

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF COLORADO]

## FLUORANE FROM THE DRY DISTILLATION OF COPPER PHTHALATE

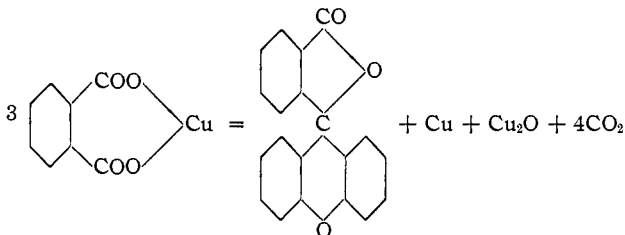
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In a previous paper,<sup>1</sup> mention was made of a product obtained by the dry distillation of copper phthalate, which was not further investigated at the time, being regarded as benzophenone from its appearance and odor. The yield seemed to be considerable and it was suggested that this might be a convenient method for the preparation of this ketone. A further examination, however, of the distillate obtained as described above reveals that the product is not benzophenone, but fluorane, and it may be obtained in yields as high as 91% of the theoretical.

It seems probable that the decomposition of the anhydrous copper phthalate takes place according to the equation



### Experimental

**Preparation of Copper Phthalate.**—Copper carbonate was added to a hot water solution of phthalic anhydride until carbon dioxide was no longer given off. The solution was filtered and evaporated to crystallization. The copper phthalate crystals thus obtained were allowed to dry in the air. The moist crystals may not be dried by heating them even at a relatively low temperature, since, if heated while wet, at a certain point in the crystalline mass they ignite and glow, the glowing quickly spreading through the whole decomposing mass. After the moist crystals had dried in the air, the anhydrous salt was obtained by heating them for some time at 120°.

**Dry Distillation of Air-Dried and of Anhydrous Copper Phthalate.**—Five grams of air-dried copper phthalate was distilled from a 50-cc. distilling flask upon the sand-bath, the flask being wrapped with asbestos and the receiver being cooled by means of a cloth wrapped around it and continually cooled with a stream of cold water. The flask was heated slowly at first and gradually raised to a dull red heat, and the heating continued until no more vapors passed over. Carbon dioxide was given off during the distillation. The residue left in the flask was a mixture of finely divided cuprous oxide and metallic copper, which when pressed out on a hard surface with a spatula showed the bright metallic luster of copper. The solidified distillate was crystalline and melted at 120°.<sup>2</sup>

<sup>1</sup> Ekeley and Banta, *THIS JOURNAL*, **38**, 767 (1917).

<sup>2</sup> R. Meyer, *Ber.*, **25**, 1386 (1892). Fluorane crystallizes from alcohol solution with one-half molecule of alcohol of crystallization. In driving off the alcohol of crystallization in an air-bath at 120°, Meyer observed the curious fact that at 120°, after the

It was soluble in concentrated nitric and in concentrated sulfuric acid with a green-yellow fluorescence. An analysis gave the following results: Calcd. for  $C_{20}H_{12}O_3$ : C, 80.00; H, 4.00. Found: C, 79.87; H, 4.22.

Recrystallized from alcohol, it yields long bright prisms, which after giving off their alcohol of crystallization melt at  $180^\circ$ . The crystals gave the following analysis. Calcd. for  $C_{20}H_{12}O_3 \cdot \frac{1}{2}C_2H_5OH$ : C, 78.32; H, 4.64. Found: C, 78.08; H, 4.86. The substance is evidently fluorane.

Two grams of anhydrous copper phthalate was distilled very carefully. The fluorane obtained weighed 1.092 g., a yield of 91.5% of the theoretical.

The temperature of distillation must be above  $300^\circ$ . The quality of the distillate is only slightly influenced by the temperature, but much larger yields are obtained by strong heating.

Copper tetrachlorophthalate yields a similar distillate, but thus far the product has presented difficulties in the combustion for carbon and hydrogen and in the determination of chlorine. Presumably the product is dodecachlorofluorane, but checking analyses for carbon have not yet been obtained, since during the combustion small quantities of the compound distil through the red-hot copper oxide unburned and condense as minute crystals in the cold part of the tube. The combustion, while giving a low value for carbon, gives only a very small fraction of a per cent. of hydrogen, this latter corresponding to a dodecachlorofluorane, which would contain no hydrogen. The Carius method for chlorine yields varying low values for chlorine, around 58%, while the calculated value is 59.49%. Other methods for chlorine also yield low results.

### Summary

Dry distillation of anhydrous copper phthalate at high temperatures (between  $300^\circ$  and dull red heat) gives fluorane, which may be obtained in as high a yield as 91.5%.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF GRINNELL COLLEGE]

## DECOMPOSITION OF OPTICALLY ACTIVE DIAZO COMPOUNDS<sup>1</sup>

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The aliphatic diazo group may be formulated as a straight chain or as a ring.



The chain structure was established largely by the work of Angeli,<sup>2</sup> Thiele,<sup>3</sup> and Staudinger,<sup>4</sup> who obtained chain derivatives of diazo compounds.

alcohol had been driven off, a portion of the alcohol-free substance was *melted*, whereas the melting point of fluorane is  $180^\circ$ .

<sup>1</sup> Presented before the 79th meeting of the American Chemical Society, Atlanta, Georgia, April 10, 1930.

<sup>2</sup> A. Angeli, *Atti accad. Lincei*, [V] 32, i, 443 (1923).

<sup>3</sup> J. Thiele, *Ber.*, 44, 2522 (1911).

<sup>4</sup> Staudinger, *Helv. Chim. Acta*, 5, 75 (1922).