organic layer was added to the ether solution, and the mixture was extracted twice with dilute hydrochloric acid. On neutralization of the acid layer with sodium hydroxide, an oil was obtained which was converted to the hydrochloride. This material amounted to 3.5 g.; m.p. 103–105°. The base which was obtained from this hydrochloride melted at 84–86°, and a mixture with the compound obtained by the action of lithium aluminum hydride on 3,3-diphenyl-5-methyl-2-furanoneimine showed no depression in m.p. The ether solution was concentrated, and the residue was distilled under reduced pressure. The fraction obtained at 153–158° and 3 mm. amounted to 4.0 g. The oil crystallized and was recrystallized several times from petroleum ether (b.p. 90–100°); m.p. 64.5–66°.

Anal. Calcd. for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 84.80; H, 7.97.

5-Dimethylamino-4,4-diphenyl-2-pentanol Hydrochloride.—A mixture of 16.7 g. of 5-amino-4,4-diphenyl-2-pentanol, 50 ml. of formalin and 50 ml. of formic acid was refluxed for seven hours. The solution was poured into an equal volume of water, the mixture was extracted with ether, and the organic layer was dried over sodium carbonate. The addition of alcoholic hydrogen chloride produced an oil that crystallized on standing. The yield of hydrochloride melting at 199–201° was 16.2 g. An analytical sample was recrystallized from ethanol–isopropyl ether solution; m.p. 200–202°.

Anal. Calcd. for $C_{19}H_{26}NOCl$: C, 71.34; H, 8.19; Cl, 11.08. Found: C, 71.40; H, 8.11; Cl, 11.10.

1-Dimethylamino-2,2-diphenyl-4-acetoxypentane.—A mixture of 4 g. of 5-dimethylamino-4,4-diphenyl-2-pentanol hydrochloride and 20 ml. of acetyl chloride was heated gently; the solid gradually dissolved and a clear solution resulted. The solution was then refluxed for a half hour. (After 10 minutes of refluxing a solid started to precipitate.) Isopropyl ether was added and the solid was collected. The yield was 4 g.; m.p. 200–202°. The melting point did not change on recrystallization from ethanol–isopropyl ether. A mixture of this compound with the hydrochloride of 5-dimethylamino-4,4-diphenyl-2-pentanol had a melting point of 182–187°.

Anal. Calcd. for $C_{21}H_{28}NO_2Cl$: Cl, 9.80. Found: Cl, 9.65.

Decomposition of Methiodide of II.—The methiodide was prepared in the usual manner and melted at 229–230°.

Anal. Calcd. for $C_{20}H_{28}NOI$: C, 56.47; H, 6.65. Found: C, 57.17; H, 6.83.

A pyrolytic decomposition of 4 g. was carried out in the usual way.[9] No appreciable amount of neutral material was obtained, but a considerable quantity of a base was formed which gave a hydrochloride melting point of 196–199°. This compound gave no depression when mixed with the hydrochloride of II.

Decomposition of the Quaternary Hydrochloride of II.—A mixture of 6.5 g. of the methiodide and 3 g. of silver oxide in aqueous alcohol was stirred vigorously until no iodide ion could be detected. The mixture was filtered and washed well with water and ethanol. The solution was concentrated at reduced pressure. The residue was transferred to a Claisen flask (with a minimum amount of ethanol) and pyrolyzed over a free flame. The distillate was crystallized from aqueous methanol, m.p. 45–46° (1.1 g.). A mixed melting point with 3,3-diphenyl-5-methyltetrahydrofuran[14] showed no depression.

Anal. Calcd. for $C_{17}H_{18}O$: C, 85.68; H, 7.61. Found: C, 85.75; H, 7.61.

Acknowledgment.—The authors wish to thank Mr. Carl Lukach for preparing the 3,3-diphenyl-5-methyl-2-tetrahydrofuranoneimine used in this work, and the Smith, Kline and French Laboratories for testing these compounds.

BETHLEHEM, PENNSYLVANIA

[CONTRIBUTION NO. 133 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TENNESSEE]

Preparation and Properties of Substituted Benzhydryl Carbonium Ions

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The behavior of the following benzhydrols and symmetrical benzhydryl ethers in 100% sulfuric acid has been studied: 4,4′-dichlorobenzhydrol, 2,3,4,5,6-pentamethylbenzhydrol, 2,2′,3,3′,4,4′,5,5′,6,6′-decamethylbenzhydrol, 2,2′,3,4,4′,5,6,6′-octamethylbenzhydrol, bis-(4,4′-dimethylbenzhydryl) ether and bis-(2,3,4,4′,5,6-hexamethylbenzhydryl) ether. All the compounds gave fairly stable carbonium ions, as indicated by their *i*-factors, colors, ultraviolet and near-visible spectra, and chemical properties, all observed in 100% sulfuric acid. With the exception of 4,4′-dichlorobenzhydrol, all the compounds were shown to undergo some sulfonation in addition to carbonium ion formation.

Introduction

It has been shown that many triphenylcarbinols[1,2] and certain benzhydrols[2–4] ionize in 100% sulfuric acid to give stable carbonium ions. The ionizations are generally represented as

$$(C_6H_5)_3COH + 2H_2SO_4 \longrightarrow (C_6H_5)_3C^+ + 2HSO_4^- + H_3O^+$$

$$(C_6H_5)_2CHOH + 2H_2SO_4 \longrightarrow (C_6H_5)_2CH^+ + 2HSO_4^- + H_3O^+$$

While triphenylcarbinols are quite stable in sulfuric acid, benzhydrol is not stable and undergoes rapid polymerization and sulfonation.

The carbonium ion studies have been extended to include several substituted benzhydrols and benzhydryl ethers. In this work it was desired to find out the influence of substituents, especially methyl groups, on the formation and stabilization of benzhydryl carbonium ions.

Results

***i*-Factors.**—Table I gives the *i*-factors for the various compounds studied. Referring to the previous equations, an *i*-factor of 4.0 should be observed for the simple carbonium ion formation in the benzhydrol series. Simple carbonium ion formation from a symmetrical benzhydryl ether would be expected to give an *i*-factor of 6.0. For example

$$(C_6H_5)_2CHOCH(C_6H_5)_2 + 3H_2SO_4 \longrightarrow 2(C_6H_5)_2CH^+ + 3HSO_4^- + H_3O^+$$

According to the above equation the same benzhydryl carbonium ion would be expected from either a symmetrical ether or its corresponding benzhydrol in sulfuric acid. In confirmation of this, the spectra of pentamethylbenzhydrol and bis-(pentamethylbenzhydryl) ether were found to be identical

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(1) H. A. Smith and R. J. Smith, THIS JOURNAL, **70**, 2401 (1948).

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

(3) H. A. Smith and C. M. Welch, *ibid.*, **72**, 4748 (1950).

(4) V. Gold and F. L. Tye, *J. Chem. Soc.*, 2172 (1952).

TABLE I

VAN'T HOFF FACTORS OF BENZHYDROLS AND BENZHYDRYL ETHERS IN 100% SULFURIC ACID

Compound	i[c]	t, min.	Approx. i at zero time (by extrapolation)
Pentamethylbenzhydrol	4.62	10	4.1–4.3
	4.82	22	
	5.09	170[a]	
Dichlorobenzhydrol[b]	3.99	32	
	4.10	720[a]	
Octamethylbenzhydrol	5.37	15	4.3–4.6
	5.54	30	
	6.00	45	
	7.58	120	
	8.84	405	
	9.83	1890	
Decamethylbenzhydrol	4.84	20	4.3–4.6
	4.96	60	
	5.07	75	
	5.15	90[a]	
Bis-(dimethylbenzhydryl) ether	6.61	15	6.4–6.5
	6.67	138	
	7.00	180[a]	
Bis-(hexamethylbenzhydryl) ether	6.97	20	6.4–6.6
	7.09	30	
	7.65	55	
	8.05	95	
	8.73	125	
	10.80	546	

[a] The i-factor did not change further for a 24-hour period. [b] Previously measured by Newman[2] as 4.01, constant after two hours. [c] The values for i were calculated using the value of the molal freezing point depression given by Hammett and Deyrup (THIS JOURNAL, 55, 1900 (1933)).

within the limit of experimental error; see Fig. 1. Further evidence is shown by the observation that sulfuric acid solutions of both symmetrical ethers studied gave simple methyl ethers when allowed to react with methanol.

In addition to carbonium ion formation the carbinols and ethers can undergo sulfonation. This causes an increase in the i-factor, depending upon the number of sulfonic acid groups introduced per carbonium ion. For the introduction of one sulfonic acid group in addition to carbonium ion formation, the reaction may be written

$$C_6H_5CHOHC_6H_5 + 4H_2SO_4 \longrightarrow HO_3SC_6H_4CH^+C_6H_5 + 3HSO_4^- + 2H_3O^+ \ (i = 6.0)$$

Further ionization of the sulfonic acid group may occur. This would lead to i-factors which are quite difficult to interpret. For example, the following reaction has been suggested as a possible route to the sulfones which are always formed in aromatic sulfonations.

$$C_6H_5SO_3H + 2H_2SO_4 \longrightarrow C_6H_5SO_2^+ + 2HSO_4^- + H_3O^+$$

As shown in Table I, extrapolation of the i-factors to zero time gives values in the neighborhood of 4.0 and 6.0 for the benzhydrols and benzhydryl ethers, respectively. These values correspond approximately to simple carbonium ion formation.

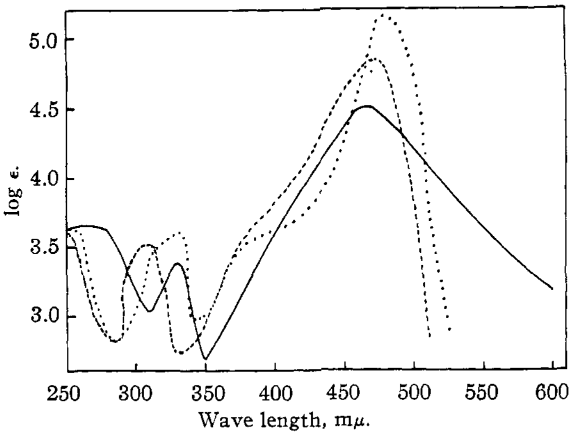

Fig. 1.—Absorption spectra of benzhydryl carbonium ions in 100% sulfuric acid: ——, pentamethyl (identical curve from ether or carbinol, 0.0122 g. and 0.009 g. per liter, respectively); ------, dimethyl (0.0150 g. of ether per liter, log ε for ethers based on one half molecular weight of ether); ...., dichloro (0.0133 g. of carbinol per liter).

Chemical Studies: Methyl Ether Preparations.—The preparation of alkyl ethers, from benzhydryl carbonium ions, as described later, serves not only as an important synthetic method, but as an excellent confirmation that the sulfuric acid solution actually contains carbonium ions. This is true since the ordinary acid-catalyzed etherification of a carbinol such as decamethylbenzhydrol would yield essentially no ether in the reaction times used.

Table II lists the ethers prepared, their melting points and analysis.

TABLE II

METHYL ETHERS OF SUBSTITUTED BENZHYDROLS

Methyl ether, benzhydryl	Yield, %	M.p., °C.[a]	Analyses,[b] % Carbon Calcd.	Found	Hydrogen Calcd.	Found
Pentamethyl-	73	78.0–78.2	85.02	85.29	9.01	8.68
Dichloro-	77.6	77.5–78	62.94	62.99	4.49	4.45
Octamethyl-	67.5	56–57	84.84	84.57	10.13	10.06
Decamethyl-	74.3	116–117	85.15	85.01	10.12	9.93
Dimethyl-	78.5	68–69	84.91	84.91	8.02	7.92
Hexamethyl-	68	72	85.05	84.48	9.28	9.13

[a] All melting points were taken on an aluminum melting point block; all melting points are uncorrected. [b] All analyses were done by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

Reactions of Carbonium Ions with Water.—It has been demonstrated that benzhydryl[3] and 4,4'-dichlorobenzhydryl[2] carbonium ions in sulfuric acid give symmetrical ethers when the solution is poured into water. It was therefore of interest to note the course of the reaction for other carbonium ions (see Table III).

Also shown in Table III are the percentages of isolated products for various reaction times. By reaction time is meant the time the solute remained in 100% sulfuric acid before addition of the solution to water. This information is of value since it indicates, as do the i-factors, that some sulfonation of the compounds occurred, giving water-soluble products.

Titrations to Form Carbonium Ions.—While 100% sulfuric acid provides optimum conditions for carbonium ion formation and existence, Newman[2] has pointed out that certain stabilized carbonium ions give their characteristic colors in aqueous solutions of as low as 30% sulfuric acid. There

TABLE III

PRODUCTS FROM REACTIONS OF CARBONIUM IONS WITH WATER

Reactant	Color in sulfuric acid	Reaction time	Product	Yield, %
Pentamethylbenzhydrol	Red-brown	5 min.	Ether[a]	80
Dichlorobenzhydrol	Red-orange	1 min.	Ether[c]	98
Dimesitylcarbinol	Red-purple	1 min.	Orig.[d,e] carbinol	93
Octamethylbenzhydrol	Violet	1 min.	Orig. carbinol	78
Octamethylbenzhydrol	Violet	1 hr.	Not identifiable[b]	
Octamethylbenzhydrol	Violet	21 hr.	Compl. water sol.	
Decamethylbenzhydrol	Violet	1 min.	Orig.[d] carbinol	97
Decamethylbenzhydrol	Violet	13 hr.	Not identifiable[b]	
Bis-(dimethylbenzhydryl) ether	Yellow-orange	1 min.	Ether[d]	90
Bis-(hexamethylbenzhydryl) ether	Wine	1 min.	Ether[d]	85

[a] Identified by Menzies molecular weight determination. *Anal.* Calcd. for $C_{36}H_{42}O$: C, 88.11; H, 8.63; mol. wt., 490.7. Found: C, 87.97; H, 8.57; mol. wt., 495. [b] A dark tarry mass was obtained from evaporation of the ether extracts; the solid could not be crystallized from ethanol or petroleum ether. [c] Identified by comparison of melting point with that previously reported by O. Grummitt and A. C. Buck, THIS JOURNAL, **67**, 693 (1945). [d] Identified by mixed-melting points with the known compounds. [e] This carbinol was studied by Fuson and Jackson[5] and Newman and Deno,[2] but the product formed when the carbonium ion solution is diluted with water was not reported. The studies reported above for this compound were made by Dr. C. M. Welch.

should be a direct relationship between the stability of carbonium ions and the concentration of ionizing solvent necessary for their formation. It was of interest to determine the minimum percentage of sulfuric acid necessary for the solutes to exhibit the colors characteristic of their carbonium ions. Titration results are shown in Table IV.

TABLE IV

TITRATION TO FORM BENZHYDRYL CARBONIUM IONS WITH 96% SULFURIC ACID

	Carbonium ion	Minimum percentage sulfuric acid for visible carbonium ion formation Run 1	Run 2	Average
1	Decamethylbenzhydryl	34.0	34.5	34.3
2	Octamethylbenzhydryl	39.2	39.8	39.5
3	Hexamethylbenzhydryl	59.4	59.1	59.3
4	Dimethylbenzhydryl	64.4	64.1	64.3
5	Pentamethylbenzhydryl	67.3	67.1	67.2
6	Dichlorobenzhydryl	68.6	69.1	68.9

Experimental

***i*-Factors.**—The apparatus, technique and solvent for the cryoscopic measurements have been described previously.[6] The only modification was that the solutions in the cryostat were kept at 7–11° throughout the period during which freezing point measurements were being made.

Since the rates of possible side reactions, such as sulfonation, are functions of temperature, it is important to know the temperature of the solution throughout the period of observation. The maintenance of a fairly constant temperature also minimized the possibility that some moist air might be sucked into the cell through several periods of cooling and warming. Trial runs using triphenylcarbinol as the solute gave values within 3% of 4.0. In addition, the *i*-factor of 4,4'-dichlorobenzhydrol was found to be within 2% of the value found by Newman and Deno[2] using a somewhat different type cryostat.

Preparation of Methyl Ethers.—A 0.25-g. sample of carbinol or symmetrical ether was dissolved in approximately 15 ml. of 100% sulfuric acid, and the solution was added immediately to 75 ml. of absolute methanol. This solution was then poured into 125 g. of an ice–water mixture and extracted quickly[7] with two 75-ml. portions of ether. After drying the ether extracts over Drierite, evaporation of the ether gave the solid methyl ether. The ether was purified by recrystallization from ethanol.

Reactions of Carbonium Ions with Water.—A 0.25-g. sample of carbinol or ether was dissolved in approximately 15 ml. of 100% sulfuric acid. After the specified time (see Table III), the solution was poured into 125 g. of an ice-water mixture and extracted with two 50-ml. portions of ether. After drying the ether extracts with solid sodium hydroxide pellets, evaporation of the ether gave the solid product. This solid was purified by recrystallization from ethanol, except when otherwise specified in Table III.

Titrations to Form Carbonium Ions.—A 0.05-g. sample of the carbinol or ether was dissolved in 10 ml. of carbon tetrachloride and this solution added to 50 ml. of water. This mixture was then titrated to the visible carbonium ion end point with 96% sulfuric acid. The sulfuric acid was added very slowly with constant stirring of the titration mixture. The mixture was kept in an ice-bath throughout the titration and its temperature maintained at approximately room temperature or below. 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 employed as the light source in the range 250–350 mμ; an ordinary tungsten filament was employed in the range 350–600 mμ.

Preparation of Compounds

4,4'-Dichlorobenzhydrol.—This compound was prepared by the lithium aluminum hydride reduction of the ketone as previously described.[2]

Pentamethylbenzhydrol.—This carbinol was prepared in 88% yield, m.p. 130°, by the reduction of the ketone for two hours with a fourfold excess of ethereal lithium aluminum hydride. A melting point of 124–125° has been reported.[8]

Anal. Calcd. for $C_{18}H_{22}O$: C, 84.99; H, 8.72. Found: C, 85.05; H, 8.70.

Decamethylbenzhydrol.—This carbinol was prepared in 20% yield, m.p. 189–190°, by a method completely analogous to that described by Fuson and Jackson[5] for the preparation of dimesitylcarbinol. The compound was purified by two recrystallizations from ethanol and one from petroleum ether.

Anal. Calcd. for $C_{23}H_{32}O$: C, 85.13; H, 9.94. Found: C, 85.27; H, 10.19.

Octamethylbenzophenone.—This ketone was prepared in 82% yield, m.p. 125.5–126°, by the reaction of mesitoyl chloride and pentamethylbenzene in the presence of anhydrous aluminum chloride; carbon disulfide was used as the solvent. After the dropwise addition of the acid chloride to the stirred reaction mixture, the mixture was refluxed for three hours on a steam-bath before hydrolysis. The ketone was purified by recrystallization from ethanol.

Anal. Calcd. for $C_{21}H_{26}O$: C, 85.66; H, 8.90. Found: C, 85.61; H, 8.89.

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(5) R. C. Fuson and H. L. Jackson, THIS JOURNAL, **72**, 351 (1950).

(6) C. M. Welch and H. A. Smith, *ibid.*, **72**, 4748 (1950).

(7) J. F. Norris and R. C. Young, *ibid.*, **52**, 753 (1950).

(8) H. Clement, *Ann. chim.*, **13**, 243 (1940).

Octamethylbenzhydrol.—Octamethylbenzophenone was reduced for three hours with a fourfold excess of ethereal lithium aluminum hydride. Upon hydrolysis of the organometallic complex with dilute sulfuric acid, a white solid separated from the ether layer and was collected by filtration. After recrystallization from ethanol, this solid melted at 155°. Evaporation of the ether layer gave a solid plus an amber colored oil. This solid, after recrystallization from ethanol, melted at 155°; it was assumed to be identical with the previous solid on the basis of a mixed melting point. The oil solidified upon stirring and, after recrystallization from ethanol, melted at 85.5°. Recrystallization of each solid from ethanol failed to change its melting point, indicating that both were probably pure compounds. Analyses were obtained for both solids.

Anal. For the lower-melting compound: C, 84.85; H, 9.67. For the higher-melting compound: C, 85.31; H, 9.89.

The theoretical carbon and hydrogen percentages for octamethylbenzhydrol are 85.08 and 9.52, respectively. Both solids gave identical colors and spectra in sulfuric acid. It is assumed that both solids are identical chemically, but that octamethylbenzhydrol can exist in two crystal forms. A mixture of the two solids melted at 83.5°, indicating that the lower melting form is probably the more stable.

As further evidence of the above assumption, sulfuric acid solutions of both solids were allowed to react with water and the products isolated. In several runs with each solid it was found either crystal form could be obtained. The conversion or non-conversion of crystal forms during this reaction may be a random process, or it may depend upon slight variations in reaction and purification conditions.

Hexamethylbenzophenone.—This ketone was prepared in 54% yield, m.p. 137–138°, by the reaction of toluyl chloride and pentamethylbenzene in the presence of anhydrous aluminum chloride; carbon disulfide was used as the solvent. After the dropwise addition of the acid chloride to the stirred reaction mixture, the mixture was refluxed on a steam-bath for two hours before hydrolysis. Evaporation of the carbon disulfide layer gave the ketone which was purified by two recrystallizations from ethanol.

Anal. Calcd. for $C_{19}H_{22}O$: C, 85.67; H, 8.33. Found: C, 85.53; H, 8.33.

Bis-(hexamethylbenzhydryl) Ether.—The ketone previously described was reduced for three hours with a fourfold excess of ethereal lithium aluminum hydride. After hydrolysis of the reaction mixture with dilute sulfuric acid, evaporation of the ether layer gave a white solid. This solid melted at 203–204° after several recrystallizations from ethanol. This high melting point as well as other evidence indicated that the expected carbinol had not been obtained even though an intense wine color was produced by the compound in sulfuric acid and the spectrum was analogous to that obtained for the benzhydryl carbonium ions. It was postulated that perhaps the symmetrical ether, bis-(hexamethylbenzhydryl) ether had been formed at some point during the lithium aluminum hydride reduction or subsequent hydrolysis. The analyses of the compound agree with the assumption of ether formation.

Anal. Calcd. for $C_{38}H_{46}O$: C, 87.97; H, 8.94. Found: C, 87.74, 87.77, 87.68; H, 9.11, 9.22, 8.91.

The theoretical percentages of carbon and hydrogen for hexamethylbenzhydrol are 85.02 and 9.01, respectively.

The molecular weight of the compound was determined by the Menzies method. Values of 503 and 540 were obtained, while the molecular weight of the assumed ether is 519.

One of the most conclusive pieces of evidence that the reduction of hexamethylbenzophenone gave an ether is the magnitude of the *i*-factors determined for the compound. The theoretical *i*-factor for the ionization of bis-(hexamethylbenzhydryl) ether is 6.0; an *i*-factor of approximately 6.4 was obtained upon extrapolation to zero time of a plot of *i*-factor *vs.* time.

The ether formation is probably due to a reaction subsequent to carbinol formation

$$R_2CHOH + H_3O^+ \longrightarrow R_2CH^+ + 2H_2O$$

$$H_2O + R_2CH^+ + R_2CHOH \longrightarrow R_2CHOCHR_2 + H_3O^+$$

The tendency for diphenylcarbinols to undergo this type reaction has been noted by many workers. The sulfuric acid used for the hydrolysis of the organometallic complex was probably sufficient to catalyze the reaction.

Bis-(dimethylbenzhydryl) Ether.—Dimethylbenzophenone was reduced for three hours with a fourfold excess of ethereal lithium aluminum hydride. After hydrolysis of the reaction mixture with dilute sulfuric acid, evaporation of the ether layer gave a white solid. This solid melted at 115° after several recrystallizations from ethanol. Since the melting point of this solid did not agree with the reported melting point of dimethylbenzhydrol,[9] it was suspected that ether formation again had occurred.

Anal. Calcd. for $C_{30}H_{30}O$: C, 88.62; H, 7.44. Found: C, 88.61; H, 7.59.

Molecular weight determinations gave values of 381 and 423. The calculated molecular weight of the ether is 407.

The yield of ether was 70% of theoretical.

Discussion

The ease with which a carbonium ion is formed is considered to be a good measure of its stability. The carbonium ions which are the hardest to form are usually the most reactive, and are, therefore, the least stable. The converse applies to the ions which are easiest to form. With respect to ease of formation the order of stability for the benzhydryl carbonium ions studied is: decamethyl > octamethyl > hexamethyl > dimethyl > pentamethyl > dichloro. This gradation in stability is based on the carbonium ion titrations.

The stability of a carbonium ion depends largely upon how well the central positive charge of the ion is neutralized or distributed over the molecule by resonance, hyperconjugation and the inductive effect. While all benzhydryl carbonium ions possess the same capacity for ordinary resonance, the resonance due to hyperconjugation increases with an increasing number of *ortho* and *para* methyl groups. With the exception of the pentamethylbenzhydryl carbonium ion, the order of stability above is in agreement with this fact; as the resonance possibilities due to hyperconjugation decrease, the stability decreases. The order of stability for the ions is also consistent with that which one would predict from a consideration of the inductive effect of methyl groups.

From a consideration of the hyperconjugation and inductive effects, it might seem that the pentamethylbenzhydryl carbonium ion should be more easily formed than the dimethylbenzhydryl ion. However spectral studies show that the steric inhibition to resonance is greater in the former ion; on this basis the pentamethylbenzhydryl ion would be less stable.

The role of ordinary steric hindrance (due to the mutual repulsion of large groups close to each other) in the stabilization of carbonium ions cannot be neglected. Gillespie and Leisten[10] have pointed out that the stability of the protonated carbinol $R_2CHOH_2^+$, which is probably the precursor to the carbonium ions, is less when there are large steric repulsions between the $-OH_2^+$ and other groups close to it. With the exception of the dimethylbenzhydryl ion, the stability order is compatible with one which would be predicted from a consideration of steric hindrance.

It has been observed that benzhydrol itself, in

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[9] J. P. Picard and C. W. Kearns, *Can. J. Research*, **28B**, 56 (1950).

[10] R. J. Gillespie and J. A. Leisten, *Quart. Revs.*, **VIII**, 40 (1954).

addition to undergoing sulfonation, polymerizes rapidly in sulfuric acid.[5,6] Any polymerization would be accompanied by the appearance of insoluble tarry masses in the sulfuric acid solutions. In addition, these solutions would be expected to exhibit i-factors lower than those predicted for carbonium ion formation. Since neither of these conditions was present in the series of compounds studied (including dimesitylcarbinol)[5] it appears that methyl substituents on benzhydryl carbonium ions make them less susceptible to polymerization. This is probably due to the fact that these substituted benzhydrols and benzhydryl ethers are more completely ionized in sulfuric acid than benzhydrol. Gillespie and Leisten[10] have pointed out that polymerization and sulfonation are partly due to a small amount of non-ionized solute.

Sulfonation was the principal reaction, other than carbonium ion formation, observed for the compounds studied. Both the change in the i-factors with time and the water-solubility of many of the reaction products are indicative of sulfonation. If sulfonation is assumed to be the only side reaction which made the observed i-factor values higher than those predicted for simple carbonium ion formation, then the relative resistances of the ions to sulfonation is as follows: dichlorobenzhydryl > dimethylbenzhydryl $\cong$ decamethylbenzhydryl $\cong$ pentamethylbenzhydryl > hexamethylbenzhydryl > octamethylbenzhydryl. It is therefore obvious that the resistance to sulfonation of a carbonium ion cannot be taken as a direct measure of its stability; the order of stability would be reversed almost completely from that previously given. Actually the same factors which contribute to carbonium ion stability increase the tendency for the molecule to sulfonate. The electron-donating tendencies of the methyl groups would be expected to neutralize the positive charge of the carbonium ion, thus increasing the stability of the ion and at the same time making sulfonation easier. As expected, sulfonation increased as the number of methyl groups on the ion increased. Only the decamethylbenzhydryl carbonium ion was inconsistent with this trend, for in that ion no positions are available for aromatic sulfonation. The resistance of the dichlorobenzhydryl ion to sulfonation was due probably to the electron-attracting tendencies of the chlorine atoms.

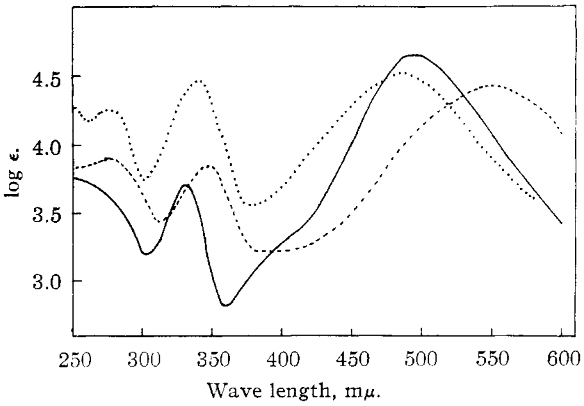

Fig. 2.—Absorption spectra of benzhydryl carbonium ions in 100% sulfuric acid: ——, hexamethyl (0.0133 g. of ether per liter); ------, decamethyl (0.0091 g. of carbinol per liter), ... , octamethyl (0.0170 g. of carbinol per liter).

It has been observed previously that triphenyl carbonium ions give triphenylcarbinol when allowed to react with water, while benzhydryl and dichlorobenzhydryl carbonium ions gave a symmetrical ether when treated similarly.[2,3] In the course of this research it was found that dimesityl-, octamethyl- and decamethylbenzhydryl carbonium ions reacted with water to give the corresponding carbinols, while the dimethyl-, dichloro-, pentamethyl- and hexamethylbenzhydryl ions gave ethers. A possible explanation for the difference in behavior is as follows: As a drop of the sulfuric acid solution of the carbonium ion hits the water, some of the ions react immediately to give the corresponding carbinol. The remaining carbonium ions then attack these carbinol molecules to form a symmetrical ether unless this attack is slowed by steric hindrance. If the effect of steric hindrance is large, all the carbonium ions will react with water before the slow etherification can occur. Of all the benzhydryl carbonium ions studied, only those with methyl groups in all four *ortho* positions gave carbinols when allowed to react with water. Apparently the carbonium ions cannot react with the methyl ether since no dibenzhydryl type ethers are formed when the carbonium ion solutions are poured into methanol.

Figures 1 and 2 show the ultraviolet and near-visible spectra for the carbonium ions studied. The spectra are analogous to the spectrum of the benzhydryl carbonium ion.[4] It was found, however, that the wave lengths of maximum absorption were shifted more than 100 mμ toward the visible. This is probably due to the increase in resonance possibilities due to the added substituents. As seen from the plots, the wave length of maximum absorption increases with the number of *ortho* and *para* methyl groups in the ion. The pentamethylbenzhydryl ion is not consistent with this trend, its wave length of maximum absorption being less than that for the dimethylbenzhydryl ion. As previously pointed out, the steric inhibition to resonance in the former ion is greater, which may account for its position.

Gold and Tye,[4] in a study of benzhydryl- and α-substituted benzhydryl carbonium ions, have attached theoretical significance to the intensity of the second absorption band occurring at about 320–340 mμ, as compared with the intensity of the principal band. Since the second band is considerably weaker in most benzhydryl carbonium ions, they suggest that it may be ascribed to a forbidden transition. The variations in intensity for this band may be associated with a varying degree of breakdown of a selection rule depending, for example, on the extent to which the benzene rings are tilted with respect to the plane of the central positive ion valencies. Thus, the transition may be more forbidden in the benzhydryl carbonium ion than in substituted benzhydryl ions where coplanarity is more difficult to achieve. The differences in intensities between the principal and second bonds for octamethyl-, decamethyl-, hexamethyl-, pentamethyl-, dimethyl- and dichlorobenzhydryl carbonium ions are 0.04, 0.57, 1.00, 1.13, 1.32 and 1.54, respectively. This is the approximate order which one would predict, assuming the explanation of Gold and Tye[4] to be correct.

It is of interest to note that the spectra of benzhydryl and triphenylcarbonium ions are quite similar.[2] Newman suggests that the steric inhibition to resonance is so great in triphenylcarbonium ions that only two or possibly one ring is involved in resonance. The greater stability of the triphenylcarbonium ions is not attributed to increased resonance, but to greater steric and inductive effects.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF VERMONT]

Oxidation of Hindered Phenols. III. The Rearrangement of the 2,6-Di-*t*-butyl-4-methylphenoxy Radical

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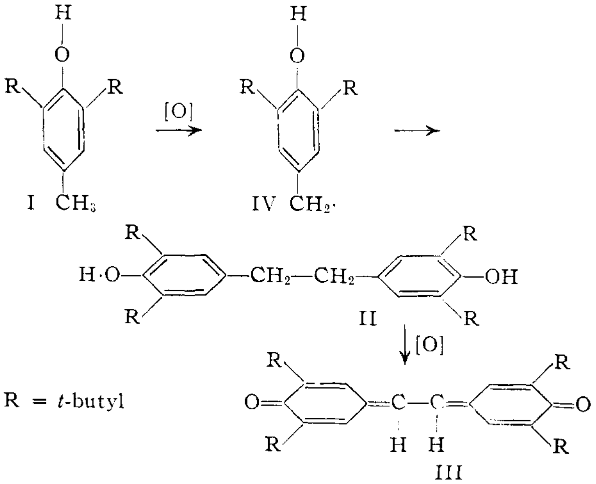
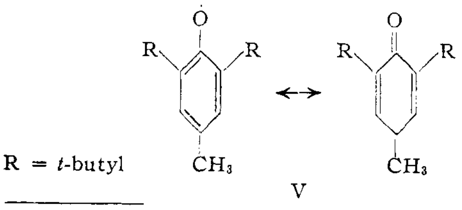
Evidence is presented for the rearrangement of the 2,6-di-*t*-butyl-4-methylphenoxy radical to give the 2,6-di-*t*-butylbenzyl radical. The implications of this rearrangement with respect to the stability of mononuclear phenoxy radicals and on the process of autoxidation inhibition are discussed. The rearrangement of 2,6-di-*t*-butyl-4-methyl-4-bromo-2,5-cyclohexadienone to yield 3,5-di-*t*-butyl-4-hydroxybenzyl bromide is reported.

The oxidation of 2,6-di-*t*-butyl-4-methylphenol (I) has been shown recently[1-3] to yield 1,2-bis-(3,5-di-*t*-butyl-4-hydroxyphenyl)-ethane (II). This compound is oxidized easily to 3,5,3′,5′-tetra-*t*-butylstilbene-4,4′-quinone (III). It has been suggested[1,2] that the dimerization occurs *via* the corresponding benzyl radical IV and that this radical is formed directly upon the oxidation of I.



There is, however, evidence suggesting that the oxidation of I may proceed through the isomeric phenoxy radical V.



Thus Campbell and Coppinger[4] have found that I reacts with *t*-butyl hydroperoxide to form 1-methyl-1-*t*-butylperoxy-3,5-di-*t*-butylcyclohexadienone-4. Cosgrove and Waters[5] obtained a similar result with 2,4,6-trimethylphenol and benzoyl peroxide. Finally, it has recently been shown[6] that the oxidation of 2,4,6-tri-*t*-butylphenol produces the corresponding phenoxy radical in excellent yields. Here, of course, the isomeric benzyl radical is an impossibility.

Since oxidative studies on I did not lead to any dimeric products suggestive of the phenoxy radical V, we were led to attempt its preparation by a different route. We have shown[6] that treatment of 2,4,6-tri-*t*-butyl-4-bromo-2,5-cyclohexadienone with alcoholic sodium iodide or with metallic mercury yields the 2,4,6-tri-*t*-butylphenoxy radical. It therefore was expected that similar treatment of 2,6-di-*t*-butyl-4-methyl-4-bromo-2,5-cyclohexadienone[7] (VI) would produce the corresponding phenoxy radical V and that the final product would be a dimer of this radical. When this reaction was performed, the main product was the substituted ethane II derived from the benzyl radical. In addition, I and III were formed. These latter products can best be explained by the oxidation of II by the benzyl radical

Quantitative measurements of the ratio of I to III confirm the stoichiometry indicated above. It therefore appears that the phenoxy radical V readily rearranges to the benzyl radical IV. This is not surprising in view of the advantage of obtaining the benzenoid configuration and the marked stability of the benzyl radical.

A number of cases of rearrangement of 4-bromocyclohexadienones have been reported. Thus, for example, Fries has shown that on gentle heating or long standing 2,5-dichloro-4-methyl-4-bromo-

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(3) G. R. Yohe, D. R. Hill, J. E. Dunbar and F. M. Scheidt, THIS JOURNAL, **75**, 2688 (1953).

(4) T. W. Campbell and G. M. Coppinger, *ibid.*, **74**, 1469 (1952).

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(6) C. D. Cook and R. C. Woodworth, THIS JOURNAL, **75**, 6242 (1953).

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