A Mechanistic Study of the Photoisomerization of Tetra-O-methylpurpurogallin to Methyl 6,7,8-Trimethoxynaphthoate[1]

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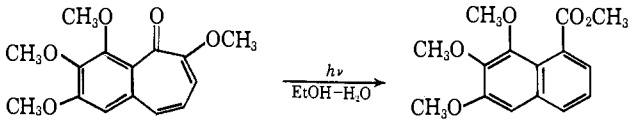
Abstract: The report[3] that tetra-O-methylpurpurogallin (I) photoisomerizes to methyl 6,7,8-trimethoxynaphthoate (II) has been confirmed. Tetra-O-methylpurpurogallin-2-^{14}C has been synthesized from diethyl malonate-2-^{14}C. Photoisomerization of labeled tetra-O-methylpurpurogallin gives methyl 6,7,8-trimethoxynaphthoate labeled in the carboxyl carbon. This result is consistent with the suggestion[3] that an oxabicyclobutane derivative is an intermediate in the photoisomerization of I to II, but does not require such an intermediate. Attempts to determine by ^{18}O-labeling whether the carbonyl oxygen atom of I becomes the carbonyl oxygen of II were frustrated by light-induced exchange of carbonyl oxygen in both I and II. The ^{18}O-labeling experiments establish that the source of the carbonyl oxygen of II must be either the carbonyl oxygen of I or solvent water. The striking observation has been made that water is absolutely necessary for the photoisomerization of I to II. In anhydrous methanol a methanol photoadduct VI is obtained. A mechanistic scheme is proposed which accounts for the observations.

The photochemistry of tropolone ethers has been the subject of several studies in recent years. Among the interesting reactions encountered in these studies, the photoisomerization of tetra-O-methylpurpurogallin (I) to methyl 6,7,8-trimethoxy-1-naphthoate (II) reported by Forbes and Ripley[3] in 1959 is unique. The photoisomerization of I to II poses an unusually difficult problem in mechanism. The difficulty encountered in writing a satisfactory mechanism for this process together with our continuing interest in tropolone photochemistry[4] prompted us to investigate the mechanistic path of this unique isomerization.

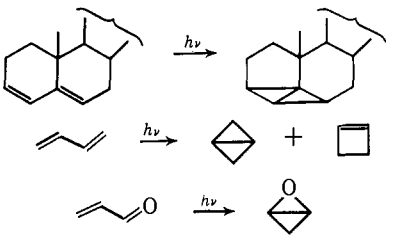
Forbes and Ripley established the structure of the product and noted that only the methyl ester is obtained when the reaction is carried out in aqueous ethanol.[3] Forbes and Ripley[3] considered two possibilities for the conversion of I to II. The first involved cleavage of the



I II

C–C bond between the benzene ring and the carbonyl carbon as the initial step. The second mechanism considered involved initial photoisomerization to an oxabicyclobutane derivative followed by thermal isomerization to the ester II. Forbes and Ripley suggested that a ^{14}C-labeling experiment would distinguish between these mechanisms since the first mechanism predicts that C-1 of the tropolone ring will become the carbonyl carbon of the product II while the second mechanism predicts that C-2 will become the carbonyl carbon. Many other rationalizations may be considered for the photoisomerization of I to II, but knowledge of the origin of the carbonyl carbon is of fundamental importance to any mechanistic study.

The observation of bicyclobutanes as products in the irradiation of 3,5-cholestadiene[5] and 1,3-butadiene[6] raised the question whether an analogous process



might be found for α,β-unsaturated carbonyl compounds.[7] It also increased interest in the possible intermediacy of an oxabicyclobutane derivative in the photoisomerization of I to II.

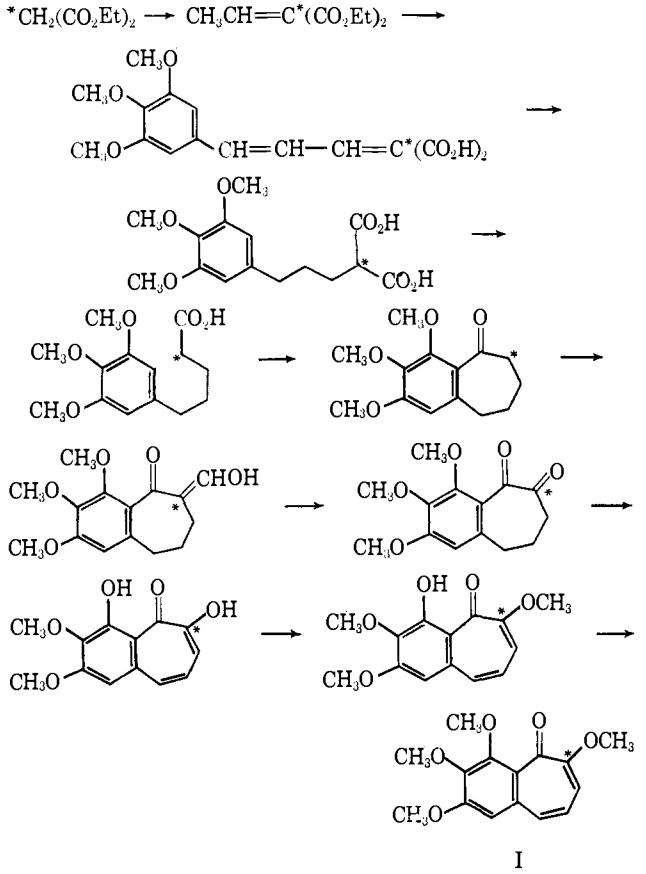
In order to establish the origin of the carbonyl carbon of II tetra-O-methylpurpurogallin labeled with ^{14}C in the 2 position was synthesized by the reactions in Scheme I which makes use of known reactions.[8-12] The over-all yield of labeled I was 0.3% (based on diethyl malonate).

Irradiation of I labeled at C-2 with ^{14}C gave the ester II. A Schmidt reaction on II gave carbon dioxide which contains all of the label. The carbonyl carbon of the ester is thus derived from C-2 of I.

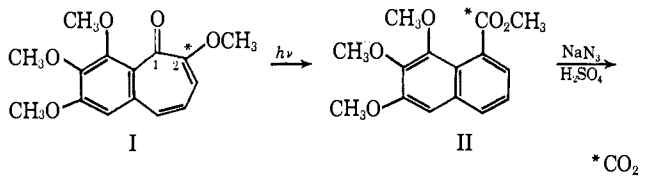
The ^{14}C-labeling result is consistent with an oxabicyclobutane intermediate but does not require it. The fact that C-2 of tetra-O-methylpurpurogallin becomes the carbonyl carbon of the ester II suggests that at some stage in the reaction a bond is formed

(1) Photochemical Transformations. XX. A preliminary account of this work was presented at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966.
(2) National Institutes of Health Predoctoral Fellow, 1965–1967.
(3) E. J. Forbes and R. Ripley, *J. Chem. Soc.*, 2770 (1959).
(4) O. L. Chapman, *Advan. Photochem.*, 1, 323 (1963).
(5) W. G. Dauben and F. G. Willey, *Tetrahedron Letters*, 893 (1962).
(6) R. Srinivasan, *J. Am. Chem. Soc.*, **85**, 4045 (1963).
(7) This possibility has been considered previously: E. J. Corey, J. D. Boss, R. LeMahieu, and R. B. Mitra, *ibid.*, **86**, 5570 (1964); E. J. Corey, M. Tada, R. LeMahieu, and L. Libit, *ibid.*, 87, 2051 (1965).
(8) F. R. Goss, C. K. Ingold, and J. P. Thorpe, *J. Chem. Soc.*, 3342 (1923).
(9) P. D. Gardner, W. J. Horton, G. Thompson, and R. R. Twelves, *J. Am. Chem. Soc.*, **74**, 5527 (1952).
(10) D. Caunt, W. D. Crow, R. D. Haworth, and C. A. Vodoz, *J. Chem. Soc.*, 1631 (1959).
(11) D. Caunt, W. D. Crow, and R. D. Haworth, *ibid.*, 1313 (1951).
(12) R. D. Haworth, B. P. Moore, and P. L. Pauson, *ibid.*, 1045 (1948).

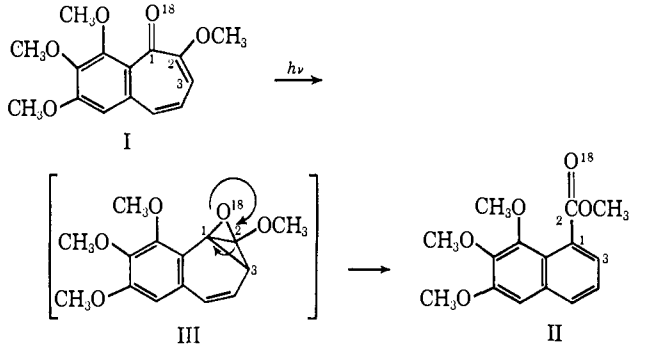
Scheme I



between carbons 1 and 3 of the tropolone ring. This bond is one of two which must be formed if III is an

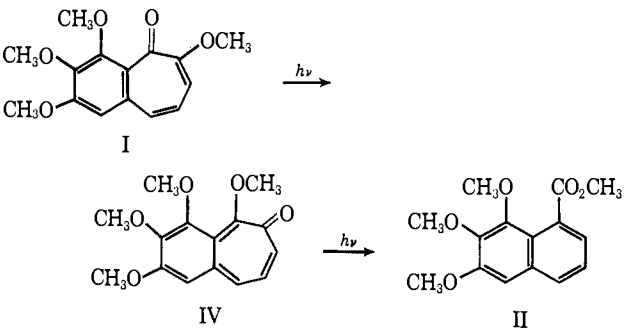


intermediate. The other required bond would involve the carbonyl oxygen of tetra-O-methylpurpurogallin

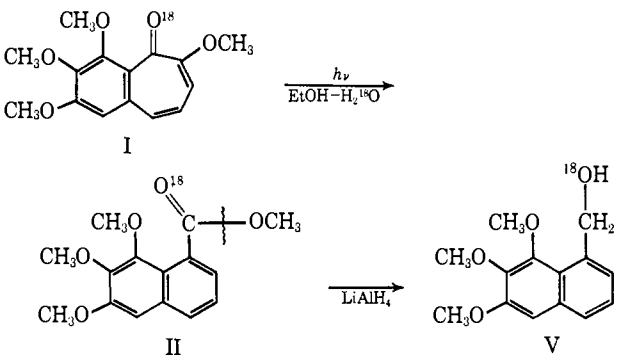


(I) and C-2. Evidence for such a bond would be available if it could be shown by ^{18}O-labeling that the carbonyl oxygen atom of I became the carbonyl oxygen atom of II. Furthermore, this labeling experiment would eliminate mechanisms which involve an oxygen–methyl shift (I → IV → II).[13]

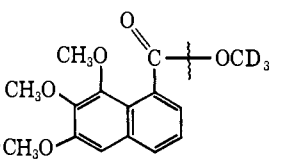
(13) Examples of oxygen-to-oxygen phenyl shifts are known in the photochemistry[14] and low-energy ionization[15] of 2-phenoxy-4,5-benztropone and carbon-to-oxygen phenyl shifts are known in the photochemistry of certain unsaturated ketones.[16-18]



Tetra-O-methylpurpurogallin labeled with ^{18}O in the carbonyl group was prepared by base-catalyzed exchange with water-^{18}O. Control experiments showed that neither I nor II exchanged carbonyl oxygen with solvent water in the dark under the conditions of the irradiations. Both I and II, however, do exchange carbonyl oxygen with solvent water when irradiated. The resistance of II to exchange of carbonyl oxygen in the absence of light is most remarkable. Samples of II retain the carbonyl-^{18}O label even after alumina chromatography. The observed exchange of the carbonyl oxygens of I and II on irradiation meant that it was necessary to use ^{18}O-labeled water in the solvent to ensure ^{18}O-labeling in the carbonyl group of I. Irradiation of I labeled with ^{18}O in the carbonyl group in solution in ethanol–water-^{18}O gave II which contained ^{18}O. The position of the label was clarified by the mass spectrum and by reduction of the product. The mass spectrum of labeled II shows loss of 31

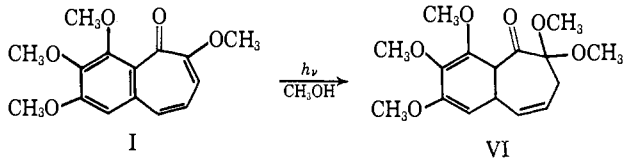


(OCH_3) from both the parent ion (unlabeled) and the parent + 2 ion (labeled). The loss of 31 from the parent ion has been shown to be due to acyl-oxygen fission of the ester to the extent of 82% by analysis of the mass spectrum of the trideuterio ester. The loss of a fragment of mass 31 from the labeled ester thus means that the ^{18}O label is not in the ester methoxyl group.



(14) O. L. Chapman, H. G. Smith, R. W. King, D. J. Pasto, and M. R. Stoner, *J. Am. Chem. Soc.*, **85**, 2013 (1963).
(15) O. L. Chapman, T. H. Kinstle, and M. Sung, *ibid.*, **88**, 2618 (1966).
(16) H. Schmidt, H. Hochweber, and H. von Halban, *Helv. Chim. Acta*, **30**, 1135 (1947).
(17) G. W. Griffin and E. J. O'Connel, *J. Am. Chem. Soc.*, **84**, 4148 (1962).
(18) H. E. Zimmerman, H. G. C. Durr, R. G. Lewis, and S. Bram, *ibid.*, **84**, 4149 (1962).

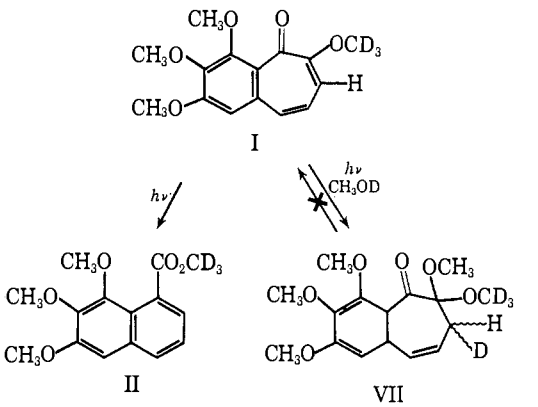
This result was confirmed by reduction of labeled II to labeled V. The mechanism of lithium aluminum hydride reduction of esters requires that alkoxide ion be expelled from the intermediate while the original carbonyl oxygen is retained. The absence of label in the oxygen of the ester methoxyl group rigorously establishes that no transfer of the methyl group from the C-2 oxygen to the carbonyl oxygen (I to IV) has occurred. This experiment, however, does not contribute directly to our knowledge of the origin of the carbonyl oxygen of II. The exchange of carbonyl oxygen of I and II with water in the solvent during irradiation means that any labeling experiment designed to test whether the carbonyl oxygen of I became the carbonyl oxygen of II (as required by the sequence I → III → II) would have to be carried out under conditions unfavorable to exchange, *i.e.*, the amount of water in the solvent would have to be reduced. Successive irradiations of I in ethanol–water (or methanol–water) in which the amount of water was progressively reduced showed that the yield of the ester II began to fall off. As the water content of the solvent approached zero, the yield of ester II approached zero. Irradiation of I in almost anhydrous methanol gave in addition to traces of ester II a new product. The new product showed $\lambda_{max}^{95\%\ EtOH}$ 251 mμ (ε 2.59 × 10⁴), 294 mμ (ε 5.5 × 10³), and 5.83 μ.[19] The mass spectrum of the product showed a parent ion at *m/e* 308 which suggested that it was a methanol adduct (confirmed by element analysis) and an intense fragment ion at *m/e* 220 (M − 88) due to elimination of 1,1-dimethoxyethylene. The nmr spectrum of the adduct showed one aromatic proton (δ 6.48), two olefinic protons (AB of ABX_2; δ 6.30, 5.60; J_{AB} = 12 cps), three methoxyl groups on the aromatic ring (δ 3.85, 3 H; 3.82, 6 H), two methoxyl groups as a singlet (δ 3.26), and two methylene protons (X_2 of ABX_2, δ 2.67). The data cited above are uniquely consistent with structure VI for the adduct. A methanol photoadduct of isocolchicine has been reported by Dauben and Cox.[20]



I VI

The formation of the methanol adduct suggested that other solvents should be used. Irradiation of I in AR grade tetrahydrofuran gave II slowly. When the same irradiation was carried out with ^{18}O-labeled I, extensive loss of label was observed. The amount of water required for the exchange is quite small, and this result suggested that sufficient water for exchange was present on the glass surface, condensed from the atmosphere when the solvent was pipetted into the irradiation vessel, or was present in the solvent. Irradiations conducted under the most anhydrous conditions we could achieve gave no ester II. In these experiments, I was placed in a Pyrex tube suitable for irradiation; the tube was sealed to a vacuum line, and the sample was carefully dried. Tetrahydrofuran was distilled into the sample from a reservoir (containing tetrahydrofuran over lithium aluminum hydride) sealed to the vacuum line. The tube containing the tetrahydrofuran solution of I was then sealed off and irradiated. Examination by column chromatography and by vapor phase chromatography showed that no ester II was formed. It is thus clear that water is essential for formation of ester II even though the conversion of I to II is formally an isomerization.[21]

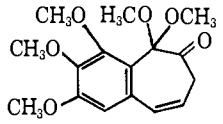
A test for the stability of the methanol adduct VI in the irradiation solution was made by irradiation of 2-O-trideuteriomethyl-7,8,9-tri-O-methylpurpurogallin in CH_3OD–D_2O.



If the deuterated adduct VII reverted to I during the course of the reaction, exchange of the OCD_3 group for OCH_3 should occur. The use of deuterium in the solvent was designed to give information about the stereochemistry of the addition–elimination sequence. The mass spectrum of ester II showed no loss (<2%) of OCD_3 and no incorporation (<1%) of deuterium from the solvent. Separate irradiation of the methanol adduct VI confirmed that the adduct is not in photoequilibrium with I. The adduct is not stable to irradiation in solution but absorbs only a small fraction of the incident light in solutions containing excess I. Irradiation of the adduct does not give either I or II.

It is clear that water is essential for the reaction and that methanol adds to I during irradiation under appropriate conditions. These facts make mechanisms which involve the addition of water to I attractive, and evidence for addition of water to I was sought. The sequence I → VIII → IX → II shows one way in which a water adduct might be involved. There are, however, difficulties with attempts to implicate a water adduct such as VIII. Addition of water to I by any means which introduces a hydroxyl group at C-2 (as in the sequence I → VIII → IX → II, for example) would lead to a C-2 hemiketal VIII which should be in equilibrium with the diketone X which should be in equilibrium with the tropolone XI. Crude reaction mixtures from the irradiations give negative ferric chloride tests;

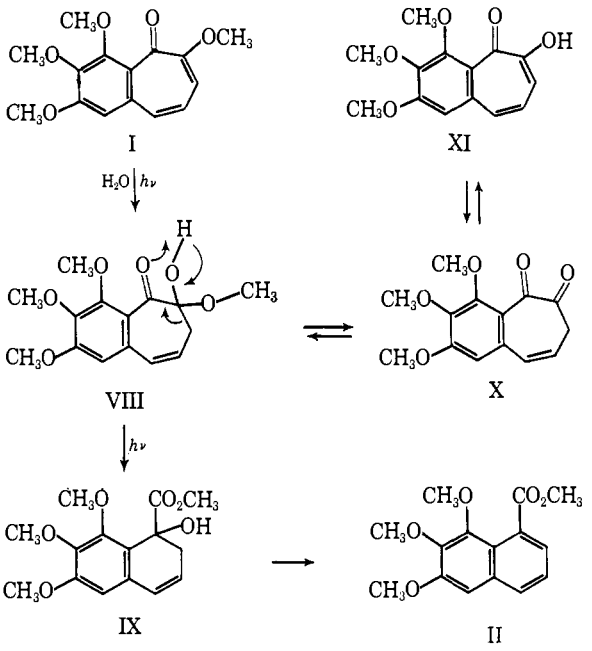
(19) The carbonyl stretching absorption in the infrared is at lower wavelength than expected for an acetophenone derivative. This is probably a result of lack of coplanarity of the aromatic ring and the carbonyl group. The alternate arrangement with the geminal methoxyl



groups between the aromatic ring and the carbonyl group is excluded by the loss of dimethoxyethylene in the mass spectrometer.

(20) W. G. Dauben and D. A. Cox, *J. Am. Chem. Soc.*, 85, 2130 (1963).

(21) This conclusion has been reached independently by Professor E. J. Forbes and co-workers: private communication.

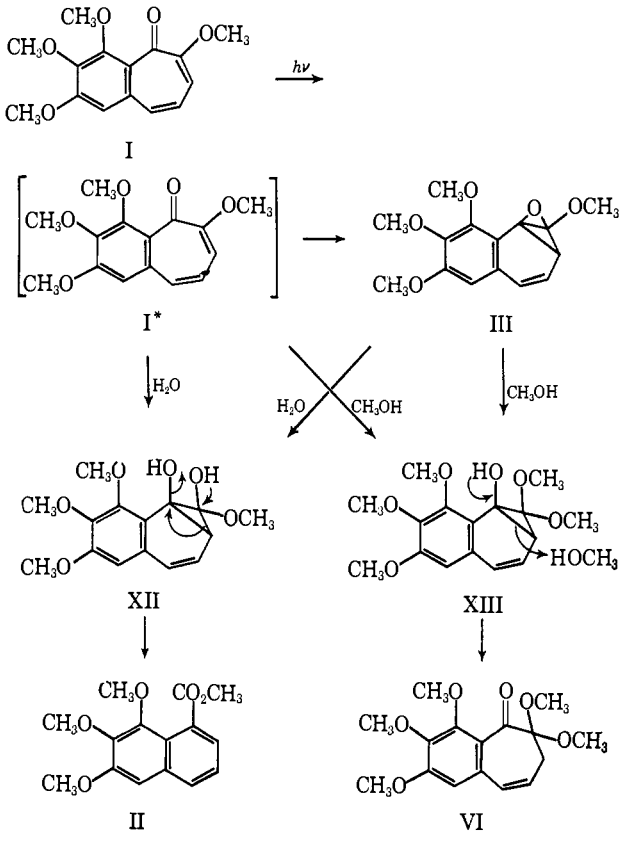


this demonstrates the absence of XI.[22] Furthermore, in the irradiations carried out in aqueous ethanol equilibration of X with the ethyl hemiketal would occur. This equilibration would lead to 2-O-ethyl-7,8,9-tri-O-methylpurpurogallin and ultimately to ethyl 6,7,8-trimethoxy-1-naphthoate. These compounds are not observed.[3] Irradiation of I in CH_3OD–D_2O gave II which did not contain any deuterium (<1%). This result places a severe constraint on any addition, rearrangement, elimination sequence (such as I → VIII → IX → II). If such a sequence were to account for this result, it would be necessary to assume that three successive reactions, addition, rearrangement, and dehydration, occur with 100% stereospecificity. This observation together with the absence of free tropolone XI, 2-O-ethyl-7,8,9-tri-O-methylpurpurogallin, and ethyl 6,7,8-trimethoxy-1-naphthoate exclude the adduct VIII from consideration.

In experiments in which the progress of the photochemical rearrangement of I to II was monitored it was noted that the ester II is formed very early in the reaction. This strongly suggests that its formation involves a single excitation and does not involve two successive photochemical reactions (as would be required in the sequence I + $h\nu$ → VIII + $h\nu$ → II). If two photochemical reactions were involved, it would be necessary for the intermediate to build up to a concentration high enough for it to compete with I for the available light.

In our system we have tried to detect the formation of a ground-state intermediate by irradiation of purpurogallin tetramethyl ether at low temperature (~77°K) in rigid glasses in which the progress of the reaction could be followed by infrared absorption spectroscopy. The cell design used was a modification of that of Wagner and Hornig.[23] The formation of ester could not be detected under these conditions, and the disappearance of tetra-O-methylpurpurogallin was quite slow. Similar experiments at Dry Ice–acetone temperatures gave similar results. If an intermediate such as III had a moderately long lifetime, it might be possible to irradiate I in nonaqueous solvents to build up a modest concentration of the intermediate and then add water to convert the intermediate to ester II. Such experiments have been uniformly unsuccessful. There is thus no evidence for a ground-state intermediate in the conversion of I to II, but the information available does not exclude formation of such an intermediate.

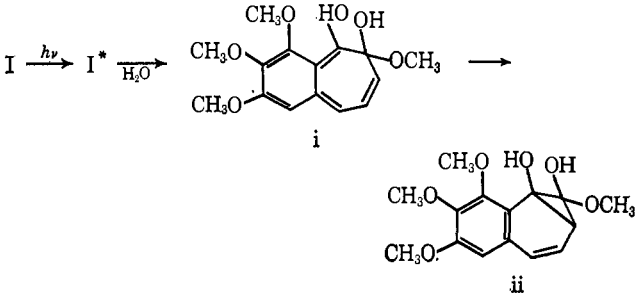
The fact that C-2 of purpurogallin tetramethyl ether I becomes the carbonyl carbon atom of the product ester II suggests that a bond is formed between C-1 and C-3 of I. This suggestion, the necessity of water for conversion of I to II, and the formation of the methanol adduct lead us to conclude that either an excited state of I[24] or a ground-state intermediate (such as III) adds water (or methanol), giving XII (or XIII). The key intermediate in the conversion of I to II then is XII, which collapses to ester II. Formation of XII would not require deuteration of the ring in accord with observation. Addition of methanol to either I* or III in similar fashion leads to XIII which is then the precursor of the methanol adduct VI. Reversion of



(22) α-Tropolones give intense colors with ferric chloride, and this is a very sensitive test for the presence of tropolones.

(23) E. L. Wagner and D. F. Hornig, *J. Chem. Phys.*, **18**, 296 (1950).

(24) One possible formulation of addition of water to an excited state of I is shown below. Isomerization of i to ii must be faster than ketonization of the enol and equilibration of the hemiketal with the ketone.



XII to I if it competes with ester formation must be stereospecific with loss of hydroxide ion since no tropolone is detected in the reaction solutions. The same ambiguity of addition to an excited state and/or a ground-state intermediate exists in the photochemical addition of alcohols[25] and acids[26] to benzene derivatives and in the addition of alcohols to dienes.[5,27] In the case of 3,5-cholestadiene derivatives there is evidence that addition of alcohols involves an excited state and a bicyclobutane derivative.[27]

Experimental Section

Preparation of Tetra-O-methylpurpurogallin. Potassium hydroxide (30 g) was dissolved in water (15 ml) and to this was immediately added 2,7,8-tri-O-methylpurpurogallin (1 g) and dimethyl sulfate (3 ml). The solution was shaken for 1 min, then additional dimethyl sulfate (3 ml) was added. The reaction was shaken vigorously and heated on a hot plate until the solution was almost colorless, at which time it was poured over ice, and concentrated ammonia solution (10 ml) was added to react with the excess dimethyl sulfate. After stirring for about 20 min, the solution was made just barely acidic with hydrochloric acid and extracted with ether. The ether extracts were dried, and the ether was removed with a rotary evaporator. The solid product was recrystallized once from cyclohexane, yield 0.90 g, mp 90–92° (lit.[28] mp 92°).

Synthesis of Tetra-O-methylpurpurogallin-2-^{14}C. Tetra-O-methylpurpurogallin-2-^{14}C was synthesized from methylene-^{14}C diethyl malonate using previously described reactions.[8-12] The over-all yield of the labeled product was 0.3% with specific activity 45.7 dpm/mg.

Photoisomerization of Tetra-O-methylpurpurogallin-2-^{14}C. Tetra-O-methylpurpurogallin-2-^{14}C (0.99 g, 45.7 dpm/mg) in 30% ethanol (333 ml) was irradiated for 165 hr with a General Electric sunlamp. The reaction was worked up in the manner described by Forbes and Ripley,[3] giving methyl 6,7,8-trimethoxynaphthoate (60 mg, mp 79.5–81.0°, 46.5 dpm/mg).

Degradation of Methyl 6,7,8-Trimethoxy-1-naphthoate. Methyl 6,7,8-trimethoxy-1-naphthoate (11.7 mg) and sodium azide (54.2 mg) was placed in a three-necked flask equipped with a glass-jacketed stirring bar, condenser, and pressure-equalizing addition funnel. Nitrogen was passed through the flask and condenser and into a tube containing toluene scintillation solution (10 ml) and Packard Instruments hydroxide of hyamine 10-X solution (1 ml). With nitrogen passing through the flask, a solution of concentrated sulfuric acid (9 ml) and water (1 ml) was added. After 3 hr, the contents of the carbon dioxide absorption solution were transferred to a counting vial and immediately counted in a Packard Tri-Carb scintillation counter. Two decarboxylations of ^{14}C-labeled methyl 6,7,8-trimethoxynaphthoate using 21.7 and 11.7 mg gave labeled carbon dioxide which contained respectively 93 ± 5% and 100 ± 5% of the label.

Preparation of Tetra-O-methylpurpurogallin-*carbonyl*-^{18}O. A solution of sodium methoxide in methanol was prepared by dissolution of sodium (8 mg) in 1 ml of anhydrous methanol (10 ml). Water (81% ^{18}O, 80 mg) and tetra-O-methylpurpurogallin (50 mg) were added, and the solution was refluxed for 6 hr. The solvent was removed with a rotary evaporator, care being taken to remove all traces of solvent. The dried solid product was leached with dry cyclohexane, from which colorless crystals of tetra-O-methylpurpurogallin were crystallized (40 mg, mp 91.5–92.0°). The percentage of ^{18}O-label and its position in the molecule were obtained from mass spectra run on an Atlas CH-4 spectrometer. Proof of the position of the label in ^{18}O-exchanged tetra-O-methylpurpurogallin as the tropolone carbonyl oxygen was obtained by the shift of the M − 28 peak, loss of CO, in the unlabeled compound to M − 30 in the labeled compound. The mass spectrum of the exchanged compound showed 75% incorporation of ^{18}O-label into the compound.

Preparation of 2-O-Trideuteriomethyl-7,8,9-tri-O-methylpurpurogallin. 7,8-Di-O-methylpurpurogallin (0.50 g) and sodium hydroxide (50 mg) were dissolved in D_2O (10 ml). This solution was saturated with carbon dioxide and extracted with methylene chloride. The extracts were dried, and the solvent was removed with a rotary evaporator. The product obtained was added to a solution of a 50% excess of CD_2N_2 in ether (100 ml), dioxane (100 ml), and D_2O (10 ml) and allowed to stand at room temperature for 20 hr. The CD_2N_2 solution was prepared by the addition of several 2-mg portions of phenol over a period of 1 hr to a solution of CH_2N_2 in ether, dioxane, and D_2O maintained at 0°. The solution was frequently swirled during this period. 2-O-Trideuteriomethyl-7,8-di-O-methylpurpurogallin was obtained by removal of the solvent with a rotary evaporator and was methylated with dimethyl sulfate as described above to yield 2-O-trideuterio-7,8,9-tri-O-methylpurpurogallin (340 mg, mp 88–91.5°).

Irradiation of Tetra-O-methylpurpurogallin-*carbonyl*-^{18}O. Tetra-O-methylpurpurogallin (carbonyl-^{18}O, 200 mg) was dissolved in absolute ethanol (8 ml), water (150 mg), and water (81% ^{18}O, 100 mg) in a 22 × 175 mm test tube. This solution was irradiated for 62 hr with a General Electric ultraviolet sunlamp. After the irradiation, the solvent was removed with a rotary evaporator and 37.5% of the crude product was chromatographed on Woelm neutral alumina (activity 1). The column was eluted with benzene–chloroform, the ester product being the first major compound eluted. The product was recrystallized twice from cyclohexane (yield 4 mg, mp 80–81.5°, lit.[3] mp 81–82°). The mass spectrum of the ester showed 21.7 ± 0.5% ^{18}O incorporation. The position of the oxygen-18 label in the ester was ascertained from the fact that both the labeled and unlabeled ester had an M − 31 peak in its mass spectrum. This peak is due to loss of the methoxyl of the ester to yield the acylonium ion. That the M − 31 peak is due predominately (82 ± 2%) to loss of the ester methoxyl and not to one of the other three methoxyl groups present in the molecule was determined from the mass spectrum of trideuteriomethyl 6,7,8-trimethoxy-1-naphthoate prepared by irradiation of 2-O-trideuteriomethyl-7,8,9-tri-O-methylpurpurogallin, the synthesis of which is described above. The presence and relative intensity of the M − 31 peak in the labeled ester indicate that the oxygen label present must be solely (±2%) in the ester carbonyl.

As an independent confirmation of the position of the oxygen-18 label, the remainder of the crude photoproduct was reduced with lithium aluminum hydride (300 mg) in ether. This reduction was worked up according to Leonard,[29] and the crude reduction product was chromatographed on Woelm neutral alumina (activity 1). The alcohol obtained was recrystallized twice from hexane (yield 0.5 mg, mp 78–81°, lit.[3] mp 85–86°). The mass spectrum of this alcohol showed 19 ± 0.5% oxygen-18 incorporation and, with allowance for the oxygen-18 incorporation, agreed exactly with the mass spectrum of unlabeled material.

Irradiation of Tetra-O-methylpurpurogallin in Deuterated Media. Tetra-O-methylpurpurogallin (110 mg) was irradiated for 17 hr in ethanol (9 ml) containing D_2O (21 ml) in a 22 × 175 mm Pyrex test tube. After the irradiation, most of the alcohol was removed with a rotary evaporator, and the remainder of the reaction mixture was extracted with dichloromethane. The extract was dried; the solvent was removed, and the product was chromatographed on Woelm neutral alumina. The ester product isolated was recrystallized twice from cyclohexane. The mass spectrum of the product showed no deuterium incorporation (<1%).

Tetra-O-methylpurpurogallin (108 mg) was irradiated as above for 19.5 hr in methanol (10 ml) containing D_2O (22 ml). The reaction was worked up as above, and the mass spectrum of the product showed no deuterium incorporation.

Irradiation of 2-O-Trideuteriomethyl-7,8,9-tri-O-methylpurpurogallin in Deuterated Media. 2-O-Trideuteriomethyl-7,8,9-tri-O-methylpurpurogallin (118 mg) was irradiated as above for 17 hr in methanol (10 ml) and D_2O (22 ml). The reaction was worked up as above, and the mass spectrum of the ester product showed no deuterium incorporation (<1%) and no loss of the trideuteriomethyl group (<2%).

Control Experiments of Tetra-O-methylpurpurogallin and Methyl 6,7,8-Trimethoxy-1-naphthoate. Tetra-O-methylpurpurogallin (50% carbonyl oxygen-18; 20 mg) was dissolved in ethanol (6 ml) and water (14 ml) and let stand for 20 hr. The solvent was removed with a rotary evaporator, and the product was recrystallized

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twice from cyclohexane. The mass spectrum of the product showed no loss of oxygen-18.

Tetra-O-methylpurpurogallin (165 mg) was dissolved in absolute ethanol (10 ml), water (81% oxygen-18; 50 mg), and water (50 mg) and irradiated in a 22 × 175 mm Pyrex test tube for 3.5 hr. The reaction was worked up exactly as for the above irradiations. Recovered, unreacted starting material showed oxygen-18 incorporation.

Methyl 6,7,8-trimethoxynaphthoate (12 mg) was dissolved in absolute ethanol (8 ml), water (81% oxygen-18; 46 mg), and water (140 mg) and let stand for 12 hr. A 1-ml sample was removed, evaporated, and recrystallized twice from cyclohexane. The mass spectrum of the product showed no oxygen-18 incorporation. The remainder of the solution was irradiated in a 22 × 175 mm test tube for 19 hr. A vpc analysis showed only the ester present after the irradiation. The solvent was removed and the product recrystallized twice from cyclohexane. The recovered ester showed oxygen-18 incorporation.

Both oxygen-18-labeled compounds were stable to the chromatographic work-up.

Irradiation of Tetra-O-methylpurpurogallin in Dry Tetrahydrofuran. Tetra-O-methylpurpurogallin (0.133 g) was added to a test tube, which had been previously flame dried and cooled, and glass sealed to a vacuum manifold. At another outlet on the manifold was affixed a flask containing analytical reagent tetrahydrofuran and solid lithium aluminum hydride. The manifold and the test tube were evacuated to 0.1-mm pressure for 1 hr. Then tetrahydrofuran (1 ml) was distilled into the test tube by isolating the manifold from the pump, while maintaining the vacuum, opening the stopcock to connect the tetrahydrofuran flask to the manifold, and cooling the test tube in a Dry Ice–acetone bath. The test tube was then isolated from the manifold and the tetra-O-methylpurpurogallin was dissolved in the tetrahydrofuran by warming the test tube. After all of the compound had dissolved, the test tube was again evacuated and pumped on for 1 hr. Then tetrahydrofuran (6 ml) was distilled into the test tube which was cooled to Dry Ice temperature, pumped to 0.1 mm, sealed, removed from the manifold, and irradiated for 25 hr with a General Electric ultraviolet sunlamp. After the irradiation, the sealed tube was opened and the composition of the product determined by vpc analysis. The vpc analysis showed no trace of the ester, methyl 6,7,8-trimethoxy-1-naphthoate.

Preparation of the Methanol Adduct of Tetra-O-Methylpurpurogallin. Tetra-O-methylpurpurogallin (138 mg) was dissolved in methanol (8 ml) and water (0.2 ml) and irradiated for 5 hr in a Pyrex test tube with a General Electric ultraviolet sunlamp. The crude reaction mixture was chromatographed on Woelm neutral alumina containing 1% added water. The adduct, first compound (50 mg) eluted from the column with benzene, was recrystallized four times from ether, mp 97–98°.

Anal. Calcd for $C_{16}H_{20}O_6$: C, 62.32; H, 6.54. Found: C, 62.16; H, 6.73.

The spectral data are as follows: ultraviolet: $\lambda_{max}^{95\%\ EtOH}$ 251 mμ (ε 18,900); infrared: 5.83 μ; nmr: 1 H (s) (δ 6.48), ABX_2, 1 H (m) (δ 6.30), 1 H (m) (δ 5.60), 2 H (q) (δ 2.67), J_{AB} = 12 cps, 6 H (s) (δ 3.26), 3 H (5) (δ 3.85), 6 H (d) (δ 3.82).

Low-Temperature Infrared Studies of the Irradiation of Tetra-O-methylpurpurogallin. The low-temperature infrared cell of Wagner and Hornig[28] was modified to contain a solution cell of variable path length.

The cell was set up with two sodium chloride plates and a $^1/_{32}$-in. Teflon spacer. A solution of tetra-O-methylpurpurogallin (0.4 mg/ml) in 9:6:1 methylcyclohexane–diethyl ether–tetrahydrofuran was injected into the cavity. Liquid nitrogen was added to cool the cell, and the cell was evacuated. When the solution had been thoroughly cooled, its infrared spectrum was taken, and the solution was irradiated through a Pyrex filter with two General Electric ultraviolet sunlamps placed approximately 5 in. from the frozen glass for 10 hr. After the irradiation the infrared spectrum was again taken, and no change was detected.

The Irradiation of Tetra-O-methylpurpurogallin in a Rigid Glass at −195°. A cell was constructed of 10-mm Pyrex tubing in the form of an H. One arm was sealed to a vacuum manifold. The tube was flame dried under vacuum, and tetra-O-methylpurpurogallin (2 mg) was added. After drying the sample, diethyl ether (2 ml) and methylcyclohexane (3 ml), which had been stored over lithium aluminum hydride in separate reservoirs affixed to the manifold, were distilled into the H tube. The H tube was sealed off, and the solution in the cell was thoroughly mixed and distributed equally between the two arms. The cross bar between the two arms was sealed, isolating the two arms.

The apparatus (Pyrex) described by Trecker and Henry[30] was used with the insert removed as the irradiation vessel. Cooling water was circulated through the outer chamber; the next chamber was evacuated, and the large inner chamber was filled with liquid nitrogen. The vessel was irradiated with eight General Electric ultraviolet sunlamps. After irradiation for 1 min, the cell was removed from the liquid nitrogen, and one of the arms was opened. Methanol (or water) was added. The addition was complete within 30 sec. The tubes were protected from ambient light and allowed to come to room temperature. After 1 hr, the other arm (control solution) was opened. Solvent was removed from each solution with a rotary evaporator, and the residues were analyzed. No trace (<0.3%) of methanol adduct VI (or ester II) could be found in the portion to which methanol (or water) had been added. The vpc scans for the runs where methanol (or water) had been added were identical with those of the control.

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