

CCXX.—*A Simple Method of Preparing Tetranitromethane.*

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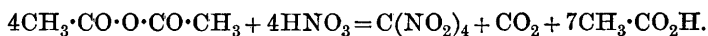
TETRANITROMETHANE can easily* be obtained without danger, and in almost theoretical amount, by allowing equal molecular amounts of nitric acid† and acetic anhydride to interact‡ at the ordinary temperature for several days. Some heat is developed on mixing, and slight cooling is necessary during this part of the process, otherwise the action may become so vigorous that loss of material results, but, so far as the author's experience goes, it never becomes explosive in character.

* The methods hitherto described for the preparation of tetranitromethane, namely, (1) nitrating nitroform (Schischkoff, *Annalen*, 1861, **119**, 247), (2) the action of diacetylorthonitric acid on acetic anhydride (Pictet and Genequand, *Ber.*, 1903, **36**, 2225), (3) distilling nitrobenzene with a large excess of a mixture of nitric and sulphuric acids containing sulphur trioxide (Claessen, D.R.-P. 184229), and (4) adding acetic anhydride to a mixture of nitrogen pentoxide and nitrogen peroxide (Schenck, D.R.-P. 211198, 211199), leave much to be desired in the way of simplicity.

† The use of more than the equivalent amount of nitric acid is of no advantage; indeed, when an excess is added, the yield is seldom so good, as the acid ordinarily employed always contains some small amount of water.

‡ On the 7th of July, since this paper was written, the Farbenfabriken vorm. F. Bayer & Co. published a method (D.R.-P. 224057) of preparing tetranitromethane exactly similar to that given above. As, however, this paper was read about a month earlier, namely, on June 16th (*Proc.*, 1910, **26**, 164), and as many details not to be found in the specification are given, it seems desirable that it should be published in full.

The action takes place almost quantitatively according to the equation:



The tetranitromethane remains dissolved in the acetic acid, and separates out as a heavy, oily layer on pouring the product into water. Carbon dioxide is given off almost from the time of mixing, but the evolution is never rapid, and the tetranitromethane appears only to be formed gradually, as the yield is small unless the mixture is kept for some days.

When nitric acid attacks acetic anhydride, a mononitro-derivative is probably first produced, which is nitrated so much more readily than the parent compound that action proceeds until the three hydrogen atoms of a methyl group have been replaced. Hydrolysis then occurs, and the trinitroacetic acid formed slowly decomposes into carbon dioxide and nitroform, which as soon as it is liberated is converted by the remainder of the nitric acid into tetranitromethane.

The operations necessary in this method are so simple and so easily carried out that the preparation is well adapted to take its place in any elementary course of practical organic chemistry to illustrate the ease with which aliphatic compounds can be nitrated, whilst the materials employed are so cheap and the yield is so satisfactory as to make tetranitromethane, which has hitherto been a somewhat unfamiliar substance, one of the most easily procurable of organic compounds.

Preparation of Tetranitromethane.

Thirty-one grams of nitric acid * ($D^{15} 1.53$) are placed in a 250 c.c. flask, and 50 grams of acetic anhydride are gradually added in quantities of about 2 c.c. at a time, the flask meanwhile being cooled in water, as some little heat is developed. If the flask is not cooled, action proceeds more and more vigorously as the temperature rises, and may, if unchecked, become violent. It is inadvisable therefore to allow the temperature to rise much above 20—25°.

When all the anhydride has been added, the flask is covered loosely by a watch-glass or inverted small beaker, and kept at the ordinary temperature for about a week. As the reaction proceeds, carbon dioxide is continuously but very slowly evolved, and the mixture, which at first is colourless, becomes brown, owing to the

* The anhydrous nitric acid required in the preparation is most easily obtained by slowly distilling ordinary fuming nitric acid from its own bulk of concentrated sulphuric acid; if ordinary concentrated nitric acid ($D 1.41$) is used, it is advisable to distil it twice from sulphuric acid. It is not necessary, although advisable if convenient, to distil off the acid under diminished pressure.

formation, in small quantity, of oxides of nitrogen. After a week, the tetranitromethane which remains dissolved in the acetic acid may be separated by pouring the mixture into about 150—200 c.c. of water. The bulk of the tetranitromethane subsides as a colourless, heavy, oily layer, which can be removed by means of a separating funnel, whilst a small quantity still remaining dissolved in the dilute acetic acid may easily be separated by means of a current of steam. The tetranitromethane passes over with the first few c.c. of the distillate, and separates as a heavy globule.

The tetranitromethane thus obtained may be freed from traces of acid by washing with water, or even better, although with slight loss, by distilling in a current of steam.* It is then separated and dried over fused calcium chloride.

Tetranitromethane as thus prepared is a heavy, very faintly yellow liquid. It can be distilled at 126° under the ordinary pressure, but the distillate is of a pale brown colour, due to oxides of nitrogen formed by some slight decomposition which takes place at this temperature, and still requires to be washed and dried to obtain it quite pure. If cooled a little below the ordinary temperature, it easily solidifies to a mass of colourless crystals.

The yield of tetranitromethane obtained is never quite the theoretical one, although by careful working it can be made to approximate to it. The small loss cannot be entirely, or even mainly, due to oxidation, as at no period of the action is there any considerable liberation of nitrous fumes; it is probably caused by some of the very heavy vapour being carried away in the escaping carbon dioxide, and lost during the processes of separation.

Using acid prepared as above, without removing the oxides of nitrogen,† the yield is approximately 80 per cent. of the theoretical, about 18—20 grams of pure, dry tetranitromethane being obtained from the weights of materials given.

It is immaterial whether the acetic anhydride be added to the nitric acid, or the nitric acid to the anhydride, but the former procedure is preferable, as the evolution of heat then occurs mainly during the first few additions of anhydride, which can be added more rapidly afterwards.

In a set of experiments to ascertain the rate of formation, a

* After distilling in a current of steam, the distillate containing the tetranitromethane as well as the residue is always bright yellow in colour, owing to the presence of dissolved nitroform, which is formed in small quantity when tetranitromethane is allowed to come into contact with water or is heated with it.

† There is no great advantage in freeing the anhydrous nitric acid from oxides of nitrogen, as even if the acid is completely colourless on mixing and the mixture is kept at 0° in a dry atmosphere it becomes coloured in a few days. The yield is slightly better if colourless anhydrous acid is employed, but the increased yield does not compensate for the extra labour involved in the preparation of the acid.

number of similar mixtures of the above quantities were made, and the amount of tetranitromethane formed was estimated after different intervals. After one day, 7.5 grams of tetranitromethane were obtained; after two days, 11.5 grams; after four days, 14.5 grams; after six days, 17 grams; and after eight days, 18.5 grams. After this, further keeping did not appreciably increase the yield.

The process can be accelerated by heating the mixed liquids cautiously until the action becomes sufficiently rapid to cause the temperature to rise even after removing the source of heat* and then checking the action by cooling; when this has been done several times, the liquid, which at first cannot be heated with safety much above 30°, may be heated to 80—100° without any violent action occurring, but on diluting the product the yield is not found to be anything like so good as when the mixture is simply allowed to remain at the ordinary temperature.

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