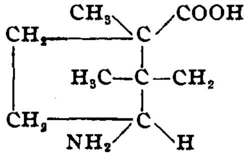
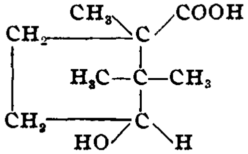
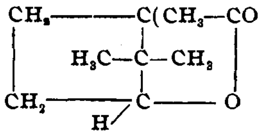
expected, still, the probability of a rearrangement was not overlooked. *Cis*-camphonololactone can be formed from isoaminocamphonanic acid by a rearrangement on the secondary carbon atom thus:


Isoaminocamphanic acid.


(Intermediate hydroxy acid.)


Cis-camphonololactone.

The alkalin portion was acidified with hydrochloric acid, and extracted with ether. From this a few drops of a light yellow oil was obtained. It was shown to be an unsaturated acid by its solubility in a solution of sodium carbonate, and by this solution instantly turning brown a solution of potassium permanganate. The acid was distilled at 150° and 60 mm., but with considerable decomposition.

The portion which contained the substances that are not distilled over with steam, presumably the hydroxy acid, was extracted with ether. From this a small amount of a dark colored oil was obtained, which did not crystallize, but became very viscous on standing. A boiling point could not be obtained, as it decomposed at 160° with considerable charring. It was shown to be a saturated acid by its conduct towards sodium carbonate and potassium permanganate.

URBANA, ILL.

THE PYROSULFATES OF SODIUM AND POTASSIUM AS CONDENSING AGENTS.

BY ALLAN F. ODELL AND CLEVE W. HINES.

Received November 18, 1912.

The availability of the pyrosulfates of sodium and potassium as condensing agents seems never to have been taken advantage of except in the preparation of acrolein from glycerol, and in the preparation of certain alkyl esters of aliphatic and aromatic acids.[1] The ready conversion of these salts into the bisulfates by the addition of water should be the means for their effective application as mediums to abstract water in organic syntheses.

Attention was drawn to this probability when an attempt was made in this laboratory to find a better method for the sulfonation of the mixed alkyl aryl ketones—acetophenone in particular. This ketone could not be sulfonated satisfactorily by the use of these salts in combination with sulfuric acid. At temperatures up to that of the water bath, acetophenone yielded triphenylbenzene in varying quantities. The greater part of the acetophenone was recovered, most of the time, unchanged.

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[1] Bogojawlenski, *Ber.*, 38, 3344 (1905).

The same experiments conducted at temperatures from 140° to 200° yielded a large amount of a brittle, dark colored resin. This was probably a decomposition product of the ketone.[1]

As a method for the preparation of triphenylbenzene, the experiment carried out at low temperatures is probably more convenient than the usual method of employing hydrochloric acid as a condensing agent.[2]

The most favorable conditions for the formation of triphenylbenzene were determined in the following experiment:

Twenty-five grams of acetophenone are mixed with 52 grams of potassium pyrosulfate, freshly prepared and finely powdered, and about 4 grams of concentrated sulfuric acid stirred into the mixture. This is then heated in a closed flask in an air bath to 45° for 30 hours. At the end of this time, the solid mass is treated once with 85% alcohol, to extract the unchanged acetophenone, then with hot water until the acid sulfate of potassium is dissolved. The residue remaining, when recrystallized from glacial acetic acid, gives glistening white needles of triphenylbenzene, m. p. 172°. The yield varies from 65% to 85% of the theory.

This particular condensation would not take place with the pyrosulfate alone, even when heated with it in a sealed tube for 6 hours to 180°. Neither would it take place with sulfuric acid alone.

With the idea of testing the applicability of the pyrosulfates in other condensations, a number of experiments were carried out. The results of these go to show that these salts may be used where a mild condensing agent is required.

The general method employed consisted of mixing the substances to be condensed in the molecular proportions required and adding one molecule of the pyrosulfate for each molecule of water to be abstracted. In the examples given below, no solvent was used to bring about the intimate mixture of the reacting substances.

The following cases were thought to be of sufficient value to give the processes in detail:

Benzal-aniline.—Twenty-one grams of benzaldehyde, 20 grams of aniline and 52 grams of potassium pyrosulfate are heated on the water bath for thirty minutes. The resulting solid is treated with ether, whereby the benzal-aniline is extracted and is obtained almost pure on evaporation of the solvent. The yield is almost quantitative.

Benzal-malonic Acid.—Nine grams of malonic acid, 10 grams of benzaldehyde and 28 grams of pulverized potassium pyrosulfate are mixed and heated in the boiling water bath for 3 hours. The resulting mass is treated with 150 cc. of boiling water, heating until everything dissolves, and

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[1] *Ber.*, 7, 1123.

[2] *Loc. cit.*

filtered. On cooling slowly, benzalmalonic acid crystallizes out in an almost pure condition, m. p. 192–195°. The yield is about 75% of the theory.

Benzal-acetophenone.—Twelve grams of acetophenone, 10 grams of benzaldehyde and 25 grams of pulverized sodium pyrosulfate are mixed and heated in the boiling water bath for 6 hours. The residue is treated with 75 cc. of water and boiled to dissolve the acid sulfate. The unchanged acetophenone and benzaldehyde form a layer on the top of the resulting solution, from which the benzal-acetophenone crystallizes out on standing. The crystals are drained off and washed with cold water, then with dilute alcohol. The compound so obtained is almost pure, with a melting point of 57° to 58°. The yield is about 30% of the theory.

Acetanilide.—Thirty grams of glacial acetic acid, 25 grams of aniline and 25 grams of pulverized sodium pyrosulfate are heated in a flask, with an air condenser, in an oil bath at 130–140° for 1 hour. The resulting mass is powdered and boiled with 300 cc. of water until everything dissolves. On cooling, acetanilide of m. p. 113° crystallizes out. The yield is almost quantitative.

Efforts to produce condensation between aniline and the phenols were not so successful. Condensation apparently took place, probably with the formation of sulfuric acid esters,[1] which were combined with aniline. The products resulting from the crystallization of the reaction mixture from water, however, consisted chiefly of aniline sulfate. These were not further examined.

When one molecule of benzaldehyde is mixed with one molecule of resorcinol and one molecule of potassium pyrosulfate and heated in the water bath for twenty minutes, a presumably quantitative yield of an insoluble, amorphous, canary yellow product results. This contains sulfur, probably as a sulfuric ester also. The compound dissolves readily in potassium hydroxide to a deep red solution, from which it may be reprecipitated on the addition of hydrochloric acid. It does not melt below 300°. This substance will receive more thorough examination at a later date.

As condensing agents, the pyrosulfates would seem to serve excellently in instances analogous to those that have been cited. They have the advantage of being clean and convenient to handle, and do not cause the formation of resinous or tarry products when used alone. This was found to be the case in a large number of experiments which were carried out qualitatively. Furthermore, it is a simple matter to prepare them quickly by fusing the normal sulfates of sodium or potassium with slightly more than the theoretical amount of sulfuric anhydride.

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[1] Cf. Lassar-Cohn, *Arbeitsmethoden*, pps. 312–3, 4th Aufl.

Summary.

The pyrosulfates of sodium and potassium are convenient and effective as mild condensing agents.

Good results were obtained by means of these agents in the preparation of triphenylbenzene, benzal-aniline, benzalmalonic acid, benzal-acetophenone, and acetanilide.

The pyrosulfates cannot be used to condense the phenols with other substances.

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[CONTRIBUTION FROM THE DIVISION OF DRUGS, BUREAU OF CHEMISTRY.]

A CHEMICAL INVESTIGATION OF THE OIL OF CHENOPODIUM. II.

BY E. K. NELSON.

Received October 19, 1912.

Rearrangement of Ascaridole.—As shown by Schimmel's chemists[1] ascaridole suffers a molecular rearrangement when heated with caution to 150°, while the author has found[2] that hydration of ascaridole by shaking it with solution of ferrous sulfate affords the same glycol which is obtained by hydrating the conversion product obtained by heating. This shows that the formation of glycol on treatment with ferrous sulfate must be accompanied by the same rearrangement which takes place on heating ascaridole.

The rearrangement of ascaridole by heating it to 150° and the substances obtained by shaking the conversion product with dilute sulfuric acid have been further studied. It has been found that in addition to the glycol which has been already described, and which is the chief product, two other crystallin water soluble substances are formed, one in considerable, the other in lesser amount. As these products are quite easily decomposed by the action of mineral acids, it was found necessary, in order to obtain them, to use very dilute sulfuric acid in hydrating. The conversion product was prepared[3] and rectified by distillation at 4 mm. Fifty grams of the product were stirred for 2 hours with 500 cc. of 0.2% sulfuric acid, the oil going almost completely into solution. The glycol of m. p. 62.5–64° was extracted directly from the solution with ether, the residue from which crystallized on seeding with the solid substance.

The acid solution was exactly neutralized, concentrated to about one-fifth its volume, and extracted with chloroform. A sirupy residue was obtained from the chloroform, which, after adding a very little water, became crystallin on standing. The substance thus isolated in small

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[1] *Schimmel's Report*, April, 1908.

[2] THIS JOURNAL, **33**, 1404.

[3] *Schimmel's Report*, April, 1908; THIS JOURNAL, **33**, 1404.