (3 × 50 ml), water (4 × 25 ml), 5% aqueous sodium carbonate solution (5 × 25 ml), water (4 × 25 ml), and saturated sodium chloride solution (2 × 25 ml). The ether solution was dried with anhydrous magnesium sulfate and evaporated to dryness. The oily residue was distilled under reduced pressure to afford a colorless liquid (11.78 g, 85%), bp 172°, at 0.025 mm. The distillate solidified and had mp 68–70°. Recrystallization from chloroform–hexane furnished white needles: mp 71–72°; $\nu_{\max}^{\text{KBr}}$ 1733, 1511, 1477, 1263, 1193, 1043, 1007 cm^{-1}; $\lambda_{\max}^{\text{EtOH}}$ 242 (sh), 275, 283 (sh), 290 (sh), mμ (log ϵ 3.90, 3.62, 3.60, 3.49); nmr ($CDCl_3$–TMS) τ 2.3–3.3 (7 H, m), 4.01 (3 H, s), 4.11 (3 H, s), 4.20 (3 H, s).

Anal. Calcd for $C_{16}H_{16}O_5$: C, 66.66; H, 5.59. Found: C, 66.80; H, 5.43.

Photolysis of *p*-Methoxyphenyl 2,3-Dimethoxybenzoate (III). The Preparation of 2-Hydroxy-2′,3′,5-trimethoxybenzophenone (IV).—A solution of III (10.05 g) was irradiated at 30–40° for 9 hr. Progress of the reaction was followed by ir and vpc by periodic examination of aliquots. The ethanol solution was evaporated to dryness and the residue was chromatographed on 320 g of neutral alumina (Woelm, activity grade II). The initial hexane eluents (fractions 1 and 2) gave a yellow oil (1.67 g, 16.5%) which was identified as ethyl 2,3-dimethoxybenzoate by its ir and nmr spectra. It was not further purified. Further elution of the column with hexane and hexane–benzene mixtures (fractions 3–21) furnished yellow crystalline IV (4.47 g, 42.5%), mp 65–75°, which showed one spot on tlc. One recrystallization from aqueous pyridine provided IV with mp 74–76°: $\nu_{\max}^{\text{KBr}}$ 1613, 1481, 1312, 1289, 1272, 1252, 1229, 1066, 826, 805, 781 cm^{-1}; $\lambda_{\max}^{\text{EtOH}}$ 225, 238 (sh), 371 mμ (log ϵ 4.34, 4.19, 3.61); $\lambda_{\max}^{\text{EtOH-NaOH}}$ 227, 262, 408 mμ (log ϵ 4.33, 3.96, 3.85); nmr ($CDCl_3$–TMS) τ −1.9 (1 H, s), 2.6–3.2 (6 H, m), 6.03 (3 H, s), 6.14 (3 H, s), 6.33 (3 H, s).

Anal. Calcd for $C_{16}H_{16}O_5$: C, 66.66; H, 5.59. Found: C, 66.56; H, 5.56.

Further elution of the column with benzene, chloroform, ethanol, and mixtures of these solvents (fractions 22–51) gave a total of 2.2 g (22% by weight) of oily material. Analysis (tlc) showed this to be a mixture containing IV and two other materials of lower mobility. This was not further examined.

2,2′,3,5′-Tetrahydroxybenzophenone (V).—A solution of IV (2.00 g) in glacial acetic acid (30 ml) and 48% hydrobromic acid (20 ml) was refluxed for 4 hr. The resulting green solution was concentrated to 25 ml, diluted with water, and filtered. The filtrate was evaporated to dryness and the resulting residue was dissolved in ethyl acetate (200 ml), treated with charcoal, and again evaporated to dryness. The resultant yellow oil was triturated with water and the yellow solid which formed was separated by filtration, washed with water, and dried to give crude V, mp 187–189° (1.28 g, 79%). After sublimation and recrystallization from aqueous ethanol, there was obtained 1.05 g (64%) of V: mp 190–191°; $\nu_{\max}^{\text{KBr}}$ 1634, 1613, 1600, 1580, 1458, 1330, 1269, 1221 cm^{-1}; nmr (acetone-d_6, TMS) τ 2.7–3.4 (6 H, m), 0.56–1.57 (4 H, s).

Anal. Calcd for $C_{13}H_{10}O_5$: C, 63.41; H, 4.09. Found: C, 62.76; H, 4.22.

2,5-Dihydroxyxanthone (Ia).—A mixture of V (1.05 g) and water (10 ml) in a stainless steel bomb was kept for 17 hr at 225°. After the mixture cooled to room temperature the material was separated by filtration and dried to give brown needles of Ia, 295–300° (0.70 g, 72%). This product was dissolved in ethyl acetate and treated with charcoal. The solution was evaporated and the residue was sublimed to give yellow needles: mp 303–305°; $\nu_{\max}^{\text{KBr}}$ 1639, 1616 (sh), 1600, 1585 (sh), 1495, 1471, 1460 (sh), 1316, 1248, 1208, 766 cm^{-1}; $\lambda_{\max}^{\text{EtOH-0.01 } N \text{ HCl}}$ 253, 282 (sh), 372 mμ (log ϵ 4.58, 3.45, 3.79); $\lambda_{\max}^{\text{EtOH-0.01 } N \text{ NaOH}}$ 252 (sh), 275, 430 mμ (log ϵ 4.44, 4.58, 3.72); nmr (pyridine-d_5, TMS) τ −1.75 (2 H, s), 1.93–3.21 (6 H, m).

Anal. Calcd for $C_{13}H_8O_4$: C, 68.42; H, 3.53. Found: C, 68.24; H, 3.66.

2,5-Dimethoxyxanthone (Ib).—Methylation of Ia (0.20 g) afforded tan needles (0.21 g, 98%), mp 167–170°. This crude material was sublimed, chromatographed through neutral alumina, and recrystallized from chloroform–hexane to give fine white needles of Ib (0.17 g, 78%), mp 176.5–177°. Two additional recrystallizations from chloroform–hexane raised the melting point to 178–179°: $\nu_{\max}^{\text{KBr}}$ 1661, 1645, 1600, 1490, 1439, 1431, 1314, 1269, 1148, 752 cm^{-1}; nmr ($CDCl_3$–TMS) τ 2.14–2.90 (6 H, m), 6.04 (3 H, s), 6.13 (3 H, s).

Anal. Calcd for $C_{15}H_{12}O_4$: C, 70.30; H, 4.72. Found: C, 70.07; H, 4.71.

2,5-Diacetoxyxanthone (Ic).—Acetylation of Ia (0.15 g) afforded a tan solid (0.20 g, 97%), mp 150–154°. Sublimation and three recrystallizations from chloroform–hexane gave pure Ic: mp 159–160°; $\nu_{\max}^{\text{KBr}}$ 1779, 1761, 1669, 1481, 1451, 1314, 1252, 1221, 1143, 912, 882, 766 cm^{-1}; nmr ($CDCl_3$–TMS) τ 1.85–2.89 (6 H, m), 7.62 (3 H, s), 7.72 (3 H, s).

Anal. Calcd for $C_{17}H_{12}O_6$: C, 65.38; H, 3.87. Found: C, 65.19; H, 3.83.

***o*-Methoxyphenyl 2,3-Dimethoxybenzoate (VII).**—A mixture of *o*-methoxyphenol (16.00 g), 2,3-dimethoxybenzoyl chloride (22.77 g), and pyridine (75 ml) was refluxed for 5 hr. Excess pyridine was removed under reduced pressure and the remaining liquid was dissolved in ether (800 ml). The ether solution was washed with water (2 × 50 ml), 2 *N* hydrochloric acid (3 × 40 ml), water (3 × 50 ml), 10% aqueous sodium bicarbonate solution (2 × 50 ml), water (2 × 50 ml), and saturated sodium chloride solution (2 × 50 ml). The ether solution was dried with anhydrous magnesium sulfate and the ether was evaporated under reduced pressure. The residual yellow oil was distilled, bp 174–178° at 0.2 mm, to give 29.38 g (90%) of colorless VII. This material crystallized from a hexane suspension to give 27.47 g (83%) of crystalline white solid: mp 49–50°; $\nu_{\max}^{\text{KBr}}$ 1748, 1504, 1486, 1312, 1285 (sh), 1261, 1238, 1170, 1111, 1044, 757 cm^{-1}; $\lambda_{\max}^{\text{EtOH}}$ 242 (sh), 273, 279, 298 mμ (log ϵ 3.66, 3.42, 3.43, 3.24); nmr ($CDCl_3$–TMS) τ 2.3–3.4 (7 H, m), 6.10 (3 H, s), 4.27 (3 H, s), 4.29 (3 H, s).

Anal. Calcd for $C_{16}H_{16}O_5$: C, 66.66; H, 5.59. Found: C, 66.53; H, 5.63.

Photolysis of *o*-Methoxyphenyl 2,3-Dimethoxybenzoate (VII). Preparation of the Benzophenones VIII and IX.—A solution of VII (9.34 g) in absolute ethanol (320 ml) was irradiated for 22 hr. The solvent was then evaporated under reduced pressure and the residue was chromatographed on 320 g of neutral alumina (Woelm, activity grade III). The initial hexane eluents (fractions 1–4) gave no residues. A yellow oil (0.16 g) was obtained from fractions 5–7 which were eluted with hexane and hexane–benzene mixtures. Thin-layer chromatography indicated the presence of three components and no attempt was made to further purify this product. Further elution of the column with hexane–benzene mixtures (fractions 8–16) furnished crystalline yellow residues. The residue from fraction 8 (0.62 g) was recrystallized from absolute ethanol to give fine yellow needles of VIII, mp 70–90° (0.46 g, 5%). The residues from fractions 9–16 showed a single spot on tlc and were combined to give an additional amount of VIII (1.05 g, 11%), mp 90–100°. Six recrystallizations from absolute ethanol raised the melting point of VIII to 110–110.5°: $\nu_{\max}^{\text{KBr}}$ 1634, 1475, 1466, 1445, 1346, 1312, 1269, 1250, 999, 992, 758, 749, 741 cm^{-1}; nmr ($CDCl_3$–TMS) τ −2.3 (1 H, s), 2.7–3.4 (6 H, m), 6.08 (6 H, s), 6.22 (3 H, s); $\lambda_{\max}^{\text{EtOH-0.01 } N \text{ HCl}}$ 227, 272, 355 mμ (log ϵ 4.41, 4.11, 3.49); $\lambda_{\max}^{\text{EtOH-0.01 } N \text{ NaOH}}$ 235 (sh), 275, 392 mμ (log ϵ 4.32, 3.95, 3.86).

Anal. Calcd for $C_{16}H_{16}O_5$: C, 66.66; H, 5.59. Found: C, 66.58; H, 5.63.

Further elution of the column with benzene (fractions 17–23) gave mixtures of VIII and IX (1.28 g, 14%). Fractions 24–31, showing two spots on tlc, and having a combined weight of 0.93 g (10%), were recrystallized from benzene to afford IX, 0.62 g, mp 137–142°, as a tan solid. Five recrystallizations from benzene furnished white crystalline IX: mp 143–143.5°; $\nu_{\max}^{\text{KBr}}$ 1650, 1595, 1582, 1513, 1477, 1466, 1427, 1316, 1279, 1248,

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(11) F. Mauthner, *J. Prakt. Chem.*, **112**, 63 (1926).

1159, 1086, 1002, 998, 766, 745 cm^{-1}; nmr ($CDCl_3$–TMS) τ 2.3–3.3 (6 H, m), 3.48 (1 H, s), 6.10 (6 H, s), 6.23 (3 H, s); $\lambda_{max}^{EtOH-0.01\ N\ HCl}$ 228, 283, 312 mμ (log ϵ 4.29, 4.04, 4.08); $\lambda_{max}^{EtOH-0.01\ N\ NaOH}$ 255, 285 (sh), 360 mμ (log ϵ 4.04, 3.57, 4.44).

Anal. Calcd for $C_{16}H_{16}O_5$: C, 66.66; H, 5.59. Found: C, 66.84; H, 5.79.

Further elution of the column with benzene, chloroform, ethyl acetate, and mixtures of these solvents gave mixtures (2.9 g, 32%) which contained both VIII and IX and at least two other components (tlc) which were not identified. Three additional portions (10 g each) of VII were photolyzed and provided, after work-up, an additional 4.1 g (14%) of VIII, mp 107–108°.

2,2′,3,3′-Tetrahydroxybenzophenone (X).—A solution of VIII (4.0 g) in glacial acetic acid (60 ml) and 48% hydrobromic acid (40 ml) was refluxed for 5 hr. The solution was concentrated to *ca.* 50 ml, diluted with water (150 ml), and filtered. The filtrate was allowed to stand for 12 hr at room temperature, whereupon the precipitate was collected by filtration, washed with water, and dried to give fine yellow needles of X (2.65 g, 78%), mp 120–121°. Sublimation followed by recrystallization from water gave X with mp 121–122°: ν_{max}^{KBr} 3600–2700 (broad), 1626, 1475, 1449, 1332, 1279, 1442, 1190, 854, 752, 740 cm^{-1}; $\lambda_{max}^{EtOH-0.01\ N\ HCl}$ 223, 275, 350 mμ (log ϵ 4.30, 4.08, 3.56); $\lambda_{max}^{EtOH-0.01\ N\ NaOH}$ 240, 273 (sh), 308, 365 mμ (log ϵ 4.35, 4.04, 4.05, 3.38).

Anal. Calcd for $C_{13}H_{10}O_5$: C, 63.41; H, 4.09. Found: C, 63.03; H, 4.12.

4,5-Dihydroxyxanthone (VIa).—A mixture of X (1.5 g) and water (15 ml) was heated in a stainless steel bomb for 19 hr between 220–230°. The mixture was then cooled and the solid material was separated by filtration, washed with water, and dried. Sublimation afforded crystalline yellow VIa (0.91 g, 65%) which decomposed at 350°. Recrystallization from absolute alcohol furnished fine yellow needles: mp >350° (dec); ν_{max}^{KBr} 1600, 1468, 1374, 1350, 1255, 1170, 742 cm^{-1}; $\lambda_{max}^{EtOH-0.01\ N\ HC}$ 247, 300, 358 mμ (log ϵ 4.66, 3.82, 3.77); $\lambda_{max}^{EtOH-0.01\ N\ NaOH}$ 264, 316, 350, 410 mμ (log ϵ 4.62, 3.76, 3.63, 3.61); nmr (DMSO-d_6, TMS) τ 2.15–3.15 (m).

Anal. Calcd for $C_{13}H_8O_4$: C, 68.42; H, 3.53. Found: C, 68.01; H, 3.85.

4,5-Dimethoxyxanthone (VIb).—Methylation of 4,5-dihydroxyxanthone (VIa) (0.20 g) afforded 0.15 g (68%) of a crystalline white solid, mp 273–275° (subl). Sublimation followed by recrystallization furnished fine white needles of VIb (0.12 g): mp 273–274° (subl); ν_{max}^{KBr} 1660, 1490, 1441, 1360, 1339, 1282, 1230, 1078, 750 cm^{-1}; nmr ($CDCl_3$–TMS) τ 2.03–2.76 (6 H, m), 5.93 (6 H, s).

Anal. Calcd for $C_{15}H_{12}O_4$: C, 70.30; H, 4.72. Found: C, 70.14; H, 4.92.

4,5-Diacetoxyxanthone (VIc).—Acetylation of VIa (45 mg) afforded a white crystalline solid (58 mg, 94%), mp 263–268°. Sublimation furnished fine white needles of VIc: mp 270–272°; ν_{max}^{KBr} 1764, 1669, 1493, 1475, 1447, 1372, 1326, 1230, 1178, 753 cm^{-1}; nmr ($CDCl_3$–TMS) τ 1.80–2.78 (6 H, m), 7.59 (6 H, s).

Anal. Calcd for $C_{17}H_{12}O_6$: C, 65.38; H, 3.87. Found: C, 65.32; H, 4.04.

Registry No.—Ia, 35040-32-5; Ib, 35040-33-6; Ic, 35040-34-7; III, 35040-35-8; IV, 35040-36-9; V, 35040-37-0; VIa, 35040-38-1; VIb, 35040-39-2; VIc, 35040-40-5; VII, 35040-41-6; VIII, 35040-42-7; IX, 35042-49-0; X, 35042-50-3.

Semihydrogenation of 1-Phenyl-4-penten-2-yn-1-one and of 1-Phenyl-3-(cyclohexen-1-yl)-2-propynone[1]

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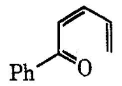
Semihydrogenation of 1-phenyl-4-penten-2-yn-1-one gave mainly 1-phenyl-2-penten-1-one. Addition of 1 mol of hydrogen to 1-phenyl-3-(cyclohexen-1-yl)-2-propynone (4) gave a mixture in which 6-phenyl-2,3-cyclohexa-2*H*-pyran and *cis*-2,3-cyclohexa-6-phenyl-3,4-dihydro-2*H*-pyran were identified by spectral methods and from which *cis*-2,3-cyclohexa-6-phenyltetrahydropyran and 3-cyclohexyl-1-phenyl-1-propanone could be isolated.

The synthesis of some cis dienones was a crucial part of a project aimed at elucidation of the electrocyclic equilibrium between α-pyrans and cis dienones. Some early studies by Schinz and his students[2] have shown that semihydrogenation of some enynones gave mixtures which appeared to contain at least the α-pyran valence isomer, and perhaps both the pyran and the cis dienone. We have investigated this semihydrogenation route to cis dienones with considerable care, and the results described here will show why we have become disenchanted with this beguilingly simple process.

Schinz[2c] indicated that partial reduction of dodec-5-en-3-yn-2-one gave mainly 2-hexyl-6-methyl-2*H*-pyran. To enhance the value of ultraviolet spectroscopy as an *a priori* device for distinguishing between cis dienone and α-pyran forms, we decided to employ phenyl rather than methyl ketones. Ring closure would then be expected to lead to a large (*ca.* 40 nm) bathochromic shift.



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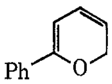
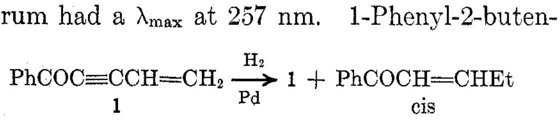


3

1-Phenyl-4-penten-2-yn-1-one (1) was prepared by Jones oxidation of the corresponding alcohol,[3] and it was reduced over a variety of palladium catalysts under varying conditions. The product inevitably contained unreacted **1**, and, when its uv absorption was subtracted from that of the mixture, the difference spectrum had a λ_{max} at 257 nm. 1-Phenyl-2-buten-1-one absorbs at 256 nm.[4] Thus the 257-nm band along with a band at 734 cm^{-1} identified the main product as *cis*-1-phenyl-2-penten-1-one. Clearly a terminal vinyl group and the triple bond are reduced competitively.



$$\underset{\mathbf{1}}{PhCOC{\equiv}CCH{=}CH_2} \xrightarrow[Pd]{H_2} \mathbf{1} + \underset{cis}{PhCOCH{=}CHEt}$$

1-Phenyl-3-(cyclohexen-1-yl)-2-propynone (4) was selected as a second substrate to reduce the competition by the double bond. Semihydrogenation of **4** gives a

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