[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

Aryl Carbonium Ions in Sulfuric Acid[1]

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The *i*-factors in 100% sulfuric acid have been measured by the freezing point method for the series R_3COH where R equals *p*-tolyl, *p*-nitrophenyl, *p*-chlorophenyl, *p*-aminophenyl, *p*-dimethylaminophenyl, and in addition di-(*p*-dimethylaminophenyl)-phenylcarbinol. The spectra of the above carbinols in 100% acid has been examined in the region 200–600 mμ. Both types of experiments indicate that all three rings are probably not involved in the resonance interaction of the carbonium ions. On the basis of further *i*-factor and spectra measurements, it was concluded that the following mono- and diarylcarbinols gave comparatively stable carbonium ions in 100% sulfuric acid: α,α,2,4,6-pentamethylbenzyl alcohol, heptamethylbenzyl alcohol, di-*p*-dichlorophenylcarbinol, di-*p*-chlorophenylmethylcarbinol and dimesitylcarbinol. A moderately stable carbonium ion is obtained by dissolving α,2,4,6-tetramethylstyrene in sulfuric acid. Its absorption spectrum is recorded.

Although the cryoscopic determination of the Vant Hoff *i*-factor in 100% sulfuric acid provides convincing evidence for the existence of stable carbonium ions, triphenylcarbinol is the only alcohol that has been shown to yield a carbonium ion by this method.[2–5] Other physical evidence for the existence of the triphenylcarbonium ion has been obtained from conductance measurements[6,7] and spectral work.[7–10] In addition reaction mechanisms involving transitory carbonium ions have been frequently advanced.

We have studied the cryoscopic behavior of a number of mono-, di- and triarylcarbinols in sulfuric acid in order to obtain evidence for carbonium ions stable in this medium. In this study an *i*-factor of 4 suggests ionization to the carbonium ion according to equation 1. Additional evidence was obtained by isolation of reaction products and from spectral studies. As a result the following carbinols have been shown to yield stable carbonium ions in sulfuric acid: tri-*p*-tolyl- (I); tri-*o*-tolyl- (II); tri-*p*-aminophenyl- (III); tri-*p*-dimethylaminophenyl- (IV); di-(*p*-dimethylaminophenyl)-phenyl- (V); tri-*p*-chlorophenyl-; tri-*p*-nitrophenyl-; dimesityl-; di-*p*-chlorophenyl-; and di-(*p*-chlorophenyl)-methyl-. α,α,2,4,5-Pentamethyl- and heptamethyl-benzyl alcohols yielded carbonium ions of limited stability in sulfuric acid.

$$ROH + 2H_2SO_4 \rightleftharpoons R^+ + H_3O^+ + 2HSO_4^- \quad (1)$$

Determination of *i*-Factors

The procedure for measuring the *i*-factors was essentially that previously described.[11] The procedure described below gives more reproducible and accurate results than any other we have tried.

Approximately 100 g. of 100% sulfuric acid was weighed into the apparatus previously described.[11] Several drops of water were added until rough cooling curves showed that the freezing point of the sulfuric acid had dropped to about 9.5°. After standing at least 20 hours, several precise cooling curves were taken. Since the chief source of error was found to be non-equilibrium between crystals and mother liquor, a rapid stirring rate (at least three strokes per second with a conventional Beckman spiral stirrer) was necessary. The time of supercooling was kept at a constant value of eight minutes. Although this caused the solution to supercool about 1°, reproducibility was improved because smaller and more numerous crystals were formed when crystallization commenced. Crystallization was initiated by holding an open tube of powdered Dry Ice against the container and applying light pressure with a plunger. The time of contact with the Dry Ice was 20 seconds and during this time stirring was interrupted. With these precautions consecutive cooling curves usually agreed to within 0.003°.

The solute was added and the process of solution conducted between 9 and 11°. We wish to emphasize the necessity of measuring the *i*-factors as a function of time, and of holding the solution at a constant specified temperature between measurements. Since many of the *i*-factors change with time (*cf.* Table I), their interpretation is only possible when the variation of *i*-factor with time is known. Since most freezing point depressions were about 0.3°, the *i*-factors are precise to about 2%.

Preparation of Compounds

The following compounds were prepared by previously described methods: tri-*p*-nitrophenylcarbinol,[12] tri-*p*-aminophenylcarbinol (III),[13] tri-*p*-dimethylaminophenylcarbinol (IV),[14] di-(*p*-dimethylaminophenyl)-phenylcarbinol (V),[15] di-*p*-chlorophenylmethylcarbinol,[16] *p*-nitrobenzyl alcohol and acetate.[17]

Tri-*p*-tolylcarbinol.—Diethyl carbonate (5.9 g.) was added dropwise with stirring to 0.2 mole of *p*-tolylmagnesium bromide in 100 cc. of ether. After two days the mixture was treated with ammonium chloride solution and the ethereal extract washed with dilute alkali. The residue from steam distillation yielded 7.5 g. of crude carbinol, b.p. 200–240° at 1 mm. The pure carbinol, m.p. 93.4–94.0°,[18] was obtained in 25% yield by crystallization from 60–70° alkanes.

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[1] This work was made possible through the support of the Office of Naval Research.

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TABLE I

i-FACTORS OF CARBINOLS IN 100% SULFURIC ACID

Sample[a]	Time, hr.	Temp.,[b] °C.	i[c]
Tri *p*-tolylcarbinol			
1	5/6	10	4.02
2	1/2	10	3.92
1 + 2	20	25	4.04
3	2	10	4.05
	Best value		4.03
Tri-*o*-tolylcarbinol			
1	1/2	10	3.16
1	1	10	4.06
1	2	10	3.99
2	4	10	3.95
3	1/2	10	3.20
1 + 2 + 3	20	25	3.97
	Best final value		3.97
Tri-*p*-chlorophenylcarbinol[d]			3.99
Tri-*p*-nitrophenylcarbinol[d]			3.85
Tri-*p*-aminophenylcarbinol[d]			6.02
Tri-*p*-dimethylaminophenylcarbinol[e]			6.00
Di-(*p*-dimethylaminophenyl)-phenylcarbinol[e]			5.74
Tri-*p*-aminophenylmethane[d,f]			3.96
Di-*p*-chlorophenylcarbinol[d]			4.01
Heptamethylbenzyl alcohol			
1	2/3	10	4.60
1	5/4	10	5.26
1	11/6	10	5.78
1	7/3	10	6.03
	Extrap. to zero time		4.0
Pentamethylphenylcarbinol			
1	5/6	10	4.73
1	4	25	8.57
2	1/2	10	2.94
p-Nitrobenzyl alcohol[d]			3.19
Di-(*p*-chlorophenyl)-methylcarbinol			
1	3/4	10	3.75
1	2	25	3.83
1	15	25	4.57
2	1	10	4.02
3	3/4	25	4.25
Dimesitylcarbinol			
1	1/2	10	4.04
1	7/6	10	4.10
1	5/3	10	4.15
1	4	10	4.83
	Extrap. to zero time		4.00
α,α,2,4,6-Pentamethylbenzyl alcohol			
1	1/2	10	4.64
1	4/3	10	5.67
1	13/6	10	6.00
1	2	25	6.54
1	18	25	8.35
	Extrap. to zero time		4.0
α,2,4,6-Tetramethylstyrene			
1	1/2	10	2.71
1	5/3	10	3.91
1	20	25	5.84
2	1/10[g]	10	2.2
2	2/3	10	3.84
3	1/20[g]	10	2.1
	Extrap. to zero time		2.1
p-Nitrobenzyl acetate			
1	1/2	10	2.54
1	2	25	3.20
1	4	25	3.44
1	20	25	3.41
2	2/3	10	2.88
2	20	25	3.32
	Best final value		3.38

[a] The samples were added in successive portions to the same sample of solute except where a line is drawn to indicate that a new sample of solvent was used. The increments were such as to cause 0.3° to 0.5° depressions of the freezing point. [b] A temp. listed as 10° means processes of solution and freezing point measurement were conducted between 7° and 11°. A temp. listed as 25° means that the solution was allowed to stand at approximately 25° for the specified time and then cooled and the freezing point determined. [c] The values for *i* have been calculated from the formula of Hammett and Deyrup (ref. 5). Recently R. J. Gillespie, E. D. Hughes and C. K. Ingold (*J. Chem. Soc.*, 2473–2551 (1950)) have introduced a more exact formula, a new cryoscopic constant for sulfuric acid, and the symbol γ to replace Hammett and Deyrup's *i*-factor. Calculation of our data by the newer formula leads to values of *i* (G., H. and I's γ) which are generally 1–2% higher. The difference in the two calculated values is almost completely due to the new value for the cryoscopic constant. Sufficient data to calculate γ is available from the authors. [d] The *i*-factors measured after $^1/_2$ hr. did not change on continued standing at 10 or 25°. [e] The *i*-factors measured after $^1/_2$ hr. did not change on continued standing at 10°. [f] Samples were dried *in vacuo* with and without sulfuric acid in the chamber, and at various time intervals. The *i*-factors were identical with all samples. This was an important point since small amounts of water in the sample would have invalidated the arguments presented to show that triply charged ions behave ideally in 100% sulfuric acid in the concentration range studied. [g] The solute was added at the bottom of the supercooling curve. Since the solute was a liquid, mixing was complete within a minute.

Tri-*o*-tolylcarbinol.—Diethyl carbonate (5.9 g.) was added to 0.2 mole of *o*-tolylmagnesium bromide in 100 cc. of ether. The solution was refluxed for four hours after addition of 50 cc. of benzene and removal of the ether. The mixture was treated with ammonium chloride solution and the ethereal extract washed with dilute alkali. The residue from steam distillation yielded 5.5 g., b.p. 195–200° at 2 mm. The pure carbinol, m.p. 102.5–103.0°,[19] was obtained in 4% yield by several crystallizations from 60–70° alkanes. This carbinol was also prepared by the previously published method.[19]

Tri-*p*-chlorophenylcarbinol.—4,4'-Dichlorobenzophenone (12 g.) was added to 0.073 mole of *p*-chlorophenylmagnesium bromide in 150 cc. of ether. After standing overnight, 50 cc. of benzene was added, the ether distilled off, and the solution refluxed for one hour. Ammonium chloride solution was added and the ethereal extract washed with dilute alkali. The solvents were removed and the residue dissolved in 50 cc. of alcohol. A considerable amount of white solid was removed by filtration. The crude carbinol from the filtrate, b.p. 250–260° at 1 mm., was triturated with 30–40° alkanes to give a 19% yield of the pure carbinol, m.p. 93.5–94.0°.[20]

Di-*p*-chlorophenylcarbinol.—This carbinol was prepared in 81% yield, m.p. 92.4–93.6°,[21] by reduction of the ketone for one hour with excess ethereal lithium aluminum hydride.

Dimesitylcarbinol.—A 93% yield of carbinol m.p. 145–159°,[22] was obtained by reducing dimesityl ketone[23] for 12 hours with excess ethereal lithium aluminum hydride.

Mesitylcarbinol.—A 53% yield of the carbinol, m.p. 86.0–87.8°,[24] was obtained by 12-hour reduction of mesitoic acid with excess ethereal lithium aluminum hydride.

Pentamethylphenylcarbinol.—Pentamethylbenzoic acid[25] (0.01 mole) was converted to the acid chloride by means of thionyl chloride and pyridine. After reduction of the acid chloride for 20 hours with excess ethereal lithium aluminum hydride, water was added and the ethereal extract washed with dilute alkali. A 95% yield of colorless crystals of pentamethylphenylcarbinol, m.p. 159.6–160.4°, was obtained by removing the ether and washing the crystals with alkanes. Clement[25] previously reported a m.p. of 136–137° for this carbinol prepared from pentamethylphenylmagnesium bromide and formaldehyde.

Anal.[26] Calcd. for $C_{12}H_{18}O$: C, 80.9; H, 10.1. Found: C, 81.1; H, 10.3.

When the reduction was carried out on the free acid, the yield of carbinol was only 8% probably because of the insolubility of the salts of the acid.

α,α,2,4,6-Pentamethylbenzyl Alcohol.—This carbinol has been reported,[27] but no yield or method of isolation was given. Acetone (2.5 moles) was added over 30 minutes to a stirred, refluxing solution of mesitylmagnesium bromide prepared from 2 moles of bromomesitylene in 1 l. of ether. After ten minutes ammonium chloride solution was added until all the precipitated salts had dissolved. The ethereal extract was washed with dilute alkali and steam distilled. A 69% yield of mesitylene was obtained by fractionation of the organic layer of the distillate. The residue from steam distillation partially crystallized on cooling. The crystals were filtered from the adhering oil with the aid of a rubber dam. By recrystallization from 60–70° alkanes 33.4 g. (9.4%), m.p. 106–111°, of α,α,2,4,6-pentamethylbenzyl alcohol was obtained. The m.p. could be raised to 112.0–112.6° by recrystallization from methanol but the recovery was poor. The residual oils were distilled after dehydrating by heating to 120° with iodine. The fraction boiling at 190–212° (the b.p. of the olefin is 206°) weighed 8.4 g. However, if this fraction was the olefin, it was very impure. Conducting the addition of acetone to the Grignard reagent at 0 or 80° did not appreciably change the yield.

α,2,4,6-Tetramethylstyrene.—A mixture of 4.5 g. of α,α,-2,4,6-pentamethylbenzyl alcohol and 50 cc. of concentrated

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hydrochloric acid was shaken for 30 minutes. The yield of olefin was 3.82 g. (95%), b.p. 203–206.5°. α,2,4,6-Tetramethylstyrene does not decolorize permanganate in aqueous acetone but does decolorize bromine in carbon tetrachloride rapidly with evolution of hydrogen bromide. The olefin was redistilled and a middle cut (205–206°) was taken for analysis.

Anal. Calcd. for $C_{12}H_{16}$: C, 89.9; H, 10.1. Found: C, 90.3; H, 10.1.

Heptamethylbenzyl Alcohol.—Pentamethylphenylmagnesium bromide was prepared from 49 g. of pentamethylbromobenzene (0.216 mole) using an equimolar amount of ethyl bromide as a promoter as previously described.[25] Excess acetone was added over 30 minutes to the stirred, refluxing Grignard reagent in ether. After stirring for an additional 30 minutes, ammonium chloride solution was added to dissolve all precipitated salts. The ethereal extract was washed with dilute alkali, dried over potassium carbonate and distilled. The fraction boiling at 55–70° (1 mm.) was principally pentamethylbenzene. The fraction boiling at 100–130° (1 mm.), wt. 10 g., was submitted to numerous alternate crystallizations from 60–70° alkanes and ethanol–water. The yield of heptamethylbenzyl alcohol, m.p. 92–94° with previous sintering at 71°, was 0.42 g. (1%). The same yield was obtained when the acetone was added to the Grignard reagent at −80°. The purest samples of the carbinol were shiny white flakes or elongated prisms melting at 90.4–91.8° (samples with higher melting points contained a high-melting impurity, probably pentamethylbromobenzene).

Anal. Calcd. for $C_{14}H_{22}O$: C, 81.5; H, 10.8. Found: C, 81.8; H, 11.0.

The above procedure is similar to that of Clement[25,28] with the exception that Clement conducted the fractional crystallization without the preliminary distillation. However, the products isolated by us were quite different than those reported by Clement. He claimed to have isolated the carbinol, m.p. 136–137°, and the olefin, m.p. 122°, in a combined yield of 25%. In our experience, samples melting in these ranges could be separated by further crystallizations into pentamethylbromobenzene and lower melting material.

Tri-*p*-aminophenylmethane.[29]—Purification of the triamine was facilitated by dissolving in dilute acetic acid and treating the solution with charcoal (Darco G-60) in the cold. The filtrate is treated with ammonia immediately and the pale yellow precipitate collected and crystallized from alcohol to yield pure white shiny flakes, m.p. 204.5–206.0°. The triamine slowly becomes pink on exposure to air.

Isolation of Reaction Products

The isolation experiments were conducted by holding a 2–5% solution of the compound in 100% sulfuric acid for the time specified in Tables II and III, followed by pouring the solutions onto ice with stirring. The non-sulfonated organic products were isolated from ethereal extracts.

Isolation experiments were not performed on the following compounds; however, the colors of their solutions in sulfuric acid are given in parentheses followed by the reason for not reporting isolation experiments: di-(*p*-dimethylaminophenyl)-phenylcarbinol (V) (orange-brown), spectral work has indicated that the carbonium ion is stable[8]; tri-*p*-aminophenylcarbinol (IV) (orange-brown) and tri-*p*-dimethylaminophenylcarbinol (IV) (orange-brown) gave stable *i*-factors and were presumed to be stable; dimesitylcarbinol (permanganate colored), satisfactory isolation experiments have been reported[30]; *p*-nitrobenzyl alcohol (orange-yellow) and its acetate (light-yellow), after two hours in sulfuric acid at 10° about half could be recovered as an uncrystallizable oil; and pentamethylphenylcarbinol (black), extensive decomposition was evident by color and sulfur dioxide evolution.

TABLE II

PRODUCTS FROM THE TREATMENT OF COMPOUNDS WITH 100% SULFURIC ACID AT 25°

Compound	Color of[a] H_2SO_4 soln.	Time, hr.	Product	Yield, %
Tri-*p*-tolylcarbinol	Orange-red	2	Carbinol	100
Tri-*o*-tolylcarbinol	Orange-red	2	Carbinol	100
Tri-*p*-chlorophenylcarbinol	Cherry-red	16	Carbinol	65[b]
Tri-*p*-nitrophenylcarbinol	Orange-red	15	Carbinol	100
Di-*p*-chlorophenylcarbinol	Brown-red	3/4	Ether	64[c]
Di-*p*-chlorophenylmethylcarbinol	Cherry-red[d]	3/4	Olefin	53[e]
Tri-*p*-aminophenylmethane	Colorless	15	Triamine	74

[a] In all cases the color was completely discharged on adding the solution to ice. [b] This product, m.p. 94–96°, was obtained by crystallization of the crude product (m.p. 71–88°, 86% yield) from alkanes. [c] This product was bis-(4,4′-dichlorodiphenylmethyl) ether, m.p. 125.8–127° (highest m.p. observed, 128.2–128.8°) (O. Grummitt and A. C. Buck, THIS JOURNAL, **67**, 693 (1945)), and was obtained by crystallization of the crude product (m.p. 107–120°, 97% yield) from alcohol. [d] The solution was orange-brown when first formed at 10°, but soon changed to cherry-red. [e] This product was 1,1-bis-(4,4′-dichlorodiphenyl)-ethylene, m.p. 84.6–85.8°,[16] and was obtained from the crude product (m.p. 78–84°, 83% yield) by crystallization from alcohol.

TABLE III

PRODUCTS FROM REACTION OF RR'_2COH WITH 100% SULFURIC ACID AT 10° FOR TEN MINUTES

R	R′	Color of solution	Yield of products, % Olefin	Olefin dimer	Sulfonation[a]
Phenyl	Methyl	Pale yellow	0	67	33
o-Tolyl	Methyl	Yellow	13	42	45
Mesityl	Methyl	Deep orange-red	70	0	30
Phenyl	Butyl	Dark red-brown	25	5	70
Phenyl	*i*-Propyl	Dark red-brown	3	9	88

[a] This water soluble material was not isolated; the yield was calculated by difference.

Methyl Ether of Tri-*o*-tolylcarbinol.—A solution of 2.67 g. of tri-*o*-tolylcarbinol in 15 cc. of 100% sulfuric acid was allowed to stand one hour and then poured into a well-stirred solution of 25 g. of sodium methoxide in 300 cc. of methanol. The temperature was held below −20° by means of Dry Ice–acetone-bath. The mixture was stirred at 25° until all traces of red color had disappeared (30 min.) and then diluted with four volumes of water. The slow disappearance of the red color may be due to mechanical trapping of the carbonium ion solution in the sodium sulfate precipitate. The tri-*o*-tolylcarbinyl methyl ether, m.p. 102–106°, wt. 1.72 g. (62%), was obtained by crystallization of the ethereal extract from 60–70° alkanes. The highest m.p. obtained was 108.2–108.6°.

Anal.[26] Calcd. for $C_{23}H_{24}O$: C, 87.4; H, 7.6. Found: C, 87.4; H, 7.7.

Discussion

The stability and spectra of the triphenylcarbonium ion and its *p*-amino derivatives, the triarylmethane dyes, have been attributed to the large number of contributing resonance structures which are possible when all three rings are coplanar.[31–34]

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(31) C. R. Bury, THIS JOURNAL, **57**, 2115 (1935).

(32) (a) G. N. Lewis and M. Calvin, *Chem. Revs.*, **25**, 308 (1939); (b) G. N. Lewis, T. T. Magel and D. Lipkin, THIS JOURNAL, **64**, 1774 (1942).

(33) G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry, Prentice-Hall, Inc., New York, N. Y., 1944, pp. 176–182.

(34) G. W. Wheland, "The Theory of Resonance and Its Application to Organic Chemistry, John Wiley and Sons, Inc., New York, N. Y., 1944, pp. 152–154, 184.

Lewis[32b] later modified his views regarding the coplanarity of the crystal violet ion (tri-*p*-dimethylaminophenylcarbonium ion). A study of the spectrum of this ion in various solvents indicated that at least two isomeric forms were present. This isomerism was attributed to sterically different nonplanar forms, since isomeric forms were incompatible with a planar model for this ion.

Szwarc[35] considered coplanar resonance forms involving all three rings to be impossible for the triphenylmethyl free radical due to repulsion between ortho-hydrogens. He thus concluded that resonance stabilization for the triphenylmethyl free radical should be comparable to that for the benzyl free radical. Since similar steric considerations probably hold for triarylcarbonium ions, we believe that the question of the geometry of such ions needs further attention.

We have studied the cryoscopic behavior and absorption spectra of a number of mono-, di- and triarylcarbinols in sulfuric acid and believe that the results are best understood in terms of the principle that resonance interaction involves at most two rings. We believe that only one ring is involved but further work will be necessary before this contention can be conclusively demonstrated.

The cryoscopic data (*cf.* Table I) was obtained by methods similar to those used previously[5,11] but improved by several refinements in technique. In this work, an *i*-factor of four is interpreted to involve carbonium ion formation according to equation 1, with the additional requirement that the starting carbinol could be isolated from the reaction mixture after diluting with water.

Triarylcarbinols.—Tri-*p*-tolylcarbinol and tri-*o*-tolylcarbinol gave *i*-factors of four (Table I) and were recovered unchanged on dilution (Table II). These facts indicate ionization to the carbonium ion according to equation 1. These two carbinols were studied to determine whether the *o*-methyl groups would prevent formation of the carbonium ion or decrease its stability. Qualitative tests showed that solutions of both carbinols in methanol developed the orange-red colors characteristic of the carbonium ion spectra when only 5% (by weight) sulfuric acid was added. In contrast methanol solutions of triphenylcarbinol required addition of nearly an equal weight of sulfuric acid before development of color. Thus, the two tri-tolylcarbinols have about the same tendency to ionize in acid media and this tendency is considerably greater than that of triphenylcarbinol. Both carbinols developed color with 40% sulfuric acid but not with 30% acid.

The similarities in the tendency of the two tritolylcarbinols to ionize suggested that the *o*-methyl groups were not inhibiting any of the resonance stabilization of the tri-*o*-tolylcarbonium ion. This result is consistent with the assumption that one or two rings are involved in resonance interaction, rather than all three. Further experiments are required to distinguish between the two possibilities. All three rings could be involved only if resonance interaction did not require completely coplanarity. The question as to the relation between resonance interaction and deviation from coplanarity is as yet unanswered.

Of all the carbinols that yielded carbonium ions, only tri-*o*-tolylcarbinol failed to give an *i*-factor of four at the first measurement. The fact that the *i*-factor of four was not reached until one hour indicates a relatively slow rate of carbonium ion formation. Formation of the carbonium ion from tri-*o*-tolylcarbinol was further confirmed by pouring a sulfuric acid solution of the carbinol into a cold solution of excess sodium methoxide in methanol. The methyl ether was isolated in 62% yield. The usual technique for preparing these methyl ethers, which consists of pouring the sulfuric acid solution of the carbonium ion into excess methanol[36] was unsuccessful. Although the 100% sulfuric acid was diluted with methanol down to a 10% solution, the deep orange-red color of the tri-*o*-tolylcarbonium ion was quite intense. When water was added, complete decolorization took place, and the starting carbinol was recovered quantitatively.

Tri-*p*-aminophenylcarbinol (III), tri-*p*-dimethylaminophenylcarbinol (IV) and di-(*p*-dimethylaminophenyl)-phenylcarbinol (V), the carbinols of pararosaniline, crystal violet and malachite green, respectively, gave *i*-factors of 6.02, 6.0 and 5.74. Before these results could be interpreted, it was necessary to demonstrate that triply charged cations behave ideally in 100% sulfuric acid. For this purpose tri-*p*-aminophenylmethane was chosen. Since an *i*-factor of four was obtained, ionization according to equation 2 was indicated. This provides evidence that the solution was ideal in behavior.

$$(p\text{-}H_2NC_6H_4)_3CH + 3H_2SO_4 \rightleftarrows (p\text{-}H_3N^+C_6H_4)_3CH + 3HSO_4^- \quad (2)$$

The *i*-factors for III and IV can now be interpreted to mean that ionization occurs as shown in equation 3.

$$\begin{array}{l} (p\text{-}R_2NC_6H_4)_3C\text{—}OH + 4H_2SO_4 \rightleftarrows \\ \quad \text{III, } R = H \\ \quad \text{IV, } R = CH_3 \\ \qquad\qquad (p\text{-}R_2NC_6H_4)(p\text{-}R_2HN^+C_6H_4)_2C^+ + \\ \qquad\qquad\qquad H_3O^+ + 4HSO_4^- \quad (3) \end{array}$$

On the basis of absorption spectra, Branch and Tolbert[8] concluded that the carbonium ion of V accepted two protons in 96% sulfuric acid. This conclusion would demand an *i*-factor of 6 whereas we found it to be only 5.74, a fact for which we have no adequate explanation. The absorption spectra of V in 100% sulfuric acid proved no different from that in 96% acid.

With the carbinols, III and IV, the fact that one *p*-amino grouping was never protonated is consistent with the view that only one of the rings is involved in resonance interactions. In fact, a remarkable difference in base strength appears to exist between the third amino group in VIA as compared with the first two. It has been reported that 68% of the carbonium ions from crystal violet add two protons in 1 *N* hydrochloric acid.[37] Our *i*-factor results show that when the acidity is in-

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[35] M. Szwarc, Discussions of the Faraday Society No. 2, 42 (1947).

[36] H. A. Smith and R. J. Smith, THIS JOURNAL, **70**, 2400 (1948).

[37] E. Q. Adams and L. Rosenstein, THIS JOURNAL, **36**, 1452 (1914).

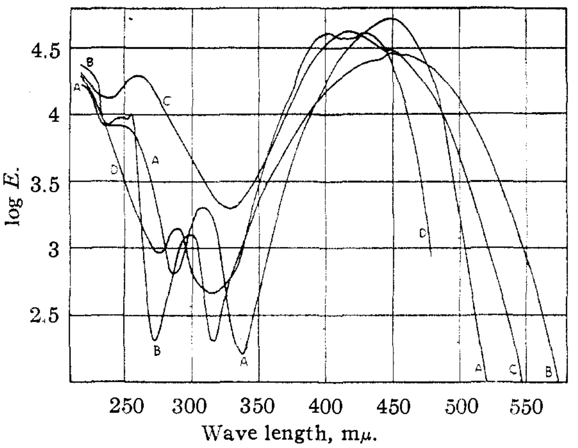


Fig. 1.—A, Tri-*p*-tolylcarbinol: B, tri-*o*-tolycarbinol; C, tri-*p*-nitrophenylcarbinol; D, triphenylcarbinol. The solvent was 100% sulfuric acid and the spectra were recorded by Mrs. Arlene Brooks on a Beckman ultraviolet spectrophotometer. $\log E = \frac{\log I_0/I}{\text{molarity} \times \text{cell width}}$. With triphenylcarbinol (D) a nearly identical spectrum has been previously reported in 93% sulfuric acid (W. R. Orndorff, R. C. Gibbs, S. A. McNulty and C. V. Shapiro, THIS JOURNAL, 49, 1551 (1927)).

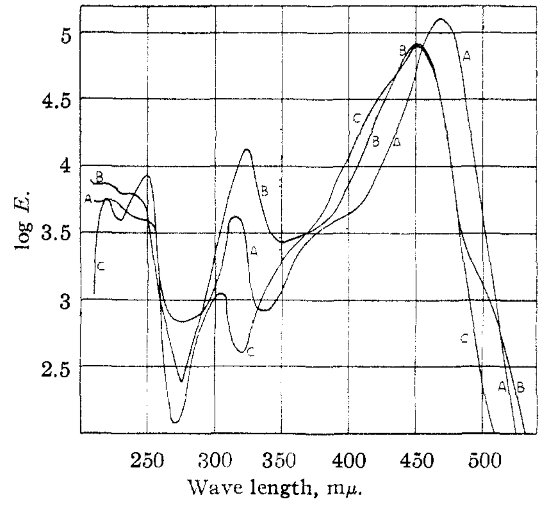
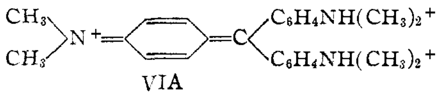
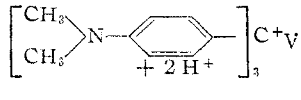


Fig. 2.—The following spectra were taken in 100% sulfuric acid: A, di-*p*-chlorophenylcarbinol; B, di-*p*-chlorophenylmethylcarbinol; C, tri-*p*-chlorophenylcarbinol.

creased about ten H_0 units in going to 100% sulfuric acid, the third amino group has still failed to accept a proton. Apparently, the quinonoid structures, such as VIA, which were used by the early investigators in this field, more accurately represent the electron distribution in the ion than does the usual carbonium ion formulation, VIB. This formula for VIA indicates that the third amino group in the ion is structurally different from the other two.



VIA



VI B

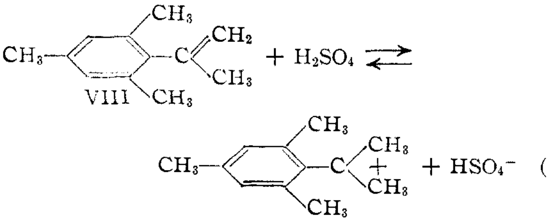
Triarylcarbinols with electron-withdrawing substituents were studied to see if carbonium ion formation could be prevented in 100% acid. Although tri-*p*-nitrophenylcarbinol has less tendency to ionize in acid than triphenylcarbinol,[38] it gave an *i*-factor of 4 indicating carbonium ion formation as previously reported.[38] Tri-*p*-chlorophenylcarbinol also yielded a carbonium ion. Thus, none of the electron-withdrawing substituents (–Cl, –NO$_2$, –NH(CH$_3$)$_2^+$ and –NH$_3^+$) prevented carbonium ion formation in 100% acid.

Diarylcarbinols.—The *i*-factors of four for di-*p*-chlorophenylcarbinol and di-*p*-chlorophenylmethylcarbinol indicated formation of carbonium ions (Eq. 1). The diarylmethylcarbinol yielded the olefin, 1,1-bis-(*p*-chlorophenyl)-ethylene, on dilution with water. The result provides the first quantitative evidence for a carbonium ion stable to 100% sulfuric acid in which the carbonium ion contains only two aromatic rings.[39]

Di-*p*-chlorophenylcarbinol yielded the symmetrical ether on adding the sulfuric acid solution to water. The *i*-factor and color of the acid solution were incompatible with ether formation so that the ether must have formed in the process of dilution.

On the basis of chemical evidence dimesitylcarbinol has recently been reported to yield a carbonium ion in sulfuric acid.[30] Our measurements of the *i*-factor gave a value of 4.04 after 30 minutes which confirms the formation of the carbonium ion. Diphenylcarbinol and diphenylmethylcarbinol were found to sulfonate rapidly in 100% acid and were not further investigated.

Monoarylcarbinols.—Among the several monoarylcarbinols investigated, only α,α,2,4,6-pentamethylbenzyl alcohol (VII) and heptamethylbenzyl alcohol gave carbonium ions stable enough to be studied. Even in these two cases, the *i*-factor increased with time because of sulfonation, so that the values of about four characteristic for carbonium ion formation were only obtained by extrapolation to zero time. The mesityldimethylcarbonium ion, which was formed from VII, was also formed when α,2,4,6-tetramethylstyrene (VIII) was dissolved in 100% sulfuric acid. In this case, extrapolation of the *i*-factor to zero time gave values around two, which is that expected for carbonium ion formation from an olefin (equation 5). With VII, after ten



(5)

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[38] F. H. Westheimer and M. S. Kharasch, *ibid.*, **68**, 1871 (1946).

[39] There is already evidence for a diarylmethylcarbonium ion in the literature. C. S. Schoepfle and J. D. Ryan (THIS JOURNAL, **54**, 3687 (1932)) found that 1,1-diphenylethyl chloride and triphenylchloromethane dissolved in ethylene chloride plus stannic chloride to give colored solutions having similar spectra. We believe that they were measuring the spectra of the diphenylmethyl- and triphenylmethylcarbonium ions. Welch and Smith, *ibid.*, **72**, 4748 (1950), and Fuson and Jackson, ref. 30, have provided qualitative evidence for the existence of other diaryl carbonium ions of moderate stability in sulfuric acid.

minutes at 10°, a 70% yield of the olefin (VIII) was obtained on dilution with water, and after 90 minutes at 10°, the yield of VIII was 30% (Table III). With both experiments, the product was composed solely of VIII and water-soluble sulfonation products. The spectrum of VIII in 100% sulfuric acid was measured at various time intervals and the results extrapolated to zero time (Fig. 3). The intensity of the principal maximum at 360 mμ decreased 30% in ten minutes at 10°. Thus, the decrease in intensity of this maximum parallels the decrease in yield of VIII that can be recovered from sulfuric acid solutions of the carbinol (VII) under comparable conditions. These results are interpreted to mean that 70% of the carbinol in the form of the carbonium ion was present when the first *i*-factor reading was made, and over 30% when the second reading was made. Thus, we feel that the extrapolations of the *i*-factor measurements to zero time are fairly sound.

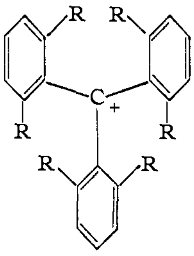
An interesting gradation in behavior was found in three carbinols of the formula $R(CH_3)_2COH$ in which R represents phenyl, *o*-tolyl and mesityl. The results are recorded in Table III. Evidently, one of the reasons for the stability of the mesityldimethylcarbonium ion is its inability to dimerize and cyclize to an *ortho* position to give a substituted indane.[40] With *o*-tolyl and phenyldimethylcarbinol, a second phase was present in the sulfuric acid solution immediately after adding the carbinol. For this reason *i*-factors were not measured.

Our results with other monoarylcarbinols were inconclusive in respect to carbonium ion formation. Benzyl alcohol has long been known to yield white insoluble polymers in 100% sulfuric acid. The transient orange-red colors that are observed in this reaction are perhaps due to carbonium ions but this would be difficult to prove. *p*-Chlorobenzyl alcohol gave red polymers in sulfuric acid. *p*-Nitrobenzyl alcohol and its acetate gave stable *i*-factors around 3.3.

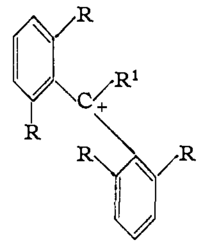
It was thought that the substitution of methyl groups into the aryl ring might inhibit sulfonation and self-alkylation and thus yield compounds which would have unchanging *i*-factors. However, 2,4,6-trimethylbenzyl alcohol and 2,3,4,5,6-pentamethylbenzyl alcohol were both rapidly attacked by sulfuric acid to give water-soluble products. Oxidation also took place as evidenced by the evolution of sulfur dioxide.

Spectra.—In the following discussion, reference will be made to two types of steric inhibition of resonance. In type A, repulsion between the R groups in IX and X prevents coplanarity of the aryl rings and thus restricts resonance interaction to one or two aryl rings. In type B, repulsion between R and R′ in XI inhibits the planar structure shown so that resonance interaction even with a single aryl ring is inhibited.

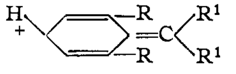
Evidence that steric inhibition of resonance of Type A is practically complete in triarylcarbonium ions was found in comparing the spectra of the tri-*p*-chlorophenyl- (XII), di-*p*-chlorophenylmethyl- (XIII) and di-*p*-chlorophenyl- (XIV) carbonium ions (Fig. 2). Although XIII contains one less aryl ring than XII, the position and intensity of the principal maximum at 450 mμ was unchanged.



IX



X



XI

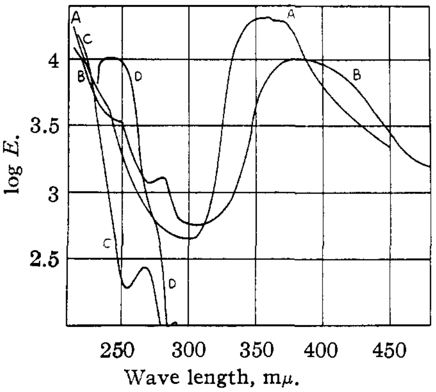


Fig. 3.—A, α,2,4,6-tetramethylstyrene in 96% sulfuric acid (an identical spectrum between 300 and 500 mμ was obtained in 100% sulfuric acid); B, heptamethylbenzyl alcohol in 96% sulfuric acid; C, α,2,4,6-tetramethylstyrene in 95% ethanol; and D, α-methylstyrene in ethanol (Mme. Ramart-Lucas, *Compt. rend.*, **198**, 267 (1934)). With the compounds giving curves A and B, which are the absorption at zero time, the compounds were dissolved in the sulfuric acid at 0° and the absorption intensities recorded as a function of time. Curves A and B were then obtained by a small extrapolation.

This may be interpreted in at least two ways: that the third aryl ring contributes little to the resonance due to steric inhibition of resonance (Type A); that each of the three rings in XII makes an equivalent contribution to the resonance, but that this contribution is small because of the angle of twist of the rings.[41] If the second alternative were adopted it would require that the similarity in the absorption band of XII and XIII at 450 mμ be explained by having the two rings in XIII more nearly coplanar than the three rings in XII and thus make up for their smaller number by increased resonance interaction. Since this explanation would require a rather fortuitous combination of effects, we prefer the former explanation.[42] It is also possible that

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(40) E. Bergmann, H. Taubadel and H. Weiss, *Ber.*, **64**, 1493 (1931).

(41) See H. B. Klevens and J. R. Platt, THIS JOURNAL, **71**, 1714 (1949), for a discussion of the effect of angle of twist on absorption spectra of *o*-substituted N-dimethylanilines. The steric inhibition of resonance discussed by these authors is of our type B.

(42) The spectra of triphenylchloromethane and 1,1-diphenylethyl chloride in stannic chloride–ethylene dichloride are reported to be remarkably similar.[39] Since these spectra are probably due to the triphenyl- and diphenylmethylcarbonium ions the result parallels ours with the chlorinated analogs.

only one ring is of importance in the resonance but we have as yet been unable to produce a sufficiently stable monoaryl carbonium ion free of other objectionable characteristics (especially steric hindrance of type B, see below) to test this possibility.

With the di-*p*-chlorophenylcarbonium ion (XIV), the principal maximum at 480 mμ was actually more intense and shifted toward longer wave lengths compared to the principal maximum of XII and XIII. Although this shift may be attributed to the smaller steric requirements of the α-hydrogen in XIV, as compared with the aryl group in XII and the methyl group in XIII, it is not certain whether the diminution in steric inhibition of resonance is of type A or B. An alternative explanation, that the change in inductive effect produced when the *p*-chlorophenyl group is replaced by hydrogen is responsible for this shift, is unlikely in view of the marked shift toward higher wave lengths shown by the tri-*p*-chlorophenylcarbonium ion (XII) as compared with the triphenylcarbonium ion (Fig. 1).

Further support for the idea that at least one of the three rings has a function different from that of the others in the over-all picture of the ions under discussion was obtained from a consideration of the spectra of the tri-*p*-tolyl- (XV) and the tri-*o*-tolyl- (XVI) carbonium ions (Fig. 1). A small steric inhibition of resonance may be indicated in XVI by the decrease in intensity of absorption at the principal maximum. However, this is partially compensated by the shift of this maximum from 450 mμ in XV to 460 mμ in XVI. We prefer to explain these small differences in terms of a small resonance inhibition of type B. If all three rings in XV had been involved in resonance interaction, a large shift in spectra would be anticipated in XVI due to the large resonance inhibition of type A caused by the *o*-methyl groups. Actually, only small differences were observed between the spectra of XV and XVI.

The above interpretations would require monoarylcarbonium ions to absorb similarly to comparably substituted di- and triarylcarbonium ions. Although both monoarylcarbonium ions studied, mesityldimethyl- and pentamethylphenyldimethyl-, absorbed strongly in the visible region of the spectrum, the actual maximum for their broad absorption band was 60 to 80 mμ less than for the tritolylcarbonium ions. We attribute this difference to steric inhibition of resonance of type B. Thus, repulsion between the two α-methyl and the two *o*-methyl groups inhibit coplanar configurations such as XI for the ion. This conclusion is supported by the complete steric inhibition of resonance in the sterically similar α,2,4,6-tetramethylstyrene. Thus, the spectrum of this olefin in ethanol resembles that of benzene rather than that of α-methylstyrene (Fig. 3). The spectrum of the pentamethylphenyldimethylcarbonium ion showed decreased intensity of absorption at the principal maximum as compared with the mesityldimethylcarbonium ion. This is another example of increased steric inhibition of resonance due to the "buttressing" effect of groups on the 3- and 5-position of aryl rings.[43]

Compared to the tritolylcarbonium ions, the principal maximum in the spectrum of the tri-*p*-nitrophenylcarbonium ion showed a small shift to shorter wave lengths while that of the tri-*p*-chlorophenylcarbonium ion showed a small shift to longer wave lengths (Figs. 1 and 2). The small shift with the nitro derivative is consistent with the frequent observation[44] that inductive effects have only a small effect on absorption spectra of aryl derivatives. The effect of the *p*-chloro substituent is to contribute structures with the positive charge on the chlorine.[43]

The shift in spectra of basically substituted triarylcarbonium ions (such as the ions from III, IV and V) in the series Ar_3C^+, $Ar_3C^+{\cdot}H^+$ to $Ar_3C^+{\cdot}2H^+$ is much greater and has usually been interpreted as due to the decrease in contributing resonance forms.[8,31,34] We feel that additional experimental work on compounds of this type with *ortho* substituents must be carried out before further discussion is warranted.

Finally, it should be pointed out that it is at present difficult in many cases to predict the effect on a spectral maximum due to a change in the steric inhibition of resonance. This shift will depend on the relative contributions of the inhibited forms to both the ground and excited states.[45] Since our arguments rest chiefly on the presence or absence of a shift and not on its direction, they are probably independent of the above consideration.

COLUMBUS 10, OHIO RECEIVED NOVEMBER 3, 1950

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

[44] W. H. Rodebush, *Chem. Revs.*, **41**, 317 (1947).

[45] L. G. S. Brooker, F. L. White, R. H. Sprague, S. G. Dent and G. van Zandt, *ibid.*, **41**, 325 (1947); L. N. Ferguson, *ibid.*, **43**, 385 (1948).