

the ether had distilled, the distillation curve rose sharply and the hydrocarbon fraction was collected over an approximately 5° range. The products were boiled for an hour over metallic sodium to remove any alkyl halide and redistilled. There was thus obtained from isobutylmagnesium bromide, 20 g. (37.5%) of 2,5-dimethylhexane, b. p. (755 mm.) 107–108.5°, d^{20}_4 0.6911, n^{21}_D 1.3922. Egloff² gives b. p. (760 mm.) 109.3°, d^{20}_4 0.6949, n^{20}_D 1.39295 as the preferred values. Similarly, from *s*-butylmagnesium bromide, there was obtained 7.5 g. (13%) of 3,4-dimethylhexane, b. p. (757 mm.) 116–117°, d^{22}_4 0.7199, n^{26}_D 1.4040. Egloff² (p. 54) gives as the preferred values, b. p. (760 mm.) 117.8°, d^{20}_4 0.7195, n^{20}_D 1.4045.

(2) G. Egloff, "Physical Constants of Hydrocarbons," Vol. I, Reinhold Publishing Company, New York, 1939, p. 53.

DEPARTMENT OF CHEMISTRY
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Morpholine Condensations

BY CHESTER B. KREMER, M. MELTSNER AND
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In the course of researches dealing with the condensation of secondary amino alcohols with *o*- and *p*-chloronitrobenzenes, we also investigated the condensing ability of the secondary amine, morpholine. The products obtained have been described by others in a recent article,¹ but were prepared in a manner somewhat different from ours. We are therefore recording our procedures and at the same time including data for one compound as yet unreported.

The general method of procedure was to reflux molar quantities of morpholine and the chloronitrobenzene in the presence of anhydrous sodium carbonate for approximately four hours. The reaction mixture was then steam distilled to rid it of unreacted material. A dark oil, slowly solidifying, remained in the distillation flask in the run with *o*-chloronitrobenzene, an orange-red solid remaining in the case of the para compound. These were recrystallized from benzene: N-(*o*-nitrophenyl)-morpholine, light orange product, m. p. 40–41°; N-(*p*-nitrophenyl)-morpholine, yellow in color, m. p. 149–150°.

Another method used in preparing N-(*p*-nitrophenyl)-morpholine was as follows: 1.0 g. of phenylmorpholine was added to 4 cc. of concentrated sulfuric acid and 4 cc. of concentrated nitric acid added dropwise. The reaction mixture turned red and foamed violently. When the reaction was complete, the mixture was poured

(1) R. H. Harradence and F. Lions, *J. Proc. Roy. Soc. N. S. Wales*, **70**, 406–412 (1937).

onto ice and finally filtered. The filtrate yielded orange crystals of the desired product.

Reduction of the nitro compounds with tin and hydrochloric acid yielded the previously reported N-(*p*-aminophenyl)-morpholine² and the new compound, N-(*o*-aminophenyl)-morpholine, m. p. 98–98.5°; calculated N, 15.73; found, 15.87.

N-(*o*-Aminophenyl)-morpholine can be purified by sublimation, yielding beautiful white platelets. In the pure state the compound is quite stable, but when somewhat impure discolors fairly rapidly on standing.

The present work proves that the compound formed in treating *o*-chloronitrobenzene with diethanolamine is not N-(*o*-aminophenyl)-morpholine as had been tentatively advanced³ in a previous publication.

(2) H. A. Lubs, U. S. Patent 2,004,763 (1935).

(3) Meltsner, *et al.*, *This Journal*, **59**, 2660 (1937).

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Hydrogen and Deuterium Exchange between Nitramide and Water

BY V. K. LA MER AND SEYMORE HOCHBERG

On the basis of measurements of the decomposition rate of proto-nitramide dissolved in mixtures of H₂O and D₂O, La Mer and Greenspan¹ suggested two mechanisms for the decomposition. The first assumed that only one H of nitramide exchanges promptly on being dissolved in D₂O; the second that both H atoms of nitramide exchange promptly.

On the basis of the data then available it was impossible to decide whether the decomposing substrate was HDN₂O₂ or D₂N₂O₂ when proto-nitramide is dissolved in D₂O.

We now present evidence based upon two independent procedures that both H atoms are exchanged promptly for D atoms in a solvent of high deuterium content, and that the rate-determining step in D₂O involves D₂N₂O₂.

I. Decomposition Rate of D₂N₂O₂.—Deutero-nitramide was prepared by the reaction of potassium nitrocarbamate with 99% D₂O and SO₃. On reaction of this nitramide with water (0.01 *N* hydrochloric acid) the observed rate constant, based upon manometric measurement² of

(1) La Mer and Greenspan, *Trans. Faraday Soc.*, **197**, XXXIII, Part 0, 1266 (1937).

(2) Greenspan, La Mer and Liotta, *This Journal*, **59**, 1606 (1937).

the nitrous oxide formed, is $k^* = 387 \times 10^{-5}$ min.⁻¹ (decadic logs) at 35°, in excellent agreement with Baughan and Bell's³ $k^* = 386 \times 10^{-5}$ min.⁻¹ obtained for proto-nitramide in H₂O.

Partially deuterized nitramide prepared from 48% D₂O and sulfur trioxide yielded $k^* = 125.5 \times 10^{-5}$ min.⁻¹ at 24.84° in 0.01 *N* hydrochloric acid in H₂O. La Mer and Greenspan¹ obtained $k^* = 126.6 \times 10^{-5}$ min.⁻¹ under the same conditions for proto-nitramide in H₂O.

II. Direct Exchange.—Proto-nitramide was dissolved in D₂O (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 deuterio-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 D₂O cannot be held constant. Since deuterio-nitramide decomposes in water at the same rate as proto-nitramide and since deuterio-nitramide containing more than one atom of D per molecule may be extracted from a solution of proto-nitramide in D₂O, it is evident that both atoms of hydrogen in nitramide exchange with D₂O 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. DOBSON

A further investigation¹ 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 Hsieh² 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 Hsieh² reported a 25-28% yield, while Tzukervanik and Tokareva³ 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-