

in water will underlie the alcohol. This last will be colored more or less.

The alcoholic solution, if any carbon disulphide was in the gas, will contain a so-called xanthate of potash, and may be boiled and tested for sulphuretted hydrogen.

A more demonstrative method is to add excess of copper salt, filter out the precipitated cupric compounds, and pour ammonia through the filter paper, when a highly characteristic precipitate of cupric xanthate will remain on the filter paper.

XIV.—UPON THE DIRECT CONVERSION OF THE AROMATIC AMIDES INTO THEIR CORRESPONDING AZO-COMPOUNDS.

BY ALBERT R. LEEDS.

I have already published in another place (JOURNAL AMERICAN CHEMICAL SOCIETY, 3, 16,) the results obtained by the action of hydrogen peroxide upon benzene. The latter is gradually converted into phenole-oxalic acid, and a small amount of a yellow coloring matter being formed at the same time.

Phenole itself is but slightly acted upon by hydrogen peroxide in the cold, but at the boiling point undergoes conversion into a tarry substance.

Naphthalene, when digested with hydrogen peroxide, yields a small amount of naphthole. Naphthole itself is not affected to any notable extent by hydrogen peroxide in the cold, but at the boiling point is changed to a tar.

When anthracene is dissolved in glacial acetic acid, and the precipitate obtained on the addition of solution of hydrogen peroxide is digested with excess of the latter re-agent, the anthracene is slowly converted into anthraquinone. Three grms of anthracene, boiled for three days with hydrogen peroxide, in a flask attached to a return-cooler, were changed almost entirely into anthraquinone, the brown coloring matter formed at the same time being too small in amount to permit of its being experimented upon successfully.

Benzenesulphonic acid was slightly acted upon, a brown color being imparted to its solution after boiling for a number of hours with hydrogen peroxide, and the acid crystallising out from the liquid in small colorless crystals, identical in appearance with the original body before its treatment with peroxide.

The preceding results show that in certain cases hydrogen peroxide operates upon organic bodies by the substitution of hydroxyl; in other cases, by direct oxidation, and in the third place, by both actions combined.

The experiments were therefore extended to the aromatic amides with the hope that hydroxylated derivatives of these compounds might be obtained. The amide was converted into the acetate, or when this not possible, it was dissolved in excess of glacial acetic acid, and a solution of hydrogen peroxide, containing 1.2 per cent. of peroxide, added in successive portions. Heating of the liquid had to be avoided, the amide in every instance being changed to a tarry substance. This result indeed happened in most instances, even when the experiment was conducted at common temperatures or with gentle warming. The following is a brief summary of the results obtained with the compounds thus far operated upon :

Diphenylamine yielded a large amount of a black liquid and a black tar.

Dimethylaniline gave a very dark red liquid with a black residue soluble in alcohol.

Xylidine formed a claret colored liquid with a blackish residue dissolving in alcohol to a dark purple solution.

Naphthylamine gave a rose colored liquid with a brownish-black residue.

Similar results were obtained with orthotoluidine, the solution acquiring a ruby color, and a blackish tarry residue soluble in alcohol being formed.

Failing to obtain by careful sublimation, or by treatment with ligroine, alcohol and other solvents, any crystalline bodies from the above products, their further study was abandoned.

Aniline and paratoluidine acted differently. The solutions of their acetates in hydrogen peroxide quickly threw down on gentle warming, copious precipitates of a brownish crystalline appearance. At higher temperatures there was a formation of tar. The precipitates came down principally on the first treatment with the peroxide. On filtering them off and adding an amount of the peroxide in excess of the calculated quantity, the second crop of crystals was small, and the larger portion of the aniline or paratoluidine acetate remained behind in the solution.

The precipitates, after washing and drying, were sublimed very slowly, since the small amounts of accompanying tarry matter interfered seriously with the operation when the temperature was not carefully regulated at the lowest practicable point. The sublimate from the paratoluidine formed yellow needles, some of them exceeding two inches in length. They were repeatedly crystallised from alcohol, in which they are not very readily soluble and were finally

obtained as magnificent orange needles. Their melting point was 143–144°.

0.2806 grm of the substance yielded on combustion 0.8123 grm carbonic acid and 0.1763 grm water. These results agree with those calculated on the supposition that the body is azotoluole, $C_{11}H_{11}N_2$:

	Calculated.	Found.
Carbon	80.00	79.28
Hydrogen	6.66	6.98
Nitrogen	13.34	13.51

The same body has recently been obtained by Barsilowsky* by the action of very dilute potassium permanganate solution upon toluidine sulphate. This reaction yielded a very small product, and Barsilowsky afterwards used a solution of potassium ferricyanide and caustic potash with better results. The orange crystals thus obtained melted at 144°, and were identical in their physical properties both with the parazotoluene, derived by Petrieff from the reduction of nitrotoluene, and with the substance described by the author. By the action of hydrogen peroxide, therefore, upon paratoluidine it is converted directly into parazotoluene.

The sublimate from the aniline product yielded large red crystals, together with some accompanying yellow oil. This sublimate had a melting point of 66°, showing that the body was azotoluene (m. pt., 66°.5).

XV.—ON THE EXAMINATION OF CARBON DIOXIDE IN THE FLUID CAVITIES OF TOPAZ.

BY ALEXIS A. JULIEN.

Literature.

- SIR DAVID BREWSTER. See for ref., J. D. Dana, system of Mineralogy, articles Brewsterline and Cryptolineite; also *Phil. Mag.*, 1847, 3, **31**, 497; 1853, 4, **5**, 235, etc.
 R. TH. SIMMLER. *Pogg. Ann.*, 1858, **105**, 460.
 H. VOGELSANG and H. GRISSLER. *Pogg. Ann.*, 1869, **137**, 56.
 ISAAC LEA. *Proc. Ac. Nat. Sci., Phil.*, May, 1876.

Recent studies of the fluid contents of the cavities of minerals, especially of the fluids separated in sufficient quantities for analytic examination, have established more definite views concerning their true character. The liquid first observed by Brewster in Brazilian topaz, and which has since passed by the name Brewsterline or Brewsterlineite, has been shown by Simmler, Vogelsang and Geissler,

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