homogeneous when only 150 g. of the solvent was used. When 70% acetone was used as a solvent hydration did not take place rapidly enough to maintain miscibility, although more solvent was used than was required to keep the 2-hexanone in solution.

When hydration of 1-hexyne was carried out in 60% acetic acid it proceeded sufficiently rapidly so that the mixture remained practically homogeneous despite the fact that much less solvent was used than required to dissolve the acetylene.

In the cases of hydration with aqueous methanol or acetic acid it is possible that the organic solvent may react with the acetylene by addition.[14,15] The resulting ketal or ester would hydrolyze to ketone under the conditions of the experiments.

(14) Killian, Hennion and Nieuwland, THIS JOURNAL, **56**, 1384 (1934).

(15) Hennion and Nieuwland, *ibid.*, **56**, 1802 (1934).

A number of experiments were performed with the object of determining the mechanical losses which resulted from washing, drying and distilling the products. These were found to amount to 10–15% of the material when half-mole quantities of the acetylenes were used. Consequently the actual extent of hydration was, in each case, considerably higher than indicated in Table III.

The application of this method to the hydration of other acetylenic compounds is being further studied in this Laboratory.

Summary

Catalytic hydration of three higher alkylacetylenes to ketones has been accomplished readily and with excellent yields by use of aqueous solvents.

NOTRE DAME, INDIANA RECEIVED NOVEMBER 29, 1937

NOTES

The Explosion of Chloroform with Alkali Metals

BY TENNEY L. DAVIS AND JOHN O. MCLEAN

The explosion which occurs when chloroform and sodium in contact with each other are subjected to shock seems to have been discussed for the first time in 1925 by Staudinger,[1] who described a safe technique for demonstrating it and reported only sodium chloride and carbon as the products. We have wished to account for the hydrogen which the chloroform contains and to identify other products in the hope that light might be thrown upon the mechanism of the reaction.

About 0.3 g. of sodium or of potassium or of the liquid alloy was sealed up in a small glass bulb, 6 to 8 mm. in diameter, which had a capillary stem 15 to 20 mm. in length. This was placed in the bottom of a narrow test-tube and held in place by a collar of glass (a section of glass tubing) which was sintered to the inner wall of the test-tube. The latter was then drawn down, chloroform (1 to 2 cc.) was introduced, and the explosive capsule was sealed. These capsules could be prepared in advance and could be kept safely as long as desired.

For studying the products of the explosion a steel bomb, such as is used for laboratory high pressure syntheses, was taken, about 25 cm. long and having a capacity of 380 cc. It was equipped with valves and copper tubes, by means of which the bomb was flushed out with nitrogen for at least fifteen minutes before each experiment, the pressure existing in the bomb after the explosion was determined, and the gaseous products were swept out with nitrogen. The inside of the bomb was fitted with a cylindrical block of steel by which the explosive capsule was gripped and by the crushing action of which it was fired. The details of the apparatus are shown in Fig. 1. The steel block and capsule being at the end of the bomb which is uppermost in the figure, the explosion was made to occur by inverting the bomb quickly or by dropping it on the floor. The explosion produced heat enough to make the bomb perceptibly warm to the touch.

When one of the capsules was dropped on the concrete pavement from a height of 2 meters, a loud explosion was produced, accompanied by a flash which was visible even in the sunlight, and a cloud of white smoke or mist which smelled distinctly of phosgene.

When the explosion occurred in the bomb in an atmosphere of nitrogen, the interior of the bomb was found to be covered with a deposit of soot. After the bomb had resumed room temperature, the pressure within it was determined by means of a manometer, and the gases were swept out by a stream of nitrogen and bubbled through water for the removal of hydrogen chloride, until a total of 1800 cc. of the mixed gases (mostly nitrogen) had been collected. Twenty-five cc. portions ($^1/_{72}$ of the whole)

(1) Staudinger, *Z. Elektrochem.*, **31**, 549 (1925).

were taken for analysis, and the results were calculated in cc. of each gas present in the bomb after the explosion. The part absorbed by sodium hydroxide solution was taken to be phosgene, for the reasons that carbon dioxide appeared improbable and that the gases precipitated barium carbonate from baryta water producing chloride ions in the solution at the same time. The amount of phosgene was greater than can be ascribed to the air which was sealed up in the capsule, and probably indicates that we had not succeeded in displacing completely the air which was originally present in the bomb. The gases contained no material which reacted with bromine water. They were mixed with oxygen and fired with an electric spark, and the resulting contraction was calculated as hydrogen. The material absorbable by sodium hydroxide which resulted from the combustion, phosgene or carbon dioxide, was taken as equal to the partial volume of chloroform vapor which had been present in the gases. The average results from three analyses on each of three different experiments are reported in Table I.

TABLE I

GASES RESULTING FROM THE EXPLOSION

	I	II	III
Phosgene, cc.	58	43	65
Hydrogen, cc.	36	17	7
Chloroform vapor, cc.	34	43	22
Total gas produced, cc.	128	103	94
Observed increase of pressure, mm.	326	...	195
Calculated increase of pressure, mm.	255	...	161

Since the actual amounts of the gases in the 25-cc. samples which were analyzed varied between 0.1 and 0.8 cc., it is probable that the figures are 20 or 30% in error—and the agreement is considered satisfactory between the observed increases of pressure and those calculated to result from the production of the gases in a space of 380 cc. already filled with nitrogen at atmospheric pressure. If it is supposed that the gaseous organic compound is not chloroform, but is one which contains two carbon atoms, then the agreement is poorer. It seems probable, moreover, regardless of the stoichiometric relations between the amounts of the alkali metal and chloroform, that a certain portion of the chloroform would be blown by the force of the explosion out of the sphere of the reaction and would survive unchanged in the gas phase.

In these experiments no hydrogen chloride was produced; in later experiments in which larger amounts of chloroform and relatively smaller amounts of alkali metal were used it was produced in considerable amount.

For a study of the non-gaseous products extra large capsules, containing 2 g. of potassium and 15 g. of chloroform, were used. Several failed to explode in the bomb designed for smaller capsules, but two of them exploded successfully. The gases contained large amounts of hydrogen chloride, evident by its odor and by test with ammonia. The sooty material in the bomb was brought together and extracted with ether. The red ether extract on evaporation yielded 0.5 cc. of a green oil and 0.5 g. of a reddish solid. The oil had a sp. gr. of 1.100 and commenced to boil at 105°, but decomposed on distillation and yielded no identifiable products. The solid in the molecular still yielded a carbonaceous residue and 0.3 g. of crystalline sublimate, and the latter, recrystallized several times from alcohol in which it was sparingly soluble, yielded pure hexachlorobenzene, colorless needles, m. p. 223°, identified by mixed melting point with a known sample.

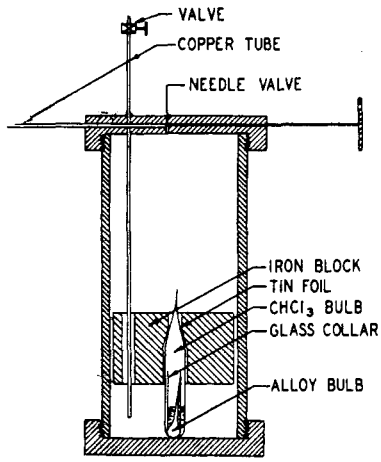

Fig. 1.—Steel bomb with capsule enclosed. The moving parts are in the position which they would occupy at the moment preceding the explosion.

Hydrogen chloride and hexachlorobenzene are known to be produced by the pyrolysis of chloroform.[2] It may be supposed that in our experiments while one portion of the chloroform enters into the explosive reaction, another portion is cracked or pyrolyzed by the energy thus liberated. This cracking however cannot be the sole source of hydrogen chloride or of hydrogen, for the hydrogen which was contained in the chloroform which was concerned in the first explosive reaction would remain to be accounted for. This hydrogen may perhaps be liberated in accordance with one or the other of the following equations, according to the amount of sodium which is available for reaction.

$$CHCl_3 + 3Na \longrightarrow 3NaCl + C + 0.5H_2 \quad (1)$$
$$CHCl_3 + 2Na \longrightarrow 2NaCl + C + HCl \quad (2)$$

These equations, however, fail to account for the hexachlorobenzene which we have found. While this substance may actually arise from a pyrolysis, it may on the other hand be explained, and the other facts accounted for, by supposing that the primary explosive reaction is in accordance with the equation

$$CHCl_3 + Na \longrightarrow NaCl + HCl + \rangle CCl \quad (3)$$

(2) Besson, *Compt. rend.*, **116**, 103 (1893); Conduché, *ibid.*, **158**, 1182 (1914).

Whether the hexachlorobenzene is formed by the explosion or by a pyrolysis, the $>CCl$ radical seems an obvious intermediate between it and chloroform.

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The Fluorescence of Double Salts of Calcium Phosphate

BY JULIAN GLASSER AND GORTON R. FONDA

Ox teeth are known to consist of 1% of organic matter combined with calcium phosphate in an apatite structure. Their fluorescence under ultraviolet radiation is destroyed by burning out their organic content at 600° or higher, but is increased by firing at an optimum temperature of 400°. After solution in acid and precipitation in alkali, the fluorescence is fully restored by refiring at 400°.

A similar product can be made synthetically by coprecipitating a calcium salt with a mixture of sodium phosphate and tartrate and firing at 400°. An optimum fluorescence bluish-white in color is obtained when the solution of sodium phosphate contains 11 molar per cent. of sodium tartrate. The 400° treatment is effective only when carried out in the presence of oxygen. It burns off most of the tartrate but leaves an oxidized residue at a concentration of about 2% by weight combined with the phosphate. The fluorescence under 3650 Å. is double that of teeth and is about 4% of the theoretical, on the basis of complete quantum conversion. The product again has the apatite structure but with an apparently slight contraction of the lattice. Its fluorescence is retained after solution in acid and reprecipitation with alkali. It is destroyed by firing at temperatures above 400°.

A fluorescent product also results by firing at 400° the coprecipitate of calcium phosphate contaminated with some other organic radical, such as succinate or lactate. In fact it appears that the contaminant may even be the calcium salt of an inorganic acid radical, such as borate or chromate. The fluorescence of solids is generally associated with the presence of a small amount of metallic impurity as activator. In this case, however, it appears that the activator may be a foreign acid radical. The possibility of such a type of fluorescence is being studied further.

JULIAN GLASSER
DEPARTMENT OF CHEMISTRY
PENNSYLVANIA STATE COLLEGE
STATE COLLEGE, PENN.

GORTON R. FONDA
RESEARCH LABORATORY
GENERAL ELECTRIC CO.
SCHENECTADY, N. Y.

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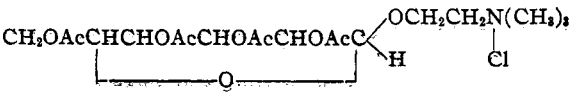
beta-Tetraacetylcholine-*d*-glucoside[1,2]

BY ERNEST L. JACKSON

Schroeter and Strassberger[3] prepared 2-chloroethyl-*d*-glucoside by the reaction of glucose with ethylene chlorohydrin containing hydrogen chloride, condensed their impure 2-chloroethylglucoside with trimethylamine, and from the products prepared a phosphomolybdate of cholineglucoside. The chloride of cholineglucoside, showing $[\alpha]^{15}D + 49.5°$ in water, was obtained in crystalline condition from the phosphomolybdate.

By the reaction of trimethylamine with pure crystalline beta-tetraacetyl-2-chloroethyl-*d*-glucoside[4] in benzene solution the writer has prepared the crystalline chloride of tetraacetylcholine-*d*-glucoside (I) which has a melting point of 230° and a specific rotation[5] of −25.6° in water and −13.5° in chloroform.



(I)

This compound must be a beta-pyranoside, since the parent tetraacetyl-2-chloroethylglucoside was prepared from ethylene chlorohydrin, acetobromoglucose and silver carbonate, a reaction which in the case of other alcohols is known generally to produce beta-pyranosides. Although the chloride of beta-cholineglucoside has not been prepared in crystalline condition, its rotation as determined by an indirect method is near −27° in water. The dextrorotation of Schroeter and Strassberger's product indicates it to be an alpha form which was separated from the mixture of glycosides expected to result from their method of preparation.

(1) Publication authorized by the Surgeon General, U. S. Public Health Service.

(2) The pharmacological properties of this compound are under investigation by Dr. M. I. Smith of this Institute.

(3) G. Schroeter and L. Strassberger, *Biochem. Z.*, **232**, 454 (1931).

(4) Walter Schoeller and Hans-Georg Allardt, German Patent 527,036 (1926); *Chem. Zentr.*, **102**, II, 1452 (1931).

(5) Except where otherwise stated, all rotations in this article are specific rotations at 20° for sodium light.