ratio.[1,2] These spectral differences have been used to follow the changes occurring prior to gelation on the addition of an ammonium salt or acid and to detect differences between silicates of the same analytical composition but different properties.

Figure 1 shows the absorption spectrum of 1.0×10^{-5} *M* pinacyanol chloride in a mixture of 0.01 *M* Na_2SiO_3 and 0.01 *M* H_2SO_4 after the acid–silicate mixtures had aged at twice this concentration for three minutes, one and five hours. The absorption spectrum changed gradually from that practically the same as in sodium metasilicate alone to the spectrum characteristic of the dye in a silicate with a silica to alkali ratio of 4 or 5 in mixtures aged for one hour.[2] The α and β bands at 600 and 548 mμ, respectively, almost disappeared and the γ band at 498 mμ became evident. During the subsequent fifteen hours the mixture changed so that the α and β bands of the dye's spectrum again became well defined and the γ band decreased in intensity and shifted to 514 mμ. Aging mixtures of 0.1 *M* $Na_2O{\cdot}3.3SiO_2$ + 0.01 *M* H_2SO_4 produced a decrease in the intensity of the γ band of the dye in these solutions with an accompanying increase in intensity of the α and β bands. These changes were reversed after about twenty hours of aging. Such results indicate that a maximum effect on the absorption spectrum of the dye is observed with particles of an intermediate molecular weight.

The absorption spectrum of pinacyanol chloride was approximately the same in a 0.01 *M* $Na_2O{\cdot}3.3SiO_2$–0.01 *M* $(NH_4)_2SO_4$ solution aged at twice this concentration for twenty-one hours as in a freshly prepared mixture. The absorption spectra were therefore determined in 0.025 *M* solutions aged at a concentration of 0.05 *M*. In contrast to the above results with sulfuric acid, the addition of 0.05 *M* ammonium sulfate to 0.05 *M* sodium metasilicate produced within three minutes a profound change in the nature of these solutions as shown by changes in the absorption spectrum of the dye in them after dilution. The α and β bands had almost disappeared and a prominent γ band appeared which increased somewhat in intensity on further aging. In mixtures of 0.05 *M* $(NH_4)_2SO_4$–0.05 *M* $Na_2O{\cdot}3.3SiO_2$ only changes in the intensity of the γ band of the dye were observed until the solution gelled.

These differences in the behavior with pinacyanol chloride of acid–silicate and ammonium sulfate–silicate mixtures during aging suggest differences in the mechanism of gelation. This is in agreement with a suggestion made previously on the basis of differences in the effect of concentration and of acid or ammonium salt to silicate ratio on the time of set.[3] Gelation of a silicate–ammonium salt mixture may involve formation of a readily coagulated ammonium salt of a silicic acid of intermediate molecular weight as well as the condensation reaction occurring on the addition of an acid.

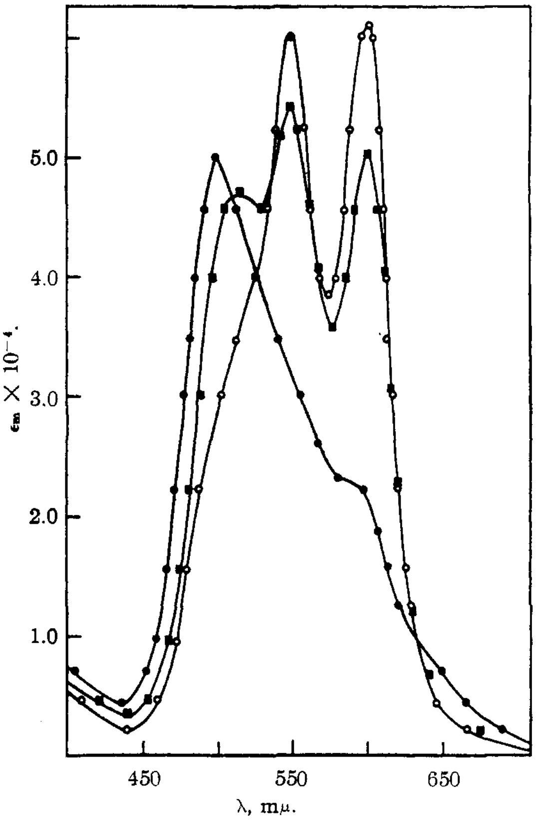

Fig. 1.—Molar extinction coefficients of 1.0×10^{-5} *M* pinacyanol chloride in 0.01 *M* Na_2SiO_3–0.01 *M* H_2SO_4 after acid–silicate mixture aged at twice this concentration for 3 min. – ○, 1 hr. – ●, and 5 hr. – ■.

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RECEIVED DECEMBER 16, 1949

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[1] R. C. Merrill, R. W. Spencer, and R. Getty, THIS JOURNAL, **70**, 2460 (1948).

[2] R. C. Merrill and R. W. Spencer, *ibid.*, **70**, 3683 (1948).

[3] R. C. Merrill and R. W. Spencer, *J. Phys. Colloid Chem.*, submitted.

The Preparation of 4-Ethyl-2-methoxy-2-phenylmorpholine

BY ROBERT H. JORDAN[1] AND ROBERT E. LUTZ

In our studies on ring-chain tautomerism of α-ethanolaminoketones[2] it was found that acid-catalyzed methanolysis of α-(ethylethanolamino)-acetophenone (Ia) gave readily and in good yield the cyclic acetal (Ib),[2b,d] and there was observed no evidence of the formation of significant amounts of any other product. The formation in

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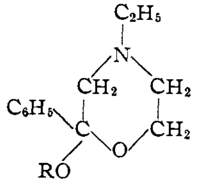
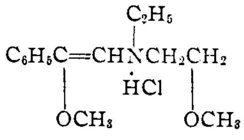
[1] Postdoctorate Fellow (1948–1949), supported by a grant-in-aid from the National Institute of Health, recommended by the National Cancer Institute.

[2] (a) Lutz, Freek and Murphey, THIS JOURNAL, **70**, 2015 (1948); (b) a paper presented at the Chicago meeting of the American Chemical Society, April 20, 1948; (c) Lutz and Murphey, THIS JOURNAL, **71**, 478 (1949); (d) Lutz and Jordan, *ibid.*, **71**, 996 (1949).



I (a) R = H
(b) R = CH_3
(c) R = C_2H_5



$\mathrm{C_6H_5\underset{OCH_3}{C}{=}CH\overset{C_2H_5}{\underset{HCl}{N}}CH_2\underset{OCH_3}{CH_2}}$

II

this reaction of a "dimethoxy" compound (II) such as was reported by Cromwell and Tsou[3] seemed to us unlikely.[4] Our attempts to repeat their preparation of "II"[3b] indeed gave only the expected cyclic acetal (Ib hydrochloride), which was identified by mixture melting point with an authentic sample,[2d] by comparison of X-ray diffraction patterns obtained from the two samples (Figs. 1–4), and by a characterizing analysis for methoxyl. Furthermore it was shown that no significant transetherification occurred when Ib hydrochloride was treated with ethanol under these conditions.

New preparations of Ib hydrochloride by methanolysis of Ia hydrochloride were carried out because Cromwell and Tsou[3] had reported that "II" is a secondary product in the reaction. On treatment of Ia hydrochloride with boiling methanol for two or five minutes, reaction was negligible; after one hour of refluxing considerable unchanged Ia hydrochloride could still be recovered; however when a small amount of free hydrogen chloride was present, reaction was at least half completed after five minutes of refluxing, but unchanged material was still present in very considerable amounts.

Ultraviolet absorption spectra of Ib and Ic hydrochlorides[5] in methanol showed slight but pronounced maxima at 256 mμ ($\epsilon \times 10^{-3} = 0.22$ and 0.24, respectively), and the curves obtained were very similar in fine structure to the curves reported by Cromwell and Tsou[3c] both for Ib hydrochloride and for their "dimethoxy" compound II.

It would therefore appear that the work of Cromwell and Tsou in respect to the formation of the compound supposed by them to be II[3] is erroneous.

Experimental[6,7]

The reliability of the mixture melting point identification of the hydrochlorides in this series is supported by the unmistakable 5° depression given by the hydrochlorides of the methoxy compound (Ib) and its ethoxy analog (Ic). The melting points, since they varied slightly when taken under different conditions, were determined simultaneously, using similarly pulverized samples, with the bath temperature initially 10° below that of the final melting and the rate of heating 1–2° per minute.

Preparation of Ib Hydrochloride.—Sample no. 1 (see Figs. 2 and 3), which proved to be unchanged Ib hydrochloride, was obtained in 48% yield in accordance with the directions of Cromwell and Tsou[3b] for the preparation of their "dimethoxy" compound (II) from Ib hydrochloride; upon crystallization from methanol–ether mixture it melted at 148–149°; the mixture melting point with a sample of Ib hydrochloride prepared according to our original directions[2d] (of m. p. 148–149°) was 148–149°. (*Anal.* Calcd. for $C_{13}H_{19}NO_2 \cdot HCl$: C, 60.57; H, 7.81; OCH_3, 12.04. Found: C, 60.43; H, 8.17; OCH_3, 11.99.) X-Ray patterns from the sample prepared according to the Cromwell–Tsou directions for their "dimethoxy" compound II, are shown in Figs. 2 and 3, and are identical respectively with those of Figs. 1 and 4 obtained from the original Ib hydrochloride.[2d] In a repetition of this experiment the recovery of purified Ib hydrochloride was 70%. In another similar experiment where absolute ethanol was substituted for methanol, Ib hydrochloride was again recovered (80%).

The original preparation of Ib hydrochloride (B[2d]) was repeated but with distillation of two-thirds of the methanol from the reaction mixture (optimum yields had not previously been given). Using purified starting materials the yield of crude (but nearly pure) hydrochloride (of m. p. 144.5–146°) was 95%; of liberated and distilled base (of b. p. 98–100° (1 mm.), $n^{25}\text{D}$ 1.5157) 85% from Ia; of pure hydrochloride (precipitated from 2 ml. of 1-1 methanol–dry ether per g. by slow addition of 0.75 *N* ethereal hydrogen chloride until acid to congo, and addition of excess ether) (of m. p. 147.5–148.5°), 79% from Ia.

A preparation involving four days of refluxing gave 79% yield of crude product.

Dimorphism of Ib Hydrochloride. Crystal form-A was obtained from methanol with solvent of crystallization which is very easily lost. Freshly prepared samples air-dried at room temperature for a half-hour lost approximately 8% of weight *in vacuo* overnight at room temperature. (*Anal.* Calcd. for $C_{13}H_{19}NO_2 \cdot HCl$: C, 60.57: N, 7.81. Found: C, 60.52; H, 7.93.) Vacuum-dried samples exclusively were used to obtain X-ray diffraction patterns. The compound crystallized from isopropyl alcohol in a different and solvent-free form (**crystal form-B**) which gave a different and characteristic X-ray diffraction pattern (Fig. 1). (*Anal.* Calcd. for $C_{13}H_{19}NO_2 \cdot HCl$: C, 60.57; H, 7.81. Found: C, 60.95; H, 8.03.) Conversion back into crystal form-A was effected by crystallization from methanol (the sample was identified by melting point and X-ray diffraction pattern). Melting points of the two forms were identical and no depression was observed upon admixing; however, there was observed in the case of crystal form-A a visible change in the texture of the sample, which occurred at 78–81° under slow heating from room temperature, and which was interpreted in terms of transition to crystal form-B. This conclusion was tested by annealing a sample of form-A at 100° for fifteen minutes; an X-ray diffraction pattern subsequently obtained from the sample was identical with that from a sample of crystal form-B obtained by crystallization from isopropyl alcohol.

The hydroxymorpholine (Ia) hydrochloride (dry) crystallized in one and the same form from both methanol and from isopropyl alcohol; the identity of the two samples was shown by the identity of the X-ray diffraction patterns. (The pattern from the sample crystallized from isopropyl alcohol is shown in Fig. 6.) It is noteworthy that there was no evidence here of etherification of Ia hydrochloride (or transetherification of Ib or Ic hydrochlorides) upon crystallizations from methanol or ethanol. Slow crystallization from methanol–dry ether mixture gave small well-formed crystals melting somewhat higher than previously reported; m. p. 128–128.5°.

Catalyst Requirement for Conversion of Ia to Ib.—In a typical experiment a solution of 1 g. of Ia in 5 ml. of methanol and 5 drops of saturated methanolic hydrogen chloride was refluxed for five minutes; the hydrochlorides were precipitated slowly portionwise by additions of dry ether. The first crops comprising 35% of the material were iden-

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[3] Cromwell and Tsou, THIS JOURNAL, **71**, (a) 993, (b) 995, (c) 994 (Fig. 4) (1949).

[4] *Cf.* Bergmann and Weil, *Ber.*, **63**, 1911 (1930); *cf.* also ref. 2d.

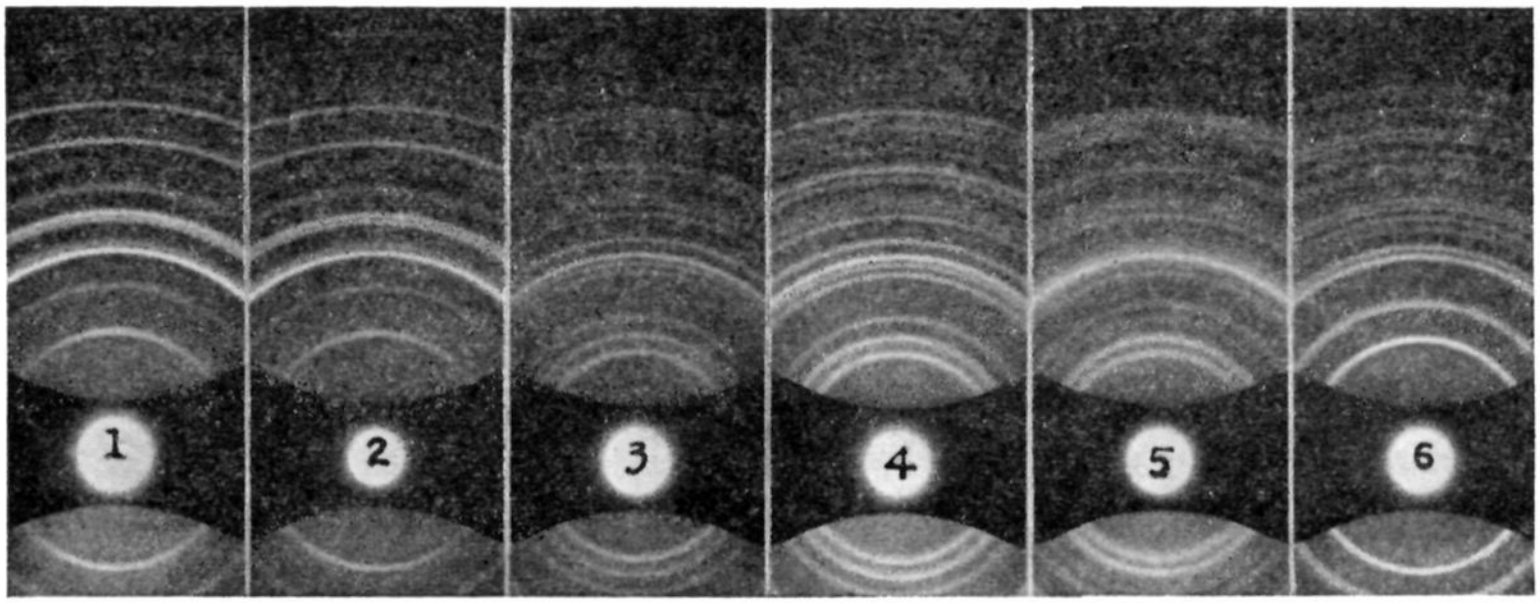
[5] Determinations were made by Mr. Spencer M. King using a Beckman type DU spectrophotometer.

[6] Melting points are corrected.

[7] Microanalyses were by Clark Microanalytical Laboratories, and by Dr. E. C. Cogbill and Mrs. Anne Wilgus of this Laboratory.

Representative X-ray diffraction patterns of crystalline hydrochlorides.

Fig. 1 Fig. 2 Fig. 3 Fig. 4 Fig. 5 Fig. 6



Ib-Form-B
Cryst. from
isopropyl alcohol

Sample No. 1.
Cryst. from
CH_3OH

Ib-Form-A.

Sample No. 2.
(Mixt. of Ia and b),
Cryst. from CH_3OH

Ia

tified by mixture melting points and X-ray diffraction patterns as nearly pure Ib hydrochloride. The next fraction (sample no. 2) was shown to be a mixture of Ib and Ia hydrochlorides by X-ray diffraction patterns (Fig. 5). In similar experiments without added hydrogen chloride Ia was recovered and was identified in the form of the base by mixture melting points; and similar experiments (without added hydrogen chloride) were carried out with similar results on Ia hydrochloride which had been freshly precipitated from an ether solution of Ia by hydrogen chloride, washed with dry ether and used directly without drying (these samples had retained very little if any free hydrochloric acid).

The representative X-ray diffraction patterns given in Figs. 1–6 are contact prints and were obtained by the powder wedge technique in a cylindrical camera with a 7.16 cm. radius exposed to radiation from a copper target X-ray tube with a nickel oxide filter giving essentially Cu K_α radiation.

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The Preparation and Properties of Diethylene Glycol Diacetate

BY SHOU CHU LIANG,[1] R. W. WALKER AND N. R. TRENNER

In connection with another investigation, a quantity of pure diethylene glycol diacetate was required, and consequently we followed the work of previous authors.[2,3] An examination of the properties of the products so obtained revealed that they were of unsatisfactory purity, whereupon the more satisfactory methods described below were developed. The physical properties of the pure diethylene glycol diacetate thus obtained were found sufficiently different from those reported by the earlier investigators to warrant publication.

Several methods of preparation were tried. Application of the classical esterification procedure, *i. e.*, refluxing diethylene glycol with glacial acetic acid in the presence of concd. sulfuric acid, yielded no diacetate. The diester, however, was obtained by a Schotten–Baumann reaction using diethylene glycol in the presence of pyridine with either acetic anhydride or acetyl chloride. Diethylene glycol monoacetate was obtained in all cases, but it was not isolated in pure form.

It has been found that acetic acid, formed during the preparation, must not be removed from the diacetate by alkali extraction for the diester was found to be extremely sensitive to bases. Thus, if a solution of the diester is shaken with aqueous potassium hydroxide (3 *N*) at room temperatures for a short time, the diester is hydrolyzed to the monoester.

It was not found possible to separate the mono- and diacetates very well by fractional distillation under vacuum as they formed a constant boiling mixture. The diacetate could be isolated, however, by extracting with ether from an aqueous solution of the mixture of the two esters. The monoester is more hydrophilic and remains in the aqueous phase.

Diethylene glycol diacetate is hygroscopic. When pure and dry, it melts at 18°. On standing in air, the melting point gradually lowers as the diester absorbs moisture from the atmosphere and finally drops to below 0°.

Quite unexpectedly, the diacetate is completely miscible with water. This is very different from the behaviors of structurally similar compounds such as ethyl acetate, diethyl ether and 1,4-butanediol diacetate.

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[2] L. H. Cretcher and W. H. Pittenger, THIS JOURNAL, **47**, 165 (1925).

[3] M. Macleod, *J. Chem. Soc.*, 3092 (1928).