It melted at 112.0 to 113.5 and showed no change in melting point on standing in a desiccator over a period of several weeks. Hydrolysis and chromatography gave only triphenylcarbinol; the chloride was entirely free from triphenylmethane.

Nitromethane was purified by two methods, both starting with Matheson nitromethane. Method I, like that used by Bentley, Evans and Halpern,[1] consists of refluxing the nitromethane over phosphorus pentoxide, distilling it, collecting the fraction boiling at 100.0 to 100.5° and storing in a glass-stoppered bottle. Method II is like that of Thompson, Coleman and Helm[3] and consists of washing with dilute sodium bicarbonate, sodium bisulfite and sulfuric acid followed by a preliminary drying over phosphorus pentoxide and distillation from phosphorus pentoxide through a 19-plate bubble cap column into ampoules which are sealed while still attached to the column. A forerun, b.p. 100.0–100.2°, is discarded and the main fraction, b.p. 100.5°, collected for use.

Spectrophotometry.—In the first experiments weighed portions of triphenylmethyl chloride were made up to a known volume with nitromethane purified by method I. Measurements were made in 1-cm. ground-glass stoppered Beckman cells at 404 and 434 mμ. The optical density decreased with time and the value extrapolated to zero time was used in calculating the equilibrium constants for ion-pair formation. Curve A of Fig. 1 shows the decay of optical density for a typical solution in nitrobenzene purified by method I. Later experiments were made using nitromethane purified by method II, carrying out the procedure of opening the ampoules, making up the solutions, and filling the cells in a dry-box. The cells were sealed around the top with Apiezon Q (method IIa). In method IIb, which gave the same results as method IIa, an ampoule of the nitromethane purified by method II is introduced into one arm of a vacuum system and allowed to stand over boric acid. An ampoule containing a known amount of triphenylmethyl chloride is fused to the system, the solvent frozen, degassed and transferred onto the triphenylmethyl chloride by distillation at 10^{-5} mm. The ampoule containing the triphenylmethyl chloride is then sealed and detached from the apparatus. After the optical density measurements the ampoule is opened, the volume of solution measured, and the ampoule calibrated against a standard Beckman cell.

In both method IIa and IIb precipitation of ammonium chloride greatly hindered accurate observation of the rate of decay of the optical density. In method IIb the ampoules were centrifuged before observation. Curve B of Fig. 1 is a typical result.

Values of K obtained from the optical densities are shown in Table I. The extinction coefficients used in the calculations were determined from solutions of triphenylcarbinol in concentrated sulfuric acid and were ϵ_{404} 35,500 and ϵ_{434} 35,900. These values of the extinction coefficient agree with those in the literature and with those used in the previous measurements.[1,7]

TABLE I

Concn. of trityl chloride, moles/liter × 10²	Equilibrium constant for ion-pair formation Measured at 434 mμ	Measured at 404 mμ
6.72[a]	1.40	1.46
5.61[b]	2.07	2.10
4.01[b]	1.72	1.77
3.12[a]	1.68	1.82

[a] Sealed ampoule technique (method IIb). [b] Dry-box technique (method IIa).

Reaction Products.—An ampoule containing 300 mg. of triphenylmethyl chloride was filled with pure nitromethane (method II) by the vapor phase transfer method. The evacuated and sealed ampoule, after five days at 92°, was opened and the precipitate removed. It consisted of 28.6 mg. of ammonium chloride, identified by its sublimation in a sealed tube at 330 to 350°, by conversion to ammonia and by conversion (90%) to silver chloride. Triphenylcarbinol and triphenylmethylamine were isolated by chromatography on alumina from the filtrate after hydrolysis. No triphenylmethane or triphenylnitroethane was observed. The amine was identified by its melting point (90–100°), its solubility in hydrochloric acid, and the melting point of its hydrochloride (230–240°).

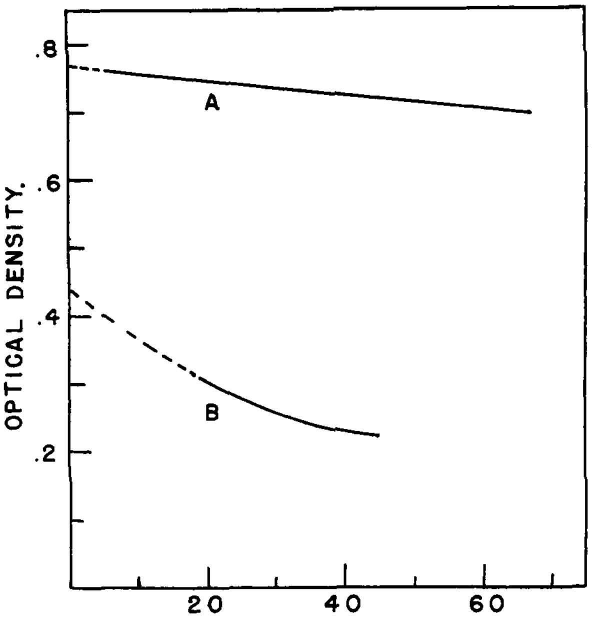

Fig. 1.—Decay of optical density with time (434 mμ): A, 0.0485 M $(C_6H_5)_3CCl$ in nitromethane, method I; B, 0.0561 M $(C_6H_5)_3CCl$ in nitromethane, method IIa.

A similar experiment with nitromethane purified by method I gave triphenylmethane, m.p. 94.5–95.5°, not depressed by an authentic sample.

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DEPARTMENT OF CHEMISTRY
FLORIDA STATE UNIVERSITY
TALLAHASSEE, FLORIDA

A New Reagent for Dehydrating Primary Amides Under Mild Conditions

BY C. R. STEPHENS, E. J. BIANCO AND F. J. PILGRIM

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In the course of structural studies on Terramycin[1] and on Aureomycin,[2] we have observed previously that arylsulfonyl chlorides in cold pyridine solution convert the antibiotics to nitrile derivatives through dehydration of the primary carboxamido group. The use of the above reagent in converting primary amides to nitriles apparently has not been reported previously, although it is known that certain acyl halides[3] (*e.g.*, 3,5-dinitrobenzoyl chloride) do bring about this transformation in the presence of pyridine. Acyl halide–pyridine

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(7) W. R. Orndorff, R. C. Gibbs, S. A. McNulty and C. V. Shapiro, THIS JOURNAL, **49**, 1551 (1927).

(1) F. A. Hochstein, C. R. Stephens, L. H. Conover, P. P. Regna, R. Pasternack, P. N. Gordon, F. J. Pilgrim, K. J. Brunings and R. B. Woodward, THIS JOURNAL, **75**, 5455 (1953). Terramycin is the registered trade-mark of Chas. Pfizer & Co., Inc., for the antibiotic oxytetracycline.

(2) C. R. Stephens, L. H. Conover, R. Pasternack, F. A. Hochstein, W. T. Moreland, P. P. Regna, F. J. Pilgrim, K. J. Brunings and R. B. Woodward, *ibid.*, **76**, 3568 (1954). Aureomycin is the registered trade-mark of Lederle Laboratories Division, American Cyanamid Co., for the antibiotic chlorotetracycline.

(3) (a) Q. E. Thompson, THIS JOURNAL, **73**, 5841 (1951); (b) J. Mitchell, Jr., and C. E. Ashby, *ibid.*, **67**, 161 (1945).

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

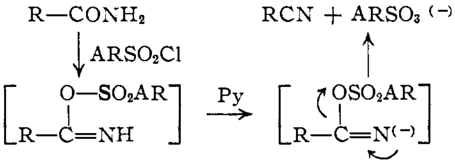
[a] In each case only one reaction was tried; yields could quite conceivably be improved. [b] See Experimental. [c] We are indebted to Dr. R. D. Drinkard for this example. He reports that usual dehydration procedures gave poor yields with this amide. [d] Reference 2. [e] As benzenesulfonate ester. Reference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

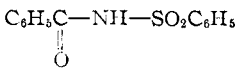
$$R\text{—}CONH_2 + ARSO_2Cl + 2Py \longrightarrow RCN + PyH^{(+)}ARSO_3{}^{-} + PyH^{(+)}Cl^{(-)}$$

(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).



$$C_6H_5\underset{\underset{O}{\|}}{C}\text{—}NH\text{—}SO_2C_6H_5$$

I

However, since compound I has been prepared in 93% yield in pyridine solution[3] (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.

RESEARCH LABORATORY
CHAS. PFIZER AND CO., INC.
GROTON, CONNECTICUT

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).