

### Summary

1. Three series of band spectra which have previously been found in benzene have been found in cyclohexene, ethyl ether, methyl-*n*-amyl ether and ethylene chlorohydrin.

2. An analysis of these spectra on the basis of the quantum theory indicates that they can be attributed to the carbon-hydrogen linkage in the molecule.

3. The direction in which the experimental determination of the relation between absorption and chemical constitution lies, is pointed out.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

## METHOXY-SUBSTITUTED TRIPHENYL CARBINOLS AND THEIR SALTS

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When to equimolecular quantities of carbinols dissolved in acetic acid containing some sulfuric acid, dil. alcohol is added until the color is discharged, the amount of dilution serves as the index of the relative ease with which the various carbinol salts are completely hydrolyzed. Although this procedure can give only approximately correct results—and this was recognized by Baeyer and Villiger<sup>2</sup>—nevertheless, it has frequently been used by later investigators, and mathematically formulated rules have been derived concerning the basic strength of these nitrogen-free bases. With Baeyer, it is assumed that the influence of the methoxy groups is as follows: triphenyl carbinol: mono-*p*-methoxy: di-*p*: tri-*p* = 1:6.3:34.0:286. The influence of each succeeding group is thus exponential. As regards orientation, it is assumed that the *para* is pre-eminently greater in its influence than the other positions: triphenyl carbinol: *m*, -*m*, -*m*: *p*, -*o*, -*o*: *p*, -*p*, -*p*: 1:1.7:7.6:286.

The possible relation between increased basic strength of the carbinols on the one hand and their tendency to give rise to monomolecular triaryl methyls on the other, has been the subject of many investigations. In this Laboratory,<sup>3</sup> a number of mono- and dimethoxy triaryl methyls have been prepared in the solid state, and their molecular state determined. The results indicate that the methoxy groups, in addition to augmenting the basicity of the carbinols, exert an appreciable positive influence as

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<sup>2</sup> Baeyer and Villiger, *Ber.*, **35**, 1189 (1902).

<sup>3</sup> Gomberg and co-workers, *THIS JOURNAL*, **45**, 190, 207 (1923); **47**, 2392 (1925).

regards the degree of dissociation of the corresponding hexa-aryl ethanes into free radicals.

The purpose of this investigation has been to further our knowledge of the questions discussed above. (a) To determine what effect an increased number of methoxy groups in the triaryl carbinol has upon the tendency of the central carbon atom to become trivalent; tri-*o*-methoxy carbinol was selected for this test. (b) To study, by the application of physical-chemical methods, the influence of methoxy groups on the basic tendencies of the carbinols; with this in view we determined the basicity constants of carbinols containing from three to seven methoxy groups. (c) To obtain further evidence concerning the constitution of these simple, colored carbinol salts, so-called halochromic salts, and for this purpose their absorption spectra were determined.

### Preparation of the Carbinols

All the carbinols described in this paper were prepared through the Grignard reaction. In some cases the magnesium reacted with the aryl iodide only with difficulty, especially when both positions *ortho* to the iodine were occupied by methoxy groups. In such cases the metal was activated, but we found it unnecessary to employ for this purpose as large amounts of iodine as prescribed by Baeyer.<sup>4</sup> The yields of the carbinols were usually good, except when the 2,6 positions of the Grignard reagent were occupied. The preparation of the carbinol chlorides presented unexpected difficulties, and when more than three methoxy groups were present in the molecule of the carbinol, then by none of the usual procedures could the chloride be obtained crystalline. Finally, the chloride of 2,4,2',4'-tetramethoxytriphenyl carbinol was obtained as crystals by salting it out from a solution in concd. hydrochloric acid. This chloride is strongly colored and, outside of the dyes, is the first known strictly triaryl methyl chloride that is colored in the solid state—all other colored chlorides except some which contain a xanthone ring,<sup>5</sup> contain a loosely bound molecule of hydrogen chloride.<sup>6</sup>

**2,2',2''-Trimethoxytriphenyl Carbinol.**—THE CHLORIDE.—Baeyer prepared tri-*o*-anisyl carbinol; he also mentions the chloride,<sup>7</sup> but no description of it is given.

Fifteen g. of the carbinol is dissolved in 100 cc. of purified chloroform; to this solution is added 15 cc. of acetyl chloride which has been freshly distilled over dimethyl-aniline. The mixture is kept at about 30° for two to three hours, and 150 cc. of dry ether is then added. On cooling the solution, the chloride precipitates in very fine crystals. The product is filtered and washed twice with dry ether, dried for a short time at 100° and then placed over soda lime in a vacuum desiccator; yield, 13 g. The

<sup>4</sup> Gomberg and Bachmann, *THIS JOURNAL*, **49**, 255 (1927).

<sup>5</sup> Gomberg and West, *ibid.*, **34**, 1529 (1912).

<sup>6</sup> Gomberg and Cone, *Ann.*, **370**, 191 (1909).

<sup>7</sup> Baeyer, *Ber.*, **42**, 2627 (1909).

chloride decomposes slowly at 170–175°, but does not melt instantly when immersed in a bath which has been preheated to 185°.

*Anal.* Calcd. for  $C_{22}H_{21}O_3Cl$ : Cl, 9.63. Found: 9.60.

**TRI-*o*-ANISYLMETHANE.**—Two g. of the carbinol is dissolved in 125 cc. of boiling alcohol, 10 cc. of concd. hydrochloric acid is added and the solution is heated on the steam-bath until the violet color disappears. Upon cooling the solution, the methane crystallizes out; yield, 1.8 g.; m. p., 136–137°.

*Anal.* Calcd. for  $C_{22}H_{22}O_3$ : C, 79.04; H, 6.59. Found: C, 79.17; H, 6.36.

**2,4,2',2''-Tetramethoxytriphenyl Carbinol** was prepared from *o*-iodo-anisole and 2,4-dimethoxybenzoic ester; yield, 55%. After recrystallization from alcohol the carbinol melts at 122°.

*Anal.* Calcd. for  $C_{23}H_{24}O_5$ : C, 72.63; H, 6.32. Found: C, 72.59; H, 6.30.

**2,4,2',4''-Tetramethoxytriphenyl Carbinol.**—This carbinol was prepared by Kauffmann and Kieser<sup>8</sup> from 2,4-dimethoxy-iodobenzene, magnesium and 2,4-dimethoxybenzophenone. We prefer to let the same Grignard reagent react with methyl benzoate, because the yield of the carbinol seems to be higher in this case, namely, about 60%. The pure carbinol melts at 137°, while Kauffmann reports 134.5°.

In the process of preparing the requisite dimethoxy-iodobenzene, there is always produced also some of the 1,3-dimethoxy-4,6-di-iodobenzene; m. p., 202°.

*Anal.* Calcd. for  $C_8H_8O_2I_2$ : I, 65.1. Found: 65.5.

**THE CARBINOL CHLORIDE.**—Five g. of the carbinol is dissolved in 100 cc. of concd. hydrochloric acid, and 15 g. of magnesium chloride dissolved in a little water is added. If seeding at this stage can be done, then the crystallization of the carbinol will proceed rapidly; otherwise it may be weeks before it commences. The crystals are filtered and washed with a little 5 *N* hydrochloric acid solution, pressed between filter papers and placed in a desiccator over phosphorus pentoxide. The desiccator is now exhausted and a few cc. of gaseous hydrogen chloride is let in, in order to prevent the moisture which adheres on the surface of the crystals from hydrolyzing the chloride back to the carbinol. Care must be taken, however, not to introduce into the desiccator too much hydrochloric acid gas, otherwise the carbinol chloride will liquefy with the formation of the chloride-hydrochloride. After the crystals have remained in the desiccator for a day, dry air is let in, the hydrogen chloride blown out, and a dish with soda lime placed beside the crystals. The yield is 4 g. of the dried product. The chloride decomposes at about 80°. The crystals are bronze colored with a metallic luster; they are soluble in acetone, chloroform and nitrobenzene; very slightly soluble in ether and benzene.

*Anal.* Calcd. for  $C_{23}H_{23}O_4Cl$ : Cl, 8.90. Found: 8.93.

**2,4,4',4''-Tetramethoxytriphenyl Carbinol** was prepared from *p*-iodo-anisole and 2,4-dimethoxybenzoic methyl ester. The carbinol crystallizes from alcohol very slowly; m. p., 111°.

*Anal.* Calcd. for  $C_{23}H_{24}O_5$ : C, 72.63; H, 6.32. Found: C, 72.19; H, 6.19.

**2,4,2',4',2''-Pentamethoxytriphenyl Carbinol** was prepared from 2,4-dimethoxy-iodobenzene and *o*-methoxybenzoic methyl ester; yield, 40%; m. p., 146–147°. In order to obtain the carbinol in perfectly colorless crystals, it is advisable to add a drop of ammonium hydroxide to the solution, when recrystallizing from alcohol. A similar procedure should be followed also in the case of the other highly methoxylated carbinols.

*Anal.* Calcd. for  $C_{24}H_{26}O_6$ : C, 70.21; H, 6.39. Found: C, 70.22; H, 6.22.

**2,4,2',4',4''-Pentamethoxytriphenyl Carbinol** was prepared from 2,4-dimethoxy-iodobenzene and *p*-anisic ester; yield, 25–30%; m. p., 91–92°.

<sup>8</sup> Kauffmann and Kieser, *Ber.*, **45**, 2334 (1912).

*Anal.* Calcd. for  $C_{24}H_{26}O_8$ : C, 70.21; H, 6.39. Found: C, 69.91; H, 6.20.

**2,6,2',6',2''-Pentamethoxytriphenyl Carbinol** was prepared from 2,6-dimethoxyiodobenzene<sup>9</sup> and *o*-anisic ester, employing anisole as the solvent. The carbinol magnesium compound is precipitated from the anisole solution by the addition of petroleum ether, filtered from the mother liquid, and is decomposed in the usual manner. The carbinol crystallizes from the ether solution when the ether is allowed to evaporate at low temperature. The yield is very poor; 1 g. or less from 15 g. of the dimethoxyiodobenzene and 5 g. of the ester. The carbinol decomposes at 143–146°.

*Anal.* Calcd. for  $C_{24}H_{26}O_8$ : C, 70.21; H, 6.39. Found: C, 70.46; H, 6.22.

**2,4,6,2',4',6'-Hexamethoxytriphenyl Carbinol** was prepared from 2,4,6-trimethoxyiodobenzene,<sup>10</sup> magnesium and methyl benzoate, with anisole as the solvent. The yield of the carbinol is very poor; m. p., 184°.

*Anal.* Calcd. for  $C_{28}H_{28}O_7$ : C, 68.15; H, 6.41. Found: C, 68.41; H, 6.47.

**2,4,6,2',4',2'',4''-Heptamethoxytriphenyl Carbinol** was prepared from 2,4-dimethoxyiodobenzene and 2,4,6-trimethoxybenzoic ethyl ester; yield, 40%; m. p., 147°.

*Anal.* Calcd. for  $C_{26}H_{30}O_8$ : C, 66.35; H, 6.43. Found: C, 66.45; H, 6.34.

### The Free Radical Tri-*o*-anisylmethyl

**Preparation.**—Five g. of the carbinol chloride and 5 g. of molecular silver are placed in a large test-tube, benzene is added and the mixture is shaken for two to three hours. The usual procedure for the isolation of the radical is followed, except that the solution is kept below 30° during the evaporation of the benzene. When the solution has been concentrated to about 10 cc., 25 cc. of dry ether is added, whereupon the radical separates in crystalline form. The crystals are washed with ether and dried under reduced pressure in a slow current of carbon dioxide; yield, 3–3.5 g. The product is pale yellow, almost white, but dissolves in benzene with a color resembling that of potassium dichromate in water. The substance decomposes at about 110°, but it does not melt at once when plunged into a bath at 125–130°.

**Tri-*o*-anisyl Peroxide.**—Weighed amounts of the carbinol chloride in bromobenzene were shaken with molecular silver for half an hour, and the rate of oxygen absorption by the resulting radical was then determined. The same was done on the crystalline triaryl methyl. The amount of oxygen theoretically necessary for the formation of the peroxide is absorbed rapidly (within a minute) and the solution is decolorized. Thereafter, further oxidation takes place at a slow rate, and the solution gradually assumes a lemon-yellow color.

For the isolation of the peroxide, a benzene solution of the radical is allowed to evaporate in the air at room temperature. The brown, sticky residue is stirred with a little ether, whereupon the peroxide crystallizes. It is best recrystallized from benzene; m. p., 157–160°, with decomposition. The peroxide is rather soluble in most solvents and insoluble in petroleum ether.

*Anal.* Calcd. for  $C_{44}H_{42}O_8$ : C, 75.63; H, 6.02. Found: C, 75.88; H, 6.12.

**The Molecular State.**—The dissociation of the di-2,2',2''-trimethoxyhexaphenylethane into free radicals is almost complete. We determined the molecular weight in two ways; by the indirect method, when the free radical was formed in the freezing-point apparatus from the carbinol chloride and silver, stirring for about an hour; and also directly upon

<sup>9</sup> Baeyer, *Ann.*, 372, 127 (1910).

<sup>10</sup> Kauffmann and Kieser, *Ber.*, 46, 3792 (1913).

the pure, crystalline radical itself. The constant for the solvents was determined by means of tri-*o*-anisylmethane.

TABLE I

MOLECULAR WEIGHT OF DI-2,2',2''-TRIMETHOXY-HEXAPHENYLETHANE			
Solvent, g.	Solute, g.	Depression, °C.	Dissociation, %
I. Solvent: benzene, $K = 534$ ; solute, carbinol chloride + silver			
17.58	0.3044	0.249	100
17.58	.4638	.382	100
17.60	.1903	.155	97
II. Solvent: benzene; solute, free radical			
17.60	0.2965	0.241	79
17.60	.5533	.451	79
III. Solvent: <i>p</i> -bromotoluene, $K = 81.6$			
26.80	0.2743	0.247	97
26.80	.4984	.445	95
27.20	.2520	.224	97
27.20	.4485	.395	96

It is evident from the results given, that the presence of methoxy groups in the molecule exerts a very great influence as regards the tendency of the central carbon atom to exist in the tervalent state. Two methoxy groups in a single nucleus<sup>11</sup> induce the dissociation of the ethane into free radicals to the extent of 25%; three groups, each in a separate nucleus, induce complete dissociation.

### Basicity Strength of Polymethoxy-triphenyl Carbinols

The triaryl carbinols themselves, as is well known, are not basic; they dissolve in neutral solvents without measurable dissociation and formation of hydroxyl ions. When, therefore, we speak of the basicity of a carbinol, we really mean the basicity of the true base which corresponds to the cation of the colored triaryl methyl salt, and this, generally, can seldom be isolated.<sup>12</sup> Obviously, in order to measure the basic strength of the true bases, we have to examine the salts and not the colorless carbinols themselves, as these are pseudo bases. The property of a salt which is characteristic for the basicity of the corresponding base is the resistance of the salt against hydrolysis, that was also the principle of the method devised by Baeyer.

In a solution containing acid and carbinol, there is an equilibrium,  $\text{ROH} + \text{H}^+ \rightleftharpoons \text{R}^+ + \text{H}_2\text{O}$ , and the hydrolysis constant of the salt is  $K_h = ([\text{ROH}] \times [\text{H}^+]) / ([\text{R}^+] \times [\text{H}_2\text{O}])$ , where R stands for the pseudo base radical and  $\text{R}^+$  for the colored base radical. The water concentration,

<sup>11</sup> Gomberg and Forrester, *THIS JOURNAL*, **47**, 2373 (1925).

<sup>12</sup> Gomberg, *ibid.*, **35**, 1035 (1913). Gomberg and Van Stone, *ibid.*, **38**, 1577 (1916). Gomberg and McGill, *ibid.*, **47**, 2392 (1925).

if sufficiently large, may be considered as constant, and then the equation  $K_h = ([ROH] \times [H^+])/[R^+]$ , defines the hydrolysis constant of the carbinol salt. This constant we have attempted to measure for a number of carbinols. The relation between the hydrolysis constant and the basicity constant is  $K_h \times K_b = [H^+] \times [OH^-] = K_w$ . In order, therefore, to determine  $K_b$  from  $K_h$  it is necessary to know the ionic product of the water in the solvent employed, in the aqueous 50% acetone.

**Determination of  $K_w$ .**—The solvent was made up from  $n$  cc. of acetone diluted with water to the volume  $2n$  cc. at the same temperature, 1.07  $n$  cc. of water being required for this. The method for the determination of the ionic product of the water has been described by Pring.<sup>13</sup>

For the dissociation measurements of acid and alkali, an Arrhenius cell was employed, the capacity of which was 0.1657.

CONDUCTIVITY OF HCL IN ACETONE-WATER AT 25°

Concn.	0.1	0.02	0.01	0.002	0.001	0.0006
$\lambda$	155.6	179.3	186.7	191.8	192.7	192.7

For infinite dilution,  $\lambda$  (calcd.) = 195.

CONDUCTIVITY OF NAOH IN ACETONE-WATER AT 25°

Concn.	0.05	0.02	0.01	0.005
$\lambda$	79.1	85.3	88.45	91.9

For infinite dilution,  $\lambda$  (calcd.) = about 99.

The corresponding values obtained by Pring for hydrochloric acid solutions were considerably greater, and those for sodium hydroxides somewhat less than ours.

In measuring the potential of the chains, acid quinhydrone electrode against acid or alkali hydrogen electrode, we encountered difficulties; this potential is dependent very much on the speed of the hydrogen current, due probably to the reduction of the acetone in the presence of platinum black. We finally determined the potentials with exactly the same gas current during all of the measurements, and even then, we fear, the results cannot claim the desired absolute accuracy; they are, however, reliable for the comparison of the basic strengths of the carbinols among themselves.

The potential of the chain Pt | H<sub>2</sub>, 0.01N . HCl | KCl | H<sub>2</sub>, 0.05N . NaOH | - Pt was found to be 0.685  $\pm$  0.001 v. From this, the value of the ionic product  $K_w$  in our water-acetone mixture is calculated as  $[H^+] \times [OH^-] = 1.0 \times 10^{-15}$ .

**Hydrolysis Constants.**—Two methods have been employed for the determination of the hydrolysis constants of our carbinols. If the original hydrogen-ion concentration is  $a$ , the carbinol concentration is  $c$ , and in

<sup>13</sup> Pring, *Trans. Faraday Soc.*, 19, 705 (1924).

the equilibrium the salt concentration is  $x$ , then the hydrolysis constant is determined by the equation

$$K_h = ([c - x] \times [a - x]) / [x] \quad (1)$$

Here  $x$  means both the concentration of the salt  $R^+$  formed and the diminution in the hydrogen-ion concentration. Therefore, we have two possibilities for the determination of  $K_h$ , namely, (1) from the depression in the hydrogen-ion concentration and (2) from the salt concentration produced.

**Potentiometric Determination of  $K_h$ .**—In the determination of potentials, two identical electrodes were employed which agreed within 0.1 millivolt or less. The depression in the hydrogen-ion concentration was measured by means of the quinhydrone electrode.<sup>14</sup> The difference in potential between an electrode in the acid and one in the mixture of acid and carbinol determines the difference in Sørensen value,  $P_H$ . If this difference is very slight, the method is not accurate. In our case, the lower limit of the applicability of the method is reached with the penta-methoxy carbinols, where the difference in potential is only a very few millivolts, but the method is reliable with the more highly methoxylated carbinols.

In Table II, from the acid concentration in Col. 2, the original hydrogen-ion concentration,  $a$ , has been calculated by the aid of the conductivity data on page 1351; the depression in hydrogen-ion concentration is obtained by the aid of potential difference in Col. 4. Only the average of four values is reported for each chain in the tables.

TABLE II  
HYDROLYSIS CONSTANTS OF METHOXY CARBINOL SALTS DETERMINED  
POTENTIOMETRICALLY

Methoxy carbinol	Acid, N	Carb., N	Potent. diff., v.	$K_h$	$K_h$ av.
2,4,6,2',4',2'',4''	0.002 H <sub>2</sub> SO <sub>4</sub>	0.002	0.0933	$1.41 \times 10^{-6}$	$1.3 \times 10^{-6}$
	.001 H <sub>2</sub> SO <sub>4</sub>	.001	.0847	$1.40 \times 10^{-6}$	
	.002 HCl	.00303	.1729	$1.23 \times 10^{-6}$	
	.001 HCl	.00160	.1680	$1.15 \times 10^{-6}$	
2,4,2',4',2'',4''	.001 H <sub>2</sub> SO <sub>4</sub>	.001	.0103	$1.35 \times 10^{-3}$	$1.37 \times 10^{-3}$
	.001 HCl	.001	.0102	$1.37 \times 10^{-3}$	
	.002 HCl	.001	.0077	$1.37 \times 10^{-3}$	
	.002 HCl	.002	.0149	$1.41 \times 10^{-3}$	
2,4,2',4',4''	.002 HCl	.002	.0016	.029	0.027
	.002 HCl	.004	.00363	.025	
2,4,2',4',2''	.001 HCl	.001	.0015	.031	.029
	.001 HCl	.005	.0041	.028	

**Spectrometric Determination of the  $K_h$ .**—The second method for obtaining the value of  $K_h$  is based on the fact that only the salts, and not the carbinols themselves, absorb visible light. In the last part of this

<sup>14</sup> Büllmann, *Ann. chim.*, **15**, 109 (1921). Büllmann and Lund, *ibid.*, **16**, 321 (1921).

paper the absorption curves are presented for some of the carbinol salts in solution. The comparison, with these curves, of the absorption by a solution of a carbinol salt of unknown concentration, permits the calculation of the concentration of the salt. The limits of applicability for this method are determined by the concentrations of acid necessary to produce proper salt concentrations for the absorption measurements. As these salt concentrations are in our case between  $10^{-5}$  and  $10^{-6} N$ , it is evident that salts which are hydrolyzed only slightly cannot be examined by this method because they would require acid concentrations of the same order of magnitude. Here the pentamethoxy carbinols form the upper limit, where the acid concentrations employed were of the order  $1/2000 N$ . The fact that both methods gave results agreeing fairly well, indicates that both are reliable within their proper intervals.

Usually six determinations of the extinction coefficients were made within about  $25m\mu$  on each side of the maximum of the absorption curve, but only the average of the six corresponding values for the salt concentration is reported in the following table. Those values agreed within 5% or less. In Table III are given the original acid concentration,  $N$  the degree of its dissociation,  $D$ , the original carbinol concentration,  $C$ , the carbinol salt concentration as found by this method,  $R^+$ , which is equal to  $X$  in Equation 1.

TABLE III  
HYDROLYSIS CONSTANTS OF METHOXY CARBINOL SALTS DETERMINED  
SPECTROMETRICALLY

Carbinol	Acid, $N$	$D$ , %	$C$	$R^+ \times 10^{-4}$	$K_h$	$K_h$ (av.)
2,4,2',4',4''	0.0003	99	0.0005	3.24	0.046	
	.0006	99	.0005	6.36	.0467	
2,4,2',4',2''	.0004	99	.0005	4.3	.046	0.046
	.0008	98	.0005	8.4	.047	
2,4,4',4''	.01	96	.00048	2.7	1.71	
	.006	97	.001	3.35	1.75	1.73
2,4,2',4'	.02	92	.001	8.45	2.20	
	.01	96	.001	4.65	2.10	2.15
2,4,2',2''	.02	92	.001	5.2	3.54	
	.04	85	.001	10.3	3.30	3.4
4,4',4''	.02	92	.001	3.08	6.0	
	.01	96	.001	1.64	5.9	5.95
2,4',4''	.1	82	.001	0.91	90	
	.2	70	.001	1.67	84	87.0

**Basicity Constants.**—The various hydrolysis constants which have been determined by the two methods, and the basicity constants derived from these are summarized in Table IV.

The results given above indicate that when several methoxy groups are present in the carbinol molecule the effect of additional methoxy groups upon the basicity strength of the carbinol does not follow Baeyer's



TABLE IV  
 HYDROLYSIS AND BASICITY CONSTANTS OF THE CARBINOLS

Carbinol	Hydrolysis const.	Basicity const.	Method
2,4,6,2',4',2'',4''	0.0000013	$7.7 \times 10^{-10}$	Potentiom.
2,4,2',4',2'',4''	.0014	$7.1 \times 10^{-13}$	Potentiom.
2,4,2',4',4''	.027	$3.7 \times 10^{-14}$	Potentiom.
2,4,2',4',4''	.046	$2.2 \times 10^{-14}$	Spectrom.
2,4,2',4',2''	.029	$3.5 \times 10^{-14}$	Potentiom.
2,4,2',4',2''	.046	$2.2 \times 10^{-14}$	Spectrom.
2,4,4',4''	1.7	$6.0 \times 10^{-16}$	Spectrom.
2,4,2',4''	2.1	$4.8 \times 10^{-16}$	Spectrom.
2,4,2',2''	3.4	$3.0 \times 10^{-16}$	Spectrom.
4,4',4''	6.0	$1.7 \times 10^{-16}$	Spectrom.
2,4',4''	87	$1.15 \times 10^{-17}$	Spectrom.

product rule, nor any other simple rule. Whether the last group introduced goes into the *ortho* or *para* position with regard to the central carbon atom, is of minor importance. The resulting configuration of the new ring, whether it becomes a resorcinol or phloroglucinol ring, is the deciding factor. Then again, in one case, the introduction of an *o*-methoxy group increases the basicity constant three times; in another case, one thousand times.

#### Electrical Conductivity of the Carbinol Salts

The choice of solvents which may be considered for salts of the weakly basic triaryl carbinols is very limited, liquid sulfur dioxide<sup>15</sup> and hydrogen cyanide<sup>16</sup> serving as the most feasible solvents. Ether, benzene and other hydrocarbons do not dissociate, while most solvents containing hydroxyl groups react with the salts. However, in the case of the polymethoxylated carbinols the tendency of the salts towards hydrolysis is greatly diminished, and so it is possible to use as solvents compounds which have hydroxyl groups, or solvents which contain water as an admixture. Alcohol is still out of the question because it reduces the salts to the corresponding triarylmethanes. We found in acetone a very suitable solvent. It dissolves the carbinols as well as their salts; free acids are only very slightly dissociated in it, while the salts are practically completely dissociated at the dilutions which we used.

**Conductivity in Pure Acetone.**—The acetone, dried over calcium chloride was distilled over freshly ignited potassium carbonate and its conductivity was then less than  $1 \times 10^{-6}$ . The salt solutions in pure acetone were prepared by adding a solution of acid in acetone to a solution of the carbinol in the same solvent. The negligible amount of water formed in the reaction need not be considered, since the solvent itself cannot be dried completely without danger of undergoing some conden-

<sup>15</sup> Walden, *Ber.*, **35**, 2018 (1902). Gomberg, *Ber.*, **35**, 2402 (1902).

<sup>16</sup> Gomberg and Sullivan, *THIS JOURNAL*, **44**, 1819 (1922).

sation. In order to neutralize the acid, an excess of carbinol was added, but in a few cases it was impossible to reach the complete transformation of acid into salt. A conductivity cell of the Washburn type was employed, the capacity of which was 0.01313. A Vreeland oscillator furnished the alternating current, and the resistance and bridge were Leeds and Northrop's calibrated and adjusted instruments. The temperature was 25°.

TABLE V

CONDUCTIVITY OF 2,4,2',4',2'',4'''-HEXAMETHOXY-TRIPHENYLMETHYL SULFATE

 $(R_3COH):(1/2H_2SO_4) = 9:1$ 

Dilution	1800	2250	4500	9000	18000
Equiv. cond.	71.5	72.1	73.7	75.3	75.3

In Table VI, a comparison is given of the conductivities of different carbinol sulfates in acetone at the *same* concentrations. The ratio carbinol: acid varies from one carbinol to another and is indicated by the number *p*. The carbinols were dissolved in 0.0005 *N* sulfuric acid in acetone.

TABLE VI

CONDUCTIVITY OF DIFFERENT CARBINOL SULFATES AT EQUAL CONCENTRATIONS IN ACETONE

Carbinol	Equiv. conduct.	<i>p</i>	Carbinol	Equiv. conduct.	<i>p</i>
4,4',4''	(32.0)	20	2,4,2',4',2'',4'''	71.8	5
2,4,2',2''	(46.5)	20	2,4,2',4',2'',4'''	71.1	2.5
2,4,2',4'	(44.7)	20	2,4,6,2',4'	76.5	10
2,4,2',4',2''	71.1	20	2,4,6,2',4'	74.4	5
2,4,2',4',2''	70.5	10	2,4,6,2',4'	72.5	2.5
2,4,2',4',4''	68.4	10	2,4,6,2',4',2'',4'''	76.7	5
2,4,2',4',4''	65.9	5	2,4,6,2',4',2'',4'''	76.7	2.5
2,4,2',4',2'',4'''	71.6	10	2,4,6,2',4',2'',4'''	72.8	1

**Conductivity of some Carbinol Salts in 50% Acetone-Water.**—Some measurements were carried out in a mixture of acetone and water. The hydrolysis constants determined in the preceding section make it possible to compute the equilibrium concentrations of acid and salt, and the conductivity of the acid being known, the conductivity of the salts can be determined. This has been done for the two most "basic" carbinols. For the mixture of water and acetone the Arrhenius cell, already mentioned,

TABLE VII

CONDUCTIVITY OF CARBINOL CHLORIDES IN DILUTE (50%) ACETONE

Methoxy carbinol	Acid, <i>N</i>	Carbinol, <i>N</i>	Salt (calcd.) <i>N</i>	$\lambda$	$\lambda$ , av.
2,4,6,2',4',2'',4'''	0.001	0.00224	0.000999	52.3	53.0
	.001	.000448	.000448	53.6	
2,4,2',4',2'',4'''	.001	.00387	.00070	44.0	42.1
	.001	.0030	.000633	42.3	
	.001	.00247	.00058	41.0	
	.001	.00170	.000473	41.2	

was used. In the calculations, the equivalent conductance of the hydrochloric acid in the solvent in question is assumed to be 192, from the data on page 1351. It will be noticed that the conductivity of the salt of the heptamethoxy carbinol is greater than that of the hexamethoxy compound, in spite of the fact that the molecule of the former is heavier than that of the latter.

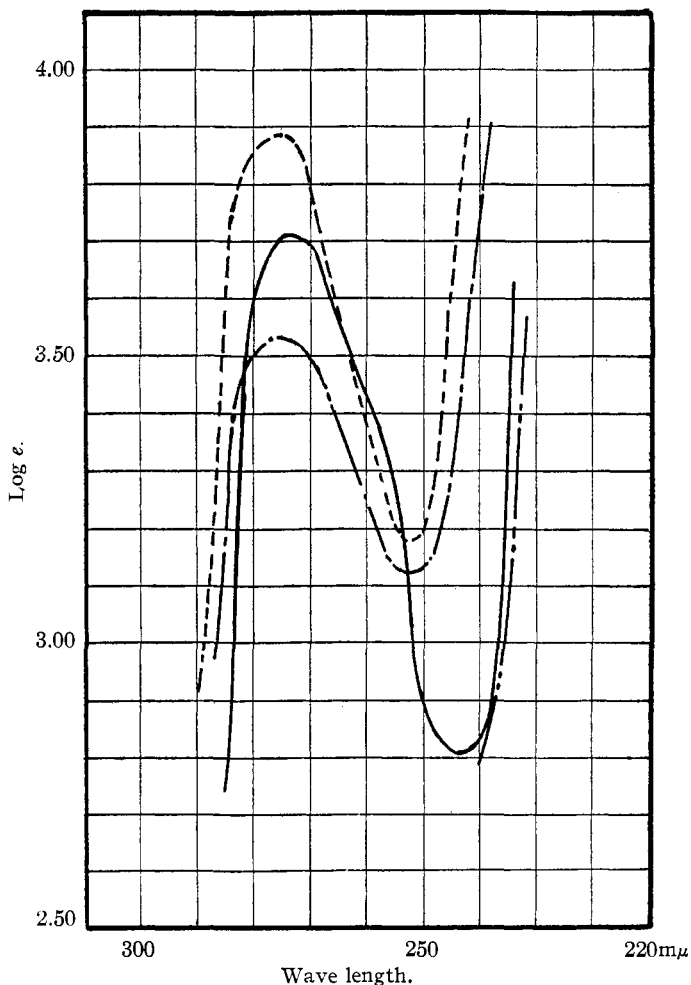


Fig. 1.— ———, 2,2',2''-trimethoxytriphenyl carbinol; - - - - -, 4,4',4''-trimethoxytriphenyl carbinol; - - - - -, 2,4,2',4',2'',4''-hexamethoxytriphenyl carbinol; - · - · - ·, triphenyl carbinol.

In a similar manner, it was found that the equivalent conductance of heptamethoxy carbinol chloride in water containing only 2% of acetone, is 92.5. As the equivalent conductance of the chloride ion is about 70—

the value in pure water—the value of the cation is about 22.5, or nearly one-third that of the anion.

### Absorption Spectra, and Constitution of the Carbinol Salts

At the present time our knowledge of atomic structure does not enable us to express the halochromism of the carbinol salts in terms of electron orbits of some definite atom or atoms in the molecule;<sup>17</sup> nor is the frequently proposed expression  $[R_3C]^+X^-$  satisfactory, for after all, it is merely a restatement of the fact that the compound is a salt, with no commitment as to the constitution. One is still obliged, therefore, to have recourse to the older explanation, namely, that there is a distinct difference in

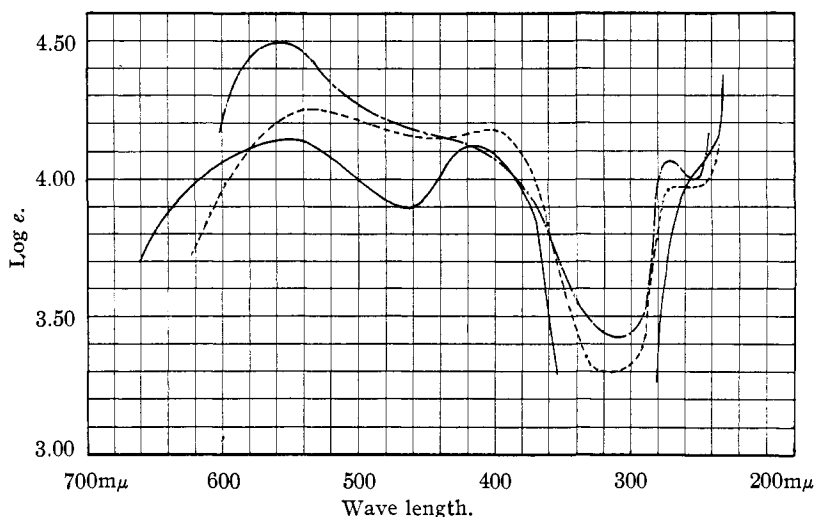


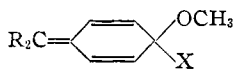
Fig. 2.— ———, 2,2',2''-trimethoxytriphenyl carbinol chloride; - - - - -, 2,4,2',2''-tetramethoxytriphenyl carbinol chloride; - · - ·, 2,4,2',4',2''-penta-methoxytriphenyl carbinol chloride.

the atomic configuration of the  $(R_3C)$  group, depending upon whether the group is in the molecule of the colorless or the colored substance. Accordingly, for salts of those triaryl carbinols which contain no oxygen, the quinocarbonium formula alone can come into consideration. For the methoxy carbinol salts, however, two views have been advanced: the quinocarbonium configuration I,<sup>18</sup> and the oxonium II,<sup>19</sup> and III; constitution III being only for such cases when there is no *p*-methoxy group in the molecule.

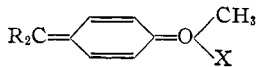
<sup>17</sup> See, for such an attempt, Lund, *Dissertation*, "Studier in Trifenylmethangruppen," Arnold Busck, Copenhagen, 1926.

<sup>18</sup> Gomberg and Cone, *Ann.*, **370**, 192 (1909).

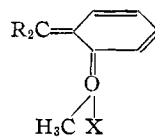
<sup>19</sup> Kehrman, Houben-Weyl's "Methoden der organischen Chemie," Georg Thieme, Leipzig, 1923, vol. III, p. 345.



I



II



III

Now, on the oxonium constitution, there is obviously a very marked difference in the constitution between *p*-methoxy and *o*-methoxy salts, since the first possess a *p*-quinone nucleus and the latter an *o*-quinone.

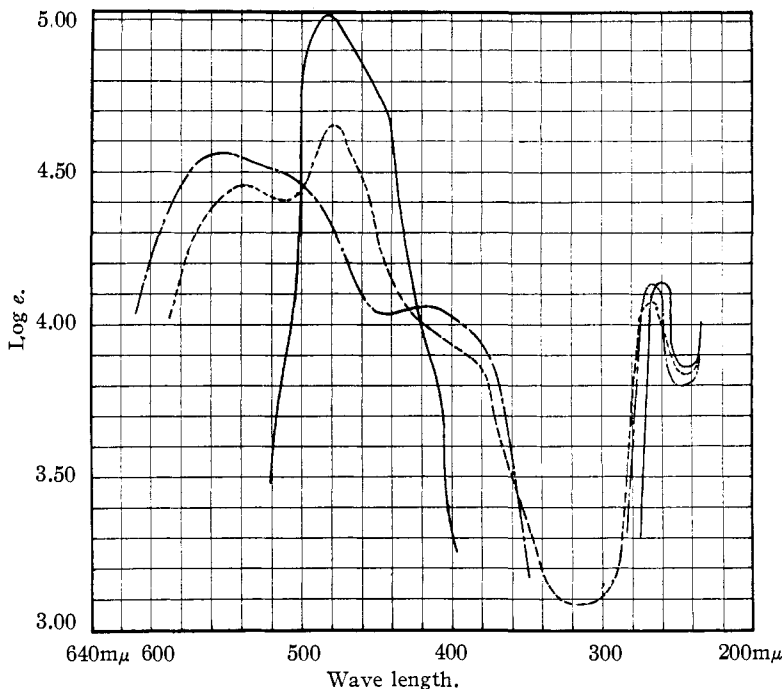


Fig. 3.—Salts of, ———, 4,4',4''-trimethoxytriphenyl carbinol; - - - - - , 2,4,2',4',4''-pentamethoxytriphenyl carbinol; - · - · , 2,4,2',4',2'',4''-hexamethoxytriphenyl carbinol.

This difference in constitution should produce a marked difference in the absorption spectra of the corresponding salts. We find, however, that there is no greater difference in the spectra of the 2, 2',2''-trimethoxy ion and the 2,4,2', 2'' ion than may be expected from the addition of merely a new substituent; the shape of the curves as a whole is identical in the two cases. Furthermore, the change, it will be noticed, is perfectly gradual when we pass through the series, 2,2',2'' - 2,4,2',2'' - 2,4,2',4',2'' - 2,4,2',4',4'' - 4,4',4'' -, although we pass here from a purely *ortho*- to a purely *para* substituted salt. Obviously, all of the salts, whether *p*- or *o*-methoxy, have fundamentally the same constitution.

The oxonium hypothesis, which postulates a differentiation between *o*- and *p*-methoxy salts, is not in harmony with the facts and, therefore, the quinocarbonium constitution is to be preferred here.

The contention of Dilthey<sup>20</sup> that the colored normal carbinol salts possess an essentially different constitution from those salts which require an extra equivalent of acid for color production, is not substantiated by the results of our experiments.

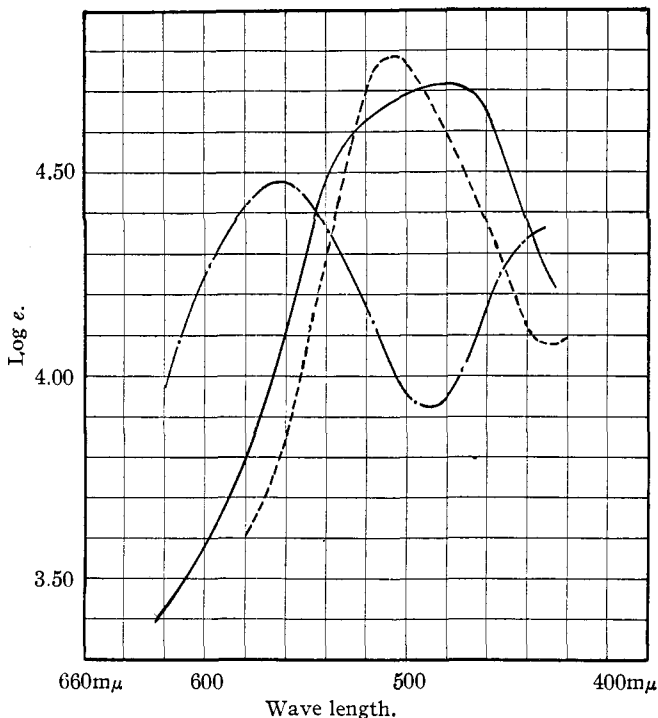


Fig. 4.—Salts of - - - - , 2,4',4''-trimethoxytriphenyl carbinol; - . - , 2,4,2',4'-tetramethoxytriphenyl carbinol; ———, 2,4,4',4''-tetramethoxytriphenyl carbinol.

The measurements in the visible part of the spectrum were made by means of a Hilger wave-length spectrometer and a Nutting photometer; the light source was a Pointolite lamp. The absorption in the ultra-violet region was determined by the method of Chr. Winther<sup>21</sup> and in his Laboratory in Copenhagen. Weighed amounts of the carbinols were dissolved in 50% acetone-water, containing enough acid to insure complete conversion of the carbinol into the corresponding salt. The absorption tube was 10 cm. long. For the calculation of the molecular extinction coeffi-

<sup>20</sup> Dilthey, *J. prakt. Chem.*, **109**, 276 (1925).

<sup>21</sup> Winther, *Z. wiss. Phot.*, **22**, 125 (1923).

cient  $\epsilon$ , the formula  $\epsilon = a/10c$  was used, where  $a$  is the measured extinction and  $c$  is the concentration of the salt per liter of solvent (Figs. 1, 2, 3, 4).

Our value for the maximum extinction for the 4,4',4'' ion in the visible light is considerably greater than that found by Brand.<sup>22</sup> His paper arrived a few days after we had plotted our curve. We are inclined to think that our value is probably correct because, on this value, the maximum for the 4,4',4''- becomes greater than for the 4,4'- disubstituted salt; Brand's attempt to explain his results to the contrary seems to us, therefore, to be unnecessary.

To Professor M. Gomberg, who suggested the problem, and in whose Laboratory this investigation was carried out, I wish to express my thanks for his interest throughout the progress of the work.

### Summary

1. A series of methoxy triaryl carbinols was prepared which contain, respectively, from three to seven methoxy groups, all in the *ortho* and *para* positions with respect to the central carbon atom. These carbinols readily form salts with acids. The basicity constants of the carbinols have been determined. It was found that the increase in the basic strength incurred with the increase in the number of methoxy groups in the carbinol, does not follow any one simple rule.

2. When more than three methoxy groups are present in the molecule, then even the normal salts of the carbinol are colored—and probably ionized—in the crystalline state. Salts of the most basic carbinols are only slightly hydrolyzed in water solution, and such carbinols may find application as indicators which are colored in acid and colorless in alkaline solutions.<sup>23</sup>

3. The absorption spectrum of the carbinol salts in the visible and ultraviolet region was determined. The spectra indicate that the salts cannot be oxonium salts, but that if considered as quinonoid in structure, they must be quinocarbonium salts.

4. In the case of the tri-*o*-anisyl carbinol, the corresponding free triaryl methyl radical was found to exist in solution almost entirely in the monomolecular state.

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<sup>22</sup> Brand, *J. prakt. Chem.*, **109**, 15 (1925).

<sup>23</sup> See Kolthoff, *THIS JOURNAL*, **49**, 1218 (1927).