TABLE I

PHENOTHIAZINES BY THIONATION

Substituent	Yield, %[a]	M.P.
2-Methyl-	38	190–191°[b]
4-Methyl-	3	129–132°[c]
2-Chloro-	26	197–199°[d]
4-Chloro-	Unable to purify	
2-Methoxy-	16	185–188°[e]
4-Methoxy-	Unable to isolate	
3-Methyl-	47	166–167°
3-Methoxy-	48	155–157°[f]
3-Chloro-	[g]	
2-Chloro-7-methoxy	35	173–174°

[a] These yields represent purified yields. For example, in the thionation of 3-methyldiphenylamine, a crude yield of 80% of the 2-isomer, melting at 175–177°, is obtained, and a crude yield of 20% of the 4-isomer, melting at 125–127°. [b] Charpentier *et. al.*, *loc. cit.*, reported a melting point of 187–188°. [c] Charpentier *et al.*, m.p., 114–118°. As noted above, our crude product melted at 125–127°. [d] Charpentier, *et al.*, m.p., 196–197°. [e] Charpentier, *et al.*, m.p., 179–180°. [f] Gilman and Shirley, *J. Am. Chem. Soc.*, **66**, 888 (1944) and Kehrmann and Nossenko, *Ber.*, **46**, 2809 (1913) report a melting point of 158–159°; Pummerer and Gassner, *Ber.*, **46**, 2322 (1916) report 163°. [g] 3-Chlorophenothiazine could not be obtained by this procedure. Complete loss of chlorine resulted and good yields of phenothiazine were obtained as the only reaction product. A similar loss occurred to some extent in the preparation of 1-chlorophenothiazine.[4]

removed by distillation. There was obtained 20.4 g. (95%) of a yellow product, melting at 135–136°.

An analytical sample was obtained by recrystallization from benzene. Colorless glistening crystals, melting at 136–137°, were obtained. On standing or exposure to air, the compound slowly turned green.

Anal. Calcd. for $C_{12}H_9ONS$: C, 67.0; H, 4.19. Found: C, 66.8; H, 4.25.

1-Acetoxy-10-acetylphenothiazine. A mixture of 0.6 g. of 1-hydroxyphenothiazine, 4 ml. of acetic anhydride, and a few drops of pyridine was refluxed for 4 hr. On cooling the mixture, colorless crystals settled out. Recrystallization from benzene gave 0.4 g. (60%) of colorless crystals, m.p., 208–209°.

Anal. Calcd. for $C_{16}H_{13}O_3NS$: S, 10.70. Found: S, 10.34.

1-Ethoxyphenothiazine.[12] A mixture of 3 g. of 1-hydroxyphenothiazine, 3 ml. of ethyl bromide, and 10 g. of anhydrous potassium carbonate in 150 ml. of dry acetone was refluxed for 24 hr. The hot reaction mixture was filtered, and the filtrate evaporated. The residue, which was insoluble in alkali, was recrystallized from ethanol to give 2.1 g. (62%) of colorless crystals, m.p., 81–82.

Anal.[13] Calcd. for $C_{14}H_{13}ONS$: C, 68.8; H, 5.35. Found: C, 68.0; H, 5.36.

2-Acetoxy-10-acetylphenothiazine. A mixture of 2 g. of 2-methoxyphenothiazine and 6 g. of pyridine hydrochloride was heated at 200° for 5 hr. When the melt was worked up as described under 1-hydroxyphenothiazine, an oil was obtained which could not be crystallized. The oil was, therefore, by a procedure similar to that for the 1-hydroxy derivative, converted into 2-acetoxy-10-acetylphenothiazine. This was crystallized with difficulty from benzene–petroleum ether to give 0.6 g. (35%) of colorless crystals, m.p., 138–140°.

Anal. Calcd. for $C_{16}H_{13}O_3NS$: S, 10.70. Found: S, 10.23.

3-Hydroxyphenothiazine.[14] The demethylation of 3 g. of 3-methoxyphenothiazine with 12 g. of pyridine hydrochloride was carried out as described for the 1-hydroxy derivative. Recrystallization from benzene acetone mixture gave 2.2 g. (76%) of steel-gray crystals, m.p. 187–188°. Because of the ease of oxidation, to a purple colored solid, the product was not analyzed but was converted, as described under the 1-derivative, into 3-acetoxy-10-acetylphenothiazine, which crystallized with difficulty from benzene–petroleum ether mixture to give a white powder, m.p., 111–116°.

Anal. Calcd. for $C_{16}H_{13}O_3NS$; S, 10.70. Found: S, 10.21.

2-Chloro-7-hydroxyphenothiazine. Demethylation of 2 g. of 2-chloro-7-methoxyphenothiazine in the usual manner gave a product which crystallized from benzene to give 1 g. (52%) of light purple crystals, m.p. 224–226°, turning deep purple on standing.

Anal. Calcd. for $C_{12}H_8ONSCl$: S, 12.83. Found S, 13.14.

10-(9-Xanthenyl)-phenothiazine. A mixture of 0.5 g. of phenothiazine, 0.5 g. of xanthydrol and 6 ml. of glacial acetic acid was heated to reflux. On cooling to room temperature, a white crystalline solid separated. Filtration and recrystallization from ethanol-acetone mixture gave a colorless solid, m.p., 205-212°, sintering at 195°. It turned violet on standing.

Anal.[13] Calcd. for $C_{25}H_{17}NOS$: C, 79.2; H, 4.48. Found C, 78.6; H, 4.86.

1-Chloro-10-acetylphenothiazine.[3] To 1.0 g. of 1-chlorophenothiazine was added 1 ml. of isopropenyl acetate[15] and 5 drops of boron trifluoride ethereate. The mixture was heated with stirring in a boiling water for a few minutes. The dark residue was cooled and triturated in ethanol to remove colored impurities. The colorless amide was filtered and recrystallized from ethyl acetate to give 1.3 g. of colorless crystals, m.p., 135–136°. By adapting the same procedure, the 10-acetyl derivatives of 1-methyl phenothiazine and 1-methoxyphenothiazine were also prepared.

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(13) Analysis by C. Beames, N. Mexico Highlands University, Las Vegas, N. M.

(14) This compound has been reported to melt at 172–174° by D. F. Houston, E. B. Kester, and F. DeEds, *J. Am. Chem. Soc.*, **71**, 3816 (1949), who prepared it by the thionation of p-anilinophenol.

(15) This material was kindly supplied by the Tennessee Eastman Co., courtesy, Dr. J. B. Dickey.

Hexagonal Urea from Acetone-Urea Adduct

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It is reported in the literature that when a urea adduct decomposes, the urea reverts to its natural tetragonal structure.[1] Urea adducts are crystalline molecular compounds of hexagonal structure.[2] We have found that a small part of the urea obtained from the decomposition of an acetone urea adduct existed in the hexagonal form. X-ray dif-

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(1) R. T. Holman, W. O. Lundberg, T. Malkin, *Progress in the Chemistry of Fats and Lipids*, Pergamon Press, Ltd., London, 1954, Vol. 2.

(2) A. E. Smith, *J. Chem. Phys.* **18**, 150 (1950).

fraction patterns were obtained, showing that a small amount, probably less than 5%, possessed hexagonal structure. The urea obtained from acetone urea adduct after the adduct was decomposed by heat at 55° was found to form fatty acid urea adducts readily in the absence of any urea solvent.

EXPERIMENTAL

Preparation of acetone activated urea.[3] Into a beaker containing *ca.* 150 ml. of acetone was added exactly 200 g. of urea of about 150 mesh, and the mixture was left to stand for 1 hr. at room temperature. The excess acetone was removed by suction filtration and the solid adduct was placed in a 55° oven until the original weight of urea was obtained. At this point decomposition of the acetone urea adduct was considered to be complete.[4]

Reactivity of acetone activated urea. To 100 g. of the above urea was added 25 g. of oleic acid, U.S.P. grade, and the mixture was left to stand for 2 hr. with occasional stirring. From the adduct formed, 24 g. of fatty acid was recovered after decomposition of the adduct by hot water. Other fatty acids and their methyl or ethyl esters reacted equally well.

Rate study. Urea, 200 g., was treated as in the first experiment. To this urea was added 370 ml. of toluene to which 40 g. of stearic acid, N.F. grade, had been dissolved, and immediately mechanical agitation was started. Small samples were taken out at definite intervals, were rapidly filtered *via* a cotton plug and of the clear liquid an aliquot was titrated in isopropyl alcohol with standard sodium hydroxide solution to a phenolphthalein end point so that the molarity of the stearic acid toluene solution could be determined at each interval. The results were plotted and fitted well the first order equation:

$$2.3 \log c/c_0 = kt$$

where c_0 = initial concentration of stearic acid
c = concentration of stearic acid after lapse of time, t
t = time, min.
k = specific reaction velocity constant

Fig. 1 represents this curve.

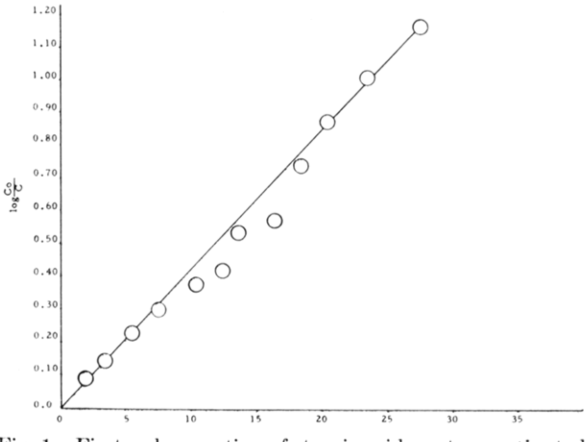


Fig. 1. First order reaction of stearic acid–acetone activated urea

Comparison of rates of acetone activated and ordinary urea. Urea, 200 g. of *ca.* 200 mesh, was reacted with stearic acid dissolved in toluene in the same manner as the acetone activated urea in the previous example. Practically no reaction took place. Fig. 2 shows the results.

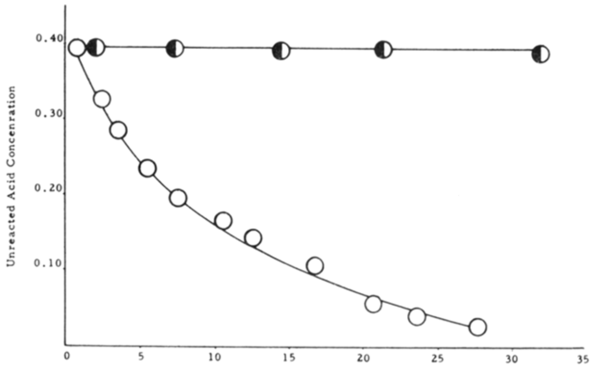
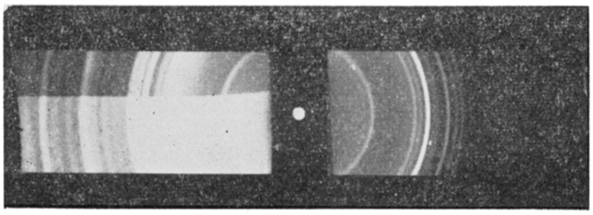


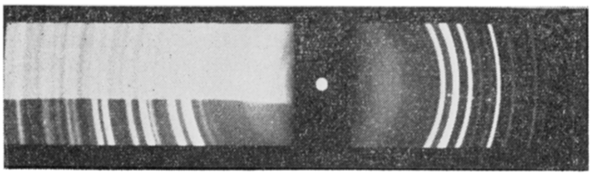
Fig. 2. Rate comparison: acetone activated urea–stearic acid, ○; ordinary urea–stearic acid, ◐

X-ray diffraction patterns. Powder diffraction patterns were obtained with copper target and wedge sample holder in a Debye-Sherrer type camera.

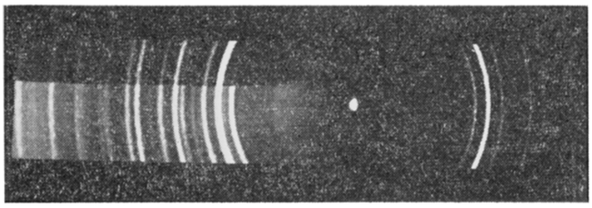
1. Sample exposed for 1.5 hr. Film #23
2. Sample exposed for 2 hr. Film #42
3. Hexagonal urea (ethyloleate adduct)[5] Film #35



Film #35. Hexagonal urea (ethyl oleate adduct)



Film #42. 2 hr. exposure. Just to left of heavy line is weak line of hexagonal urea



Film #23. Exposure 1.5 hr.

Figure 3

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[3] Urea from decomposed acetone adduct.

[4] The urea was weighed to the nearest tenth of a mg. to make sure that no acetone or acetone adduct was present when this urea was caused to react with the fatty substances. Small traces of acetone or acetone adduct might still be present; however, these small traces could not have catalyzed the reaction to any great extent. It was found that when ordinary urea, 100 g., was mixed with 25 g. of oleic acid in the presence of *ca.* 0.5 g. acetone adduct and 0.5 ml. of acetone, less than 3 g. of oleic acid had reacted after 2 hr. at room temperature. It is not probable that traces of free acetone or acetone adduct could have catalyzed the reaction of acetone activated urea with the fatty acids or their esters, in these experiments.

[5] This adduct was freshly made in saturated urea methanol solution with excess ethyl oleate.

Exactly 5 g. of urea, C.P., was caused to react with excess acetone as in the first experiment. A specimen of this urea was investigated. Film #23 did not show much evidence for hexagonal urea. Film #42 did show a weak line at about 21° 12/(20). This corresponds to the most intense line of the hexagonal urea adduct, Film #35. The intense line of tetragonal urea was very dark on the film because of the long exposure. A densitometer was used to compare the line of the hexagonal with the intense line of the tetragonal urea. Only an estimate could be made on account of the high darkening of the tetragonal line. This estimate put the amount of hexagonal urea at probably less than 5%. Diffraction patterns are shown in Fig. 3.

DISCUSSION

The existence of the small portion of hexagonal urea, after the acetone urea adduct is decomposed by heating the adduct, could perhaps justify a conjecture that the hexagonal channels of urea do not all collapse instantly upon the escape of the acetone molecules. Some of them may retain their hexagonal configuration or assume some metastable structure before reverting to the natural tetragonal form. Such a crystalline configuration would favor adduct formation with adduct forming substances without the use of a urea solvent. A phenomenon similar to adsorption[6] may take place when acetone activated urea is contacted with a substance such as oleic acid. The catalytic effect of acetone, and perhaps of other ketones, may be explainable not only on the basis that acetone is a mutual solvent for both urea and adduct forming substances but also that it forms its urea adduct which decomposes to provide *in situ* acetone activated urea.

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[6] W. J. Zimmerchied, R. A. Dinerstein, A. W. Weitkamp, and Robert F. Marsener, *Ind. Eng. Chem.*, **42**, 1300 (1950).

New Simple Preparation of Diphenylsilanediol and Its Condensation Products; Cyclodiphenylsiloxanes

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In the previous works[1–7] related to the preparation of diphenylsilanediol (hereafter called diol) from diphenyldichlorosilane, the hydrolysis of the chlorosilane under carefully controlled mild conditions to minimize the formation of high polymers has generally been aimed at for successful preparation.

The author now finds that diol in pure form can be obtained readily from the reaction of diphenyldichlorosilane with ammonium carbonate monohydrate, the yield being 90–94%.

The new method can be represented summarily by the following equation:

$$(C_6H_5)_2SiCl_2 + (NH_4)_2CO_3\text{-}H_2O \longrightarrow (C_6H_5)_2Si(OH)_2 + 2NH_4Cl + CO_2$$

When 1 mole of diphenyldichlorosilane was added to 1.2–1.5 mole of ammonium carbonate monohydrate covered with an inert anhydrous organic solvent preheated at 50–60°, the ammonium salt decomposed readily, evolving carbon dioxide, and ammonium chloride precipitated as fine crystals. After cooling to room temperature, the reaction product was filtered, whereupon pure diol was obtained from the filtrate upon evaporation. The most effective result was obtained by use of acetone as the reaction medium: The hydrophilic character of this would make the first stage of the reaction, hydrolysis of diphenyldichlorosilane with water produced by the decomposition of ammonium carbonate, fairly homogeneous.

The proposed method has the advantage that throughout the preparation procedure no byproducts other than ammonium chloride and carbon dioxide were produced. Both of these have no disadvantageous effect on the hydrolysed product and can be separated easily from the liquid part, allowing ready isolation of diol.

As has been described by Burkhard,[4] diol was converted readily into cyclodiphenylsiloxanes on being refluxed in an appropriate solvent in the presence of acid or caustic alkali as catalyser; hydrochloric acid and sodium hydroxide gave hexaphenylcyclotrisiloxane and octaphenylcyclotetrasiloxane, respectively.

EXPERIMENTAL

Reagents. Reagent grade ammonium carbonate monohydrate was used after prolonged drying in a vacuum desiccator. Highest purity diphenyldichlorosilane was received from the Shin-etsu Chemical Industrial Co. Acetone was purified according to the ordinary method.

Preparation and some properties of diol. In a 2-l. flask surrounded by a water bath heated at 50° was placed 80 g.

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[1] G. Martin, *Ber.*, **45**, 403 (1912).

[2] F. S. Kipping, *J. Chem. Soc.*, **101**, 2108 (1912).

[3] F. S. Kipping and R. Robinson, *J. Chem. Soc.*, **105**, 487 (1914).

[4] C. A. Burkhard, *J. Am. Chem. Soc.*, **67**, 2173 (1945).

[5] J. F. Hyde and R. C. DeLong, *J. Am. Chem. Soc.*, **63**, 1194 (1941).

[6] S. Fukukawa, *Science & Industry (Japan)*, **30**, 71 (1956).

[7] T. Takiguchi, "Studies on organochlorosilanes, VII," *J. Chem. Soc. Japan (Ind. Chem. Sect.)*, in press.