

oxymethylene and ethyl malonate with acetic acid as a condensing agent, and Knoevenagel<sup>4</sup> obtained it from 40% formaldehyde and ethyl malonate in the presence of a secondary amine.

Evidently in Kamm and Waldo's  $\beta,\beta'$ -dichloro-diethyl ether the ether linkage is very much more stable than in the isomeric  $\alpha,\alpha'$ -dichloro-diethyl ether or the lower homolog, *sym*-dichloro-dimethyl ether which is likewise an  $\alpha$ -derivative.

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**Beta Naphthol.**—In teaching laboratory courses in organic chemistry, the writer has the conviction that not enough emphasis is being placed on the reaction in which an aromatic sulfonic acid is converted into a phenol by fusion of the sodium salt of the acid with sodium hydroxide. Lately, this reaction has become of first importance. The reaction has a wide application, and for that reason examples of it should be in our courses. In our modern laboratory manuals the preparation of  $\beta$ -naphthol which is one of the simplest and most readily made phenols, is either left out or is described by directions that will not yield the substance in good amount and of good quality.

In working with the preparation of the sodium salt of  $\beta$ -naphthalene sulfonic acid and its conversion to  $\beta$ -naphthol, certain observations not specifically mentioned in the literature have been made. These facts should be helpful to other teachers and to those engaged in research problems involving work with sulfonic acids and phenols.

After sulfonation of an aromatic hydrocarbon, the usual procedure is to neutralize the mixture with lime. This leaves the unsulfonated hydrocarbon and most of the calcium sulfate undissolved. On filtration, the filtrate contains the soluble calcium sulfonate, together with quite a little dissolved calcium sulfate. The latter will continue to crystallize from solution for at least several days.<sup>1</sup> The filtrate from the calcium sulfate contains the calcium sulfonate, and usually this solution is treated directly with a solution of sodium carbonate until the calcium is all precipitated as the normal carbonate. We have found that the only way to obtain a satisfactory precipitation at this point is to use pure anhydrous sodium carbonate from a freshly opened container. The use of the hydrated

<sup>4</sup> Knoevenagel, *Ber.*, **27**, 2346 (1894).

<sup>1</sup> Namba, *J. Soc. Chem. Ind.*, **40**, 281T (1921).

sodium carbonate always led to unsatisfactory results.<sup>2</sup> The sodium salt thus formed was not found to yield  $\beta$ -naphthol on fusion with sodium hydroxide. All preparations of hydrated sodium carbonate available to us seemed to contain considerable bicarbonate. This formed a soluble calcium hydrogen carbonate that was very difficult to convert to the normal carbonate. Repeated boilings and evaporations did not completely remove the carbon dioxide. The use of pure anhydrous sodium carbonate gave a product that was completely soluble in water and did not effervesce when moistened with strong mineral acid.

In the conversion of the sulfonate into the phenol, a second precaution necessary for the success of the reaction is a fusion in the absence of conditions that can oxidize the product and bring about a decreased yield. To this end, iron crucibles are avoided and commercial hydrochloric acid is not used in the recovery of the product of the fusion.

We have found the following to be the best conditions for the laboratory preparation of  $\beta$ -naphthol.

In a 75cc. nickel or silver crucible fuse 30 g. of sodium hydroxide and 3 cc. of water. Heat to 270° and add 10 g. of finely pulverized sodium naphthalene sulfonate that is completely soluble in water and shows the presence of no carbonates.<sup>3</sup> Gradually increase the temperature of the contents of the crucible to 315°. There is a tendency toward boiling over and the mixture requires slow heating. In about 20 minutes after the sodium salt has been added, the mixture reaches the latter temperature where it is allowed to remain for about 3 minutes. If the sodium salt is quite pure, no marked tendency toward boiling over will be observed. After fusion, pour the mixture onto a cement floor or table top, dissolve in water, cool slightly and acidify strongly with chemically pure hydrochloric acid. Allow the mixture to stand overnight, filter, wash with a little water and allow to dry in the funnel. The product will be only slightly colored and on sublimation will yield beautiful flakes resembling naphthalene. The above directions have been used repeatedly in our classes and give a high grade product in good yield. Almost all such fusions give lower yields than a calculation calls for, but by watching the details the yield can be increased.

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<sup>2</sup> Our attention has been called lately to the fact that is not widely known perhaps, that pure anhydrous sodium carbonate left exposed to the air for several days will absorb carbon dioxide in an amount sufficient for the conversion of 20% of the original carbonate into bicarbonate. Sodium carbonate of this latter quality should not be used in converting a calcium sulfonate into a sodium sulfonate.

<sup>3</sup> We have found an ordinary army rifle shell partly filled with a high boiling paraffin serves well as a protector for the thermometer bulb. The fused sodium hydroxide dissolves some zinc out of the brass shell but one shell has been used for more than 50 fusions and is still practically unchanged.