The *p*-bromophenacyl derivative of α-XIII was obtained as flat, elongated, very small blades after 3 recrystallizations from aqueous ethanol; m.p. 157–158°.

Anal. Calcd. for $C_{24}H_{23}BrO_4$: C, 63.31; H, 5.09. Found: C, 63.28; H, 4.93.

Concentration of the filtrates from the purification of α-XIII gave 1.39 g. (32%) of a solid which after 3 recrystallizations from aqueous ethanol had m.p. 171–172°. This material proved to be a eutectic mixture of α-XIII and β-XIII (*cf.* below for further details) containing about 2 parts of α-isomer to 1 part of β-isomer. On this basis it can be estimated that the hydrolysis product contained about 8 parts of α-XIII to one part of β-XIII.

Treatment of 0.1 g. of α-XIII with ethereal diazomethane gave 0.08 g. (76%) of the starting ester, α-XII; m.p. 156–156.5°.

The β-isomer of 6,7,7a,8,9,10,11,11a-octahydro-7-carboxy-5-keto-5H-dibenzo[a,c]cycloheptatriene (β-XIII) could not be obtained in pure form. When a 0.60-g. sample of β-XII (m.p. 96–97°) was saponified under the conditions described above, 0.55 g. (97%) of an acidic product was obtained, m.p. 170–172°. After 4 recrystallizations from aqueous ethanol the m.p. was 171–172.5°. That this product was actually a mixture of α-XIII and β-XIII was indicated by remethylation experiments. When this material was treated with ethereal diazomethane the resulting product could be separated, by fractional crystallization, into 48–64% of α-XII (m.p. 156–157°) and 38–27% of β-XII (m.p. 96–97°). On this basis it can be estimated that the hydrolysis product contained about 2 parts of α-XIII to one part of β-XIII.

α-Isomer of 1,2,3,4,4a,9a,10,10a-Octahydro-9-ketophenanthryl-10-acetic Acid (α-XI). (a) **By Saponification of α-X.**—A 0.59-g. sample of α-X (m.p. 75–76°) was saponified under the conditions described above to yield, after one recrystallization from aqueous ethanol, 0.49 g. (88%) of α-XI, m.p. 173–175°. Further recrystallization gave colorless, very small needles, m.p. 175–176.5°; $\lambda_{\max}^{EtOH}$ (ϵ) 248 mμ (11,600), 289 mμ (1800).

Anal. Calcd. for $C_{16}H_{18}O_3$: C, 74.39; H, 7.02. Found: C, 74.42; H, 6.75.

The S-benzylthiouronium salt of α-XI was obtained as colorless, thick, square blades after several recrystallizations from ethanol; m.p. 157–157.5°.

Anal. Calcd. for $C_{24}H_{28}N_2O_3S$: C, 67.89; H, 6.65. Found: C, 67.91; H, 6.62.

Remethylation of α-XI with ethereal diazomethane gave a quantitative yield of α-X, m.p. 75–76°.

(b) **By Saponification of β-X.**—A 0.500-g. sample of β-VI (m.p. 127–128°) was treated with an excess of anhydrous hydrogen fluoride and the mixture allowed to stand at room temperature for 2 hr. The neutral product, isolated in the usual fashion, consisted of an oil which did not crystallize and which is presumed to be β-X (*cf.* below). Saponification of the neutral fraction yielded, after recrystallization of the product, 0.220 g. (50%) of colorless needles of m.p. 173–175° which showed no depression in m.p. when admixed with a sample of α-XI prepared as described above.

β-Isomer of 1,2,3,4,4a,9a,10,10a-Octahydro-9-ketophenanthryl-10-acetic Acid (β-XI).—When a 8.16-g. sample of β-VI was cyclized with aluminum bromide in carbon disulfide as described previously[2] a 91% yield of β-XII was obtained. In addition, 4% of an acidic fraction was isolated and shown to be β-XI. It was purified by recrystallization from aqueous ethanol and obtained as a white powder, m.p. 129–131°; $\lambda_{\max}^{EtOH}$ (ϵ) 249 mμ (12,100), 290 mμ (1800).

Anal. Calcd. for $C_{16}H_{18}O_3$: C, 74.39; H, 7.02. Found: C, 74.12; H, 6.94.

The methyl ester of β-XI (β-X) was obtained by treatment of the acid described above with diazomethane. The product was obtained, after evaporative distillation at 80–90° (0.001 mm.), as an oil; $\lambda_{\max}^{EtOH}$ (ϵ) 249 mμ (10,900), 290 (1800).

Anal. Calcd. for $C_{17}H_{20}O_3$: C, 74.97; H, 7.40. Found: C, 75.08; H, 7.66.

Ultraviolet Spectra.—The spectra of compounds α-X, β-X, α-XII, β-XII and XIV have been reported previously,[2,15] the data having been obtained on a Beckman model DU spectrophotometer. The spectra of these compounds were redetermined for purposes of a closer comparison using, in the present instance, a Cary recording spectrophotometer. The data agreed very closely with those in the literature, and the differences in extinction coefficient between α-XII, β-XII and XIV appear to be real and reproducible. As a further check, the areas under the curves for the 250 mμ bands were compared (oscillator strengths) and were found to fall in exactly the same order as the extinction coefficients.

ST. LOUIS, MO.

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

The Properties of Some Phenylpyridylmethanols in Sulfuric Acid Solution

BY HILTON A. SMITH AND C. W. HOLLEY

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The behavior of the following compounds in 100% sulfuric acid has been studied: phenyl-2-pyridylmethanol, phenyl-4-pyridylmethanol, diphenyl-2-pyridylmethanol and diphenyl-4-pyridylmethanol. The first two compounds show no evidence of carbonium ion formation, but appear to give polymers. The last two compounds form fairly stable carbonium ions. The properties of the solutions were investigated, utilizing *i*-factors, ultraviolet and near-visible spectra, titration studies and chemical reaction with methanol and water. The influence of the protonation of the pyridine nitrogen on carbonium ion stability of the phenylpyridylmethanols is discussed.

Introduction

The dissociation of diphenyl- and triphenylmethanols in 100% sulfuric acid to give relatively stable carbonium ions has been the subject of a number of investigations.[1-9] The influence of substituents on the stability of such ions has been studied by means of freezing point lowering, reaction with water and alcohols, ultraviolet absorption spectra and minimum sulfuric acid concentration necessary to produce a visible color. It has been demonstrated that the substitution of electron-releasing groups in the phenyl rings of diphenylmethanol increases the stability of the carbonium ion formed in sulfuric acid solution while electron-withdrawing groups decrease the thermodynamic stability and also promote the tendency for polymerization. Compounds such as tri-*p*-aminophenylmethanol and tri-*p*-dimethylaminophenylmethanol when dissolved in sulfuric acid form stable

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

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

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

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

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

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

(7) R. G. Thompson and H. A. Smith, *ibid.*, **77**, 4432 (1955).

(8) H. A. Smith and B. B. Stewart, *ibid.*, **79**, 3693 (1957).

(9) B. B. Stewart and H. A. Smith, *ibid.*, **79**, 5457 (1957).

carbonium ions in spite of the strong electron-withdrawing groups present in the form of protonated amino substituents. However, the measured *i*-factors for these compounds are only 6.0 instead of the predicted value of 7.0. Apparently protons can exist on only two of the amino groups of the carbonium ion.[3,7]

$$((CH_3)_2NC_6H_4)_3COH + 4H_2SO_4 \longrightarrow H_3O^+ + 4HSO_4^- + ((CH_3)_2\overset{+}{N}HC_6H_4)_2\overset{-}{C}C_6H_4N(CH_3)_2 \quad (i = 6.0)$$

If one of the benzene rings in diphenyl- or triphenylmethanol is replaced by a pyridine ring, protonation of the nitrogen atom would be expected to decrease the stability of the carbonium ion produced in sulfuric acid. Four such methanols were prepared and their solutions in sulfuric acid were studied.

Results

i-Factors.—Table I gives the *i*-factors for the phenylpyridylmethanols studied. For all of these compounds solution was relatively rapid, and the initial freezing point measurement was recorded within the first 15–20 minutes. Formation of a carbonium ion together with protonation of the nitrogen in the pyridine ring should give an *i*-factor of 5.0 as shown, for example, by the equation

$$(C_6H_5)_2(C_5H_4N)COH + 3H_2SO_4 \longrightarrow (C_6H_5)_2(C_5H_4\overset{+}{N}H)C^+ + H_3O^+ + 3HSO_4^- \quad (i = 5)$$

This represents the initial behavior of the diphenylpyridylmethanols. The increase in the freezing point depression as the sulfuric acid solutions are allowed to stand is probably caused by sulfonation of the benzene rings. Each sulfonic acid group which is introduced in the carbonium ion will cause an increase of 2 in the value of *i*.

TABLE I

VAN'T HOFF FACTORS OF PHENYLPYRIDYLMETHANOLS IN 100% SULFURIC ACID

Methanol	*i* At zero time (extrapolated)	 At 24 hours
Phenyl-2-pyridyl-	3.85	3.98 (constant)
Diphenyl-2-pyridyl-	5.00	7.30 (constant)
Phenyl-4-pyridyl-	3.65	3.70 (constant)
Diphenyl-4-pyridyl-	4.90	5.66 (increasing slowly)

Simple solution of the methanol in sulfuric acid together with protonation of the nitrogen would give an *i*-factor of only two

$$C_6H_5(C_5H_4N)CHOH + H_2SO_4 \longrightarrow C_6H_5(C_5H_4\overset{+}{N}H)CHOH + HSO_4^- \quad (i = 2)$$

while polymerization together with protonation of the nitrogen would give values of 2.5–3.0. If the carbinol group of the polymer reacted with the acid to form a carbonium ion, the values of *i* would vary from 4 ($n = 2$) to 3 ($n \rightarrow \infty$)

$$nC_6H_5(C_5H_4N)CHOH + H_2SO_4 \longrightarrow (C_5H_4\overset{+}{N}H)CHOHC_6H_4\ CHC_6H_4(C_5H_4\overset{+}{N}H)_{n-2}\text{-}CHC_6H_5(C_5H_4\overset{+}{N}H) + n\text{-}1\ H_3O^+ + (3n-2)HSO_4^- \quad (i = 4 \text{ for } n = 2 \text{ to } 3 \text{ for } n \rightarrow \infty)$$

The values of *i* for the phenylpyridylmethanols do not correspond to simple solution or to solution and polymerization unless some sulfonation takes place. The lack of color and other evidence indicates that carbonium ions are not formed.

Reactions of Sulfuric Acid Solutions with Methanol and Water.—When solutions of the pyridyldiphenylmethanols in sulfuric acid were poured into methanol and then water and the products isolated, the corresponding methyl ethers were obtained. These were identified by elemental analysis. When the same solutions were poured into water, the original carbinols were regenerated. These are the expected reactions if diphenylpyridylcarbonium ions are present in the solution.

When sulfuric acid solutions of the phenylpyridylmethanols were poured into methanol and then water or into water directly, elastic materials of variable composition were isolated which slowly crystallized on standing. These charred and sintered at temperatures from 220–260° and appeared to be polymeric in nature.

Titrations to Form Carbonium Ions.—When diphenyl-2-pyridylmethanol is dissolved in sulfuric acid, an intense wine color is produced and with the corresponding 4-pyridyl compound a dark reddish-brown color is obtained. Titrations of the diphenylpyridylmethanols dissolved in an inert solvent in contact with water were carried out with 100% sulfuric acid until the color of the carbonium ion was barely visible. The minimum weight per cent. of sulfuric acid necessary to produce the characteristic color of the diphenyl-2-pyridylcarbonium ion was 66.0, while for the corresponding diphenyl-4-pyridylcarbonium ion the corresponding value was 56.5. For triphenylmethanol the value is 49.3 and for diphenylmethanol it is 72.0. No such titrations were performed with the phenyl-2-pyridylmethanol which gives no color with 100% acid or with phenyl-4-pyridylmethanol which forms a very light yellow color.

Experimental

i-Factors.—The apparatus, technique and solvent for the cryoscopic measurements have been described previously.[2,10] The temperature was maintained below 15° during an entire run. Preliminary experiments with triphenylmethanol as the solute were used to check the reproducibility of the apparatus.

Reaction of the Phenylpyridylmethanol Solutions with Water.—A 0.25-g. sample of each diphenylpyridylmethanol was added with constant stirring to 18 g. (10 ml.) of 100% sulfuric acid. Solution was completed in approximately one minute. Each solution was poured onto 100 g. of cracked ice, neutralized with sodium hydroxide and extracted with ether. The extracts yielded 60 to 80% of the original methanols on evaporation and these showed no depression of the melting point when corresponding reactants and products were mixed.

Sulfuric acid solutions of phenyl-2-pyridylmethanol and phenyl-4-pyridylmethanol were allowed to stand for 24 hours and then poured over cracked ice. After neutralization with sodium hydroxide, the solutions were extracted with ether which yielded no residue on evaporation. The solutions were then extracted with pyridine, evaporation of which gave solid polymeric materials which charred and sintered at about 220° for the 2-pyridyl derivative and 230–260° for the 2-pyridyl compound.

Reaction of the Phenylpyridylmethanol Solutions with Methanol.—A 0.25-g. sample of each diphenylpyridylmethanol was added with constant stirring to 18 g. (10 ml.) of 100% sulfuric acid and this solution added cautiously with vigorous stirring to 100 ml. of cold absolute methanol. The mixture was then poured into 100 g. of cracked ice, neu-

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

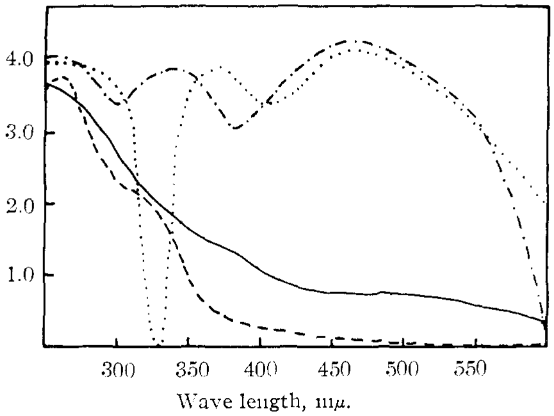

Fig. 1.—Absorption spectra of sulfuric acid solutions of phenylpyridylmethanols: ———, phenyl-4-pyridyl; – – – –, phenyl-2-pyridyl; – · – · –, diphenyl-4-pyridyl; . . . . , diphenyl-2-pyridyl.

tralized with sodium hydroxide and extracted with ether. Evaporation of the solution gave a 30% yield for the methyl ether of diphenyl-2-pyridylmethanol which melted at 53.0–54.2°.

Anal. Calcd. for $C_{19}H_{17}NO$: C, 82.87; H, 6.22. Found: C, 82.14; H, 6.00.

For the methyl ether of diphenyl-4-pyridylmethanol the yield was 35% of a compound melting at 93.4–94.3°.

Anal. Calcd. for $C_{19}H_{17}NO$: C, 82.87; H, 6.22. Found: C, 82.71; H, 5.97.

Sulfuric acid solutions of the phenyl-2-pyridyl- and phenyl-4-pyridylmethanols were allowed to stand and then poured into methanol and then over ice. The solutions were extracted with ether. An elastic material was observed between the ether and aqueous layers for preparations from both of the phenylpyridylmethanols. These materials were collected and dried under vacuum. They became hard and brittle, and their weights were approximately the same as for the starting pyridylphenylmethanols. No residue was obtained from the ether extracts. The product from the 2-pyridyl compound charred and sintered at 220–230° while that from the 4-pyridyl compound started to sinter at 240°.

Titrations to Form Carbonium Ions.—Small samples (0.0002 mole) of each of the pyridyldiphenylmethanols were dissolved in 10 ml. of carbon tetrachloride in a 125-ml. erlenmeyer flask. To this was added 25 ml. of water and with vigorous shaking the two-phase mixture was titrated with 100% sulfuric acid until a faint but permanent color was observed. The temperature of the solution was maintained at 22 ± 2° throughout the titration by means of an ice-bath. 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 with 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. The spectra were taken as quickly as possible after solution of the pyridylphenylmethanols in sulfuric acid. The spectra are shown in Fig. 1.

Preparation of Compounds. Phenyl-4-pyridylmethanol.—4-Benzoylpyridine obtained commercially from Reilly Tar and Chemical Co. was reduced with aluminum isopropoxide to give the desired product in 92% yield. The general procedure given by Wilds[11] was followed. The melting point of the product was 121–122°. The literature[12] value is 123–125°.

Phenyl-2-pyridylmethanol was obtained in 86% yield by aluminum isopropoxide reduction of 2-benzoylpyridine which was purchased from Reilly Tar and Chemical Co. The product melted at 75.5–76° which compares with a literature value of 76–78°.[13]

Diphenyl-4-pyridylmethanol was obtained commercially from Reilly Tar and Chemical Co.

Diphenyl-2-pyridylmethanol was prepared in 73% yields by the Grignard reaction of benzoyl-2-pyridine with phenylmagnesium bromide. The product melted at 104.6–105.6° which compares to the literature value of 105°.[14]

Discussion

The results of this research support the expectation that substitution of a pyridine ring for a benzene ring in a phenyl-substituted methanol decreases the ease of formation of carbonium ions in sulfuric acid solution. For the two diphenylpyridylmethanols, the initial *i*-factor of approximately 5, the characteristic spectra shown in Fig. 1, and the reaction of the sulfuric acid solution with water and methanol to form the original compound and the ether all indicate stable carbonium ion formation. The titration experiments show that the stabilities of these ions are less than for the triphenylcarbonium ion but greater than for the diphenylcarbonium ion. They also show that the 2-pyridyldiphenylcarbonium ion is less stable than the 4-pyridyldiphenylcarbonium ion. This might be expected since the protonated nitrogen atom in the former compound is closer to the central carbon than in the 4-pyridyl derivative. The increase in the *i*-factor with time is apparently due to slow sulfonation of the benzene ring.

The spectra of the sulfuric acid solutions of the two phenylpyridylmethanols give little if any indication of carbonium ion formation, for there is no major absorption band in the neighborhood of 450–500 mμ. If simple solution and nitrogen protonation had occurred, an *i*-factor of 2 would have been anticipated. The values of 3.7–4 indicate that something more than simple solution and nitrogen protonation did occur, and the chemical experiments give evidence that a process of polymerization took place. The spectra suggest that the polymer in solution was a methanol derivative rather than a carbonium ion. The constancy of the *i*-factors indicates that the polymers were formed rapidly, and that slow sulfonation of the benzene rings did not occur.

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[11] A. L. Wilds in "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 178.

[12] M. Kharasch, D. Schwartz, M. Zimmerman and W. Nudenburg, *J. Org. Chem.*, **18**, 1051 (1953); M. R. Kegelman and E. V. Brown, THIS JOURNAL, **75**, 4649 (1953).

[13] H. Gilman and S. Spatz, *J. Org. Chem.*, **16**, 1485 (1951).

[14] A. E. Tschitschibabin and S. W. Benewolenskaja, *Ber.*, **61**, 551 (1928).