the excess strontium carbonate was filtered off and washed with cold water. The filtrate and washings were shaken with silver carbonate until free from bromide ion; the solids were then filtered off and washed. Silver was removed from the filtrate as the sulfide. After filtration and aeration, a slight acidity was neutralized to phenolphthalein with strontium hydroxide solution. The solution was then filtered through carbon and concentrated under reduced pressure to 50 cc., filtered, and the concentration continued to 10 cc. The addition of a few drops of alcohol caused a turbidity which increased slightly after a few hours at room temperature. After filtering, the addition of a little more alcohol caused crystallization to begin. Several crops of fine needles were obtained by alternately adding alcohol and chilling; yield of trihydrate of the salt, 3 g. or 54%. After four recrystallizations of the salt[12] from 8 parts of water the rotation of the anhydrous substance became constant at −56.6° (*c*, 1.2108; *l*, 2).[11] The corresponding free acid rotated −11.5° (*c*, 0.9648; *l*, 4).[11]

Anal. Calcd. for $C_5H_6O_6Sr\cdot 3H_2O$: H_2O, 17.8. Found (loss in wt. at 105° *in vacuo*); 17.6. Calcd. for $C_5H_6O_6Sr$: Sr, 35.01. Found: Sr, 34.94.

Oxidation of β-Methyl-*d*-arabinopyranoside.—The procedure was the same as reported for α-methyl-*d*-lyxoside. The yield of strontium salt was 65%. The anhydrous substance rotated +55.0° (*c*, 1.0080; *l*, 2).[11] The corresponding free acid rotated +11.9° (*c*, 0.8390; *l*, 1).[11]

Anal. Calcd. for $C_5H_6O_6Sr\cdot 3H_2O$: H_2O, 17.8. Found (loss in wt. at 105° *in vacuo*): 17.6. Calcd. for $C_5H_6O_6Sr$: Sr, 35.01. Found: Sr, 34.32.

Oxidation of α-Methyl-*d*-mannopyranoside.—This oxidation proceeds more rapidly than in the previous cases so the total reaction time was reduced to one and a half hours. The yield of strontium salt (IV) was 55% after correcting for a small amount of mannoside which was recovered unchanged. The anhydrous form rotated −52.2° (*c*, 0.6280; *l*, 4).[11] The corresponding free acid rotated +25.2° (*c*, 1.044; *l*, 1).[11]

Anal. Calcd. for $C_6H_8O_7Sr\cdot 2H_2O$: H_2O, 11.41. Found: (loss in wt. at 105° *in vacuo*), 12.18. Calcd. for $C_6H_8O_7Sr$: Sr, 31.25. Found: Sr, 31.08.

Oxidation of α-Methyl-*d*-glucopyranoside.—The total reaction time was three and a half hours, and the yield of strontium salt (VI) was 59% after correcting for a small amount of unchanged glucoside. The anhydrous salt rotated −50.7° (*c*, 0.6492; *l*, 2).[11] The corresponding free acid rotated +24.7° (*c*, 1.1440; *l*, 4).[11]

Anal. Calcd. for $C_6H_8O_7Sr\cdot 2H_2O$: H_2O, 11.41. Found: (loss in wt. at 105° *in vacuo*), 11.8. Calcd. for $C_6H_8O_7Sr$: Sr, 31.25. Found: Sr, 31.13.

Summary

1. Several methyl-pyranosides have been oxidized with lead tetraacetate in glacial acetic acid and in chloroform solutions.

2. There has been observed in each case cleavage of the carbon chain with elimination of one carbon and formation of a dialdehyde through the consumption of two moles of oxidizing agent per mole of glycoside.

3. Further oxidation of these dialdehydes with strontium hypobromite has led to isolation of strontium salts of dibasic acids identical with those produced by Jackson and Hudson and Maclay and Hudson through the action of periodic acid and strontium hypobromite on the same methyl-glycosides.

4. In the case of α-methyl-*d*-mannoside it has been shown that in acetic acid at room temperature the removal of carbon three from the first fission product proceeds at a more rapid rate than does the initial cleavage.

CAMBRIDGE, MASS. RECEIVED JUNE 24, 1938

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[12] Mother liquors from this salt developed growths of mold during several weeks' exposure to the laboratory air. A small quantity of a water-insoluble organic compound containing strontium was found as a product.

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

The Coupling Action of the Grignard Reagent. VI. A New Synthesis of Hexaalkylbenzils

BY REYNOLD C. FUSON AND JOSEPH CORSE

The coupling action of the Grignard reagent on halogen compounds has been shown to take place according to the general equation $2RMgX + 2R'X \longrightarrow R{-}R + R'{-}R' + 2MgX_2$.[1] The reaction seems to be conditioned largely by the activity of the halogen atom in the R'X molecule. In fact, similar results are obtained when the alkyl halide is replaced by other types of halogen compounds, notably certain metal halides such as cupric chloride[2] and silver bromide.[3] The metals suffer reduction—a change which is analogous to coupling. It would appear that any halogen compound in which the halogen atom is loosely bound might serve to bring about such effects.

It occurred to us that the halogen atoms of

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[1] Fuson, THIS JOURNAL, **48**, 2681 (1926).

[2] Krizewsky and Turner, *J. Chem. Soc.*, **115**, 559 (1919).

[3] Gardner and Borgstrom, THIS JOURNAL, **51**, 3375 (1929); Gardner, Joseph and Gollub, *ibid.*, **59**, 2583 (1937).

acyl halides should possess sufficient activity for this purpose. However, experience has shown that these react with Grignard reagents to give ketones or carbinols, and it is reasonable to suppose that addition to the carbonyl group takes precedence over other possible types of reactions. By the introduction of steric hindrance, however, it is possible to reduce the rate of the addition reaction and so favor any tendency there may be to undergo coupling.

To test this suggestion, we have made 2,4,6-trimethylbenzoyl chloride and 2,4,6-triethylbenzoyl chloride and treated them with solutions of methylmagnesium iodide. The results verified our prediction; both alkylation and coupling occurred. By analogy with similar types of reactions the equations for the alkylation and the coupling would be as follows

$$\text{Coupling: } 2R_3C_6H_2COCl + 2CH_3MgI \longrightarrow R_3C_6H_2COCOC_6H_2R_3 + C_2H_6 + 2MgICl$$

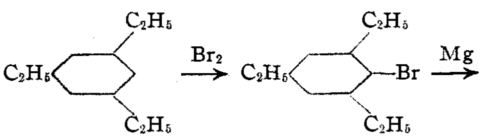
$$\text{Alkylation: } R_3C_6H_2COCl + CH_3MgI \longrightarrow R_3C_6H_2COCH_3 + MgICl$$

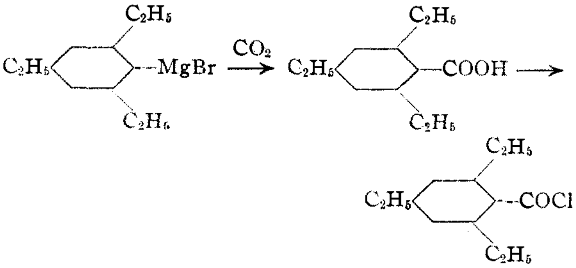
Alkylation alone occurred when the acid chloride was added to the solution of the Grignard reagent. In order to bring about coupling it was necessary to add the reagent to a dilute ether solution of the acid chloride. Under these conditions the yields of hexamethylbenzil and hexaethylbenzil were 39 and 32%, respectively. The alkylation products, acetomesitylene and 2,4,6-triethylacetophenone, were obtained in yields of 35 and 38.5%, respectively.

As a synthetic method for the preparation of hexamethylbenzil this is far superior to those of Kohler and Baltzly,[4] Gray and Fuson[5] and Fuson, Matuszesky and Gray.[6] It is somewhat more convenient than the method of Arnold and Fuson.[7] The hexaethylbenzil had not been made previously.

The work with triethylbenzene derivatives was greatly facilitated by the fact that this hydrocarbon has recently been made readily available by the excellent method of Norris and Rubinstein.[8]

The 2,4,6-triethylbenzoyl chloride was made by the following series of transformations





2,4,6-Triethylacetophenone, the product which accompanied the hexaethylbenzil, had been reported previously by Kunckell[9] but was not characterized. In the present work this ketone and its dinitro and benzal derivatives were synthesized and characterized.

Experimental Part

2,4,6-Triethylacetophenone.—A mixture of 162 g. of 1,3,5-triethylbenzene, 500 cc. of carbon disulfide and 300 g. of anhydrous aluminum chloride was placed in a 2-liter three-necked flask equipped with dropping funnel, stirrer and reflux condenser leading to a gas absorption trap. The mixture was heated to reflux and 101 g. of acetic anhydride was added over a period of one and one-half hours, the rate of addition being adjusted to keep the mixture boiling slightly. The mixture was stirred for an additional hour and allowed to stand for three hours. It was decomposed by pouring into 2 kg. of cracked ice to which 100 cc. of concentrated hydrochloric acid had been added. The layers were separated and the aqueous portion was extracted twice with 100-cc. portions of carbon disulfide. The extracts were added to the separated layer and the combined liquid was dried with calcium chloride. The solution was then filtered and the solvent removed on the steam-bath. The ketone distilled at 115–118° (5 mm.). The yield was 163 g. or 80% of the theoretical amount; $n^{20}{}_D$ 1.5097; $d^{20}{}_4$ 0.9475.

Anal. Calcd. for $C_{14}H_{20}O$: C, 82.26; H, 9.86. Found: C, 82.20; H, 9.79.

3,5-Dinitro-2,4,6-triethylacetophenone.—To 15 cc. of fuming nitric acid cooled to 0° was added 1 g. of 2,4,6-triethylacetophenone. The mixture was allowed to stand for ten minutes and then was poured into 50 g. of chipped ice. The precipitate was collected on a filter and recrystallized from aqueous alcohol. The yield of dry product was 1.3 g. or 90% of the theoretical amount. The compound crystallizes from alcohol in needles which melt at 112–113°.

Anal. Calcd. for $C_{14}H_{18}O_5N_2$: C, 57.13; H, 6.16. Found: C, 57.05; H, 6.06.

Benzal-2,4,6-triethylacetophenone.—A solution of 2.8 g. of sodium hydroxide in 22 cc. of water was made in a 50-cc. flask. To this was added 10 g. of 2,4,6-triethylacetophenone, 30 cc. of 95% ethyl alcohol and 5.8 g. of freshly distilled benzaldehyde. The flask was placed on the shaking machine for eighteen hours. The mixture was then diluted with 10 cc. of water and cooled. The crystalline product was separated and washed with 15 cc. of cold 80% alcohol. The yield of crude product was 14.2 g. or 90% of

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(4) Kohler and Baltzly, THIS JOURNAL, **54**, 4015 (1932).

(5) Gray and Fuson, *ibid.*, **56**, 739 (1934).

(6) Fuson, Matuszesky and Gray, *ibid.*, **56**, 2099 (1934).

(7) Arnold and Fuson, *ibid.*, **58**, 1295 (1936).

(8) Norris and Ingraham, *ibid.*, **60**, 1421 (1938).

(9) Kunckell, *Ber. deut. pharm. Ges.*, **23**, 188 (1913).

the theoretical amount. The compound crystallizes in slightly tinted prisms which melt at 66°.

Anal. Calcd. for $C_{21}H_{24}O$: C, 86.24; H, 8.28. Found: C, 86.14; H, 8.25.

2,4,6-Triethylbromobenzene.—Three hundred and twenty-four grams of 1,3,5-triethylbenzene was added to 200 cc. of carbon tetrachloride in a 2-liter three-necked flask equipped with a stirrer, dropping funnel and reflux condenser which was attached to a gas absorption trap. Ten grams of powdered iron was added and the mixture cooled to 0°. The flask was protected from light as much as possible and 320 g. of bromine dissolved in 200 cc. of carbon tetrachloride was added with vigorous stirring over a period of five hours. The reddish-brown solution was allowed to stand overnight. It was then washed twice with 500-cc. portions of water. once with 500 cc. of 10% sodium hydroxide and with water until the aqueous layer was neutral to litmus. The carbon tetrachloride solution was dried with calcium chloride, filtered and the carbon tetrachloride removed by distillation. The residue was then refluxed one-half hour with an alcoholic solution of sodium hydroxide prepared from 400 cc. of 95% ethyl alcohol and 20 g. of sodium. The solution turned dark red and some sodium bromide precipitated. After standing overnight the solution was diluted with 1 liter of water and the bromide layer separated. The aqueous portion was extracted with three 200-cc. portions of carbon tetrachloride which were added to the halide layer The carbon tetrachloride layer was dried with calcium chloride, filtered and solvent removed on the water pump. The remaining solution was fractionated with the oil pump. Three hundred and forty grams of product boiling at 96–99° (2–3 mm.) was obtained. The yield amounted to 70% of the theoretical; $n^{20}{}_D$ 1.5366; $d^{20}{}_4$ 1.2076.

Anal. Calcd. for $C_{12}H_{17}Br$: C, 59.76; H, 7.11. Found: C, 59.89; H, 7.06.

2,4,6-Triethyl-3,5-dinitrobromobenzene.—Five grams of 2,4,6-triethylbromobenzene was added to 50 cc. of fuming nitric acid cooled to 0°. The mixture was allowed to stand at room temperature for twenty minutes and then poured into 250 cc. of water. The precipitate was collected and recrystallized from alcohol, giving needles which melt at 78.5–79°. The yield amounted to 4.6 g. or 67% of the theoretical.

Anal. Calcd. for $C_{12}H_{15}O_4N_2Br$: N, 8.46; Br, 24.13. Found: N, 8.66; Br, 23.72.

2,4,6-Triethylbenzoic Acid.[10]—Twelve and one-half grams of magnesium turnings was placed in a 1-liter three-necked flask equipped with stirrer, reflux condenser and dropping funnel. A solution of 120.5 g. of 2,4,6-triethylbromobenzene in 200 cc. of dry ether was then added at such a rate that, after the reaction started, gentle refluxing ensued. The addition of reagent takes about two and one-half hours. Stirring was continued for an additional hour, with heating the last twenty minutes. The mixture was then cooled in an ice–salt bath to −5°, and small pieces of dry ice were added cautiously. Care was taken not to add very large pieces because considerable heat is produced in spite of the coldness of the dry ice. After the reaction had spent its force and no appreciable heating took place on addition of dry ice, 50 to 75 g. of dry ice was added and the ice–salt bath removed. The mixture was allowed to come up to room temperature unaided and was then poured into 300 cc. of ice water containing 40 g. of ammonium chloride and 20 cc. of concentrated hydrochloric acid. The ether layer was separated and the aqueous layer washed twice with 100-cc. portions of 0.25 normal hydrochloric acid. The ether was then extracted with one 200-cc. and two 100-cc. portions of 10% sodium hydroxide solution. These were combined, made acid and the precipitate collected. The precipitate was dissolved in a 10% potassium bicarbonate solution. This solution was then extracted with 200 cc. of ether, the aqueous layer separated and boiled a little to remove dissolved ether. The aqueous solution was then cooled and made acid with dilute hydrochloric acid. The yield amounts to 68 g. or 66% of the theoretical. After recrystallization the acid melted at 113–113.5°.

Anal. Calcd. for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.71; H, 8.86.

3,5-Dinitro-2,4,6-triethylbenzoic Acid.—One gram of 2,4,6-triethylbenzoic acid was mixed with 20 cc. of fuming nitric acid and warmed on the steam-bath for thirty minutes. The yellow solution was then poured into 100 cc. of ice water and allowed to stand. The crystals were collected and after recrystallization from ligroin the melting point was 128.5–129°, as compared with 128–129° in the literature.[10]

2,4,6-Triethylbenzoyl Chloride.—To 51.5 g. of 2,4,6-triethylbenzoic acid in a 200-cc. modified Claisen flask, 51 g. of phosphorus pentachloride was added in small portions. When all the phosphorus pentachloride had been added and the reaction subsided, the mixture was warmed slightly for five minutes. The phosphorus oxychloride was removed by the water pump and the acid chloride was then distilled. The acid chloride boiled at 112–113° (4–5 mm.); the yield was 47 g. or 83% of the theoretical amount; $n^{20}{}_D$ 1.5182; $d^{20}{}_4$ 1.0424.

Anal. Calcd. for $C_{13}H_{17}OCl$: Cl, 15.78. Found: Cl, 15.54.

2,4,6-Triethylbenzamide.—To 40 cc. of concentrated aqueous ammonia was added 3.4 g. of 2,4,6-triethylbenzoyl chloride. The mixture was shaken for one hour. The precipitate was then collected and recrystallized from aqueous alcohol. The yield was 2.6 g. or 83% of the theoretical amount. The melting point was 148–150°, and after recrystallization rose to 154.5–155.5°. The literature[10] gives 155–156°.

2,4,6,2′,4′,6′-Hexaethylbenzil.—To a solution of 28.3 g. of 2,4,6-triethylbenzoyl chloride in 200 cc. of absolute ether placed in a 1-liter three-necked flask equipped with stirrer, reflux condenser and dropping funnel, was added 200 cc. of 1.35 molar methylmagnesium iodide solution. The Grignard reagent was added at a regular rate over a two-hour period, and the solution was stirred vigorously. The reaction mixture was then decomposed with an ice–ammonium chloride solution. The ether layer was separated and washed with water twice. The aqueous portion was extracted with two 100-cc. portions of ether, which were added to the ether layer. This ether solution was dried with anhydrous sodium sulfate, then filtered, the ether removed on the steam cone and the residue distilled

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(10) Gattermann, Fritz and Beck, *Ber.*, **32**, 1123 (1899).

with the oil pump. Nine and eight-tenths grams of 2,4,6-triethylacetophenone came over at 112–114° (4–5 mm.). The distillation slowed up and was discontinued at this point. After standing overnight at room temperature, the flask contained yellow crystals. These were removed, filtered and washed with a little 85% alcohol. On recrystallization from petroleum ether, 7.75 g. of product was obtained. The yields of diketone and monoketone were 32.5 and 38.4%, respectively.

The monoketone was identified by means of a mixed melting point of its benzal derivative with an authentic specimen. The diketone crystallized in golden-yellow prisms melting at 75–75.5°.

Anal. Calcd. for $C_{26}H_{34}O_2$: C, 82.49; H, 9.06. Found: C, 82.53; H, 9.01.

2,4,6,2′,4′,6′-Hexamethylbenzil.—The Grignard reagent prepared from 23.7 g. of methyl iodide and 4.06 g. of magnesium diluted to 200 cc. with absolute ether was added with vigorous stirring over a period of seventy minutes to 10.95 g. of 2,4,6-trimethylbenzoyl chloride dissolved in 200 cc. of absolute ether. The reaction mixture was then decomposed and treated in a manner similar to that described for the triethyl compound. The yield of acetomesitylene was 3.44 g. and that of the benzil was 3.45 g., or 35 and 39%, respectively. The acetomesitylene was converted to the benzal derivative which was identified by means of a mixed melting point with an authentic specimen. The dimesityl diketone was likewise identified by comparison with an authentic specimen.

When the acid chloride was added to the solution of the Grignard reagent, it was not possible to isolate any benzil from the reaction products. Instead, acetomesitylene was formed in 88% yields.

Summary

2,4,6-Trimethylbenzoyl chloride and 2,4,6-triethylbenzoyl chloride are coupled by the action of methylmagnesium iodide to give, respectively, 2,4,6,2′,4′,6′-hexamethylbenzil and 2,4,6,2′,4′,6′-hexaethylbenzil.

URBANA, ILLINOIS RECEIVED MAY 23, 1938

[CONTRIBUTION FROM THE CHEMICAL DIVISION OF THE PROCTER & GAMBLE COMPANY]

A Phase Study of the System Sodium Palmitate–Sodium Chloride–Water at 90°

BY ROBERT D. VOLD[1] AND R. H. FERGUSON

It is the aim of this paper to present a complete equilibrium diagram of the system sodium palmitate–sodium chloride–water at 90° with greater precision than that which has characterized any previous published account of a similar system of soap, inorganic electrolyte and water. Especial emphasis is directed to the support of the interpretation of those parts of the diagram where the curd phase[2] is shown.

The practical soap maker has long been familiar with curd soap as an intermediate, distinctive form, differing markedly in its properties from neat soap, the usual finished product of the soap boiling process. However, the first clear concept of curd as a separate and discontinuous phase from neat soap, and of the relations of both these forms of soap to the other coexisting phases is of recent origin. This concept has been developed in a remarkable group of papers by McBain,[3] dealing with the properties and behavior of soap. In these papers both the experimental results and the imagination exhibited in the interpretation are of the first importance in the whole field of soap chemistry.

Inevitably, however, the evidence is not equally convincing with respect to all parts of the diagram constructed by McBain and his co-workers. For example, it is possible to derive conflicting views[4] relating to the presence of definite hydrates in the system at high temperatures, and the early dew-point results[5] do not support the existence of the three-phase invariant equilibrium, neat soap–curd phase–lye. In fact no definite constancy of phase composition has been clearly established hitherto for this equilibrium.

In general, the results of the present work, involving careful, systematic vapor pressure measurements of the system at 90°, are in agreement with McBain's conception of the equilibrium diagram. There are some quantitative divergencies, as may be noted by comparing the McBain diagrams with Fig. 6 below. In particular we have obtained definite proof that crystalline curd phase of sodium palmitate exists at 90° as a distinct phase different from neat soap, and that the neat–

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[2] The term *curd phase* will be used herein to refer to a homogeneous solid phase. In the literature, in addition to this meaning, the word curd has been used to describe variously a heterogeneous mixture of solid soap and other phases, any cooled and solidified soap system, and the upper curdy layer of soap in the soap kettle.

[3] Alexander, "Colloid Chemistry," Vol. I, Chapter by McBain; bibliography, McBain, Lazarus and Pitter, *Z. physik. Chem.*, **A147**, 87 (1930).

[4] Ostwald and Erbring, *Kolloid-Beihefte*, **31**, 345–346 (1930).

[5] McBain and Salmon, *J. Chem. Soc.*, **119**, 1374 (1921).