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]

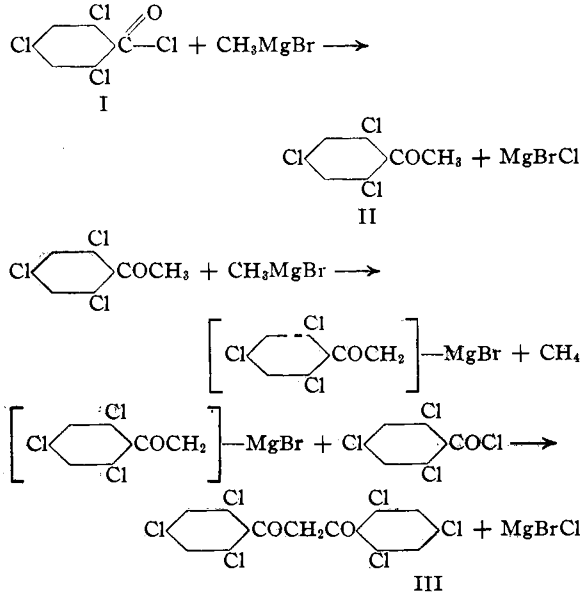
The Action of Methylmagnesium Bromide on 2,4,6-Trichlorobenzoyl Chloride

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).

phenone is dibromodi-(2,4,6-trichlorobenzoyl)-methane.

Experimental

Di-(2,4,6-trichlorobenzoyl)-methane.—When 2,4,6-trichlorobenzoyl chloride is refluxed with one or two mole equivalents of methylmagnesium bromide, iodide, or chloride in ether solution for twenty-four hours, di-(2,4,6-trichlorobenzoyl)-methane is produced in 30 to 50% of the theoretical yield. The melting point of the purified compound is 160–161°.

Anal. Calcd. for $C_{15}H_{16}O_2Cl_6$: C, 41.7; H, 1.4; Cl, 49.38. Found: C, 41.84; H, 1.69; Cl, 48.94.

2,4,6-Trichloroacetophenone.[4]—Three hundred cubic centimeters of 1.47 molar methylmagnesium bromide in ether was placed in a 500-cc., three-necked flask fitted with a sealed stirrer and a condenser set for distillation. The flask was heated until 200 cc. of ether had distilled. The condenser was turned upward for refluxing and 16 g. of 2,4,6-trichlorobenzoyl chloride dissolved in 10 cc. of dry benzene was added to the vigorously stirred solution over a period of fifteen minutes. The mixture was kept hot and the stirring continued for thirty minutes longer. The contents of the flask were diluted with 200 cc. of ether and the mixture poured onto ice and hydrochloric acid Ten grams of product melting at 46–50° was obtained. The purified product melts at 51°.

Anal. Calcd. for $C_8H_5OCl_3$: C, 42.9; H, 2.23; Cl, 47.61. Found: C, 42.68; H, 2.26; Cl, 47.55.

The benzal derivative formed by shaking the ketone with an equal molecular amount of benzaldehyde in an excess of 10% sodium hydroxide solution for twenty hours melts at 100–101°.

Anal. Calcd. for $C_{15}H_9OCl_3$: C, 57.77; H, 2.91; Cl, 34.15. Found: C, 58.03; H, 3.00; Cl, 34.4.

Di-(2,4,6-trichlorobenzoyl)-methane from 2,4,6-Trichloroacetophenone and 2,4,6-Trichlorobenzoyl Chloride.—One gram of ketone was dissolved in 10 cc. of dry benzene and 2.7 cc. of 1.61 molar methylmagnesium bromide was added. The mixture was heated under reflux for one hour. Seven-tenths cubic centimeter (1.1 g.) of the acid chloride was added and the mixture was refluxed for twenty-four hours. On decomposition with dilute hydrochloric acid, 0.78 g. of di-(2,4,6-trichlorobenzoyl)-methane and an oily residue was obtained. The residue was heated with 100 cc. of 5% sodium hydroxide solution for two hours. The solution was cooled and extracted with ether. Evaporation of the ether left a semi-solid material from which 0.2 g. of ketone was recovered. Acidification of the alkaline solution deposited a small amount of 2,4,6-trichlorobenzoic acid. This oily residue was therefore very likely a mixture of unreacted acid chloride and ketone.

α,α,α - Tribromo - 2,4,6 - trichloroacetophenone.—Two grams of finely ground 2,4,6-trichloroacetophenone was shaken with 200 cc. of 10% sodium hypobromite solution for six days. After one day the material suspended in the solution had liquefied. On the second day it had again solidified. The solid material was broken up as finely as possible by means of a stirring rod and the shaking resumed for four days more. The yield of crude material was 4 g. After two crystallizations from alcohol the product melted at 77–78°.

Anal. Calcd. for $C_8H_2OCl_3Br_3$: C, 20.96; H, 0.44. Found: C, 20.93; H, 0.77. Mixed halogen, 1127 g. required 14.64 cc. of 0.1 *N* $AgNO_3$. Found: 14.66 cc.

Forty per cent. sodium hydroxide solution made by dissolving 20 g. of sodium hydroxide in 50 cc. of 20% alcohol, failed to cleave the compound. After refluxing 1 g. with the alkaline solution for twenty-four hours, most of the compound was recovered unchanged. On refluxing with 20% sodium hydroxide solution in 95% alcohol for twenty hours decomposition was effected, but no 2,4,6-trichlorobenzoic acid was obtained.

α,α,α,2,4,6-Hexachloroacetophenone.—Five grams of 2,4,6-trichloroacetophenone was shaken with a mixture of 500 cc. of 10% sodium hypochlorite solution and 100 cc. of ether in a two-liter flask for four days. The ether layer was separated and the aqueous layer was extracted with three 50-cc. portions of ether. The ether extracts were combined, dried with calcium chloride and the ether evaporated. The residue was subjected to vacuum distillation. Four grams of material boiling at 134–137° (3 mm.) was collected. The forerun deposited about half a gram of 2,4,6-trichloroacetophenone after standing for several days. The 4 g. of material boiling at 134–137° was redistilled from a small modified Claisen flask. One gram of material boiling at 127–128° (1.5 mm.) was obtained.

Anal. Calcd. for $C_8H_2OCl_3$: C, 29.37; H, 0.618; Cl, 65.1. Found: C, 29.62; H, 0.927; Cl, 65.3.

Cleavage of α,α,α,2,4,6-Hexachloroacetophenone with Alkali.—One-half gram of α,α,α,2,4,6-hexachloroacetophenone was refluxed with 20 g. of sodium hydroxide dissolved in 100 cc. of 10% alcohol for twenty-four hours. The mixture was allowed to cool and extracted with two 25-cc. portions of ether to remove any alkali insoluble material. The alkaline solution was acidified with hydrochloric acid and extracted with two 25-cc. portions of ether. These extracts were evaporated to dryness, the residue was taken up in 30 cc. of dilute sodium hydroxide solution and filtered. On acidification a small amount of material precipitated. After two reprecipitations from alkaline solution the material melted at 156–159°. A mixed melting point showed it to be 2,4,6-trichlorobenzoic acid.

Dichloro - di - (2,4,6 - trichlorobenzoyl) - methane.—One gram of di-(2,4,6-trichlorobenzoyl)-methane was dissolved in 100 cc. of glacial acetic acid. Chlorine was passed slowly into the solution for thirty minutes. The stream of chlorine was stopped and the flask allowed to stand for twenty hours. The contents were poured into 500 cc. of water. After standing for several hours the precipitate was collected on a filter. Nine-tenths of a gram of compound was obtained. After two crystallizations from alcohol the compound melted at 106–108°.

Anal. Calcd. for $C_{15}H_4O_2Cl_8$: C, 36.02; H, 0.806; Cl, 56.76. Found: C, 35.99; H, 0.848; Cl, 57.13.

The same compound can also be obtained by the prolonged action of 10% sodium hypochlorite solution on finely powdered di-(2,4,6-trichlorobenzoyl)-methane.

Dibromo - di - (2,4,6 - trichlorobenzoyl) - methane.—One gram of di-(2,4,6-trichlorobenzoyl)-methane was dis-

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(4) Lock, *Ber.*, **70**, 916 (1937).

solved in 100 cc. of glacial acetic acid and a large excess of bromine (5 cc.) was added at one time. The mixture was allowed to stand for three days and then poured into a liter of water. Sodium bisulfite was added to discharge the bromine color and after standing for several hours the product was collected on a filter. One and two-tenths grams of crude product was obtained. After two recrystallizations from a carbon tetrachloride–petroleum ether (low-boiling) mixture the material melted at 135–136°.

Anal. Calcd. for $C_{15}H_4O_2Cl_6Br_2$: C, 30.58; H, 0.685. Found: C, 30.84; H, 1.05. Mixed halogen, 0.1176 g. required 15.99 cc. of 0.1 *N* $AgNO_3$. Found: 16.11 cc.

The same material can be made by treating finely powdered di-(2,4,6-trichlorobenzoyl)-methane with 10% sodium hypobromite solution for a period of seven days.

Summary

2,4,6-Trichlorobenzoyl chloride reacts with methylmagnesium bromide to give di-(2,4,6-trichlorobenzoyl)-methane (III). When a large excess of the reagent is used 2,4,6-trichloroacetophenone (II) can be obtained. These compounds react with sodium hypohalites to give the expected halogenation products.

URBANA, ILLINOIS RECEIVED JUNE 3, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Deviations of Carbon Tetrachloride and Silicon Tetrachloride Solutions from Raoult's Law[1]

BY SCOTT E. WOOD[2]

Hildebrand[3] has defined regular solutions as those solutions in which there is no change of entropy when a mole of solute is transferred from an ideal solution to a regular solution of the same concentration. Thus

$$\overline{S}^{r} - \overline{S}^{i} = 0 \qquad (1)$$

where $\overline{S}$ represents the partial molal entropy of a component and the superscripts represent regular and ideal solutions. This definition postulates that the distribution of the molecules in a regular solution would be random or the same as in an ideal solution. The study of the deviations of regular solutions from Raoult's law is thus greatly facilitated, since

$$\overline{F}^{r} - \overline{F}^{i} = \overline{H}^{r} - H^{0} = \Delta\overline{H} \qquad (2)$$

and, when the volumes of the components are additive

$$\overline{F}^{r} - \overline{F}^{i} = \overline{E}^{r} - E^{0} \qquad (3)$$

In these equations, $\overline{F}$, $\overline{H}$, and $\overline{E}$ designate the partial molal free energy, heat content, and energy, respectively, and E^0 the internal energy of one mole of the pure component.

Hildebrand and Wood[4] derived the equation

$$E = \frac{2\pi N^2}{V}\left[n_1^2 \int_{\tau_{11}}^{\infty} \phi_{11}(r)\, W_{11}(r)\, r^2 \mathrm{d}r + n_2^2 \int_{\tau_{22}}^{\infty} \phi_{22}(r)\, W_{22}(r) r^2\, \mathrm{d}r + 2\, n_1 n_2 \int_{\tau_{12}}^{\infty} \phi_{12}(r)\, W_{12}(r)\, r^2 \mathrm{d}r\right] \qquad (4)$$

for the potential energy of $n_1 + n_2$ moles of solution, and also the equation

$$\overline{E}_1 - E_1{}^0 = 2\pi\, N^2 \left(\frac{n_2 v_2}{n_1 v_1 + n_2 v_2}\right)^2 v_1 \left[\frac{2}{v_1 v_2}\int_{\tau_{12}}^{\infty} \phi_{12}(r)\, W_{12}(r)\, r^2 \mathrm{d}r - \frac{1}{v_1{}^2}\int_{\tau_{11}}^{\infty} \phi_{11}(r)\, W_{11}(r)\, r^2 \mathrm{d}r - \frac{1}{v_2{}^2}\int_{\tau_{22}}^{\infty} \phi_{22}(r)\, W_{22}(r)\, r^2 \mathrm{d}r\right] \qquad (5)$$

Here n represents the number of moles of a component; N, Avogadro's number; $\phi(r)$, the intermolecular energy between a pair of molecules; $W(r)$, the radial distribution of molecules about a central one; v, the molal volume of a component of the solution; V, the total volume of the solution; and τ, the distance of closest approach of two molecules. The subscripts (11), (22), (12) indicate the type of molecular pairs. Equation (4) is perfectly general and is applicable to gases, liquids, and solids; however, equation (5) is valid only when the volumes of the components are additive. Letting $n_2 v_2/(n_1 v_1 + n_2 v_2) = z_2$, equation (5) may be reduced to

$$\overline{E}_1 - E_1{}^0 = z_2{}^2\, v_1 \left[\left(\frac{E_1{}^0}{v_1}\right)^{1/2} - \left(\frac{E_2{}^0}{v_2}\right)^{1/2}\right]^2 \qquad (6)$$

with the aid of the following assumptions: (1) that k_{12}, the attractive force constant between un-

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(1) Condensed from a thesis submitted by S. E. Wood in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of California.

(2) Present address, Massachusetts Institute of Technology, Cambridge, Mass.

(3) Hildebrand, THIS JOURNAL, **51**, 66 (1929).

(4) Hildebrand and Wood, *J. Chem. Phys.*, **1**, 817 (1933). *Cf.* Scatchard, *Chem. Rev.*, **8**, 321 (1931); van Laar, *Z. physik. Chem.*, **A137**, 421 (1928); and Heitler, *Ann. Physik*, **4**, 80, 630 (1928).