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THE PREPARATION OF THIO-ACETIC ACID

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RECEIVED MAY 2, 1924 PUBLISHED JULY 7, 1924

In a search for a more convenient method for the preparation of thio-acetic acid than that described by Schiff,[1] which consists in the action of phosphorus pentasulfide upon acetic acid, attempts were made to acetylate hydrogen sulfide by passing this gas into acetic anhydride and into acetyl chloride. In neither case was there obtained any evidence of reaction; but when hydrogen sulfide was passed into acetic anhydride containing about 2% of acetyl chloride, absorption took place readily, with rise in temperature, until the gain in weight of the mixture amounted approximately to 80% of the calculated quantity according to the equation

$$(CH_2.CO)_2O + H_2S = CH_3.COSH + CH_3.COOH.$$

On fractional distillation with the use of a column, an approximately 70% yield of thio-acetic acid boiling at 88–91.5° was obtained. The residue boiling above 115° proved to consist principally of acetic acid, though it possessed a powerful and disagreeable odor of sulfur compounds, and appeared to contain an appreciable proportion of high-boiling polysulfides.

On further experimentation it was found, as might be expected, that the reaction between acetic anhydride and hydrogen sulfide could equally well be promoted by a corresponding amount of hydrogen chloride. Concd. sulfuric acid acts in a similar way, except that it tends to oxidize the hydrogen sulfide. A more effective catalyst was found in acetyl bromide, which induces a more rapid reaction.

A study of the amounts of hydrogen sulfide taken up on successive additions of catalyst disclosed the remarkable fact that an absorption of 20 to 30% of the calculated amount is made possible by the presence of about 0.15% of acetyl chloride or 0.22% of acetyl bromide, which are only one-tenth of the amounts necessary to permit the absorption to proceed to above 80%. It is also noteworthy that the superiority of acetyl bromide as a catalyst over acetyl chloride is much more pronounced in this first stage than later.

The catalytic effect of the above-mentioned substances bears a striking similarity to the effect of the same agents on the bromination of acetic anhydride, recently studied by Orton, Watson and Bayliss,[2] who showed that hydrogen bromide was a more effective catalyst than hydrogen chloride. These authors consider that the catalyst induces the formation of

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[1] Schiff, *Ber.*, **28**, 1204 (1895).

[2] Orton, Watson and Bayliss, *J. Chem. Soc.*, **123**, 3081 (1923).

an enolic form of acetic anhydride, $CH_3.CO.O.C(OH) = CH_2$, which adds bromine at the instant of its formation, with subsequent cleavage of the molecule into bromo-acetic acid and acetyl bromide. The action of hydrogen sulfide can be explained by the catalytically induced formation of a reactive form of acetic anhydride, though the exact mechanism of the reaction is still obscure. A strict examination by physicochemical methods would be highly desirable, but cannot be undertaken by the authors.

Experimental Part

When dry hydrogen sulfide was passed into 1020 g. of redistilled acetic anhydride of approximately 85% anhydride content, at room temperature and with continual stirring, no rise in temperature could be noted, and at the end of two days' treatment the gain in weight had amounted to 12 g. The solubility of hydrogen sulfide would thus appear to be around 1.2% at 15–20°.

A parallel experiment with pure acetyl chloride indicated not only the absence of reaction but the negligible solubility of hydrogen sulfide, as no gain in weight was observed.

A mixture of 2040 g. of the same acetic anhydride and 40 g. of acetyl chloride was then treated with a current of dry hydrogen sulfide, with continual stirring, at such a rate that very little gas passed through unabsorbed. The temperature rose rapidly to 45°; and when this fell to 30° it was held at this point by means of a bath. At the end of about 40 hours no further absorption could be observed, and the total weight was found to have increased by 538 g. or 90% of the calculated amount. The mixture was then treated with 45 g. of anhydrous sodium acetate to remove hydrogen chloride, and subjected to systematic fractional distillation through a column; by this means 960 g. of pure thio-acetic acid distilling at 88–91.5° was obtained. This yield corresponds to 72% of the calculated amount based on anhydride of 85% strength, or 80% on the hydrogen sulfide absorbed.

In a subsequent experiment a mixture of 3000 g. of 85% acetic anhydride and 60 g. of acetyl chloride absorbed 804 g. of hydrogen sulfide, or 92% of the calculated amount. In another, 8000 g. of anhydride and 160 g. of chloride absorbed 1750 g., or 75%.

A similar result was obtained on the addition of 1% of hydrogen chloride: 1500 g. of acetic anhydride containing 15 g. of hydrogen chloride absorbed 290 g. (70% of the calculated amount) of hydrogen sulfide in 30 hours at 30–40°.

A mixture of 1490 g. of acetic anhydride and 20 g. of concd. sulfuric acid rapidly absorbed hydrogen sulfide, the temperature rising to 40°. Sulfur separated at the beginning of the reaction, but subsequently redissolved. Absorption was complete at the end of 8 hours, or little more than one-quarter of the time necessary in the case of acetyl chloride or hydrogen chloride. The proportion of hydrogen sulfide absorbed, however, was considerably less, amounting to only 230 g., or 55% of the calculated amount.

Attempts were made to determine the minimum practicable amounts of acetyl chloride and acetyl bromide, by adding successive small quantities of the catalysts and noting the amounts of hydrogen sulfide taken up and the time when absorption ceased after each addition.

With 2 cc. of acetyl chloride, 1500 g. of acetic anhydride at 35–40° absorbed 85 g. of hydrogen sulfide in 27 hours; on the further addition of 12 cc. of acetyl chloride only 7 g. more of hydrogen sulfide was absorbed in nine hours, but the addition of 10 cc. more permitted 78 g. more of the gas to be taken up in seven hours, when absorption again ceased. Another 10 cc. allowed 108 g. of hydrogen sulfide to be absorbed in eight hours; while with one more addition of 10 cc., 60 g. of gas was finally taken up in six hours. The total amount of catalyst was thus 44 cc. (50 g.), and the total weight of hydrogen sulfide absorbed was 338 g. (80% of the calculated amount).

On the other hand, with 2 cc. of acetyl bromide, 135 g. of hydrogen sulfide was absorbed by 1500 g. of anhydride at 35–40°; on the further addition of 2 cc. no more gas was taken up during three hours. At this point 10 cc. more of acetyl bromide was added, when 116 g. of gas was absorbed in six hours, whereupon absorption ceased. On addition of another 10 cc. of bromide, absorption was resumed and 234 g. of sulfide was taken up in 19 hours. The total amount of catalyst was thus 24 cc. (40 g.), and the total weight of hydrogen sulfide absorbed was 485 g. (14% more than the calculated amount). This batch was treated with 25 g. of anhydrous sodium acetate and fractionally distilled, when 660 g. (68% of the calculated quantity) of pure thio-acetic acid was obtained.

Summary

1. Thio-acetic acid may be conveniently prepared in approximately 70% yield by passing hydrogen sulfide into acetic anhydride containing about 2% of acetyl chloride, hydrogen chloride, or acetyl bromide.
2. Acetic anhydride alone and acetyl chloride alone do not react with hydrogen sulfide.
3. Acetyl bromide is a more effective catalyst than acetyl chloride.
4. The progress of the reaction shows two stages, the first of which (20–30%) requires only one-tenth of the amount of catalyst necessary for the completion of the reaction.

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ISOXAZOLINE OXIDES

II. BENZOYL-DIPHENYL-ISOXAZOLINE OXIDE

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RECEIVED MAY 21, 1924 PUBLISHED JULY 7, 1924

It has been shown that the removal of hydrogen bromide from certain α-bromo-γ-nitro ketones leads to the formation of a new type of cyclic compound which was called an isoxazoline oxide.[1] The presence of an isoxazole ring in the new substance was established beyond reasonable doubt but details of structure and the mechanism of many of the peculiar reactions were left for later consideration. The present paper deals with some of these problems.

In order to secure less sensitive compounds, to diminish the number of possible reactions, and to get products with more favorable physical properties, it seemed best, if possible, to introduce an additional group in the 3 position of the oxide. It has now been found that oxides with a phenyl group in this position can be made without difficulty by means of a series of reactions similar to those employed in the earlier work. Thus, phenyl-

[1] Kohler, THIS JOURNAL, **46**, 503 (1924).