TABLE I

X-Ray diffraction powder data for bayerite-*a* and bayerite-*b*

	Bayerite-*a*		Bayerite-*b*			
Line	d_{obs}	I/I_1	d_{obs}	I/I_1	d_{calc}*	$hk.l$
1	4.745	7	4.745	100	4.730	00.1
2	4.381	100	4.385	90	4.371	10.0
3	3.209	9	3.210	34	3.210	10.1
4	2.706	2	2.705	2	—	—
—	—	—	—	—	2.523	11.0
5	2.468	4	2.468	2	—	—
6	2.365	1	2.368	7	2.365	00.2
7	2.222	62	2.227	90	2.226	11.1
—	—	—	—	—	2.185	20.0
8	2.176	3	2.171	2	—	—
9	—	—	2.079	3	2.080	10.2
10	1.989	4	1.987	4	1.984	20.1
11	1.722	11	1.725	45	1.726	11.2
12	1.647	4	1.653	3	1.652	12.0
13	1.605	4	1.604	10	1.605	20.2
—	—	—	—	—	1.577	00.3
14	1.558	5	1.560	15	1.560	12.1
—	—	—	—	—	1.483	10.3
15	1.458	6	1.460	25	1.457	30.0

*d_{calc} from $a = 5.047$ Å, $c = 4.730$ Å for bayerite-*b* (4).

and *b* in the relative intensities of some of the X-ray diffraction powder lines, particularly the abnormally weak 00.1 line of type *a*, are the result of preferred orientation of the crystals of type *a* parallel to their length.

Grateful acknowledgment is made to Dr. S. Nishimura for helpful advice regarding the preparation of bayerite-*a*.

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DIPHENYLCYANAMIDE DERIVATIVES. IV. 1,1-bis(4-CHLOROPHENYL)-UREA*

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The synthesis of 1,1-bis(4-chlorophenyl)-urea was reported as resulting from the aqueous alkaline hydrolysis of 4,4′-dichlorodiphenylcyanamide; it was described as a white solid, m.p. 220°–222° (1). Subsequent investigation has shown this material to be a complex mixture containing 1,1-bis(4-chlorophenyl)-urea, some 4,4′-dichlorodiphenylamine, and a polymeric compound containing silicon leached from the Pyrex flask. (No

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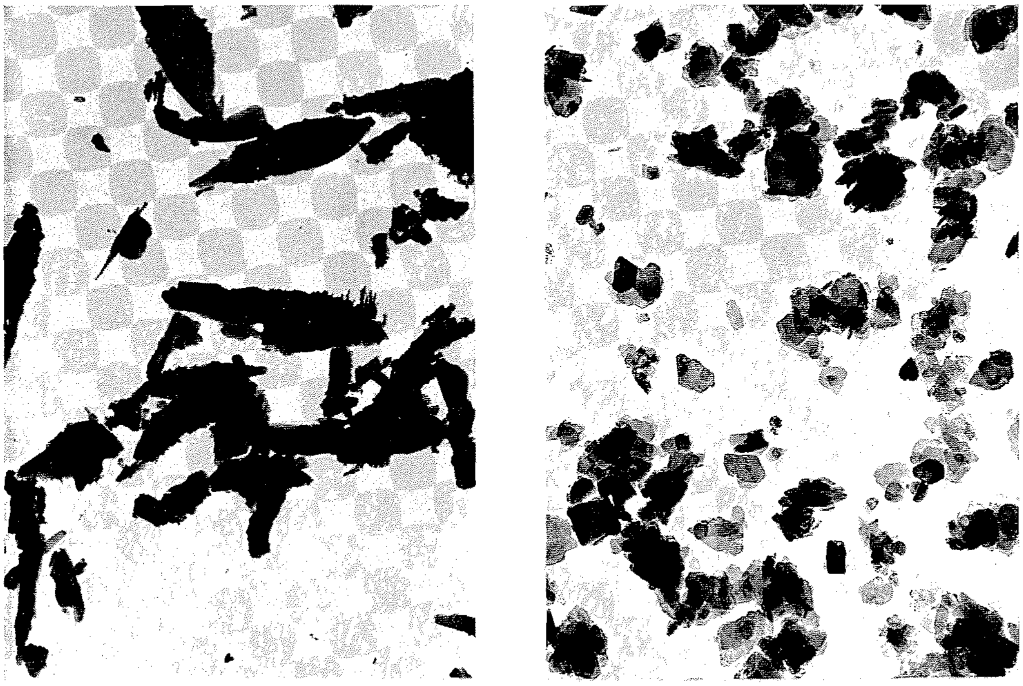
PLATE I



TYPE — a 2 TYPE — b

3

FIG. 2 Electron micrographs of bayerite-*a* and bayerite-*b* (×27,000).
FIG. 3. Electon microdiffraction pattern of bayerite-*a* (acceleration voltage 100 kv).

silicone grease was used.) The purpose of this note is to record a corrected description of 1,1-bis(4-chlorophenyl)-urea in the pure state.

This unsymmetrically substituted urea has now been obtained by a different method and characterized through conversion to known derivatives by the well-established reactions illustrated in Fig. 1.

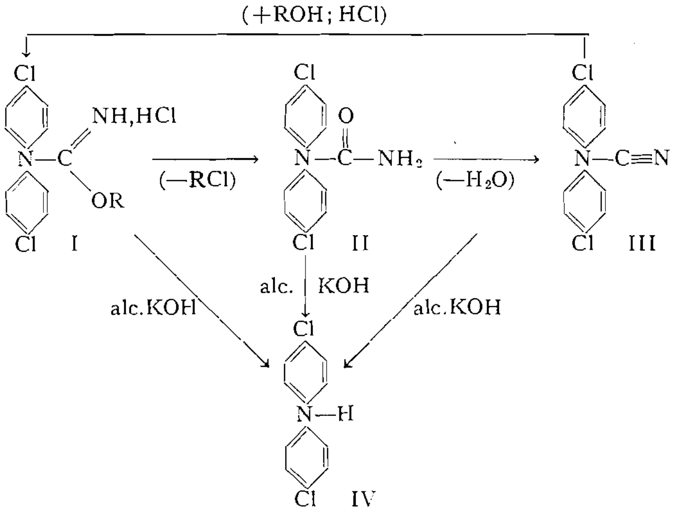


FIG. 1. The synthesis and hydrolysis of 1,1-bis(4-chlorophenyl)-urea.

Although the 3,3-diphenyl-2-alkylpseudoureas are known to undergo rearrangement and cleavage on heating to form diphenylamine and the corresponding alkyl isocyanate (2), their hydrochloride salts, when heated, retain the urea skeleton resulting in the formation of unsymmetrical diphenylurea and the corresponding alkyl chloride (3). Similar behavior of the 3,3-dialkyl-2-alkylpseudoureas was reported by McKee (4). This property has provided a convenient method for synthesis of 1,1-bis(4-chlorophenyl)-urea (II, Fig. 1). The reaction of water with the pseudourea salts, at room temperature, is observed to produce the same material, though slowly.

Evidence for the structure of II is provided by its ready dehydration to 4,4′-dichlorodiphenylcyanamide (III) using Kurzer's technique (5), as well as by its hydrolysis to 4,4′-dichlorodiphenylamine (IV) in alcoholic potassium hydroxide. Further, the infrared spectrum* of the material in the region 3600–3200 cm^{-1} is identical with that of 1,1-diphenylurea and 1,1-bis(4-methoxyphenyl)-urea, each having absorption peaks characteristic of —NH_2 at 3540 and 3430 cm^{-1}, as well as a strong peak at 1675 cm^{-1} typical of an amide carbonyl; a peak at 830 cm^{-1} is further indication of the paradisubstituted phenyl groups in this material.

The degradation of the 3,3-bis(4-chlorophenyl)-2-alkylpseudourea salts (I) to 4,4′-dichlorodiphenylamine may also be accomplished directly in boiling alcoholic potassium hydroxide; 4,4′-dichlorodiphenylcyanamide undergoes similar conversion (1).

Acknowledgment is made to Mr. R. W. White of this laboratory for recording and interpreting the infrared spectra of these materials.

EXPERIMENTAL*

3,3′-Bis(4-chlorophenyl)-2-alkylpseudoureas

3,3-Bis(4-chlorophenyl)-2-alkylpseudoureas (Fig. 1, I where R = C_1 to C_{12} alkyl groups) were prepared by the alkoxide catalyzed addition of alcohols to 4,4′-dichlorodiphenylcyanamide (1, 3).

1,1-Bis(4-chlorophenyl)-urea

(a) By Thermal Decomposition of 3,3-Bis(4-chlorophenyl)-2-n-heptylpseudourea Hydrochloride

The pseudourea salt (2.0 g, 4.8 mmoles) was spread thinly over a watch glass and kept in a 90° oven until odorless and no longer water-soluble (5 days). The residue was recrystallized from methanol–water, ethanol–water, then dried *in vacuo* over calcium chloride. The yield of purified material (fine, colorless needles) was 1.0 g (75%); it gave a positive test for organic halogen, a negative test for halide, and melted at 187°–188° C. Its infrared absorption characteristics are described above. Anal. Calc. for $C_{13}H_{10}N_2OCl_2$: C, 55.53; H, 3.58%. Found: C, 55.75; H, 3.57%.

(b) By Thermal Decomposition of 3,3-Bis(4-chlorophenyl)-2-n-butylpseudourea Hydrochloride

The salt (1.17 g, 3.18 mmoles) was kept at the melting point, under vacuum (0.2 mm of mercury), on a manifold to which a cold trap was attached. After 90 minutes the crude residue weighed 0.87 g (97%) and repeated recrystallization from ethanol–water gave fine, colorless needles, m.p. 187°–188°.

The distillate in the cold trap weighed 0.265 g (90%) and had the boiling point (77°–78°) and refractive index (1.4014) of *n*-butylchloride.

(c) By the Action of Water on 3,3-Bis(4-chlorophenyl)-2-methylpseudourea Hydrochloride

An aqueous solution of the salt (0.5 g, 1.5 mmoles in 100 ml of water) was left standing in the dark at room temperature. After several days, long needle-like crystals began to grow. After 7 months the material was filtered off and recrystallized from methanol–water and ethanol–water, giving colorless needles, m.p. 187°–188°.

The three products (*a*, *b*, and *c*) were identical in chemical and physical properties.

4,4′-Dichlorodiphenylcyanamide

A solution of 0.84 g (2.98 mmoles) of 1,1-bis(4-chlorophenyl)-urea (above) in 25 ml of pyridine was treated with 1.77 g (10 mmoles) of benzenesulphonyl chloride and left standing at room temperature for 12 hours. The reaction product, after precipitation with water, filtration, and washing, was recrystallized from methanol yielding 0.58 g (73%) of long colorless needles of 4,4′-dichlorodiphenylcyanamide, m.p. 114°–115°. The material was confirmed by a mixed melting point with an authentic sample (1).

4,4′-Dichlorodiphenylamine

A 5-ml methanolic potassium hydroxide solution of 1,1-bis(4-chlorophenyl)-urea (0.12 g, 0.42 mmole) was boiled under reflux for 24 hours; some ammonia was evolved. After crystals of potassium carbonate were filtered off, the product was precipitated by adding water and recrystallized from 110° petroleum ether yielding 0.085 g (85%) of 4,4′-dichlorodiphenylamine, colorless needles, m.p. 77°–78°.

The identical product was obtained in 80–90% yield, by the same technique, starting with any of the 3,3-bis(4-chlorophenyl)-2-alkylpseudourea hydrochlorides.

**Melting points were obtained using a Fisher–Johns block and are uncorrected. Carbon and hydrogen analyses were by J. F. Alicino, Metuchen, N.J.*

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