percentage of color (hydrogen absorption), and the composition (derivatization of the cleavage products), may be determined with one sample which need not be greater than 10 g.

Acknowledgment.—A supply of water soluble sulfonated azo dyes, together with assays, was generously donated by Mr. Fred Hope. The assistance of Mr. Henry D. Lewis in making the carbon and hydrogen determinations is deeply appreciated.

Summary

The utility of the Raney nickel catalyst in the reduction of some common azo compounds at from 1–4 atmospheres absolute pressure and room temperature has been demonstrated.

BROOKLYN, N. Y. RECEIVED MAY 7, 1937

[CONTRIBUTION FROM THE LABORATORY OF PLANT NUTRITION, UNIVERSITY OF CALIFORNIA AGRICULTURAL EXPERIMENT STATION]

The Molecular Structure of Canna Starch

BY W. Z. HASSID AND W. H. DORE

The investigations of Haworth and collaborators[1-3] have shown that the structure of the starch molecule is a continuous unbranched chain of from 26 to 30 anhydroglucose units joined uniformly by α-glucosidic linkages between the first and fourth carbon atoms of contiguous hexose units. This structure has been shown to hold equally well for starch from potato, maize or waxy maize although these three starches have markedly different physical properties. It appears important to determine whether still other types of starch have the same molecular structure, hence the present contribution which reports the results of an investigation of starch obtained from the canna plant (*Canna edulis*).[4]

Canna starch is characterized by the large size of its granules, some of which are more than 0.1 mm. in diameter. Like potato starch it gives a blue color with iodine and is not soluble in either hot or cold water. It does not gelatinize as readily as potato starch. Its specific rotation in 4% sodium hydroxide solution is +156°, in reasonably good agreement with values obtained by Hirst, Plant and Wilkinson[2] for potato amylose (+151°) and amylopectin (+151°) and by Haworth, Hirst and Woolgar[3] for regenerated waxy maize starch (+152°), all of these determinations being made in either 4 or 5% sodium hydroxide solution. Canna starch is hydrolyzed at the same rate as potato starch and this suggests that the two have similar glucosidic linkages.

Canna starch was acetylated by two methods: (a) the method of Haworth, Hirst and Plant[5] using pyridine as a catalyst and (b) the method of Barnett[6] as modified by Irvine and Hirst[7] and by Haworth, Hirst and Webb[8] using chlorine and sulfur dioxide as catalysts. Both products had the full acetyl content for triacetyl starch. The starch which was regenerated from the acetate prepared by method (a) was insoluble in water and gave the same specific rotation (+156°) in 4% sodium hydroxide solution as the original starch. The starch, regenerated from the acetate which was prepared by method (b), was soluble in water but otherwise it was similar to the original canna starch in its properties. Its specific rotation in water solution was +198°, which is comparable with the value +190° reported for potato amylose[2] and +212° reported for waxy maize,[3] both in water solution.

The methylation of starch as carried out by the early investigators was very laborious, involving as many as forty treatments to complete the methylation. Later Irvine and Macdonald[9] improved this procedure by applying methyl sulfate and sodium hydroxide directly to the original starch and obtained trimethyl starch after twenty-four methylation treatments but in rather poor yield. Haworth, Hirst and Webb[8] reduced the number of treatments to six by employing a specially prepared triacetyl starch and methylating it in an acetone solution. After the first methylation

(1) Haworth, *Ann. Rev. Biochem.*, **5**, 81 (1936).
(2) Hirst, Plant and Wilkinson, *J. Chem. Soc.*, 279 (1932).
(3) Haworth, Hirst and Woolgar, *ibid.*, 177 (1935).
(4) The canna starch was obtained through the courtesy of Professor R. S. Bean, University of Hawaii, Honolulu.
(5) Haworth, Hirst and Plant, *J. Chem. Soc.*, 1214 (1935).
(6) Barnett, *J. Soc. Chem. Ind.*, **40**, 8T (1921).
(7) Irvine and Hirst, *J. Chem. Soc.*, **121**, 1585 (1922); **125**, 15 (1924).
(8) Haworth, Hirst and Webb, *ibid.*, 2681 (1928).
(9) Irvine and Macdonald, *ibid.*, 1502 (1926).

with methyl sulfate and 30% sodium hydroxide they obtained a product with a methoxy content of 36%. After five additional methylations the starch was completely methylated to a methoxyl content only slightly under the theoretical value for trimethyl starch, *i. e.*, 45.6%.

The present authors have been able to methylate starch directly, *i. e.*, without preliminary acetylation, in seven treatments, to the practical limit of methylation, approaching closely to the composition of trimethyl starch. The first stage of the methylation was carried out in carbon tetrachloride as a medium and followed an adaptation of the procedure used by West and Holden[10] for the methylation of glucose. One methylation treatment at room temperature, using 35% sodium hydroxide solution, gave a product with 37% methoxy content, a degree of methylation comparable to that obtained by Haworth, Hirst and Webb at a temperature of 50–55° in the first treatment of their specially prepared triacetyl starch. Further methylation of this partially methylated starch by the same procedure did not raise the methoxyl content. To complete the methylation the method of Haworth, Hirst and Webb was thereafter employed using acetone as a solvent. Six additional methylations by this method gave a product with methoxyl content of 44.4%. The complete methylation of both canna and potato starch has been accomplished with equal success by the present authors through the use of this method.

The fully methylated canna starch was hydrolyzed and the cleavage products were separated quantitatively by chloroform-water extraction according to the procedure used by Bell.[11] Approximately 4% of the product was obtained as tetramethylglucose, indicating a chain length of about 27 glucose units for methylated canna starch. This is in agreement with the chain lengths of from twenty-six to thirty glucose units which have been reported for potato, maize and waxy maize starches.

Carrington, Haworth and Hirst[12] have contended that a sharp separation of tetra- and trisubstituted methyl glucoses cannot be effected by chloroform and water extraction since it is not true that all the tri-substituted sugar remains in the water while the tetra- is extracted by chloroform. Macdonald[13] has calculated the partition coefficients of trimethylglucose and tetramethylglucose distributed between chloroform and water and has presented data to show that a reasonably sharp separation of the sugar derivatives may be effected by repeating the extractions with chloroform a sufficient number of times and thereafter washing the combined chloroform extracts with water. Bell[11,14] has used this method for the separation of the hydrolysis products of methylated glycogen with satisfactory results.

Using the partition coefficients which were given by Macdonald for the distribution of trimethylglucose and tetramethylglucose between chloroform and water, the authors have calculated the results which should be obtained by treating a mixture containing 4.75 g. of trimethylglucose with 0.25 g. of tetramethylglucose according to the procedure of Bell. Theoretically, the final chloroform phase would contain 0.2289 g. of tetramethylglucose or 91.56% of the original amount and 0.0182 g. of trimethylglucose. The combined weight of the products would be 0.2471 g. and as an analytical procedure this value would be considered as representing tetramethylglucose only and corresponding to 98.84% of the original amount taken. Thus by a compensation of errors an analytical result would be obtained which has a value in agreement with the actual amount present. Although the analytical product does not consist of pure tetramethylglucose, the amount of trimethylglucose which is present is not large enough to change materially the optical rotation or the methoxyl content of pure tetramethylglucose, hence these criteria when applied to the products of this separation would not afford conclusive evidence for their purity. Actually the constants of the products obtained by this separation agreed within experimental error with authentic values for these derivatives. As a practical analytical separation, the procedure here outlined appears to meet the requirements of a satisfactory method for estimating the end groups in the starch chain.

The two acetates of canna starch prepared by using (a) pyridine and (b) chlorine and sulfur dioxide as catalysts had different solubilities and different viscosities. The acetylated starch prepared by method (a) was difficultly soluble in chloroform and acetone while the starch prepared

(10) West and Holden, THIS JOURNAL, **56**, 930 (1934).

(11) Bell, *Biochem. J.*, **29**, 2031 (1935).

(12) Carrington, Haworth and Hirst, THIS JOURNAL, **55**, 1084 (1933).

(13) Macdonald, *ibid.*, **57**, 771 (1935).

(14) Bell, *Biochem. J.*, **30**, 1612 (1936).

by method (b) was very readily soluble in those solvents. The viscosities of these acetylated starches and therefore their molecular weights, as determined viscosimetrically by Staudinger's[15] method, differed greatly. The starch acetate prepared by the pyridine method was more viscous, and had an apparent molecular weight of 22,500, corresponding to a chain length of about seventy-eight glucose units, while the starch acetate prepared by the chlorine and sulfur dioxide method was less viscous and showed a molecular weight of 8700, corresponding to about thirty glucose units. It is significant to note that the latter value approximately agrees with the molecular weight of the methylated starch determined by the method of chemical assay of the "end group," namely, twenty-seven glucose units.

Recently McBain and Scott[16] have shown that molecules comprising substances of colloidal nature, such as soap or cellulose, possess the property of association and formation of more complicated structure or micelles. The degree of association determines the viscosity of the solution. These authors point out that an increase in degree of association can be accomplished by simple physical treatment. For example, the relative viscosity of nitrocellulose can be altered by varying the solvent, or in the same solvent by varying the temperature, or by various treatments at one temperature.

These results suggest that the different viscosities of the starch acetates, obtained by the writers, may be due to two different states of dissociation or aggregation of the anhydroglucose chains constituting the starch molecule. Since the starch acetate prepared by the use of chlorine and sulfur dioxide has a molecular weight, as determined by the Staudinger method, which corresponds to a chain length of the same order or magnitude as that of the methylated starch determined by the chemical assay of the "end group," it appears that this product is a derivative of a starch which was completely disaggregated without chemical degradation to a single molecular chain.

The other canna starch acetate, prepared by the use of pyridine, has an apparent molecular weight as measured by the Staudinger method which is approximately three times that of the simple single chain starch acetate just described. It appears probable that the more viscous acetate is an aggregate of simple molecules held together by secondary valence forces rather than a single larger molecule. It was found by Sponsler and Dore[17] that physical properties of cellulose, such as swelling and dispersion, are explainable as a disturbance of the secondary valence attractions between the molecular chains. It would seem that the differences in solubility and viscosity that are shown by the canna starch acetates are perhaps likewise explainable in terms of an aggregate of starch molecules held together by means of secondary valence attractions. Thus the aggregates of canna starch and its acetates could be represented respectively by the formulas $[(C_6H_{10}O_5)_m]_n$ and $[(C_{12}H_{16}O_8)_m]_n$ in which m is the number of anhydroglucose or acetylglucose units in the molecular chain and n the number of molecular chains in the aggregate. The value of m is from 26 to 30; the value of n is 1 for the low-viscosity canna starch acetate and 3 for the high-viscosity form.

Haworth and his associates have repeatedly expressed the belief that aggregation plays an important role in the behavior of starch.

The low-viscosity canna starch acetate here described appears to be the first example of a derivative of a single unaggregated starch molecule obtained directly from a natural source without preliminary disaggregation. Similar acetyl and methyl derivatives of a "simplified amylose" have been described by Haworth and his associates[18,19] but these preparations were obtained from material that had undergone special pretreatment for the purpose of disaggregating it and the disaggregated material showed a tendency to revert to a reaggregated state.

The phosphorus in canna starch persisted throughout the processes of acetylation, deacetylation and also after methylation. The phosphorus content of the original starch was about 0.05% while in the acetylated starch it was 0.03%; when allowance is made for the relative sizes of the molecules, the amount of phosphorus is virtually unchanged. After deacetylation and regeneration of the starch the phosphorus content is very close to its value in the original starch.

(15) Staudinger, "Die Hochmolekularen organischen Verbindungen Kautschuk und Cellulose," Julius Springer, Berlin, 1932, pp. 56–75.

(16) McBain and Scott, *Ind. Eng. Chem., Anal. Ed.*, **28**, 470 (1936).

(17) Sponsler and Dore, *Colloid Symposium Monograph*, **4**, 174 (1926).

(18) Baird, Haworth and Hirst, *J. Chem. Soc.*, 1201 (1935).

(19) Haworth, *Chemistry and Industry*, **54**, 859 (1935).

These facts seem to indicate that the phosphorus is an integral part of the starch molecule. The view of Samec and his collaborators[20,21] that the insolubility of starch in water, and its gelatinizing power are due to its phosphorus content could not be substantiated in the case of canna starch. After regeneration of the acetylated starch a product was obtained which retained the full phosphorus content and yet was soluble in water. Hirst, Plant and Wilkinson[2] also found that a soluble amylose fraction containing its original phosphorus content could be obtained from potato starch. The claim of Samec that insolubility of starch is due to its phosphorus content is therefore not sustained.

Experimental

Reprecipitation of Canna Starch.—The canna starch used in this study was first treated by bursting the granules and reprecipitation from alcohol according to the procedure of Haworth, Hirst and Webb.[8] A 3% suspension of the starch was heated on the steam-bath with continuous stirring until a paste was formed. After heating for thirty more minutes the starch was precipitated by the addition of 95% alcohol. The supernatant liquid was poured off and the precipitated starch was filtered off in a Büchner funnel. It was then ground in a mortar in the presence of alcohol, filtered again, washed with alcohol and ether and dried in a vacuum desiccator. The specific rotation of the starch (*c*, 0.1) in 4% sodium hydroxide $[\alpha]_D$ was +156°. Its P content was 0.05%; C, 44.3; H, 6.34 calculated on a dry basis. (Calcd. for $C_6H_{10}O_5$: C, 44.4; H, 6.2.)

Hydrolysis.—The canna starch was hydrolyzed with amylase prepared from saliva and its rate of hydrolysis was compared with that of potato starch. The amylase was prepared as follows: about 25 cc. of saliva was poured into 1 liter of 95% alcohol, allowed to stand for two days and then filtered. The precipitate which formed was filtered off, washed with absolute alcohol and dried in a vacuum desiccator. It was then extracted with water at 40° and the filtrate was diluted to 75 cc. and used for hydrolysis.

Two-gram portions of canna and potato starch were each heated with 10 cc. of water on the steam-bath until gelatinized and then boiled for a few minutes. After cooling to room temperature 25 cc. of the prepared amylase and 2 cc. of 0.01 *N* sodium chloride were added to each flask. A third flask containing 100 cc. of water, 25 cc. of amylase and 2 cc. of 0.01 *N* sodium chloride was also made up and used as a blank. The three flasks were placed in a constant temperature bath at 40°, and the progress of hydrolysis was followed by determining the reducing value every half an hour of a 1-cc. portion of each solution. The rate of hydrolysis of both starches was the same and after five hours both were completely hydrolyzed to the theoretical amount of maltose. The maltose from each was identified by its phenylosazone prepared from the hydrolyzed solution.

(20) Samec, *Chemistry and Industry*, **52**, 389 (1933).

(21) Samec and Mayer, *Kolloid-Beihefte*, **13**, 284 (1921).

Acetylation.—The following two methods were used with slight modification: (a) the method of Haworth, Hirst and Plant[5] using pyridine as a catalyst and (b) the method of Barnett[6] as modified by Irvine and Hirst[7] with chlorine and sulfur dioxide as a catalyst.

(a) To 5 g. of starch, which was ground and screened through a 100-mesh sieve, 50 cc. of pyridine was added. The mixture was kept at 80° for two hours with occasional shaking and then continuously shaken with a mechanical shaker for four hours at room temperature. Fifty cc. of acetic anhydride and 17 cc. of pyridine were added and the mixture again shaken continuously for twelve hours. It was then kept at 60° for four hours, cooled to room temperature and the clear solution poured into a large excess of cold water. The acetylated starch which separated in the form of a flaky white precipitate was washed with water until free of acid, then with alcohol and ether, and dried in a vacuum at 40°. This acetylated starch did not reduce Fehling's solution, gave no color with iodine, and it was difficultly soluble in chloroform and acetone. Its specific rotation (*c*, 0.2) in chloroform, $[\alpha]_D$ was +164. P, 0.024%; $COCH_3$, 45.0%; (calculated $COCH_3$, 44.8%). Its specific viscosity in 0.1% solution in *m*-cresol at 25°, $\eta_{sp.}$ was 0.157. This corresponds to an apparent molecular weight of 22,500, using Staudinger's formula.[15,22]

(b) Five grams of canna starch was ground and sieved as before. It was then allowed to stand in 30 cc. of glacial acetic acid, through which chlorine gas was bubbled, for thirty seconds. Fifty cc. of acetic anhydride, through which sulfur dioxide was bubbled for thirty seconds, was added and shaken for an hour with a mechanical shaker. The solution was filtered, using suction, and poured into a large excess of cold water. The acetylated starch was washed with water, alcohol and ether and dried in vacuum at 40°. The starch triacetate prepared by this method did not reduce Fehling's solution, gave no color with iodine, was readily soluble in chloroform and acetone. Its specific rotation (*c*, 0.2) in chloroform $[\alpha]_D$ was +164°; P content 0.028%; $COCH_3$, 44.8%. The specific viscosity in 0.4% solution in *m*-cresol, at 25°, $\eta_{sp.}$ was 0.121. This corresponds to a molecular weight of 8700, using Staudinger's formula, and indicates that the starch acetate consists of about thirty acetylated glucose units.

Deacetylation.—One gram of the acetylated starch prepared by method (a), using pyridine as a catalyst, was shaken with 25 cc. of 0.5 *N* alcoholic potassium hydroxide for one hour, and the alkali was neutralized with 0.1 *N* acetic acid. The regenerated starch was filtered off, washed with alcohol, and ground in a mortar under alcohol acidified with acetic acid. The deacetylated starch was washed with alcohol until free of acid, then with ether, and dried in vacuum at 35°. The properties of the regenerated product were similar to those of the original canna starch. It stained blue with iodine and was insoluble in water.

(22) Staudinger found the following empirical relation between the molecular weights of certain polymers and the viscosity of their dilute solutions: specific viscosity, $\eta_{sp.} = CK_mM$, where $\eta_{sp.} = \eta_r - 1$; η_r = relative viscosity, or viscosity of solution divided by that of solvent; C = concentration, base moles/liter; K_m = a constant; M = molecular weight. "Base molecular weight" means the molecular weight of the occurring unit in the compound, such as 288 in triacetyl starch. The constant K_m is determined from some independent measurement of molecular weight. Staudinger determined K_m for starch to be 10^{-4}.

Its specific rotation (c, 0.1) in 4% sodium hydroxide was +156°. Its P content was 0.036%.

One gram of the acetylated starch prepared by method (b), using chlorine and sulfur dioxide as catalysts, was deacetylated by the same method as above. This regenerated canna starch was similar in all its properties to the original starch with the exception that it was soluble in water. It stained blue with iodine. Its specific rotation in water was (c, 0.1), $[\alpha]_D$ +198°; P content 0.052%.

Methylation.—The methylation was carried out as follows: 20 g. of canna starch which had been ground and sieved through a 100-mesh sieve was treated with a mixture of 125 cc. of carbon tetrachloride and 90 cc. of methyl sulfate, and stirred vigorously with a mechanical stirrer for fifteen minutes. Two hundred cc. of 35% sodium hydroxide was then added, the stirring being maintained throughout the entire process. The methylating reagents were admitted in portions of 3.3 cc. of methyl sulfate and 7.5 cc. of sodium hydroxide every ten minutes from two dropping funnels. At the end of this process the carbon tetrachloride was evaporated off, the mixture cooled, almost neutralized with sulfuric acid and then treated with an excess of carbon dioxide. Four hundred cc. of hot water was added, and when the mixture was heated to 100° the methylated starch floated to the top. It was then washed several times with boiling water, and dried in the vacuum oven at 80°. The methoxyl content of this methylated starch was 37.4%.

Sixteen grams of the methylated starch (37.4%) was dissolved in 250 cc. of acetone, and treated with 200 cc. of methyl sulfate and 500 cc. of 30% sodium hydroxide. The methylating reagents were added with vigorous stirring in twenty equal portions at intervals of ten minutes, the temperature being maintained between 50 and 55°. At the end of the reaction 400 cc. of hot water was added and the temperature was raised to 100°. After half an hour the methylated starch separated out, was washed with boiling water and dried. The methylated product was redissolved in acetone, and methylated again by the same procedure. After six more methylations a product was obtained with a methoxyl content of 44.4% (calculated OCH_3 content for trimethyl starch 45.6%). Another methylation did not raise this methoxyl content. The methylated starch was then dissolved in chloroform, reprecipitated by the addition of petroleum ether, dried, extracted with ether, and dried again. Its specific rotation $[\alpha]_D$ (c, 0.4) in chloroform was +210°; P content, 0.029%.

Hydrolysis of Methylated Starch and Separation of the Cleavage Products.—Seven and one-half grams of the methylated starch was permeated with 40 cc. of glacial acetic acid by keeping it in a flask for an hour under reduced pressure. Seventy-five cc. of 5% hydrochloric acid was added, and the mixture was kept on a steam-bath for twenty-four hours. Barium carbonate, 10% in excess of the hydrochloric acid used, was then added to the solution, and the mixture evaporated to dryness under reduced pressure at 45°, water being added from time to time to remove the acetic acid. The residue was dried by a mixture of alcohol and benzene, and the cleavage products were separated by repeated chloroform–water extraction.

The procedure followed for the quantitative separation of the cleavage products of the methylated canna starch was similar to that described by Bell[11] in the case of methylated glycogen. The dry residue containing the cleavage products of the methylated starch and the barium salts were exhaustively extracted with benzene. This extract contained the trimethyl- and tetramethylglucoses. The benzene was evaporated off, and the dry residue was dissolved in 8 parts of boiling water. The aqueous solution was cooled and extracted fifteen times with one-twentieth its volume of chloroform. The chloroform solutions were combined then washed three times with one-fortieth of its volume of water. The total water was concentrated in vacuum to one-quarter of its volume and extracted six times with one-fifth of its volume of chloroform. The chloroform solution was washed with water as before.

The combined chloroform solution was evaporated to dryness and extracted with boiling petroleum ether. The extract after evaporation of the petroleum ether yielded 0.304 g. of 2,3,4,6-tetramethylglucose. Its specific rotation $[\alpha]_D$ (c, 1.0) in water was +81.6°. Its methoxyl content OCH_3 was 52.1% (calculated, 52.5%). A small amount of residue which was left after the extraction with petroleum ether was not examined.

The combined water extract was also evaporated to dryness and extracted with a mixture of equal parts of benzene and ether. After evaporation of this mixture a yield of 5.15 g. of 2,3,6-trimethylglucose was obtained. Its specific rotation $[\alpha]_D$ (c, 1.0) when first dissolved in water was about +80°. The solution, however, mutarotated downward and after a few hours came to a constant value of $[\alpha]_D$ +69.4°. Its methoxyl content was 41.7% (calculated OCH_3 content, 41.9%).

The residue, containing the barium salts, after extraction with benzene, was extracted with ethyl acetate. After evaporation of the ethyl acetate 0.15 g. of a thick sirup was obtained. The methoxyl content of this sirup corresponded to dimethylglucose. Its methoxyl content was 30.2% (calculated OCH_3, 29.8%).

From the above figures, the yield of 0.304 g., approximately 4% of 2,3,4,6-tetramethylglucose obtained from 7.5 g. of trimethyl starch, corresponds to an estimated chain length of about twenty-seven α-glucopyranose units.

Summary

1. The molecular structure of canna starch was investigated, and was shown to be closely similar to that of starches obtained from other plant sources. Hydrolysis of the fully methylated starch, followed by a quantitative separation of the cleavage products into 2,3,4,6-tetramethylglucose and 2,3,6-trimethylglucose, showed the starch molecule to be built up of about twenty-seven anhydroglucose units.

2. The data obtained are in favor of the hypothesis that the chemical units of starch, consisting of chains of about twenty-seven anhydroglucose units bound by primary valences, are associated, probably by secondary valences, to form a larger colloidal unit, $[C_6H_{10}O_5)_m]_n$, where n is the number of associated chains, and m is

the number of glucose units in the chain and has a value of from twenty-six to thirty.

3. A starch triacetate containing a single unaggregated molecule has been prepared directly from canna starch without special preliminary disaggregation.

4. A methylation method was developed which does not require previous acetylation of the starch.

5. Samec's correlation of the insolubility of starch with its phosphorus content could not be substantiated in the case of canna starch.

Berkeley, Calif. Received June 8, 1937

[Contribution from the Chemical Laboratory of the University of Illinois]

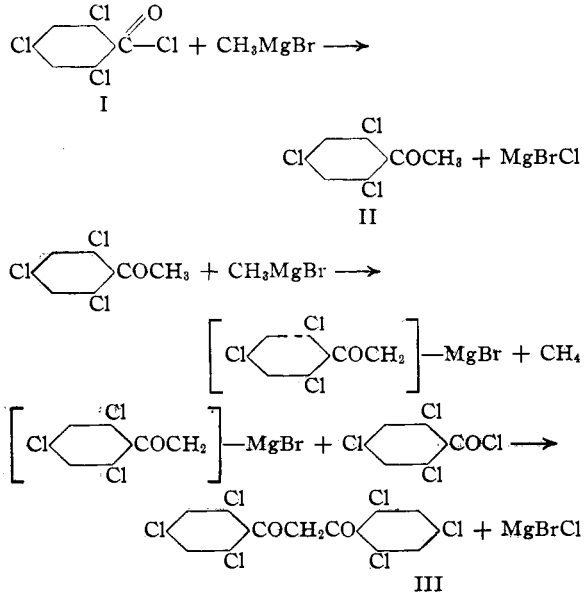
The Action of Methylmagnesium Bromide on 2,4,6-Trichlorobenzoyl Chloride

By W. E. Ross and Reynold C. Fuson

2,4,6-Trichlorobenzoyl chloride (I) when it was treated with methylmagnesium bromide gave rise to either 2,4,6-trichloroacetophenone (II) or to di-(2,4,6-trichlorobenzoyl)-methane (III), depending on the conditions under which the reaction was carried out.

If, for example, the acid chloride was dropped slowly into a great excess (tenfold) of concentrated methylmagnesium bromide solution, the monoketone was produced in yields of from 50 to 60%. However, if the acid chloride was refluxed with one or two molecular equivalents of methylmagnesium bromide for twenty-four hours, the diketone was produced in approximately 50% yields.

Under these last specified conditions the reaction apparently involved the following steps



The diketone gave a red color with ferric chloride, formed a copper derivative when an ether solution was shaken with copper acetate, and liberated two moles of methane when treated with methylmagnesium iodide in the Grignard machine.[1] One mole was liberated in fifteen minutes at room temperature, the second only on heating for fifteen hours.

Treatment with sodium hypochlorite or a solution of chlorine in acetic acid gave dichlorodi-(2,4,6-trichlorobenzoyl)-methane, sodium hypobromite or bromine in acetic acid gave dibromodi-(2,4,6-trichlorobenzoyl)-methane. Both of these compounds were cleaved by concentrated alkali to yield 2,4,6-trichlorobenzoic acid. The unsubstituted diketone was stable to alkalies.

When crystallized from alcohol the dibromodi-(2,4,6-trichlorobenzoyl)-methane lost bromine.[2] Its alcohol solution gave an immediate color with potassium iodide–starch paper.

The monoketone formed the benzal derivative readily. Treatment with sodium hypobromite and hypochlorite solutions resulted in the formation of α,α,α-tribromo-2,4,6-trichloroacetophenone and α,α,α,2,4,6-hexachloroacetophenone, respectively. These two compounds were decomposed by strong alkali containing a solubilizing agent such as alcohol or pyridine. The latter compound yielded a small amount of 2,4,6-trichlorobenzoic acid. No acid was detected in the decomposition of the former.

The compound (m. p. 157°) erroneously reported by Fuson, Bertetti and Ross,[3] as 2,4,6-trichloroacetophenone, is the diketone which melts at 160–161° when pure. Their α,2,4,6-tetrachloroacetophenone is in reality dichlorodi-(2,4,6-trichlorobenzoyl)-methane and the compound reported as α,α,α-tribromo-2,4,6-trichloroaceto-

(1) Kohler, Stone and Fuson, This Journal, **49**, 3181 (1927).
(2) *Cf.* Kröhnke, *Ber.*, **69**, 921 (1936).
(3) Fuson, Bertetti and Ross, This Journal, **54**, 4380 (1932).