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THE ACTION OF SULFURIC ACID IN THE PREPARATION OF CERTAIN ALKYL HALIDES

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During the course of our work, we had occasion to prepare alkyl halides of higher purity than ordinarily obtained. Michael and his co-workers³ came to the conclusion that the purest halides were made by heating the corresponding alcohols with aqueous hydrobromic acid, according to Norris'⁴ suggestion. They removed the small amount of unsaturated materials formed with potassium permanganate.

However, sulfuric acid is commonly used in the preparation of these halides.⁵ While we have suspected for a long while the detrimental effects attending the use of this acid, we now have definite experimental proof that halides prepared by its aid tend to spoil more easily on keeping, developing colors and free halogen acid. We have shown that sulfuric acid splits out halogen acid, forming small quantities of olefins, which are then polymerized, the polymers adding on halogen acid to form unstable products and violet colors.

We have found that distilling the halide from a mixture containing sulfuric acid results in a decided increase in high-boiling products, particularly in the case of sensitive bromides, such as *isopropyl*, *sec.-butyl* and *isobutyl*. Except in the cases of *sec.-* and *isobutyl* bromides, all the bromides from ethyl to *n*-amyl contained very little high-boiling products when they were prepared by slowly distilling the alcohol from hydrobromic acid alone, according to Norris'⁴ procedure. The amount of such products was greater for *isobutyl* than for *sec.-butyl* bromide. If the bromide obtained from the first distillation in the Norris method was returned to the acid flask and redistilled to improve the yield, as sometimes recommended, the additional time of heating resulted in an increase in polymers and other undesirable materials.

Allyl chloride and allyl bromide are commonly prepared by the aid of heat, and also by the use of sulfuric acid.⁵ These halides, as ordinarily prepared, soon develop an extremely pungent odor, becoming lachrymators, and the bromide also develops a color. A simple cold process has been worked out for preparing these halides. The high-boiling residue

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³ Michael, Scharf and Voigt, *THIS JOURNAL*, **38**, 653 (1916); Michael and Zeidler, *Ann.*, **393**, 81, 104 (1912); Michael and Leupold, *ibid.*, **379**, 263, 305 (1910).

⁴ Norris, *Am. Chem. J.*, **38**, 639 (1907); *THIS JOURNAL*, **38**, 1075 (1916).

⁵ "Organic Syntheses," John Wiley and Sons, Inc., New York, **1**, 1 (1920).

is very small in this process. Furthermore, one distillation gives a product which remains for months water-white and maintains a perfectly clean odor, without any trace of sharpness, when stored in the dark in an ordinary bottle. The yields are poorer than those obtained in "Organic Syntheses,"⁵ but our process is recommended when one wishes to sacrifice yield for quality, in making these halides for special work. The process also involves a minimum of apparatus and hardly any attention, although it requires a few days' time.

Experimental

Allyl Alcohol.—Solid potassium carbonate is added to Eastman practical allyl alcohol. The upper layer is removed and given the same treatment. After twenty-four hours it is filtered and used without distillation.

Allyl Chloride.—The alcohol is mixed with 8 times its volume of commercial hydrochloric acid (sp. gr., 1.19) in a suitable well-corked bottle. After ten days the upper layer is washed once with 10% sodium hydroxide and twice with 15% sodium chloride, which minimizes emulsion formation. It is dried over calcium chloride and distilled. The yield of material boiling from 45–47° is from 55–65%. As an example: 204 cc. of crude alcohol with 1632 cc. of acid gave 144 g. of chloride.

If a small amount of halide is wanted in a hurry, the reaction is carried out in a sealed Pyrex bottle immersed in hot water (60°). Most of the yield, over 80%, is obtained in three hours.

Allyl Bromide.—A similar process is used. The alcohol: 48% acid ratio in cc. is 1:7. The yields are 60–65%. Example: 410 cc. of crude alcohol with 2870 cc. of acid gave 478 g. of bromide, boiling from 69–73°. The excess acid is recovered by distillation.

Allyl Iodide.—The alcohol: acid (sp. gr. 1.7) ratio in cc. is 1:6. The time is five days and the yield is 75–80%. Example: ten cc. of crude alcohol gave 10.3 cc. of iodide boiling from 99–103°.

Washing the Crude Halides.—In preparing *sec.*-butyl and *sec.*-amyl bromides by the Norris⁴ method, the final products were extracted several times with concentrated sulfuric acid before washing. In some cases the halides were distilled from sulfuric acid. Invariably they turned pink on drying over calcium chloride. During distillation, hydrogen bromide was evolved, the material in the flask gradually assuming colors from pink through lavender to violet-red. The higher the temperature and the longer the contact with sulfuric acid, the worse were the colors and acid evolution. Repeated distillation tended to decrease these evils. We have found Norris' original recommendation of washing with concentrated hydrochloric acid a much better way of getting out the unchanged alcohol. By washing alkyl chlorides in this way and alkyl bromides with 48% hydrobromic acid, the troubles mentioned were reduced to a minimum.

In preparing pure bromides for the determination of their physical properties, to be reported by one of us in a forthcoming paper, the crude samples made by the Norris method were washed repeatedly with small portions of 48% hydrobromic acid until no volume change occurred. All alcohol and possibly some unsaturated products were thus removed. On returning the washings to the preparation flask and redistilling, a further quantity of bromide of a somewhat poorer quality was obtained. Bromides washed in this way gave no emulsion difficulties and on distillation gave very small light colored residues. Washing with sulfuric acid gave emulsions and highly colored residues with a disagreeable odor in the case of bromides easily attacked, *e. g.*, *sec.*-butyl, particularly if the time of contact was long, even in the cold.

Careful fractionation of the products dried after the hydrobromic acid washing gave

good yields of bromide of excellent purity. Constant boiling *isopropyl* bromide was obtained in 42% yields and *sec.*-butyl bromide, boiling over a 0.05° range, in 18% yields. These pure bromides gave no test for unsaturated materials.

The Formation of Olefin and the Polymerizing Action of Sulfuric Acid.—Fifty cc. of secondary butyl bromide was made according to Norris' procedure and washed with hydrobromic acid. The colorless distillate had no odor of hydrogen bromide, but smelled somewhat unsaturated. The residue in the flask amounted to 3 cc. and had a deep violet color. On redistillation, the first 3 cc. smelled highly unsaturated and used up 1.5 cc. of a 10% bromine solution in carbon tetrachloride. A fraction of a cc. of the colored residue was diluted with chloroform until the color just faded. On adding 1 cc. of acetic anhydride and then one small drop of concentrated sulfuric acid (Burchard test)⁶ a faint violet color appearing in one-half minute, developed to a distinct color in a few minutes. A fraction of a cc. was diluted with chloroform to a light pink. The Burchard test gave an immediate blue-violet tint and increased depth of color. In ten minutes it was fairly deep greenish violet. After two days the color had faded badly and a ring of purplish red resin had formed around the surface of the liquid. This substantiates the theory proposed by one of us (to be published later) that the Burchard test reagents and similar reagents cause polymerization to form colloidal particles. The color effects are then understood by applying Wo. Ostwald's colloidal theory of color.⁷

In making secondary butyl bromide, by heating the alcohol with acid in a sealed tube at 60°, the amount of unsaturation found was 1%, calculated as dibutene. Five cc. of secondary butyl bromide containing 2% of *sec.*-butyl alcohol was shaken with 5 cc. of concentrated sulfuric acid at room temperature. The volume change indicated that the alcohol had been extracted but even after a few minutes' shaking a small amount of emulsion had formed. After standing for two hours the attack on the bromide was pronounced and standing overnight gave a viscous, dark brown mixture. The use of 70% sulfuric acid reduced the trouble but a small amount of viscous oil also was formed after standing overnight.

Isopropyl, *sec.*-butyl and *sec.*-amyl bromides, especially after sulfuric acid treatment, on drying with calcium chloride assume delicate light blues, pinks, violets and lavenders and become opalescent, the degree of opalescence depending on the depth of the shade of red. Experiment showed that these effects are chargeable to the sulfuric acid treatment.

Three cc. of pure *isopropyl* bromide was added to 2 cc. of chloroform. One cc. of acetic anhydride and one drop of concentrated sulfuric acid were then added. In forty-eight hours a dark violet color resulted.

One drop of a 2,4-hexadiene dimer was dissolved in 5 cc. of chloroform. One drop of concentrated hydrochloric acid was added and the whole was shaken. Within half a minute the solution had assumed the typical pink color developed by ordinary *sec.*-butyl bromide on standing over calcium chloride, showing that the colors also could be produced by the action of the halogen acid on the unsaturated polymers.

Not all bromides are noticeably attacked by sulfuric acid. *n*-Butyl bromide seems to be the most stable of all those studied by us. When washed with either sulfuric or hydrobromic acid, it gave an equally good product. The residues from the distillations show only a faint color. Ethyl and *n*-propyl bromides are more sensitive. In fact, they are sufficiently sensitive for us to recommend only the hydrobromic acid treatment. *Isobutyl* bromide is quite sensitive and the secondary bromides are so easily attacked that we feel it is very undesirable to use sulfuric acid when pure products are desired.

⁶ Burchard, *Chem. Zentr.*, I, 25 (1890).

⁷ Wo. Ostwald, *Kolloidchem. Beihefte*, 2, 409-488 (1911); *Chem. Zentr.*, II, 1407 (1911).

Summary

1. Convenient methods for making allyl halides are described. Allyl bromide and allyl chloride made in this way do not develop objectionable odors and colors on standing.

2. Sulfuric acid is to be condemned in the preparation of pure alkyl halides.

3. In the preparation of pure alkyl halides, even by the Norris method, a small amount of unsaturated materials is formed.

4. Sulfuric acid not only polymerizes these materials but attacks sensitive halides to form more unsaturated materials.

5. The colors of decomposing halides are caused by the action of sulfuric acid and halogen acid on the unsaturated materials.

6. The Norris procedure gives the purest products.

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OXIDATION OF UNSATURATED COMPOUNDS.

I. OXIDATION OF CROTONIC AND ISOCROTONIC ACIDS, OF THE LACTONE OF 3-HYDROXY-ISOCROTONIC ACID AND OF MALEIC ANHYDRIDE

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I. Oxidation of Crotonic and Isocrotonic Acids

According to the van't Hoff-Wislicenus theory there are two isomeric 2-methylacrylic acids, the *cis* and *trans*. In the opinion of Auwers² the *cis* form represents *isocrotonic* and the *trans* form crotonic acid. Since this pair of acids has active double bonds and has been thoroughly studied from the point of view of *cis-trans* isomerism, these acids are very well suited for the study of the addition of hydroxyl groups.

Several different methods for the oxidation of crotonic acid are reported in the literature. Melikoff³ oxidized it with hypochlorous acid and prepared a dihydroxybutyric acid (m. p. 80°) through the intermediate formation of 2-methylglycidic acid. Fittig and Kochs⁴ used barium permanganate, Glattfeld and Woodruff⁵ potassium chlorate; in both cases the identical dihydroxybutyric acid, m. p. 74–75°, was obtained.

The pure, crystallizable *isocrotonic* acid had not previously been used for oxidation. Melikoff and Petrenko-Kritschenko⁶ succeeded in pre-

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² Auwers and Wissebach, *Ber.*, **56**, 715 (1923).

³ Melikoff, *Ann.*, **234**, 197 (1886).

⁴ Fittig and Kochs, *ibid.*, **268**, 7 (1892).

⁵ Glattfeld and Woodruff, *THIS JOURNAL*, **49**, 2309 (1927).

⁶ Melikoff and Petrenko-Kritschenko, *Ann.*, **266**, 359 (1891).