gave $\alpha = +4.70$ or $[\alpha]^{25}_{D}$ +104.5°. Ten grams of the *l*-salt ($[\alpha]^{25}_{D}$ −45.0°, m. p. 168.5–169°) was converted into the free amine in a similar manner; 0.5031 g. of this amine in 25 cc. of ethyl alcohol gave $\alpha = -4.19$ or $[\alpha]^{25}_{D}$ −104.2°.

Summary

A number of β-ethoxyamines have been partially or completely resolved. A study has been made of the procedure of resolution of these amines with *d*-camphorsulfonic acid and *d*-tartaric acid. It has been shown that it is possible to recrystallize a less soluble salt until a constant rotation is obtained and still not have effected a complete resolution. It is also possible that a salt may be recrystallized twenty or more times without reaching a constant rotation. If the salts of the enantiomorphic forms have a markedly different crystalline form, it is possible to crystallize either from a saturated solution of the active salt of the racemic compound (such as *d*A-*dl*B) by seeding with the pure active salt of the active compound (such as *d*A*d*B or *d*A*l*B).

COLUMBUS, OHIO

RECEIVED NOVEMBER 7, 1932
PUBLISHED APRIL 6, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NEBRASKA]

The Action of Chlorine on *p*-Toluenearsonic Acid under the Influence of Ultraviolet Light and its Chlorination with Hypochlorous Acid

BY CLIFF S. HAMILTON AND WILLIAM N. KING

It has been shown that the presence of phosphorus trichloride, phosphorus pentachloride[1] or ultraviolet light[2] greatly increases the rate of substitution of chlorine into the side chain of an aromatic hydrocarbon, when treated with chlorine. Book and Eggert[3] found that at a temperature of −80° it was possible to obtain a sixty to seventy per cent. yield of benzyl chloride if the reacting mixture was irradiated with ultraviolet light. *p*-Nitrotoluene has been chlorinated in the side chain, by passing the chlorine into the substance heated to 185–190°.[4]

Since toluene and especially *p*-nitrotoluene can be chlorinated in the side chain, it was thought that the analogous *p*-toluenearsonic acid, converted into the corresponding dichloroarsine by means of phosphorus trichloride and dissolved in a suitable solvent such as carbon tetrachloride, could likewise be chlorinated, the idea being to introduce one, two or three chlorine atoms into the side chain, and then by hydrolysis to obtain the corresponding alcohol, aldehyde and acid. In none of the experiments

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[1] F. Berlstein, *Ann.*, **116**, 336 (1860).

[2] Sabatier and Reid, "Catalysis in Organic Chemistry," D. Van Nostrand Co., New York, 1922, p. 105.

[3] Book and Eggert, *Z. Elektrochem.*, **29**, 521 (1923).

[4] Wachendorff, *Ann.*, **185**, 271 (1877).

carried out in this manner was there any indication of side chain substitution. When hexachloroethane, a much higher boiling substance, was used as a solvent the 4-methylphenyltetrachloroarsine formed by the action of chlorine on 4-methylphenyldichloroarsine was decomposed and the product obtained after hydrolysis proved to be *p*-chlorobenzoic acid.

One of the characteristic reactions of tetrachloroarsines is decomposition according to the equation[5]

$$R—AsX_4 = RX + AsX_3$$

However, the literature indicates that most of these reactions are sealed tube reactions, at temperatures around 200°, and no record could be found of the use of chlorine in breaking the arsenic to carbon linkage under normal pressure at temperatures around 180°. Similar results were obtained at temperatures ranging between 75–120° when the reaction was carried out under the influence of ultraviolet light. At temperatures around 100°, the orange colored 4-methylphenyltetrachloroarsine would suddenly decompose into *p*-chlorotoluene and arsenic trichloride after being exposed to the ultraviolet light for about two hours. With continued chlorination at the same temperature and in the presence of ultraviolet light, there was a rapid gain in weight, indicating that the *p*-chlorotoluene was being chlorinated.

Toluene has also been chlorinated by means of hypochlorous acid,[6] the chlorine substituting in the ring or side chain, depending upon the conditions.[7] Hypochlorous acid will chlorinate the side chain if it is more concentrated than one normal or if the temperature is above 40°. Low concentration of hypochlorous acid or low temperature will favor ring substitution.[7] The literature does not reveal an instance where toluenearsonic acids have been chlorinated by means of hypochlorous acid in an aqueous medium. It was found in the case of *p*-toluenearsonic acid that chlorine substituted in the nucleus and not in the side chain. In order to prove the position of the chlorine in the ring, the arsonic acid was converted into the corresponding tetrachloroarsine, the arsenic to carbon linkage broken by the action of chlorine under the influence of ultraviolet light, and the dichlorotoluene thus formed was chlorinated and hydrolyzed to yield 2,4-dichlorobenzoic acid. 3-Chloro-4-methylphenylarsonic acid has not been described previously.

In view of the fact that work in this Laboratory has shown that the arsenic to carbon linkage can be ruptured readily by the use of chlorine in the presence of ultraviolet light, the method should prove of value in the determination of the structure of more complex arsenicals.

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(5) La Coste and Michaelis, *Ann.*, **201**, 198 (1880).

(6) Levinstein and Bader, British Patent 134,909 (1918).

(7) Clark, *Chem. News*, **143**, 265 (1931).

Experimental

4-Methylphenyldichloroarsine.—It was necessary to reduce *p*-toluenearsonic acid since it is insoluble in carbon tetrachloride. The reduction was accomplished by the action of phosphorus trichloride on the arsonic acid.[8]

4-Methylphenyltetrachloroarsine.—This was prepared by the action of dry chlorine on a carbon tetrachloride solution of 4-methylphenyldichloroarsine according to the method of La Coste and Michaelis.[9]

Chlorination with Hexachloroethane as the Solvent.—To 4-methylphenyltetrachloroarsine prepared from 10 g. of *p*-toluenearsonic acid was added 125 g. of hexachloroethane and the temperature held at 140° for the chlorination. The increase in weight was slow, approximately twelve hours being required for the chlorination. One hundred cc. of water was added to the reaction mixture, and after refluxing for a few minutes enough 6 *N* sodium hydroxide was added to make the mixture alkaline to litmus paper. On cooling, the hexachloroethane layer solidified and the water layer was poured off. The water layer was acidified to litmus paper with concentrated hydrochloric acid, and the white crystalline precipitate which formed was filtered off and recrystallized twice from an alcohol–water mixture; yield of *p*-chlorobenzoic acid 70–80%, sublimed at 230–232°. The *p*-chlorobenzoic acid was identified by preparing the amide, which melted at 174°. The neutralization equivalent for the obtained acid was 157.9 (calcd. 156.6).

Optional Method.—Ten grams of *p*-toluenearsonic acid, dissolved in 125 g. of hexachloroethane at a temperature of 140°, was heated to 185–190° and chlorinated for ten hours or until the weight had increased the calculated amount. The mixture was then treated as outlined above and an 80% yield of *p*-chlorobenzoic acid, subliming at 231°, was obtained.

Chlorination in the Presence of Ultraviolet Light.—4-Methylphenyltetrachloroarsine was prepared from 10 g. of *p*-toluenearsonic acid, as outlined above, and the carbon tetrachloride removed under diminished pressure. The resulting product was transferred as a liquid to a 100-cc. quartz flask fitted with a small stirrer which could be rotated rapidly, and a long condenser as well as an inlet tube for dry chlorine. The source of ultraviolet light was a carbon arc lamp placed about six inches from the quartz flask. With rapid stirring the chlorine was allowed to bubble slowly through the 4-methylphenyltetrachloroarsine at a temperature of 90–100°. After the mixture had been exposed to the ultraviolet light for two to three hours, it suddenly lost its orange color and became practically colorless. With continued chlorination in the presence of ultraviolet light, the weight of the flask increased 7.8 g. The solution was cooled to room temperature, 20 cc. of water added slowly through the condenser and then enough 6 *N* sodium hydroxide was added to make the solution alkaline to litmus paper. After refluxing the mixture with stirring for thirty minutes, it was cooled to room temperature, made acid to litmus paper with concentrated hydrochloric acid, decolorized with activated charcoal and finally made acid to Congo red paper. The *p*-chlorobenzoic acid which separated was filtered off and recrystallized twice from an alcohol–water mixture; yield 70–75% of the calculated amount, sublimed 230–232°; identified by preparing its amide.

In another experiment carried out as above, the chlorination was stopped at the point where the orange color of the 4-methylphenyltetrachloroarsine disappeared. The solution was subjected to fractional distillation, three fractions being collected. The first fraction (75–100°) consisted of phosphorus trichloride; the second fraction (100–130°) consisted largely of arsenic trichloride, while the third fraction (130–165°) was almost entirely *p*-chlorotoluene. This final fraction (130–165°) was refractionated

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(8) La Coste, *Ann.*, **208**, 16 (1881).

(9) La Coste and Michaelis, *ibid.*, **201**, 249 (1880).

and 5 cc. of a liquid boiling at 161° was obtained. It was identified as *p*-chlorotoluene by placing it in a quartz flask and chlorinating in the presence of ultraviolet light. Hydrolysis of the product as carried out above gave *p*-chlorobenzoic acid, which was finally converted to the amide. The fraction boiling between 100–130° was dissolved in 6 *N* sodium hydroxide solution, the solution made just acid with hydrochloric acid and hydrogen sulfide passed through. Arsenous sulfide precipitated out, thus identifying the fraction as arsenic trichloride.

Chlorination of *p*-Toluenearsonic Acid with Hypochlorous Acid

3-Chloro-4-methylphenylarsonic Acid.—Fifty grams of sodium hydroxide dissolved in 125 cc. of water was placed in a one-liter round-bottomed flask, fitted with a mechanical stirrer, chlorine inlet, and a tube to lead away the excess chlorine. The flask was placed in an ice-bath and when the temperature of the solution had fallen to 5° or less, chlorine was passed through until the solution acquired a yellow tinge. The temperature of the solution was raised to 20°, and then, with continuous stirring, 10 g. of *p*-toluenearsonic acid dissolved in the minimum quantity of 6 *N* sodium hydroxide was added. The hypochlorous acid was released by the action of 2 *N* hydrochloric acid on the sodium hypochlorite solution, the hydrochloric acid being added just rapidly enough to keep a plentiful supply of hypochlorous acid (bleaches Congo red paper) in the solution at all times. About eight hours were required to add sufficient hydrochloric acid to make the solution definitely acid to Congo red paper. The final addition of hydrochloric acid precipitated the arsonic acid, which was filtered off and recrystallized from a 50% alcohol–water mixture; yield 60%, m. p. > 250°.

Anal. Calcd. for $C_7H_{11}O_3ClAs$: As, 30.20. Found: 30.22, 30.39.

Structure Proof.—In order to prove that the chlorine was substituted in the meta position with respect to the arsono group, the acid was reduced to the dichloroarsine, and treated with chlorine in the presence of ultraviolet light at a temperature around 100°. The characteristic change of color was noted at the end of two hours, and then chlorination was continued in order fully to chlorinate the side chain. Following the method already outlined, 2,4-dichlorobenzoic acid was obtained, m. p. 160°.

3-Chloro-4-carboxyphenylarsonic Acid.—This was prepared by the oxidation of 3-chloro-4-methylphenylarsonic acid with an alkaline solution of potassium permanganate. 3-Chloro-4-carboxyphenylarsonic acid is readily soluble in hot water, ether, and alcohol, m. p. 233°.

Anal. Calcd. for $C_6H_6O_5ClAs$: As, 26.72. Found: 26.62, 26.67.

Summary

1. When *p*-toluenearsonic acid dissolved in hexachloroethane was treated with chlorine at 180–190°, the arsenic to carbon linkage was broken, and then the methyl group of the *p*-chlorotoluene thus formed was chlorinated.

2. At 100°, in the absence of a solvent, but in the presence of ultraviolet light, 4-methylphenyltetrachloroarsine and 3-chloro-4-methylphenyltetrachloroarsine decomposed when treated with chlorine, the arsenic to carbon linkage being ruptured.

3. Chlorine was substituted in the ring by the action of hypochlorous acid on *p*-toluenearsonic acid. 3-Chloro-4-methylphenylarsonic acid and 3-chloro-4-carboxyphenylarsonic acid have been described for the first time.

LINCOLN, NEBRASKA

RECEIVED NOVEMBER 7, 1932
PUBLISHED APRIL 6, 1933