of m.p. 148°. A mixture m.p. determination with pure *p*-nitroaniline (reported[10a] m.p. 148°), indicated no depression; a mixture m.p. with IC showed the mixture to melt at 103–113°. Thus IC was 5-methylmercapto-1-*p*-nitrophenyltetrazole.

*Reduction of* IC. To 1.0 g. of IC dissolved in 75 ml. of 90% ethanol was added 1 g. of aluminum foil (which had been amalgamated by immersion for 10 minutes in an aqueous, 6%, solution of mercuric chloride). The mixture was allowed to stand at room temperature for three hours, during which time a slow evolution of gas was detectable. The resulting sludge then was filtered off and on cooling to 0° for 24 hours, the filtrate yielded 0.69 g. (81% yield) of light-brown colored needles of m.p. 156–159°. After 4 recrystallizations from absolute ethanol, the 5-methylmercapto-1-*p*-aminophenyltetrazole (ID) was obtained as cream needles of m.p. 160–161°.

*Anal.* Calc'd for $C_8H_9N_5S$: C, 46.4; H, 4.3; N, 33.8; S, 15.5. Found: C, 46.9; H, 4.2; N, 33.2; S, 15.3.

*Diazotization and coupling of* ID. To a suspension of 0.5 g. of ID in 30 ml. of water was added 0.45 ml. of hydrochloric acid. To the well stirred mixture, whose temperature was maintained below 10° throughout, was added, dropwise, a solution of 0.5 g. of sodium nitrite in 5 ml. of water. After a further 10 minutes, during which most of the suspended ID went into solution, *ca.* 1 g. of urea was added to remove excess nitrite. The mixture was stirred, its temperature being still kept below 10°, for a final 15 minutes, then it was filtered and the filtrate was added dropwise to a solution of 0.7 g. of β-naphthol in 30 ml. of *ca.* 0.1 *N* sodium hydroxide solution. Immediate deposition of IE as a deep red solid began. After 2 hours, it was filtered and washed with warm water, dried, and obtained as 0.77 g., 87.5% yield, of material of m.p. 230–232°. This, after recrystallization from chloroform, separated as fine orange-red needles of m.p. 233.5–234.0°.

*Anal.* Calc'd for $C_{13}H_{14}N_6OS$: C, 59.7; H, 3.9; N, 23.2; S, 8.8. Found: C, 59.9; H, 4.0; N, 22.8; S, 8.8.

The coupling product with N,N-dimethylaniline was formed analogously, except that the amine substrate was dissolved in ethanolic hydrochloric acid solution prior to coupling. The product (IF) was formed in 88% yield and was crystallized as fine red needles, of m.p. 190–191°, from chloroform.

*Anal.* Calc'd for $C_{16}H_{17}N_7S$: C, 56.6; H, 5.0; N, 28.9; S, 9.4. Found: C, 56.4; H, 4.8; N, 28.8; S, 9.5.

With phenol, an analogous compound was formed in similar yield, m.p. 208–209°.

*Anal.* Calc'd for $C_{14}H_{12}N_6OS$: C, 53.8; H, 3.8; N, 26.9; S, 10.3. Found: C, 53.2; H, 3.7; N, 27.0; S, 10.3.

Reaction of the above 5-methylmercapto-1-*p*-diazoniumphenyltetrazole salt with benzal guanyl- or phenylhydrazones, or with benzal diaminoguanidine or anisal guanyl hydrazone resulted in failure to isolate a coupling product under a variety of conditions.

*Bromination of* IB. To a solution of 3 g. of IB in 25 ml. of glacial acetic acid was added 2 ml. of bromine, dissolved in 25 ml. of the same solvent. The addition was effected dropwise and the mixture was continuously agitated. After 60 minutes stirring at room temperature, the mixture was heated, at 100°, for 30 minutes, during which time the odor of methyl mercaptan was noted. On cooling and concentrating in a stream of air, 0.43 g. (9% yield) of an amorphous solid of m.p. 118–120°, was obtained. This on recrystallization from aqueous ethanol was obtained as tiny platelets, m.p. 120–122°, which did not depress the m.p. of authentic 2,4,6-tribromoaniline (reported[10(b)] m.p. 122°).

*Anal.* Calc'd for $C_6H_4Br_3N$: C, 21.8; H, 1.2; N, 4.2; Br, 72.7. Found: C, 22.6; H, 1.2; N, 4.4: Br, 72.5.

On working up the filtrate a further portion (0.22 g., 4% yield) of this material was obtained, together with 0.51 g., (9% yield) of 2,4,6-tribromoacetanilide which was obtained as white needles m.p. 232° (reported[10(b)] m.p. 232°) which did not depress the m.p. of an authentic sample.

*Anal.* Calc'd for $C_8H_6Br_3NO$: C, 25.8; H, 1.6; N, 3.8; Br, 64.5. Found: C, 26.3; H, 1.3; N, 4.0; Br, 64.7.

Comparable results were obtained when the bromination was effected in refluxing anhydrous chloroform solution with, or without, magnesium oxide as base.

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## The Ultraviolet Absorption Spectra of the Pyridine Analogs of Chalcone

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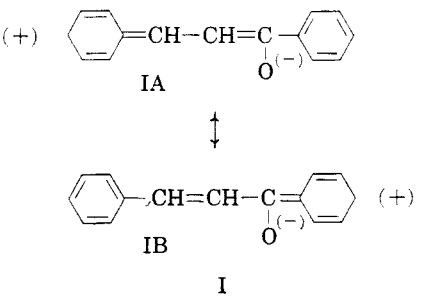
*Received June 6, 1956*

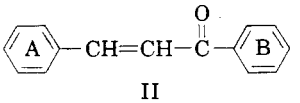
In connection with work on the synthesis of new monomers for free radical polymerization studies, a series of nine pyridine analogs of chalcone were prepared by the base-catalyzed condensation of the appropriate aldehyde and acetophenone or acetylpyridine.[2] The ultraviolet spectra of these *trans*-α,β-unsaturated ketones are of interest since they provide an opportunity for comparison with chalcone and its 2-furyl and 2-thienyl analogs. Szmant and co-workers[3] correlated the absorption spectra of substituted chalcones with the electronic nature of the substituents by considering the whole molecule of the chalcone as one conjugated system. The principal absorption band is assumed to originate from electronic oscillations represented by I.



IA ↕ IB

I

Szmant found from experimental data that in α,β-unsaturated ketones represented by II, electron-attracting groups on ring A cause large hypsochromic shifts, but when present on ring B they tend to give bathochromic effects.



II

(1) Present address: Materials Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio.

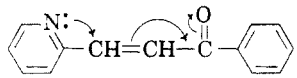
(2) Marvel, Coleman, and Scott, *J. Org. Chem.*, **20**, 1785 (1955).

(3) Szmant and Basso, *J. Am. Chem. Soc.*, **74**, 4397 (1952).

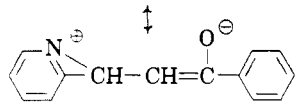
In other papers, Szmant[4,5] studied the absorption spectra of the 2-thienyl and 2-furyl analogs of chalcone. Results of these investigations indicated that replacement of the phenyl group by the 2-furyl or 2-thienyl group gave a consistent bathochromic effect. This effect was greater when replacement 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 | $\lambda_{max}$ | $\epsilon \times 10^{-4}$ |
|---|---|---|---|
| 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.

(4) Szmant and Basso, *J. Am. Chem. Soc.*, **73**, 4521 (1951).
(5) Szmant and Planinsek, *J. Am. Chem. Soc.*, **76**, 1193 (1954).

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

## The Preparation of 4-*p*-Tolylpyridine

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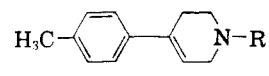
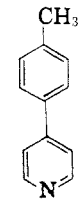
*Received June 6, 1956*

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-

(1) Schmidle and Mansfield, *J. Am. Chem. Soc.*, **78**, 1702 (1956).
(2) Meek, Merrow, and Cristol, *J. Am. Chem. Soc.*, **74**, 2667 (1952).