Factors Influencing the Basicities of Triarylcarbinols. The Synthesis of Sesquixanthydrol[1]

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Synthetic routes to the novel 2,6,2',6',2'',6''-hexasubstituted triphenylcarbinols (I and II) have been developed. Both carbinols are of considerable theoretical interest. The hexamethoxytriphenylcarbinol I, because its six *ortho* substituents provide large steric interactions between rings, is a precursor of a carbonium ion which must exist in an exaggerated "propeller" conformation, or at any rate a highly nonplanar conformation. Sesquixanthydrol (II) is of interest since its derivative carbonium ion (and radical) appear from models to be capable of attaining complete coplanarity. Both carbinols yield well-characterized carbonium ions at unusually high pH. Some of the chemistry of these carbonium ions is discussed and quantitative measurements of basicity are reported.

The question of the detailed structures of the triphenylmethyl carbonium ion and radical has provided, over the past 20 years, a persistent impetus to the study of their properties. The conflicting requirements for maximizing the resonance stabilization of the ion or radical and minimizing the steric interactions between *o*-substituents on neighboring rings demand a compromise which has been accommodated to several different models.

The aryl groups may be twisted out of the plane of the central carbon atom to form a symmetrical "propeller" which may be converted to an unsymmetrical analog by reversing the "pitch" of one of the rings.[3] Such a model, in which the angle of twist has been estimated[4,5] to be of the order of 50–60°, must involve a loss of resonance stabilization. Much evidence concerned with the basicity of substituted triphenylcarbinols has been interpreted[6–11] in terms of this model for the carbonium ion.

An alternative hypothesis advanced by Deno[4,12–14] explains the stabilization of the ion in terms of a model in which only one or two of the phenyl rings attains coplanarity at any given time. In this model one of the rings, not contributing to the resonance stabilization of the ion, is regarded as essentially perpendicular to the plane of the central carbon atom. The greater basicities of triarylcarbinols, as compared to the corresponding diarylcarbinols, would be considered to be attributable primarily to the greater relief of steric strain resulting from the change from tetrahedral to trigonal geometry on going to the triarylmethylcarbonium ion.

This paper reports the preparation and properties of 2,6,2',6',2'',6''-hexamethoxytriphenylcarbinol (I), and 12c-hydroxy-4,8,12-trioxadibenzo[c,d,m,n]pyrene

or sesquixanthydrol[15] (II) and the corresponding carbonium ions III and IV.

I   II

III   IV
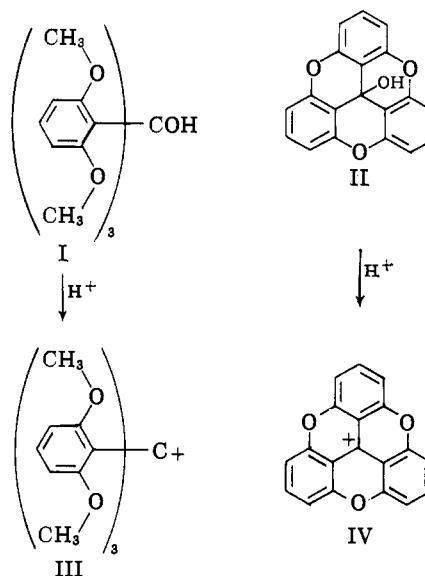
Results and Discussion

Carbinols I and II are conveniently prepared from 2,6-dimethoxyphenyllithium, which is available from resorcinol dimethyl ether by metalation with butyllithium.[16] The synthetic sequences and reactions interrelating these compounds are outlined in Scheme I.

The additions of 2,6-dimethoxyphenyllithium to the sterically hindered ketones or esters intermediate in this synthetic sequence do not occur in ether or tetrahydrofuran solution. In a solvent mixture with a large percentage of benzene, however, one obtains addition to give the highly hindered carbinol, I.

The use of other catalysts (AlBr₃, AlCl₃, HBr) for the ring closure to II results in yields inferior to those obtained using molten pyridinium chloride as a reaction medium.

The second methylation step in the conversion of VI to VII, involving the strongly hydrogen-bonded hydroxyl group, could not be effected with diazomethane, even in the presence of catalytic amounts of methanol[17] or boron trifluoride etherate.[18,19] The use of trimethyl-

(1) From the Ph.D. Thesis of R. G. Smith, University of Illinois, 1961. Presented in part before the 138th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1960, p. 81 P of Abstracts.

(2) Rohm and Haas Co. Fellow, 1959–1960.

(3) G. N. Lewis, T. T. Magel, and D. Lipkin, *J. Am. Chem. Soc.*, **64**, 1774 (1942).

(4) N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *J. Org. Chem.*, **19**, 155 (1954).

(5) H. O. Pritchard and F. H. Sumner, *J. Chem. Soc.*, 1041 (1955).

(6) P. D. Bartlett, *Bull. soc. chim. France*, **18**, C100 (1951).

(7) V. Gold, *J. Chem. Soc.*, 3944 (1956).

(8) D. Bethell and V. Gold, *Quart. Rev.* (London), **12**, 173 (1958).

(9) A. Streitwieser, Jr., *J. Am. Chem. Soc.*, **74**, 5288 (1952).

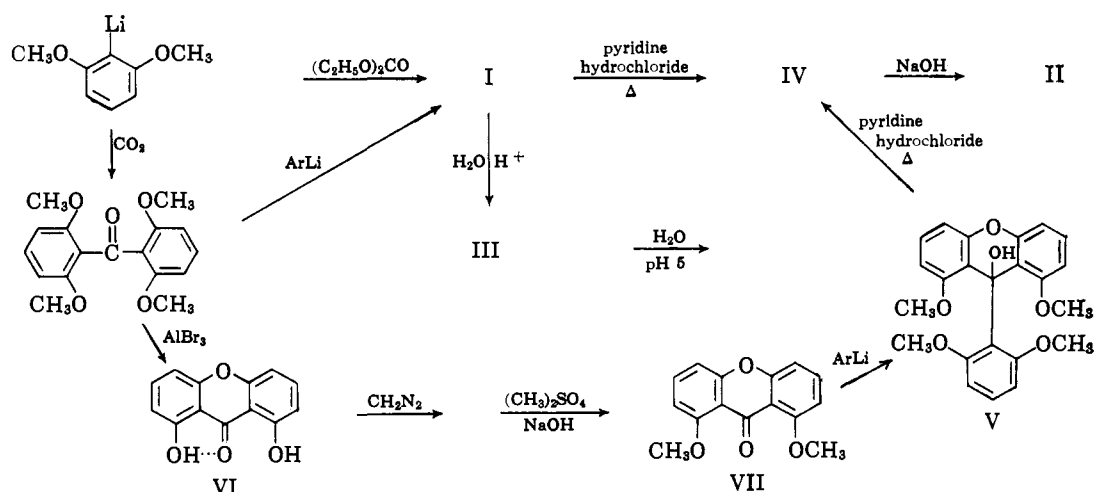(10) S. F. Mason, *J. Chem. Soc.*, 808 (1958).

(11) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p. 362 ff.

(12) N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *J. Am. Chem. Soc.*, **77**, 3044 (1955).

(13) N. C. Deno and A. Schriesheim, *ibid.*, **77**, 3051 (1955).

(14) N. C. Deno, P. T. Graves, and G. Saines, *ibid.*, **81**, 5290 (1959).

(15) The name sesquixanthydrol, suggested for this compound by Professor P. D. Bartlett, will be used throughout.

(16) H. Gilman and J. W. Morton, Jr., in "Organic Reactions," Vol. VIII, John Wiley and Sons, Inc., New York, N. Y., 1954.

(17) A. Mustafa and O. H. Hishmat, *J. Org. Chem.*, **22**, 1644 (1957).

(18) M. C. Caserio, J. D. Roberts, M. Neeman, and W. S. Johnson, *J. Am. Chem. Soc.*, **80**, 2584 (1958).

(19) E. Muller and W. Rundel, *Angew. Chem.*, **70**, 105 (1958).

SCHEME I

anilinium hydroxide or dimethyl sulfate on the salt of the phenol provides low, but synthetically practical, conversions to the desired product.

Carbinols I and II react in faintly acidic media to yield the corresponding carbonium ions III and IV. The proton n.m.r. spectra of the carbinols and their corresponding carbonium ions, summarized in Table I,

TABLE I

NUCLEAR MAGNETIC RESONANCE SPECTRA

Com-pound	Chemical shift, τ^a			$J_{H_{meta} \cdot H_{para}}{}^b$	Solvent
	H_{para}	H_{meta}	$H_{methoxy}$		
I	3.03	3.59	6.58	8.4 ± 0.2	CCl$_4$
II	2.67	3.00	..	9.0 ± .2	Dioxane
III	2.21	3.25	6.29	8.7 ± .2	CF$_3$CO$_2$H
IV	1.44	2.12	..	8.9 ± .2	CF$_3$CO$_2$H
V		2.88^c	6.22^d		CF$_3$CO$_2$H

^{a} Parts per million relative to the internal standard, tetra-methylsilane, which is taken as 10; see G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958). ^{b} Obtained by interpolation from the tables of K. B. Wiberg and B. J. Nist, "The Interpretation of NMR Spectra," W. A. Benjamin, Inc., New York, N. Y., 1962. ^{c} For the 9-aryl group; other shifts not determined. ^{d} All methoxy protons of V have the same chemical shift.

provide good evidence for the proposed structures.[20] In each case the region of the spectrum assigned to the aromatic proteins shows the expected AB$_2$ multiplet structure. Electronic spectral data for these species are summarized in Table II.

Basicities of Carbinols.—The ease of formation of a carbonium ion from a carbinol in acidic medium may be considered to reflect what has been termed the "secondary basicity"[21] of the carbinol. The expression of this basicity in terms of values of pK_{R+}[22] provides a basis for comparisons of carbinols (Table III). A modification of conventional methods,[4] using spectrophotometric measurements of carbonium ion concentrations, in a series of borate buffer solutions, was used to obtain the pK_{R+} for II. This carbinol (II) is 50% converted to its carbonium ion IV in solutions of pH 9.05 (corresponding to a pK_{R+} value of 9.05). Its aqueous solutions may be titrated potentiometrically with hydrochloric acid, giving typical weak-base titration curves. It is particularly instructive to note that the analogous tris-*p*-anisylcarbinol, which gives a carbon-

(20) For a discussion of these spectra see J. C. Martin, *J. Chem. Educ.*, **38**, 286 (1961). The values of Table I are more accurate than those reported previously.
(21) V. Gold and B. W. V. Hawes, *J. Chem. Soc.*, 2102 (1951).
(22) The negative logarithm of the equilibrium constant for the reaction.

TABLE II

ELECTRONIC SPECTRA

Compound	λ_{max}, mμ (log ϵ)
Carbinol II^a	280 (3.86)
	288 (3.95)
Carbonium ion IV^b	240 (4.68)
	282 (4.47)
	330 (4.52)
	452 (3.95)
	475 (3.93) (sh)
Carbinol V^a	215 (4.77)
	276 (4.03)
	285 (shoulder)
Carbonium ion^c from V	288 (4.62)
	357 (4.34)
	450 (4.00)
	525 (3.62) (sh)
Carbinol I^a	277 (3.66)
	284 (3.65)
Carbonium ion III^d	272 (4.04)
	315 (sh)
	522 (4.25)
Carbonium ion IIIe	522 (4.30)
Carbonium ion III^f	522 (4.29)
Carbonium ion III^g	522 (4.28)

^{a} In ethanol. ^{b} In 0.1 M aqueous CH$_3$CO$_2$H. ^{c} In 0.1 M aqueous HCl. ^{d} In 0.5 M aqueous HCl. ^{e} In 0.5 M ethanolic HCl. ^{f} In 0.5 M methanolic HCl. ^{g} In 90% aqueous dioxane containing 0.5 M HCl.

TABLE III

BASICITIES OF TRIARYLCARBINOLS

Compound	pK_{R^+}
4,4',4''-Tri(dimethylamino)triphenylcarbinol^a	9.36
Sesquixanthydrol (II)	9.05
4,4',4''-Triaminotriphenylcarbinol^a	7.57
2,6,2',6',2'',6''-Hexamethoxytriphenylcarbinol	>6.5
9-(2,6-Dimethoxyphenyl)-1,8-dimethoxyxanthydrol (V)	2.5
4,4',4''-Trimethoxytriphenylcarbinol	0.82
Triphenylcarbinol^b	- 6.63
4,4',4''-Trinitrotriphenylcarbinol^b	-16.27

^{a} R. J. Goldacre and J. N. Phillips, *J. Chem. Soc.*, 1724 (1949). ^{b} Reference 12.

ium ion stabilization by oxonium-type resonance structures related to those important in the sesquixanthylium ion (structure VIII), has a pK_{R+} of only 0.82. This difference of 10^6 in the equilibrium constants for the ionizations of the two carbinols reflects an unusual stabilization of IV which deserves comment.

VIII   IX
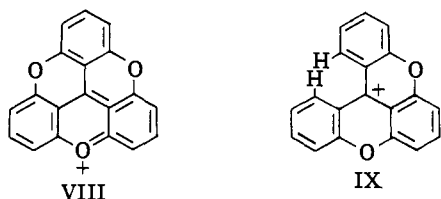
An examination of molecular models (Stuart–Briegleb) indicates that ion IV may exist in a completely copolanar configuration with little if any more strain than is present in the tetrahedral carbinol. By contrast the analogous ion IX, having only two ether bridges, which was reported[23] during the course of this work, cannot be completely coplanar. It is forced into a helical configuration by hydrogen–hydrogen interactions.

The usual basicity of both carbinols is reflected in the ionic nature of the corresponding chlorides. The chloride hydrochloride of IX is a red solid, described[23] as being insoluble in most organic solvents but dissolving in water with decomposition. Sesquixanthydryl chloride was isolated as an orange crystalline dihydrate which yields, on heating, its yellow unhydrated form. Both forms are hygroscopic, insoluble in ether or benzene, and soluble in water, methanol, ethanol, or acetone. An aqueous solution shows an electronic spectrum identical with that obtained when II is dissolved in aqueous acid.

The evidence at hand does not allow a quantitative assessment of the importance of the possible coplanarity of IV as a factor in explaining its stability with respect to II. It is interesting to compare II with the closely analogous carbinols I and V, which also bear oxygen substituents at each o-position, but have quite different geometry. Formation of the intensely purple carbonium ion III from I is rapid at pH 6.0. It is not, however, possible to obtain an accurate value of the pK_{R+}, since this reaction does not give a true equilibrium. The addition of excess sodium hydroxide to an aqueous solution of III gives no regeneration of the carbinol I, as evidenced by the failure to get any of the characteristic color of the carbonium ion on treatment of the solid reaction product with acid. The product mixture does contain carbinol V, in addition to a complex mixture of colored products giving infrared absorption in the region characteristic of quinone-like carbonyl groups. Quinonoid products might be expected from the nucleophilic attacks by hydroxide ion (or water) at the o-position of III.[24]

A solution of III in dilute aqueous hydrochloric acid loses its purple color over a few hours at room temperature, depositing crystalline carbinol V in excellent yield. Since the rate of this ring closure approaches that of formation of the carbonium ion from the carbinol in media of low acidity, our data allow us to do no more than place a lower limit on the value of pK_{R+}. We know that the rate of nucleophilic attack by hydroxide ion (and presumably water) on the central carbon of the carbonium ion is extremely small, relative to the rate of attack at the o-positions. We also know that the ion is formed with a rate large enough to provide an appreciable steady state concentration of carbonium ion at

pH 6.0–6.5. It is therefore conservative to say that the pK_{R+} has a value greater than 6.5, probably considerably greater.

The failure to regenerate carbinol I from III can be understood by considering the geometry of III. The steric interactions of the six o-methoxy substituents must result in an exaggerated angle of twist of the aryl groups in the propeller-like ion. This places three methoxyl groups above and three below the central carbon, effectively shielding it from nucleophilic attack.

This twisting of the aryl groups out of the plane of the ring must result in a decrease in resonance stabilization and charge delocalization in III.[25] It is therefore necessary to look elsewhere for an explanation of the great basicity of I.

The steric repulsion between methoxyl groups on different rings would be expected to be less unfavorable in the sp^2-hybridized, trigonal carbonium ion than in the tetrahedral carbinol.[26] It is impossible to construct a Stuart–Brieglev model of this molecule. Relief of strain in the ionization step provides an obvious driving force in a manifestation of steric effects reminiscent of the rapid ionizations observed with derivatives of tri-t-butylcarbinol.[6]

The 9-arylxanthydrol derivatives V in which this source of driving force for ionization is obviously much less important, has a pK_{R+} of 2.5. The establishment of one of the ether bridges forming the xanthydryl nucleus would be expected to have a very favorable electronic effect on the stability of the carbonium ion. Even so, the comparison of V with I ($pK_{R+} > 6.5$) clearly indicates the importance of an unusual factor, probably steric, favoring the ionization of I.

Electronic Absorption Spectra.—The unusual, very intense purple color of solutions of III suggests a possible effect of the pronounced lack of coplanarity of the conjugated systems in this hexamethoxytriphenylcarbonium ion. The substitution of methoxy groups into the p-positions of the triphenylcarbonium ion produces[14] a shift of the low energy bond of the parent ion (431 mμ, log ϵ 4.60) to longer wave lengths and higher intensity; for the 4,4',4''-trimethoxy derivative this bond is shifted to 483 mμ (log ϵ 5.02). The expected[28] effect of the twisting of the aryl rings out of the central plane of the ion is to produce a bathochromic shift accompanied by a lowering of the extinction coefficient.

(23) O. Neunhoeffer and H. Haase, *Chem. Ber.*, **91**, 1801 (1958); the pK_{R+} of the corresponding carbinol was not determined.

(24) R. Möhlau, *Ber.*, **16**, 2855 (1883); see also ref. 28a.

(25) This effect is mirrored in the n.m.r. spectra of Table 1 which show the downfield shift, as one goes from carbinol to carbonium ion, for the protons at the p-positions to be much greater in the planar IV than in III. See ref. 20 for a discussion of this effect. This exaggerated deviation from coplanarity in III is also evident in the corresponding free radical from electron spin resonance studies of hyperfine interactions with the m- and p-protons (studies with C. S. Johnson, Jr., H. S. Gutowsky, and M. J. Sabacky).

(26) Unpublished results of R. K. Howe (B.S. Thesis, University of Illinois, 1961) reflect the importance of this effect in another reaction of the carbinol. Heating a mixture of carbinol I with 30% of its sodium salt to 165° for 30 min. gives a quantitative yield of m-dimethoxybenzene and 2,6,2',6'-tetramethoxybenzophenone. Under these conditions carbinol V gives only 59% conversion to the xanthone and m-dimethoxybenzene after 2.5 hr. The analogous reaction of triphenylcarbinol requires 4 hr. at 280–320° for 49% conversion.[27] These reactions, the reverse of the addition of arylsodium to a ketone, involve in the slow step cleavage of the bond joining an aryl group to the carbinol carbon, a step accompanied by a considerably greater relief of strain for the reaction of I than for the other carbinols.

(27) H. D. Zook, J. March, and D. F. Smith, *J. Am. Chem. Soc.*, **81**, 1617 (1959).

(28) (a) C. C. Barker in G. W. Gray's "Steric Effects in Conjugated Systems," Butterworths Scientific Publications, London, 1918, p. 34; (b) M. J. S. Dewar, *ibid.*, p. 46, p. 59; (c) S. F. Mason and R. Printner, *ibid.*, p. 52.

From Table II we see that the long wave length absorption of the sesquixanthylium ion IV very closely resembles that of the tri-p-anisylcarbonium ion (at about 50 mμ longer wave length than that of the triphenylcarbonium ion). In each case a double peak is observed, unresolved in the case of IV. Although the close resemblance of these spectra is surprising in view of the differences in the electronic systems, the shift is in the direction predicted from a consideration of electronic substituent effects.

The predicted bathochromic shifts and lowered intensities (relative to IV) are observed for the carbonium ion derived from V. The ion III shows the bathochromic shift but, contrary to prediction, shows an increase in extinction coefficient relative to IV or relative to the ion derived from V. All of these ions have oxygen substituents at all six o-positions and fall in an order of increasing coplanarity of III < V (as the carbonium ion) < IV. We might therefore expect that the absorption for III might be less intense than that for the other ions though at longer wave length. It is actually more intense.

In an analogous case, the methylated derivatives of crystal violet (X, $R_1 = R_2 = R_3 = H$), the introduction of o-methyl substituents into the ion, with the at-

N(CH₃)₂ structure figure X
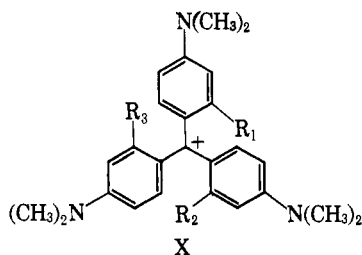
tendant exaggeration of the angle of twist of the aryl rings, produces the expected lowering of extinction coefficient. For the parent ion, the 2-methyl, the 2,2'-dimethyl, and the 2,2',2''-trimethyl analogs, the value of $\epsilon \times 10^{-4}$ decreases from 11.7 to 11.0 to 10.3 to 10.00 as λ_{max}(mμ) increases from 589 to 597 to 605 to 614.[28a]

The only surprising feature of the spectrum of III is, therefore, the very large value of the extinction coefficient for the long wave length bond. An explanation of this must await the study of further models.

Experimental[29]

1-Hydroxy-8-methoxyxanthone.—Crude 1,8-dihydroxyxanthone (20.0 g., 0.088 mole) prepared from 2,6,2',6'-tetramethoxybenzophenone by the method of Baeyer[30,31] was dissolved in 1000 ml. of tetrahydrofuran and treated with a threefold excess of diazomethane in 200 ml. of ether at room temperature for 1 day. Removal of solvent and recrystallization from ethanol yielded 18.5 g. (87.5%) of 1-hydroxy-8-methoxyxanthone, m.p. 146.8–150.9°. A pure sample, yellow needles, m.p. 153.0–153.7°, was obtained by four recrystallizations from ethanol.

Anal. Calcd. for C₁₄H₁₀O₄: C, 69.40; H, 4.12. Found: C, 69.31; H, 4.02.

1,8-Dimethoxyxanthone (VII). A.—Phenyltrimethylammonium benzenesulfonate was prepared by heating dimethylaniline (18.0 g., 0.015 mole) and methyl benzenesulfonate (25.0 g., 0.016 mole) on a steam bath for 30 min. The solid mass obtained in this manner was purified by one recrystallization from ethanol.

An ethanol solution of phenyltrimethylammonium ethoxide was prepared by the addition of phenyltrimethylammonium benzenesulfonate (16.0 g., 0.0546 mole) in 200 ml. of ethanol to sodium (0.91 g., 0.0395 g.-atom) in 50 ml. of ethanol. The solution was filtered to remove sodium benzenesulfonate and was then added to 1-hydroxy-8-methoxyxanthone (5.0 g., 0.0206 mole). Ethanol was removed from the mixture by vacuum distillation at 50° to leave a yellow residue which was heated on an oil bath for 1 hr. at 110°, then extracted with chloroform. A yellow material (7.5 g.), which remained undissolved after the chloroform extraction, was converted to 1-hydroxy-8-methoxyxanthone (2.32 g., 46.5%) on treatment with hydrochloric acid. The chloroform extract was recrystallized from ethanol to yield 1,8-dimethoxyxanthone (1.56 g., 29.6%), m.p. 217.9–223.3°. A pure sample, white needles, m.p. 223.7–225.4°, was obtained by three recrystallizations from benzene.

Anal. Calcd. for C₁₄H₁₂O₄: C, 70.28; H, 4.71. Found: C, 70.51; H, 4.66.

B.—Partially purified 1-hydroxy-8-methoxyxanthone (m.p. 146–150°, 5.0 g., 0.0204 mole) was dissolved in 500 ml. of boiling methanol and a solution of sodium (0.50 g., 0.0218 g.-atom) in 25 ml. of ethanol was added. The solution was concentrated to dryness and the residue was heated at 110° for 1 hr. with 10 ml. of toluene and 15 ml. of dimethyl sulfate. The product mixture yielded 2.22 g. (44.5%) of recovered starting material and 1.78 g. (34.0%) of 1,8-dimethoxyxanthone.

2,6,2',6',2'',6''-Hexamethoxytriphenylcarbinol (I). A. From 2,6,2',6'-Tetramethoxybenzophenone.—A solution of phenyllithium was prepared by the dropwise addition of bromobenzene (25.0 g., 0.159 mole) in 150 ml. of ether to lithium wire (2.20 g., 0.317 g.-atom) and 100 ml. of ether. Resorcinol dimethyl ether (20.0 g., 0.145 mole) was added and the reaction mixture was allowed to stand at room temperature for 60 hr. under nitrogen. Pure 2,6,2',6'-tetramethoxybenzophenone (15.0 g., 0.0497 mole), prepared in 61% yield by the method of Wittig and Pockels,[30] in 1 l. of hot benzene[32] was added and the reaction mixture was boiled for 3 days under nitrogen. The reaction mixture was poured into 1 l. of water and the organic layer was concentrated to yield 17.0 g. (77.8%) of I, m.p. 165.2–165.9°. A pure sample, white needles, m.p. 165.2–165.9°, was obtained by one recrystallization from ether; Infrared spectrum: 3420, 1590, 1470, and 1430 cm.⁻¹.

Anal. Calcd. for C₂₅H₂₈O₉: C, 68.16; H, 6.43. Found: C, 67.90; H, 6.17.

B. From Ethyl Carbonate.—A solution of phenyllithium was prepared by the addition of bromobenzene (39.2 g., 0.250 mole) in 125 ml. of ether to lithium wire (4.0 g., 0.577 g.-atom) and 60 ml. of ether. Resorcinol dimethyl ether (30.0 g., 0.218 mole) was added and the reaction mixture was allowed to stand at room temperature under nitrogen for 60 hr. Ethyl carbonate (8.50 g., 0.072 mole) in 400 ml. of benzene was added and the reaction mixture was refluxed for 3 days under nitrogen. The reaction mixture was poured into 600 ml. of water and the organic phase was concentrated to yield a gray residue. Recrystallization from ether gave 18.0 g. (57.0%) of I, m.p. 163.0–164.8° (mixture m.p. with material from part A, 164.2–166.1°).

9-(2,6-Dimethoxyphenyl)-1,8-dimethoxyxanthydrol (V). A. From 1,8-Dimethoxyxanthone.—A solution of 2,6-dimethoxyphenyllithium was prepared as before from resorcinol dimethyl ether (17.2 g., 0.125 mole). Unpurified 1,8-dimethoxyxanthone from methylation with dimethyl sulfate (4.20 g., 0.0164 mole) in 400 ml. of hot benzene was added and the reaction mixture was stirred at reflux under nitrogen for 3 days. The reaction mixture was cooled and poured into 300 ml. of water. A solid material present after pouring the solution into water was brought into solution by the addition of 400 ml. of chloroform. Concentration of the organic phase gave a solid which was recrystallized from benzene to yield 4.22 g. (65.2%) of 9-(2,6-dimethoxyphenyl)-1,8-dimethoxyxanthydrol, m.p. 268–289°. A pure sample, white needles, m.p. 294.0–297.2°, was obtained by seven recrystallizations from benzene.

Anal. Calcd. for C₂₃H₂₂O₆: C, 70.05; H, 5.62. Found: C, 69.85; H, 5.66.

B. From Carbinol I.—A solution of I (2.0 g., 0.00454 mole) and 5 ml. of concentrated hydrochloric acid in 500 ml. of water was heated for 12 hr. on a steam bath. The initially deep purple solution became colorless during this time and a white precipitate

(29) The authors wish to thank Mr. J. Nemeth, Mr. O. Norton, Miss C. Juan, and Mr. P. McMahon for the microanalytical and spectroscopic data. Melting points are uncorrected. Spectra are reproduced in full in the Ph.D. Thesis of R. G. Smith, University of Illinois, 1961, available from University Microfilms, Inc., Ann Arbor, Mich.

(30) G. Wittig and U. Pockels, *Ber.*, **72B**, 89 (1939).

(31) A. Baeyer, *Ann.*, **372**, 80 (1910).

(32) Preliminary experiments pointing up the necessity of adding benzene to the solvent mixture were carried out by Mr. R. Ekrlide.

was formed. The precipitate was collected by suction filtration and dried under vacuum to yield 1.81 g. (100%) of 9-(2,6-methoxyphenyl)-1,8-dimethoxyxanthydrol. The product was purified by one recrystallization from benzene–acetone to give 1.30 g. of material, m.p. 300.5–303.3°. This product gave an infrared spectrum identical with that of the product from procedure A.

Sesquixanthydrol (II). A. From Carbinol V.—Pyridine hydrochloride (7.0 g., 0.061 mole) and V (3.70 g., 0.0094 mole) were mixed and heated at 205° in an oil bath for 1 hr. At the end of this time the semiliquid reaction product was poured into water and the solids remaining in the reaction flask were washed out with water. The dark yellow solution was filtered to remove an insoluble red material and was then basified with sodium hydroxide which discharged the yellow color of the solution and produced a white precipitate. The precipitate was collected and dried under vacuum to yield 2.10 g. (74.0%) of sesquixanthydrol, m.p. 200–229° dec.; infrared spectrum (KBr pellet): 3460, 1615, 1485, 1460, and 1265 cm.$^{-1}$.

Anal. Calcd. for $C_{19}H_{10}O_4$: C, 75.48; H, 3.34. Found: C, 75.31; H, 3.38.

Recrystallization from benzene–ethanol yields sesquixanthydryl ethyl ether,[33] 1.16 g. (37.5%).

Anal. Calcd. for $C_{21}H_{14}O_4$: C, 76.35; H, 4.27. Found: C, 76.36; H, 4.22.

B. From Carbinol I.—Pyridine hydrochloride (50.0 g., 0.435 mole) and compound I (10.0 g., 0.023 mole) were treated as in the above procedure. The initial purple mass gradually became liquid under these conditions and took on a red color. The mixture yielded 4.22 g. (61.4%) of crude sesquixanthydrol which on recrystallization from benzene–ethanol yielded 3.45 g. (46.0%) of pure sesquixanthydryl ethyl ether.

Sesquixanthene.—Anhydrous aluminum chloride (10.6 g., 0.080 mole) was dissolved in 200 ml. of dry diglyme (purified by distillation from calcium hydride) and lithium aluminum hydride (1.61 g., 0.042 mole) was added. After stirring for 5 min., addition of sesquixanthydryl methyl ether (2.0 g., 0.00604 mole) in 400 ml. of dry diglyme was carried out over a 1 hr. period. The excess lithium aluminum hydride was decomposed by the addition of water, the reaction mixture was filtered, and the resultant colorless solution was poured into 2 l. of water to produce a white solid, 1.33 g. (76%) of sesquixanthene. The compound was found to be unstable in boiling chloroform and in boiling glacial acetic acid, in both cases decomposing to give yellow solutions. However, solutions in hot benzene, hot acetone, and hot ethanol remained colorless. Solutions in acidic ethanol slowly became yellow and the rate of color formation was found to be increased greatly by irradiation of the solution with a sunlamp with air passing through the solution. No color formation occurred in acidic ethanol on irradiation under nitrogen and no color formed on passage of air through acidic ethanol solutions in the dark.

The compound was purified by recrystallization from benzene–acetone to give 0.950 g. (55%) of sesquixanthene, m.p. 280–300° dec.

Anal. Calcd. for $C_{19}H_{10}O_3$: C, 79.71; H, 3.52. Found: C, 79.69; H, 3.76.

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(33) Unpublished results of M.-D. Steinhardt indicate this. We are indebted to Mrs. Steinhart for the material used in this analysis.

Autoxidation of Sesquixanthene in Ethanol.—Sesquixanthene (0.100 g.) was dissolved in 300 ml. of ethanol and 5 ml. of concentrated hydrochloric acid. The solution was irradiated with a sunlamp under reflux for 7 days. Air was passed through the solution during this time and the solution gradually took on a yellow color. When the solution was made basic with aqueous potassium hydroxide, concentrated under vacuum, then diluted with water, a yellow-red solid resulted. Purification by dissolving in dilute hydrochloric acid, filtering, and making the filtrate basic with KOH produced a white solid with an infrared spectrum identical with that of sesquixanthydrol (~10%).

Sesquixanthydryl Chloride.—Sesquixanthydryl ethyl ether (1.0 g., 0.00302 mole) was dissolved in 500 ml. of benzene and the solution was saturated with hydrogen chloride to produce an orange precipitate. After filtration and drying under vacuum, 1.16 g. (98.4%) of the dihydrate of sesquixanthydryl chloride was obtained. A portion of the product was recrystallized from ethanol–ether to yield orange needles, unmelted at 350°. A portion of the pure sample dried under vacuum at room temperature was analyzed.

Anal. Calcd. for $C_{19}H_9O_3Cl·2H_2O$: C, 63.97; H, 3.67. Found: C, 63.95; H, 3.41.

A portion of the pure sample, dried under vacuum at 110°, underwent a color change from orange to yellow; m.p. 350°.

Anal. Calcd. for $C_{19}H_9O_3Cl$: C, 71.13; H, 2.79. Found: C, 70.81; H, 3.15.

The hydrated chloride was found to be moderately soluble in water, ethanol, methanol, and acetone and was found to be insoluble in ether and in benzene. The visible and ultraviolet spectra of the chloride in water were found to be identical with those for sesquixanthydrol in dilute acid solution.

Basicity of Sesquixanthydrol.—The pK_{R+} of sesquixanthydrol was evaluated from the relationship

$$pK_{R+} = pH + \log [R^+]/[ROH]$$

The concentration of carbonium ion in a series of 0.1 M borate buffer solutions was determined by spectrophotometric measurements of the absorbance of the solutions at 330 mμ where the carbonium ion shows intense absorption and sesquixanthydrol does not absorb. The extinction coefficient for the 330 mμ peak was evaluated by a study of several concentrations of sesquixanthydrol in 0.1 M boric acid in which the alcohol is completely ionized.

Electronic Spectroscopic Studies of Ion III.—Spectral studies on 2,6,2',6',2'',6''-hexamethoxytriphenylcarbinol in acid solution were carried out immediately after preparation of the samples to avoid errors due to ring closure of the 2,6,2',6',2'',6''-hexamethoxytriphenylcarbonium ion to form 9-(2,6-dimethoxyphenyl)-1,8-dimethoxytriphenylcarbinol. This ring-closure reaction was found to be relatively slow and changes in the spectrum of 2,6,-2',6',2'',6''-hexamethoxytriphenylcarbonium ion due to this reaction were negligible over a 10-min. period.