the nitrous oxide formed, is $k^* = 387 \times 10^{-5}$ min.$^{-1}$ (decadic logs) at 35°, in excellent agreement with Baughan and Bell's[3] $k^* = 386 \times 10^{-5}$ min.$^{-1}$ obtained for proto-nitramide in H_2O.

Partially deuterized nitramide prepared from 48% D_2O and sulfur trioxide yielded $k^* = 125.5 \times 10^{-5}$ min.$^{-1}$ at 24.84° in 0.01 *N* hydrochloric acid in H_2O. La Mer and Greenspan[1] obtained $k^* = 126.6 \times 10^{-5}$ min.$^{-1}$ under the same conditions for proto-nitramide in H_2O.

II. **Direct Exchange.**—Proto-nitramide was dissolved in D_2O (temp., approx. 5°). The nitramide produced by exchange was extracted with ether (dried over sodium) by the freezing method of Marlies and La Mer.[4,5] The exchange and extraction required less than one hour.

To ensure the complete removal of possible traces of deutero-solvent, the nitramide was kept over phosphorus pentoxide for one week. It was then decomposed by gentle heating in the presence of a trace of anhydrous sodium carbonate. The liberated water was redistilled and the density determined by the falling drop method.[6]

The following results show that the deuterium content of the nitramide approximated the deuterium content of the water from which it had been extracted.

Mole fraction of D in the solvent water in which exchange takes place	0.28	0.87	0.97
Mole fraction of D in the water from the decompn. of the extracted nitramide	.25	.65	.94

There is no point in calculating an exchange constant because, due to the method of extraction, the equilibrium temperature and the equilibrium concentration of D_2O cannot be held constant. Since deutero-nitramide decomposes in water at the same rate as proto-nitramide and since deutero-nitramide containing more than one atom of D per molecule may be extracted from a solution of proto-nitramide in D_2O, it is evident that both atoms of hydrogen in nitramide exchange with D_2O before decomposition occurs.

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(3) Baughan and Bell, *Proc. Roy. Soc.* (London), **A894**, 158, 464–478 (1937).
(4) Marlies and La Mer, THIS JOURNAL, **57**, 2008 (1935).
(5) Marlies, La Mer, and Greenspan, "Inorganic Syntheses," McGraw-Hill Book Co., Inc., New York, N. Y., Vol. I, p. 72.
(6) Hochberg and La Mer, *Ind. Eng. Chem., Anal. Ed.*, **9**, 291 (1937).

Ferric Chloride as a Condensing Agent

BY W. M. POTTS AND R. J. DODSON

A further investigation[1] of anhydrous ferric chloride as a condensing agent in the alkylation of benzene has been carried out using butyl alcohols.

1. Condensation products were not formed with *n*-butyl alcohol and benzene. This agrees with the results reported by Huston and Hsieh[2] using aluminum chloride and primary alcohols up to and including *n*-hexyl alcohol.

2. *s*-Butyl alcohol gave evidence of a reaction but no product was identified. With aluminum chloride under the same conditions, a 69% yield of *s*-butylbenzene was obtained. Huston and Hsieh[2] reported a 25–28% yield, while Tzukervanik and Tokareva[3] reported a 70% yield. The *s*-butylbenzene was identified by its physical constants and the diacetamino derivative, m. p. 193°.[4]

3. At room temperature, one mole of *t*-butyl alcohol, one mole of ferric chloride and five moles of benzene gave an 82% yield of *t*-butylbenzene. With aluminum chloride under the same conditions a 50% yield of *t*-butylbenzene was obtained. Using two moles of *t*-butyl alcohol, one mole of benzene and one mole of ferric chloride, a 24% yield of mono-*t*-butylbenzene and 64% of 1,4-di-*t*-butylbenzene was obtained. The acetamino derivative of the former melted at 168°.[4] The latter was identified by the method reported by Potts and Carpenter.[1]

Better yields of *t*-butylbenzene were obtained with ferric chloride than with aluminum chloride, but ferric chloride does not effect the condensation of primary and secondary alcohols with benzene. Higher temperatures and larger quantities of ferric chloride lower the yields of *t*-butylbenzene.

(1) Potts and Carpenter, THIS JOURNAL, **61**, 663 (1939).
(2) Huston and Hsieh, *ibid.*, **58**, 439 (1936).
(3) Tzukervanik and Tokareva, *J. Gen. Chem.* (U. S. S. R.), **5**, 764 (1935); *C. A.*, 442 (1936).
(4) Ipatieff and Schmerling, THIS JOURNAL, **59**, 1056 (1937).

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α-Hydrindone

BY CHARLES C. PRICE AND FREDERICK M. LEWIS

Although ring closures of many β- and γ-aryl butyric acids to the corresponding cyclic ketones have been accomplished successfully by the ac-

tion of sulfuric acid, it has been reported[1] that this reagent will not effect such a ring closure for the simplest β-arylpropionic acid, hydrocinnamic acid, to yield α-hydrindone.

By varying the conditions for the reaction of hydrocinnamic acid in sulfuric acid it has been found possible to obtain a very pure product rapidly and conveniently although in only moderate yield.

The concentration of acid was varied from 15% fuming to 85% sulfuric acid, the time of heating from one minute to three hours and the reaction temperature from 100 to 160°. Optimum conversion was obtained by using 5% fuming sulfuric acid at 140° for five minutes. In each case the sulfuric acid (20 cc.) was heated to the desired temperature in an oil-bath, the hydrocinnamic acid (5 g., m. p. 49–50°) added with stirring and, at the end of the specified time, the reaction mixture poured over cracked ice (100–150 g.). The α-hydrindone was extracted with two 25-cc. portions of benzene. After drying over sodium sulfate, the benzene was removed by evaporation on a steam plate, leaving a pale yellow oil which crystallized on cooling to room temperature, maximum yield 1.2 g. (27%), m. p. 40–41°. A mixture of these crystals with the starting material was liquid at room temperature. The identity of the product was established further by preparation of the 2,4-dinitrophenylhydrazone, m. p. 254–255°. No starting material was isolated in any case.

The addition of boron fluoride or aluminum chloride to the sulfuric acid lowered the yield considerably.

(1) Von Miller and Rohde, *Ber.*, **23**, 1887 (1890).

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Some Schiff Base Hydrochlorides. A Test for Arylamines[1]

BY J. V. SCUDI, H. D. RATISH AND J. G. M. BULLOWA[2]

In the course of certain studies,[3] a very simple color test was devised for the estimation of sulfanilamide and other arylamines. The test is not as sensitive (1 part in 200,000) as diazotization procedures,[4,5] but its simplicity has made it useful in following various concentrates in a semi-quantative way. Recently the Ehrlich reagent has been more rigorously standardized[6] for the determination of sulfanilamide, although the reaction mechanism was left in doubt. It was therefore decided to record our observations.

The test consists in adding 1 cc. of 10% hydrochloric acid to 5 cc. of a 1% solution of cinnamaldehyde in alcohol followed by 5 cc. of a 2–4 mg. % solution of the arylamine. A yellow color is instantly formed. This is stable for several days, but unstable to alkali. Other aldehydes may be used, but not benzaldehyde. Toluenesulfonamide does not give the test. The sensitivity is increased ten-fold by performing the test in absolute alcohol in the presence of concentrated sulfuric acid.

The color producing substances were shown to be the somewhat labile hydrochlorides of the Schiff bases of sulfanilamide and sulfapyridine. These were converted to the free bases. In accord with the finding of Dimroth and Zoeppritz[7] and Moore and Gale,[8] the color appears to be produced by the halochromic effect of the acid upon the Schiff base. The compounds reported are not submitted as crystalline derivatives for the characterization of the arylamine, but as evidence of the mechanism of the color development.

Experimental

Schiff Base Hydrochlorides.—These were prepared essentially by the method of Dimroth and Zoeppritz[7] with the exception that one mole of cinnamaldehyde was dissolved in alcohol prior to addition to the arylamine in dilute hydrochloric acid. Yields of 85–95% of the products were precipitated instantly as golden-orange plates. The cinnamylidene sulfanilamide hydrochloride, melting at 203–205° dec., was recrystallized with some hydrolysis from dilute hydrochloric acid. Calculated for $C_{15}H_{14}O_2N_2S\cdot HCl$: Cl, 11.01. Found: Cl, 11.35.

The cinnamylidene sulfapyridine hydrochloride was too labile to be crystallized. Washed with a minimal amount of alcohol and ether, the product melted at 178–180° dec. Calculated for $C_{20}H_{17}O_2N_3S\cdot HCl$: N, 10.52; Cl, 8.90. Found: N, 10.15; Cl, 9.65.

Free Bases.—Crystallization of cinnamylidene sulfanilamide hydrochloride from water gave 70–80% yields of the base, m. p. 213–215° dec. The melting point was unchanged when mixed with an authentic sample,[9] although

(1) Presented at the Baltimore meeting of the American Chemical Society, April, 1939.

(2) These studies received financial support from the Littauer Pneumonia Research Fund, from the Metropolitan Life Insurance Company, and from Mr. Bernard M. Baruch, Mr. Bernard M. Baruch, Jr., Miss Belle N. Baruch, and Mrs. H. Robert Samstag.

(3) H. D. Ratish, J. G. M. Bullowa, J. B. Ames and J. V. Scudi, *J. Biol. Chem.*, **128**, 297 (1939).

(4) E. K. Marshall, Jr., *J. Biol. Chem.*, **122**, 263 (1938).

(5) J. V. Scudi, *ibid.*, **122**, 539 (1939).

(6) A. E. A. Werner, *Lancet*, **1**, 1095 (1938).

(7) O. Dimroth and R. Zoeppritz, *Ber.*, **35**, 984 (1902).

(8) F. J. Moore and R. D. Gale, THIS JOURNAL, **30**, 394 (1908).

(9) W. H. Gray, G. A. H. Buttle and D. Stephenson, *Biochem. J.*, **31**, 724 (1937).