combinations, however, had been observed to be generally non-specific in their action on Terramycin and Aureomycin. It thus was indicated that the arylsulfonyl halide–pyridine mixture might be a new, preferential reagent for use in converting sensitive amides to nitriles under mild conditions. Some preliminary studies on known amides thus have been carried out and tend to substantiate this belief. These studies, together with speculations regarding the mechanism of the acid chloride–pyridine amide dehydration reaction, are the subject of this communication.

In general, the amides studied (Table I) were converted smoothly to nitriles in good yield by the new reagent. Dehydration occurred much more readily with the arylsulfonyl chloride–pyridine combination than with 3,5-dinitrobenzoyl chloride–pyridine. There was some indication that saturated aliphatic amides may react less rapidly than α,β-unsaturated amides or aromatic amides. Acetamide seems to be an exception; it reacted vigorously to give a water-soluble solid which has not been characterized.

TABLE I

DEHYDRATION OF PRIMARY AMIDES WITH $ArSO_2Cl$–PYRIDINE

Amide	Yield[a] of nitrile, %	Procedure[b]
Benzamide	76	A
n-Caproamide	58	A
Nicotinamide	66	A
Cinnamamide	75	B
9-Xanthene carboxamide[c]	82	B
Aureomycin	30[d]	B
Terramycin	80[e]	B

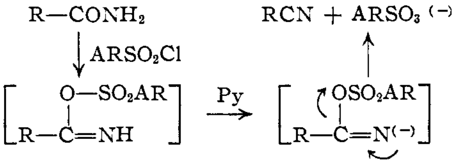
[a] In each case only one reaction was tried; yields could quite conceivably be improved. [b] See Experimental. [c] We are indebted to Dr. R. D. Drinkard for this example. He reports that usual dehydration procedures gave poor yields with this amide. [d] Reference 2. [e] As benzenesulfonate ester. Reference 1.

In studies on the dehydration mechanism we have established that a base is essential and have found the stoichiometry of the reaction to be

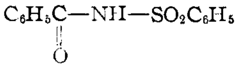
$$R\text{—}CONH_2 + ARSO_2Cl + 2Py \longrightarrow RCN + PyH^{(+)}ARSO_3{}^{-} + PyH^{(+)}Cl^{(-)}$$

(Py = pyridine)

The following mechanism seems likely



The proposed O-sulfonation step finds strong support in the following consideration: We observe (Table I) that benzamide is converted to benzonitrile in high yield (76%) by benzenesulfonyl chloride–pyridine. Now if attack occurred on nitrogen, we would expect to obtain as an intermediate N-benzoylbenzenesulfonamide (I).



$$C_6H_5C(=O)\text{—}NH\text{—}SO_2C_6H_5$$

I

However, since compound I has been prepared in 93% yield in pyridine solution[3a] (by the interaction of benzoyl chloride and benzenesulfonamide) and is perfectly stable in this solvent, it can be ruled out as an intermediate. Thus, an O-sulfonated intermediate is indicated.

The final step in the proposed mechanism, involving dissociation of the O-sulfonated intermediate, would be facilitated by the high stability of the sulfonate anion. Support for this concept is found in the work of Thompson[3a] on the interaction of acyl halides and amides in pyridine solution. He observed that halides of strong carboxylic acids frequently dehydrate amides to nitriles whereas halides of weak carboxylic acids lead to acylated products.

Experimental

Amide Dehydration. General Procedures. A.—Benzenesulfonyl chloride or *p*-toluenesulfonyl chloride (1 mole) was added gradually to a stirred mixture of the amide (1 mole) and pyridine (2.25 moles) at such a rate that the temperature did not exceed 70° (*i.e.*, usually the reaction is strongly exothermic). The resulting mixture, a thick slurry of pyridine salts and the nitrile, was allowed to cool slowly to room temperature, then treated with excess anhydrous ether. The salts were removed by filtration and the ether was washed with water, then evaporated. The residual nitrile was then purified by distillation or crystallization as required by the specific example.

B.—A solution of the amide in excess pyridine was treated with an excess of either benzenesulfonyl chloride or *p*-toluenesulfonyl chloride. Appropriate temperature control was used depending on the compound. When the exothermic reaction was over (usually after five to ten minutes), the solution was cooled to 25° and poured into excess water. The nitrile was then isolated by filtration or solvent extraction.

Specific procedures for Terramycin and Aureomycin have been reported previously.[1,2] In this work, it was observed that the dehydration proceeds readily even at 0°.

The nitrile products were identified by comparison of their physical constants and infrared absorption spectra with those of authentic samples.

Comparison of 3,5-Dinitrobenzoyl Chloride–Pyridine with the Arylsulfonyl Halide Pyridine Reagent in Amide Dehydration.—When 3,5-dinitrobenzoyl chloride was substituted for the arylsulfonyl chloride in procedure B (specific example: 5 g. of benzamide, 20 ml. of pyridine, 10 g. of 3,5-dinitrobenzoyl chloride), no significant heat effect was noted. After three hours at room temperature, only a trace of nitrile could be detected.

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Concerning the Reaction of Kojic Acid with Potassium Cyanide[1]

BY L. L. WOODS

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The fact that kojic acid reacts with potassium cyanide nearly quantitatively and without complicating side reactions was unexpected. Previously, Armit and Nolan[2] have reported that 2-(chloromethyl)-5-hydroxyl-1,4-pyrone when permitted to combine with potassium cyanide produced a resinous material.

Although the carbonyl group of 1,4-pyrones is commonly thought to be unreactive, reports have

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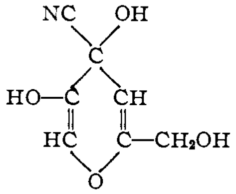
(1) The author expresses his thanks to the Research Corporation for their support of this project and the Corn Products Refining Company for the kojic acid used in these experiments.

(2) J. W. Armit and T. J. Nolan, *J. Chem. Soc.*, Pt. 2, 3023 (1931).

appeared[3,4] describing its reactivity and in no case were drastic conditions required.

The reaction of potassium cyanide with kojic acid takes place at the carbonyl to form the potassium salt of the cyanhydrin; which, when acidified, gives 2-(hydroxymethyl)-4-cyano-1,4-pyran-4,5-diol (I).



I

Compound I is still phenolic as indicated by a positive ferric chloride test, and has three hydroxyl groups in the molecule as shown by acetylation and phenylcarbamate formation.

The heating of 2-(chloromethyl)-4,5-dihydroxy-1,4-pyran-4-carboxylic acid with hydrochloric acid results in the regeneration of the carbonyl group and 2-(chloromethyl)-5-hydroxy-1,4-pyrone is formed.

Finally, the hydrolysis of I did not permit the isolation of the corresponding acid as did the 2-chloromethyl derivative of I, but produced a compound which is probably the lactide.

In consideration of the experimental data described no structure other than that proposed can fulfill the requirements as to the site and nature of the reaction of potassium cyanide with kojic acid.

Experimental[5]

A mixture of 100 ml. of ice-cold absolute methanol and 6.5 g. of potassium cyanide was stirred to break up any lumps of the cyanide, and 14.2 g. of powdered kojic acid was added all at once. The resulting mixture was thoroughly shaken. The reaction was apparently complete within a few minutes; however, the material was placed in the freezer and allowed to stand overnight. The solid product was stirred with a dilute solution of glacial acetic acid in absolute ethanol, chilled, collected and air-dried. Twenty and one-half grams of pale yellow crystalline material was obtained. An analysis gave an ash content of greater than 23%. The substance was therefore recrystallized from ethanol containing 7 ml. of hydrochloric acid. The 11.3 g. of tan needles thus obtained was recrystallized twice from absolute ethanol to produce colorless needles, m.p. 160°. The compound gave an orange-red solution with a 1% solution of ferric chloride.

Anal. Calcd. for $C_7H_7NO_4$: C, 49.70; H, 4.14; N, 8.28. Found: C, 49.66; H, 4.21; N, 8.06.

Gentle hydrolysis of the above compound was attempted by placing a small portion of the substance in 3 volumes of water, containing a small amount of hydrochloric acid, and refluxing the mixture for 2 hours, but only the starting material was obtained. The failure of the compound to be hydrolyzed under the conditions described diminished the likelihood that compound I was an aldimine.

The trisphenylcarbamate derivative was formed by refluxing a mixture of 1 g. I, 2.2 g. of phenyl isocyanate, 70 ml. of benzene and 1 ml. of pyridine for 30 minutes. The mixture was filtered and allowed to stand overnight, giving 2.5 g. of colorless crystals. Recrystallization from hot benzene produced a white amorphous material which progressively decomposed above 208°.

Anal. Calcd. for $C_{23}H_{22}N_4O_7$: N, 10.64. Found: N, 10.50.

When 5 g. of I was allowed to react with an excess of thionyl chloride and then recrystallized from hot water 3.6 g. of yellow prisms was obtained which was sublimed to yield colorless needles, m.p. 166. Only the 2-chloromethyl derivative was obtained. This was to be expected, since a chlorine replacing the hydroxyl on the carbon in position 4 is 1,3 from unsaturated groupings in three directions and is easily displaced by water.

Anal. Calcd. for $C_7H_6ClNO_3$: C, 44.81; H, 3.22. Found: C, 44.85; H, 3.07.

Hydrolysis of the nitrile group of the 2-chloromethyl derivative of I was effected by using the procedure of Cheronis and Entrikin.[6] The acid was recrystallized several times from absolute ethanol to give colorless needles, m.p. 167–168°.

Anal. Calcd. for $C_7H_7ClO_5$: C, 40.68; H, 3.39. Found: C, 40.44; H, 3.12.

The above acid was decarboxylated by slowly heating 1 g. of the compound with 10 ml. of concentrated hydrochloric acid over a steam-bath to dryness. The resulting tan solid weighed 0.8 g. The analytical sample was obtained by subliming the substance to a white powder, m.p. 166–167°, which is the accepted value for the melting point of 2-(chloromethyl)-5-hydroxy-1,4-pyrone.[7]

Anal. Calcd. for $C_6H_5ClO_3$: C, 44.85; H, 3.11. Found: C, 44.78; H, 3.40.

One gram of 2-(hydroxymethyl)-4-cyano-1,4-pyran-4,5-diol (I) was hydrolyzed exactly as previously described in the case of the 2-chloromethyl derivative of I. However, upon diluting the mixture with the requisite amount of water no crystals were obtained. Storage in the freezer for three days produced 0.4 g. of needles of the lactide, which were recrystallized twice from ethanol, m.p. 156°.

Anal. Calcd. for $C_{14}H_{12}O_{10}$: C, 49.41; H, 3.52. Found: C, 49.59; H, 3.68.

Acetylation of I was carried out in the usual manner with acetic anhydride, the reaction mixture was diluted with water, neutralized with sodium bicarbonate, and the precipitate was collected and air-dried. The sample was taken up in hot benzene, decolorized with Norit and allowed to crystallize. Colorless needles of the triacetyl derivative melting at 99–100° were formed.

Anal. Calcd. for $C_{13}H_{13}NO_7$: C, 52.88; H, 4.40. Found: C, 52.44; H, 4.30.

The phenacyl ether of I was prepared by allowing a mixture of 2 g. of phenacyl bromide, 1 g. of sodium bicarbonate, 2 g. of I and 40 ml. of ethanol to reflux for two hours. Isolation of the phenacyl derivative was accomplished by diluting the mixture with 120 ml. of water and collecting the precipitate. The resulting tan solid was purified by recrystallization first from ethanol, then from benzene to give colorless crystals, m.p. 150°.

Anal. Calcd. for $C_{15}H_{13}NO_5$: C, 62.71; H, 4.52. Found: C, 62.38; H, 4.30.

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[3] H. N. Barham and B. L. Smits, *Trans. Kansas Acad. Sci.*, **37**, 112 (1934).

[4] D. N. Bedekar, *et al.*, *J. Indian Chem. Soc.*, **12**, 465 (1935) [*C. A.*, **30**, 459 (1936)].

(5) All analyses were performed by Dr. Carl Tiedcke. All melting points were determined on a Fisher–Johns melting point assembly.

(6) N. D. Cheronis and J. B. Entrikin, "Semimicro Qualitative Organic Analysis," Thomas Y. Crowell Co., New York, N. Y., 1947, p. 296.

(7) T. Yabuta, *J. Chem. Soc.*, **125**, 575 (1924).

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The Structure of Quaternary Salts from 1-Alkyl-1,2,3-triazoles

BY RICHARD H. WILEY AND JAMES MOFFAT

RECEIVED NOVEMBER 19, 1954

The commonly encountered[1] problem of assigning the proper isomeric structure to N-substituted 1,2,3-triazoles which involve 1- and 2-alkyl isomerism is one for which no satisfactory attack has been devised. An unavailable type of basic information needed for such studies is that establishing the

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(1) R. H. Wiley, N. R. Smith, D. M. Johnson and James Moffat, THIS JOURNAL, **76**, 4933 (1954).