oxidation of curium only, while allowing *ca.* 100% oxidation of americium in the same solution.

No evidence for the existence of Cm(IV), -(V) or -(VI) was found in the oxidation of Cm(III)–Am(III) mixtures in either acid or alkaline media under conditions where Am(III) yielded Am(VI) or Am(V), quantitatively. Consequently, the potential of Cm(III) to Cm(IV), (V), or Cm(VI) is at least more negative than the corresponding americium couples. The Cm(III)–(VI) couple is probably more negative than −2 volts (the peroxydisulfate–argentic couple).

A rapid separation method based on the precipitation of CmF_3 from Am(VI) was developed. For macro amounts of curium, CmF_3 is precipitated without carrier, leaving Am(VI) in the supernatant; for amounts of curium where the solubility of CmF_3 is a limiting factor, lanthanum fluoride carrier is used. Where lanthanum is introduced as carrier for CmF_3, a later purification from this element must be performed. This is readily accomplished by means of a column elution using 13 *f* HCl.[6] Where no lanthanum carrier was used, the solubility of CmF_3 was found to be *ca.* 12 μg./ml.

(6) K. Street, Jr., and G. T. Seaborg, This Journal, 72, 2790 (1950).

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Toluene-Soluble Copper and Silver Fluoborates. Decomposition of Diazonium Fluoborates[1]

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During the course of some investigations concerning copper hydrides, a variety of copper compounds was treated with lithium aluminum hydride under various conditions. Compounds of copper soluble in organic media (solvents stable toward lithium aluminum hydride) were sought, and phenylcopper seemed a promising material. Phenylcopper was prepared by Reich[2] *via* the action of Grignard reagents on copper(I) iodide at 0°, as a reactive and unstable substance. Gilman and Straley[3] also prepared phenylcopper and related compounds by Reich's method. Bolth, Whaley and Starkey,[4] and later Whaley and Starkey,[5] decomposed aromatic diazonium fluoborates in the presence of copper and boiling benzene or toluene, and observed that some of the copper was dissolved. They attributed this to the formation of arylcopper compounds, largely on the basis of examination of derivatives with pyridine and other materials. Thus they claimed the identification of the phenylcopper–pyridine derivative as $C_6H_5Cu\cdot3C_5H_5N$, a blue, water-soluble compound.

Phenylcopper *via* Grignard and Diazonium Reagents.—The above preparative methods both were repeated, but gave products widely different, especially in stability and in behavior toward pyridine. Phenylcopper prepared by Reich's method decomposed in toluene solution slowly at 0°, more rapidly at room temperature, forming a copper mirror on the walls of the vessel; further it gave no blue coloration with pyridine. Neither Reich nor Gilman and Straley had noted coloration on dissolving phenylcopper in pyridine. On the other hand, toluene solutions prepared

using benzenediazonium fluoborate and copper, according to Whaley, *et al.*, deposited no copper even on boiling, and with pyridine (and air) yielded blue crystals. Work was, therefore, undertaken to clarify this discrepancy, and possibly employ both types of copper compounds in the copper hydride studies.

The general techniques of Whaley, *et al.*, were followed in work with the diazonium compounds. The principal deviation from their procedure was the use of an all-glass apparatus designed to permit refluxing, stirring, filtration and introduction of pyridine in a strictly air-free system. Pyridine was distilled from aluminum chloride directly into the filtrate. Nitrogen, freed of oxygen by passage through activated cobalt(II) oxide[6] was employed to exclude air and to pressure the solutions through sintered glass disks. Benzene- and *p*-nitrobenzenediazonium fluoborates were prepared using fluoboric acid according to Roe,[7] and dried over sulfuric acid in vacuum desiccators. These compounds, especially the *p*-nitro derivative, were observed to decompose slowly, and preparations two or more weeks old gave some tarry products.

Toluene solutions of phenylcopper were prepared by Gilman and Straley's method; substitution of phenyllithium for phenylmagnesium iodide was found to be advantageous.

Treatment of the filtrate from the benzenediazonium fluoborate–copper reaction with pyridine under air-free conditions caused precipitation of a pale yellow material, and no blue color developed until the mixture was aerated. The yellow and blue substances thus appeared to be copper(I) and copper(II) compounds, respectively. Whaley, *et al.*, supposed the blue material to be formed without air oxidation, and to be $C_6H_5Cu\cdot3C_5H_5N$.

Tetrapyridinecopper(II) Fluoborate.—The blue crystals (A) from benzenediazonium fluoborate were recrystallized from ethanol. *p*-Nitrobenzenediazonium fluoborate, when decomposed similarly in boiling toluene in the presence of copper, gave two reaction products with pyridine and air. Treatment with hot ethanol yielded blue crystals (B) from the soluble portion, and a green residue (C). Substance C was insoluble in the common solvents except glacial acetic acid, which on cooling deposited blue-green crystals (D). Qualitative analysis of A and B disclosed the presence of fluoborate ion, and analysis identified both as tetrapyridinecopper(II) fluoborate, $Cu(C_5H_5N)_4(BF_4)_2$, a substance previously prepared by Lange[8] and by Wilke-Dörfurt and Balz.[9]

The blue crystals were prepared in quantity by dissolving basic copper(II) carbonate in fluoboric acid and adding pyridine, and recrystallizing from ethanol. This preparation (E) was shown by analysis to have the same composition as A and B. Substance C was evidently impure copper(II) hydroxide, and D a partially hydrated copper(II) acetate.

Carbon, hydrogen and nitrogen analyses were made[10] using standard methods. Copper determinations were made iodometrically employing the blue crystals directly, or after successive digestions with alkali and nitric acid, both methods giving identical results. Fluoborate analyses were made gravimetrically by precipitating nitron fluoborate.[8,9,11]

Anal. Calcd. for $Cu(C_5H_5N)_4(BF_4)_2$: Cu, 11.48; C, 43.39; H, 3.64; N, 10.12; BF_4, 31.37. Found for A: Cu, 11.7; C, 43.5; H, 4.1; N, 9.71; BF_4, 31.1. For B: Cu, 11.5; C, 43.5; H, 4.5; N, 8.4; BF_4, 31.5. For E: Cu, 11.5; C, 43.4; H, 4.5; N, 9.0; BF_4, 31.8.

Anal. Calcd. for $Cu(OH)_2\cdot0.5H_2O$: Cu, 59.5; H, 2.8. Found for C: Cu, 60.0; C, 0.0; H, 3.5.

Anal. Calcd. for $Cu(C_2H_3O_2)_2\cdot0.63H_2O$: Cu, 32.9; C, 24.8; H, 3.8. Found for D: Cu, 32.9; C, 25.0; H, 4.5.

Hydrogen analyses of the fluoborates were high, probably on account of partial absorption of boron trifluoride in the weighing tubes. Nitrogen analyses were somewhat low and variable, probably owing to partial loss of pyridine during recrystallization and drying; a portion of A, freshly recrystallized from alcohol–pyridine mixtures, had a nitrogen content of 10.48%.

(1) Presented at the XII International Congress of Pure and Applied Chemistry, New York, N. Y., September, 1951.

(2) R. Reich, *Compt. rend.*, 177, 322 (1923).

(3) H. Gilman and J. M. Straley, *Rec. trav. chim.*, 55, 821 (1936).

(4) F. A. Bolth, W. M. Whaley and E. B. Starkey, This Journal, 65, 1456 (1943).

(5) W. M. Whaley and E. B. Starkey, *ibid.*, 68, 793 (1946).

(6) H. A. Pagel and E. D. Frank, *ibid.*, 63, 1468 (1941).

(7) A. Roe, "Organic Reactions," Vol. V, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 193 ff.

(8) W. Lange, *Ber.*, 59, 2107 (1926).

(9) E. Wilke-Dörfurt and G. Balz, *Z. anorg. allgem. Chem.*, 159, 197 (1927).

(10) Microanalyses were carried out by Mr. J. Piric.

(11) V. L. Berkovich and Y. V. Kulyashev, *J. Applied Chem.* (U.S.S.R.), 10, 192 (1937).

That A, B and E were identical was confirmed through X-ray diffraction patterns made using powdered specimens. The three materials gave patterns identical in every respect. While no structure determination was made, the material had a low order of symmetry, being orthorhombic, monoclinic or triclinic. According to the conclusions of Whaley, *et al.*, substances A and B should be different, namely, C_6H_5-Cu·3C_5H_5N and p-$NO_2C_6H_4Cu$·3C_5H_5N, and it now seems certain that these compositions are erroneous.

Copper(I) Fluoborate via Diazonium Fluoborates.—Identification of the blue crystals as a derivative of copper(II) fluoborate suggested that the intermediate, toluene-soluble copper(I) compound, formed through the attack of copper metal during decomposition of the diazonium fluoborates, was copper(I) fluoborate. This idea was supported by consideration of the well-known solubility of silver perchlorate in aromatic hydrocarbons, the comparable size of copper(I) and silver(I) ions and the similarity of their compounds, the structural resemblance of the fluoborate and the perchlorate ions, and the failure of the copper compound to form when non-aromatic solvents are substituted.[5] Accordingly, the proposed reaction, in the case of the unsubstituted diazonium fluoborate, is

$$2C_6H_5N_2BF_4 + 2Cu \longrightarrow 2CuBF_4 + 2N_2 + (C_6H_5)_2$$
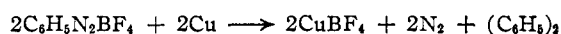
Treatment of toluene filtrates from p-nitrobenzenediazonium fluoborate–copper reaction mixtures with water or very dilute sulfuric acid gave a green copper(II) solution and metallic copper, corresponding to the disproportionation of the copper(I) ion. Moreover, the p,p'-dinitrobiphenyl was isolated and identified as follows. The toluene was steam distilled and the resulting tarry residue recrystallized from alcohol several times. This gave yellow crystals of p,p'-dinitrobiphenyl, m.p. 231–233° (literature, 233°). A portion was reduced to benzidine, which was converted to p,p'-bis-(p-tolylsulfonamido)-biphenyl, m.p. 241–243° (literature, 243°); a mixed melting point of this derivative with an authentic specimen showed no depression.[12]

Silver Fluoborate.—Silver powder was substituted for copper in the decomposition of p-nitrobenzenediazonium fluoborate in boiling toluene, and small but unmistakable quantities of silver as a toluene-soluble substance were detected in the filtrate. The concentration of silver was so low, however, that attempts were made to prepare silver fluoborate in quantity by other means, and investigate its behavior toward toluene.

Silver fluoborate monohydrate was prepared by a slight modification of the procedure of Wilke-Dörfurt and Balz.[9] The evaporation and final drying, which was carried out in vacuum over anhydrous magnesium perchlorate, requiring about five weeks at room temperature, yielded white flakes assaying approximately 93% $AgBF_4·H_2O$. This material was found to dissolve abundantly in toluene with slight evolution of heat, forming a viscous solution. Using the phase data of Hill and Miller[13] on the silver perchlorate–toluene–water system as a guide, it was predicted that addition of water to a toluene solution of the fluoborate should cause it to separate first into two and then into three liquid phases. Accordingly, water was slowly added (temperature 25°) to a toluene solution which was 3.61% H_2O and 39.4% $AgBF_4$ (all percentages by weight). When the water content reached 6.22% (38.4% $AgBF_4$), a second liquid phase began to separate. When the water content reached 9.47% (37.0% $AgBF_4$), a third liquid phase began to separate. More water was added, the three phases separated, and each analyzed. The lower layer was 69.3% $AgBF_4$; the middle layer was 50.0% $AgBF_4$; and the top layer was 0.56% $AgBF_4$, and approximately 91% toluene. These data differ somewhat quantitatively from those of the silver perchlorate system, but are very similar qualitatively.

It was believed profitable to examine the anhydrous system, and accordingly the synthesis was attempted by the action of boron trifluoride on silver fluoride suspended in boiling toluene. Anhydrous silver fluoride was prepared by the method of Moles and Batuecas,[14] modified in that the final dehydration was carried out at 70–75° under vacuum using a large iron vessel. The silver fluoride (0.30 mole) was transferred to the all-glass system employed in the diazonium fluoborate decomposition work, covered with 300

ml. of toluene, stirred vigorously, and boiled under reflux. Boron trifluoride from a tank of compressed gas was bubbled into the suspension for 14 hours. Filtration was effected by nitrogen pressure; essentially all of the silver fluoride had dissolved. The filtrate consisted of two layers, the volume of the upper phase being roughly three times that of the lower.

The existence of a two-liquid phase system was ascribed to adventitious introduction of moisture during transfer of the extremely hygroscopic silver fluoride into the system or to incomplete dehydration of the original material. Relatively little water is required to split either the silver perchlorate–toluene or silver fluoborate–toluene system into two liquid phases. Analysis of each layer showed Ag:BF_4 ratios of 1.12:1 for the lower phase, indicating some excess silver fluoride, and 1.01:1 for the upper phase. The concentrations were 119 and 16.5 mg. of silver per gram for the lower and upper phases, respectively.

Copper(I) Fluoborate via Boron Trifluoride.—It also proved possible to prepare a toluene solution of copper(I) fluoborate through the use of boron trifluoride. Since copper(I) fluoride does not exist at room temperature,[15] a stoichiometric mixture of copper metal and copper(II) fluoride was used instead. The latter compound was prepared by hydrofluorinating basic copper carbonate at 500°. Employing the same apparatus and technique as in the case of the silver compound, the boron trifluoride treatment was carried out for 2.5 hours. The toluene filtrate was treated with very dilute sulfuric acid, when metallic copper and a green copper(II) solution resulted from disproportionation of the copper(I) fluoborate. The copper in each state was determined; the copper(II) constituted slightly more than half of the total. The original toluene filtrate contained 0.382 mg. of Cu per gram of solution.

Attempted Preparation of Copper(I) and Silver Fluoborates via Metathesis.—Stoichiometric quantities of ammonium fluoborate with copper(I) chloride on the one hand and with silver sulfate on the other were refluxed with toluene 24 and 6 hours, respectively. In neither case, however, did detectable amounts of the metal enter the hydrocarbon phase.

Discussion.—If it is supposed that the constitution of silver fluoborate in toluene resembles that of the perchlorate,[16] *i.e.*, ion pairs in dilute solutions, molecular aggregates in more concentrated solution, the existence of solid compounds such as $AgBF_4·C_6H_5CH_3$ is predicted. This behavior may be regarded as another manifestation of the resemblance of fluoborate and perchlorate ions, which, as pointed out by Wilke-Dörfurt,[17] have similar structures, size (Cl–O = 1.63 Å., B–F = 1.53 Å.) and crystal packing behavior. The interaction of silver ions with aromatic hydrocarbons evidently plays the deciding role in the solubility of the perchlorate and fluoborate, and stabilizes the latter; evidently pure silver fluoborate is incapable of existence, except possibly at low temperatures and high boron trifluoride pressure. Apparently a similar situation exists in the case of copper(I) fluoborate. The single bond covalent radii of copper and silver,[18] 1.17 and 1.34 Å., respectively, are not widely different. The subtle factors influencing solubilities of these and related compounds in aromatic hydrocarbons are illustrated by the insolubility of thallium(I) perchlorate, thallium(I) fluoborate,[19] and silver permanganate in toluene, and the moderate solubility of silver trifluoroacetate in benzene.[20]

(15) H. von Wartenberg, *Z. anorg. allgem. Chem.*, **241**, 381 (1939).

(16) A. E. Hill, THIS JOURNAL, **43**, 254 (1921); **44**, 1163 (1922).

(17) E. Wilke-Dörfurt, *Z. angew. Chem.*, **37**, 712 (1924).

(18) L. Pauling, THIS JOURNAL, **69**, 542 (1947).

(19) Prepared by vacuum dehydration of TlBF₄·H₂O at 108°; H. Funk and F. Binder, *Z. anorg. allgem. Chem.*, **159**, 121 (1927).

(20) F. Swarts, *Bull. soc. chim. Belg.*, **48**, 176 (1939).

(12) This part was done by N. Schwartz.

(13) A. E. Hill and F. W. Miller, THIS JOURNAL, **47**, 2702 (1925).

(14) B. Moles and T. Batuecas, *J. chim. phys.*, **17**, 537 (1919).

From molecular weight determinations using benzene solutions, Hill[15] concluded that at higher concentrations, two or even three ion pairs of silver perchlorate associated into clusters. Estimations of the size of the solute particle by Luder, et al.,[21] also indicate dimerization. It may prove possible to determine the solute particle geometry by an

(21) W. L. Luder, P. B. Kraus, C. A. Kraus and R. M. Fuoss, THIS JOURNAL, **58**, 255 (1936).

X-ray diffraction technique, using concentrated solutions of silver perchlorate or fluoborate in toluene, such as was carried out by Vaughan, et al.,[22] with complex ions of certain heavy metals.

(22) P. A. Vaughan, J. H. Sturdivant and L. Pauling, ibid., **72**, 5477 (1950).

DEPARTMENT OF CHEMISTRY
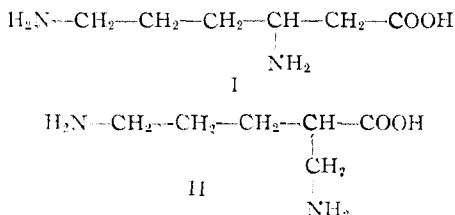UNIVERSITY OF SOUTHERN CALIFORNIA
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COMMUNICATIONS TO THE EDITOR

STRUCTURE OF THE DIAMINOHEXANOIC ACID FROM STREPTOTHRICIN[1]

Sir:

Previously we have reported that streptothricin on hydrolysis yields three ninhydrin-positive products, one of which, the fastest-moving on papergrams, was characterized as a diaminohexanoic acid.[2,3] The same amino acid has been isolated from viomycin[3,4,5] and appears to be present also in streptolin.[3,6]

Possible structures for this substance were limited to isomers I and II on the basis of the following data[2,3]: negative Kuhn–Roth, negative

$$H_2N-CH_2-CH_2-CH_2-CH-CH_2-COOH$$
$$|$$
$$NH_2$$
$$I$$

$$H_2N-CH_2-CH_2-CH_2-CH-COOH$$
$$|$$
$$CH_2$$
$$II \qquad |$$
$$NH_2$$

periodate, and negative α-amino acid tests; degradation via the Curtius reaction to a triaminopentane which reacted with periodate (one mole) yielding ammonia and formaldehyde.

Since further degradation studies were unproductive, the synthesis of isomers I and II was undertaken. I was obtained from α-N-phthalyl-δ-N-benzoyl-L-ornithine by application of the Arndt-Eistert reaction in a manner similar to that described by Balenović, et al.,[7] for derivatives of tyrosine. The resulting β,ϵ-diamino-n-caproic acid

(1) Supported by a grant from the Abbott Laboratories, Eli Lilly and Company, and the Upjohn Company.

(2) H. E. Carter, W. R. Hearn and W. R. Taylor, "Abstracts of Papers," 119th Meeting, American Chemical Society, Cleveland, Ohio, April, 1951, p. 25A.

(3) H. E. Carter, W. R. Hearn and W. R. Taylor, "Abstracts of Papers" 120th Meeting, American Chemical Society, New York, N. Y., September, 1951, p. 3L.

(4) T. H. Haskell, S. A. Fusari, R. P. Frohardt and Q. R. Bartz, THIS JOURNAL, **74**, 599 (1952).

(5) We are indebted to Parke, Davis and Company for a generous supply of viomycin.

(6) E. E. Smissman, R. W. Sharpe and E. E. van Tamelen, "Abstracts of Papers" 121st Meeting, American Chemical Society, Milwaukee, Wisconsin, April, 1952, p. 80.

(7) von K. Balenović, V. Thaller and I. Filipović, Helv. Chim. Acta, **34**, 744 (1951).

was optically active ($[\alpha]^{28}D$ +24°, c 1.1 in 1 N hydrochloric acid), and yielded the following derivatives: p-hydroxyazobenzene-p'-sulfonate, m.p. 246–249°; N,N-dibenzoyl acid, m.p. 113–116° (found: C, 67.94; H, 6.30; N, 7.73); N,N-dibenzoyl methyl ester, m.p. 147–150° (found: C, 68.47; H, 6.42; N, 7.77). The corresponding derivatives of the natural substance ($[\alpha]^{28}D$ +25°, c 1.1 in 1 N hydrochloric acid) melted at 224–246° (found: C, 51.52; H, 4.44; N, 12.23; S, 9.30), 113–116° (found: C, 68.02; H, 5.73; N, 7.93), and 148–150° (found: C, 68.63; H, 6.22; N, 7.86), respectively. The infrared spectra of the N,N-dibenzoyl acids and esters of the synthetic and natural substances were respectively identical. Moreover, crystallization from ethanol of the crude benzoylation products of both the synthetic and natural substances yielded neutral dibenzoyl derivatives (synthetic, m.p. 143–146°, found: C, 68.95; H, 6.77; N, 7.43; natural, m.p. 146–148°, found: C, 68.71; H, 6.97; N, 7.89) having superimposable infrared spectra.

Isomer II was prepared in racemic form by reduction of ethyl α,γ-dicyanobutyrate in a glacial acetic–sulfuric acid mixture with platinum oxide as catalyst. The racemic N,N-dibenzoyl acid (m.p. 156–158°, found: C, 68.13; H, 5.92; N, 7.66) and N,N-dibenzoyl methyl ester (m.p. 119–122°) of II gave infrared spectra differing significantly from those of the corresponding derivatives of the natural substance.

These data establish conclusively that the diaminohexanoic acid from streptothricin and viomycin has structure I (β,ϵ-diamino-n-caproic acid). It is suggested that the trivial name β-lysine be assigned to this compound.

Structural studies upon streptothricin and its hydrolytic products will be reported later in more detail.

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