NOTES

Optical Properties of Sulfamic Acid

By W. M. D. Bryant

Sulfamic acid, $NH_2 \cdot SO_3H$, has been the subject of crystallographic studies at widely different times by at least two experimenters.[1,2] Only very meager optical data incidental to goniometric observations were reported, and these were inadequate for purposes of identification. Recently M. E. Cupery[3] described a new process for industrial scale preparation of pure sulfamic acid and kindly placed some of this substance at the writer's disposal for optical crystallographic examination.

The methods employed in this study were those described in an earlier paper.[4] The refractive indices and optic axial angles were measured in green monochromatic light (5461 Å.) from the mercury arc. Due to the weak dispersion optic axial angles in white light were not appreciably different. The observed optical data are tabulated.

Refractive indices at 25 $\pm$ 3°: $\alpha = 1.553$; $\beta = 1.563$; $\gamma = 1.568$ all ± 0.003.

Optic axial angle: $2 H_a = 65 \pm 1°$; $2 H_0 = 120 \pm 5°$; $2V = 64°$ (calculated from $2 H_a$ and $2 H_0$ by the tangent relation); $2 V = 63°$ (calculated from $2 H_a$ and β).

Dispersion: weak, indeterminate.

Optical character: negative.

Crystal system: orthorhombic bipyramidal, according to both Fock and Jaeger. However, these investigators each used a different setting, so that the crystallographic b- and c-axes are transposed in their respective treatments.

Crystal habit: tablets and compact prisms from cold aqueous solution; large lozenge-shaped plates on cooling hot aqueous solution; the fused material is glassy.[5]

Optical orientation: the optic axial plane coincides with the principal pinacoid, which is 001 according to Jaeger or 010 according to Fock. The obtuse bisectrix apparently coincides with the a-axis for both settings.

The only numerical optical constant found in the earlier literature is the optic axial angle re-

(1) A. Fock, Z. Krist., 14, 531 (1888); E. Raschig, Ann., 241, 177 (1887).

(2) F. M. Jaeger, Verslag Akad. Wetenschappen, Amsterdam, [1] 35, 68 (1926).

(3) M. E. Cupery, Ind. Eng. Chem., 30, 627 (1938).

(4) W. M. D. Bryant, This Journal, 60, 1394 (1938).

(5) The writer is indebted to Dr. Cutler D. West (private communication) for a measurement of the refractive index of the amorphous phase obtained on cooling molten sulfamic acid. The value reported, $n^{27.5}D$ 1.5048, was measured on an Abbe refractometer using the pure Lamotte product.

ported by Fock[1] as $2 E = circa$ 85°. $2 E$ calculated from the present $2 H_a$ value is about 109 $\pm$ 2°. Since no indications of a second crystal modification of sulfamic acid have been obtained to date, it is believed that Fock's $2 E$ value is erroneous.

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Wilmington, Delaware   Received June 28, 1939

A Method of Coupling Organic Radicals by Means of the Grignard Reagent: A Correction

By John H. Gardner and Lionel Joseph

In a paper of this title published in 1929[1] the statement was made that when iso- and s-butylmagnesium bromides were allowed to react with silver bromide, there is formed a mixture from which no pure compound could be isolated. In connection with some other work in progress in this Laboratory, some results were obtained which led us to doubt the correctness of this statement. Consequently, the experiments were repeated using more effective distilling apparatus than was available at the time the earlier work was done. In this way, we obtained the dimethylhexanes which would be expected from the coupling of the radicals in high purity but in rather poor yield. The other products were gases, very likely the corresponding butanes and butenes, although definite proof of their identity has not as yet been obtained. It is thus definitely established that in all cases so far studied of the action of Grignard reagents on silver bromide, there is no rearrangement.

Experimental

Reaction of Iso- and s-Butylmagnesium Bromides with Silver Bromide.—To an ethereal solution of 1 mol of the Grignard reagent in a flask provided with a mechanical stirrer and two reflux condensers, and cooled in an ice-salt bath, there was added a slight excess of silver bromide, with continual stirring. The mixture was stirred in the cooling bath for a half hour and then for an hour at the boiling point. After the addition of very dilute hydrochloric acid, the organic products were separated by steam distillation, dried over calcium chloride and distilled through a 70-cm. Vigreux column. In both cases, after

(1) J. H. Gardner and P. Bergstrom, This Journal, 51, 3375 (1929).

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 isobutyl-magnesium 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. Egloff[2] gives b. p. (760 mm.) 109.3°, d^{20}_4 0.6949, n^{20}D 1.39295 as the preferred values. Similarly, from s-butyl-magnesium 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. Egloff[2] (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.

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ST. LOUIS, MISSOURI   RECEIVED JULY 3, 1939

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 chloro-nitrobenzene 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-nitro-phenyl)-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)-morpholine[2] 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 advanced[3] 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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NEW YORK, N. Y.   RECEIVED JUNE 27, 1939

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 H_2O and D_2O, La Mer and Greenspan[1] suggested two mechanisms for the decomposition. The first assumed that only one H of nitramide exchanges promptly on being dissolved in D_2O; 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 HDN_2O_2 or $D_2N_2O_2$ when proto-nitramide is dissolved in D_2O.

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 D_2O involves $D_2N_2O_2$.

I. Decomposition Rate of $D_2N_2O_2$.—Deutero-nitramide was prepared by the reaction of potassium nitrocarbamate with 99% D_2O and SO_3. On reaction of this nitramide with water (0.01 N hydrochloric acid) the observed rate constant, based upon manometric measurement[2] of

(1) La Mer and Greenspan, Trans. Faraday Soc., 197, XXXIII, Part 9, 1266 (1937).
(2) Greenspan, La Mer and Liotta, THIS JOURNAL, 59, 1606 (1937).