CCCLV.—*The Attempted Isolation of Copper Benzaldehyde.*

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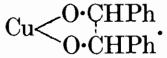
BERNOULLI and SCHAAF state (*Helv. Chim. Acta*, 1922, **5**, 721) that, although copper has no direct action on pure benzaldehyde, combination may be brought about by allowing a solution of benzaldehyde in toluene, benzene, or ethyl acetate to react with the metal at 50° : the copper slowly dissolves to give a deep green solution, from which green crystals can be isolated. In the earlier experiments the crude product was recrystallised from toluene and assigned the empirical formula $Cu(Ph{\cdot}CHO)_2$. Later Schaaf (*ibid.*, 1923, **6**, 535) described a better method of purification : the crude substance is dissolved in pyridine and the pyridine derivative, $2[Cu(Ph{\cdot}CHO)_2],5C_5H_5N$, is isolated and heated to 150°, whereby pure copper benzaldehyde is stated to remain. The stability of this product is remarkable. Not only is it resistant to heat, but it is said to be unattacked by dilute hydrochloric acid or alkalis. By analogy with the sodium derivative, $ONa{\cdot}CHPh{\cdot}CHPh{\cdot}ONa$, prepared by Church (*Annalen*, 1863, **128**, 295) and Beckmann and Paul (*ibid.*, 1891, **266**, 25), Bernoulli and Schaaf suggest that the compound is  $Cu\begin{matrix}\diagup O{\cdot}CHPh \\ \diagdown O{\cdot}CHPh\end{matrix}$. Commenting on this work (*Ann. Reports*, 1922, 123), Professor R. Robinson states : "The constitution of the compound is not yet clear, the obvious possibility that it is copper hydrobenzoin being difficult to reconcile with the stability to acid."

In view of the theoretical interest of copper benzaldehyde and the possibility that other metallic derivatives might be prepared we have reinvestigated the method of preparation of the copper salt. Although we have carefully observed all the experimental details given by the authors and repeated the preparation many times, yet in no case have we isolated copper benzaldehyde. The *substance* we invariably obtain from the reaction between copper and benzaldehyde, dissolved in toluene, is copper benzoate associated with one molecule of water and one molecule of benzaldehyde. When this product is recrystallised from pyridine, the *compound* isolated is $Cu(Ph{\cdot}CO_2)_2,2C_5H_5N,H_2O$, which on careful heating loses one molecule of water and one molecule of pyridine to form an emerald-green *substance*, $Cu(Ph{\cdot}CO_2)_2,C_5H_5N$. On prolonged heating at 150°, anhydrous copper benzoate and not copper benzaldehyde is left. To prove the existence of the compound $Cu(Ph{\cdot}CO_2)_2,Ph{\cdot}CHO,H_2O$ we heated copper benzoate, $Cu(Ph{\cdot}CO_2)_2,2H_2O$, with a solution of benzaldehyde in toluene. A deep green solution was obtained from which crystals of the required composition separated. It is noteworthy that the copper retains its covalency of four—a molecule of benzaldehyde replacing a molecule of water. Both in crystalline form and in composition these crystals were identical with our product isolated from the reaction described by Bernoulli and Schaaf. On theoretical grounds the formation of copper benzoate when copper is heated with benzaldehyde and toluene is not unexpected. It is well known that benzoyl hydrogen peroxide is formed by the aerial oxidation of benzaldehyde (Baeyer and Villiger, *Ber.*, 1900, **33**, 1582), and it appears highly probable, therefore, that the following reactions will take place :

$$\mathrm{Ph{\cdot}CHO + O_2 \longrightarrow Ph{\cdot}CO{\cdot}O{\cdot}OH}$$
$$\mathrm{Ph{\cdot}CO{\cdot}O{\cdot}OH + Ph{\cdot}CHO \longrightarrow 2Ph{\cdot}CO{\cdot}OH}$$
$$\mathrm{Ph{\cdot}CO{\cdot}O{\cdot}OH + Cu \longrightarrow CuO + Ph{\cdot}CO{\cdot}OH}$$
$$\mathrm{CuO + 2Ph{\cdot}CO{\cdot}OH \longrightarrow Cu(Ph{\cdot}CO_2)_2 + H_2O}$$

In addition there is no doubt that benzoic acid in toluene slowly attacks copper at room temperature. It is very significant that *p*-nitrobenzaldehyde in toluene does not attack copper when maintained in contact with it at 50° for several days. The formation of a peroxide in this case would not be anticipated. Using the method outlined by Bernoulli and Schaaf, we have not been able to obtain copper benzaldehyde and accordingly the existence of such a substance appears to us very doubtful.

EXPERIMENTAL.

Preparation of Benzaldehyde Copper Benzoate.—Pure electrolytic copper together with 32 c.c. of pure benzaldehyde and 168 c.c. of pure toluene (16% benzaldehyde-toluene solution by volume) was heated under reflux at 50° for several hours until the solution had attained a deep green colour; it was then allowed to cool. After several hours, brilliant bluish-green crystals separated, which were washed with toluene and air-dried. The yield was small [Found : Cu, 14·86, 14·82, 14·80; C, 59·57; H, 4·15. $\mathrm{Cu(Ph{\cdot}CO_2)_2,Ph{\cdot}CHO,H_2O}$ requires Cu, 14·79; C, 58·66; H, 4·19%]. The method outlined above is that given by Bernoulli and Schaaf for the preparation of copper benzaldehyde. They state that their product can be recrystallised from toluene. Our product was so slightly soluble in this solvent that it was useless as a medium for recrystallisation. Moreover, toluene appeared to decompose our substance, for the crystals became light blue. *Benzaldehyde copper benzoate* was also prepared by replacing the copper in the above experiment with copper benzoate; bluish-green crystals separated, which were washed with toluene and air-dried (Found : Cu, 14·8 ; C, 59·5 ; H, 4·15%).

Benzaldehyde copper benzoate is insoluble in water, but very soluble in aqueous ammonia. In contact with ether, it turns light blue, copper benzoate being formed. The ethereal layer leaves, on evaporation, a white residue smelling strongly of benzaldehyde. A similar observation is made with alcohol. Hydrochloric acid liberates benzoic acid from the compound. When boiled with concentrated caustic soda solution, it yields a black residue containing copper and sodium benzoate. The solid on distillation first melts to a brown liquid, white fumes with the odour of benzaldehyde being evolved. Benzene distils at 70—80°, benzoic acid at 245°, and finally phenol at 300°, free copper remaining in the flask. This result is interesting, since the literature reveals that the distillation of copper benzoate gives benzene, benzoic acid, phenol, diphenyl ether, and phenyl benzyl ether. Steam distillation yields benzoic acid. When the crystals are heated with potassium permanganate, manganese dioxide is formed.

Preparation of Dipyridine Copper Benzoate.—The product obtained from the reaction between copper and the benzaldehyde–toluene solution was dissolved in the minimum quantity of warm pyridine, in a nitrogen atmosphere. From the deep blue liquid obtained—still maintained in a nitrogen atmosphere—dark blue needles (A) slowly separated, which were washed with toluene and air-dried [Found : Cu, 13·4 ; C, 60·1 ; H, 4·8 ; N, 5·9.

$$Cu(Ph{\cdot}CO_2)_2,2C_5H_5N,H_2O$$

requires Cu, 13·2 ; C, 59·8 ; H, 4·6 ; N, 5·8%].

The same compound was prepared by dissolving copper benzoate in hot pyridine and filtering the resulting blue solution into excess of toluene. The blue needles (B) which separated were washed with toluene and air-dried. To ensure a product of constant composition the crystals were kept in contact with pyridine for several days. They were then drained on a porous tile and air-dried until all odour of pyridine had disappeared (Found : Cu, 13·3 ; C, 59·8 ; H, 4·9%). The method outlined in the first case is essentially that by which Schaaf (*loc. cit.*) claims to have isolated the compound $2[Cu(Ph{\cdot}CHO)_2],5C_5H_5N$.

Properties of dipyridine copper benzoate. When heated, the compound changes first to the monopyridine copper benzoate, then to copper benzoate, and finally to metallic copper. In other respects it behaves similarly to benzaldehyde copper benzoate [Found after prolonged heating of compound (A) at 150° : Cu, 20·68 ; C, 55·0 ; H, 3·5. $Cu(Ph{\cdot}CO_2)_2$ requires Cu, 20·80 ; C, 55·0 ; H, 3·3%].

Preparation of Monopyridine Copper Benzoate.—When the dark blue crystals (A) were heated for a short time at *ca.* 150° in an air-oven, they became dull green [Found: Cu, 16·5; C, 58·8; H, 4·1. $Cu(Ph{\cdot}CO_2)_2,C_5H_5N$ requires Cu, 16·5; C, 59·3; H, 3·9%]. This new *compound* was prepared in better-formed crystals by dissolving the crude product from the reaction between copper and benzaldehyde–toluene in hot pyridine, filtering the solution into excess of toluene and allowing it to cool. The blue needles which separated were washed with toluene, then transferred to a beaker, a very small amount of toluene was added, and the whole heated to 150° in an air-oven. Emerald-green crystals were produced [Found: Cu, 16·35; C, 59·2; H, 4·1; N, 3·65. $Cu(Ph{\cdot}CO_2)_2,C_5H_5N$ requires N, 3·6%].

This new substance was also obtained by heating pure copper with pyridine (60 c.c.) and benzaldehyde (40 c.c.) in a nitrogen atmosphere and then concentrating the greenish solution at 130° in an air-oven. At first the solution turned blue and, as the concentration increased, this altered to bluish-green and then emerald-green. At the same time dark green crystals were deposited. The large crystals were washed with toluene, crushed to a powder, and heated at 140° till benzaldehyde could no longer be detected (Found: Cu, 16·8; C, 58·7; H, 3·9%).

Monopyridine copper benzoate behaves similarly to dipyridine copper benzoate.

Action of p-*Chlorobenzaldehyde and Toluene on Copper.*—Pure electrolytic copper foil was heated at 50° with *p*-chlorobenzaldehyde in toluene solution. The solution quickly became green and, on cooling, deposited a greenish flocculent solid.

Action of Benzoic Acid in Toluene on Copper.—Pure electrolytic copper foil was kept with benzoic acid in toluene solution. The solution immediately acquired a bluish colour, and copper benzoate finally separated.

Preparation of Monoquinoline Copper Benzoate.—When monopyridine copper benzoate is kept in contact with quinoline for several days, the pyridine is replaced by quinoline. The solid product is washed with toluene and air-dried and proves to be *monoquinoline copper benzoate* [Found: Cu, 14·63; H, 4·4; N, 3·3. $Cu(Ph{\cdot}CO_2)_2,C_9H_7N$ requires Cu, 14·63; H, 3·9; N, 3·2%]. The compound is light green and behaves similarly to the pyridine derivative.

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