

EXPERIMENTAL⁷

Phenyl 2-pyridyl ketoxime, m.p. 126–140°, as a mixture of the geometrical isomers, was prepared from 2-benzoylpyridine.⁸

According to the method of Kolloff and Hunter,⁹ α -cyano-pyridine was reduced, using Raney nickel,¹⁰ to *2-pyridylmethyl amine*, b.p. 102–104° (26 mm.)¹¹ in 57% yield.

In a similar procedure phenyl 2-pyridyl ketoxime was hydrogenated over 24 hr. The product, *phenyl-2-pyridylmethyl amine*, distilled as a yellow liquid, b.p. 110–114° (0.1 mm.), 6.0 g. (54%). Attempted redistillation led to polymerization and/or decomposition. A *picrate* derivative separated from 95% ethanol as yellow needles and was further purified by recrystallization from ethyl acetate and hexane mixtures. A sample, m.p. 181–182° (dec.), was analyzed.

Anal. Calcd. for $C_{12}H_{12}N_2 \cdot C_6H_3N_3O_7$: C, 52.31; H, 3.66; N, 16.94. Calcd. for $C_{12}H_{12}N_2 \cdot C_6H_3N_3O_7 \cdot \frac{1}{2}H_2O$: C, 51.19; H, 3.82; N, 16.58. Found: C, 51.15; H, 3.63; N, 16.71.

Reduction of 2-benzoylpyridine by the Leuckart reaction. According to a general procedure of Crossley and More¹² for the Leuckart reaction, 35 g. (0.57 mole) of 28% ammonium hydroxide and 29.3 g. (0.57 mole) of 90% formic acid were added to a three-necked flask equipped with a dropping funnel, thermometer, and distilling condenser. As water was removed by distillation, the temperature was raised to 160° and 21.0 g. (0.115 mole) of 2-benzoylpyridine was added all at once. The mixture was held at 160–170° for 9 hr., cooled, treated with 40 ml. of concentrated hydrochloric acid, refluxed for 8 hr., cooled, diluted with 70 ml. of water, and extracted with benzene. The aqueous layer was treated with a little charcoal and made alkaline with concentrated ammonium hydroxide. An oil was extracted into benzene, washed with water, dried over sodium sulfate, and distilled. Benzene was removed at 1 atm. and 2.8 g. (12.6%) of a viscous yellow liquid, b.p. 168–174° (0.5 mm.) was obtained. It rapidly darkened upon standing. The structural assignment, 1-phenyl-2:3a-diazaindene was in agreement with elemental analyses of its *picrate* derivative, m.p. 209–212° (dec.) in a bath preheated to 204°. Blue fluorescence under ultraviolet light was reported for 2:3a-diazaindene⁴ and was also observed for 1-phenyl-2:3a-diazaindene.

Anal. Calcd. for $C_{13}H_{10}N_2 \cdot C_6H_3N_3O_7$: C, 53.90; H, 3.10; N, 16.55. Found: C, 54.14; H, 3.39; N, 16.56.

Preparation of amides. One ml. of benzoyl chloride was added dropwise to a solution of 1.0 g. (0.005 mole) of phenyl 2-pyridylmethyl amine in 10 ml. of dry pyridine and 20 ml. of dry benzene. The mixture was heated at 60–70° for 30 min., poured into 200 ml. of water, the aqueous layer separated and washed with benzene. The combined benzene layer and washings were washed with 20 ml. of water and 20 ml. of 5% sodium carbonate solution, dried over anhydrous sodium sulfate, concentrated to 10 ml., and added to 20 ml. of hexane whereupon *N-benzoyl phenyl(2-pyridyl)methyl amine* separated as colorless needles, m.p. 124–125°, 0.76 g. (49%), and was recrystallized from aqueous ethanol.

Anal. Calcd. for $C_{13}H_{10}N_2O$: C, 79.13; H, 5.59; N, 9.92; O, 5.55. Found: C, 79.25; H, 5.65; N, 9.91; O, 5.47.

(7) Semi-micro analyses by Alfred Bernhardt, Microanalytisches Laboratorium, Mülheim (Ruhr), Germany.

(8) E. H. Huntress and H. C. Walter, *J. Am. Chem. Soc.*, **70**, 3702 (1948) reported m.p. 116–145°.

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(11) A b.p. 81° (12 mm.) for a sample from the reduction of α -cyanopyridine with lithium aluminum hydride was reported.⁴

(12) F. S. Crossley and M. L. More, *J. Org. Chem.*, **9**, 529 (1944).

N-p-nitrobenzoyl 2-pyridylmethyl amine, m.p. 135–137°,¹³ was prepared in a similar manner from 2-pyridylmethyl amine and *p*-nitrobenzoyl chloride.

N-nitrosoamides. To a solution of 0.85 g. (0.003 mole) of *N-p*-nitrobenzoyl 2-pyridylmethyl amine in 3 ml. of acetic acid and 17 ml. of acetic anhydride cooled to 0°, 5.0 g. (0.07 mole) of sodium nitrite was added over a period of 4 hr. The mixture was then kept at 0° for 10 hr., poured into ice water, and extracted with ether. The ether layer was washed with water, 5% sodium bicarbonate, again with water, and dried over anhydrous sodium sulfate. Upon removal of solvent *in vacuo*, an unstable orange oil, assumed to be *N-2-picoyl-N-nitroso-p-nitrobenzamide*, was dissolved in 30 ml. of toluene and heated at 100–110° for 5 hr. The mixture was extracted with 5% sodium bicarbonate solution, and then with 5% hydrochloric acid. Upon neutralization of the combined acid extracts crude *2-pyridylmethyl p-nitrobenzoate* precipitated. It recrystallized from ethanol as colorless needles, 0.17 g. (20% based on *N-p*-nitrobenzoyl 2-pyridylmethyl amine), m.p. and mixture m.p. 90–92°.¹⁴

In attempts to nitrosate *N*-benzoyl phenyl(2-pyridyl)methyl amine with nitrogen tetroxide or with isoamyl nitrite starting material was quantitatively recovered. Impure unidentified products were obtained upon all attempts to combine nitrous acid and either phenyl 2-pyridylmethylamine or 2-pyridylmethylamine in aqueous media. An unidentified yellow liquid, b.p. 94–98° (3.2 mm.), was obtained from 2-pyridylmethyl amine and isoamyl nitrite in glacial acetic acid. It solidified upon standing and then decomposed into a dark oil. A *picrate* derivative after repeated recrystallizations had a melting range 155–163°.

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(13) R. Graf, G. Perathoner, and M. Tatzel, *J. prakt. Chem.*, **146**, 88 (1936) reported 136°.

(14) The ester was identical with the product obtained from *p*-nitrobenzoic acid and pyridotriazole [J. H. Boyer and L. T. Wolford, *J. Am. Chem. Soc.*, **80**, 2741 (1958)].

Hydrogenation of Thiophene Compounds with Hydrogen and Carbon Monoxide and a Cobalt Catalyst

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Previous attempts to hydrogenate the thiophene nucleus to thiolane have been only partly successful.⁴ Thiophenes have been reduced to thiolanes over a palladium catalyst, but very large quantities of catalyst were required to overcome the poisoning effect.⁵ Alkyl derivatives of thiophene and thiolane

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(3) Department of Chemistry, University of Cincinnati, Cincinnati 21, Ohio.

(4) H. D. Hartough, *Thiophene and Its Derivatives*, Interscience Publishers, Inc., New York, 1952, p. 167.

(5) R. Mozingo, S. A. Harris, D. E. Wolf, C. E. Hoffine, Jr., N. R. Easton, and K. Folkers, *J. Am. Chem. Soc.*, **67**, 2092 (1945).

TABLE I
REDUCTION OF THIOPHENE COMPOUNDS WITH SYNTHESIS GAS (2H₂:1CO)^a AND A COBALT CATALYST^b AT 180–190°

Starting Compound	Moles of Starting Compound	Benzene, Ml.	Weight of Cobalt, g.	Time, Hr.	Products	
					Composition	% yield
Thiophene	1.15	20	6	5	Thiophene	25
					Thiolane ^c	50
Thiophene	1.01	80	10	4	Thiophene ^d	24
					Thiolane ^d	66
2-Methylthiophene	0.89	20	1.4	4	2-Methylthiophene	39
					2-Methylthiolane ^{e,f}	51
2-Methylthiophene	1.00	80	2.6	5 ^g	2-Methylthiophene ^d	5
					2-Methylthiolane ^d	77
2-Ethylthiophene	0.40	80	2.6	3	2-Ethylthiophene ^d	6
					2-Ethylthiolane ^d	82
2,5-Dimethylthiophene	0.44	50	1.4	5	2,5-Dimethylthiophene ^h	53
					2,5-Dimethylthiolane ^h	22
2-Thenyl alcohol	0.36	50	1.4	4	2-Methylthiophene	24
					2-Methylthiolane ^f	57
2-Acetylthiophene	0.72	20	2.7	9 ⁱ	2-Ethylthiophene	52
					2-Ethylthiolane	26

^a Initial pressure of 3500–4000 p.s.i. at room temperature. ^b Dicobalt octacarbonyl or a mixture of dicobalt octacarbonyl and cobaltous carbonate. ^c Mercuric chloride addition product melted at 130.1–131.0° and did not depress melting point of an authentic sample; reported melting point, 129–130°. ^d Identified and analyzed by mass spectrometry. ^e Identified by mass spectrometry. Mercuric chloride addition product melted at 160.3–161.0° after recrystallization from ethanol; reported melting point, 162°. ^f n_D^{25} 1.4880; reported value, 1.4884. ^g After pressure dropped to 3200 p.s.i. in 4 hr., autoclave was repressured to 4000 p.s.i. at 190°. ^h Yields estimated from boiling point–refractive index curve of mixture. Geometric configuration of 2,5-dimethylthiolane not determined. ⁱ After pressure dropped to 3000 p.s.i. in 4 hr., autoclave was cooled and repressured to 3500 p.s.i. at room temperature.

have been obtained by hydrogenation of 2-acylthiophenes in the presence of sulfur and cobalt polysulfide;⁶ however, thiophene and 2-methylthiophene were not reduced by this method. Thiophene has been hydrogenated to thiolane with a molybdenum sulfide catalyst, but in low yield.^{7–10} Rhenium heptasulfide is reported to be a satisfactory catalyst for the hydrogenation of thiophene to thiolane¹⁰ and merits further investigation.

Earlier work in this laboratory had shown that a cobalt catalyst and synthesis gas (a mixture of hydrogen and carbon monoxide) may be used to reduce 2-thiophenecarboxaldehyde to 2-thenyl alcohol and 2-methylthiophene,^{11,12} 2-acetylthiophene to 2-ethylthiophene,^{12,13} and thiophene to thiolane in low yield.¹³

It has now been found that thiophene can be reduced to thiolane and that alkylthiophenes, 2-

thenyl alcohol, and 2-acetylthiophene, can be reduced to the corresponding alkylthiolanes at 180° to 190° by using longer reaction times with excess synthesis gas and larger amounts of cobalt catalysts. The yields are high enough for the reaction to be of preparative interest. These hydrogenations are probably homogeneously catalyzed by cobalt carbonyl and/or cobalt hydrocarbonyl.^{14,15}

In general the reduction of substituted thiophenes proceeded more readily than that of thiophene itself, and it was not difficult to obtain good yields of substituted thiolanes. That the hydrogenation of thiophene to thiolane was not reversible was demonstrated by treating thiolane with cobalt carbonyl and synthesis gas at 180° to 190°; mass spectrometric analysis of the products showed that no thiophene had been formed under these conditions. Attempts (not reported herein) to increase the yield of thiolane by employing even larger amounts of catalyst with very long reaction times and repressuring with fresh synthesis gas were not successful. Desulfurization occurred and the catalyst was partly converted to cobalt sulfide and metallic cobalt, as shown by x-ray diffraction analysis. It is possible that higher partial pressures of carbon monoxide would have preserved the catalyst as cobalt carbonyl.

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Melting points are corrected.

Synthesis gas (a mixture of hydrogen and carbon monoxide) was manufactured and compressed by the Bureau of Mines at Bruceton, Pa. Dicobalt octacarbonyl¹³ and 2-ethylthiophene¹⁶ were prepared by methods described in the literature. 2-Acetylthiophene was obtained from commercial sources. Thiophene, 2-methylthiophene, and 2,5-dimethylthiophene were gifts of the Socony-Vacuum Oil Co. 2-Thenyl alcohol was prepared in 85% yield by the lithium aluminum hydride reduction of 2-thiophenecarboxaldehyde in refluxing ethyl ether.

Each experiment was conducted at 180–190° with an initial pressure of 3500–4000 p.s.i. of 2:1 synthesis gas (2H₂:1CO) at room temperature, using benzene as solvent and dicobalt octacarbonyl, or a mixture of dicobalt octacarbonyl and cobaltous carbonate, as catalyst in a 500-ml., type 347 stainless steel, rocking autoclave purchased from the American Instrument Co. A 2-foot Heligrad Podbielniak column was used for precision fractional distillations.

The results are shown in Table I. A detailed description of the reduction of 2-acetylthiophene is given as an example.

Reduction of 2-acetylthiophene. In the 500-ml. autoclave were placed 90.0 g. (0.72 mole) of 2-acetylthiophene, 3.0 g. of cobaltous carbonate, and 20 ml. of a benzene solution containing 1.3 g. of dicobalt octacarbonyl. The autoclave was pressured to 3500 p.s.i. with 2:1 synthesis gas at room temperature and heated at about 185°. After the pressure had dropped to 3000 p.s.i. in 4 hr., the autoclave was cooled to room temperature and repressured from 1700 to 3500 p.s.i. It was then heated at about 185° for an additional 5 hr. The final pressure at room temperature was 3100 p.s.i. A total of 2.6 moles of gas had been absorbed. Fractional distillation of the reaction mixture gave 41.7 g. (52%) of 2-ethylthiophene, b.p. 133–135°, and 21.7 g. (26%) of 2-ethylthiolane, b.p. 154–158°. After purification by chromatographic absorption through silica gel, followed by azeotropic distillation with Cellosolve, the 2-ethylthiolane had the following physical constants: b.p. 156° at 736 mm., n_D^{25} 1.4870, d_4^{20} 0.9405.

Anal. Calcd. for C₆H₁₂S: C, 62.00; H, 10.41. Found: C, 62.08; H, 10.42.

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An Anomalous Reaction of Michler's Ketone with Grignard Reagents

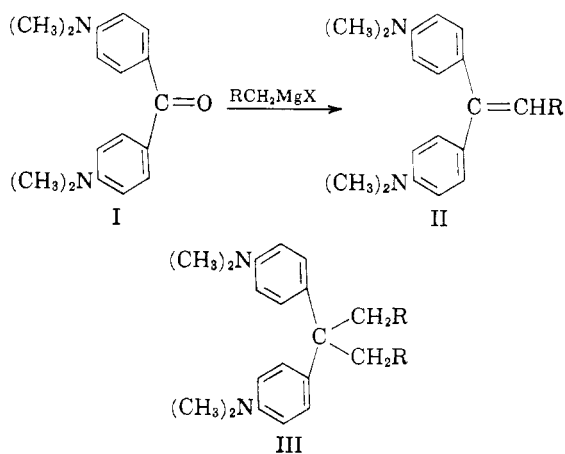
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The reaction of Michler's ketone (I) with Grignard reagents to give the corresponding di- or triphenylmethane dyes is the basis for a very sensi-

tive color test for Grignard reagents.¹ As a preparative tool, however, this reaction is often unsatisfactory and wide variations in yields of the corresponding 1,1-bis(*p*-dimethylaminophenyl)ethylenes have been reported.²

Roleff^{2f} reported quantitative yields of II (R=H) when Michler's ketone was heated with four moles of methylmagnesium bromide in benzene. Repetition of his procedure furnished 40–50% of 2,2-bis(*p*-dimethylaminophenyl)propane (III, R=H) in addition to II. Under similar conditions, benzylmagnesium chloride and I gave an 80% yield of III (R=C₆H₅ or the *o*-tolyl isomer) and no detectable II (R=C₆H₅).



Although this anomalous reaction of Grignard reagents with Michler's ketone to form the corresponding dialkyl compounds has not been described, several examples of similar reactions of Grignard reagents with carbonyl compounds have been reported.³ In all examples, an amino nitrogen is adjacent to or conjugated with the carbonyl group. This suggests that the reaction proceeds through a resonance-stabilized carbonium ion. Thus, the intermediate IV may be converted to V by a process in which a molecule of Grignard reagent, or the magnesium halide in equilibrium with the Grignard reagent, functions as a Lewis acid. The ion V then reacts with more Grignard to give the product III.

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