the remaining oil was distilled to give a small amount of colorless oil (*ca.* 0.3 g) and a large pot residue.

Hydride Transfer to 1,2-Dimethylcyclohexene.—To the same amount of polyphosphoric acid was slowly added a solution of 1,2-dimethylcyclohexene (1.10 g, 0.010 mol, 78% 1,2-dimethylcyclohexene) and tropilidene (0.92 g, 0.010 mol). The reaction mixture was heated on the steam bath for an additional 15 min, cooled, poured over ice, neutralized with solid sodium carbonate, and extracted with pentane (two 25-ml portions). The combined pentane extracts were washed with brine and dried over anhydrous sodium sulfate. The majority of the pentane was removed and the residual oil was distilled (0.15 g, bp 50–170°). Analysis of the distillate by vpc indicated a 1.85:1 *cis*/*trans* ratio of dimethylcyclohexanes.

Registry No.—I, 493-03-8; II, 1674-10-8.

The Reaction of Primary Amides with Phosgene in the Presence of Hydrogen Chloride

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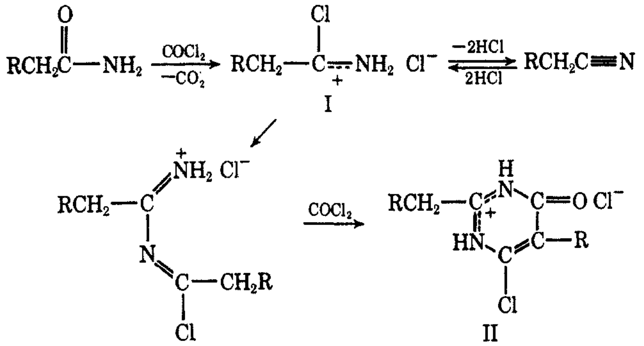
It has previously been reported[1] that the reaction of primary amides with phosgene, especially in the presence of bases, gives nitriles through the formation of imidoyl chloride hydrochloride (I) (Scheme I). In the preceding papers,[2,3] we have reported that nitriles react with phosgene in the presence of hydrogen chloride to give 6-chloro-2,5-dialkyl-4(3H)-pyrimidone hydrochlorides (II), and that this reaction proceeds *via* I and a N-(1-chloroalkylidene)alkylamidine hydrochloride (Scheme I).

SCHEME I



Noting these observations, we carried out the reaction of primary amides with phosgene in the presence of hydrogen chloride and found a satisfactory one-step synthesis of the pyrimidone hydrochlorides (II). The results are summarized in Table I.

Acetamide is basic enough to react violently with phosgene to give acetamide hydrochloride, but, when acetamide hydrochloride which had been prepared previously was allowed to react with excess phosgene in nitrobenzene at 60–65° using a sealed glass tube, 6-chloro-2-methyl-4(3H)-pyrimidone hydrochloride was isolated by filtration of the reaction mixture as the only pure product. We examined the yields of the reaction with varying molar ratios of the reactants, and found that more than 2 mol of phosgene to 1 mol of acetamide hydrochloride is essential for pyrimidone formation.

TABLE I

THE REACTION OF FATTY AMIDES WITH PHOSGENE IN THE PRESENCE OF HYDROGEN CHLORIDE[a]

Fatty amides	Reaction time, hr	Yield of products, % Pyrimidones (II)	Nitriles[b]
Acetamide[c]	200	83	
Propionamide[d]	115	54	22
Butyramide[d]	191	34	28
Caproamide[d]	197	44	32
Lauroamide[d]	206	22	78

[a] Conditions: 60–65°; solvent, nitrobenzene. [b] Determined by glpc. [c] Molar ratio of acetamide hydrochloride/$COCl_2$, 1:8. [d] Molar ratio of amide/$COCl_2$/HCl, 1:3:1.

A solvent effect was also observed in this reaction. Table II gives the yield of product and the dielectric constant of the solvent. Taking into account the ionic mechanism proposed for the reaction yielding the pyrimidones (II) from nitriles and phosgene,[3] it is expected that a high dielectric constant should give a high yield of the pyrimidone hydrochloride. However, the lack of reaction in nitromethane suggests that solubility also plays an important part. Acetamide hydrochloride did not dissolve in nitromethane during the reaction and was recovered unchanged. Analogous results were obtained on the reactions in benzene and toluene, and without solvent. In dioxane, acetonitrile was detected by glpc but the pyrimidone hydrochloride was not obtained.[4] In acetonitrile [ϵ 37.5 (20°)], acetamide hydrochloride readily disappeared as the reaction proceeded and the pyrimidone hydrochloride was formed in a shorter time. It is clear that some product is formed from acetonitrile used as solvent. Thus it is of interest to compare the reactivity of acetamide hydrochloride with that of acetonitrile under comparable conditions. The molar ratios of the reactants were determined as shown in Figure 1 in order to maintain, during the reaction, identical concentrations of hydrogen chloride and phosgene, for each experiment. Figure 1 shows that they have

TABLE II

EFFECT OF SOLVENT ON THE YIELD[a]

Solvent	Yield, %	Dielectric constant,[b] ϵ (temp, °C)
Nitrobenzene	83	34.8 (25)
Benzonitrile	53[c]	25.2 (25)
Chlorobenzene	28	5.6 (25)
Nitromethane	0	35.9 (30)
Toluene	0	2.4 (25)
Benzene	0	2.3 (25)
Dioxane	0	2.2 (25)
None	0	

[a] Conditions: 60–65°; 200 hr; concentration, see Experimental Section; molar ratio of acetamide hydrochloride/phosgene 1:8. [b] H. A. Lange, "Handbook of Chemistry", 10th ed, McGraw-Hill Book Co., New York, N. Y., 1967, p 1233. [c] 72 hr; with longer reaction time, another reaction occurred, which is now under investigation.

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(1) A. J. Speziale and L. R. Smith, *J. Org. Chem.*, **28**, 1805 (1968).

(2) S. Yanagida, M. Ohoka, M. Okahara, and S. Komori, *Tetrahedron Lett.*, 2351 (1968).

(3) S. Yanagida, M. Ohoka, M. Okahara, and S. Komori, *J. Org. Chem.* **34**, 2972 (1969).

(4) It has recently been reported that phosgene in dioxane is an easy and convenient agent for the dehydration of amides, and that this dehydration is free of side reaction [M. Wilchek, S. Ariely, and A. Patchornik, *ibid.*, **33**, 1258 (1968)].

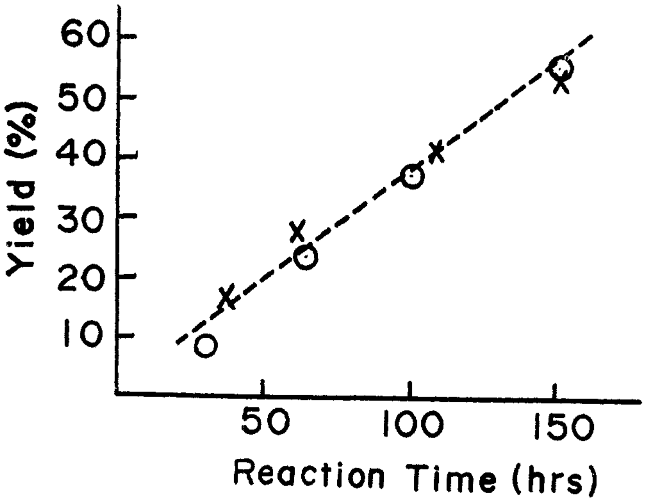

Figure 1.—Comparison of the reactivity to phosgene of acetamide hydrochloride with that of acetonitrile in the presence of hydrogen chloride: O, acetamide, 60–65°, $(CH_3CONH_2)_2$-HCl (0.5 g, 3.23 mmol) and $COCl_2$ (2.6 g, 26.2 mmol) molar ratio 1:8, nitrobenzene (17 g); ×, acetonitrile, 60–65°, CH_3CN (0.266 g, 6.48 mmol) and $COCl_2$ (1.93 g, 19.5 mmol) molar ratio 1:3:2.6, nitrobenzene (15 g).

similar reactivity. On the other hand, the reaction of primary amides with phosphorus pentachloride is well known to give imidoyl chloride hydrochloride (I) as an intermediate,[5,6] but the addition of phosphorus pentachloride to the reaction mixture did not affect the yield of the pyrimidone hydrochloride. In view of these facts, it is clear that the formation of imidoyl chloride hydrochloride (I) is not rate determining in the formation of pyrimidone hydrochlorides (II).

The reaction of amides with phosgene in the presence of hydrogen chloride has been extended to propionamide, butyroamide, caproamide, and lauroamide, the products being the corresponding pyrimidone hydrochlorides (II) and nitriles (Table I). Glpc analysis of the reaction mixture showed the formation of a small amount of 4,6-dichloro-2,5-dialkylpyrimidines as in the reaction of nitriles with phosgene in the presence of hydrogen chloride.[3]

Experimental Section

Acetamide hydrochloride $[(CH_3CONH_2)_2HCl]$ was prepared by the method of Strecker.[7] The other amides were purchased and purified by boiling.

Procedure.—*Caution. Because carbon dioxide and hydrogen chloride are evolved during the reaction, the reaction should be conducted on a small scale to avoid any dangerous explosion of the glass tube. The reaction temperature should also be kept below 70°.*

In a 50-ml glass tube were placed acetamide hydrochloride (0.003 mol) and 15 ml of phosgene solution (0.02–0.03 mol of phosgene). The tube was stoppered, cooled in Dry Ice–acetone, sealed carefully, and heated to 60–65° in a water bath. After the usual reaction period (*ca.* 200 hr), the reaction tube was chilled in Dry Ice–acetone and opened carefully. After removal of phosgene and hydrogen chloride, the resulting precipitate was separated by filtration, washed with ether, and dried *in vacuo.* It was identified as 6-chloro-2-methyl-4(3H)-pyrimidone hydrochloride by direct comparison with the ir spectrum of the authentic sample.[3]

Since the hydrochlorides of other amides were found too hygroscopic to isolate, they were prepared *in situ* by introducing dry hydrogen chloride into a solution of the amide and then allowing the mixture to react with phosgene in the same manner as mentioned above (0.01 mol of amide and hydrogen chloride, and 0.03 mol of phosgene in 15 g of nitrobenzene). The yield of nitriles was determined by glpc [on a column of silicone DC 550 10% on Diasolid L (60–80 mesh), 1 m × 4 mm]. The pyrimidone hydrochlorides except that from caproamide were identified by direct comparison with authentic samples.[3] 6-Chloro-2-pentyl-5-butyl-4(3H)-pyrimidone prepared from caproamide was recrystallized from acetonitrile and identified on the basis of its elemental analysis and ir spectrum: mp 109.5–111.0°; ir (mull) 1690 and 1590 cm^{-1}.

Anal. Calcd for $C_{13}H_{21}N_2ClO$: C, 60.80; H, 8.24; N, 10.90. Found: C, 61.10; H, 8.47; N, 10.88.

Registry No.—Phosgene, 75-44-5; hydrogen chloride, 7647-01-0; 6-chloro-2-pentyl-5-bentyl-4(3H)-pyrimidone, 21691-18-9.

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Rotational Isomerism in Vinylethylene Oxide

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In recent years, various spectroscopic methods have been employed to determine the electronic interactions of three-membered rings with unsaturated systems. Thus, with respect to benzene, cyclopropane is electron donating whereas oxirane and thiirane are electron withdrawing.[1] Recently, a large number of uv[2] and nmr[3] data have suggested a stereochemical requirement for maximum interaction between the cyclopropyl group and an adjacent p orbital. Maximum overlap occurs when the plane of the three-membered ring is parallel to the axis of the p orbital, *i.e.*, the bisected conformation.

Two bisected conformations exist for vinylcyclopropane, the *s-trans* and *s-cis* conformations.[4] However nmr evidence has been presented for a three-well torsonial potential for vinylcyclopropane.[5,6] It appears that the lower energy conformer is the *s-trans* form with two upper state forms corresponding to dihedral angles of *ca.* 80°, *i.e.*, the two *gauche* conformations. The energy separation between the *s-trans* and *gauche* conformations has been determined by nmr[6] and electron diffraction[7] to be *ca.* 1.0 kcal/mol. It is of interest to compare the results obtained for vinylcyclopropane with those obtained for the similar molecule, vinylethylene oxide (I). We wish to report our studies on the temperature variation of the nmr spectrum of

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