

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_D^{21} 1.3922. Egloff² gives b. p. (760 mm.) 109.3°, d_{20}^4 0.6949, n_D^{20} 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_D^{26} 1.4040. Egloff² (p. 54) gives as the preferred values, b. p. (760 mm.) 117.8°, d_{20}^4 0.7195, n_D^{20} 1.4045.

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

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Morpholine Condensations

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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).