to 50 ml. To this was added 75 ml. of water and concentrated ammonia to alkalinity, followed by acetic acid to *p*H 4.5. The S-benzyl-*dl*-cysteine was filtered off and partially purified by suspending in 70 ml. of water followed by the addition of sufficient 10% sodium hydroxide to cause solution. The brown solution was filtered free of gummy material and the product was precipitated with acetic acid. Repetition of this treatment followed by a crystallization from water yielded 17 g. (67.5% of theory) of S-benzyl-*dl*-cysteine, melting at 209–211°. Another recrystallization gave material melting at 213–214°, no depression of the melting point with synthetic S-benzyl-*l*-cysteine, melting 213–214°, prepared according to du Vigneaud, *et al.*[11]

Anal. Calcd. for $C_{10}H_{13}NO_2S$: N, 6.64; S, 15.18; neut. equiv., 211. Found: N, 6.64; S, 15.26; neut. equiv.,[12] 213.

5-Benzylmercaptomethylhydantoin.—The procedure used was similar to that of Pierson, *et al.*,[10] for the preparation of 5-(β-methylmercaptoethyl)-hydantoin.

Twenty grams (0.12 mole) of benzylmercaptoacetaldehyde, 57 g. (0.59 mole) of ammonium carbonate, 12.7 g. (0.26 mole) of sodium cyanide and 340 ml. of 50% ethyl alcohol were heated under reflux, and with stirring, at 40–45° for four hours. The reaction mixture was cooled and filtered and the filter cake was washed with a small amount of 95% alcohol. The filtrate and washings were combined and concentrated *in vacuo* to one-half volume. The concentrated solution was heated under reflux to 100° and then 25 ml. of concentrated hydrochloric acid was added. The reaction mixture was allowed to remain at this temperature for ten minutes. It was then cooled and the hydantoin filtered off and recrystallized from hot water to yield 20 g. (70% of theory) of 5-benzylmercaptomethylhydantoin, white needles, m. p. 118–119°.

For purposes of comparison by mixed melting points, the *levo* 5-benzylmercaptomethylhydantoin, melting at 129–130°, was prepared from S-benzyl-*l*-cysteine and was racemized with dilute aqueous sodium hydroxide solution. The *dl*-form prepared in this fashion melted at 118–119° and showed no depression of the melting point on admixture with the hydantoin prepared from benzylmercaptoacetaldehyde.

Preliminary attempts at hydrolysis of 5-benzylmercaptomethylhydantoin with alkali or ammonium sulfide or acid resulted in decomposition without yielding S-benzyl-*dl*-cysteine.

Anal. Calcd. for $C_{11}H_{12}N_2O_2S$: C, 55.90; H, 5.12; N, 11.88; S, 13.58. Found: C, 56.10; H, 4.94; N, 11.87; S, 13.32.

Summary

Benzylmercaptoacetaldehyde has been synthesized and used as a starting material for the preparation of S-benzyl-*dl*-cysteine by a modified Strecker reaction.

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[11] du Vigneaud, Audrieth and Loring, *ibid.*, **52**, 4500 (1930).

[12] The determination was carried out by a modified formol titration. The compound was dissolved in excess standard sodium hydroxide in the presence of formaldehyde and the excess sodium hydroxide was titrated with standard acid.

NOTES

Carbonyl-cyanyls of Nickel(0)

BY ANTON B. BURG AND JUNE CHASE DAYTON[1]

The compound $K_4Ni(CN)_4$, discovered by Eastes and Burgess,[2] has been interpreted as an analog of nickel carbonyl, in that the cyanide ion is isoelectronic with carbon monoxide, and could replace it in complex compounds.[3] Such cyanide complexes, having the central atom in oxidation state zero, have been designated as "cyanyls" by Ormont.[4] In a search for chemical reality in this analogy, we have carried on reactions in which cyanide ion displaces carbon monoxide from nickel carbonyl, and others in which carbon monoxide displaces cyanide ion from $K_4Ni(CN)_4$. Under the conditions of the experiments, neither reaction could be brought to completion, and the products appeared to be mixtures of the intermediate compounds $KNiCN(CO)_3$, $K_2Ni(CN)_2(CO)_2$, and possibly $K_3Ni(CN)_3CO$.

Reaction of $Ni(CO)_4$ with KCN.—The first experiments showed that a yellow to orange solid (containing no dark material) is formed with the evolution of carbon monoxide when nickel carbonyl is allowed to react with solid potassium cyanide at ordinary temperatures. The solid product proved to be soluble in methyl cyanide, which then was adopted as the reaction medium. The solubility of potassium cyanide (0.03%) aided the reaction but was too low to interfere with the isolation of the product.

The apparatus employed for the reaction is shown in Fig. 1. Potassium cyanide was placed at A and dried by evacuation of the apparatus. Then methyl cyanide and nickel carbonyl were distilled in from the high-vacuum system with A at −196°, and warmed to room temperature. After three days, the carbon monoxide was removed through a trap at −196°, collected by a Töpler pump and measured. With the methyl cyanide solution at −196°, the lower part of the apparatus was sealed off *in vacuo* at D. Now the solution was melted and decanted into the weighed tubes designated as 1, 2 and 3. Next the solvent and any excess nickel carbonyl were distilled off through a vacuum tube-opener[5] operating at F, with the sample tubes 1, 2 and 3 in ice-salt to avoid decomposition of the solid product. Finally at half-hour intervals, the sample tubes were sealed off at E (leaving a tip suitable for the tube-opener) and the contents subjected to analysis. The sample-weight (usually about 0.3 g.) was determined as the gain in weight of the sealed tube and joint-socket.

The first step of the analysis was decomposition *in vacuo* at 200°, with collection and measurement of carbon

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[1] Abstracted from a thesis presented by June Chase Dayton to the Graduate School of the University of Southern California in partial fulfillment of the requirements for the degree of Master of Science.

[2] J. W. Eastes and W. M. Burgess, THIS JOURNAL, **64**, 1189 (1942).

[3] J. J. Burbage and W. C. Fernelius, *ibid.*, **65**, 1484 (1943).

[4] Ormont, *Acta Physicochim.*, *U. R. S. S.*, **19**, 571 (1944).

[5] A. Stock, *Ber.*, **51**, 985 (1918).

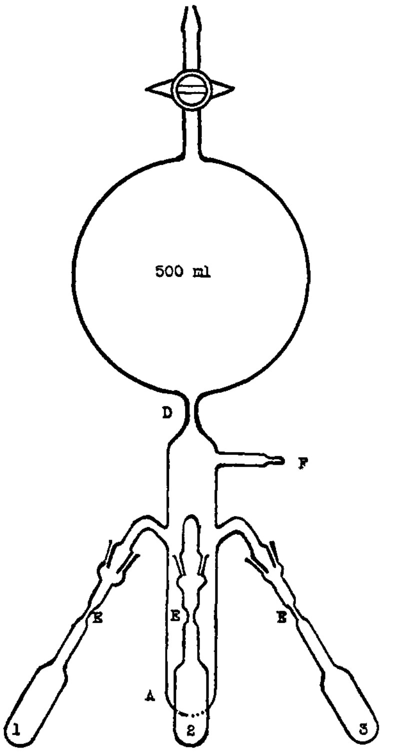

Fig. 1.—Apparatus used for the preparation of carbonyl-cyanyl compounds.

monoxide. Nickel carbonyl (perhaps due to disproportionation of a cyanyl-carbonyl) was condensed in a trap and decomposed on a hot glass surface, with collection and measurement of carbon monoxide. Finally all solids were dissolved in concentrated hydrochloric acid and analyzed for nickel by dimethylglyoxime and potassium by the cobaltinitrite method,[6] using aliquots of the solution.

One result was 43.4% KCN, 25.9% Ni, and 31.3% CO, corresponding perfectly to the formula $(KCN)_3Ni_2(CO)_5$. This could mean equal molar proportions of $K_2Ni(CN)_2(CO)_2$ and $KNiCN(CO)_3$. The average of all the results was: 39.8% KCN, 26.3% Ni, and 35.6% CO, corresponding to $(KCN)_4Ni_3(CO)_8$, or two moles of $KNiCN(CO)_3$ to one of $K_2Ni(CN)_2(CO)_2$. These simple formulas probably are fortuitous since the mixtures seem to vary continuously as indicated by measurements of carbon monoxide evolved in numerous experiments in which the composition of the solute was not determined.

It is also to be noted that in some experiments an insoluble yellow solid was obtained. This was not collected for analysis.

Reaction of $K_4Ni(CN)_4$ with CO.—The displacement of cyanide ion from $K_4Ni(CN)_4$ by the action of carbon monoxide was qualitatively demonstrated as follows. A sample of the salt $K_4Ni(CN)_4$ was prepared by the reaction of $K_2Ni(CN)_4$ with potassium in liquid ammonia.[3] After evaporation of all the ammonia *in vacuo*, methyl cyanide was distilled into the reaction tube, partially dissolving the copper-colored solid. Carbon monoxide now was introduced to a total pressure of 726 mm. During a week, at constant temperature (25°), the pressure fell to 654 mm. and a white precipitate (presumably KCN) appeared. A yellow solid apparently distinct from $K_4Ni(CN)_4$ also was noticed. More carbon monoxide was added and the pressure fell to the same point, 656 mm. Although the question of an established equilibrium was quite uncertain in this and preceding experiments, the fact that carbon monoxide could be either absorbed or evolved depending upon the conditions left no doubt of the reversibility of a series of displacements.

Discussion.—In view of the higher base strength of cyanide ion, it would seem surprising that carbon monoxide is capable of displacing it. The apparent similarity in the strength of bonding to nickel can be understood in terms of the double bonded situation in nickel carbonyl and the argument that the cyanide is chiefly single bonded.

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Preparation of Arylethynylcarbinols[1]

By E. T. Clapperton and W. S. MacGregor

Vanillin, veratraldehyde, 4-ethoxy-3-methoxybenzaldehyde and piperonal were converted to the corresponding arylethynylcarbinols by reaction with sodium acetylide in liquid ammonia.[2,3,4] The yields, Table I, ranged from 77 to 93% only when anhydrous conditions were carefully maintained. Hurd and McPhee[5] found that 0.0032 mole of water in a one-fifth mole reaction of acetone with sodium acetylide reduced the yield of dimethylethynylcarbinol from 86 to 49%. In the reaction of benzaldehyde 0.02 mole of water reduced the yield of phenylethynylcarbinol in a one-half mole reaction to 17.5%. The water in this case caused incomplete reaction and induced side reactions yielding nitrogen-free polymers, benzoic acid and benzyl alcohol.

When sodium acetylide and a nine-fold excess of benzaldehyde reacted in the presence of excess acetylene, 139% of phenylethynylcarbinol (based on sodium) was isolated. The high yield would be expected if the anion of phenylethynylcarbinol and acetylene were in equilibrium with the free carbinol and the acetylide anion as suggested by Campbell, Campbell and Eby.[2]

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Experimental

General Procedure.—The procedure used was adapted from those previously described.[2-5] The reactions were run in a 2-liter 3-neck flask fitted with a Hershberg stirrer having a hollow shaft for introducing gases. All outlets were protected from atmospheric moisture by Drierite tubes. Commercial acetylene, passed through water, a calcium chloride tube and a Dry Ice trap, was bubbled through a stirred mixture of one-half mole of sodium and 500 ml. of refrigeration-grade ammonia. After the blue

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(6) L. V. Wilcox, *Ind. Eng. Chem., Anal. Ed.*, **9**, 137 (1937).

(1) From the thesis of E. T. Clapperton presented in May, 1948, in partial fulfillment of the requirements for the Master of Science Degree at the University of Portland. Presented before the Cellulose Division of the American Chemical Society at the 114th meeting.

(2) Campbell, Campbell and Eby, This Journal, **60**, 2882 (1938).

(3) Hennion and Murray, *ibid.*, **64**, 1220 (1942).

(4) Jones and McCrombie, *J. Chem. Soc.*, 733 (1942).

(5) Hurd and McPhee, This Journal, **69**, 239 (1947).