

0.1380 g. required 13 cc. 0.1 *N* thiosulfate; Cl as : NCl = 33.31. 0.0933 g. gave 12.2 cc. N₂ at 29.8° and 763 mm., N = 19.80. 0.1701 g. gave 0.1387 g. CO₂ and 0.0379 g. H₂O, C = 22.24; H = 2.47. Calc. for C₄H₆O₂N₂Cl₂, C = 22.43; H = 2.34; N = 19.62; Cl = 33.17.

All attempts to prepare the chloroderivative of benzoylbiuret were unsuccessful. It appears that the increment of the acidic nature of the substance by a substitution of the benzoyl group has interfered with the formation of the chloroderivative.

The chloroderivative of other substituted biurets are in the course of preparation, as also other substituted nitrogen chlorides.

CHEMICAL LABORATORY,
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CONTRIBUTIONS TO THE KNOWLEDGE OF HALOGENATION.

VIII. NEW SERIES OF CHLOROXY COMPOUNDS.

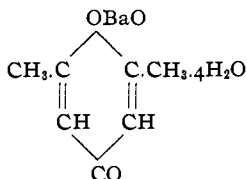
THE HYDROLYTIC CHLORINATION OF DIMETHYL- PYRONE. THE ISOLATION OF 2,6-DICHLORO- HYDROXY-3,5-DICHLORO-4-KETOHEPTANE AND ITS DECOMPOSITION INTO 3,5- DICHLORO-2,4,6-TRIOXYHEPTANE.

BY RASIK LAL DATTA AND SATYARANJAN DAS GUPTA.

Received January 12, 1915.

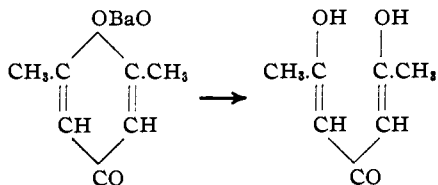
The chlorination of dimethylpyrone has been effected by a variety of reagents. Chlorine has been found quite satisfactory to effect the change, although potassium chlorate and hydrochloric acid and also aqua regia, which give chlorine in the nascent state, can effect the chlorination of dimethylpyrone with the taking up of a water molecule and the opening of the pyrone ring.

The action of barium hydrate on 2,6-dimethylpyrone¹ presents a close analogy to the case in question. When an aqueous solution of dimethylpyrone is boiled with baryta water, there separates an insoluble barium salt, containing four molecules of water of crystallization,

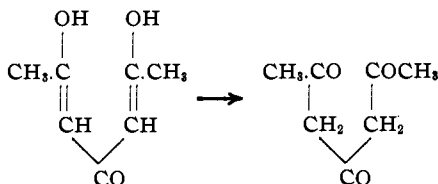


When this salt is dissolved in hydrochloric acid and the resulting solution is extracted with ether, diacetylacetone is formed. By the removal of barium as barium chloride, the hypothetical dihydroxy compound is first formed, thus:

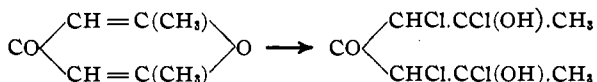
¹ Feist, *Ann.*, 257, 276 (1890).



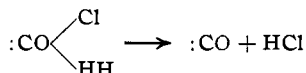
But according to Erlenmeyer's rule¹ free hydroxyl cannot exist as such, it rearranges itself, the oxygen of the hydroxyl unites doubly with carbon and, as a result of such molecular rearrangement, diacetylacetone or 2,4,6-triketetoheptane is produced.



When dimethylpyrone is subjected to the action of chlorine, potassium chlorate and hydrochloric acid and also aqua regia, the compound becomes chlorinated, first four atoms of chlorine attach themselves to the two unsaturated double bonds and, secondly, the pyrone ring opens up, taking a water molecule thus:



Unlike the hydrolytic product from dimethylpyrone itself, the hydroxyl groups are on the doubly united carbon atoms, hence they remain as such, yielding a compound of a new type and remarkable interest. The compound so formed has been found to be 2,6-dichlorohydroxy-3,5-dichloro-4-ketoheptane. In this compound, a chlorine atom and a hydroxyl group are both united with the same carbon atom. The above compound is very unstable, as might be easily inferred from the nature of the groups attached. The attempts at preparing such types of compounds by direct chlorination of compounds containing hydroxyl group have hitherto been a failure, since there is a strong tendency for the splitting off of hydrochloric acid according to the following scheme:

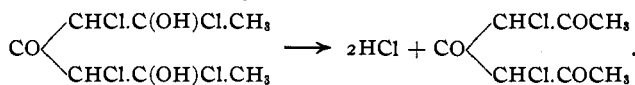


But the formation of such a compound is possible in the case in question by the addition of chlorine atoms to the unsaturated bonds and the simultaneous taking up of water molecule without any side reaction.

As can be well anticipated from the nature of the groups attached,

¹ *Ber.*, 13, 309 (1880); 25, 1781 (1892).

such a compound would readily lose hydrochloric acid and this has been found to be the case. When the compound, which is a fairly viscous oil, was kept in a stoppered bottle, its viscosity diminished in a few days and fumes of hydrochloric acid could be detected with ammonia vapor. The decomposed oil, on treatment with water, gives a white solid which has the formula $\text{CO}(\text{CHClCOCH}_3)_2$, which is 3,5-dichloro-2,4,6-triketoheptane or dichlorodiacetylacetone and is formed from the original substance with the loss of two molecules of hydrochloric acid.



As by the direct hydrolysis of 2,6-dimethylpyrone we get diacetyl acetone, so by the simultaneous chlorination and hydrolysis of 2,6-dimethylpyrone and subsequent hydrolysis of the resulting compound, dichlorodiacetylacetone has been prepared, which is a dichloroderivative of a triketone and it is interesting on account of the fact that similar chloroderivatives have not hitherto been prepared.

(1). **Preparation of 2,6-Dichlorohydroxy-3,5-dichloro-4-ketoheptane.**

(a) **From Chlorine.**—When chlorine is passed to an aqueous solution of dimethylpyrone, the compound separates as a pale yellow oil which could be separated, washed and dried as usual. The yield obtained was nearly quantitative.

(b) **From Potassium Chlorate and Hydrochloric Acid.**—Potassium chlorate and hydrochloric acid acts primarily as a chlorinating and oxidizing reagent; but in this case it acts purely as a chlorinating agent. The best yield of the substance is obtained when the following directions are carried out: Dimethylpyrone is dissolved in an excess of dilute hydrochloric acid (1 : 1) and potassium chlorate in fine crystals is added in small quantities, when it dissolves without any evolution of gas. Repeated shaking with further quantities of potassium chlorate results in its solution, the solution turning yellowish. If the test tube be left to itself, the color appears after a considerable time but if briskly shaken it appears in about fifteen minutes. At the same time a peculiar odor is noticed. When more strong hydrochloric acid is added an immediate haziness is produced, which collects to a colorless oil. The direct precipitation of the oil points to the fact that it is insoluble in water in the presence of hydrochloric acid. After allowing the mixture to stand for some time the pale yellow oil which now collects at the bottom is separated by a separating funnel, washed with small quantities of water and dried by keeping in a desiccator.

The yield obtained is nearly theoretical.

Having no regard to the yield, the oil can be most rapidly prepared thus: Dimethylpyrone is dissolved in excess of strong hydrochloric acid (sp. gr.

1.16) and to it solid specks of potassium chlorate are gradually added with shaking, no second batch being added until the first batch dissolves. Turbidity results almost immediately and more and more of the oil collects. When no further turbidity is produced the addition of potassium chlorate is stopped. The oil can be separated and dried as usual.

(c) **From Aqua Regia.**—The action of aqua regia has been found to be destructive in almost all cases, except in the case of hydrocarbons, where it acts as a simple chlorinating agent¹ chiefly owing to the resisting power of the hydrocarbons. But it is very peculiar that this reagent acts simply as a chlorinating agent to form this substance which is so unstable. Dimethylpyrone is chlorinated quantitatively if the reaction is allowed to take place in the cold, whereas if the reaction be carried out at a slightly higher temperature, the product is a mixture of the chloro derivative and chloropicrin. Again, if the reaction is carried out at 100° pure chloropicrin, which is generally a product of the action of aqua regia on organic bodies, is produced.

For the preparation of the compound, dimethylpyrone in powder is gradually added to a mixture of nitric and hydrochloric acids, the latter being kept cold, preferably by immersion in cold water. Gradually the oil separates, increasing with continued addition of dimethylpyrone. The addition of dimethylpyrone is stopped when no more of the oil separates. The oil is next separated, washed and dried.

0.1824 g. gave 0.1908 g. CO₂ and 0.0417 g. H₂O, C = 28.52; H = 2.54. 0.0733 g. gave 0.1497 g. AgCl, Cl = 50.49. Calc. for C₇H₁₀O₃Cl₄, C = 29.58; H = 3.54; Cl = 50.00.

The substance is a pale yellow, moderately viscous oil which on heating first turns brown, then deep brown, finally leaving a black charred mass behind. The substance slowly decomposes on keeping, with the evolution of hydrochloric acid and a considerable diminution in the viscosity of the oil.

(2). Preparation of 3,5-Dichloro-2,4,6-triketoheptane.

A quantity of the oil which had been kept for some time in a stoppered bottle and whose viscosity had diminished considerably, was heated on the water bath for some time in order to remove any free hydrochloric acid which might be present. The halogen of the resulting oil was determined to ascertain its probable composition,

0.1458 g. gave 0.2914 g. AgCl, Cl = 48.56. Calc. for C₇H₁₀O₃Cl₄, Cl = 50.00.

The nearly equivalent chlorine content of this oil with that of the original oil led us to suspect that although the substance had decomposed into hydrochloric acid yet it might be in a mechanical mixture with the oil. In order to wash out the hydrochloric acid formed, the oil was repeatedly washed with water, when it became more and more viscous,

¹ Datta and Fernandes, THIS JOURNAL, 36, 1007 (1914).

finally showing signs of crystallization. The oil was left under water for some days to allow its crystallization to become complete. The substance was obtained in colorless crystals having a melting point of 145–146°. It was analyzed and was found to be 3,5-dichloro-2,4,6-tri-ketoheptane.

0.1852 g. gave 0.2708 g. CO₂ and 0.0551 g. H₂O, C = 39.58; H = 3.40. 0.2331 g. gave 0.3157 AgCl, Cl = 33.50. Calc. for C₇H₃Cl₂, C = 39.81; H = 3.79; Cl = 33.65.

Further investigations on similar lines are being continued.

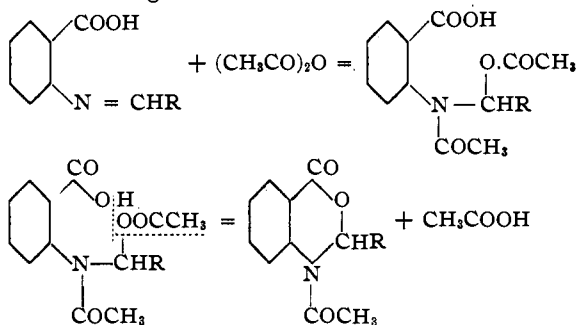
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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF COLORADO.]
THE ACTION OF ACETIC ANHYDRIDE ON SOME BENZYLIDENE ANTHRANILIC ACIDS. IV.

BY JOHN B. EKELEY AND CHARLES F. POE.

Received January 14, 1915.

Eighteen members of a series of acetketodihydrobenzmetoxazines have been described in previous papers.¹ These were obtained by the action of acetic anhydride upon the corresponding benzylidene anthranilic acids, according to the following reactions:



The previous members of this series, as described, were made by heating the benzylidene anthranilic acid with excess of acetic anhydride on the water bath for several hours, then evaporating off the excess of anhydride, and allowing the benzmetoxazine to crystallize out of the cooled concentrated solution. This method failed with certain benzylidene anthranilic acids, notably those derived from anisaldehyde and from piperonal, acetanthranilic acid being obtained instead of the expected benzmetoxazine. By a variation of the method, these benzmetoxazines have also been prepared. The benzylidene anthranilic acid was heated with molecular proportions of acetic anhydride in xylol solution for several hours, the excess of xylol was then distilled off, and the solution cooled in ice water. The benzmetoxazine derivative then crystallized out in a very

¹ THIS JOURNAL, 34, 161; 35, 282; 36, 604.