0.066 expressed as minutes and decimal logarithms), $[\alpha]^{20}_{\rm D}$ +93° (c 9.9, water, final value). The accepted values[20] for the usual crystalline form of D-fructose are: m. p. 102–104°; $[\alpha]^{20}_{\rm D}$ $-132° \rightarrow -93°$ (c 4, water), $k_{20} = 0.0548$ expressed as minutes and decimal logarithms and in 0.001 N potassium acid phthalate (pH 4.4).

The material crystallized in spherical clusters of anhydrous needles. The X-ray powder diagram of this crystal is depicted in Fig. 1, and analyzed in Table I in comparison with the known orthorhombic form of D-fructose.

Anal. Calcd. for $C_6H_{12}O_6$: C, 40.00; H, 6.72. Found: C, 39.72; H, 6.64.

L-Fructose possessed a very sweet taste and was not fermentable by yeast. It readily formed a crystalline, slightly water-soluble compound with calcium hydroxide. It yielded L-glucose phenylosazone; m. p. 211–213° (dec.), a value within the accepted range for the melting point of D-glucose phenylosazone.

D,L-Fructose.—This substance was prepared by dissolving a portion of crystalline D-fructose in methanol and adding this to a solution of a like amount of sirupy L-fructose in methanol. The product crystallized on standing overnight at ice-box temperature; m. p. 132°. Schmitz[7] recorded the m. p. 129–130° for racemic fructose.

Phenyl-L-glucosotriazole.—L-Glucose phenylosazone (4.0 g.) was converted to the phenylosotriazole according to the procedure of Hann and Hudson[21] for the enantiomorph; yield 1.1 g. of m. p. 192°. Pure material was obtained on recrystallization from water; m. p. 194–195°, $[\alpha]^{26}_{\rm D}$ +81.3° (c 1.1, pyridine). Hann and Hudson[21] reported for the enantiomorph: m. p. 195–196°, $[\alpha]^{20}_{\rm D}$ −81.6° (c 0.8, pyridine).

Anal. Calcd. for $C_{12}H_{15}O_4N_3$: C, 54.33; H, 5.70; N, 15.84. Found: C, 54.62; H, 5.72; N, 16.07.

Phenyl-D,L-glucosotriazole.—This substance was prepared by crystallizing equal portions of the enantiomorphs from water; m. p. 185–187°, $[\alpha]^{25}_{\rm D}$ ± 0° (pyridine).

Anal. Calcd. for $C_{12}H_{15}O_4N_3$: C, 54.33; H, 5.70; N, 15.84. Found: C, 54.41; H, 5.52; N, 16.21.

Acknowledgment.—Preliminary work on this problem was carried out in this Laboratory by Messrs. Irving L. Miller and Evan F. Evans. One of us (A. T.) acknowledges a stipend from the funds of The Ohio State University Research Foundation administered by the Graduate School.

Summary

1. Syntheses are described for L-arabonyl chloride tetraacetate, 1-diazo-1-desoxy-*keto*-L-fructose tetraacetate and *keto*-L-fructose pentaacetate.

2. Saponification of *keto*-L-fructose pentaacetate led to the synthesis of L-fructose in crystalline form, further characterized by its crystalline phenylosazone, phenylosotriazole and racemate.

3. The crystalline structure of the L-fructose herein reported is not enantiomorphous with the presently known usual form of D-fructose.

4. Racemic forms of the following have been synthesized: arabonic acid tetraacetate, 1-diazo-1-desoxy-*keto*-fructose tetraacetate, *keto*-fructose pentaacetate, phenyl-glucosotriazole.

COLUMBUS, OHIO RECEIVED[22] FEBRUARY 6, 1946

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[20] H. S. Isbell and W. W. Pigman, *J. Research Natl. Bur. Standards*, **20**, 773 (1938); W. C. Vosburgh, THIS JOURNAL, **42**, 1696 (1920); C. S. Hudson and D. H. Brauns, *ibid.*, **38**, 1222 (1916).

[21] R. M. Hann and C. S. Hudson, THIS JOURNAL, **66**, 735 (1944).

[22] Original manuscript received October 11, 1945.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, SCHOOL OF PHARMACY, UNIVERSITY OF MARYLAND]

Diazonium Borofluorides. V. A Study of Arylcopper Complexes

BY W. M. WHALEY[1] AND E. B. STARKEY[2]

The preceding article of this series[3] recorded the preparation of organocopper compounds from diazonium borofluorides. Preparation was given of several phenylcopper compounds and their stable complexes with pyridine.

The present article describes a further study of this reaction and the compounds produced under varying conditions. Use of two rather than one equivalent of copper did not increase the yield. An important factor was the purity of the diazonium compound as reflected in the yield, the amount of tar formed and the quantity of boron trifluoride evolved. Apparently the reaction proceeds smoothly in any aromatic hydrocarbon of suitable boiling point. No arylcopper compound was formed when the decomposition was carried out in ligroin, diisopropyl ether or dioxane. The decomposition temperature in all cases was definite.

Such basic substances as pyridine cause destruction of diazonium borofluorides and could not be used to stabilize copper compounds as formed. Since amides form stable complexes with organocopper compounds, they were added to the reaction mixture in an attempt to increase the yield. Use of formamide resulted in a definitely increased yield, while dry, powdered acetamide seemed even better. Urea gave an insoluble complex which could not be displaced by pyridine.

Addition of propionitrile to a solution of p-nitrophenylcopper resulted in a white compound, unstable in air. It was thought that addition had occurred at the triple bond of the nitrile, forming the cuprous salt of an imine (I), while its complex with pyridine (II) analyzed correctly and seemed to support the idea. Attempts to obtain p-nitropropiophenone by hydrolysis of I and II were attended with failure, thus reinforcing a previous report that phenylcopper does not react addi-

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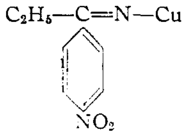
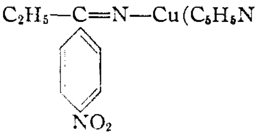
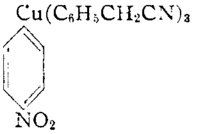
[1] Naval Research Laboratory, Washington, D. C.

[2] The Bunting Chemical Co., Baltimore, Md.

[3] Bolth, Whaley and Starkey, THIS JOURNAL, **65**, 1456 (1943).


I


II


III

tively with benzonitrile.[4] Following this, *p*-nitrophenylcopper was treated with phenylacetonitrile, and analysis of the product showed it to be a complex containing three molecules of nitrile (III). Coördination compounds of other phenylcopper derivatives with nitriles were also prepared as the stable pyridinium complexes.

Several attempts were made to prepare organocadmium compounds[5] through diazonium borofluorides. The results obtained in these experiments indicate that a reaction does occur in dioxane between *p*-nitrophenyldiazonium borofluoride and cadmium–magnesium couple, but whether an arylcadmium compound results is not decided.

Experimental

Diazonium Borofluorides.—The diazonium borofluorides used were sometimes prepared in the usual way,[6] although the amount of fluoboric acid necessary may be reduced one-half by adding two moles of concd. hydrochloric acid. A purer product resulted than in the alternative method of first preparing the diazonium chloride, then adding the fluoboric acid all at once.[7] It was deemed advisable to increase slightly the quantity of sodium nitrite.[8] Substitution of technical sodium fluoborate for the fluoboric acid was tried but yielded a more difficultly purified product.

Arylcopper Compounds.—The general procedure for producing arylcopper compounds was as previously reported,[3] except that rapid filtration in air was feasible and caused little loss of organocopper. Purity was essential: an old sample of phenyldiazonium borofluoride sometimes gave only 1% phenylcopper, and impure *p*-nitrophenyldiazonium borofluoride would produce *p*-nitrophenylcopper without evolving boron trifluoride and with much accompanying tar.

Phenylcopper.—Phenylcopper was produced smoothly in aromatic hydrocarbons.[3] When the decomposition was carried out in dry dioxane the reaction began at 60° and proceeded with violence, producing no copper compound. In ligroin the reaction proceeded at 78°, the filtered solvent containing no copper compound, diphenyl or other solid substance. It is assumed that fluorobenzene was produced.

***p*-Nitrophenylcopper.**—Synthesis of *p*-nitrophenylcopper has been described.[3] The decomposition of *p*-nitrophenyldiazonium borofluoride in diisopropyl ether did not produce any organocopper compound.

***m*-Nitrophenylcopper.**—Decomposition of *m*-nitrophenyldiazonium borofluoride required heating one hour at 120–125° in dry xylene. The supernatant solution was dark, but contained a high concentration of organocopper (34%).

***p*-Sulfonamidophenylcopper.**—*p*-Sulfonamidophenyldiazonium borofluoride reacted rapidly with copper powder at 115° in dry xylene. The water-white filtrate contained 2% of the product.

A decomposition in the presence of formamide resulted in a red gum which was extracted with hot water to give a green solution of the *p*-sulfonamidophenylcopper–formamide complex, which was so stable that it did not decompose in hot, aqueous sodium hydroxide, though it reacted at once with sodium sulfide. By weighing the pyridine complex, the yield was found to be 10%.

Substitution of dry, powdered acetamide for the formamide caused decomposition of the diazonium borofluoride to begin at 50° and proceed exothermally, giving a better yield (15–20%).

If urea was used in the decomposition, reaction began at 70°, filling the flask with red-brown precipitation. The fraction soluble in hot water contained no copper. The insoluble fraction was collected, precipitated from benzene with ligroin, and then appeared as a light-green powder containing copper.

Anal. Calcd. for $H_2NSO_2C_6H_4Cu(H_2NCONH_2)$ (280): Cu, 22.7. Found: Cu, 22.5.

***p*-Sulfonamidophenylpyridinium-copper.**—Prepared by adding pyridine to *p*-sulfonamidophenylcopper or to a complex of the organocopper compound with an amide other than urea.

Anal. Calcd. for $C_{21}H_{21}O_2N_4SCu$ (457): Cu, 14.0. Found: Cu, 13.8.

***p*-Nitrophenylcopper-propionitrile.**—A mixture of propionitrile and *p*-nitrophenylcopper solution slowly formed white prisms which were fairly stable in a closed container, but hydrolyzed in the air and water. The complex was insoluble in benzene and ether, melted at 110° and decomposed at 205°. The compound could not be weighed for analysis.

***p*-Nitrophenylcopper-phenylacetonitrile.**—Addition of benzyl cyanide to a solution of *p*-nitrophenylcopper caused the separation of white crystals which were filtered, washed with ligroin, and stored under ligroin. The complex was fairly stable in air, had a soft, soapy feeling, m. p. 121–123°.

Anal. Calcd. for $O_2NC_6H_4Cu(C_6H_5CH_2CN)_3$ (534): Cu, 11.8. Found: Cu, 11.5.

Phenylpyridinium-copper-octadecenonitrile.—Addition of octadecenonitrile[9] to phenylcopper solution, followed by addition of pyridine, produced a purple precipitate. If the nitrile was placed directly in the mixture during decomposition of the phenyldiazonium borofluoride, then pyridine added at the completion of the reaction, a 9% yield was obtained. The complex was crystallized from alcohol by adding ether. The purple hexagons were soluble in water.

Anal. Calcd. for $(C_6H_5Cu)(C_{17}H_{33}CN)(C_5H_5N)_3$ (641): Cu, 10.0. Found: Cu, 10.4.

***p*-Nitrophenylpyridinium-copper-propionitrile.**—Addition of pyridine to *p*-nitrophenylcopper-propionitrile caused the formation of a blue complex, soluble in water and alcohol, insoluble in ether and benzene.

Anal. Calcd. for $(O_2NC_6H_4Cu)(C_2H_5CN)(C_5H_5N)_3$ (478): Cu, 13.4. Found: Cu, 13.2.

Discussion

Analyses of the nitrile–pyridinium complexes support a pentacovalent formula (IV) for the compounds, and it is this fact that lends the com-

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[4] Gilman and Straley, *Rec. trav. chim.*, **55**, 821 (1936).

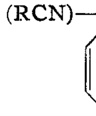
[5] Not obtained from diazonium salts by Waters, *J. Chem. Soc.*, 864 (1939).

[6] The method of Balz and Schiemann, *Ber.*, **60**, 1186 (1927), as used by Starkey, "Organic Syntheses," Coll. Vol. 11, p. 225.

[7] Schiemann and Winkelmüller, *ibid.*, pp. 188, 299; Flood, *ibid.*, p. 295.

[8] Analysis of good quality material indicates a "molecular weight" of 70-71. Saunders, "The Aromatic Diazo Compounds," Longmans, New York, N. Y., 1936, p. 5.

[9] The high molecular weight nitriles were supplied by the Armour Research Foundation.


$(RCN)-Cu\equiv(C_5H_5N)_3$

IV

pounds most of their interest. The covalency of cuprous copper seldom exceeds 3, hence the compounds should be cupric and possess an anion other than the covalent phenyl group. This is supported by their color and their reaction with potassium ferricyanide (yellow-green precipitate). However, uncoördinated arylcopper compounds react with water,[10] organic halides,[4] hydrochloric acid and chloroacetyl chloride[3] to yield inorganic cuprous compounds. In support of the cuprous condition is the analogy with copper iodide, which is only stable in the cuprous state. When considering the coördinated arylcopper compounds it should be noted that cupric iodide forms a complex with ethylenediamine which shows no tendency to revert to the cuprous condition.[11]

From theoretical considerations a 5-covalent copper should be cupric, since its effective atomic number (E. A. N.) would be 37, with krypton at 36 and pentacovalent cuprous copper at 38. By Sidgwick's maximum-covalency rule[12] a covalency of 6 is possible for copper. Werner long ago recorded cuprous halogen complexes with 3, and cupric halogen complexes with 6 molecules of pyridine.[13]

Another possibility is complete ionization of the copper–carbon bond. It may be that the influence of electrons donated by nitrogen decreases the apparent electronegativity of the metal and the arylpyridinium-copper-nitrile complexes could conform to the known cuprous type (V) (E. A. N. = 36).

$$[Cu(RCN)(C_5H_5N)_3]^+[Ar]^-$$

Conclusions

The facts lead the authors to suggest a hypothesis for arylcopper compounds and their complexes: All organocopper compounds themselves and their nitrile complexes contain copper in the colorless cuprous state. The addition of pyridine to either causes a rapid transformation to colored pyridinium complexes with copper in the cupric state. The oxidizing agent and the new anion joining the copper are unknown. However, the oxidizing agent in such cases may be very weak, as shown by the rapid oxidation of cuprous-ammines in air. This idea lends a much greater significance to the study of organocopper compounds, and it suggests new lines of work on electrode-potentials of such systems, on X-ray diffraction of the compounds, and on possible oxygen-carrying power of the compounds in biological systems.

Summary

1. Several new organocopper compounds have been synthesized from the corresponding diazonium borofluorides, and the reaction conditions have been studied.
2. Complexes of arylcopper compounds with nitriles have been prepared and also complexes containing both pyridine and a nitrile.
3. The latter complexes appear to be pentacovalent cuprous compounds, but the hypothesis is proposed that organocopper compounds and their nitrile complexes are cuprous, while the pyridinium complexes are all cupric.

BALTIMORE, MARYLAND RECEIVED NOVEMBER 2, 1945

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[10] Reich, *Compt. rend.*, **177**, 322 (1923).

[11] Sneed and Maynard, "General Inorganic Chemistry," D. Van Nostrand, New York, N. Y., 1942, p. 823.

[12] Sidgwick, "The Electronic Theory of Valency," Oxford, London, 1927, p. 169.

[13] Werner, "Neuere Anschauungen auf dem Gebiete der anorganischen Chemie," 1923, pp. 182, 189.

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 1027]

An Instrument for Determining the Partial Pressure of Oxygen in a Gas[1]

BY LINUS PAULING, REUBEN E. WOOD, AND J. H. STURDIVANT

On October 3, 1940, at a meeting in Washington called by Division B of the National Defense Research Committee, mention was made of the need for an instrument which could measure and indicate the partial pressure of oxygen in a gas. During the next few days we devised and constructed a simple and effective instrument for this purpose. This instrument measures the volume magnetic susceptibility of the gas; its use as an oxygen meter is based on the fact that the magnetic susceptibility of molecular oxygen is very much greater than that of any other common gas. The volume magnetic susceptibility of oxygen at 20° and one atmosphere pressure (standard conditions) is $+142 \times 10^{-9}$ c. g. s. m. u.; all other common gases are diamagnetic, with susceptibilities very much smaller in magnitude: nitrogen -0.40×10^{-9}; hydrogen -0.165×10^{-9}; carbon dioxide -0.83×10^{-9}; helium -0.078×10^{-9}; etc. The magnetic susceptibility of a mixture of common gases is hence de-

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[1] This work was done in whole under the Contracts Nos. NDCrc-38, NDCrc-200, OEMsr-326, and OEMsr-584 between the California Institute of Technology and the Office of Scientific Research and Development, which assumes no responsibility for the accuracy of the statements contained herein. A brief description of this instrument has been published in *Science*, **103**, 2672 (1946).