most favorable and 4 and 5 positions are most unfavorable for hydroxyl groups; (3) the influence of hydroxyl groups on fluorescence is greater when they occur in the benzene nuclei than when they occur in the phenyl residue, whereas the influence of carboxyl groups is greater in the phenyl residue than in the benzene nuclei.

3. Bromo derivatives of these compounds which have been studied do not fluoresce in any other ordinary solvents except alcohol.

CALCUTTA, INDIA

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

SOME CACODYL DERIVATIVES

BY FRANK A. LEE, CURTIS THING AND WILLIAM M. DEHN

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General

The classical investigations of Robert Bunsen in the cacodyl series have remained substantially free from revision[1] since their publication (1837–1843). This paper develops some new compounds of this series and also concerns itself with reinvestigations of some of Bunsen's compounds, for the purposes both of fixing their formulas and of improving their yields. Though some have been obtained through substitution and oxidation, most of the new compounds herein described are additive or are hydrolytic products of such additive compounds. It is of special interest to note that one chlorine atom of the pentavalent arsenic compounds is characteristically susceptible to hydrolysis.

Experimental Part

Cacodyl was prepared in large quantities by the usual method[2] and was then converted into cacodyl chloride[3] by the use of mercuric chloride. It boiled[4] at 109°.

Preparation of Cacodyl Bromide.[5]—Molecular quantities of potassium bromide and cacodyl chloride with 3 to 4 volumes of absolute alcohol were heated for 4 to 5 hours on a water-bath under a return condenser. Practical exclusion of air is advisable to avoid formation of the hydrated oxybromide. The reaction mixture was distilled from a sand bath as long as any distillate was obtained. The latter was treated with 5 to 10 volumes of water to precipitate the cacodyl bromide, which was then separated, dried with calcium chloride and fractionated. The yield of the bromide, boiling at 130°, was nearly quantitative.

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[1] Ostwald's "Klassiker der Exakten Wissenschaften," No. 27, pp. 138–148. Baeyer recalculated some of Bunsen's data with revised atomic weights and proposed some alternate formulas.

[2] (a) Bunsen, *Ann.*, **37**, 6 (1841); (b) **107**, 257 (1858). THIS JOURNAL, **35**, 2 (1906).

[3] (a) Ref. 2a, p. 30; (b) *Ann.*, **42**, 22 (1842).

[4] Bunsen gave the boiling point as "over 100°."

[5] Ref. 2a, p. 33. Bunsen prepared this compound in accordance with the reaction, $[(CH_3)_2As]_2O + 2HgCl_2 + 2HBr \longrightarrow 2(CH_3)_2AsBr + 2HgCl_2 + H_2O$.

Cacodyl Iodide.[6]—This was prepared in an analogous manner in nearly quantitative yields. It boiled[7] at 155–160°.

Cacodyl Cyanide.[8]—This was prepared from cacodyl chloride and potassium cyanide in an analogous manner. Satisfactory yields of oil boiling at 138° were obtained. Since the cyanide was not found to be excessively poisonous, it probably has the cyanide and not the isocyanide structure. This compound will be studied further.

Cacodyl Chloride and Metallic Sodium.—Equimolecular quantities of the two materials in absolute ether slowly yielded cacodyl and sodium chloride. $2(CH_3)_2AsCl + 2Na \longrightarrow [(CH_3)_2As]_2 + 2NaCl$.

Bunsen's "Basic Cacodyl Superchloride."—Cacodyl chloride was found to be oxidized when in contact with moist air, giving rise to odorless, glistening, transparent, prismatic needles. The compound[9] is best prepared by drawing moist air through an ether solution of cacodyl chloride. Dry air gives no crystals.

Analyses. Calc. for $(CH_3)_2As(OH)_2Cl$: C, 13.75; Cl, 20.32. Found: C, 13.66; Cl, 20.10.

The substance melts at 85°, is soluble in water and alcohol, and is insoluble in ether, chloroform and carbon disulfide. When dissolved in alcohol and reprecipitated by ether it melted at 92° and then contained only 18.00% of chlorine. Bunsen prepared this compound by the action of concd. hydrochloric acid on cacodylic acid: $(CH_3)_2AsO.OH + HCl \longrightarrow (CH_3)_2As(OH)_2.Cl$. Our method of preparation led to the same compound: $2(CH_3)_2AsCl + O_2 + 2H_2O \longrightarrow 2(CH_3)_2As(OH)_2Cl$. A better name for it is *hydrated cacodyl oxychloride* or simply *basic cacodyl chloride.*

Reactions of Cacodyl Chloride with Metallic Chlorides

Mercurous Chloride.—Equimolecular quantities of the two compounds under water slowly yielded a white powdery additive compound. This mixture when boiled yielded cacodyl chloride, mercury, hydrochloric acid and cacodylic acid.[10] $(CH_3)_2AsCl + 2\ HgCl + 2H_2O \longrightarrow (CH_3)_2AsO.OH + 3HCl + 2Hg$.

Mercuric Chloride.—Equimolecular quantities of the compounds quickly yielded an odorless, white, solid additive compound. When this was heated with water it yielded mercury, mercurous chloride, hydrochloric and cacodylic acids. The hot aqueous filtrate gave odorless glistening white rhombic leaflets, which were decomposed but not melted at 210°.

Analysis. Calc. for $(CH_3)_2AsCl(OH)HgCl$: Cl, 18.02. Found: 17.98.

Mol. wt. Calc. 393. Found (ebullioscopic method with water): 320.

This compound develops with hydrochloric acid the odor of cacodyl chloride. It is easily decomposed by hot aqueous solutions of alkalies and alkali carbonates. Its formation is explained by the equations, $(CH_3)_2AsCl + HgCl_2 \longrightarrow (CH_2)_2AsCl_2.HgCl$; $2(CH_3)_2AsCl_2.HgCl + 3H_2O \longrightarrow (CH_3)_2AsCl(OH)HgCl + (CH_3)_2AsO_2H + 3HCl + HgCl$. Obviously the substance is an additive compound of mercuric chloride and

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[6] Ref. 2a, p. 32. Prepared by Bunsen like the bromide.

[7] *Ann.*, **92**, 364 (1854).

[8] Ref. 2a, p. 23. Bunsen distilled mixtures of cacodyl and mercuric cyanide and obtained a very poisonous product melting at 33° and boiling at 140°.

[9] Bunsen's "hydrated cacodyl chloride," $(CH_3)_2As_2O.2HCl$, is closely related. Bunsen's "basic chlorcacodyl" and "cacodyl superchloride" were shown by Baeyer to be, respectively, a mixture of cacodyl oxide with cacodyl chloride, and $(CH_3)_2As(OH)Cl_2$.

[10] Compare this reaction with that of mercurous chloride and dimethylarsine. *Am. Chem. J.*, **35**, 35 (1906).

cacodyl hydroxide.[11] Its solubility in water and easy decomposition by acids and alkalies suggests its possible usefulness in therapeutics. The yield when the substance was prepared above was about 20%. When 1 g. of magnesium oxide was added to 20 g. of the initial additive compound in 400 cc. of water, a 42% yield was obtained. With 2 g. of magnesium oxide, however, no yield at all was obtained. When the 1 g. of magnesium oxide was replaced by 2.5 g. of calcium carbonate, a 61% yield was recovered, but with 5 g. of calcium carbonate no yield was obtained. These experiments show that one molecular equivalent of alkali leads to a maximum yield, but two molecular equivalents destroy it.

Cuprous Chloride.—When 1.5 g. of anhydrous cuprous chloride and 2.4 g. of cacodyl chloride were brought together under petroleum ether, the mixture shaken and permitted to stand, a white additive compound was formed. It was filtered, washed with petroleum ether and dried in a vacuum.

Analysis. Calc. for $(CH_3)_2AsCl.2CuCl$: Cl, 31.42. Found: 31.79.

Cupric Chloride.—When equal weights of anhydrous cupric chloride and cacodyl chloride were brought together in petroleum ether, a dark gray-green, additive compound was formed.

Analysis. Calc. for $(CH_3)_2AsCl.CuCl_2$: Cl, 38.69. Found: 39.19.

The substitution of ordinary ether for the petroleum ether in this preparation yielded a white hydrolytic product.[12]

Analysis. Calc. for $(CH_3)_2AsOH.CuCl_2$: Cl, 27.64. Found: 27.70.

When the anhydrous cupric chloride and cacodyl chloride were brought together in absolute ether, the gray product first formed changed to tan and finally to white. Ethyl chloride was found in the reaction ether.

Analysis. Calc. for $[(CH_3)_2As]_2O.2CuCl_2$: Cl, 28.65. Found: 28.66.

Ferric Chloride.—A mixture of equimolecular quantities of cacodyl chloride and ferric chloride was allowed to stand for months in absolute ether. Green crystals of ferrous chloride were deposited. That the ether contained $(CH_3)_2AsCl_3$, was proved by its hydrolysis of the latter to cacodylic acid.

Summary

Methods are described for the preparation of the bromide, iodide and cyanide of cacodyl and of basic cacodyl chloride, from the chloride. Bunsen's work on "Mercuric chloride cacodyl oxide" has been reinvestigated and the new data are presented. Four new compounds of cacodyl chloride and the copper chlorides are described.

SEATTLE, WASHINGTON

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[11] This compound agrees in all of its properties with the "Mercuric chloride cacodyl oxide" prepared by Bunsen: $[(CH_3)_2As]_2O + 2HgCl_2 \longrightarrow [(CH_3)_2As]_2O.2HgCl_2$.
This formula, however, is disproved by the molecular weight and by Bunsen's own analytical data.

Analyses. Calc. for $(CH_3)_2AsCl(OH)HgCl$: C, 6.09; H, 1.80; Cl, 18.02; Hg, 50.97. Calc. for $[(CH_3)_2As]_2O.2HgCl_2$: C, 6.24; H, 1.57; Cl, 18.44; Hg, 50.17. Found (by Bunsen): C, 6.25; H, 10.76; Cl, 18.01; Hg, 50.76.

It is formed by hydrolysis of the initial additive compound of Bunsen. See *Am. Chem. J.*, **40**, 127 (1908).

[12] See Ostwald, Ref. 1, p. 77, for the instability of Bunsen's compound prepared from cacodyl oxide, hydrochloric acid and cuprous chloride.