FRIEDEL AND CRAFTS REACTION. II.

THE CONDENSATION OF ortho- AND meta- DICHLOROBENZENE WITH CHLOROFORM AND CARBON TETRACHLORIDE

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Triphenylmethane derivatives with two or more halogen atoms on each of the three benzene rings were needed in one of our studies. A search of the literature indicated that while numerous triphenylmethane compounds with two or more halogens on one or two of the three rings have been prepared, there was no report of any with two or more on each of the three rings. Norris and Green (1) attempted to prepare this type of compound by condensing p-dichlorobenzene with carbon tetrachloride in the presence of aluminum chloride with carbon disulfide as a solvent. They obtained only tetrachlorobenzophenone chloride.

In a previous paper from this laboratory (2), we have shown that in the absence of solvents *p*-dichlorobenzene will condense with chloroform to give the expected hexachlorotriphenylmethane. But with carbon tetrachloride the product of the reaction is 1,4,7,9-tetrachloro-9-(2,5dichlorophenyl)fluorene (I) if the reaction is carried out at 55°, while if the reaction is carried out at room temperature the product is the tetrachlorobenzophenone chloride.



We have recently extended this study to include the condensation of the o- and m-dichlorobenzenes with chloroform and carbon tetrachloride. Further study of these compounds is planned, but the disturbed conditions in China, together with the approaching furlough of the senior author leads us to make a record of our present results.

o-Dichlorobenzene condenses with chloroform in the absence of solvents and in the presence of aluminum chloride to give a product which is probably 3,4,3',4',3'',4''-hexachlorotriphenylmethane (II), though the structure 2,3,2',3',2'',3''- has not been definitely ruled out for this compound.

m-Dichlorobenzene under similar conditions gives a product which is most probably 2,4,2',4',2'',4''-hexachlorotriphenylmethane (III), since, when carbon tetrachloride condenses with this dichlorobenzene under the same conditions, it gives a known tetrachlorobenzophenone with the chlorines in the 2,4,2',4' positions.

When these dichlorobenzenes are treated with carbon tetrachloride in the absence of solvents and in the presence of aluminum chloride we have so far obtained only derivatives with two benzene rings rather than those with three rings attached to the central carbon atom. With the ortho compound the product first formed was probably 3,4,3',4'-tetrachlorobenzophenone chloride, but the purification of this product proved somewhat difficult, and in this process it was hydrolyzed to give the corresponding tetrachlorobenzophenone. However, it is possible that the chlorine atoms in these two compounds occupy positions 2,3,2',3'.

On the other hand, the product from *m*-dichlorobenzene was purified without hydrolysis, and proved to be 2,4,2',4'-tetrachlorobenzophenone chloride.

We have thus found it possible to obtain triphenylmethane derivatives with each of the three dichlorobenzenes when we condense them with chloroform in the presence of aluminum chloride and in the absence of solvents. But when carbon tetrachloride is used, it has been proved possible only with p-dichlorobenzene to obtain a compound with three benzene rings joined to the central carbon atom. However, one molecule of hydrogen chloride splits off between two of these rings to give a fluorene compound. With the o- and m-dichlorobenzenes, only two rings have been joined to the central atom. We are carrying on further work to enable us to determine the conditions under which the triphenyl compounds can be obtained, and to determine why these condensations with carbon tetrachloride take a course different from that taken when chloroform is used.

EXPERIMENTAL

The chloroform, carbon tetrachloride, and aluminum chloride employed were obtained from E. Merck, Darmstadt. The dichlorobenzenes were from the Eastman Kodak Company and were employed without further purification.

Condensation product with o-dichlorobenzene and chloroform (III). Our best yields were obtained as follows. To a mixture of 7 g. of chloroform and 26 g. of o-dichlorobenzene was added 10 g. of powdered anhydrous aluminum chloride. This was heated at 55-60° for eight hours. Condensation at higher temperatures gave chiefly tarry products while at lower temperatures the reaction was slow. On cooling, the reaction-product solidified. This was broken up and poured into cold water. The mixture of water and solid was extracted three times with ether. The ether solution was washed with dilute hydrochloric acid to remove aluminum compounds, and finally with water. On evaporation of the ether, a reddish-yellow liquid remained. On standing two weeks, abundant crystals separated from this oil. These were washed with small portions of acetone and finally recrystallized from hot acetone. The final product consisted of white crystals in the form of elongated microscopic plates with beveled sides and square ends, m.p. 160.5-162°. The yield was 15% of that calculated from the chloroform used. These crystals were soluble in hot benzene, ether, and acetone.

Anal. Calc'd for C₁₉H₁₀Cl₆: C, 50.57; H, 2.24; Cl, 47.19.

Found: C, 50.82; H, 2.25 (semi-micro); Cl, 47.04 (semi-micro bomb).

2,4,2',4',2'',4''-Hexachlorotriphenylmethane (III). This was prepared from chloroform and m-dichlorobenzene, as above, except that the best yields were obtained by heating at 60-65° for 12-14 hours. The condensed mass was a dark red, viscous liquid. This was poured into cold water, the mixture was then extracted with ether, and the ether solution washed first with dilute hydrochloric acid and finally with water. On evaporation of the ether a red liquid was obtained. This was purified in two different ways. On treatment with alcohol, one fraction of the oil dissolved. The alcohol solution was then diluted with water, when white crystals separated. The second method consisted in washing the original oil with acetone. The colored portion dissolved in the acetone and a white residue remained. The two white products proved to be the same substance, which was further purified by recrystallization from hot acetone, to give characteristic white crystals that melted at 227-228.5°. The yield was 18% of the calculated. These crystals are soluble in benzene, toluene, ether, acetone, and alcohol.

Anal. Calc'd for C19H10Cl6: C, 50.57; H, 2.24; Cl, 47.19.

Found: C, 50.88; H, 2.28 (semi-micro); Cl, 46.90 (semi-micro bomb).

Condensation product of o-dichlorobenzene and carbon tetrachloride. In this reaction, the condensation was carried out between carbon tetrachloride and somewhat more than three equivalents of o-dichlorobenzene in the presence of powdered anhydrous aluminum chloride. Many runs were made, with the time varying from 2 to 24 hours and temperature varying from 20° to 100°, in efforts to obtain products with three rings on the methane carbon, but only products with two rings resulted. These products were gummy and proved difficult to purify except by treating with hot 95% alcohol, which caused hydrolysis of the chlorine on the methane carbon, and gave the ketone as the final product. This ketone was isolated by treating the gummy products with hot alcohol and diluting the alcohol solution with water, when white crystals separated. By recrystallization from hot alcohol or hot acetone, the pure white, flat, rod-shaped crystals were obtained, m.p. 141-142°. The yield was 40% of the theory, based on carbon tetrachloride used. Anal. Cale'd for C₁₂H₆Cl₄O: C, 48.77; H, 1.89; Cl, 44.33.

Found: C, 49.04; H, 1.88 (semi-micro); Cl, 44.44 (semi-micro bomb).

2,4,2',4'-Tetrachlorobenzophenone chloride. Attempts here were again made to obtain products with three rings on the methane carbon, but without success, even though the temperature was varied from 60-140° in various runs, and the time of heating extended from 2 to 24 hours. In all experiments, carbon tetrachloride was treated with somewhat more than 3 equivalents of *m*-dichlorobenzene in the presence of powdered anhydrous aluminum chloride. The product of the condensation was poured into cold dilute hydrochloric acid. The aluminum compounds dissolved, leaving slightly pinkish crystals, which were washed with cold water followed by small amounts of cold alcohol, and were finally recrystallized from hot acetone, giving crystals in the form of white plates, m.p. 139-140.5°. Here the yield was 60% of the theory, based on carbon tetrachloride used. Jaeger (3) reports that this compound melts at 140°.

Anal. Calc'd for C18H6Cl6: C, 41.62; H, 1.61; Cl, 56.78.

Found: C, 41.73; H, 1.69; Cl, 56.50.

All these compounds proved to be difficult to decompose in the sodium peroxide bomb.

SUMMARY

1. o- and m-Dichlorobenzene have been condensed with chloroform in the presence of aluminum chloride and in the absence of solvent to give the corresponding hexachlorotriphenylmethane. These compounds are new.

2. *o*-Dichlorobenzene, when condensed with carbon tetrachloride in the presence of aluminum chloride as above, gave a tetrachlorobenzophenone chloride which most probably has the chlorine in the 3,4,3',4' positions. During purification this was hydrolyzed to tetrachlorobenzophenone. This is also a new compound.

3. *m*-Dichlorobenzene with carbon tetrachloride gave 2, 4, 2', 4'-tetrachlorobenzophenone chloride.

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REFERENCES

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