1.6×10^{-2} at 25°.[11] By analogy with other systems, however, it is apparent that the constants for tetra-*n*-propyl- and tetraethylammonium bromide will be successively smaller than this value while those for pyridinium and tri-*n*-butylammonium bromides will be of the order of 10^{-4}. In chloroform the corresponding values of the constant for the two types of salts should be about 10^{-9} and 10^{-14}, respectively.

Since the effectiveness of the salts as catalysts increases with decreasing dissociation constant and dielectric constant, the catalysis probably is not due to free ions in solution. Also, it does not seem to result from an increase in the activity of the reactants since the "salting in" of the hydrogen bromide indicates a decrease in activity which is not likely to be outweighed by an increase in the activity of the ether.

The equilibrium of reaction 1 in which the ether and hydrogen bromide form a complex involves an increase in the dipole moment associated with the HBr and the presence of other ions and dipoles will tend to increase K and so accelerate the observed cleavage of the ether. However, it is doubtful if such an increase in K would account for more than a small part of the catalysis. Walvekar, *et al.*,[12] found no correlation between the values of K for different ethers and their rates of cleavage as measured by Ghaswalla and Donnan.[13] However, the very slow cleavage of diethyl ether in chloroform is markedly catalyzed by tetra-*n*-butylammonium bromide. Since diethyl ether certainly forms an oxonium complex much more readily than benzyl phenyl ether, it must be stage 2 of the reaction, cleavage of the complex, which is significantly affected by the catalyst.

It seems then that the catalysis is due to the ion pairs in solution accelerating the rate of cleavage of the C–O bond, a process which probably is closely related to the heterogeneous catalysis observed in carbon tetrachloride. The catalysis by ionic crystals is of such a general nature that it must be due primarily to the electrical inhomogeneity of the crystal surface but in solution specific ion effects must be of considerable importance because the catalytic activities of the salts do not seem to be related to the dipole moments. It seems probable therefore that the ion pair of the salt is closely associated with the transition state where it acts as a sort of bridge between the appearing and disappearing ions.

Finally it should be noted that our solubility measurements suggest that Walvekar, *et al.*, were dealing with heterogeneous systems and not solutions.

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(12) S. P. Walvekar, N. L. Phalnikar and B. V. Bhide, *J. Univ. Bombay*, **11A**, Pt. 5, 69 (1943).

(13) R. P. Ghaswalla and F. G. Donnan, *J. Chem. Soc.*, 134 (1936).

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Studies of Some Methyl-substituted Benzhydryl Carbonium Ions

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The behavior of the following methylbenzhydrols in 100% sulfuric acid has been studied: 2,2',3,4,5,6-hexamethylbenzhydrol, 2,2',4,6-tetramethylbenzhydrol and 3-methylbenzhydrol. The first two compounds gave fairly stable carbonium ions; the last gave a less stable and more reactive carbonium ion. The properties were investigated utilizing *i*-factors, ultraviolet and near-visible spectra, titration studies, and chemical studies, all using sulfuric acid. Evidence for the steric effect of three *ortho*-methyl groups and the "buttressing" effect of methyl groups in the 3- and 5-positions of the hexamethylbenzhydryl carbonium ion is discussed.

Introduction

It has been shown that many benzhydrols[1-4] ionize in 100% sulfuric acid to give stable carbonium ions. The ionization can be represented as

$$(C_6H_5)_2CHOH + 2H_2SO_4 \longrightarrow (C_6H_5)_2\overset{+}{C}H + 2HSO_4^- + H_3O^+ \quad (1)$$

Actually benzhydrol is rather unstable in sulfuric acid and undergoes rapid polymerization and sulfonation.[1] In the present work it was desired to find out the effect of certain methyl-substitutions on the formation and stabilization of benzhydryl carbonium ions. In addition, it had been noted that benzhydryl carbonium ions with two or less *ortho*-methyl substituents formed benzhydryl ethers, while those with four *ortho*-methyl substituents formed benzhydrols when poured into water. It was therefore of interest to ascertain the behavior of such ions when three *ortho*-methyl substituents were present.

Results

***i*-Factors.**—Table I gives the *i*-factors as extrapolated to zero time for the compounds studied. For the hexamethyl and tetramethyl compounds, solution was rapid, and the first *i*-factors could be determined within 10 or 15 minutes after addition of the benzhydrol to the sulfuric acid. The freezing points slowly changed as sulfonation took place. The *i*-factor of approximately 4.0 obtained by extrapolation to zero solution time is that expected for ionization according to eq. 1. For 3-methylbenzhydrol, however, solution in the sulfuric acid was very slow, for an insoluble polymer was formed which dissolved slowly as sulfonation occurred

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(1) C. M. Welch and H. A. Smith, THIS JOURNAL, **72**, 4748 (1950).

(2) M. S. Newman and N. C. Deno, *ibid.*, **73**, 3644 (1951).

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(4) H. A. Smith and R. G. Thompson, THIS JOURNAL, **77**, 1778 (1955).

TABLE I

CHARACTERISTICS OF BENZHYDROLS IN SULFURIC ACID

Benzhydrol	Color in sulfuric acid	Initial i-factors (extrapolated)	% Yield Methyl ether	M.p., °C.[a]	Methyl ether analyses,[b] %			
					Carbon		Hydrogen	
					Calcd.	Found	Calcd.	Found
2,2′,3,4,5,6-Hexamethyl	Red-brown	3.9	65[c]	69.5–70.1	85.05	85.60	9.28	9.12
2,2′,4,6-Tetramethyl-	Red-purple (iridescent)	3.9–4.0	64[d]	61.7–62.2	84.99	84.94	8.72	8.69
3-Methyl-	Red-brown (with polymer)	5.0–5.1[e]	0	(Polymer; no methyl ether isolated)				

[a] Melting points were taken on an aluminum melting point block and are uncorrected. [b] Analyses were done by Galbraith Microanalytical Laboratories, Knoxville, Tennessee. [c] Based on the crude compound. [d] Based on the purified product; the crude product was an oil and not weighed. [e] Obtained by extrapolation of the slow sulfonation curve.

After five or six hours, complete solution was achieved, and i-factors could be determined. Extrapolation of these slowly increasing values to zero solution time gave the figure of 5.0 recorded in Table I. Polymerization gives lower values and sulfonation gives larger values. The polymerization reaction can be represented for benzhydrol as

$$(n+2)(C_6H_5)_2CHOH + (n+3)H_2SO_4 \longrightarrow C_6H_5\underset{+}{C}HC_6H_4[CH(C_6H_5)C_6H_4]_n\ CH(C_6H_5)_2 + (n+2)H_3O^+ + (n+3)HSO_4^- \qquad (2)$$

The i-factor would be $(2n+6)/(n+2)$ for dissolved polymer if no sulfonation occurred. For dimerization, $n = 0$, and $i = 3.0$. For dimerization and monosulfonation of two rings the i-factor would be 5.0. After this sulfonation complete solution should be achieved, with further sulfonation occurring rather slowly. Higher polymers with more extensive sulfonation could also give i-factors around five.

Chemical Studies. Methyl Ether Preparations.—The preparation of alkyl ethers from benzhydryl carbonium ions, as described later, is not only an important synthetic method, but gives excellent confirmation that the sulfuric acid solutions actually contain carbonium ions. The ordinary acid-catalyzed etherification of a highly methylated carbinol would yield essentially no ether in the reaction times used.

The yields are given in Table I for the methyl ethers prepared. Both polymethylated-benzhydrols gave the methyl ethers. However only a polymeric material melting at 150–160° and a small amount melting at 200–210° could be obtained from the 3-methylbenzhydrol.

Reactions of Carbonium Ions with Water.—It has been demonstrated that four *ortho*-methyl groups on a benzhydryl carbonium ion are sufficient to prevent the formation of the bis ether.[1,4] Both hexamethyl- and tetramethylbenzhydrol have three *ortho*-methyl groups and therefore are sterically hindered so that formation of the bis ether is prevented. The original carbinol is obtained when the sulfuric acid solution is added to water.

A solution obtained by adding 0.25 g. of 2,2′,3,4,5,6-hexamethylbenzhydrol to 18 g. of 100% sulfuric acid and stirring for one minute was poured into an ice–water mixture. A 96% yield of the original carbinol (identified by mixed melting point) was obtained. The solution of the same benzhydrol which had stood for 21 hours in the process of cryoscopic determinations was also poured into an ice–water mixture to give a product which was completely water soluble and was not identified.

A solution obtained by the addition of 0.25 g. of 2,2′,4,6-tetramethylbenzhydrol to 18 g. of 100% sulfuric acid was stirred for one minute and then poured into an ice–water mixture to give a 100% yield of the original carbinol which was identified by mixed melting point. The solution from a 24-hr. cryoscopic run was poured into water to give an essentially clear solution.

Six solutions of 3-methylbenzhydrol in 100% sulfuric acid solution (generally in the ratio of 1 g. of benzhydrol per 100 g. of acid) were allowed to stand for times of from 10 seconds to 15 minutes and subsequently poured into ice–water mixtures. Yellow gums with different melting ranges between 130 and 250° were obtained. For one gum, some softening was noted at 50° which is close to the melting point of 3-methylbenzhydrol. The solution from a 27 hour cryoscopic run when poured into an ice–water mixture gave a clear solution. Yields of 46–90% for the gums indicate that rapid sulfonation must have occurred to give water-soluble products. This material probably gives a protonated species initially, but this undergoes a rapid reaction with undissolved benzhydrol to give a polymer which is not very soluble in sulfuric acid. Subsequently, the polymer is slowly sulfonated and is finally completely dissolved. No conditions were found where any bis ether was obtained when the sulfuric acid solution was poured into ice-water. Only polymeric materials and the original carbinol were found in the water-insoluble products. The yellow polymeric gums could be separated into two portions by extraction with ligroin, methanol or ethanol. A small fraction of insoluble, brittle material melted over the range of 180–250°, while the large fraction of soluble material melted between 130–160°.

Titrations to Form Carbonium Ions.—Titrations of the compounds dissolved in an inert solvent and water mixture using 96% sulfuric acid were made to obtain the relative stabilities from the minimum

TABLE II

TITRATION TO FORM CARBONIUM IONS WITH SULFURIC ACID

Compound	Wt. of cpd., g.	Min. % acid for visible color
2,2′,3,4,5,6-Hexamethylbenzhydrol	0.05	62.4
2,2′,4,6-Tetramethylbenzhydrol	.05	65.0
3-Methylbenzhydrol	.05	68.7
Benzhydrol	.05	71.2
Benzhydrol	.01	72.0
Benzhydrol	.25	65.6
2,2′,4,4′,6,6′-Hexamethylbenzhydrol	.05	47.7

percentage of sulfuric acid necessary for the permanent appearance of the characteristic carbonium ion color. The procedure has been described previously.[4] It was found in the present work that a suitable choice of concentration is needed to achieve satisfactory reproducibility. Reducing the concentration of the carbinol one-fifth did not affect the results appreciably whereas increasing the concentration fivefold gave very low results. Temperature control during titration is also necessary. Titration results are shown in Table II.

Experimental

***i*-Factors.**—The apparatus, technique and solvent for the cryoscopic measurements have been described previously.[1,5] Trial runs using triphenylcarbinol as the solute gave values of 4.02 and 3.96. Since the rates of possible side reactions, such as sulfonation, increase with increasing temperature, it is very important that the temperature of the solutions used remain as low as possible. The range actually encountered was 7–14°. Also the maintenance of a fairly constant temperature minimizes the amount of moist air drawn into the cryostat through the silicone-lubricated sleeve and stirring stem.

For the run with 3-methylbenzhydrol the polymer formed was very slow to dissolve, and the freezing point measurements were not commenced until the compound was dissolved. The cryostat, with a ground glass stopper, was fitted with an outside rubber stopper which was inserted into the container of a motor-driven shaker. Powdered solid carbon dioxide and crushed ice were added to the bottom of the shaker container to maintain a small amount of frozen solvent and to ensure that the temperature was held essentially constant. After five hours of shaking at 180–200 c.p.m., the Beckmann thermometer was inserted and the freezing run was begun.

Preparation of Methyl Ethers.—A 0.25-g. sample of carbinol was dissolved in approximately 18 g. of 100% sulfuric acid, and the solution was added immediately to 100 ml. of absolute methanol. This solution was then poured into 125 g. of an ice–water mixture and extracted quickly with two 100-ml. portions of ether. After drying the ether extracts over Drierite, evaporation of the ether gave the methyl ether which was then purified by recrystallization from ethanol.

Reactions of Carbonium Ions with Water.—A sample of carbinol was dissolved in 100% sulfuric acid. After a definite reaction time the solution was poured into an ice–water mixture and extracted with several portions of ether. After drying the ether extracts with solid sodium hydroxide pellets, evaporation of the ether gave the products. The solid was purified by recrystallization from ethanol. The polymers were extracted with methanol, ethanol or ligroin in the attempt to separate any bis ether which might have been formed. No bis ether was indicated in the products.

Titrations to Form Carbonium Ions.—The carbinol was dissolved in 10 ml. of carbon tetrachloride and this solution added to 50 ml. of water. This mixture was then titrated to the barely visible carbonium ion end-point with 96% sulfuric acid. The acid was added very slowly with constant stirring of the mixture which was maintained at approximately room temperature. From the volume of acid required, the percentage of acid necessary for visible carbonium ion formation in the aqueous layer was determined.

Spectra.—The ultraviolet and near-visible spectra were obtained using a Beckman DU spectrophotometer and quartz cells 1 cm. thick. A hydrogen discharge lamp was used for the range 250–350 mμ; a tungsten filament lamp was used for the range 350–600 mμ. For 3-methylbenzhydrol a solution in cyclohexane was prepared and added to sulfuric acid contained in a volumetric flask. The cyclohexane was evaporated under the vacuum produced with a water aspirator while the flask was swirled to effect extraction of the compound into the sulfuric acid layer. The flask was then filled to the mark with sulfuric acid. By this procedure solid polymer did not form and the spectrum could be measured. The reference solvent was treated exactly as just described. The spectra are shown in Fig. 1.

Preparation of Compounds. 2,2',3,4,5,6-Hexamethylbenzophenone.—This compound was prepared by the reaction of pentamethylbenzene and 2-methylbenzoyl chloride in the presence of anhydrous aluminum chloride; carbon disulfide was used as the solvent. After the addition of the acid chloride to the reaction mixture, the mixture was refluxed for two hours before hydrolysis. The ketone was purified by recrystallization from ethanol. A yield of 80.3% was obtained of white crystals very soluble in benzene; soluble in ether, ethanol and acetone; and slightly soluble in carbon disulfide. The compound melted at 155.5–155.7°.

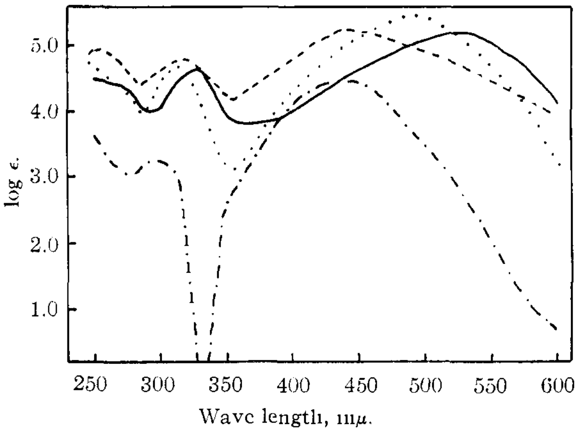

Fig. 1.—Absorption spectra of benzhydryl carbonium ions in 100% sulfuric acid: — · —, 3-methyl; . . . . , 2,2',4,6-tetramethyl; ———, 2,2',4,4',6,6'-hexamethyl; - - - -, 2,2',3,4,5,6-hexamethyl.

Anal. Calcd. for $C_{19}H_{22}O$: C, 85.73; H, 7.61. Found: C, 85.44; H, 7.58.

2,2',3,4,5,6-Hexamethylbenzhydrol.—The hexamethylbenzophenone was reduced for two hours using a fourfold excess of ethereal lithium aluminum hydride. After hydrolysis of the complex with 10% hydrochloric acid, and separation of the ether layer, evaporation gave a white solid in 99.3% yield which melted at 132.7–133.0°. Using excess lithium aluminum hydride to reduce a sterically hindered ketone evidently gives excellent yields of the carbinol. A less sterically hindered ketone, 4,4'-dimethylbenzophenone, gave an unsatisfactory yield of the carbinol but the bis ether was obtained in 70% yield.[4]

Anal. Calcd. for $C_{19}H_{24}O$: C, 84.95; H, 8.39. Found: C, 84.73; H, 8.19.

2,2',4,6-Tetramethylbenzophenone.—This ketone was prepared in 48% yield by the reaction of 2-methylbenzoyl chloride with mesitylene in the presence of anhydrous aluminum chloride; carbon disulfide was used as the solvent. After addition of the acid chloride to the reaction mixture, the mixture was refluxed for two hours, before hydrolysis. Evaporation of the carbon disulfide layer gave the ketone which was purified by recrystallizations from ethanol. The melting point was 111.9–112.2°. A melting point of 111° has been reported.[6]

Anal. Calcd. for $C_{17}H_{18}O$: C, 85.67; H, 8.32. Found: C, 85.44; H, 8.50.

2,2',4,6-Tetramethylbenzhydrol.—The tetramethylbenzophenone was reduced for two hours using a four-fold excess of ethereal lithium aluminum hydride. A white solid melting at 123.5–124.5° was obtained. The yield was 99.2%. This compound is sterically hindered also and is obtained in an excellent yield with no bis ether impurities.

Anal. Calcd. for $C_{17}H_{20}O$: C, 85.02; H, 9.01. Found: C, 85.01; H, 9.16.

3-Methylbenzhydrol.—This compound was prepared by the Grignard reaction using *m*-tolylmagnesium bromide and

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(5) L. P. Hammett and A. J. Deyrup, THIS JOURNAL, **55**, 1900 (1933); H. P. Treffers and L. P. Hammett, *ibid.*, **59**, 1708 (1937).

(6) J. Coops, W. Nauta, M. Ersting and A. Faber, *Rec. trav. chim.*, **59**, 1109 (1940).

benzaldehyde. The compound melted at 53.0-53.3° and was obtained in 80% yield. The literature gives melting points of 53°[7] and 61°.[8] In this work the higher melting compound could not be obtained.

Anal.[9] Calcd. for $C_{14}H_{14}O$: C, 84.82; H, 7.11. Found: C, 84.75; H, 7.29.

2,2',4,4',6,6'-Hexamethylbenzhydrol (Dimesitylcarbinol).—This material was prepared by "Method B" of Fuson and Jackson.[10] It melted at 150.6-151.4°.

Discussion

The ease of formation for a carbonium ion, determined from the concentration of ionizing solvent needed to give visibility, is considered to be a measure of its stability. The decreasing ease of formation for the benzhydryl carbonium ions discussed here as well as previously[1] is as follows: decamethyl- > 2,2',3,4,4',5,6,6'-octamethyl- > 2,2',4,4',6,6'-hexamethyl- > 2,3,4,4',5,6-hexamethyl- > 2,2',3,4,5,6-hexamethyl- > 4,4'-dimethyl- > 2,2',4,6-tetramethyl- > 2,3,4,5,6-pentamethyl- > 3-methyl- > benzhydryl carbonium ion. It is interesting to note that while, in general, stability increases with increasing methyl substitution, the accumulation of methyl groups is not so effective when all substituents are on one ring as when they are distributed over both rings.

Another interesting comparison involves compounds which should show the "buttressing effect."[11] According to Newman and Deno[12] resonance in the mesityldimethylcarbonium ion is sterically hindered by the introduction of methyl groups in the 3- and 5-positions to form the pentamethylphenyldimethylcarbonium ions. A similar effect should be found when methyl groups are introduced into the 3- and 5-positions of the 2,2',4,6-tetramethylbenzhydrylcarbonium ion and into the 3,5- and 3',5'-positions of the dimesitylcarbonium ion. These introductions should give for the relative ease of formation the following orders: 2,2',4,6-tetramethyl- > 2,2',3,4,5,6-hexamethyl- and 2,2',4,4',6,6'-hexamethyl- > 2,2',3,4,4',5,6,6'-octamethyl- > decamethylbenzhydryl carbonium ions. Exactly the reverse order is noted. One must conclude that the "buttressing" effect is not of considerable importance in these ions. It is possible that steric hindrance is not as great when methyl groups are substituted in the *ortho* positions of the benzhydryl carbonium ions as is found for similar substitution in the benzyldimethyl carbonium ions studied by Newman and Deno. However scale models indicate little difference.

When one studies the absorption spectra of these ions, the opposite conclusions concerning the "buttressing effect" can be drawn. The order of increasing extinction coefficient should be decamethyl- < 2,2',3,4,4',5,6,6'-octamethyl- < 2,2',4,4',6,6'-hexamethyl- and also 2,2',3,4,5,6-hexamethyl- < 2,2',4,6-tetramethyl. This is the observed order. One might also anticipate that λ_{max} would be shifted toward shorter wave lengths as resonance is hindered by the 3,5-methyl substituents, but the decamethylbenzhydryl carbonium ion has the largest rather than the smallest value.

Gold and Tye[3] attach theoretical significance to the intensity of the second absorption occurring at about 320–340 mμ as compared with the intensity of the principal band for several benzhydryl and α-substituted benzhydryl carbonium ions. They predict greater stability for smaller values of the intensity difference. The differences in the logarithms of the intensities between the principal and secondary bands for 2,2',4,4',6,6'-hexamethylbenzhydryl, 2,2',3,4,5,6-hexamethylbenzhydryl, tetramethylbenzhydryl, methylbenzhydryl and benzhydryl carbonium ions are 0.57, 0.64, 0.87, 1.18 and 1.32, respectively. This order of decreasing stability is in agreement with the titration results.

2,2',3,4,5,6-Hexamethylbenzhydrol and 2,2',4,6-tetramethylbenzhydrol gave fairly stable carbonium ions which did not polymerize. The solutions as initially formed reacted with water to give the original carbinol and with methanol to give the methyl ether. These results are explained best by the existence of carbonium ions. Carbonium ions in sulfuric acid when poured into water usually give the bis ether but evidently three as well as four[4] *ortho*-methyl groups prevent this reaction and permit regeneration of the original benzhydrol.

From the cryoscopic runs the rate of sulfonation of the hexamethylbenzhydryl carbonium ion appears to be somewhat faster than that of the tetramethylbenzhydryl carbonium ion. The factors that contribute to carbonium ion stability also increase the tendency for sulfonation as previously noted.[4] It appears that monosulfonation presumably in the unsubstituted ring takes place readily. Further sulfonation, if any, is very slow. Sulfonation of one ring for all molecules is also suggested from the fact that the contents of the cryostat when poured into an ice–water mixture after the cryoscopic run gave a clear solution indicating no unsulfonated material.

The "*i*" value of 5.0 listed in Table I for 3-methylbenzhydrol is believed to correspond to dimerization with monosulfonation in one ring of each unit in the dimer. Obviously the fast initial reaction was polymerization which caused insolubility until sulfonation had occurred. Formation of a trimer followed by sulfonation in each unit would give an "*i*" factor of 4.67. Further sulfonation is apparently quite slow, for the slope in the plot of freezing point *vs.* time after complete solution was less than 0.002° per hour.

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[7] P. J. Montagne and J. M. van Charante, *Rec. trav. chim.*, **31**, 348 (1912).

[8] W. D. Cohen, *ibid.*, **38**, 118 (1919).

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[11] G. W. Wheland, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 212.

[12] M. S. Newman and N. C. Deno, THIS JOURNAL, **73**, 3650 (1951).