

ON THE PREPARATION OF THIOPHENE.

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Pursuing the investigation in regard to the formation of anthraquinone from thiophenalddehyde¹ it was found that thiophene could be prepared at about one-fifth of the price of the imported article (nearly forty dollars per pound), and it was therefore made in the laboratory.

Although the preparation of thiophene is not new², nor especially difficult, it may be useful to others to have a description of the method in detail.

The preparation of thiophene involves the use of sodium succinate and phosphorus trisulphide. Thiophene is produced when these two substances are jointly subjected to destructive distillation.

Sodium Succinate.—Succinic acid is more easily obtainable than its salts. In each case 450 grms. of succinic acid (about one pound) were dissolved in a litre of boiling distilled water. The acid used was the intermediate one of the three kinds offered in the market, called "pure." It was clean, white and of very nearly the correct melting point, between 178° C. and 185° C. It is sufficiently pure for our purpose. The gently boiling solution was very gradually saturated with the so-called dry sodium carbonate. This latter is *not* dry, *nor* pure, but loses, when fused, 31.66 per cent., which loss is due to water and also to carbon dioxide, bicarbonate being present. It does *not* contain ammonium salts, as proved by Nessler's test. 600 grms. of such sodium carbonate, finely powdered, were used.

After neutralization, the liquid was allowed to stand over night. About 800 grms. of well formed, colorless crystals of sodium suc-

¹ J. Am. Chem. Soc., **12**, 26.

² Ber., **18**, 454.

cinates were obtained the following morning. The mother liquor was poured off and evaporated on the water bath, stirring towards the end of the process. The resulting mass was more yellow than the crystals first obtained. The crystals were allowed to drain in a large funnel on a tuft of glass wool, a small cylinder of wrapping paper being inserted in the tube of the funnel. Both crops were then dried in a steam oven. The crystals offer no difficulty in drying, but the evaporated mass must be put into a dish, because it liquifies partly during the first hours of drying. After two days treatment in this way all of the salt was spread upon filter paper and put into a drying oven kept constantly at about 110°C . Continuing this treatment for a week, the six mols. of water, with which sodium succinate crystallizes, were finally expelled. The mass does not powder very easily and spreads an irritating dust. It is passed through a sixty mesh sieve and kept in well-stoppered bottles.

Phosphorus Trisulphide.—This mixture, which, as a dehydrating agent we owe to Kekulé, was prepared in the following manner. Absolutely dry red phosphorus, and dry washed flowers of sulphur were most intimately mixed in the proportion of 62 P to 96 S, first on a large sheet of paper with a broad spatula, crushing every small lump of phosphorus which might remain, then in a mortar. The mixture has to be fused together. Since I prepared $2\frac{1}{2}$ kilos. of it in a very short time, with little loss of material, I will give the mode of procedure.

Take two sound Berlin porcelain crucibles, 2 in. deep, $3\frac{1}{4}$ in. upper and $1\frac{1}{2}$ in. lower diameter, with covers. Put each into an iron ring on a tripod, so that the ring clasps the crucible at about two-thirds of its height. Work under a good hood to carry off vapors. With a porcelain spatula, nearly as broad as the mouth of the crucible, put as much as the spatula will comfortably hold into the crucible. Cover and heat gently with a Bunsen burner. A slight explosion is heard, a faint flame becomes visible through the translucent crucible and white vapors are forced out at the edge of the cover. Remove the burner; it is unnecessary to heat the crucible further. The next charge is added as soon as no spontaneous combustion occurs on lifting the cover of the crucible.

Gradually and in small portions, as indicated, the crucibles are filled, finally almost to the edge, with the quietly flowing molten mass. The covers must not be opened unnecessarily. The crucibles are allowed to cool. When quite cool they are tilted over a clean piece of paper and a gentle tap brings out the cone. The mass is crystalline in part, waxy and of a dark grayish yellow. It is broken into large pieces and these are at once transferred to quite dry, wide salt-mouthed bottles and the stoppers are sealed with paraffine.

The loss of material by burning, if the process is carried out as above, is slight, being between six and eight per cent. I obtained, for instance, from a charge consisting of 124 grms. of phosphorus and 192 grms. of sulphur, 298 grms. of the so-called phosphorus trisulphide, thus having lost but 18 grms. The average charge for *two* crucibles of the size mentioned is a little greater. Most of the loss involved occurs at the beginning of the operation, when the crucibles are then only partly filled and air is more abundant within them than afterwards.

*Thiophene.*¹—The process of destructive distillation of sodium succinate with phosphorus trisulphide was carried out in a tubulated, two litre retort, higher than broad, connected with a Liebig's condenser, four feet long. A smaller cooler may do as well or even a well cooled flask, into which the neck of the retort reaches, might serve, but a long condensing tube retains more of a semi-solid yellow substance, which is also formed in this process, and thus the distillate obtained is purer.

Not more than about 155 grms. of sodium succinate are weighed out and mixed intimately with the double quantity, viz., 310 grms. of well crushed phosphorus trisulphide. The powdering of the trisulphide is facilitated by adding a little of the dry succinate powder from the start. The mixture is run, by means of a wide funnel, into the retort, which it nearly half fills. The bottom of the retort rests free in a ring, *without* either wire gauze or iron plate underneath it.

¹ J. Am. Chem. Soc., **12**, 29, foot note.

By means of the full flame of a broad round burner a uniform heat is applied. The mass soon begins to assume a dark brown color in spots. The burner is removed and the reaction continues. The mass swells a little, vapors which contain much hydrogen sulphide are given off, so that most perfect ventilation is necessary during the process. Soon the neck of the retort and the condenser tube become lined with yellow drops, condensing in the cooler to a half solid substance, while an abundant flow of an almost colorless liquid fills the receiving flask. After some time (generally in about ten minutes) the distillate runs less briskly. Then the heat under the retort is renewed, until the dropping becomes so slow as to make further work unprofitable.

The distillate, which has a golden yellow color, is at once redistilled from a water bath, yielding an easy flowing, almost colorless oil, still slightly impure from presence of H_2S .

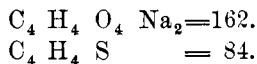
I remark here, that it is more profitable *not* to distill such a small quantity as we obtain from 155 grms. of sodium succinate, but to repeat the process, just described, four times with little or no interruption with new quantities of mixture, in new retorts and then to redistill the united crude distillates. All this can be done in two hours.

The redistilled oil is then shaken with dilute alkali, which turns brown, while the oil (which, according to the strength of the alkali used, floats upon it or sinks below it) assumes its purer, colorless appearance. The two liquids are separated, either by a siphon or by a separating funnel, this latter being better for vigorous shaking and subsequent washing of the oil. The thiophene obtained, being but slightly opalescent from water retained in it, is filtered through a small, dry, fluted filter into a flask with good stopper.¹ Some long, thin strips of clean sodium, showing metallic lustre, are put into the thiophene and the liquid is allowed to stand with the metal over night. Then the thiophene

¹ A previous shaking with calcium chloride is *not* necessary, nor is it advisable. In one instance, when I tried to dry the oil with a little solid, very pure $CaCl_2$, a faintly rose colored solid was formed at the expense of the oil, and I had to dissolve in water and distill again.

is distilled from the sodium on a water bath. It is thus perfectly pure. The sodium assumes the color of "old gold."

From nearly 610 grms. of sodium succinate and 1,200 grms. of phosphorus trisulphide, treated in the manner described above, I obtained 150 grms. of pure thiophene. This is the obtainable yield, it is almost fifty per cent. of that indicated theoretically :



At first I worked with quantities of sodium succinate up to 200 grms. and more at a time. I also purified each raw distillate as soon as obtained, but got only 100 grms. of pure thiophene from 600 grms. of succinate. Most of this discrepancy I have to attribute to the visible loss by adhesion of drops of oil to the wash liquids and in the distilling flasks ; some of it, of course, also to the large quantities used for destructive distillation. I therefore recommend most strongly to use the figures given in my directions.

The yellow substance, semi-solid in the cooler (some of it had also run down into the receiver), was allowed to drop slowly into a dish. It continued for days to give off $\text{H}_2 \text{S}$, and when put into a tube, closed by a cork, was puffed up towards the latter ; it gradually became harder, however. The black, uniformly caked mass in the original retort can be used to advantage for the preparation of hydrogen sulphide, this latter being developed from it by the addition of water. If, after the development of $\text{H}_2 \text{S}$, the mass is filtered, leached with water and the extracts filtered, the liquids evaporated to almost a syrup (which process gives rise to a new evolution of $\text{H}_2 \text{S}$), then put over a dessicator, white crystalline crusts begin to deposit and more $\text{H}_2 \text{S}$ is given off. The liquid is of acid reaction. With reagents it answers neither to the phosphoric acid, nor to the sodium sulphide tests,¹ but acts in general as a strongly reducing substance, indicative of *phosphorous* acid. The following reactions, which were performed with it, speak for themselves :

¹ J. Am. Chem., Soc., 12, 29; foot note.

Neutral lead acetate: White ppt., not changed on boiling.

Alkaline sol. of lead acetate: White ppt., not changed on boiling.

Acetic acid sol. of lead acetate: White ppt., not changed on boiling.

Silver nitrate: Yellow ppt., turning brown and ultimately black on boiling.

Mercuric chloride: White ppt., heavy gray on boiling.

Mercurous nitrate: White, brown, finally black ppt.

Cupric sulphate: Green ppt., on boiling reduced to red oxide and even to metallic copper.

Ammoniacal sol. of $Cu SO_4$: Blue ppt., green on boiling.

Ammoniacal sol. of $Ag NO_3$: Brown ppt., then black and reduced to silver.

Ammonium molybdate: No precipitate, the liquid turned blue, indicating reduction to molybdic oxide. The same reaction took place when the liquid tested was previously neutralized with $Na_2 CO_3$.

Barium chloride: No precipitate.

Ferric chloride: Acid and neutral, white ppt., unchanged on boiling.

Magnesium sulphate (after $N H_4 Cl$ and $N H_4 O H$): white ppt. cold or boiling.

Ammoniacal Ammonium molybdate: also reduced to clear blue liquid.

Platinic chloride: nothing, cold, on heating the liquid turned mahogany brown and a black precipitate formed.

Potassium iodide: no ppt., no coloration, cold or hot.

Iodic acid: abundant reduction to iodine.

Potassium permanganate (neutral): strongly reduced, first with simple decoloration. On adding more, until distinctly red and then boiling, chocolate brown precipitate.

Sodium hydrate (saturated sol.): black ppt.

Nitric acid (conc.): Flocks of sulphur separate on boiling. The liquid filtered off did *not* give a ppt. with ammonium molybdate.

Conc. $H_2 SO_4$ or $H Cl$ produced opalescence and evolution of $H_2 S$.

When the original salt solution was evaporated to dryness in a porcelain crucible, spontaneously inflammable hydrogen phos-

phide was evolved in abundance. Finally the mass turned black and fused to a black, translucent glass. At the end of a platinum wire in a Bunsen flame (outer or inner) the glass swelled and gave a clear colorless bead. This, dissolved in water, did *not* yield a ppt. with molybdate solution.

I cannot decide, as yet, whether the liquid giving the above tests is the solution of a uniform salt, or whether it contains several salts, and if so, what may be the nature of these. It is very apparent, however, that *phosphorous* acid, or phosphites, or both, are present in it. The formation of these is easily explained, if we consider the substances present in the retort in which destructive distillation of sodium succinate with P_2S_3 was taking place, after the formation of thiophene had begun. The probability that a phosphoric acid, containing sulphur for some of its oxygen atoms, may have formed, is also indicated.

This salt mixture, which doubtless retains some sodium sulphide, invites future study. (J. Am. Chem. Soc. **12**, 29, footnote.)

On redistilling the first *crude* oil from the waterbath, a considerable amount of an oil, non-volatile at steam heat, remained, together with a yellow solid substance. This oil, of peculiar odor, faintly amber colored, did not permit of fractional distillation at once. It amounted to about 25 c. c. At $87^\circ C.$ it began to boil and gave some distillate, evidently containing thiophene. The temperature rose soon to 95° and then more rapidly to $120^\circ C.$ Then suddenly a large amount of gas was given off. This effervescence subsided and gave way to a quiet flow of the liquid, which meanwhile had assumed a dark brown color. Finally, and almost instantaneously, the temperature rose to $220^\circ C.$ and the mass was driven up into the neck of the retort. The distillate was treated several times with solution of alkali, then washed, dried with a pinch of fused sodium chloride, filtered, shaken with metallic sodium and distilled from the same. I fractioned out of it six c. c. of an oil which gave the indophenin reaction and boiled at 86° to $99^\circ C.$

In regard to the properties of thiophene I refer to my paper on anthraquinone¹. In addition, it may be remarked that the

¹ J. Am. Chem. Soc., **12**, 26 *et seq.*

specific gravity of thiophene, at 23° C. is 1.062. For this and other particulars see "Die Thiophen Gruppe."¹

The two most characteristic reactions of thiophene being the indophenin and the phenanthraquinone reactions, care should be taken to use pure isatin and pure phenanthraquinone.

The brown commercial isatin is not fit to be used for the purpose. It is very simply purified by dissolving in a solution of potassium hydrate and then carefully adding hydrochloric acid, drop by drop. A leather-brown precipitate is formed, which is filtered at once. The filtrate, on addition of a little more HCl, yields a bright brick-red or vermilion precipitate of pure isatin. A drop of thiophene is mixed with ten c. c. of pure benzol. *Very* little isatin is introduced into this mixture and then conc. H₂SO₄ is slowly run into the same, shaking the test tube all the time. The mixture assumes a deep color, more green than blue. On addition of water, indophenin is precipitated in dark blue flocks. These are soluble with marine-blue color in chloroform, the solution showing its tint also by gaslight.

The phenanthraquinone is obtained from commercial phenanthrene, which can be bought quite pure and of the correct melting point, 99° C.

21 grms. of such phenanthrene are oxidized in a mixture of :

30	grms. potassium dichromate,
15	" conc. H ₂ SO ₄ ,
54	" water,

according to Fittig and Ostermeyer². These authors recommend a recrystallization from equal volumes of glacial acetic acid and water. The phenanthroquinone thus obtained crystallizes in remarkably pretty tufts of gold bronze lustre³.

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¹ Pages 20 *et seq.*

² Ann. Chem. (Liebig), **166**, 361; see also **196**, 38.

³ For the reaction between thiophene and phenanthraquinone, see J. Am. Chem. Soc., **12**, 30.