hydroxide and then allowed to stand for three days. On acidification a solid separated which on recrystallization from Skellysolve B melted at 133°. A mixed melting point with a sample of cinnamic acid showed no depression.

Anal. Calcd. for $C_9H_8O_2$: C, 73.0; H, 5.4; neutral equivalent, 148. Found: C, 73.1; H, 5.1; neutral equivalent, 150.

Carbethoxymethyl-β-carbethoxy-α-phenylethyl Sulfide (IV).—A mixture of 11.7 g. (0.67 mole) of ethyl cinnamate, 8 g. (0.67 mole) of ethyl thioglycolate and five drops of piperidine was heated on the steam-bath for four and one-half hours and then distilled. Five grams of a forerun consisting of unreacted materials and 13.5 g. (69%) of product boiling at 163–165° at 2 mm. were collected.

Anal. Calcd. for $C_{15}H_{20}O_4S$: C, 60.8; H, 6.8. Found: C, 61.0; H, 7.2.

5-Carbethoxy-2-phenyl-3-thiolanone (V).—A solution of 34.5 g. of IV in 120 cc. of dry ether was added with stirring and cooling with an ice-salt mixture, to a suspension of 18.7 g. of sodium ethylate in 30 cc. of ether. Stirring and cooling were continued for six hours. After standing at room temperature overnight the reaction mixture was poured into ice water containing about 25 g. of acetic acid and extracted with ether. The ether was extracted with 5% potassium hydroxide and the alkaline extracts acidified with acetic acid. The oil which separated was taken up in ether and the ether was dried with sodium sulfate. Distillation of the product gave 10 g. of a light yellow oil boiling at 158–160° at 1 mm. It gives a bluish color with ferric chloride solution.

Anal. Calcd. for $C_{13}H_{14}O_3S$: C, 62.4; H, 5.6. Found: C, 62.7; H, 5.3.

2,4-Dinitrophenylhydrazone, m. p. 158–159°.

Anal. Calcd. for $C_{19}H_{18}N_4O_6S$: N, 13.02. Found: N, 13.02.

Anil-anilide, m. p. 153–154°.

Anal. Calcd. for $C_{23}H_{20}N_2OS$: N, 7.53. Found: N, 7.57.

Hydrolysis of V.—One and one-half grams of V was refluxed for four hours in 20 cc. of 15% sulfuric acid. The oil which separated on cooling was taken up in ether, the ether dried and evaporated. The residual oil (0.8 g.) was shaken with 10% sodium carbonate solution and again taken up in ether. After removing the ether the residue was recrystallized from Skellysolve A to give a product melting at 54°. It gave a semicarbazone melting at 199–200°. A mixed melting point with the semicarbazone prepared from III showed no depression.

Summary

A method is described for the preparation of 3-carbethoxy-2-phenyl-4-thiolanone from ethyl γ-chloroacetoacetate.

A series of reactions leading from this thiolane keto-ester to two isomeric thiolenedicarboxylic acids is described.

An isomeric keto-ester, 5-carbethoxy-2-phenyl-4-thiolanone, was prepared by ring closure of carbethoxymethyl β-carbethoxy-α-phenylethyl sulfide with sodium ethoxide.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POMONA COLLEGE]

The Catalytic Action of Cupric Ion on the Oxidation of Ascorbic Acid in Pyridine Solution

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The catalytic action of cupric ion on the oxidation of *l*-ascorbic acid has been noted and discussed for some years.[2] By the use of magnetic susceptibility measurements, it has been found possible to determine the function of cupric ion in the oxidation of ascorbic acid, when the reaction is carried out in pyridine solution.

Experimental

Synthesis.—In the following syntheses J. T. Baker and Co., C. P. cupric chloride was used as the source of the cupric and cuprous ion. The cuprous chloride was specially prepared by reduction of cupric chloride, using the Proust method as modified by Wohler.[3] The *l*-ascorbic acid and pyridine were obtained from Eastman Kodak Company, and the pyridine was carefully distilled, using only the fraction that boiled within 0.2 degree of the proper corrected temperature.

The reaction flask found most convenient to use was constructed from a 200-ml. Pyrex florence flask which had two 25-ml. florence flasks opening into the neck of the larger flask. The entire system could then be connected by means of Pyrex glass tubing and carefully ground stopcock to a Cenco vacuum pump, and reasonable elimination of oxygen obtained by evacuation to incipient boiling of the solvent for some minutes to sweep out the air in the system. The pyridine–copper salt solution was placed in the large flask, and the quantitatively weighed dry ascorbic acid in the small side flask. Removal of oxygen was then effected by evacuation and boiling of the pyridine solution at room temperature, and the dissolving of the dry ascorbic acid by the pyridine–metal salt solution could be done in the virtual absence of oxygen by tipping and shaking the sealed system.

The equipment also allowed for the introduction of measured amounts of air into the evacuated flasks for oxidation. The compositions of the various solutions are shown in Table I.

Magnetic Measurements.—The magnetic susceptibility measurements were made on the solutions using the Gouy method, at a temperature of 22°. The susceptibilities due to the metal ion are shown in Table I. In the column listing the Bohr magnetons, the calculations have been made assuming complete quenching of the orbital contribution to the magnetic moment. In the conversion of the experimental data into Bohr magnetons, a correction has been made for the diamagnetism of the non-metal portion of the molecule.

Discussion

Cupric ion in pyridine solution (I) exhibits the expected paramagnetism due to one unpaired electron, as shown in Table I. It is a reasonable

(1) Present addresses, (a) Pacific Coast Borax Company, Pasadena, Calif.; (b) Du Pont Chemical Company, El Monte, Calif.

(2) For very recent work in this field, see Weissberger and LuValle, THIS JOURNAL, **66**, 700 (1944).

(3) Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., New York, N. Y., 1923, Vol. III, p. 158.

TABLE I

Soln.	Molal concentrations Cu^{++}	Cu^{+}	Ascorbic acid	O_2	Bohr magnetons Exptl.	Calcd.	Unpaired electrons	Color of solution
I	0.030				2	1.73	1	Deep blue
II	.030		0.015		Diamagnetic		0	Yellow
III[a]	.030		.015	0.0075	2	1.73	1	Deep green
IV		0.030			Diamagnetic		0	Green
V		.030	.015		Diamagnetic		0	Yellow
VI		.030	.015	.015	2	1.73	1	Green

[a] When pyridine solutions of dehydroascorbic acid, and cupric chloride, respectively, are prepared in separate containers, the color shown by light passing through the two containers is a slightly lighter blue than the color of cupric ion in pyridine.

assumption that the ascorbic acid is oxidized by cupric ion to dehydroascorbic acid in (II), with the reduction of the cupric ion to the diamagnetic cuprous form, as shown in Table I. The preferential oxidation of the cuprous ion to the paramagnetic cupric form, rather than the further oxidation of the dehydroascorbic acid, is shown by (III), when (II) is treated with the stoichiometric volume of air to convert the cuprous to the paramagnetic cupric form, as seen from Table I.

The experimental evidence found from the work with cuprous ion is in agreement with the foregoing. Cuprous ion in pyridine solution (IV) shows the expected diamagnetism, and no significant change is observed when the ascorbic acid is dissolved in the cuprous ion solution in the absence of air. To obtain the solution comparable to (III), sufficient oxygen must be added to (V) to convert both the cuprous to the cupric form, (see Table I) as well as converting the ascorbic to the dehydroascorbic form (VI). In view of (III), it is possible to suggest that the oxygen changes cuprous to cupric ion, and that the cupric ion then oxidizes the ascorbic to the dehydroascorbic form. The cuprous ion so produced will be converted back to the cupric form after the conversion of the ascorbic to the dehydroascorbic acid.

From the foregoing, it is reasonable to write the reaction

$$2Cu^{++} + \text{ascorbic acid} \longrightarrow 2Cu^{+} + 2H^{+} + \text{dehydroascorbic acid}$$

The yellow color of (II) indicates the possibility that a complex of cuprous ions and dehydroascorbic acid is formed. As it has been shown that the color in (III) is not a physical combination of the blue color of cupric ion, and the yellow color of dehydroascorbic acid in pyridine solution, it is likely also that a complex of the dehydroascorbic acid and cupric ion has been formed.

Summary

It has been shown that in the absence of oxygen and using pyridine as the solvent, two cupric ions quantitatively oxidize ascorbic acid, presumably to dehydroascorbic acid, with the simultaneous production of two cuprous ions, and two hydrogen ions. When cuprous dehydroascorbate solutions are oxidized by oxygen from air, the cuprous is oxidized to the cupric ion, and the dehydroascorbic acid is not further attacked under the conditions used. Cuprous ascorbate requires sufficient oxygen to convert both the cuprous to the cupric form, as well as converting the ascorbic to the dehydroascorbic acid form.

Using visual color as the criterion, the possibility of complexes between cuprous ion and dehydroascorbic acid, cuprous ion and ascorbic acid, and cupric ion with dehydroascorbic acid, respectively, has been suggested.

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