

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

The Absorption Spectra of Some Methylpyridine Derivatives

BY LEIGH C. ANDERSON AND NELSON V. SEEGER

The structures of the 2- and 4-methylpyridines have not been definitely determined and one finds both the pyridine and pyridone-methide structures used for 2-methylpyridine. Tschitschibabin¹ postulated that both the 2- and 4-isomers existed as tautomeric mixtures of the two forms. Cartwright and Errera² presented evidence based on infrared absorption spectral curves of the 2- and 3-methylpyridines which indicated the existence of only the pyridine structure for the 2-isomer.

In order to obtain data which might be of value in determining the structure of 2-methylpyridine, the ultraviolet absorption curve of the compound was compared with that of 1-methyl-2-pyridone-methide in ether solution. The absorption curves are shown in Fig. 1. The pyridonemethide has two distinct bands at 2370 mm.^{-1} and at 3620 mm.^{-1} while 2-methylpyridine has only one band

at 3850 mm.^{-1} . One would expect 2-methylpyridine to have an absorption curve with two bands if it consists of a tautomeric mixture of the 2-pyridonemethide and 2-methylpyridine forms and since it has only one band in the region where pyridine absorbs light, the conclusion must be drawn that only the pyridine ring structure can be assigned to it.

In the preceding paper, it was shown that 1-methyl-2-pyridoneimine reacted with water to give a quaternary ammonium hydroxide and there was a corresponding change from the pyridone-imine absorption type of curve to that of pyridine. The absorption curves of 1-methyl-2-pyridone in ether, hexane, 72% dioxane-28% water, and pure water are presented in Fig. 1. These curves show absorption in the same spectral region. Apparently there is little tendency to form the quaternary compound and this is also shown by the fact that a water solution of 1-methyl-2-pyridone reacts neutral to litmus. There is comparatively little change in absorption in these different types of solvent. There is a pronounced change in absorption, however, when the

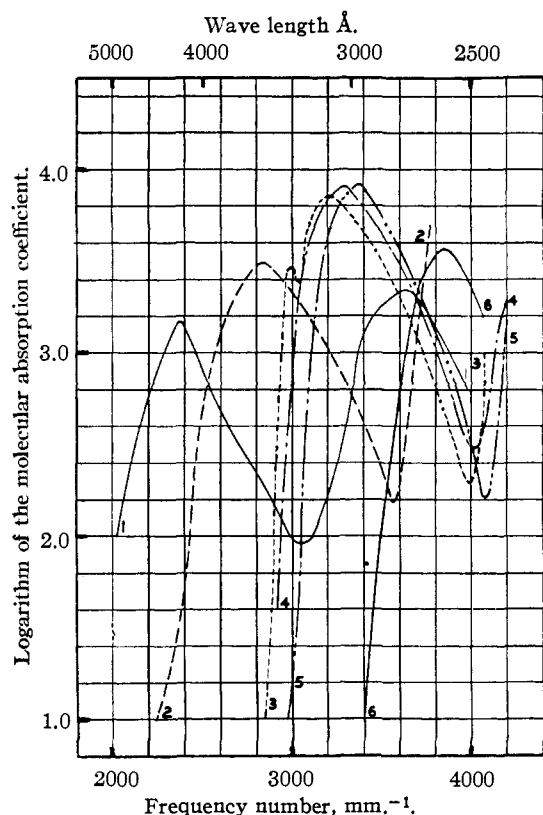


Fig. 1.—1, 1-Methyl-2-pyridonemethide in ether; 2, 1-methyl-2-pyridoneimine in ether; 3, 1-methyl-2-pyridone in ether and hexane; 4, 1-methyl-2-pyridone in 72%:28% dioxane-water; 5, 1-methyl-2-pyridone in water; 6, 2-methylpyridine in ether.

(1) Tschitschibabin, *Ber.*, **60B**, 1607 (1927).

(2) Cartwright and Errera, *Compt. rend.*, **300**, 914 (1935).

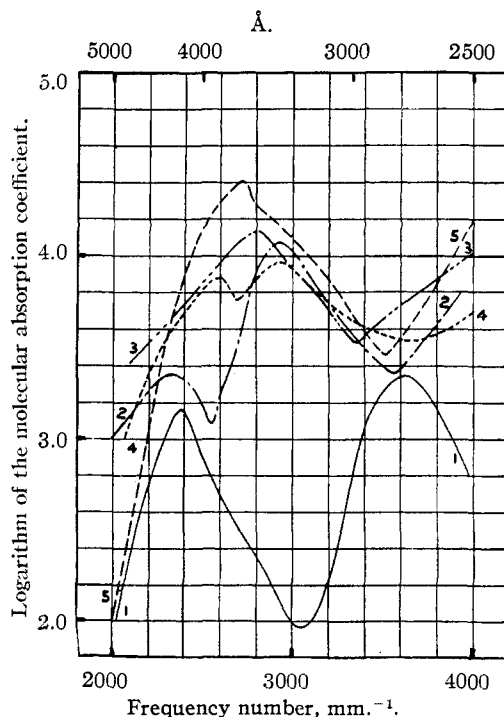


Fig. 2.—Absorption of ether solution of: 1, 1-methyl-2-pyridonemethide; 2, 1-methyl-2-pyridone-phenylmethide; 3, 1-methyl-2-pyridone-diphenylmethide; 4, 1-methyl-4-pyridone-phenylmethide; 5, 1-methyl-4-pyridone-diphenylmethide.

ketonic oxygen is replaced by an imine group and a still more marked change when the oxygen is replaced by a methylene group.

Figure 2 presents the curves of the following compounds wherein the methide hydrogens of 1-methyl-2- and 1-methyl-4-pyridone methides have been replaced with phenyl groups.

The compound with two hydrogens on the methide group has two bands, one at the edge of the visible, the other in the ultraviolet. Each of the compounds having one hydrogen replaced by a phenyl group also has two absorption bands but they occur much closer to each other than in the unsubstituted compound, there being a shift of the ultraviolet band toward the visible and of the band in the visible region toward the ultraviolet. When both hydrogens of the methide group have been replaced, only one intense band is found. In Fig. 3 a comparison between the curves of 1-methyl-4-pyridonediphenylmethide and of diphenylquinomethane shows a very striking similarity. The maximum absorption for both compounds is in the same region, 2750 mm.^{-1} for diphenylquinomethane and 2700 mm.^{-1} for the pyridone. The intensities of the bands are also very similar.

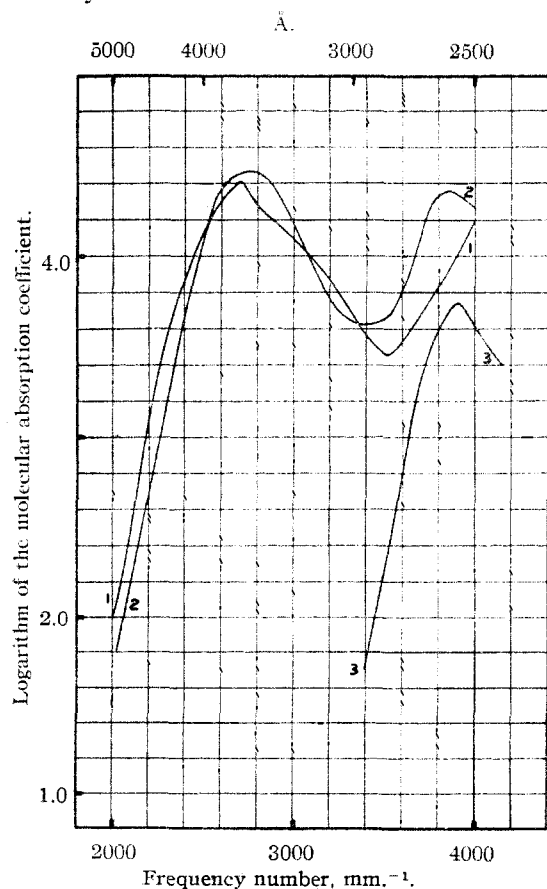


Fig. 3.—1, 1-Methyl-4-pyridone-diphenylmethide in ether; 2, diphenylquinomethane in ether; 3, 4-pyridyldiphenylcarbinol in dioxane.

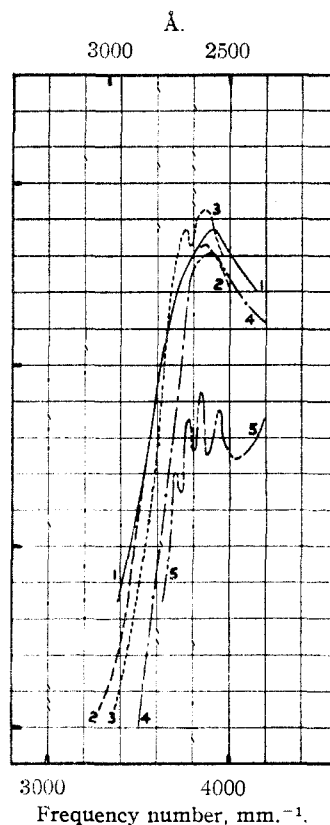


Fig. 4.—1, 4-Pyridyldiphenylcarbinol in dioxane; 2, 3-pyridyldiphenylcarbinol in ether; 3, 2-pyridyldiphenylcarbinol in ether; 4, pyridine in 72%:28% dioxane-water; 5, triphenylcarbinol in ether.

Figure 4 shows the curves of triphenylcarbinol, 2-pyridyldiphenylcarbinol and 3-pyridyldiphenylcarbinol in ether, 4-pyridyldiphenylcarbinol in dioxane, and pyridine in dioxane-water. Dioxane was used as a solvent for the 4-pyridyldiphenylcarbinol because the material was insoluble in ether. A comparison of the four carbinols shows that the replacement of a phenyl group by a pyridyl residue causes a considerable increase in the intensity of absorption. This increase is approximately the same regardless of the position of the pyridine substitution. The curves of the three pyridylcarbinols are strikingly similar to pyridine, the series of small bands in triphenylcarbinol being absent in the pyridylcarbinols except for the two peaks in 2-pyridyldiphenylcarbinol. Each of the pyridylcarbinols gives an intense red solution in concentrated sulfuric acid.

Experimental

2-Methylpyridine.—Eastman Kodak Co. product was purified in the same manner as pyridine according to the method of Spiers and Wibaut³; b. p. 127° .

1-Methyl-2-pyridonemethide.—This compound was prepared by the action of concentrated potassium hydroxide on the methiodide of 2-methylpyridine¹; it is a red oil which decomposes on distillation, even under reduced pressure.

(3) Spiers and Wibaut, *Rec. trav. chim.*, **56**, 579 (1937).

1-Methyl-2-pyridone.—This compound was prepared by the action of potassium ferricyanide on 1-methylpyridinium hydroxide according to the directions given in "Organic Syntheses"⁴; b. p. 250° (740 mm.).

2-Pyridyldiphenylcarbinol.—2-Pyridylmagnesium bromide, prepared by the method of Overhoff and Proost,⁵ was added to an ether solution of benzophenone. The carbinol which resulted was recrystallized from alcohol; m. p. 103–104°.⁶

1-Methyl-2-pyridone-diphenylmethide.—2-Pyridyldiphenylmethane was prepared by the method of Tschitschibabin and Benewolenskaja.⁷ It was recrystallized from a mixture of alcohol and water; m. p. 63°.

2-Pyridyldiphenylmethane was heated with methyl iodide in a sealed tube and the product was recrystallized from hot water; m. p. 222–224°. This methiodide upon treatment with concentrated potassium hydroxide solution gave 1-methyl-2-pyridone-diphenylmethide which crystallized from alcohol in long, dark red-violet needles; m. p. 147°.

3-Pyridyldiphenylcarbinol.—In order to prepare 3-pyridylmagnesium bromide, the procedure of Overhoff and Proost for the preparation of the 2-isomer had to be modified somewhat. A few drops of ethyl bromide were added to 8 g. of magnesium under 20 cc. of absolute ether. When the reaction had started, a mixture of 20 g. of redistilled Eastman 3-bromopyridine and 10 g. of ethyl bromide in 100 cc. of ether was added drop by drop with heating and constant stirring, a reddish brown precipitate being formed. The solution was boiled for two hours.

To obtain 3-pyridyldiphenylcarbinol, 36 g. of benzophenone in ether was added to the 3-pyridylmagnesium bromide solution and after some time the addition compound was decomposed with an ice-cold solution of ammonium chloride. The ether layer was extracted with dilute hydrochloric acid and the carbinol precipitated with ammonia. On recrystallization from ethyl acetate, the carbinol melted at 115–116°.

Anal. Calcd. for C₁₈H₁₆ON: N, 5.36. Found: N, 5.32.

The picrate of 3-pyridyldiphenylcarbinol was formed by adding a hot alcoholic solution of picric acid to a hot alcoholic solution of the carbinol; m. p. 195°.

Anal. Calcd. for C₁₈H₁₆ON·C₆H₃O₇N₃: N, 11.42. Found: N, 11.46.

(4) Prill and McElvain, "Organic Syntheses," Vol. XV, John Wiley and Sons, New York, N. Y., 1935, p. 41.

(5) Overhoff and Proost, *Rec. trav. chim.*, **57**, 184 (1938).

(6) Proost and Wibaut, *ibid.*, **59**, 971 (1940).

(7) Tschitschibabin and Benewolenskaja, *Ber.*, **61B**, 551 (1928).

4-Pyridyldiphenylcarbinol.—A mixture of 2- and 4-benzylpyridines was obtained by the action of benzyl chloride and pyridine according to the directions of LaForge.⁸ Following the procedure of Tschitschibabin⁹ this mixture was oxidized with permanganate to the 2- and 4-benzoylpyridines. For the preparation of 4-pyridyldiphenylcarbinol, previous investigators⁷ used pure 4-benzoylpyridine. However, this requires a tedious separation of the mixture of 2- and 4-benzoylpyridines by means of the picrate. Therefore, in this work, the mixture of benzoylpyridines was added directly to phenylmagnesium bromide forming a mixture of 2- and 4-pyridyldiphenylcarbinols. The 2-pyridyldiphenylcarbinol dissolved readily in ether and the 4-isomer which is insoluble in ether was filtered off. After two recrystallizations from ethyl acetate, the melting point was 234–235°.

1-Methyl-4-pyridonediphenylmethide.—4-Pyridyldiphenylmethane was prepared by the method of Tschitschibabin and Benewolenskaja using gaseous hydrogen iodide to reduce 4-pyridyldiphenylcarbinol; m. p. 125°. To obtain the methiodide, 4-pyridyldiphenylmethane was heated with methyl iodide in a sealed tube and the product recrystallized from alcohol; m. p. 159–161°. The methiodide was treated with concentrated potassium hydroxide and 1-methyl-4-pyridonediphenylmethide was formed; recrystallization from alcohol gave yellow needles, m. p. 113°.

1-Methyl-2- and 4-Pyridonephenylmethides.—Each of these compounds was prepared according to the directions of Decker¹⁰ by the addition of a concentrated solution of potassium hydroxide to the methiodides of 2- and 4-benzylpyridines.

Summary

1. Quantitative absorption spectral data indicate that 2-methylpyridine possesses only a pyridine structure in ether solution.

2. The absorption spectrum curve for 1-methyl-4-pyridonediphenylmethide in ether solution is very similar to the curve for diphenylquinomethane.

3. Curves for 2-, 3- and 4-pyridyldiphenylcarbinols show the presence of a pyridine structure only.

(8) LaForge, *This Journal*, **50**, 2484 (1928).

(9) Tschitschibabin, *J. Russ. Phys. Chem. Soc.*, **33**, 300 (1901).

(10) Decker, *Ber.*, **38**, 2494 (1905).

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The Kinetics and Mechanism of the Uncatalyzed Alkylation of Phenol

BY HAROLD HART AND J. H. SIMONS

Although the alkylation of the aromatic nucleus has long been an important reaction to the organic chemist, there have been relatively few kinetic studies of the mechanism of this reaction. Ionic intermediates for this reaction have been postulated,^{1,2} but some recent kinetic studies³ on the hydrogen fluoride catalyzed alkylation of toluene with *t*-butyl chloride present strong evidence against any high energy intermediate for that re-

action. These conclusions were based on the fact that various oxygen-containing (basic) promoters affected the rate only as a function of their concentration, and independent of the structure of the particular promoter, upon the retardation effect of hydrogen chloride, and upon the energy requirements for the reaction.

Following the discovery that phenols could be alkylated in the para-position with tertiary alkyl halides in the absence of any added catalysts^{4,5}

(1) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 309.

(2) C. C. Price, *Chem. Rev.*, **29**, 44–51 (1941).

(3) (a) W. H. Pearson and J. H. Simons, *This Journal*, **67**, 352 (1945); (b) J. W. Sprauer and J. H. Simons, *ibid.*, **64**, 648 (1942).

(4) J. H. Simons and H. Hart, *ibid.*, **66**, 1309 (1944).

(5) (a) G. M. Bennett and F. M. Reynolds, *J. Chem. Soc.*, 131 (1935); (b) J. van Alphen, *Rec. trav. chim.*, **46**, 287 (1927).