of tricyclohexylamine (m. p. 267–268°). *Anal.* Calcd. for $C_{18}H_{34}NBr$: Br, 23.21. Found: Br, 23.15. Hydrochloride of tricyclohexylamine (m. p. 264°). *Anal.* Calcd. for $C_{18}H_{34}NCl$: Cl, 11.63. Found: Cl, 11.89. Picrate of tricyclohexylamine (m. p. 172.5–173°). "Tricyclohexylamine" from hydrogenation over platinum, b. p. 171–173° (4 mm.). *Anal.* Calcd. for $C_{18}H_{33}N$: C, 82.04; H, 12.64. Found: C, 84.48, 84.27; H, 10.69, 10.62.

Summary

Experimental conditions for the successful hydrogenation over nickel of triphenylcarbinol, triphenylmethane, dicyclohexylphenylmethane, 1,3,5-triphenylbenzene, triphenylamine, 1,3,5-trimethylbenzene and 2,2′,4,4′-6,6′-hexamethyldiphenyl have been determined. Water and ethanol have been found to inhibit the hydrogenation of dicyclohexylphenylmethane. 1,3,5-Tricyclohexylcyclohexane and 2,2′4,4′,6,6′-hexamethyldicyclohexyl have been prepared for the first time. Tricyclohexylmethane and tricyclohexylamine have been found to have physical properties very different from those previously reported.

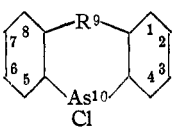
MADISON, WISCONSIN

DERIVATIVES OF THE ARSENIC ANALOG OF 9,10-DIHYDROACRIDINE. I[1]

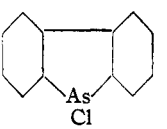
BY WILLIAM GUMP AND HUGO STOLTZENBERG

RECEIVED NOVEMBER 25, 1930 PUBLISHED APRIL 6, 1931

Compounds of the type represented by the Formula I are known in which R is: NH, (10-chloro-9,10-dihydrophenarsazine);[2] O, (10-chloro-



I



II

9,10-dihydrophenoxarsine);[3] S, (10-chloro-9,10-dihydrophenthiarsine);[4] AsCl, (9,10-dichloro-9,10-dihydroarsanthrene).[5] This series contains the arsenic as a hetero atom in a six-membered ring; an example of a five-membered ring is the *o,o′*-diphenylylene arsenious chloride (II).[6]

The synthesis of these compounds can be accomplished in the cases of R=NH and O by heating arsenic trichloride with diphenylamine and with diphenyl ether, but this reaction does not take place with diphenyl,

[1] Read before the Division of Organic Chemistry at the 77th meeting of the American Chemical Society, Columbus, Ohio, April 29 to May 3, 1929.

[2] Bayer and Co., German Patent 281,049 (1913); Wieland and Rheinheimer, *Ann.* **439**, 1 (1921).

[3] Lewis, Lowry and Bergeim, THIS JOURNAL, **43**, 891 (1921); Turner and Sheppard, *J. Chem. Soc.*, **127**, 544 (1925).

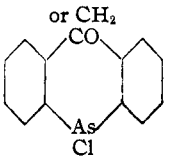
[4] Roberts and Turner, *ibid.*, **129**, 1207 (1926).

[5] Kalb, *Ann.*, **423**, 39 (1921).

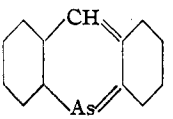
[6] Aeschlimann and co-workers, *J. Chem. Soc.*, **127**, 66 (1925).

diphenylsulfide, diphenylmethane or benzophenone, and other methods have to be used to synthesize these arsenical ring compounds.

Analogs of acridone, 9,10-dihydroacridine and acridine where the nitrogen is replaced by arsenic and which have the structure shown by the Formulas III and IV, thus belonging to the general type I, have not yet



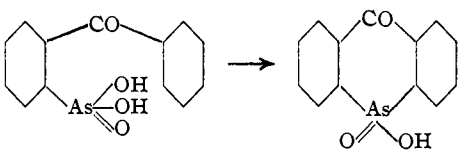
III



IV

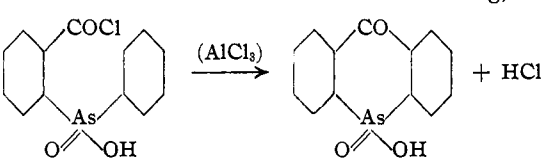
been prepared although several attempts have been made to secure such compounds.

Aeschlimann and McCleland[7] had studied the synthesis of the acridone analog (III) by different methods. They tried to close the ring from ben-



zophenone-*o*-arsonic acid by removing the elements of water by means of sulfuric acid or phosphorus pentoxide in the same way that anthraquinone is prepared from *o*-benzoylbenzoic acid. This method was used successfully in some syntheses of arsenic ring compounds, but the ring formation did not occur here.

Another way was to start from *o*-carboxydiphenylarsinic acid. Aeschlimann prepared the acid chloride and tried to split off hydrogen chloride by means of aluminum chloride in order to close the ring, but the desired



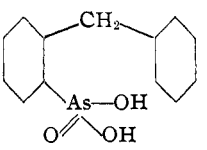
compound could not be obtained. Sakellarios[8] was also unsuccessful in his attempts to form the ring from the *o*-carboxydiphenylarsinic acid, using water-removing condensation agents.

The work done already showed that the synthesis of an arsenic acridone analog is a difficult task. The object of our research was to see if the CH_2 group instead of the CO group would make the ring formation easier and would give the possibility of obtaining acridine and acridone rings with arsenic instead of nitrogen. We propose the name acridarsine for this new

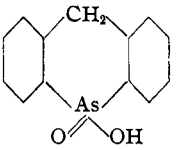
[7] Aeschlimann and McCleland, *J. Chem. Soc.*, **125**, 2025 (1924).

[8] Sakellarios, *Ber.*, **59**, 2552 (1926).

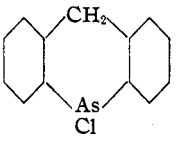
series. We were able to prepare the acridarsinic acid (VI) and the 10-chloro-9,10-dihydroacridarsine (VII).



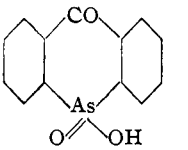
V



VI



VII

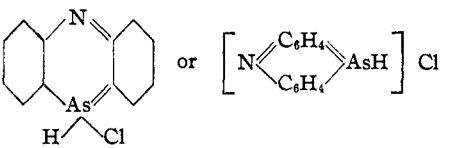


VIII

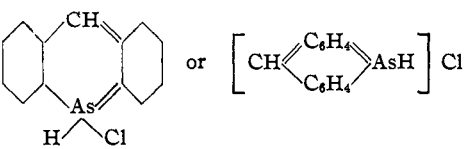
The first step was the preparation of diphenylmethane-*o*-arsonic acid (V) from *o*-aminodiphenylmethane. The well-known method of Bart was used; the diazo solution of *o*-aminodiphenylmethane was coupled with sodium arsenite to the diphenylmethane-*o*-arsonic acid. This arsonic acid could be closed to a ring by means of concentrated sulfuric acid without difficulty, in contrast to the benzophenone-*o*-arsonic acid. Acridarsinic acid (VI) was so formed.

The acridarsinic acid was then reduced to the 10-chloro-9,10-dihydroacridarsine (VII) by means of sulfur dioxide and hydrochloric acid. This compound forms beautiful, yellow-greenish prisms and has distinct physiological properties. It shows the disagreeable qualities of acridine in an increased degree. When dusted in the air in smallest amounts, it causes severe burning of the face, the lips and the tongue. In addition to that, the trivalent arsenic strongly irritates the mucuous surfaces of the bronchial organs in the same way as 10-chloro-9,10-dihydrophenarsazine and other organic arsenic compounds.

In a recent publication, Kappelmeier[9] suggested a new formula for 10-chloro-9,10-dihydrophenarsazine by reason of his experimental results, namely



As the 10-chloro-9,10-dihydroacridarsine behaves like acridine in its skin-irritating properties, it may be also an arsonium salt and have a figuration which is derived from acridine and not from 9,10-dihydroacridine.



The preparation of the acridine analog (III) from the 10-chloro- or the 10-methoxy-9,10-dihydroacridarsine will be investigated.

[9] Kappelmeier, *Rec. trav. chim.*, **49**, 64 (1930).

Another reaction which will be studied is the oxidation of acridarsinic acid. By means of chromic acid–sulfuric acid mixture a new acid, melting above 260°, was obtained from acridarsinic acid. This is probably the 9-oxo-acridarsinic acid (VIII) and the oxidation would lead to the compounds which Aeschlimann was not able to synthesize.

Experimental Part

o-**Aminodiphenylmethane.**—The preparation of this starting material is quite troublesome. Commercial *o*-nitrotoluene was chlorinated to *o*-nitrobenzyl chloride according to the method of Häussermann and Beck[10] using sulfur as chlorine transporter. The yield was always low and could not materially be increased by exposing the reaction mixture to sun or artificial light. For future experiments, it may be more advantageous to nitrate benzyl chloride and to separate the *o*- and *p*-nitrobenzyl chlorides.

The *o*-nitrobenzyl chloride, benzene and aluminum chloride resulted in *o*-nitrodiphenylmethane in a yield of about 75%; the method of Geigy and Königs,[11] modified by Tanasescu,[12] was applied.

o-Nitrodiphenylmethane was reduced to the amino compound with tin and hydrochloric acid. Fischer and Schütte[13] claim that the reduction proceeds very slowly; we found, however, that 50 g. of nitrodiphenylmethane was reduced completely in about one hour. The yield of pure *o*-amino diphenylmethane is at least 80%.

The alkaline reduction of *o*-nitrodiphenylmethane, described by Carre,[14] did not give satisfactory results.

Diphenylmethane-*o*-arsonic Acid.—Thirty-seven grams of *o*-aminodiphenylmethane was dissolved in about 100 cc. of ether. The ether solution was allowed to drop with stirring upon a mixture of 70 cc. of hydrochloric acid and 700 g. of finely crushed ice. The separated hydrochloride was brought into solution by diazotizing with *N*/10 sodium nitrite solution.

Forty grams of arsenious oxide was dissolved in 120 cc. of 5 *N* sodium hydroxide and 300 cc. of sodium carbonate solution (106 g. of anhydrous sodium carbonate in a liter of solution), 25 cc. of an ammoniacal solution of copper sulfate (1:10) and 600 cc. of water were added. This mixture and the diazonium solution were dropped onto 500 g. of ice under stirring during one hour. On the next morning the tar was filtered off, the boiling liquor was decolorized with Darco or Nuchar and hydrochloric acid was added until the solution was neutral. The small amounts of a by-product were filtered off, and the arsonic acid (16 g.) was precipitated by the further addition of hydrochloric acid until congo paper showed blue color.

The diphenylmethane-*o*-arsonic acid is obtained in beautiful, white needles by recrystallization from a large amount of water. The acid, melting at 161–162°, is very slightly soluble in cold water, and somewhat soluble in boiling water. Glacial acetic acid is a good solvent for the arsonic acid.

Anal. Subs., 0.2034: $Mg_2As_2O_7$, 0.1070. Calcd. for $C_{13}H_{13}O_3As$: As, 25.7. Found: As, 25.4.

Acridarsinic Acid.—Ten grams of diphenylmethane-*o*-arsonic acid was dissolved in 40 cc. of concentrated sulfuric acid; the solution was heated in boiling water for five

[10] Häussermann and Beck, *Ber.*, **25**, 2445 (1892).

[11] Geigy and Königs, *ibid.*, **18**, 2402 (1885).

[12] Tanasescu, *Bull. soc. chim.*, [4] **39**, 1453 (1926).

[13] Fischer and Schütte, *Ber.*, **26**, 3086 (1893).

[14] Carre, *Bull. soc. chim.*, [4] **5**, 119 (1909).

minutes, and poured into about 500 cc. of water. Glittering, colorless crystals separated which were filtered and washed with water. The yield is almost quantitative. The crystals melt at 230–235°, becoming yellow at 200° and brown shortly before melting. The acid is obtained in small needles by recrystallization from dilute acetic acid, which melt at 235–236° with disintegration. The acridarsinic acid is almost insoluble in cold and also in boiling water; in warm glacial acetic acid, it is easily soluble.

Anal. Subs., 0.2026: $Mg_2As_2O_7$, 0.1164. Calcd. for $C_{13}H_{11}O_2As$: As, 27.5. Found: As, 27.7.

10-Chloro-9,10-dihydroacridarsine.—Ten grams of acridarsinic acid was finely pulverized and suspended in 100 cc. of hydrochloric acid; 100 cc. of chloroform was added to the suspension. By means of a wide tube which was submerged below the surface of the chloroform, sulfur dioxide and hydrogen chloride were passed through. After five minutes, a little potassium iodide was added and the reduction was completed on the steam-bath under refluxing.

The chloroform solution was separated from the aqueous liquor and the chloroform was distilled off on the steam-bath. The 10-chloro-9,10-dihydroacridarsine (9 g.) remained in large crystals of brownish color. The substance was obtained in beautiful, yellow prisms by recrystallization from benzene. The 10-chloro-9,10-dihydroacridarsine is soluble in the common organic solvents and melts at 114–115°.

Anal. Subs., 0.1411: $Mg_2As_2O_7$, 0.0778. Subs., 0.2318: AgCl, 0.1200. Calcd. for $C_{13}H_{10}ClAs$: As, 27.1; Cl, 12.83. Found: As, 26.7; Cl, 12.81.

Summary

Starting with *o*-aminodiphenylmethane, the diphenylmethane-*o*-arsonic acid and derivatives of the arsenic analog of 9,10-dihydroacridine, such as acridarsinic acid and 10-chloro-9,10-dihydroacridarsine have been synthesized.

BINGHAMTON, NEW YORK

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

THE PIRIA REACTION. I. THE OVER-ALL REACTION[1]

BY W. H. HUNTER AND MURRAY M. SPRUNG

RECEIVED NOVEMBER 28, 1930 PUBLISHED APRIL 6, 1931

Aminosulfonic acids can be obtained directly from aromatic nitro compounds by heating the latter with metal sulfites and then boiling with mineral acids. This reaction was discovered by Piria[2] in 1851, and will therefore be referred to in the following pages as "the Piria reaction." Piria, at that time, subjected α-nitronaphthalene to the action of ammonium sulfite in dilute alcoholic solution, and isolated two reduction products: the ammonium salts of naphthionic acid and of α-naphthylsulfaminic acid, respectively.

[1] The work described in this paper formed part of a thesis submitted to the Graduate Faculty of the University of Minnesota by Murray M. Sprung in partial fulfilment of the requirements for the degree of Doctor of Philosophy, September, 1928. Presented before the Division of Organic Chemistry of the American Chemical Society at the Minneapolis Meeting, September 9–16, 1929.

[2] Piria, *Ann.*, **78**, 31 (1851).