

NOTES

Optical Properties of Sulfamic Acid

By W. M. D. BRYANT

Sulfamic acid, $\text{NH}_2\text{SO}_3\text{H}$, 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. Cupery³ 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 $25 \pm 3^\circ$: $\alpha = 1.553$; $\beta = 1.563$; $\gamma = 1.568$ all ± 0.003 .

Optic axial angle: $2H_a = 65 \pm 1^\circ$; $2H_0 = 120 \pm 5^\circ$; $2V = 64^\circ$ (calculated from $2H_a$ and $2H_0$ by the tangent relation); $2V = 63^\circ$ (calculated from $2H_a$ 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_D^{25} 1.5048, was measured on an Abbe refractometer using the pure Lamotte product.

ported by Fock¹ as $2E = \text{circa } 85^\circ$. $2E$ calculated from the present $2H_a$ value is about $109 \pm 2^\circ$. Since no indications of a second crystal modification of sulfamic acid have been obtained to date, it is believed that Fock's $2E$ value is erroneous.

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

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In a paper of this title published in 1929¹ 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).