that I have tried to derive the most rational conclusions possible under the circumstances from the experiments described in this and the previous papers, and that I shall be ever ready to acknowledge any false conclusions I may have arrived at. The processes described by me have simplified the problem of the preparation of the unsaturated hydrocarbons, and I hope that they will be made use of in the systematic study of this branch of organic chemistry which is still in a more or less chaotic[1] state.

In conclusion, I would like to express my indebtedness to my colleague, R. B. Earle, for many valuable suggestions, and to thank him again for his constant help in carrying out a good many of the experiments described in this and the previous papers.

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# THE PREPARATION OF ALLYL IODIDE.

BY RASIK LAL DATTA.

Received March 12, 1914.

The preparation of large quantities of allyl amine for conversion into the nitrite, necessitated the preparation of still greater quantities of allyl iodide, since allyl amine was obtained from this through the isothiocyanate. The method used for the preparation of allyl iodide was the action of yellow phosphorus on iodine in glycerol. This method is attended with some difficulty, and hence it has engaged the attention of chemists who have published modifications of the method from time to time. On undertaking the preparation of the compound, the various methods were tried, but it was found that in no case had the real difficulties been overcome. After a series of careful experiments, a modified method was devised, in which, as will be shown later, the difficulties were reduced to a minimum, and by which the preparation could be completed smoothly and in a very short time. Behal[2] in order to obviate the use of yellow phosphorus, employed red phosphorus in conjunction with a solution of iodine in allyl iodide and glycerol. This method does not, however, come under our consideration.

Claus[3] described the preparation of this compound in detail for the first time. His results were confirmed by James.[4] Claus did not use carbonic acid gas in this method. The yield obtained was 220 g. of pure allyl iodide from 240 g. of iodine.

Later, Kanonikoff and Saytzeff published a modification of the method

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[1] This is especially the case with the higher members of the unsaturated hydrocarbon series, where the possibility for the formation of a number of isomers, and their presence in the products obtained in the reactions, make their identification quite difficult and highly desirable.

[2] *Bull. soc. chim.*, 47, 876 (1887).

[3] *Ann.*, 131, 58 (1864).

[4] *Ibid.*, 185, 191 (1877).

in which, by the use of carbonic acid during the preparation, the yield was improved to 1000 g. allyl iodide from 1000 g. of iodine and the preparation of large quantities at a time was made possible. As a result of incorrect observation, they stated, moreover, that by following the method of Claus, without the use of carbonic acid gas, the yield could not be raised over 700 g. allyl iodide from 1000 g. of iodine. That the yield stated by Claus can actually be obtained has been verified by me. Moreover, Kanonikoff and Saytzeff held that their method alone enabled one to operate with large quantities. Experiments show, however, that the method of Claus does not require operating on a small scale, but that as large a quantity can be taken in one operation as in the other method. It is necessary to point out that both the above methods are attended by the usual difficulties of preparing this compound.

After a series of careful experiments, the following method is proposed. In it the use of carbonic acid gas is avoided altogether, and no difficulty is experienced, the operation is carried through smoothly and quickly, while the yield is equally satisfactory.

The first difficulty attending the method is that the addition of phosphorus is tedious and the addition of several grams takes hours. Moreover, the pieces which are added are not easily brought into interaction but must be stirred with a glass rod pushed through the tubulus of the retort. Sometimes, even on stirring, no action takes place for a considerable time; and if, in the belief that the action is over, more pieces are added before the previous portion has been used up the reaction may suddenly set in with explosive violence. Local warming with a flame is not safe. The following details have been found to give the most satisfactory results:

The apparatus consists of a retort, fitted with a funnel having a glass stopper. The retort is connected with a condenser and receiver as usual. The retort is kept dipped in a larger-sized water bath, which can be heated from beneath. Glycerol is next poured into the retort and then the iodine, taking care that all of it drops on the glycerol and that none sticks to the side of the retort. When all the iodine is added, the water bath is heated to boiling. A small piece of phosphorus is then added, the stopper of the funnel being removed temporarily. When this comes into contact with iodine in the hot glycerol, it reacts at once. As a result of the interaction, some allyl iodide is formed which takes up some iodine into solution. A second piece is immediately added and takes part in the reaction in like manner. On continuing the addition of larger pieces of phosphorus, more and more allyl iodide is formed, which, taking up increasing quantities of iodine into solution, facilitates the reaction. After a considerable quantity of phosphorus has been added in this manner, the allyl iodide formed distils off, being heated on the water bath and the heat generated by the reaction. Proceeding in this manner, after the addition of only a few grams of phosphorus (which takes but a short time), large pieces weighing as much as 3-4 g. can be added in quick succession. The operation can, therefore, be very smoothly and quickly completed. Since some isopropyl iodide (b. p. 89°) is invariably produced in this reaction, the mixture boils at less than 100° and, hence, the major part of the distillation is finished on the water bath. The last traces can be distilled off by heating with a constantly moving luminous flame. The allyl iodide is dried and purified in the usual manner.

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# CHLORINATION BY MEANS OF AQUA REGIA. THE CHLORINATION OF BENZENE, THIOPHENE, TOLUENE AND MESITYLENE.

BY RASIK LAL DATTA AND FRANCIS V. FERNANDES.

Received March 12, 1914.

Although several processes have been used for the chlorination of organic compounds, there has always been difficulty in finding a method which could be carried out economically, both as regards the time and the chemicals. The only method which has been applied rather extensively is the one in which chlorine is passed through a liquid, usually in the presence of a carrier. In this case, however, the chlorination of a single compound means the work of some hours, not to speak of the trouble necessitated by the conditions demanded, *viz.*, the influence of direct sunlight, etc.

Some of the difficulties, mentioned above, seem to be obviated by the use of a mixture of nitric and hydrochloric acids as a chlorinating agent. Some investigators have used it in some oxidizing experiments, but they have pronounced it as an unsatisfactory reagent, chiefly owing to its exceedingly active properties. While this is true for some compounds, it has been found that the reagent in many cases acts as a powerful chlorinating agent, and in others both as an oxidizing and chlorinating agent. It acts as a simple chlorinating agent towards compounds which are not easily susceptible of oxidation with nitric acid, while, if the substance in question is susceptible of oxidation by nitric acid, both the processes of oxidation and chlorination occur simultaneously. In fact, the changes that can occur under any circumstances may be described thus: We know that a mixture of nitric and hydrochloric acids yields chlorine and nitrosyl chloride, the latter decomposing in the presence of water into nitrous fumes and hydrochloric acid. Hence, either or both of the following reactions may take place: first, the strong nitric acid may oxidize or nitrate the body coming into contact with it; and secondly, the nascent chlorine may unite with great energy with such compounds. In the case of hydrocarbons, generally, the reagent acts simply as a chlorinating agent, with the production of the several chloroderivatives, according to the