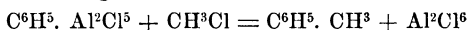


tomic chloride present, the organic radicle entering the benzol nucleus, and aluminium chloride being reformed.



A small quantity of aluminium chloride serves for the preparation of an indefinite quantity of the new hydrocarbon.

By the action of aluminium chloride on the monatomic chlorides alone, hydrochloric acid is also eliminated, and the radicle is condensed. Hence, the reaction which would take place between benzol and a polyatomic chloride under the same circumstances cannot be entirely foreseen. It seems possible that in the case of ethylene chloride, for example, both atoms of chlorine might be replaced by phenyl groups, but it would seem more probable that, after the first substitution, one molecule of hydrochloric acid would be removed from the ethylene chloride, and that a more condensed hydrocarbon, styrol, would be formed. However, the first reaction is that which actually occurs.

When aluminium chloride is introduced into a mixture of benzol and ethylene chloride, the reaction begins in the cold, and becomes energetic on the application of heat. Hydrochloric acid is disengaged abundantly; when the reaction has ceased, the mixture is thrown into water to separate the aluminium chloride, and the oily liquor which separates is heated with alcoholic potassium hydrate, in order to decompose any remaining ethylene chloride.

After washing and drying the product, it yields, on fractional distillation, very nearly the theoretical quantity of dibenzyl, after which a thick oily mixture remains, which does not completely distill at 200° in a vacuum. This mixture consists of condensation products, and yields no satisfactory results, as it cannot well be fractionated, and does not solidify in a freezing mixture.

Pure dibenzyl melts at 52.5–53°, and boils at 279°, under a pressure of 767 millimetres, the thermometer being entirely immersed in the vapor. This boiling point is lower than that given by Cannizarro and Rossi (284°), and higher than that indicated by Fittig (272°).

On Dioxyethyl-methylene, and the Preparation of Methylene chloride. By Wm. H. Greene, M.D.

(Read before the American Philosophical Society, November 21, 1879.)

With the exception of the diethyl ether of methylene glycol, all of the oxyethyl substitution compounds of methane have already been described. Orthoformic ether, $\text{CH}(\text{OC}^2\text{H}^5)^3$, was studied by Kay and Williamson, and is generally known as Kay's ether: orthocarbonic ether, $\text{C}(\text{OC}^2\text{H}^5)^4$, was discovered and described by H. Bassett: methyl-ethyl oxide has long been known.

By a reaction similar to that by which these ethers are formed, I have

isolated dioxyethyl-methylene, the reaction between sodium ethylate and methylene chloride taking place as indicated by theory.

The chief difficulty lies in the preparation of pure methylene chloride; the process described by Perkin, and depending upon the reduction of chloroform by zinc and ammonia, yields only small quantities of methylene chloride, and the direct chlorination of methylchloride yields equally unsatisfactory results. The method which, after numerous experiments, I have found to answer best, consists in the reduction of an alcoholic solution of chloroform by zinc and hydrochloric acid.

The zinc and chloroform mixed with several times its volume of alcohol are placed in a flask connected with a suitable condensing apparatus, and hydrochloric acid is added in small portions. The reaction develops considerable heat, and methylene chloride and chloroform distill over; when the reaction has somewhat subsided, and no more liquid distills, more hydrochloric acid is added, and a moderate heat is applied, if necessary. In any case, the mixture is heated towards the close of the operation, until alcohol begins to distill in quantity. The operation is then arrested, and the product in the receiver is washed, dried and rectified, that portion which passes below about 53° being retained. The residue is returned to the flask and again submitted to the action of the zinc and hydrochloric acid. By several careful rectifications of the product passing below 53° , pure methylene chloride, boiling at $40-41^{\circ}$, is obtained.

By several operations in this manner the yield of methylene chloride may be brought up to about twenty per cent. of the chloroform employed.

Little or no advantage is gained by attempting to fractionate the product as it distills from the flask, so that the chloroform may flow back into the reducing mixture, for such distillation necessarily takes place in a stream of hydrogen which carries with it about as much chloroform as methylene chloride.

DIOXYETHYL-METHYLENE.—This compound was prepared by gradually introducing one molecule of sodium into a mixture of one molecule of methylene chloride and about four times the theoretical quantity of absolute alcohol, contained in a flask connected with a reflux condenser. After all of the sodium has been introduced, the mixture is heated on a water-bath for about an hour, and is then distilled. The distillate is fractionated, and the portion which passes below 78° contains all of the diethyl ether. It is agitated with a tolerably concentrated solution of calcium chloride, and the light ethereal layer is separated, dried over calcium chloride and carefully rectified, until a liquid is obtained which boils at $86-89^{\circ}$.

Dioxyethyl-methylene so obtained is an ethereal liquid, having a penetrating, pleasant odor, somewhat recalling that of mint. Its specific gravity at 0° is 0.851, and it boils at 89° , under a pressure of 769 millimetres. It is slightly soluble in water, from which it may be separated by the addition of calcium chloride; it mixes in all proportions with ether and alcohol, and it cannot readily be separated from its alcoholic solution if much alcohol be present; in such a case, fractional distillation and treatment of the portion which passes below 78° with solution of calcium chloride, effect the separation.