and stirrer, 160 g. (1 mole) of bromine was mixed with 130 g. (1 mole) of α-picoline hydrochloride. The resulting red liquid was heated at 120-130° for fifteen hours during which time the hydrogen halide that was evolved was collected in water. Titration of an aliquot of this acid solution indicated that 1 mole of hydrogen chloride had been driven from the perbromide. If the remaining reaction mixture was treated with cold, dilute aqueous sodium hydroxide the orange-colored, solid picoline perbromide separated and could be filtered off. If this product or the original reaction product was warmed carefully to 50-60° with a 20% aqueous solution of sodium hydroxide until the red color disappeared, an insoluble oil separated. This oil was taken up in benzene. Fractionation of this benzene solution yielded 70 g. (75%) of unchanged α-picoline and 5 g. of a nuclear monobrominated product, b. p. 73-74° (17 mm.); $n^{25}\text{D}$ 1.5580; $d^{25}{}_4$ 1.5584.

Anal. Calcd. for C_6H_6NBr; N, 8.14. Found: N, 7.98.

This monohalogen compound had an odor and chemical behavior similar to 3-bromopyridine with no indication of lachrymatory properties that would be expected if the bromine had entered the methyl group. An attempt was made to determine the position of the halogen in this compound by converting it to the corresponding nitrile by means of cuprous cyanide. While this method is very satisfactory for the preparation of nicotinonitrile from 3-bromopyridine,[11] no nitrile could be obtained from the bromo-α-picoline. The reaction product was a tar from which nothing could be distilled.

Heating the α-picoline hydrochloride perbromide for a longer time (forty-eight hours) did not increase the yield of the brominated product, a fact that shows the bromination reaction involves the hydrochloride and is competitive with the pyrolysis to the α-picoline perbromide and hydrogen chloride. When the α-picoline hydrochloride perbromide was heated to higher temperatures (140-200°), the only reaction product was black polymeric material similar to that obtained below when the picoline perbromide was heated. At these temperatures, apparently, the picoline perbromide undergoes oxidative polymerization as rapidly as it forms from the pyrolysis of the perbromide of the hydrochloride.

Similar experiments in which β-picoline and γ-picoline were used instead of α-picoline gave practically the same results, except that it was not possible to isolate any nuclear bromination product from either of these picolines.

Pyrolysis of α-Picoline Perbromide.—An orange, crystalline perbromide of α-picoline was obtained by carefully mixing equivalent amounts of bromine (34.4 g.) and α-picoline (20 g.). This perbromide was carefully heated in an oil-bath; it melted completely at a bath temperature of 95°. At 135° a violent exothermic reaction took place, the bromine color disappeared, and a viscous black solid remained in the reaction flask. From the reaction product was isolated 3 g. of unchanged α-picoline through a steam distillation from a basic solution, saturating the distillate with sodium hydroxide and extracting with 25 cc. of ether. The weight of non-volatile, black polymer that was insoluble in both water and alcohol amounted to 11.6 g.

Reaction of α-Picoline Perbromide with an Excess of α-Picoline.—Twenty grams of α-picoline (0.22 mole) and 10 g. of bromine (0.06 mole) were carefully heated in a round-bottom flask equipped with a reflux condenser and thermometer extending below the surface of the liquid. On raising the temperature to 90° an extremely violent exothermic reaction took place resulting in considerable loss of material through the reflux condenser. The temperature of the reaction mixture rose to 250°. The reaction product, after removal of the excess α-picoline by steam distillation, consisted of the same black polymeric material that was obtained in the previous experiment.

Summary

The rate of the vapor phase bromination of pyridine at 500° to form 2-bromopyridine is found to be substantially increased by preheating the vapors of the reactants.

Various methods for the preparation of 3-bromopyridine have been studied and evaluated and a procedure by which this compound may be prepared in relatively large quantities and in 35-40% yields by the pyrolysis of pyridine hydrochloride perbromide has been developed.

The properties of some of the other products that are formed along with or instead of 3-bromopyridine in the various bromination procedures are described and the probable structures discussed.

Extension of the preferred bromination procedure to chlorine and iodine indicates that 3-bromopyridine is the only one of the 3-halogenopyridines that may be prepared satisfactorily by direct halogenation of pyridine.

The behavior of the three picolines and their hydrochlorides in this bromination procedure is described and compared to that of pyridine.

MADISON, WISCONSIN RECEIVED AUGUST 5, 1943

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[11] McElvain and Goese, THIS JOURNAL, 63, 2283 (1941).

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

The Sulfonation of Pyridine and the Picolines

BY S. M. MCELVAIN AND M. A. GOESE

O. Fischer[1] and his collaborators first obtained pyridine-3-sulfonic acid in varying yields by heating pyridine with concentrated sulfuric acid in sealed tubes at 300-350° for twenty-four hours or at the boiling point of the reaction mixture for from thirty hours to twenty days. Later workers used fuming sulfuric acid in combination with aluminum,[2] vanadyl[3] and mercuric[4] sulfates as catalysts for the sulfonation. With these catalysts higher yields of pyridine-3-sulfonic acid were obtained in considerably shorter periods of reaction. Mercuric sulfate was particularly valuable as a catalyst because it caused the sulfonation to occur at lower reaction temperatures; using it with fuming sulfuric acid, Wulff reported 37% yields of sulfonic acids from pyridine and the α- and γ-picolines after three and one-half hours at

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[1] Fischer *et al.*, *Ber.*, **15**, 62 (1882); **16**, 1183 (1883); **17**, 763 (1884).

[2] Weidel and Murmann, *Monatsh.*, **16**, 751 (1895).

[3] (a) Meyer and Ritter, *ibid.*, **35**, 765 (1914); (b) Craig, THIS JOURNAL, **55**, 2855 (1933).

[4] (a) French Patent 685,062, *Chem. Zentr.*, **101**, II, 2576 (1930); (b) Wulff, German Patent 541,036, *Chem. Abs.*, **26**, 1945 (1932); (c) Wulff, U. S. Patent 1,880,646, *ibid.*, **27**, 515 (1933); (d) van Gastel and Wibaut, *Rec. trav. chim.*, **53**, 1031 (1934); (e) Machek, *Monatsh.*, **72**, 77 (1938).

225°. Van Gastel and Wibaut[4d] reported a 25% yield of the pyridine-3-sulfonic acid with this catalyst in fuming sulfuric after seven hours at 225°, while Machek[4e] obtained a 35–40% yield in twelve to fourteen hours at 230°. The sulfonic acids were isolated from all of the above mentioned sulfonations by removing the excess sulfate ion as the insoluble calcium or barium salt and recovering the sulfonic acid from its soluble calcium or barium salt by treatment with sulfuric acid to precipitate the insoluble sulfates of these metals.

The present paper reports the results of a study of the sulfonation of pyridine and the 3 picolines in which the conditions for optimum yields and the structures of the sulfonated picolines have been determined. It was found that the best yields of the various sulfonic acids are dependent upon at least three factors, (a) the presence of mercuric sulfate[5] in catalytic amounts in the sulfonation mixture—this requirement has been emphasized by Wulff,[4c] (b) the presence of one equivalent of sulfur trioxide in the amount of fuming sulfuric acid used in the sulfonation (*cf.* run 5, Table I) and (c) the length of time that the sulfonation reaction mixture is heated at 220–230°. The effects of this time factor on the yields of the sulfonic acids are shown in Table I.

Table I

Reaction Times and Yields in the Sulfonation of Pyridine and the Picolines at 220–230°

Run	Compound sulfonated	Reaction time, hr.	Yield, %	Compound formed
1	Pyridine	12	41	Pyridine-3-sulfonic acid
2	Pyridine	18	55	
3	Pyridine	24	71	"
4	Pyridine	36	68	"
5	Pyridine	24	22[a]	"
6	α-Picoline	24	60[b]	6-Methylpyridine-3-sulfonic acid
7	α-Picoline	12	54[c]	
8	α-Picoline	4	12	"
9	β-Picoline	24	0[d]	—
10	β-Picoline	16[e]	23	5-Methylpyridine-3-sulfonic acid
11	γ-Picoline	4	35	4-Methylpyridine-3-sulfonic acid
12	γ-Picoline	8	40	
13	γ-Picoline	12	0[d]	—

[a] In this run only one-half of an equivalent of sulfur trioxide was present in the sulfonation mixture. [b] This product was dark brown in color, but gave the same yield of nitrile as the product of run 7. [c] The shorter sulfonation time in this run gave a product that was light tan in color. [d] The yield in this case refers to water-soluble material. The only reaction product in this run was a black, water-insoluble tar. [e] Longer heating periods gave lower yields and more tar. Shorter heating periods gave lower yields.

Another factor that undoubtedly contributed to the improvement in yields in the present work is the method of isolation of the sulfonic acids. Instead of removing the excess of sulfuric acid from the reaction mixture by the precipitation and filtration of insoluble sulfates, it is removed by distillation under diminished pressure. This procedure leaves the sulfonic acids in a form in which they may be readily precipitated and recrystallized in maximum yields.

It is seen from the data in Table I that the picolines generally give lower yields of sulfonic acids than does pyridine. This is due, no doubt, to their greater tendency to be converted to black tarry products by the fuming sulfuric acid. Among the picolines, the α- and γ-compounds, in spite of their more reactive methyl group, give higher yields of sulfonic acids than does β-picoline. This is probably related to the fact that the orientation of the methyl group in both the α- and γ-picolines is to the same position as that of the nitrogen of the pyridine nucleus, while the directive influence of the methyl group of β-picoline is to ring positions (2, 4 and 6) that are rendered strongly cationoid by the nitrogen of the nucleus. Consequently, the only anionoid reactivity that is present in β-picoline is at the 5-position and it is of the same order as that of pyridine. This, together with the greater instability of the methyl pyridines toward the sulfonating agent, are the probable reasons for the low yield of 5-methylpyridine-3-sulfonic acid.

Each of the sulfonic acids listed in Table I was characterized by conversion of its sodium salt to the corresponding nitrile by fusion with sodium cyanide. The conversion of sodium pyridine-3-sulfonate to nicotinonitrile (3-cyanopyridine) was first reported by Fischer,[1] but he gave no yield of the product. Craig,[3b] however, using Fischer's procedure reported a 34% yield of the nitrile. In the present work a 46% yield of this nitrile was obtained from the sodium pyridine-3-sulfonate. Among the salts of the picoline sulfonic acids only the one derived from β-picoline gave a satisfactory yield (35%) of the nitrile. This nitrile, 5-methylnicotinonitrile, was characterized by hydrolysis to 5-methylnicotinic acid and the oxidation of this latter acid to dinicotinic acid. The salts of the sulfonic acids obtained from α- and γ-picolines gave very low yields (8 and 12%, respectively) of the corresponding nitriles. In each of these cases there was a considerable amount of the original picoline produced in the fusion. Even though the yields of these nitriles were low, these compounds served to establish the structures of the parent sulfonic acids, because the melting points of each of these latter compounds were found to be sufficiently sharp to preclude the admixture of isomeric substances (see footnote *a*, Table II).

Experimental

Pyridine-3-sulfonic Acid.—An all-glass distillation apparatus was used in this preparation. The distilling flask (500-ml. capacity) of this apparatus, which was fitted with

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(5) The use of vanadyl sulfate instead of mercuric sulfate and a reaction temperature of 220–230° gave no pyridinesulfonic acid by the procedure reported in the present paper. The workers (ref. 3) who used vanadyl sulfate as a catalyst also used much higher (above 300°) reaction temperatures.

TABLE II

THE PICOLINE SULFONIC ACIDS, $C_6H_7O_3NS$, AND THE CORRESPONDING NITRILES, $C_7H_6N_2$

-Pyridine-3-sulfonic acid	M. p., °C.[a]	Analyses, % N Calcd.	Analyses, % N Found	-Nicotinonitrile	M. p., °C.	Yield, %	Analyses, % N Calcd.	Analyses, % N Found
6-Methyl-	338–341[b]	8.80	8.74	6-Methyl-	84–85[c]	8	—	—
5-Methyl-	312–314[d]	8.80	9.09	5-Methyl-	83–84	35	23.7	23.5
4-Methyl-	353–355[e]	8.80	8.93	4-Methyl-	43–44	12	23.7	23.9

[a] These melting points were determined in a copper block with a standardized Anschütz thermometer. The melting points of mixtures of these sulfonic acids generally were found to be 50–70° lower than either component and over a considerable range (25–35°). [b] Begins to darken at 318°. Wulff (ref. 4b) does not report the melting point of this sulfonic acid. He reports its structure as the α-picoline-β-sulfonic acid (2-methylpyridine-3-sulfonic acid) which is in disagreement with the structure assigned to the acid in the present work. [c] This nitrile has been reported by Räth and Schiffmann, *Ann.*, **487**, 127 (1931). The 2-methyl-nicotinonitrile, which would have been obtained if the sulfonic acid had the structure ascribed to it by Wulff (*cf.* footnote *b*), melts at 58° (Baumgarten and Dornow, *Ber.*, **72**, 563 (1939). [d] Begins to darken at 308°. [e] Begins to darken at 310°. Wulff (ref. 4b) does not report the melting point of this acid. However, he does assign to it the same formula as that indicated in the above table.

a short still head, was used as the reaction flask. In it was placed 400 g. of 20–22% fuming sulfuric acid; the density of the fuming sulfuric acid furnishes a convenient measure of its sulfur trioxide content (d^{20} of 20% fuming sulfuric acid is 1.911 and of 22% fuming sulfuric acid is 1.919). To this acid 80 g. of pyridine was added dropwise. This addition may be completed safely and in about ten minutes if the pyridine is added through a short (30 cm.) air condenser that, for this step, replaces the still head and if the sulfuric acid is kept cooled by swirling the reaction flask in cold water. Then 2.5 g. of mercuric sulfate[6] was added to the reaction mixture, the still head put in place and the reactants heated in an oil-bath at 220–230° for twenty-four hours. During the period of sulfonation the side arm of the still head was attached to a tube that dipped into 10 ml. of concentrated sulfuric acid in a test-tube. This acid served to collect any sulfur trioxide that escaped from the reaction mixture.

After this time the tube leading from the still head to the sulfuric acid was replaced by a 1-liter round-bottom flask that served as a receiver and the excess sulfuric acid removed from the reaction mixture by distillation under diminished pressure. At 2 mm. the sulfuric acid distils at about 180° and a total of 230–240 g. of this acid was recovered. The dark brown, oily residue that remained from the distillation was cooled, diluted with 200 ml. of absolute alcohol and the resulting alcoholic solution cooled to 0°. After standing at this temperature for a few hours, the precipitate was filtered off. This crude sulfonic acid was redissolved in 500 ml. of water and treated with hydrogen sulfide to precipitate mercuric sulfide. After warming the suspension of the sulfide to 80°, it was filtered. The filtrate was evaporated to the point of crystallization and treated with 150 ml. of absolute alcohol and the precipitated sulfonic acid filtered off. After drying under diminished pressure at 100°, the product weighed 113 g. (71%) and melted at 352–356° (see footnote *a*, Table II).

By the same procedure, except that 93 g. of the picoline was used instead of the pyridine, the sulfonic acids of the three picolines were obtained. The optimum times of heating for maximum yields of these sulfonic acids are shown in Table I; the melting points and analyses are listed in Table II.

Nicotinonitrile (3-Cyanopyridine) from Pyridine-3-sulfonic Acid.—A thorough mixture of 33 g. (0.18 mole) of sodium pyridine-3-sulfonate and 26 g. (0.53 mole) of powdered sodium cyanide was placed in a 125-ml. distilling flask with a side arm of 10 mm. diameter. The flask was equipped with a stirrer and its side arm fitted with a 50 ml. distilling flask to serve as a receiver. The reaction flask was heated in a potassium nitrate–sodium nitrite bath. At 340° evidence of reaction, as indicated by fusion and frothing of the reaction mixture, appeared. After a small forerun of pyridine, nicotinonitrile began to collect in the receiver. The bath temperature then was raised to 400° and held there for forty to fifty minutes. After this time the distillate in the receiver was fractionated and yielded 2.6 g. (18%) of pyridine after which solid nicotinonitrile, b. p. 204–206°, was collected. This product, after recrystallization from an ether–petroleum ether (60–68°) mixture, weighed 8.7 g. (46%) and melted at 49–50°.

The same procedure was applied to the salts of the three picoline sulfonic acids. With the sodium 5-methylpyridine-3-sulfonate the reaction went much the same as it did with sodium pyridine-3-sulfonate, but with the salts of the sulfonic acids derived from α- and γ-picolines relatively much larger amounts of the corresponding picoline distilled from the fusion mixture before any of the nitrile appeared. For example, from 34.5 g. of sodium 6-methylpyridine-3-sulfonate 5.6 g. (34%) of α-picoline was obtained. The melting points, yields and analyses of the nitriles derived from the picoline sulfonic acids are listed in Table II.

Hydrolysis of 5-Methyl- and 4-Methylnicotinonitriles.—Each of these nitriles was hydrolyzed as follows: a solution of 0.5 g. of the nitrile and 0.75 g. of sodium hydroxide in 50 ml. of 70% alcohol was refluxed for three hours. The solvent then was removed by distillation, the residue dissolved in 5 ml. of water and the resulting solution treated with the exact amount of a solution of hydrochloric acid to neutralize the alkali that was originally used. Any precipitate that appeared at this point was filtered off and then the filtrate was evaporated to dryness. The residue was treated with 10 ml. of hot alcohol and the resulting alcoholic solution filtered from the insoluble salt. On cooling, the methylnicotinic acid crystallized from the alcoholic solution. The 5-methylnicotinic acid,[7] m. p. 215–216°, was obtained in 90% yield and the 4-methylnicotinic acid,[8] m. p. 211–213°, in 80% yield.

The 5-methylnicotinic acid was further characterized by oxidation to the dicarboxylic acid. A solution of 0.5 g. of 5-methylnicotinic acid, 0.2 g. of sodium hydroxide and 2 g. of potassium permanganate in 50 ml. of water became colorless after three hours of refluxing. The precipitated manganese dioxide was filtered off and the filtrate, after concentration to 20 ml., was carefully made acid to congo red with dilute hydrochloric acid. The precipitated dinicotinic acid, after recrystallization from alcohol, weighed 0.35 g. and melted at 320–323°.[9]

Summary

A procedure by which pyridine-3-sulfonic acid and certain of the picoline sulfonic acids may be prepared in quite satisfactory yields by the direct sulfonation of pyridine and the picolines is

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(6) This amount of mercuric sulfate is approximately 0.8 mole % and represents about the limit of solubility of this salt in the amount of fuming sulfuric acid that is used. If the amount of this catalyst is materially reduced the yield of the pyridine-3-sulfonic acid drops noticeably. For example, the use of 1 g. of mercuric sulfate in the above procedure gave only 50% (instead of 71% with 2.5 g. of catalyst) of the theoretical amount of the pyridinesulfonic acid.

(7) Dürkopf and Göttsch, *Ber.*, **23**, 1110 (1890).

(8) Hoogewerff and Van Dorp, *Rec. trav. chim.*, **2**, 21 (1883).

(9) (a) Weber, *Ann.*, **241**, 12 (1887); (b) Meyer and Tropsch, *Monatsh.*, **35**, 207 (1914).

described. The sulfonic acid group in each of these sulfonations enters the 3-position of the pyridine nucleus.

The structures of the picoline sulfonic acids were determined by conversion to the corresponding nitriles and the hydrolysis of these compounds to the known methylnicotinic acids.

Nicotinonitrile was obtained from sodium pyridine-3-sulfonate in 46% yields.

Madison, Wisconsin Received August 5, 1943

[Contribution from the Laboratory of Organic Chemistry of the University of Wisconsin]

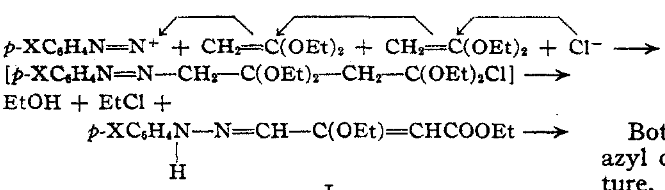
Ketene Acetals. XII. The Reaction of Ketene Diethylacetal with Diazonium Salts

By S. M. McElvain and Arthur Jelinek[1]

In previous papers[2] from this Laboratory the reactions of a variety of cationoid reagents with the anionoid center of ketene acetal have been described. It seemed that a continuation of this study with the very reactive diazonium cation as the reagent would be of interest, particularly since it would make possible a comparison of the behavior of ketene acetal with other types of compounds, such as β-ketoesters, phenols and aromatic amines, of lower anionoid reactivity which react quite readily with diazonium compounds.

This paper describes the course of the reaction of ketene acetal with four representative diazonium salts, phenyl-, *p*-ethoxyphenyl-, *p*-nitrophenyl- and *p*-carbethoxyphenyldiazonium chlorides. Since the acetal reacts rapidly with water and other hydroxylic compounds, these reactions were carried out with the dry diazonium salt in the presence of an excess of the acetal. In some exploratory experiments, in which a 10:1 ratio of reactants was used, it was found that for each mole of diazonium salt 5 moles of ketene acetal were consumed in reactions with the salt and with such reaction products as alcohol and hydrogen chloride; the remaining 5 moles of acetal were recovered unchanged. Consequently a 5:1 molar ratio of the acetal to the diazonium salt was used in subsequent reactions.

In each case the main reaction product was a 1-phenyl-4-ethoxypyridazone-6 (II) the formation of which may be rationalized as a cyclization of the phenylhydrazone (I) that is formed by the addition of the diazonium salt—the cation of which is in the resonance form,[3] ArN=N$^+$—across two molecules of ketene acetal, thus

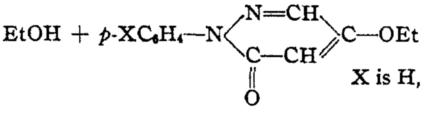


$$p\text{-XC}_6\text{H}_4\text{N}{=}\text{N}^+ + \text{CH}_2{=}\text{C(OEt)}_2 + \text{CH}_2{=}\text{C(OEt)}_2 + \text{Cl}^- \longrightarrow$$

$$[p\text{-XC}_6\text{H}_4\text{N}{=}\text{N—CH}_2\text{—C(OEt)}_2\text{—CH}_2\text{—C(OEt)}_2\text{Cl}] \longrightarrow$$

$$\text{EtOH} + \text{EtCl} + p\text{-XC}_6\text{H}_4\underset{\text{H}}{\underset{|}{\text{N}}}\text{—N=CH—C(OEt)=CHCOOEt} \longrightarrow$$

I



X is H, EtO,NO$_2$ or COOEt

II

The yields of the pyridazones (II) were 25–35% of the theoretical and in each case they dropped to about one-half of these values if the reaction was carried out in pyridine in which both reactants are soluble. With none of the diazonium salts was the yield of nitrogen more than 20% of the theoretical, a fact that indicates that no more than this amount of the salt underwent decomposition to produce free radicals.[4]

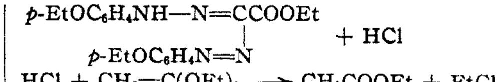
In addition to the pyridazone (II) varying quantities of products, the formation of which requires the addition of the diazonium salt to a single molecule of ketene acetal, were isolated from the reaction of all of the diazonium salts except phenyldiazonium chloride. The largest yield of such a product was obtained with *p*-ethoxyphenyldiazonium chloride. This compound, which was identified as ethyl *p,p'*-diethoxydiphenylformazyl formate (IV), was obtained as beautiful dark red leaflets in 27% yields. Its formation is the result of coupling of the diazonium compound with the hydrazone (III) that is formed by the addition of the diazonium salt to a single molecule of ketene acetal, thus

$$p\text{-EtOC}_6\text{H}_4\text{N}{=}\text{N}^+\ \text{Cl}^- + \text{CH}_2{=}\text{C(OEt)}_2 \longrightarrow$$

$$[p\text{-EtOC}_6\text{H}_4\text{N}{=}\text{NCH}_2\text{—C(OEt)}_2\text{Cl}] \longrightarrow \text{EtCl} +$$

$$p\text{-EtOC}_6\text{H}_4\text{NH—N=CHCOOEt} \xrightarrow{p\text{-EtOC}_6\text{H}_4\text{N=N}^+\ \text{Cl}^-}$$

III



$$\begin{array}{l} p\text{-EtOC}_6\text{H}_4\text{NH—N=CCOOEt} \\ \qquad\qquad\qquad\qquad\quad | \\ \qquad p\text{-EtOC}_6\text{H}_4\text{N=N} \end{array} + \text{HCl}$$

$$\text{HCl} + \text{CH}_2{=}\text{C(OEt)}_2 \longrightarrow \text{CH}_3\text{COOEt} + \text{EtCl}$$

IV

Both the pyridazone (II, X is H) and the formazyl compound (IV) are described in the literature. Sonn[5] prepared the former compound by the ethylation of 1-phenyl-4-hydroxypyridazone-6 (VI, X is H) which was obtained through the following sequence of reactions starting with phenyl-

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[1] Wisconsin Alumni Research Foundation Research Assistant, 1941–.

[2] (a) McElvain, *et al.*, This Journal, **60**, 2210 (1938); (b) **62**, 1281 (1940); (c) **64**, 254 (1942); (d) **64**, 260 (1942).

[3] *Cf.* Hauser and Breslow, *ibid.*, **63**, 418 (1941).

[4] *Cf. Ann. Rep.*, **37**, 278 (1940).

[5] Sonn, *Ann.*, **518**, 290 (1935).