130–140 °C (0.01 mm); mass spectrum, m/e 381, 379, 377 (M^+); ^1H NMR ($CDCl_3$) δ 0.27 (9 H, s, $SnCH_3$, $J_{^{119}Sn-^1H}$ = 52 Hz) and δ 1.42 (CCH_3) are associated with the major (7) isomer, while corresponding signals at δ 0.24 and δ 1.45 characterize the 6-NO_2 isomer. Consistent alkyl proton absorption (CH_2CH_2) (δ 1.20–2.1) and two regions of aromatic resonance (ca. δ 7.0–7.42 and 7.9–8.2) are observed. (Some impurities are revealed by the ^1H and ^{13}C NMR spectra.)

^{13}C spectra were obtained on the JEOL FX-100 spectrometer at 25.04 MHz. The solvent employed was a mixture (60:40) of deuteriochloroform and dichloromethane, and spectra were referenced to $^{13}CDCl_3$ as 77.00 ppm. ^{199}Hg spectra were obtained on the same spectrometer modified for multinuclear observation. The operating frequency was 17.82 MHz (benzylmercuric chlorides) and 17.83 MHz (dibenzylmercury series). The solvent was again 60:40 $CDCl_3$–CH_2Cl_2 and 10-mm tubes were used. The chemical shifts are referenced to the (unsubstituted) parent compounds, so that the differences represent the substituent chemical shifts. The variation in shift between the mono- and dibenzyl mercurials is in excess of 400 ppm, and relative to $(CH_3)_2Hg$, the shifts can be calculated to be ca.–1120 and –700 ppm, respectively (i.e., upfield). Concentrations of mercurials were very close to 0.4 M, and in most cases, known mixtures of two compounds were examined, and the ^{199}Hg shifts obtained were little different from those when single compounds were examined. Usually a fluoro-substituted benzyl mercurial was a member of the mixture, as this ^{199}Hg resonance (with ^{199}Hg–^{19}F coupling) could be easily recognized. The dibenzyl mercurials provide sharp spectra, whereas some broadening characterized the spectra of the mercuric chlorides. ^{119}Sn spectra were obtained on the JEOL FX-100 spectrometer at a frequency of 37.70 MHz for solutions 0.5 M in 65:35 $CDCl_3$–CH_2Cl_2 solvent. Internal tetramethyltin $(CH_3)_4Sn$ was used as reference, and dilution studies showed very minor concentration effects.

Acknowledgment. We are grateful to the Australian Research Grants Committee for funding parts of this research and for providing access to the National NMR Centre, Canberra (Director Dr. Alan Jones).

Registry No. $C_6H_5CH_2HgCl$, 2117-39-7; o-$CH_3C_6H_4CH_2HgCl$, 4109-87-9; m-$CH_3C_6H_4CH_2HgCl$, 19224-35-2; p-$CH_3C_6H_4CH_2HgCl$, 4158-22-9; m-$FC_6H_4CH_2HgCl$, 2357-53-1; p-$FC_6H_4CH_2HgCl$, 2357-55-3; m-$ClC_6H_4CH_2HgCl$, 4109-90-4; p-$ClC_6H_4CH_2HgCl$, 4109-88-0; m-$CF_3C_6H_4CH_2HgCl$, 76807-70-0; $C_6H_5CH_2HgCH_2C_6H_5$, 780-24-5; o-$CH_3C_6H_4CH_2HgCH_2C_6H_4$-$o$-$CH_3$, 76807-71-1; m-$CH_3C_6H_4CH_2HgCH_2C_6H_4$-$m$-$CH_3$, 35597-66-1; p-$CH_3C_6H_4CH_2HgCH_2C_6H_4$-$p$-$CH_3$, 10507-46-7; m-F-$C_6H_4CH_2HgCH_2C_6H_4$-m-F, 10507-43-4; p-$FC_6H_4CH_2HgCH_2C_6H_4$-p-F, 10507-45-6; p-$ClC_6H_4CH_2HgCH_2C_6H_4$-p-Cl, 10507-42-3; m-$CF_3C_6H_4CH_2HgCH_2C_6H_4$-$m$-$CF_3$, 76807-72-2; $C_6H_5CH_2Sn(CH_3)_3$, 4314-94-7; p-$FC_6H_4CH_2Sn(CH_3)_3$, 706-26-3; p-$OCH_3C_6H_4CH_2Sn(CH_3)_3$, 51755-57-8; p-$CH_3C_6H_4CH_2Sn(CH_3)_3$, 19962-42-6; p-$C_6H_5C_6H_4CH_2Sn(CH_3)_3$, 61760-10-9; m-$OCH_3C_6H_4CH_2Sn(CH_3)_3$, 51517-27-2; p-$ClC_6H_4CH_2Sn(CH_3)_3$, 41037-63-2; m-$FC_6H_4CH_2Sn(CH_3)_3$, 30590-70-6; m-$ClC_6H_4CH_2Sn(CH_3)_3$, 27640-06-8; m-$CF_3C_6H_4CH_2Sn(CH_3)_3$, 27640-07-9; o-$CH_3C_6H_4CH_2Sn(CH_3)_3$, 19962-44-8; trimethyl(2-naphthalenylmethyl)stannane, 61760-08-5; trimethyl(6-methyl-2-naphthalenylmethyl)stannane, 61760-09-6; trimethyl(1-naphthalenylmethyl)stannane, 51220-36-1; 4-methyl-1,4-ethano-1,2,3,4-tetrahydronaphthalene, 33673-05-1; 1-(trimethylstannyl)-4-methyl-1,4-ethano-1,2,3,4-tetrahydronaphthalene, 76807-73-3; 4-methyl-6-fluoro-1,4-ethano-1,2,3,4-tetrahydronaphthalene, 76807-74-4; 1-(trimethylstannyl)-4-methyl-6-fluoro-1,4-ethano-1,2,3,4-tetrahydronaphthalene, 76807-75-5; 4-methyl-7-fluoro-1,4-ethano-1,2,3,4-tetrahydronaphthalene, 76807-76-6; 1-(trimethylstannyl)-4-methyl-7-fluoro-1,4-ethano-1,2,3,4-tetrahydronaphthalene, 76807-77-7; 1-(trimethylstannyl)-4-methyl-6-(dimethylamino)-1,4-ethano-1,2,3,4-tetrahydronaphthalene, 76807-78-8; 1-(trimethylstannyl)-4-methyl-7-(dimethylamino)-1,4-ethano-1,2,3,4-tetrahydronaphthalene, 76807-79-9; 1-(trimethylstannyl)-4-methyl-6-nitro-1,4-ethano-1,2,3,4-tetrahydronaphthalene, 76807-80-2; 1-(trimethylstannyl)-4-methyl-7-nitro-1,4-ethano-1,2,3,4-tetrahydronaphthalene, 76807-81-3; 1-iodo-4-methyl-1,4-ethano-1,2,3,4-tetrahydronaphthalene, 76807-82-4; 1-iodo-4-methyl-6-fluoro-1,4-ethano-1,2,3,4-tetrahydronaphthalene, 76807-83-5; 1-iodo-4-methyl-7-fluoro-1,4-ethano-1,2,3,4-tetrahydronaphthalene, 76807-84-6; 1-iodo-4-methyl-6-(dimethylamino)-1,4-ethano-1,2,3,4-tetrahydronaphthalene, 76807-85-7; 1-iodo-4-methyl-7-(dimethylamino)-1,4-ethano-1,2,3,4-tetrahydronaphthalene, 76807-86-8.

Acylation of Multiple Anions of Poly-β-ketones by Hydroxy- and Alkoxybenzoates. Cyclization of the Resultant Tetraketones to Benzophenones and Xanthones

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Received August 6, 1980

The dianion (**2**) of 2,4-pentanedione and the trianion (**10**) of 2,4,6-heptanetrione were acylated by lithium salts of the unprotected hydroxybenzoates methyl 2-hydroxy-4-methoxy-6-methylbenzoate (**1b**), methyl 2,6-dihydroxy-4-methoxybenzoate (**7b**), and methyl 2,4-dimethoxy-6-hydroxybenzoate (**7c**), as well as by the alkoxybenzoates methyl 2,4,6-trimethoxybenzoate (**7d**) and methyl 2,4,6-tribenzoxybenzoate (**7e**). The aryl 1,3,5,7-octanetetraones (**11b-d** and **12**) resulting from acylation of **10** were cyclized in biomimetic processes to naturally occurring benzophenones and xanthones. Hydrogenolysis of 1-(2,4,6-tribenzoxyphenyl)-1,3,5,7-octanetetraone (**11e**) and cyclization gave norlichexanthone (**20**).

Acylation by benzoate esters bearing oxy substituents provides a convenient approach to several classes of secondary metabolites including coumarins,[1] coumestans,[2] xanthones,[3] and alternariol.[3] Examples have generally involved O-alkylated hydroxybenzoates; for example, the synthesis of 9-*O*-methylalternariol (**4**) has been accomplished by a route involving acylation of the dianion (**2**) of 2,4-pentanedione with ester **1a** to give triketone **3a**[3] (Scheme I). After carboxylation of the trianion of **3a**, a deprotection step is subsequently required to form **4**. It would be advantageous if acylations with hydroxy-sub-

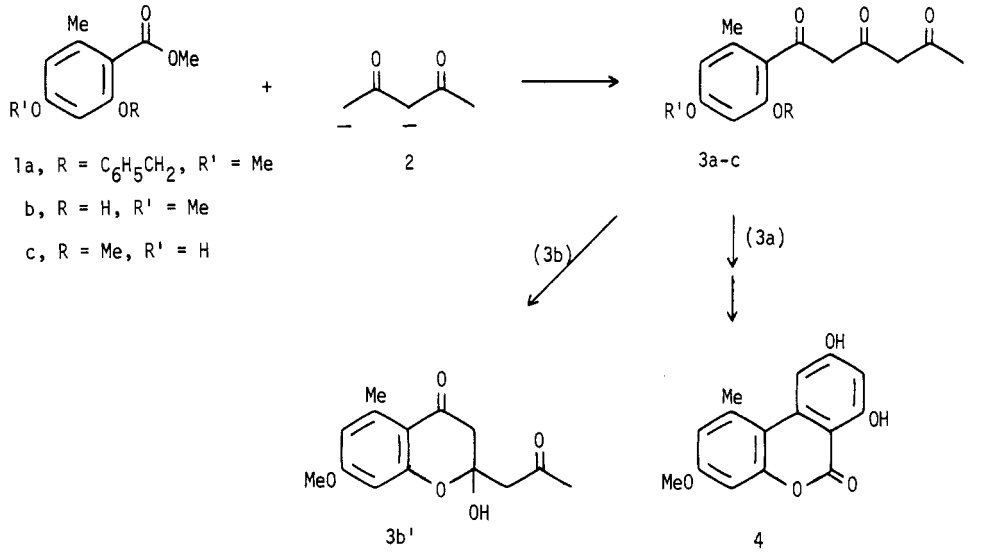
(1) Ellis, G. P., Ed. "Chromenes, Chromanones, and Chromones"; Wiley: New York, 1977; pp 273, 541–542.

(2) Nakanishi, K.; Goto, T.; Ito, S.; Natori, S.; Nozoe, S., Eds. "Natural Products Chemistry"; Kodansha, Ltd.: Tokyo; Academic Press: New York, 1975; pp 248–249.

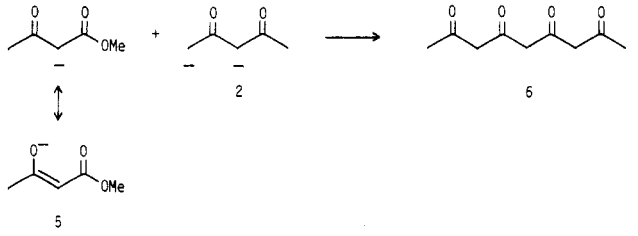
(3) Harris, T. M.; Hay, J. V. *J. Am. Chem. Soc.* **1977**, *99*, 1631.

0022-3263/81/1946-2260$01.25/0

Scheme I



Scheme II



stituted benzoate esters could be accomplished without the need for protection and deprotection steps. Moreover, undesirable side reactions are sometimes observed in anionic reactions of phenolic compounds protected as benzyl ethers.[3] The complication in use of unprotected phenolic esters as acylating agents is that the phenols become ionized under the strongly basic conditions required for such condensations; consequently, one anionic species must attack another one in the acylation process. Precedents are available which suggest the feasibility of such anion–anion condensations. For example, the monoanion (**5**) of methyl acetoacetate acylates the dianion (**2**) of 2,4-pentanedione to give tetraketone **6**[4] (Scheme II). *o*-Hydroxy- and, to a lesser extent, *p*-hydroxybenzoate esters are structurally related to β-keto esters. Precedents involving hydroxybenzoate esters include acylations of the sodium salt of dimethyl sulfoxide with ethyl 2-hydroxy- and 2,4-dihydroxybenzoate to give β-keto sulfoxides.[5] Recently the fungal xanthone bikaverin was synthesized by a route which involved acylation of lithiated 3,5-dimethylisoxazole, which is a masked β-diketone, by the sodium salt of ethyl 2-hydroxy-4-methoxy-6-methylbenzoate.[7]

We report herein the results of an investigation of the acylation of the dianion (**2**) of 2,4-pentanedione and the trianion (**10**) of 2,4,6-heptanetrione with various *o*-hydroxybenzoate esters (Table I).[6] The general procedure involved use of lithium diisopropylamide (LDA) as the ionizing base for both the β-keto compound and the phenolic ester. The β-keto compound was added to a solution of the base in tetrahydrofuran (THF) followed, after ionization was complete, by the phenolic ester. Acylation reactions employing esters require a 2:1 ratio of nucleophile to acylating agent.

Table I. Condensations of Benzoate Esters with the Dianion (2) of 2,4-Pentanedione and the Trianion (10) of 2,4,6-Heptanetrione

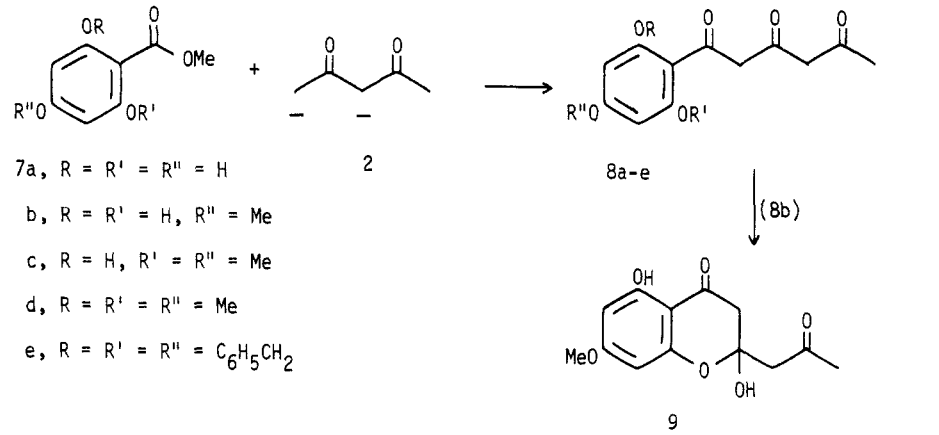
ester	anion	product	yield, %
1b	**2**	**3b'**	42
1c	**2**	**3c**	failed
7a	**2**	**8a**	failed
7b	**2**	**9**	62
7c	**2**	**8c**	100
7d	**2**	**8d**	61
7e	**2**	**8e**	100
7b	**10**	**12**	59
7c	**10**	**11c**	48
7d	**10**	**11d**	42-55
7e	**10**	**11e**	65

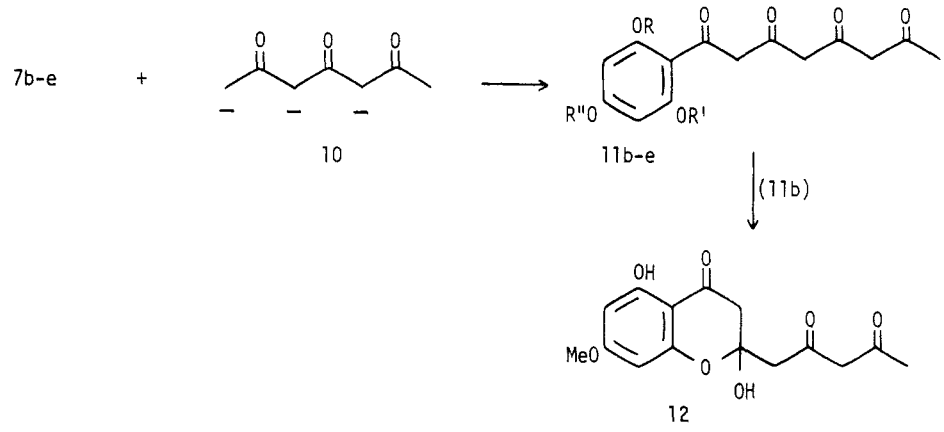
The initial study involved the 4- and 2-*O*-methyl derivatives (**1b** and **1c**) of methyl orsellinate. Treatment of **1b** with the dilithium salt of **2** for 14 h from 0 to 25 °C gave triketone **3b** in 42% yield (Scheme I); **3b** existed mainly as cyclic hemiacetal **3b'**. Similar treatment of **1c** failed to give detectable amounts of **3c** even when the condensation was allowed to proceed for 24 h. Unaltered ester **1c** was recovered in high yield from the reaction mixture. The failure of **1c** to undergo reaction is ascribed, at least in part, to the insolubility of the lithium salt in THF. In contrast, the lithium salt of **1b** was partially soluble in the reaction medium.

Attention was turned to the reactions of the methyl ester of phloroglucinolcarboxylic acid and the corresponding methyl ethers. The unprotected ester **7a** formed a highly insoluble trilithium salt which failed to condense with the dilithium salt of **2** to give aryl triketone **8a** (Scheme III). However, the dilithium salt of 4-methyl ether **7b** reacted with **2** to give aryl triketone **8b**. The monolithium salt of 4,6-dimethyl ether **7c** reacted similarly to give triketone **8c**. Triketone **8c** existed mainly as a mixture of enol and keto forms whereas **8b** was isolated as cyclic hemiacetal **9**, in which the remaining phenolic hydroxyl group was hydrogen bonded to the oxygen of the ketone carbonyl. The hemiketal structure of **9** was indicated in the ^{1}H NMR spectrum by the AB patterns for the prochiral methylene groups and in the ^{13}C NMR spectrum by the number of

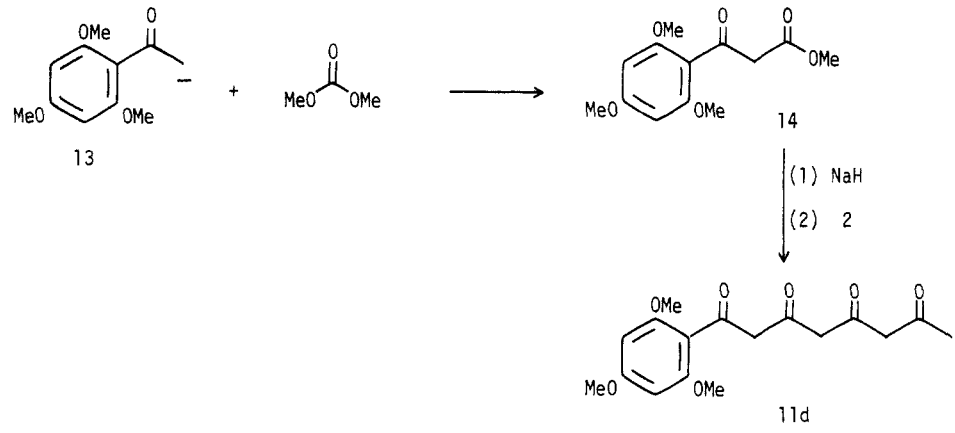
(4) Murray, T. P.; Harris, T. M. *J. Am. Chem. Soc.* **1972**, *94*, 8253.
(5) (a) Klutchko, S.; Cohen, M. P.; Shavel, J. Jr.; von Standtmann, M. *J. Heterocycl. Chem.* **1974**, *11*, 183. (b) von Standtmann, M.; Klutchko, S.; Cohen, M. P.; Shavel, J., Jr. *Ibid.* **1972**, *9*, 171.
(6) Sandifer, R. M.; Harris, T. M. *J. Chem. Soc., Chem. Commun.* **1979**, 442.
(7) Iijima, I.; Taga, N.; Miyazaki, M.; Tanaka, T.; Uzawa, J. *J. Chem. Soc., Perkin Trans. 1* **1979**, 3190.

Scheme III





Scheme IV

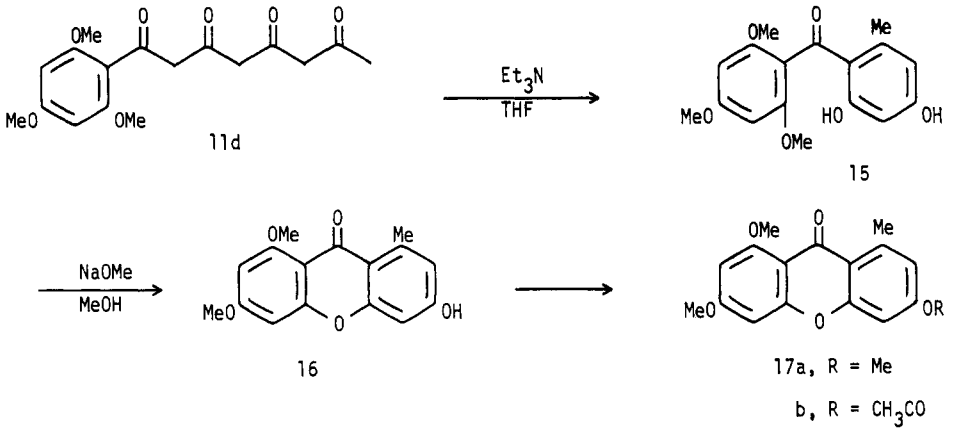


carbon signals and their chemical shifts. The condensation of trialkyl ethers **7d** and **7e** with the dilithium salt of **2** gave triketones **8d** and **8e** in good yield. In general, the bulk of alkoxy substituents at positions 2 and 6 on the aromatic ring causes the reactions to be sluggish, requiring higher temperatures and longer periods of reaction. Less steric hindrance is encountered in condensations with dilithio **7b** and lithio **7c** because coordination of the lithium cation between the phenoxide anion and the carbonyl oxygen of the ester group holds the ester in the plane of the aromatic ring, rendering the ester more susceptible to nucleophilic attack.

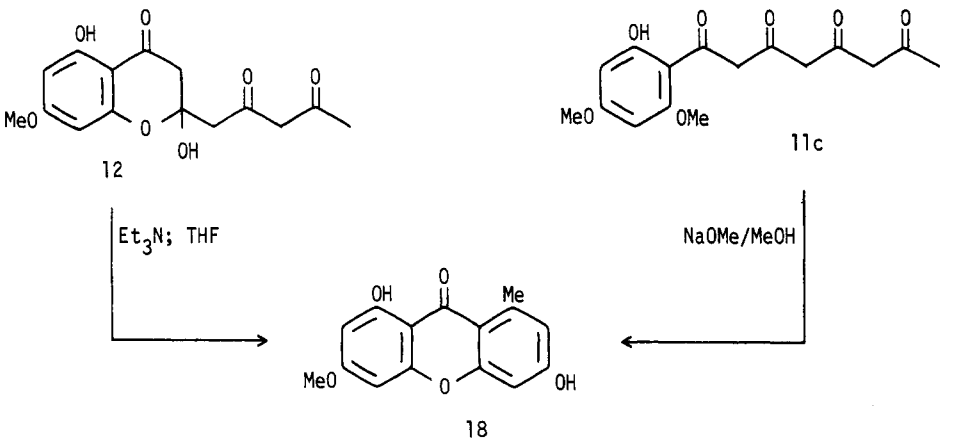
Reactions of esters **7b–e** with the trilithium salt (**10**) of 2,4,6-heptanetrione were also investigated. Condensation with dilithium salt **7b** gave tetraketone **11b** which existed mainly as enol/keto tautomers of hemiacetal β-diketone **12**. Ester **7c** gave tetraketone **11c** which existed as a complex mixture of mono- and dienol forms. Initial attempts to effect the reaction of trimethoxy ester **7d** with the trilithio triketone were unsuccessful, but reaction to give tetraketone **11d** was subsequently achieved in 55% yield by carrying out the reaction at 0–25 °C for 17 h. Similarly, tribenzoxy ester **7e** gave **11e** in 60% yield after 22 h at 45 °C.

Our interest in tetraketones **11** and in hemiacetal **12** lay in the possibilities for cyclization to griseophenones and xanthones. Prior to the development of the conditions for formation of tetraketone **11d** by condensation of trianion **10** with ester **7d**, a less direct route was developed which involved acylation of the enolate anion (**13**) of 2,4,6-trimethoxyacetophenone with dimethyl carbonate. The resulting β-keto ester (**14**) was converted to its sodium salt

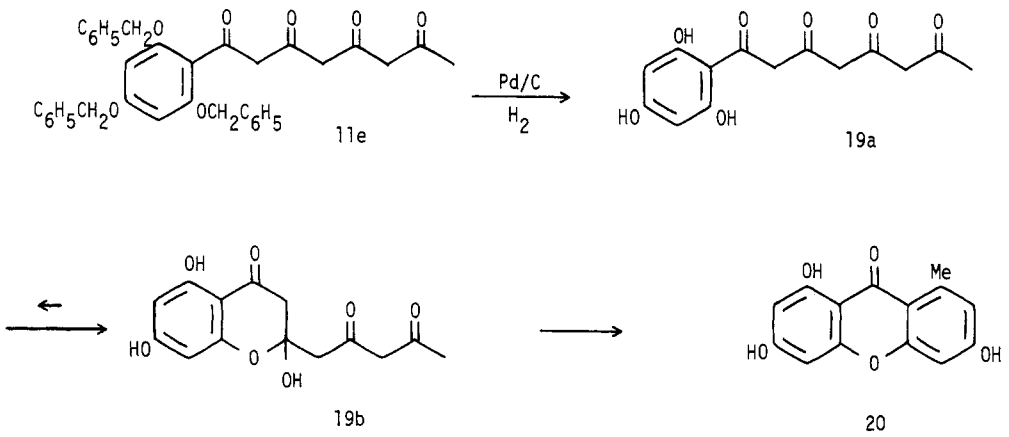
Scheme V



Scheme VI



Scheme VII



and used to acylate the dianion (**2**) of 2,4-pentanedione to give **11d** (Scheme IV).

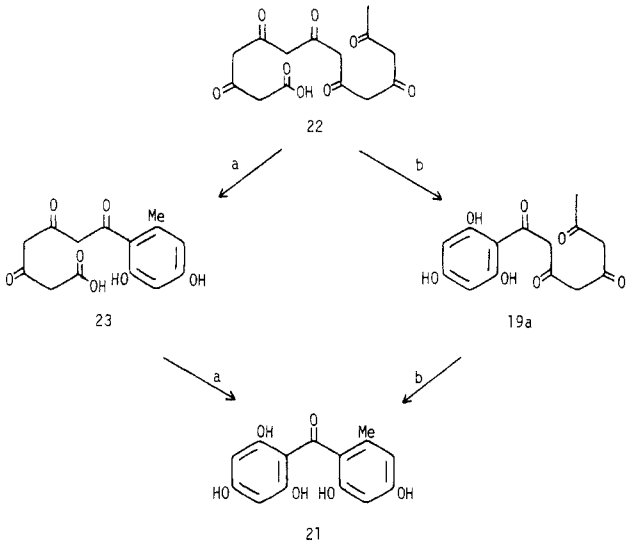
Aldol-type closures of the tetraketones gave naturally occurring benzophenones and xanthones in biomimetic processes. Under mildly basic conditions, tetraketone **11d** cyclized to benzophenone **15** (Scheme V), which could also be obtained directly from the reaction of β-keto ester **14** and the dilithium salt of **2** by quenching the intermediate lithium salts with water. A second ring closure to 1-*O*-methylgriseoxanthone C occurred when benzophenone **15** was treated with sodium methoxide in methanol. Methylation of xanthone **16** gave the fungal metabolite *O*-methyllichexanthone (**17a**). Xanthone **16** was further characterized as the monoacetate derivative (**17b**).

Hemiacetal **12** underwent a rapid conversion to griseoxanthone C (**18**) even under mildly basic conditions (Scheme VI), while tetraketone **11c** gave **18** only after treatment with sodium methoxide in methanol. 2-Hydroxy-2′-methoxybenzophenones similar to the one intermediate in the latter reaction have been observed to undergo a loss of a molecule of methanol under both acidic and basic conditions.[8]

Hydrogenolysis of tetraketone **11e** gave tetraketone **19a** with liberated phenolic groups (Scheme VII); the compound was isolated as hemiacetal **19b** after chromatography. The latter compound proved to be surprisingly stable, being recovered almost quantitatively from reflux with triethylamine in THF and from sodium acetate/acetic acid buffer of pH 5. Cyclization to norlichexanthone (**20**) was

(8) McMaster, W. I.; Scott, A. I.; Trippett, S. *J. Chem. Soc.* **1960**, 4628.

Scheme VIII



finally effected by heating **19b** with potassium hydroxide in ethanol/water. Neither tetraketone **19a** nor benzophenone **21**, both likely intermediates in the formation of **20**, was observed in this process. Dehydration of benzophenone **21** is known to be particularly facile.[9]

Indirect evidence indicates benzophenone **21** to be the biosynthetic precursor to the antibiotic griseofulvin[9a] and to the various fungal[9a] and lichen[9b,10] xanthones, the latter metabolites being derived either from shunt metabolic pathways or from nonenzymatic closures of **21** or its chloro and *O*-alkyl derivatives. Benzophenone **21** itself is derived biogenetically from a polyketide chain (**22**) of seven acetate units via Claisen- and aldol-type closures of the chain (Scheme VIII); the order of these closures is not known. A chemical model study which gives indirect support to path b[3] has been reported.

The present study gives further support to the possibility of path b but offers no proof as to what occurs in the enzymatic pathway. A successful biogenetic-type synthesis means the proposed biosynthetic process is plausible not that it necessarily occurs, and it does not make a final distinction between alternative pathways (note that alternariol has been synthesized by routes modeled after *each* of two alternative pathways[3,11]).

A survey of fungal metabolites by Turner produced no examples in which the uncyclized residues of the carboxy end of the polycarbonyl chain outnumbered those of the methyl end.[12] The natural existence of such compounds (e.g., **23**) may have been obscured, however, by the extreme lability of poly-β-keto acids[13] toward cyclization in the pH ranges likely both in fermentation media and in aqueous solutions involved in the process of extraction.

Experimental Section

Tetrahydrofuran (THF) and ether were distilled from sodium/potassium alloy and used immediately. Lithium diisopropylamide (LDA) was prepared by addition of 1.1 equiv of *n*-butyllithium to 1 equiv of diisopropylamine (distilled from sodium) in an ethereal solvent at 0 or −70 °C under a nitrogen atmosphere. All glassware was dried for at least 1 h at 130 °C, assembled for the reaction, and cooled under a stream of nitrogen. All reactions involving anionic intermediates were performed under nitrogen. Thin-layer chromatography (TLC) was done with Merck GF(254) plates (0.25 mm), visualized under UV light and developed by I_2, alcoholic $FeCl_3$, or diazotized benzidine. Column chromatography was done by using silica gel (Matheson Coleman and Bell, grade 62, 60–200 mesh) that had been washed previously with 2 N HCl, rinsed to pH 4.5, and dried to 25% water content. ^1H NMR spectra were recorded on a JEOL MH-100 or FX-90Q spectrometer. ^{13}C NMR spectra were done on the latter instrument, IR spectra on a Perkin-Elmer 727 spectrophotometer, and mass spectra on an LKB-9000 mass spectrometer (70 eV). Melting points, taken on a MelTemp device, are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc.

Methyl 2-hydroxy-4-methoxy-6-methylbenzoate (**1b**),[3] methyl 4-hydroxy-2-methoxy-6-methylbenzoate (**1c**),[14] 2,4,6-heptanetrione,[15] methyl 2,6-dihydroxy-4-methoxybenzoate (**7b**),[16] methyl 2,4,6-trimethoxybenzoate (**7d**),[17] methyl 2,4-dimethoxy-6-hydroxybenzoate (**7c**),[18] and 2,4,6-trimethoxyacetophenone (**13**)[21] were prepared according to published procedures. The preparation of methyl 2,4,6-tribenzoxybenzoate (**7e**) was modeled after that of benzyl 2,4,6-tribenzoxybenzoate.[9b] The dilithium salt of 2,4-pentanedione (**2**)[19] and the trilithium salt of 2,4,6-heptanetetraone (**10**)[20] were prepared as described previously.

2-Hydroxy-7-methoxy-5-methyl-2-(2-oxopropyl)-2,3-dihydro-4*H*-1-benzopyran-4-one (3b). A solution of methyl 2-hydroxy-4-methoxy-6-methylbenzoate (**1b**) (0.526 g, 2.68 mmol) in 15 mL of THF was added dropwise to 8.05 mmol of the dilithium salt of **2**, prepared with LDA (15.1 mmol) in THF at 0 °C, to form a pale yellow solution, which was allowed to warm to room temperature over 14 h. The clear orange solution was evaporated, an ethereal slurry of the resultant lithium salts was partitioned with cold dilute HCl, and the layers were separated. Extraction of the aqueous layer (pH 3) with ethyl acetate (twice), washing of the combined organic layers (brine), drying ($MgSO_4$), and evaporation gave an orange solid. Removal of excess 2,4-pentanedione in vacuo by use of a Dewar condenser at −78 °C and chromatography (10 g of acidic silica gel, 0–90% ether/hexane) gave 0.829 g (42%) of **3b′** as an orange solid: mp 110–114 °C (lit.[3] mp 116.5–117.5 °C); identical by TLC and NMR and mass spectroscopy with authentic material.

Methyl 2,4,6-Tribenzoxybenzoate (7e). Anhydrous K_2CO_3 (30 g, heated 6 h, 130 °C) was added to 5 g (27.2 mmol) of methyl 2,4,6-trihydroxybenzoate[17] in 100 mL of acetone (dried over K_2CO_3), and the system was flushed thoroughly with nitrogen before 9.7 mL (13.9 g, 81.5 mmol) of benzyl bromide was added. The mixture was heated under reflux 50 h. The solids were filtered and rinsed (2 × 100 mL of acetone), and the filtrate and rinsings were evaporated to a golden oil which was partitioned with ether and iced dilute HCl. After separation, the aqueous layer was extracted (3×, ether); the combined organic layers were washed (2×, saturated $NaHCO_3$), dried ($MgSO_4$), and evaporated to a cloudy tan oil. Trituration with hexane (15 min) caused tan crystals to form; after an additional 15 min of being stirred, these were filtered and washed (2 × 50 mL of hexane). Three recrystallizations (methanol) gave 6.3 g (51%) of **7e** as analytically pure colorless crystals: mp 111.5–112 °C; ^1H NMR ($CDCl_3$) δ 4.10 (s, 3 H), 5.29 (s, 2 H), 5.38 (s, 4 H), 6.62 (s, 2 H), 7.78 (m, 15 H); IR (CH_2Cl_2) 1720, 1600, 1430, 1270, 1160, 1115 cm^{-1}; mass

(9) (a) Harris, C. M.; Roberson, J. S.; Harris, T. M. *J. Am. Chem. Soc.* **1976**, *98*, 5380. (b) Sundholm, E. G. *Acta Chem. Scand., Ser. B* **1974**, *B28*, 1102.
(10) Sundholm, E. G. Doctoral Dissertation; University of Uppsala, Sweden, 1979.
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spectrum, m/e (relative intensity) 454 ($M^{\cdot+}$, 16), 422 (10), 363 (24), 331 (6), 195 (10), 181 (17), 180 (14), 91 (100).

Anal. Calcd for $C_{29}H_{26}O_5$: C, 76.63; H, 5.77. Found: C, 76.82; H, 5.90.

1-(2,4,6-Trimethoxyphenyl)-1,3,5-hexanetrione (8d). A solution of 0.365 g (1.16 mmol) of methyl 2,4,6-trimethoxybenzoate (**7d**) in 20 mL of THF was added dropwise to 4.83 mmol of the dilithium salt of **2**, prepared with LDA (9.66 mmol) in THF at 0 °C, to give a light yellow-green solution which was allowed to warm to room temperature over 19 h. The THF was evaporated, and the slurry resulting from addition of ether (100 mL) was partitioned with cold, dilute HCl. The organic layer and extracts (3×, ether) of the aqueous layer (pH 3) were combined, dried ($MgSO_4$), and evaporated. Removal of excess 2,4-pentanedione in vacuo by use of a Dewar condenser at −78 °C gave 0.501 g of yellow oil. Chromatography (10 g of acidic silica gel, 0–80% ether/hexane) gave a yellow oil. Further chromatography (5 g of acidic silica gel, ether/hexane) gave 0.290 g (61%) of **8d**. Crystallization (cold ether/hexane) gave yellow crystals, and recrystallization (2×) gave analytically pure material: mp 68.5–71.5 °C; ^1H NMR ($CDCl_3$, a mixture of tautomers) δ 1.98 (s), 2.03 (s), 2.25 (s), 2.31 (s), 3.42 (s), 3.80 (s, 6 H), 3.86 (s, 3 H), 5.22 (s), 5.38 (s), 5.65 (s), 5.79 (s), 6.10 (s), 6.14 (s); IR (CH_2Cl_2) 1670–1710 (br), 1600, 1200, 1160, 1130 cm^{-1}; mass spectrum, m/e (relative intensity) 294 ($M^{\cdot+}$, 15), 263 (18), 195 (100), 168 (13).

Anal. Calcd for $C_{15}H_{18}O_6$: C, 61.22; H, 6.17. Found: C, 61.06; H, 6.22.

2,5-Dihydroxy-7-methoxy-2-(2-oxopropyl)-2,3-dihydro-4*H*-1-benzopyran-4-one (9). Methyl 2,6-dihydroxy-4-methoxybenzoate (**7b**; 0.600 g, 3.03 mmol) dissolved in 10 mL of THF was added dropwise to 6.06 mmol of the dilithium salt of **2**, prepared with LDA (18.2 mmol) in THF at 0 °C. Precipitation of a white solid occurred; the reaction mixture, a yellow suspension after 10 min, was allowed to warm to room temperature over 14.4 h and was then evaporated to give orange-yellow lithium salts. After an ethereal slurry of these salts was partitioned with dilute HCl, the layers were separated, the aqueous layer was extracted (3×, ether), and the combined organic layers were dried ($MgSO_4$) and evaporated to a viscous orange oil. Excess 2,4-pentanedione was removed in vacuo by use of a Dewar condenser at −78 °C to give 0.74 g of oil. Chromatography (15 g of acidic silica gel, 0–100% ether/hexane, followed by 10% methanol/ether) gave an orange-yellow oil which was dissolved in ethyl acetate, dried ($MgSO_4$), and evaporated to give 0.498 g (62%) of **9** as an orange-yellow solid, mp 112–117 °C. Three recrystallizations (methanol/water) gave analytically pure pale yellow crystals: mp 131.5–133 °C (dried in vacuo); ^1H NMR (acetone-d_6) δ 2.29 (s, 3 H), 2.77 (d, 1 H, J = 17 Hz), 3.04 (d, 1 H, J = 16 Hz), 3.27 (dd, 1 H, J = 17, 2 Hz, irradiation at δ 6.39 collapsed 2-Hz splitting), 3.32 (d, 1 H, J = 16 Hz), 3.85 (s, 3 H), 5.98 and 6.04 (2 d, 1 H each, J = 2 Hz), 6.39 (d, 1 H, J = 2 Hz), 12.01 (s, 1 H); ^{13}C NMR (acetone-d_6) δ 32.0 (q), 46.5 (t), 51.7 (t), 56.2 (q), 95.5 (d, approximately 2 times the intensity of other protonated carbons), 101.9 (s), 103.5 (s), 160.7 (s), 164.6 (s), 168.8 (s), 196.3 (s), 207.1 (s); IR (CH_2Cl_2) 1700, 1630, 1580, 1315, 1150 cm^{-1}; mass spectrum, m/e (relative intensity) 266 ($M^{\cdot+}$, 39), 198 (69) 197 (29), 192 (19), 178 (10), 177 (10), 167 (10), 166 (75), 140 (25), 125 (14), 85 (38), 43 (75).

Anal. Calcd for $C_{13}H_{14}O_6$: C, 58.65; H, 5.30. Found: C, 58.85; H, 5.55.

1-(2,4-Dimethoxy-6-hydroxyphenyl)-1,3,5-hexanetrione (8c). Methyl 2,4-dimethoxy-6-hydroxybenzoate (**7c**; 0.500 g, 2.35 mmol) in 15 mL of THF was added dropwise to 7.08 mmol of the dilithium salt of **2**, prepared with LDA (16.5 mmol) in THF at 0 °C, to give a light yellow solution which was allowed to warm to room temperature over 26.75 h to give a medium-orange solution. An ethereal slurry of the lithium salts resulting from evaporation of the solvent was partitioned with cold dilute HCl. After separation, the aqueous layer (pH 3) was extracted (3×, ether), and the combined organic layers were dried ($MgSO_4$) and evaporated to give a yellow solid. Removal of excess 2,4-pentanedione in vacuo gave 0.673 g (100%) of **8c**. An NMR spectrum and TLC showed no contaminants. Rapid chromatography (5 g of acidic silica gel, ether/hexane) gave orange crystals, mp 74–82 °C. Recrystallization (2×, methanol/water) afforded analytically pure apricot-orange crystals: mp 95–98 °C; ^1H NMR ($CDCl_3$, a mixture of tautomers) δ 2.04 (s), 2.27 (s), 2.30 (s), 3.68 (s), 3.80 (s), 3.95 (s), 4.14 (s), 5.48 (s), 5.92 (d, 1 H, J = 2 Hz), 6.11 (d, 1 H, J = 2 Hz), 13.18 (br s), 13.45 (br s), 13.57 (s); IR (Nujol) 1710, 1620, 1580 cm^{-1}; mass spectrum, m/e (relative intensity 280 ($M^{\cdot+}$, 22), 223 (37), 181 (100), 154 (12), 149 (13).

Anal. Calcd for $C_{14}H_{16}O_6$: C, 60.00; H, 5.75. Found: C, 60.12, H, 5.98.

1-(2,4,6-Tribenzoxyphenyl)-1,3,5-hexanetrione (8e). Methyl 2,4,6-tribenzoxybenzoate (**7e**; 1.00 g, 2.20 mmol) in 15 mL of THF was added dropwise to 4.40 mmol of the dilithium salt of **2**, prepared with LDA (8.80 mmol) in THF at 0 °C, to produce a green solution which was allowed to warm to room temperature over 2.5 h. The mixture was heated at 40–45 °C for 28 h to produce a yellow suspension, which was cooled to room temperature and evaporated. Cold, dilute HCl (100 mL) was added to an ethereal suspension (50 mL) of the resultant lithium salts. After partition and separation, the aqueous layer was extracted (3×, ether), dried ($MgSO_4$), and evaporated to a yellow-orange oil. Excess 2,4-pentanedione was removed in vacuo to give 1.16 g of orange oil which appeared by NMR and TLC analysis to be essentially pure **8e** (100%). Chromatography (2×, acidic silica gel, ether/hexane) gave analytically pure **8e** as a yellow oil: ^1H NMR ($CDCl_3$, a mixture of tautomers) δ 1.83 (s), 1.97 (s), 2.02 (s), 2.12 (s), 3.33 (s), 3.48 (s), 3.77 (s), 3.96 (s), 4.75 (s), 5.00 (s), 5.04 (s), 5.07 (s), 5.18 (s), 5.47 (s), 5.87 (s), 6.02 (s), 6.27 (s), 6.30 (s), 6.82–7.85 (m), 12.72 (s), 14.5 (br s), 15.3 (br s); mass spectrum, m/e (relative intensity) 522 ($M^{\cdot+}$, 0.9), 423 (11), 396 (11), 350 (9), 333 (10), 306 (9), 181 (12), 92 (16), 91 (100).

Anal. Calcd for $C_{30}H_{30}O_6$: C, 75.84; H, 5.79. Found: C, 76.09; H, 5.97.

2,5-Dihydroxy-7-methoxy-2-(2,4-dioxopentyl)-2,3-dihydro-4*H*-1-benzopyran-4-one (12). Methyl 2,6-dihydroxy-4-methoxybenzoate (**7b**; 0.848 g, 4.42 mmol) in 15 mL of THF was added to 13.3 mmol of the trilithium salt of **10**, prepared with LDA (44.2 mmol) in THF at 0 °C, to form an orange suspension which was allowed to warm to room temperature over 16 h. The mixture was heated at 40 °C for 46 h to form a brick-red suspension which was evaporated to give lithium salts. Dilute HCl (100 mL) was added to an ethereal slurry (100 mL) of the salts and the mixture partitioned. The aqueous layer (pH 2) was extracted (3×, ethyl acetate), and the combined organic layers were washed (brine) and dried ($MgSO_4$). Evaporation of the yellow solution gave an orange-red oil, chromatography (40 g of acidic silica gel, 0–80% ether/hexane) of which gave 0.800 g (59%) of hemiacetal **12**. Crystallization from a large volume of ether and recrystallization (methanol) gave **12** as analytically pure light yellow crystals: mp 140–142 °C; ^1H NMR ($CDCl_3$, varying tautomer composition) δ 2.03 (s), 2.15 (s), 2.49 (s), 2.57 (d, 1 H, J = 16 Hz, overlapped with s at 2.79), 2.79 (s, overlapped with d at 2.57) 2.99 (s, 1 H, OH), 3.00 (d, 1 H, J = 16 Hz), 3.70 (s), 5.52 (s), 5.80 (d, 1 H, J = 3 Hz), 5.85 (d, 1 H, J = 3 Hz), 6.80 (s, OH), 11.60 (s, OH); IR (KBr) 1610, 1570, 1150 cm^{-1}; mass spectrum, m/e (relative intensity) 308 ($M^{\cdot+}$, 21), 290 (9), 209 (100), 208 (96), 167 (79), 166 (90), 138 (24), 100 (9), 85 (25), 43 (64).

Anal. Calcd for $C_{15}H_{16}O_7$: C, 58.44; H, 5.23. Found: C, 58.62; H, 5.52.

1-(2,4-Dimethoxy-6-hydroxyphenyl)-1,3,5,7-octanetetraone (11c). A solution of 1.78 g (8.40 mmol) of methyl 2,4-dimethoxy-6-hydroxybenzoate (**7c**) in 15 mL of THF was added to 21.0 mmol of the trilithium salt of **10**, prepared with LDA (7.20 mmol) in THF at 0 °C, to form a dark red mixture, which was allowed to warm to 30 °C over 28.2 h. Evaporation of the solvent gave lithium salts which were suspended in ether and partitioned with cold dilute HCl (100 mL). After separation, the aqueous layer was extracted (3×, ether), and the combined organic layers were washed (brine), dried ($MgSO_4$), and evaporated to 4.05 g of dark red oil. The product mixture, adhered to ca. 2 g of silica gel, was placed on the surface of a column of 80 g of acidic silica gel. Chromatography (0 to 100% ether/hexane) gave 1.30 g (48%) **11c** as a red oil. Crystallization (cold ether/hexane) gave orange-yellow crystals, mp 59–64 °C. Repeated recrystallizations did not improve the purity. Chromatography (2×, acidic silica gel, ether/hexane) gave analytically pure **11c** as a dark orange oil: ^1H NMR ($CDCl_3$, mixture of tautomers) δ 2.02 (s), 2.13 (s), 2.30 (s), 2.89 (s), 3.37 (s), 3.45 (s), 3.58 (s), 3.92 (s), 4.08 (s), 4.20 (s), 4.24 (s), 5.28 (s), 5.72 (s), 5.74 (s), 5.83 (s), 6.07 (d, 1 H, J = 2 Hz), 6.12 (s, 1 H, J = 2 Hz), 7.48 (s, OH), 7.55 (s, OH), 13.62

(s, OH), 13.85 (s, OH), 13.93 (s, OH), 13.94 (s, OH), 14.51 (s, OH), 15.39 (s, OH); mass spectrum, m/e (relative intensity) 322 ($M^{\cdot+}$, 4), 265 (12), 223 (23), 181 (61), 145 (16), 140 (16), 127 (53), 125 (26), 100 (18), 85 (100), 83 (17), 82 (25), 43 (49).

Anal. Calcd for $C_{16}H_{18}O_7$: C, 59.62; H, 5.63. Found: C, 59.44; H, 5.56.

1-(2,4,6-Tribenzoxyphenyl)-1,3,5,7-octanetetraone (11e). A solution of methyl 2,4,6-tribenzoxybenzoate (**7e**; 0.610 g, 1.34 mmol) in 10 mL of THF was added dropwise to 3.36 mmol of the trilithium salt of **10**, prepared with LDA (10.1 mmol) in THF at 0 °C, to form an orange solution. The reaction mixture was warmed to room temperature over 18 h and then heated at 40–45 °C for 22 h, after which the mixture was cooled and the solvent evaporated. An ethereal slurry of the resultant lithium salts was partitioned with cold dilute HCl, and the layers were separated. The aqueous layer (pH 3) was extracted (3×, ether), and the combined organic layers were washed (brine), dried ($MgSO_4$), and evaporated to give 0.902 g of yellow-orange oil, chromatography (10 g of acidic silica gel, 0–30% ether/hexane) of which gave 0.488 g (65%) of **11e** as an orange oil. Further chromatography (2×) gave analytically pure material as an orange-red oil: ^1H NMR ($CDCl_3$, a mixture of tautomers) δ 1.96 (s), 2.01 (s), 2.15 (s), 2.18 (s), 2.28 (s), 3.17 (s), 3.29 (s), 3.39 (s), 3.49 (s), 3.66 (s), 3.73 (s), 3.83 (s), 4.03 (s), 5.04 (s), 5.10 (s), 5.22 (s), 5.65 (s), 5.98 (s), 6.30 (s), 6.32 (s), 7.40 (m), 11.4 (br s); IR (CH_2Cl_2) 1730, 1600 (br), 1430, 1375, 1155, 1115 cm^{-1}; mass spectrum, m/e (relative intensity) (no $M^{\cdot+}$ at 564) 546 (1), 527 (1), 487 (1), 486 (1), 439 (2), 422 (7), 396 (14), 333 (10), 306 (16), 181 (9), 91 (100).

Anal. Calcd for $C_{35}H_{32}O_7$: C, 74.45; H, 5.71. Found: C, 74.15; H, 5.75.

Methyl 3-(2,4,6-Trimethoxyphenyl)-3-oxopropanoate (14). 2,4,6-Trimethoxyacetophenone (**13**; 11.8 g, 56 mmol) dissolved in 80 mL of THF was added dropwise to a suspension of 4.0 g (160 mmol) of sodium hydride (prepared from an oil dispersion by washing with hexane) in 70 mL of THF at room temperature under nitrogen with stirring. After 45 min, 11.0 g (120 mmol) of dimethyl carbonate was added rapidly. The mixture was stirred 1 h and then heated under reflux for 15 h. The solvent was evaporated, and the pale yellow, solid residue was added carefully to dilute HCl. The extracts (CH_2Cl_2) of this solution were washed (brine), dried ($MgSO_4$), and evaporated to give a solid residue which was washed (ether) to give 14.0 g (93%) of **14**, mp 94–97 °C. Recrystallization (3 × 75 mL of ethanol) afforded 12.4 g (82%) of analytically pure **14** as colorless crystals: mp 96–97 °C; ^1H NMR ($CDCl_3$) δ 3.68 (s, 2 H), 3.73–3.83 (2 s, 12 H), 6.06 (s, 2 H); IR (CH_2Cl_2) 1738, 1685, 1598 cm^{-1}; mass spectrum, m/e 268 ($M^{\cdot+}$).

Anal. Calcd for $C_{13}H_{16}O_6$: C, 58.21, H, 5.97. Found: C, 58.13; H, 5.96.

1-(2,4,6-Trimethoxyphenyl)-1,3,5,7-octanetetraone (11d). A solution of 2.68 g (10.0 mmol) of methyl 3-(2,4,6-trimethoxyphenyl)-3-oxopropanoate (**14**) in 25 mL of THF was added dropwise to a suspension of 0.5 g (20 mmol) of sodium hydride (prepared from an oil dispersion by washing with hexane) in 25 mL of THF at 0 °C under nitrogen and stirred for 0.5 h. A solution of 30 mmol of the dilithium salt of **2**, prepared in THF at 0 °C, was added to the suspension of the sodium salt of **14** at room temperature to produce a light orange mixture which changed to a deep scarlet solution after 15 min. After 5 h at room temperature, this solution was heated 22 h at 40–42 °C and then evaporated to give lithium salts which were added to a solution of KH_2PO_4 (3.0 g, 22 mmol) and 4 mL of 12 M HCl in 75 mL of iced water which was extracted (CH_2Cl_2) immediately. The combined extracts were washed (2×, brine), dried (Na_2SO_4), and evaporated to a yellow oil. Chromatography (35 g of acidic silica gel, 0–100% ether/hexane) gave 1.42 g (42%) of **11d** as a yellow oil. Crystallization (ethanol) and recrystallization (acetone/hexane) gave analytically pure **11d** as yellow crystals: mp 176–179 °C; ^1H NMR ($CDCl_3$, a mixture of tautomers) δ 1.91 (s), 2.04 (s), 2.22 (s), 3.26 (s), 3.52 (s), 3.75 (s, 6 H), 3.78 (s, 3 H), 3.92 (s), 4.05 (s), 5.10 (s), 5.22 (s), 5.24 (s), 5.27 (s), 5.35 (s), 5.51 (s), 5.51 (s), 5.62 (s), 5.78 (s), 6.03 (s), 6.06 (s); IR (neat) 3680–3320, 1735–1680, 1640–1550 cm^{-1}; mass spectrum, m/e 336 ($M^{\cdot+}$).

Anal. Calcd for $C_{17}H_{20}O_7$: C, 60.71; H, 5.95. Found: C, 60.99; H, 6.04.

In a second preparation, methyl 2,4,6-trimethoxybenzoate (**7d**; 1.00 g, 4.42 mmol) in 15 mL of THF was added to 13.3 mmol of the trilithium salt of **10**, prepared with LDA (39.8 mmol) in THF at 0 °C, to give an orange solution which was stirred 17 h at room temperature. The resultant clear, dark red solution was evaporated to give lithium salts, which were suspended in ether and partitioned with iced dilute HCl. The separated aqueous layer was extracted (3×, ether), and the combined organic layers were washed (brine), dried ($MgSO_4$), and evaporated to give 2.44 g of brown-red oil. Chromatography (50 g of acidic silica gel, 0–100% ether/hexane, followed by 10% methanol/ether) gave 0.816 g (55%) of **11d** as a red oil, identical by TLC and mass and NMR spectroscopy with material prepared earlier.

2′,4′-Dihydroxy-2,4,6-trimethoxy-6′-methylbenzophenone (15). The reaction of the sodium salt of **14** (4.02 g, 15 mmol) and 45 mmol of dianion **2** was accomplished as described above. The dry lithium salts obtained from evaporation of the THF were added in portions to ice–water to form a yellow solution which was acidified (HCl) and immediately extracted (CH_2Cl_2). The combined extracts were washed (brine), dried (Na_2SO_4), and evaporated to give 7.4 g of yellow oil. Chromatography (60 g of acidic silica gel, 0–1% CH_2Cl_2/hexane, followed by 100% ether) gave 4.0 g of bright yellow solid. Further chromatography (50 g of acidic silica gel, ether/hexane) gave 2.79 g of yellow solid which was washed with CH_2Cl_2. An unidentified white solid (0.200 g) did not dissolve. The rinsings were concentrated to a yellow residue which was crystallized (ethanol) to give **15**: 1.70 g (35.6%); mp 169–173 °C; ^1H NMR (2:1 $CDCl_3/CD_3COCD_3$) δ 1.90 (s, 3 H), 3, 78 (s, 6 H), 3.88 (s, 3 H), 6.2–6.4 (m, 4 H), 8.68 (br s, 1 H), 13.72 (s, 1 H); IR (CH_2Cl_2) 1625–1570 cm^{-1}; mass spectrum, m/e 318 ($M^{\cdot+}$).

Anal. Calcd for $C_{17}H_{18}O_6$: C, 64.15; H, 5.66. Found: C, 64.00; H, 5.72.

In a more satisfactory preparation, a mixture of 0.280 g (0.833 mmol) of **11d**, 0.060 g of triethylamine (distilled from sodium), and 25 mL of THF was heated under reflux in a nitrogen atmosphere for 38 h and then evaporated to a yellow residue. Addition of ethanol and crystallization gave **15** in essentially quantitative yield; the material was identical by TLC and mass and NMR spectroscopy with material prepared previously.

1,3-Dimethoxy-6-hydroxy-8-methyl-9*H*-xanthen-9-one (16). A mixture of 2′,4′-dihydroxy-2,4,6-trimethoxy-6′-methylbenzophenone (**15**; 0.105 g, 0.330 mmol), 0.351 g (6.50 mmol) of sodium methoxide, and 9 mL of methanol was heated under reflux in a nitrogen atmosphere for 63 h. The mixture was cooled to room temperature, and 2 mL of water was added. Acidification with dilute HCl precipitated 95 mg of yellow solid. An additional 40 mg of solid was obtained from partial evaporation of the mother liquor. The combined solids were dissolved in ethanol and crystallized to give 90 mg of pale yellow crystals, which were heated in THF and filtered to give 80 mg (85%) of **16** as off-white crystals: mp 319 °C dec; ^1H NMR (C_5D_5N) δ 3.06 (s, 3 H), 3.78 (s, 3 H), 3.87 (s, 3 H), 6.50 (m, 2 H), 6.96 (m, 2 H), 8.72 (s, 1 H); IR (Nujol) 1630, 1598 cm^{-1}; mass spectrum, m/e 286 ($M^{\cdot+}$).

Anal. Calcd for $C_{16}H_{14}O_5$: C, 67.13; H, 4.90. Found: C, 67.06; H, 5.04.

Xanthone **16** was characterized as the monoacetate, 6-acetoxy-1,3-dimethoxy-8-methyl-9*H*-xanthen-9-one (**17b**): colorless crystals; mp 154.5–155.5 °C (ethanol); ^1H NMR ($CDCl_3$) δ 2.34 (s, 3 H), 2.91 (s, 3 H), 3.92 (s, 3 H), 4.01 (s, 3 H), 6.38 (d, 1 H, J = 2 Hz), 6.45 (d, 1 H, J = 2 Hz), 6.90 (d, 1 H, J = 2 Hz), 7.10 (d, 1 H, J = 2 Hz); IR (Nujol) 1760, 1665 cm^{-1}.

Anal. Calcd for $C_{18}H_{16}O_6$: C, 65.85; H, 4.88. Found: C, 66.06; H, 4.94.

1,3,6-Trimethoxy-8-methyl-9*H*-xanthen-9-one (17a). A mixture of 1,3-dimethoxy-6-hydroxy-8-methyl-9*H*-xanthen-9-one (**16**; 69 mg, 0.241 mmol), 200 mg of sodium methoxide, 4 mL of methanol, and dimethyl sulfate (1.5 mL, 2.0 g, 15.8 mmol) was heated under reflux for 13.5 h. The methanol was evaporated, and triethylamine was added dropwise to an aqueous suspension of the residue. After further dilution with water, the mixture was extracted (CH_2Cl_2), and the extracts were washed (brine) and evaporated to give a brownish yellow solid. Chromatography (acidic silica gel) gave 31 mg (50%) of **17a** as white crystals: mp 204–206 °C (lit.[20] mp 206 °C); ^1H NMR (4:1 $CDCl_3/CD_3OD$) δ 2.82 (s, 3 H), 3.92 (s, 6 H), 3.96 (s, 3 H), 6.36 (d, 1 H, J = 3 Hz), 6.46 (d, 1 H, J = 3 Hz), 6.66 (m, 2 H); IR (Nujol) 1665–1595, 1570 cm^{-1}.

1,6-Dihydroxy-3-methoxy-8-methyl-9*H*-xanthen-9-one (18). A mixture of 2,5-dihydroxy-7-methoxy-2-(2,4-dioxopentyl)-2,3-dihydro-4*H*-1-benzopyran-4-one (**12**; 0.197 g, 0.640 mmol), 0.7 mL of triethylamine, and 20 mL of THF was heated under reflux for 22 h. The 215 mg of orange residue remaining after evaporation of the solvent was subjected to chromatography (5 g of acidic silica gel, 0–80% ether/hexane) to give 140 mg (80%) of **18** as a yellow solid. Recrystallization (ethanol) gave 47 mg of light yellow crystals, mp 257–258 °C (lit.[9a] mp 255 °C), identical by TLC and NMR and mass spectroscopy with authentic material.

In a second synthesis of **18**, 0.126 g (0.39 mmol) of 1-(2,4-dimethoxy-6-hydroxyphenyl)-1,3,5,7-octanetetraone (**11c**) in 10 mL of methanol was added to excess sodium methoxide in methanol under nitrogen. The dark orange mixture was heated under reflux for 19.5 h, acidified (6 N HCl), and partitioned with water and ethyl acetate. After separation, the aqueous layer was extracted (2×, ethyl acetate), and the combined organic layers were dried ($MgSO_4$) and evaporated to give 102 mg (96%) of **18** as rust-orange crystals, identical by TLC and NMR and mass spectroscopy with authentic material. Recrystallization (ethanol/water) gave rust-orange crystals, mp 255–257 °C.

2-(2,4-Dioxopentyl)-2,5,7-trihydroxy-2,3-dihydrobenzopyran-4-one (19b). 1-(2,4,6-Tribenzoxyphenyl)-1,3,5,7-octanetetraone (**11e**; 0.723 g, 1.28 mmol) dissolved in 50 mL of 1:1 ethanol/THF was added to 70 mg of 10% Pd/C in a Brown hydrogenator and subjected to a H_2 atmosphere for 12 h. Filtration of the catalyst and evaporation of the solvent gave a yellow-brown residue which was partitioned between ethyl acetate and iced dilute HCl. After separation, the aqueous layer was extracted (2×, ethyl acetate), and the combined organic layers were washed (iced 5% $NaHCO_3$) and evaporated to give a yellow-brown oil which solidified in vacuo to give 0.38 g (100%) of crude **19a**, essentially pure by TLC, the NMR spectrum indicating a mixture of **19a** and **19b**. Chromatography (8 g of acidic silica gel, 0–50% ether/hexane) gave **19b** as a yellow-orange oil which solidified in vacuo. Recrystallization (3×, ether/pentane) gave analytically pure off-white crystals: mp 139.5–141.5 °C (dried in vacuo to remove solvent trapped in crystals); ^1H NMR (CD_3CO-CD_3) δ 2.08 (s), 2.21 (s), 2.79 (d, J = 19 Hz), 2.80 (s), 2.99 (s), 3.22 (s), 3.25 (d, J = 19 Hz), 3.85 (br s), 5.82 (s), 5.91 (s), 5.93 (s), 12.02 (s); IR (CH_2Cl_2) 1637 (br) cm^{-1}; mass spectrum, m/e (relative intensity) 294 (6), 276 (4), 195 (34), 194 (36), 153 (31), 152 (43), 125 (17), 100 (30), 85 (34), 43 (100).

Anal. Calcd for $C_{14}H_{14}O_9$: C, 57.14; H, 4.80. Found: C, 57.45; H, 4.97.

1,3,6-Trihydroxy-8-methyl-9*H*-xanthen-9-one (20). Aqueous KOH (3 mL, 4 M) was added to a solution of 0.138 g (0.469 mmol) of 2-(2,4-dioxopentyl)-2,5,7-trihydroxy-2,3-dihydro-4*H*-1-benzopyran-4-one (**19b**) in 40 mL of ethanol in a system flushed throughly with nitrogen. The mixture was heated (70–90 °C) for 22.5 h and then acidified; evaporation gave a brown solid residue which was dissolved in ether, washed (dilute HCl, brine), and dried ($MgSO_4$) to give 123 mg (100%) of **20** [mp 280 °C (lit.[9a] mp 285–90 °C)], which gave a gray $FeCl_3$ test and had NMR and mass spectra and TLC identical with those of authentic material.

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Registry No. 1b, 520-43-4; **1c**, 3465-63-2; **2** dilithium salt, 56830-66-1; **3b'**, 62643-40-7; **7a**, 3147-39-5; **7b**, 19722-76-0; **7c**, 51116-92-8; **7d**, 29723-28-2; **7e**, 72327-94-7; **8c**, 76631-00-0; **8d**, 76631-01-1; **8e**, 76631-02-2; **9**, 76631-03-3; **10** trilithium salt, 72327-95-8; **11c**, 76631-04-4; **11d**, 76631-05-5; **11e**, 72327-93-6; **12**, 76631-06-6; **13**, 832-58-6; **14**, 76631-07-7; **14** sodium salt, 76631-08-8; **15**, 76631-09-9; **16**, 76631-10-2; **17a**, 15222-54-5; **17b**, 76631-11-3; **18**, 3569-83-3; **19a**, 72327-96-9; **19b**, 72327-97-0; **20**, 20716-98-7; benzyl bromide, 100-39-0; dimethyl carbonate, 616-38-6.

Photochemistry of 3-Oxacycloalkenes

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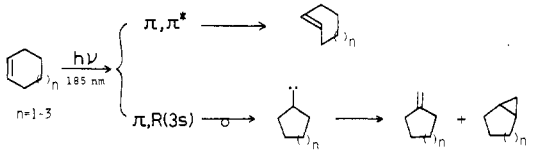
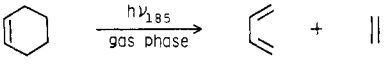
Direct and sensitized photolyses of 3-oxacycloalkenes **1a–c** has been studied in *n*-pentane and in alcohols. In contrast to the photochemistry of cycloalkenes, the direct photolyses of **1a** and **1b** in pentane gave the products **2**, **3**, and **4**, **5**, respectively, which are derived from an allylic O–C bond cleavage. In addition, in the case of **1b**, a small amount of the carbene-derived product **6** was also obtained. The seven-membered oxacycloalkene **1c** gave no volatile product upon direct irradiation in pentane. Upon direct or sensitized photolyses in methanol, oxacycloalkenes **1b** or **1c** gave the adducts **7b,c** as major products. Irrespective of the method of excitation, the yield of the adduct in the photolyses in a series of alcohols decreased with decreasing pK_a value of the alcohol which can be explained in terms of the formation and subsequent trapping of the intermediate trans isomer **14** by the alcohol. These results can be rationalized in terms of the reactivities of the π,σ^* and π,π^* states and the increased stability of the Rydberg state.

Recent reports from these laboratories[1,2] have shown that, upon direct irradiation in the liquid phase at 185 nm, medium-sized cycloalkenes (C_6–C_8) undergo cis–trans photoisomerization as well as skeletal rearrangements to give carbene intermediates as illustrated in Scheme I. A similar photochemical rearrangement has also been reported by Kropp and his co-workers[3] upon direct irradiation of some tri- and tetraalkylethylenes at longer wavelengths. The carbene formation, which appears to be a general reaction path in the direct photolysis of non-

Scheme I



Scheme II



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