The System $CuCl_2$–CH_3OH–$C_4H_8O_2$ at 30.0° C.

3-Copper (II) Chloride–Bis(1,4)dioxane

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The phase diagram for the system $CuCl_2$–methanol–1, 4-dioxane was determined by the wet residue method. The solid component in the two-phase region of the diagram was $3(CuCl_2)\cdot 2(C_4H_8O_2)$.

THE PRODUCT of the reaction between copper (II) chloride and 1,4-dioxane has been reported previously (*2, 4, 6*) as one or more of the following compounds: $CuCl_2\cdot C_4H_8O_2$, $CuCl_2\cdot 2(C_4H_8O_2)$, and $2(CuCl_2)\cdot C_4H_8O_2$. A study of the ternary system $CuCl_2$–$C_4H_8O_2$–CH_3OH has shown the product to be $3(CuCl_2)\cdot 2(C_4H_8O_2)$.

EXPERIMENTAL PROCEDURE

Reagent grade dioxane, methanol, and anhydrous $CuCl_2$ were used without further purification (*1*).

Mixtures of varying composition of copper (II) chloride, dioxane, and methanol were prepared, equilibrated at 30.0° C., and analyzed by the wet residue method (*5*). The experimental procedures have been described in detail in an earlier paper (*1*). The validity of the analyses of the liquid and wet residue phases was checked by analyzing samples of known composition of $CuCl_2$, CH_3OH, and $C_4H_8O_2$.

RESULTS AND DISCUSSION

The data listed in Table I and displayed in Figure 1 are representative of thirty-four tie lines obtained that extrapolated to within ±2% of 69.6% on the $CuCl_2$–$C_4H_8O_2$ axis. The tie-lines were extrapolated analytically by the method described by Heric (*3*). The results of the extrapolation are shown in the last column. The percentages of the three components in the saturated liquid and in the wet residue, as well as the extrapolated values, were obtained from the raw data (*1*) using a digital computer.

Table I. Distribution of Methanol and Copper (II) Chloride in the Ternary System

Liquid Phase, %		Wet Residue, %		% $CuCl_2$ Where Tie Line Intersects the $CuCl_2$–$C_4H_8O_2$ Axis
Methanol	$CuCl_2$	Methanol	$CuCl_2$	
62.18	37.82	...	...	...
64.40	35.28	45.05	45.53	69.4
68.66	30.64	46.66	43.30	70.1
73.79	24.20	56.75	34.69	69.6
78.43	18.22	42.20	41.79	69.3
79.30	14.60	51.30	34.39	70.6
78.05	11.90	59.00	25.78	68.8
74.28	9.25	40.93	36.04	68.9
68.70	7.59	39.70	33.70	69.4
56.36	5.27	45.04	17.88	68.0
43.49	3.78	29.29	25.00	68.8
30.68	2.31	25.04	14.54	68.9
19.43	1.22	14.86	16.99	68.3
9.27	0.36	7.24	15.79	71.0

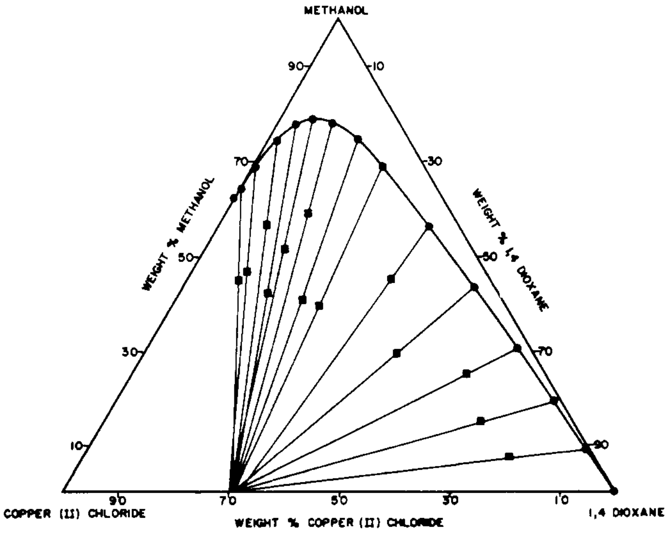

Figure 1. Ternary phase diagram for the system $CuCl_2$–CH_3OH–$C_4H_8O_2$ at 30° C.

● Liquid points

■ Wet residue points

The color of the solid phase varied with the percentage methanol in the saturated liquid phase. A high percentage of methanol in the liquid phase resulted in a bright reddish-orange solid; a pale orange solid was observed in equilibrium with saturated solutions containing low methanol percentages.

The solid from several of the mixtures was freed of excess solvent by pressing the wet solid with filter paper in a dry box. The solid was then ground with a mortar and pestle and allowed to remain in the dry box for periods of from 1 to 15 hours.

After removal from the dry box, the solid was analyzed for $CuCl_2$ content by EDTA determination of the copper (II) ion. In one series of three analyses on solid samples derived from solutions of low (about 30%) methanol concentration, the average $CuCl_2$ percentage was 69.77 ± 0.09%. In a similar series of four samples of solid derived from solutions with a high (> 75%) methanol concentration,

Table II. Percentage Composition of Possible $CuCl_2$–Dioxane Compounds

Compound	% $CuCl_2$	% C	% H	% O
$CuCl_2 \cdot C_4H_8O_2$	60.41	21.59	3.62	14.37
$CuCl_2 \cdot 2(C_4H_8O_2)$	43.28	30.93	5.19	20.60
$2(CuCl_2) \cdot C_4H_8O_2$	75.32	13.46	2.26	8.96
$3(CuCl_2) \cdot 2(C_4H_8O_2)$	69.60	16.58	2.78	11.04
Sample 1 (dull orange)[a]	69.77	16.56	2.82	11.27
Sample 2 (reddish orange)[a]	69.56	16.25	2.70	11.27

[a] Analyses for the reaction product isolated in this work (see discussion).

the average $CuCl_2$ percentage was 69.56 ± 0.10. A mixture of dioxane and $CuCl_2$ that was allowed to stand for several months produced the dull orange solid described above. This solid contained 69.43% $CuCl_2$. Table II shows the results of a carbon-hydrogen-oxygen analysis (Schwarzkopf Laboratories) on samples of the dried solid.

The compound $3(CuCl_2) \cdot 2(C_4H_8O_2)$, insoluble in dioxane, is stable in dry air, but absorbs water readily (and turns green on the surface) from moist air.

The color of the saturated liquid phase varied from a dark green near the methanol–$CuCl_2$ axis to a lighter green near the dioxane apex. The absorption spectrum of $CuCl_2$ in the solution is dependent upon the percentage dioxane in the mixture. For the system dioxane–isopropyl alcohol–$CuCl_2$, (saturated $CuCl_2$) solutions high in dioxane content are orange-red, while those high in isopropyl alcohol content are dark green. The same dark green was observed in the high methanol solutions studied in this paper, but the spectral shift as the per cent dioxane increased was not so marked. No color was observed in the liquid phase for $CuCl_2$–dioxane mixtures.

A previous study (*1*) has shown the existence of $CuCl_2 \cdot CH_3OH$. Therefore, samples were prepared with compositions (1% dioxane or less) near the CH_3OH–$CuCl_2$ axis in order to locate the $CuCl_2 \cdot CH_3OH$–$3(CuCl_2) \cdot 2(C_4H_8O_2)$–saturated solution invariant point. These mixtures were made by adding a few drops of dioxane to a saturated solution of $CuCl_2$ in methanol in equilibrium with the green $CuCl_2$–CH_3OH. The resultant solid phase appeared to be a mixture of the green solid and the reddish solid that appeared immediately upon addition of the dioxane. Addition of more than several drops of dioxane led to the disappearance of the green solid and to a sharp reduction (see Figure 1) in the $CuCl_2$ concentration in the liquid phase.

The analyses of the saturated liquids from these samples yielded $CuCl_2$ percentages from 37.61 to 37.74 (note first row of Table I). The refractive indices of the distillates from the saturated liquids corresponded to dioxane contents of the liquid phase between 0 and 0.4%. These results indicate that the per cent dioxane in the invariant liquid is less than 0.4, and that $CuCl_2 \cdot CH_3OH$ is unstable in the presence of even trace amounts of dioxane.

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Some Novel Ketones and Quinolines

Intermediates 2,4,6-Tris(*m*-trifluoromethylphenyl)-*s*-triazine, Bis(*m*-trifluoromethyl)dibenzamide, and Tris(*m*-trifluoromethyl)tribenzamide

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SOME ANALOGS of acetophenone (I), such as *m*-trifluoromethylpropiophenone (II), *m*-trifluoromethylbutyrophenone (III), *m*-trifluoromethylvalerophenone (IV), and 3′-trifluoromethyl-2-phenylacetophenone (V), have been prepared as intermediates in the synthesis of a number of trifluoromethyl derivatives of quinoline, which are expected to produce interesting pharmacological effects. These ketones were obtained by a process similar to that used for *m*-trifluoromethylphenylacetophenone (*2*), by interaction of *m*-trifluoromethylbenzonitrile (*5*) and the appropriate organomagnesium halide. The preparation of III, IV, and V led to a common byproduct which was obtained in maximum yield from interaction of *m*-trifluoromethylbenzonitrile and benzylmagnesium bromide, and was shown to be