

4. The change from diethyl oxalate to potassium methyl oxalate is represented as, first, the change of diethyl oxalate to dimethyl oxalate and, second, the change of dimethyl oxalate to potassium methyl oxalate.

5. The presence of potassium ethyl oxalate in the solution of diethyl oxalate in methyl alcohol does not cause the formation of any dimethyl oxalate.

6. If the solution of potassium hydroxide in methyl alcohol be said to contain potassium hydroxide and potassium methylate, the potassium methylate is a stronger factor than the potassium hydroxide in causing the change from diethyl oxalate to dimethyl oxalate.

These experiments were done under the direction of Professor F. B. Allan and it is proposed to continue them using solutions of other alkalies.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRESIDENCY COLLEGE.]

HALOGENATION. XI. CHLORINATION WITH AQUA REGIA. THE CHLORINATION OF HYDROCARBONS.

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In continuation of the study of the chlorination of hydrocarbons by means of aqua regia,¹ several other hydrocarbons were subjected to its action. The results obtained were, however, mostly unsatisfactory, except in the case of a few hydrocarbons whose chloro-derivatives could be isolated by distillation or crystallization. Aqua regia has a nitrating influence on account of the nitric acid, as well as a chlorinating influence on account of the nascent chlorine. The lower hydrocarbons give only chloro-derivatives while the higher homologs usually give a mixture of both chloro- and nitro-derivatives. The reagent is quite unsuitable for chlorinating the higher hydrocarbons, while it can be successfully applied for the chlorination of the lower ones. The chlorination of the xylenes, ethyl benzene and dibenzyl gives good results; the rest of the hydrocarbons treated, either give a complicated product which cannot be separated, or break up with the formation of chloropicrin, which, as will be shown later on, is the general decomposition product under these circumstances.

Experimental.

m-Xylene.—In a typical experiment, 30 cc. of *m*-xylene were chlorinated for about six hours with 360 cc. of the mixture of HCl and HNO₃ (2 : 1). The mixture was heated in a flask on the wire gauze with a reflux condenser. The product was well washed with water and alkali, and kept overnight over calcium chloride.

The liquid, 25 cc., was decanted, and distilled with a stillhead. The dis-

¹ Datta and Fernandes, THIS JOURNAL, 36, 1007 (1914).

tillate was collected in two fractions, *viz.*, (1) from 140–190°, (2) from 190–224°. The volumes of the two fractions were 15.5 cc. and 9.5 cc., respectively. Thus it seemed that monochloroxylylene was formed in predominant quality, while the 4,6-dichloroxylylene was formed in slightly smaller proportion.

The two fractions were subjected to fractional distillation. After carrying out the process repeatedly, about 9 cc. of pure monochloroxylylene were obtained from the first fraction. The second fraction similarly yielded 5 cc. of pure 4,6-dichloroxylylene. These were identified in the usual manner.

The residue that was left in the distilling flask crystallized on cooling. Thin, white needles were obtained, which were pressed between the folds of filter paper and then dried in the desiccator. The melting point of the crystals was not sharp at all: it extended over a range of 15° from 195 to 210°. Thus it appeared that a mixture of chloro-derivatives was formed. Hence the solid was fractionally crystallized from hot alcohol. After the first crystallization the substance deposited from the alcoholic solution gave the m. p. 208°, although not sharp. A second crystallization gave the pure 2,4,5,6-tetrachloroxylylene with the m. p. 210°.

0.1037 gave 0.2432 AgCl; Cl = 58.01; Calc. for $C_6Cl_4(CH_3)_2$: Cl = 58.19.

The main portion of the substance insoluble in alcohol gave, on repeated crystallization, a small amount of trichloroxylylene, m. p. 117°. Hence the solid from the residue of distillation consisted mainly of the 2,4,5,6-tetrachloroxylylene contaminated with trichloroxylylene.

In a second experiment 25 cc. of *m*-xylene were subjected to prolonged chlorination under the conditions described above. The action was allowed to proceed for 35 hours and the mixture of acids was renewed every 5 hours, 180 cc. being used each time. After about 10 hours crystals were seen all over the liquid. The product was treated as before and kept in the vacuum desiccator. After 24 hours, it was found that crystals were deposited from the liquid. They were filtered out and drained well with suction. The liquid chloro-derivatives on distillation behaved as in the first experiment and consisted of mono- and dichloro-xylenes. The residue in the distilling flask solidified. The solid melted at about 188°. The crystals which were deposited from the liquid in vacuum also melted at about 190°. By fractional crystallization both products could be separated into the tri- and tetrachloroxylenes. The total solid product weighed 1.3 g. and on fractional crystallization gave 1.1 g. of 2,4,5,6-tetrachloroxylylene. Hence the method is specially applicable for the preparation of the tetrachloro-derivative of *m*-xylene.

***o*-Xylene.**—20 cc. of *o*-xylene were mixed with 360 cc. of the mixture of acids, and the whole heated on the wire gauze with a reflux condenser,

for about 8 hours. The product, after being separated and washed was dried in the desiccator.

The liquid deposited crystals, m. p. 210° .

The filtrate (16.5 cc.) was distilled with a stillhead and the distillate collected as follows: (1) from 142 to 200° , and (2) from 200 to 230° . The amounts of the two fractions were 11 cc. and 3.5 cc., respectively. These fractions were then distilled fractionally till they yielded products which had constant boiling points. The first gave 8.5 cc. of monochloroxylylene with the boiling point 191.5° , and the second about 1.2 cc. of 4,5-dichloroxylylene which boils at 227° .

The residue in the distilling flask solidified and the solid had the m. p. 208° . The two solids obtained must have been identical. They were crystallized from acetone, and in each case a pure solid was obtained which had the m. p. 215° and could be sublimed.

0.0917 gave 0.2177 AgCl; Cl = 58.73%. Calc. for $C_6Cl_4(CH_3)_2$: Cl = 58.19.

Hence the product was 3,4,5,6-tetrachloroxylylene.

p-Xylene.—25 cc. of *p*-xylene were mixed with 180 cc. of the mixture of acids and heated on the wire gauze in a flask with a reflux condenser. The operation was conducted for about ten hours, the acids being renewed after five hours. The product was separated, washed and dried over calcium chloride.

In distilling the product, the maximum temperature attained was 230° . The following fractions were collected: (1) 170 – 200° , (2) 201 – 230° . The fractions were purified by fractional distillation; the first gave the b. p. 186.8° , and the second 222° . Thus the chloro-derivatives formed were chloroxylylene, $C_6H_3Cl(CH_3)_2$, and 2,5-dichloroxylylene, $C_6H_2Cl_2(CH_3)_2$. The quantities obtained were as follows: Volume of the whole product, 22.5 cc.; volume of chloroxylylene, 4.3 cc.; volume of 2,5-dichloroxylylene, 5 cc.

The residue in the distilling flask solidified on cooling. The solid was fractionally crystallized from hot alcohol. The pure crystals melted at 217.5° , and were soluble in ether and benzene.

0.1258 gave 0.2976 AgCl; Cl = 58.53. Calc. for $C_6Cl_4(CH_3)_2$: Cl = 58.19.

Thus the solid was tetrachloroxylylene. Its weight was about 0.8 g.

Hence the method is suitable for the preparation of all the derivatives mentioned above, as they are produced in fair quantities in a single operation.

In another experiment 25 cc. of *p*-xylene were treated as above for double the length of time, in order to see whether the amount of the end product had increased. There was a slight increase, but the chloroxylylene was also formed in an appreciable quantity.

Ethyl Benzene.—25 cc. of ethyl benzene were mixed with 360 cc. of the mixture of acids and heated on the wire gauze for about six hours.

The product was treated as usual and distilled. The temperature rose to 206° . The fraction collected between 180 and 206° was subjected to fractional distillation. The pure sample gave the b. p. 201° .

0.0917 gave 0.0925 AgCl; Cl = 24.95. Calc. for C_8H_9Cl : Cl = 25.26.

Hence monochloroethylbenzene, $C_6H_5CH_2CH_2Cl$, was formed. The quantity of this chloro-derivative was about 6 cc.

As indicated in the above investigation, the chlorine is introduced in the side-chain. To ascertain whether it was at all possible to replace the hydrogen in the nucleus, the following elaborate chlorination process was carried out: 25 cc. of the hydrocarbon were chlorinated for 37 hours, the reagent being renewed every four hours. After about 8 hours the liquid became heavy and sank beneath the acids, thus showing that the product had greater density. When the liquid was cooled a fine crop of silky white crystals was noticed, which dissolved on shaking. The crystals were formed in larger quantities at the end of the experiment.

The product was very thick in consistency. It was washed with water and alkali by decantation, the water being removed as much as possible by means of blotting paper. It was finally dried over sulfuric acid in a vacuum desiccator.

The liquid was found to have deposited crystals which had the m. p. $160-170^{\circ}$. The little remaining liquid was subjected to distillation. The temperature rose to 210° . Thus the monochloro-derivative was formed in small quantity.

The crystals were fractionally crystallized from acetone until pure. The final product had the m. p. 171.5° . As no known chloro-derivative of ethylbenzene has this m. p. the sample is being completely investigated.

Dibenzyl.—The substance was treated with the mixture of acids for about four hours, the heating being done on the water bath. A brown, oily liquid was obtained, which was separated, washed with water and alkali, and dried in the vacuum desiccator. Crystals were deposited, which had the m. p. 111° . Analysis indicated the product to be pure *p*-dichlorodibenzyl, $C_6H_4ClCH_2CH_2C_6H_4Cl$.

0.0719 gave 0.0830 AgCl; Cl = 28.57. Calc. for $C_6H_4ClCH_2CH_2C_6H_4Cl$: Cl = 28.28.

1,3,5-Butyl Xylene.—By the chlorination of 1,3,5-butyl xylene a yellow oil was obtained from which no pure chloro-derivatives could be isolated. The smell of chloropicrin was noticed, which is a product of the action of aqua regia on several organic bodies.

Anthracene is chlorinated, to a certain extent, but the greater part of it is oxidized to anthraquinone by the nitric acid. With phenanthrene a sticky mass is obtained which does not contain any nitrogen and which is a mixture of monochlorophenanthrene and phenanthrene which could not be separated. Triphenylmethane gives a mixture of chloro-derivatives

which could not be separated. Diphenylmethane and fluorene give a mixture of chloro-derivatives, respectively, which could not be separated and isolated and in these cases no nitration takes place. In the case of naphthalene it has been found that no chlorination at all takes place, but the naphthalene is nitrated. Cymene, styrene and tetrahydronaphthalene are nitrated and chlorinated. Hydrocarbons which undergo decomposition under the influence of aqua regia, such as cymene, styrene, amylene, diisobutylene, triisobutylene, give chloropicrin which is generally a product of such decompositions, as will be shown later on. Cyclohexane, on account of its volatile nature, could not be chlorinated by means of aqua regia, whereas dimethylcyclohexane is simultaneously nitrated and chlorinated.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE PRESIDENCY COLLEGE.]

HALOGENATION. XII. THE FORMATION OF CHLOROPICRIN AND TETRACHLOROQUINONE BY THE ACTION OF AQUA REGIA ON ORGANIC SUBSTANCES.

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In a previous communication¹ it has been shown that chloropicrin is formed by the action of aqua regia on several organic substances. It has now been found that whenever an organic compound breaks up destructively under the influence of aqua regia, chloropicrin is invariably produced. The chloropicrin formed is sometimes accompanied by very small quantities of other chloronitroderivatives of methane. In the case of certain aromatic compounds, tetrachloroquinone is formed as the end product of the action of aqua regia on them. As tetrachloroquinone itself breaks up to chloropicrin under the influence of aqua regia, the latter is also formed under such decompositions. The formation of chloropicrin has been noticed only in isolated cases by previous workers.

Stenhouse² showed that chloropicrin is formed by the distillation of nitro compounds with bleaching powder solution. Kekulé³ obtained it by the distillation of alcohol with sodium chloride, potassium nitrate and sulfuric acid. Later on, he again prepared the substance by the action of strong nitric acid on chloral.⁴ The action of the same reagent on chloroform was found to give chloropicrin.⁵ Levy and Jedicka⁶

¹ Datta and Chatterjee, *THIS JOURNAL*, 37, 567 (1915).

² *Ann.*, 66, 241 (1848).

³ *Ibid.*, 101, 212 (1857).

⁴ *Ibid.*, 106, 144 (1858).

⁵ Mills, *Ibid.*, 160, 117 (1871).

⁶ *Ann.*, 249, 86 (1888).