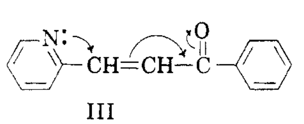
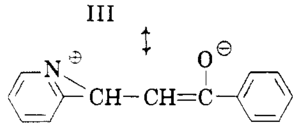
In other papers, Szmant[4,5] studied the absorption spectra of the 2-thienyl and 2-furyl analogs of chalcone. Results of these investigations indicated that replacement of the phenyl group by the 2-furyl or 2-thienyl group gave a consistent bathochromic effect. This effect was greater when replacement occurred in position A.

The spectra of the unsubstituted pyridine analogs of chalcone exhibit a distinct maximum between 280 mμ and 318 mμ with an ϵ value of approximately 20,000. This band is analogous to the 312 mμ band of *trans*-chalcone and the observed shifts of this band in the pyridine analogs when compared with chalcone can be explained in terms of the greater electron-withdrawing effect of the pyridine ring as compared with benzene.

In Table I, it can be seen that replacement of phenyl by a 2-, 3-, or 4-pyridyl group in position A causes a hypsochromic shift of 9–32 mμ while replacement of the phenyl group by pyridine in position B causes a small bathochromic effect. All of the pyridine analogs reported are *trans* and have a planar configuration. However, 2-pyridalacetophenone (III) which should be similar to 4-pyridalacetophenone is an exception. The behavior of III is probably caused by some unusual electronic effect due to the position of the nitrogen in the ring. One possible explanation would be the resonance stabilization of the IA structure by formation of a three-membered ring containing nitrogen (IV) similar to that proposed by Cram[6] for the intermediate in the Neber rearrangement.



III



IV

TABLE I

ULTRAVIOLET ABSORPTION SPECTRA OF A—CH=CH—CO—B

A	B	λ_{max}	$\epsilon \times 10^{-4}$
2-Pyridyl	Phenyl	303	2.10
3-Pyridyl	Phenyl	298	2.47
4-Pyridyl	Phenyl	280	2.83
Phenyl	2-Pyridyl	318	1.86
Phenyl	2-Methyl-5-pyridyl	315	2.24
Phenyl	4-Pyridyl	317	2.00
2-Pyridyl	2-Pyridyl	304	1.60
Phenyl	Phenyl	312[a]	2.67
2-Thienyl	Phenyl	345[a]	1.92
2-Furyl	Phenyl	344[a]	2.68
Phenyl	2-Thienyl	320[a]	1.93
Phenyl	2-Furyl	324[a]	1.07

[a] Reported in ref. 5.

EXPERIMENTAL

All of the pyridine analogs of chalcone have been recently reported and characterized.[2] The absorption spectra were determined in 95% ethanol using a Cary recording spectrophotometer and the values for the two 4-pyridyl derivatives represent corrections of reference 2. The spectral characteristics discussed here are summarized in Table I.

Acknowledgment. The author is indebted to Dr. C. S. Marvel and Dr. N. A. Nelson for their suggestions.

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[4] Szmant and Basso, *J. Am. Chem. Soc.*, **73,** 4521 (1951).

[5] Szmant and Planinsek, *J. Am. Chem. Soc.*, **76,** 1193 (1954).

[6] Cram and Hatch, *J. Am. Chem. Soc.*, **75,** 33 (1953).

The Preparation of 4-*p*-Tolylpyridine

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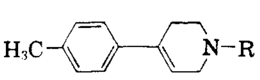
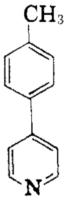
Received June 6, 1956

The preparation of 4-phenylpyridine from the starting materials α-methylstyrene, formaldehyde, and ammonium chloride or methylamine hydrochloride has been reported in a previous communication.[1] The purpose of this paper is to report the synthesis of 4-*p*-tolylpyridine (III) using the same sequence of reactions, but starting with *p*,α-dimethylstyrene.

During the preparation of 2-*p*-tolylpyridine picrate, Meek, Merrow, and Cristol[2] also obtained two other picrates, presumably those of 3- and 4-*p*-tolylpyridines, but 4-*p*-tolylpyridine itself has not been reported.



I; R = Me
II; R = H



III

The reaction of *p*,α-dimethylstyrene, formaldehyde, and methylamine hydrochloride to give 3,6-dimethyl-6-*p*-tolyltetrahydro-1,3-oxazine and 1-methyl-4-*p*-tolyl-4-piperidinol, and the rearrangement of this oxazine to 1-methyl-4-*p*-tolyl-1,2,3,6-

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[1] Schmidle and Mansfield, *J. Am. Chem. Soc.*, **78,** 1702 (1956).

[2] Meek, Merrow, and Cristol, *J. Am. Chem. Soc.*, **74,** 2667 (1952).

tetrahydropyridine (I) have already been described.[3,4]

4-*p*-Tolyl-1,2,3,6-tetrahydropyridine (II) was prepared by reacting *p*,α-dimethylstyrene, formaldehyde, and ammonium chloride and then treating the reaction mixture with excess hydrochloric acid to effect rearrangement and dehydration.

4-*p*-Tolylpyridine (III) was obtained by dehydrogenation of either I or II with palladium and nitrobenzene.

EXPERIMENTAL[5]

1-Methyl-4-p-tolyl-1,2,3,6-tetrahydropyridine (I). This compound, b.p. 110–115° (0.9 mm.), m.p. 76–78°, was prepared in 61% yield from methylamine hydrochloride, formaldehyde, and *p*,α-dimethylstyrene using the procedure (Method C) described previously[4] for the preparation of 1-methyl-4-phenyl-1,2,3,6-tetrahydropyridine.

Anal. Calc'd for $C_{13}H_{17}N$: C, 83.37; H, 9.15; N, 7.48. Found: C, 82.95; H, 9.08; N, 7.36.

4-p-Tolyl-1,2,3,6-tetrahydropyridine (II). This compound, b.p. 110–125° (0.75 mm.), m.p. 55–57°, was prepared in 33% yield from ammonium chloride, formaldehyde, and *p*,α-dimethylstyrene using the direct preparation procedure described previously[1] for the preparation of 4-phenyl-1,2,3,6-tetrahydropyridine.

Anal. Calc'd for $C_{12}H_{15}N$: C, 83.19; H, 8.73; N, 8.09. Found: C, 83.06; H, 8.71; N, 8.30.

The *hydrochloride* melted at 193–195° after recrystallization from a 10:1 mixture of acetone and isopropyl alcohol.

Anal. Calc'd for $C_{12}H_{16}ClN$: C, 68.72; H, 7.69; N, 6.68; Cl, 16.9. Found: C, 68.65; H, 7.54; N, 6.77; Cl, 16.8.

4-p-Tolylpyridine (III). *A. From 1-methyl-4-p-tolyl-1,2,3,6-tetrahydropyridine* (I). This compound (III) was prepared from 76 g. (0.41 mole) of 1-methyl-4-*p*-tolyl-1,2,3,6-tetrahydropyridine (I), 5 g. of 5% palladium on alumina catalyst, and 150 g. (1.22 moles) of nitrobenzene at 150–60° during 2½ hours using the procedure described previously[1] for the preparation of 4-phenylpyridine from 1-methyl-4-phenyl-1,2,3,6-tetrahydropyridine. There was obtained 37 g. (54%) of 4-*p*-tolylpyridine (III), b.p. 122–127° (0.7 mm.). This solidified and melted at 90–91° after recrystallization from heptane.

Anal. Calc'd for $C_{12}H_{11}N$: C, 85.17; H, 6.55; N, 8.28. Found: C, 84.89; H, 6.45; N, 8.28.

The *picrate* melted at 199–201° after recrystallization from ethanol containing a small amount of acetone.

Anal. Calc'd for $C_{18}H_{14}N_4O_7$: C, 54.27; H, 3.54; N, 14.07. Found: C, 54.49; H, 3.87; N, 13.80.

B. From 4-p-tolyl-1,2,3,6-tetrahydropyridine (II). A mixture of 5 g. of 5% palladium on alumina catalyst, 190 g. (1.54 moles) of nitrobenzene, and 46 g. (0.27 mole) of 4-*p*-tolyl-1,2,3,6-tetrahydropyridine (II) was stirred in a nitrogen atmosphere at 130–160° during two hours while water was removed by a water separator. The mixture was cooled, filtered, and distilled to give 39 g. (87%) of 4-*p*-tolylpyridine (III), b.p. 90–110° (0.1 mm.). This solidified and melted at 90–91° after recrystallization from heptane. The m.p. of a mixture with III prepared from I was 90–91°.

Anal. Calc'd for $C_{12}H_{11}N$: C, 85.17; H, 6.55; N, 8.28. Found: C, 85.14; H, 6.53; N, 8.43.

The *picrate* melted at 199–201° after recrystallization from ethanol containing a small amount of acetone. The m.p. of a mixture with the picrate of III prepared from I was 199–201°.

Anal. Calc'd for $C_{18}H_{14}N_4O_7$: C, 54.27; H, 3.54; N, 14.07. Found: C, 54.52; H, 3.78; N, 14.15.

Acknowledgment. We wish to thank Mr. C. W. Nash and his staff for analytical data reported.

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The Aminomethylation of *p*-Isopropyl-α-methylstyrene

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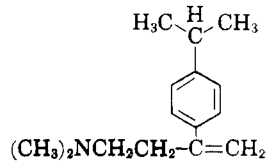
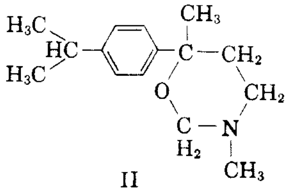
It is the purpose of this paper to report the aminomethylation of *p*-isopropyl-α-methylstyrene. The reaction of dimethylamine, formaldehyde, and *p*-isopropyl-α-methylstyrene gave N,N-dimethyl-3-*p*-isopropylphenyl-3-butenylamine (I).

The reaction of *p*-isopropyl-α-methylstyrene, formaldehyde, and methylamine hydrochloride gave 3,6-dimethyl-6-*p*-isopropylphenyltetrahydro-1,3-oxazine (II) and 1-methyl-4-*p*-isopropylphenyl-4-piperidinol (III). Rearrangement and dehydration of the crude reaction mixture in the presence of excess sulfuric acid gave 1-methyl-4-*p*-isopropylphenyl-1,2,3,6-tetrahydropyridine (IV). This substance was dehydrogenated and demethylated, using nitrobenzene and palladium on alumina, to 4-*p*-isopropylphenylpyridine (VI).

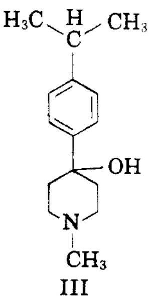
Treatment of the reaction product of *p*-isopropyl-α-methylstyrene, formaldehyde, and ammonium chloride with excess hydrochloric acid gave 4-*p*-



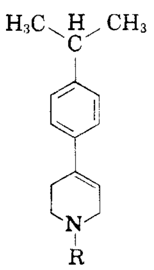
I



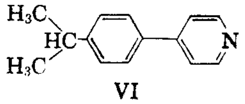
II



III



IV; R = CH_3
V; R = H



VI

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[3] Schmidle and Mansfield, *J. Am. Chem. Soc.*, **77**, 5698 (1955).

[4] Schmidle and Mansfield, *J. Am. Chem. Soc.*, **78**, 425 (1956).

[5] All melting points are uncorrected.