

Figure 6.—A schematic representation of the nitrate absorption in aralkyl nitrates. High intensity bands correspond to  $\pi_N^* \rightarrow \pi_N$  and  $\phi^* \leftarrow \phi$  excitations.

the  $\pi_N^* \leftarrow n$  mode of excitation.<sup>22,23</sup> Very recently the discovery of a second, higher energy,  $\pi_N^* \leftarrow n$  band in the circular dichroism spectrum has been reported.<sup>24</sup> The present work indicates the presence of still more low intensity bands in this region, some of which are associated with a charge transfer from the alkyl or aryl group to the nitrate  $\pi_N^*$  orbitals. From this viewpoint the photochemical reactions<sup>25–28</sup> of nitrate esters ( $\text{RONO}_2$ ) may be associated with an excited dipolar species  $\text{R}^\delta + \text{ONO}_2^{\delta-}$ , the chemical behavior of

(22) H. McConnell, *J. Chem. Phys.*, **20**, 700 (1952).

(23) C. N. R. Rao, "Ultraviolet and Visible Spectroscopy," Butterworths, London, 1961, p 21.

(24) L. D. Hayward and S. Claesson, *Chem. Commun.*, 302 (1967).

(25) J. A. Gray and D. W. G. Style, *Trans. Faraday Soc.*, **49**, 52 (1953).

(26) S. Claesson, G. Palm, and G. Wettermark, *Ark. Kemi*, **17**, 579 (1961).

(27) L. D. Hayward, R. A. Kitchen, and D. J. Livingstone, *Can. J. Chem.*, **40**, 434 (1962).

(28) I. G. Csizmadia and L. D. Hayward, *Photochem. Photobiol.*, **4**, 657 (1965).

which must be more than a mere superimposition of the properties of the cation ( $\text{R}^+\text{ONO}_2$ ) generated in the mass spectrometer and the anion ( $\text{RONO}_2^-$ ) generated by electrolytic or chemical reductions. It is hoped that the information provided here will aid in the interpretation of the photochemical reactions.

Finally the electron distribution which indicated a net positive charge on nitrogen and carbon as well as  $\alpha$  and  $\beta$  hydrogens is in agreement with the reaction mechanistic conclusions<sup>29–32</sup> of base-catalyzed reactions while the net negative charge on the three oxygen atoms predicts the sites of protonation which occur during acid catalyzed reactions.

**Registry No.**—Benzyl alcohol, 100-51-6;  $\beta$ -phenethyl alcohol, 60-12-8.

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(29) L. D. Hayward and I. G. Csizmadia, *Tetrahedron*, **19**, 2111 (1963).

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(32) J. W. Baker and D. M. Easty, *J. Chem. Soc.*, 1193 (1952).

## Reactions of Enaminonitriles with Phosgene. Synthesis of Enaminocarboxylic Acid Chlorides

MASATAKA OHOKA,\* KATSUHIKO ASADA, SHOZO YANAGIDA, MITSUO OKAHARA, AND SABURO KOMORI

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamada-ka, Suita, Osaka, Japan

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Reactions of enaminonitriles with phosgene have been investigated. Enaminonitriles with an  $\alpha$  hydrogen or  $\alpha$  halogen gave enaminocarboxylic acid chlorides in moderate to good yields together with low yields of isocyanates. Reactions of enaminonitriles with an  $\alpha$ -cyano or  $\alpha$ -ethoxycarbonyl group resulted in the quantitative recovery of the starting materials. The acid chlorides obtained were characterized by spectral analyses and by conversion to derivatives such as esters and amides.

Halleux and Viehe<sup>1</sup> have recently reported the formation of enaminocarboxylic acid chlorides from reactions of tertiary enamines with phosgene in the presence of triethylamine. However, isolation of the acid chlorides was unsuccessful because of their instability, and therefore they were identified by conversion to derivatives such as esters and amides.

In the course of our studies on the reactions of enaminonitriles with phosgene,<sup>2</sup> we have found that enaminonitriles possessing an  $\alpha$  halogen gave relatively stable enaminocarboxylic acid chlorides. We have

succeeded in their isolation and have characterized them by spectral analyses and by conversion to esters or amides.

### Results and Discussion

Treatment of enaminonitriles **1a–f** with phosgene in refluxing ethyl acetate gave enaminocarboxylic acid chlorides **2a–d** in moderate to good yields (Table I). It is of much interest that in addition to **1a** enaminonitriles **1e** and **1f** possessing an  $\alpha$  halogen also gave acid chloride **2a**. However, reactions of **1i** and **1j** with phosgene resulted in the quantitative recovery of the starting materials. The acid chlorides **2a–d** are either

(1) A. Halleux and H. G. Viehe, *J. Chem. Soc. C*, 881 (1970).

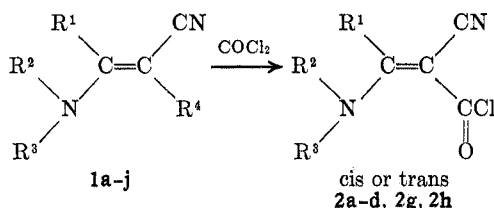
(2) M. Ohoka, S. Yanagida, and S. Komori, *J. Org. Chem.*, **37**, 3030 (1972).

TABLE I

Compd <sup>b</sup>	Yield, %	State	Mp, °C	ENAMINOCARBOXYLIC ACID CHLORIDES <sup>a</sup>			Nmr, $\delta$ (ppm)	$\lambda_{\max}$ (CH <sub>3</sub> CN), nm ( $\epsilon \times 10^{-4}$ ) Acid chloride Starting nitrile (no.)	
				$\text{C}\equiv\text{N}$	$\text{C}=\text{O}$	$\text{C}=\text{C}$			
<b>2a</b>	64 (from <b>1a</b> )	Powder	130-132	2220	1700	1655	2.34 (s, 3 H), 7.20 (br, 0.7 H) 8.90 (br, 0.7 H)	288 (1.63)	( <b>1a</b> ) <sup>c</sup> 255 (1.24)
	48 (from <b>1e</b> )								( <b>1e</b> ) 254 (1.66)
	31 (from <b>1f</b> )								
<b>2b</b>	72	Powder	140	2216	1690	1625	ca. 7.55 (m, 5 H), 8.45 (br, 0.7 H), 9.25 (br, 0.7 H)	306 (1.52), 243 (sh) (0.47)	( <b>1b</b> ) 289 (1.02), 225 (1.08)
<b>2c</b>	67	Needles	~140	2212 (2220)	1710 (1682)	1570 (1577)	2.34 (s, 3 H), 7.30 (m, 5 H), 11.35 (br s, 1 H)	308 (2.09), 222 (1.17)	( <b>1c</b> ) 287 (1.64), 225 (sh) (0.83)
<b>2d</b>	88	Needles	85-87	2210	1690	1585	2.40 (s, 3 H), 4.60 (d, 2 H, $J = 6.0$ Hz), 7.25 (m, 5 H), 10.10 (br s, 1 H)	301 (2.03)	( <b>1d</b> ) 258 (1.98), 205 (0.74)
<b>2g</b>		Viscous liquid		2205	1708	1565	2.50 (s, 3 H), 3.34 (s, 6 H)		
<b>2h</b>		Viscous liquid		2205	1713	1550	2.54 (s, 3 H), 3.22 (s, 3 H), 4.78 (s, 2 H)		

<sup>a</sup> Satisfactory analytical values ( $\pm 0.3\%$  for C, H, and N) were obtained for **2a-d**. <sup>b</sup> Recrystallization solvents: **2a-c**, AcOEt; **2d**, C<sub>6</sub>H<sub>6</sub>-CCl<sub>4</sub> 2:1 (v/v). <sup>c</sup> **2a**, **2b**, and **2d** decompose at their melting points. **2c** begins to decompose at ca. 140° without melting. <sup>d</sup> **2a-d**, KBr; **2g**, **2h**, and **2c** (data in parentheses), CDCl<sub>3</sub>. <sup>e</sup> Solvents: **2a**, liquid SO<sub>2</sub> (measured at -25°); **2b**, AcOEt; **2c**, **2d**, **2g**, and **2h**, CDCl<sub>3</sub>. <sup>f</sup> Coupling with a NH proton. <sup>g</sup> J. J. Conn and A. Taurins, *Can. J. Chem.*, **31**, 1211 (1953).

powder-like or crystalline solids and all of them decompose at their melting points. In addition, **2a** and **2b** are very sensitive to moisture. Results are summarized in Table I.



- a**, R<sup>1</sup> = CH<sub>3</sub>; R<sup>2</sup> = R<sup>3</sup> = R<sup>4</sup> = H  
**b**, R<sup>1</sup> = C<sub>6</sub>H<sub>5</sub>; R<sup>2</sup> = R<sup>3</sup> = R<sup>4</sup> = H  
**c**, R<sup>1</sup> = CH<sub>3</sub>; R<sup>2</sup> = C<sub>6</sub>H<sub>5</sub>; R<sup>3</sup> = R<sup>4</sup> = H  
**d**, R<sup>1</sup> = CH<sub>3</sub>; R<sup>2</sup> = C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>; R<sup>3</sup> = R<sup>4</sup> = H  
**e**, R<sup>1</sup> = CH<sub>3</sub>; R<sup>2</sup> = R<sup>3</sup> = H; R<sup>4</sup> = Cl  
**f**, R<sup>1</sup> = CH<sub>3</sub>; R<sup>2</sup> = R<sup>3</sup> = H; R<sup>4</sup> = Br  
**g**, R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = CH<sub>3</sub>; R<sup>4</sup> = H  
**h**, R<sup>1</sup> = R<sup>2</sup> = CH<sub>3</sub>; R<sup>3</sup> = C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>; R<sup>4</sup> = H  
**i**, R<sup>1</sup> = CH<sub>3</sub>; R<sup>2</sup> = R<sup>3</sup> = H; R<sup>4</sup> = CN  
**j**, R<sup>1</sup> = CH<sub>3</sub>; R<sup>2</sup> = R<sup>3</sup> = H; R<sup>4</sup> = CO<sub>2</sub>C<sub>2</sub>H<sub>5</sub>

The structures of the acid chlorides **2** were confirmed on the basis of ir, nmr, uv, and mass spectra and elemental analyses. Ir spectra of **2a-d** showed conjugated C≡N, C=O, and C=C stretching bands at 2210-2220, 1690-1710, and 1585-1655 cm<sup>-1</sup>, respectively. The unusually low frequencies of the absorptions due to the carbonyl groups compared to ordinary acid chlorides are reasonable in view of their conjugations with double bonds of enamines. The ir spectrum of **2a** (CH<sub>3</sub>CN solution) showed two NH absorptions at 3250 and 3390 cm<sup>-1</sup> characteristic of primary amines.

Nmr spectra of **2a-d** showed one or two broad signals assignable to NH protons in low fields. Further, all the nmr spectra of **2a**, **2c**, and **2d** showed a singlet assignable to methyl protons attached to a double bond carbon atom. This shows that the acid chlorides are composed of only one geometrical isomer (cis or trans).

Uv absorption maxima of **2a-d** were observed at longer wavelengths than those of the corresponding starting enaminonitriles as a result of spread of conjugated systems.

Mass spectra of **2a-c** showed molecular ion peaks, and molecular weights of **2c** and **2d** measured by VPO

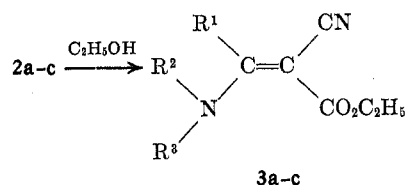
(benzene solutions) agreed closely with the calculated values.<sup>3</sup>

Reactions of **2a-c** with ethanol gave the corresponding enamino esters **3a-c** in high yields (Table II). Ester

TABLE II  
ENAMINO ESTERS<sup>a</sup>

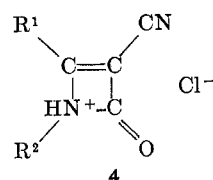
Compd	Yield, %	Mp, °C	Recrystn solvent
<b>3a</b>	86	192-193 <sup>b</sup>	EtOH
<b>3b</b>	95	125-126	EtOH
<b>3c</b>	93	82-85	<i>n</i> -Hexane

<sup>a</sup> Satisfactory analytical values ( $\pm 0.3\%$  for C, H, and N) were obtained for **3a-c**. Ir, nmr, and mass spectral data were consistent with the enaminoester structures. <sup>b</sup> Mp 190°: R. Hull, B. J. Lovell, H. T. Openshaw, L. C. Payman, and A. R. Todd, *J. Chem. Soc.*, 357 (1946).



**3a** was identified by comparison with an authentic sample<sup>4</sup> and others were characterized by their ir, nmr, and mass spectra and elemental analyses.

It is concluded, on the basis of the above data, that the products have enaminocarbonyl acid chloride structures. The alternative structure **4** when R<sup>3</sup> = H, can be excluded on the basis of the low carbonyl stretch-

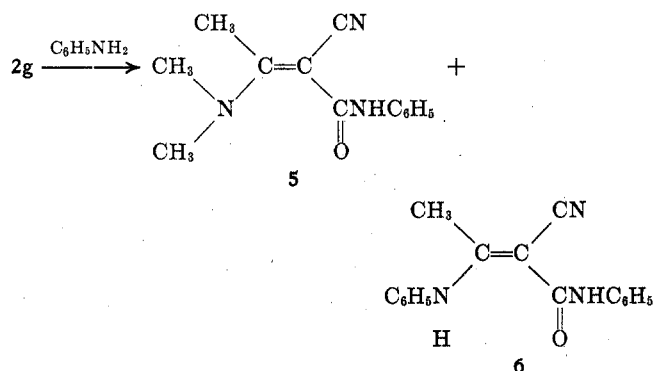


(3) Molecular weight: **2c**, found 217 (calcd 221); **2d**, found 224 (calcd 235).

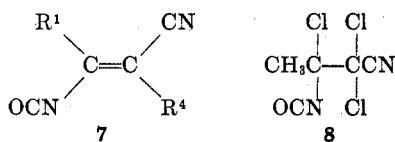
(4) R. Hull, B. J. Lovell, H. T. Openshaw, L. C. Payman, and A. R. Todd, *J. Chem. Soc.*, 357 (1946).

ing frequencies<sup>5,6</sup> and the fact that addition of **2c** to a  $10^{-3}$  *N* solution of  $\text{LiClO}_4$  in  $\text{CH}_3\text{CN}$  did not increase the conductance of the solution, whereas the addition of tetraethylammonium bromide increased the conductance of the solution by a factor of about 9.<sup>7,8</sup>

The reaction was extended to enamionitriles with a tertiary nitrogen atom. Reactions of **1g** and **1h** with phosgene gave corresponding acid chlorides **2g** and **2h**, which were very viscous liquids and could not be purified. Their ir spectra revealed characteristic absorptions of acid chlorides already described. Their nmr spectra also support the acid chloride structures. In addition, treatment of **2g** with aniline gave anilides **5** and **6** in 13 and 24% yield (overall), respectively; **6** was apparently formed by the reaction of **5** with aniline.<sup>9,10</sup>



By-products of the reaction were also examined. Enaminonitriles **1a** and **1b** gave corresponding unsaturated isocyanates **7a** ( $\text{R}^1 = \text{CH}_3$ ;  $\text{R}^4 = \text{H}$ ) (trace) and **7b** ( $\text{R}^1 = \text{C}_6\text{H}_5$ ;  $\text{R}^4 = \text{H}$ ) (23%, determined by nmr),<sup>11</sup> respectively. Enaminonitrile **1e** afforded, instead of **7e**



( $\text{R}^1 = \text{CH}_3$ ;  $\text{R}^4 = \text{Cl}$ ), 3-isocyanato-2,2,3-trichlorobutyronitrile (**8**) in 18% yield. **8** was probably produced by addition of chlorine formed during the reaction (*vide infra*) to initially formed isocyanate **7e**.

Isocyanate **8** was identified by ir, nmr, and mass spectra and elemental analyses. The assigned structure was supported by the fact that the isocyanate gave on treatment with an excess of aniline a 77% yield of *N*-phenyl-*N'*-phenylcarbamoylacetylamidine (**10**), which was probably formed *via* intermediate **9**. Amidine **10** was characterized by spectral and elemental analyses and by independent synthesis from *N*-phenylacetamide and phenyl isocyanate.<sup>12</sup>

In the case of **1c** and **1d**, phenyl isocyanate (**11**)

(5) Carbonyl stretching bands of azetidinones and azetidinones appear around  $1750 \text{ cm}^{-1}$ . Since **4** has a protonated nitrogen adjacent to the carbonyl group, its carbonyl stretching band is expected to appear at a much higher frequency than  $1750 \text{ cm}^{-1}$ .

(6) D. Cook, *Can. J. Chem.*, **40**, 2362 (1962).

(7) Product **2c** and tetraethylammonium bromide were added to the solution so that their concentrations became  $10^{-2}$  mol/l.

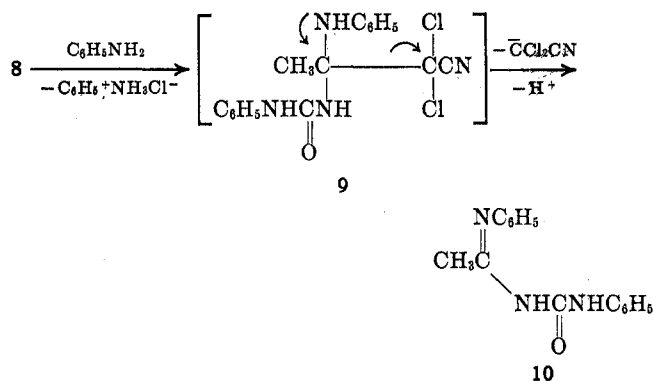
(8) The authors wish to express their thanks to Professor Hideo Tamura, Mr. Masayuki Tsunaga, and Mr. Mikio Miyake for their assistance in the measurement of the conductance.

(9) H. Ahlbrecht, *Tetrahedron Lett.*, 211 (1969).

(10) R. Helmers, *Angew. Chem.*, **83**, 756 (1971).

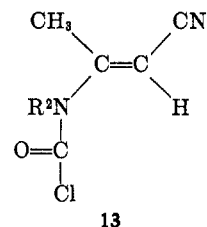
(11) Ir spectra (liquid film): **7a**, 2250 (NCO), 2210 ( $\text{C}\equiv\text{N}$ ), and 1640  $\text{cm}^{-1}$  ( $\text{C}=\text{C}$ ); **7b**, 2250 (NCO), 2210 ( $\text{C}\equiv\text{N}$ ), and 1610  $\text{cm}^{-1}$  ( $\text{C}=\text{C}$ ).

(12) A. J. Hill and I. Rabinowitz, *J. Amer. Chem. Soc.*, **48**, 732 (1962).



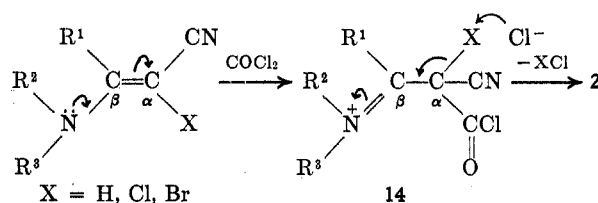
(8%)<sup>13,14</sup> and benzyl isocyanate (**12**) (3%)<sup>13</sup> were obtained, respectively. They were characterized by respective conversion to *N,N*-diphenylurea and *N*-benzyl-*N'*-phenylurea by reaction with aniline.

The formation of isocyanates **11** and **12** may be visualized to occur by the following two pathways: (a) decomposition of acid chlorides **2c** and **2d** *via* azetidinone hydrochloride **4**; (b) decomposition of carbamoyl chloride **13**. Pathway a is excluded on the basis of the



fact that treatment of acid chloride **2c** with phosgene in refluxing ethyl acetate resulted in the quantitative recovery of **2c**. Thus, the isocyanates were probably formed by pathway b, although no evidence for the intermediacy of carbamoyl chloride **13** was obtained and the decomposition mechanism of **13** has not been clarified.

The formation of acid chloride **2** is evidently initiated by the  $\alpha$  carbon attack of phosgene as follows.



Since two very electronegative groups, a cyano and a chloroformyl group, are attached to the  $\alpha$  carbon, the iminium salt **14** easily loses a proton or a positive halogen from the  $\alpha$  carbon to give **2**.

Whereas reactions of enamionitriles possessing an  $\alpha$  alkyl group with phosgene have been found to give good yields of unsaturated isocyanates *via* initial *N*-phosgenation,<sup>2</sup> enamionitriles with an  $\alpha$  hydrogen or an  $\alpha$  halogen give acid chlorides **2** as the major products. Prevalence of C-phosgenation over N-phosgenation in the present cases may be due to a decrease in the nucleophilicity of the nitrogen atom of enamionitriles on replacement of an  $\alpha$  alkyl group by a more electronegative substituent such as hydrogen or halogen.

(13) Isolation yields (based on the enamionitrile) as phenylureas.

(14) Ir spectrum of **11** agreed with that of an authentic sample.

It may be explained in the same way that the acid chlorides **2**, in spite of the high reactivity between carboxylic acid chlorides and amines, can possess an amino group in the same molecule without further cyclization to azetidinone hydrochloride **4**.

It is of much interest to know interactions between amino and chloroformyl group of the acid chlorides in solid states. Thus, the analysis of their crystal structures by X-ray diffraction is now in progress.

### Experimental Section<sup>15</sup>

**Materials.**—Enaminonitriles **1a**-**d**<sup>16,17</sup> and **1g**-**j**<sup>4,9,10</sup> were prepared according to the known methods: **1d**, mp 78–80°, **1i**, 230–231°; **1g**, bp 110–113° (2.5 mm), **1h**, 150–155° (0.15 mm). **1e** (mp 120–121°) was obtained by chlorination of **1a** with NaOCl in water. **1f** (mp 120–123°) was prepared by reaction of **1a** with Br<sub>2</sub> in aqueous Na<sub>2</sub>CO<sub>3</sub>.

**Reaction of Enaminonitrile with Phosgene.**—A typical procedure is as follows. In a 100-ml round-bottomed four-necked flask, equipped with a stirrer, a condenser, a dropping funnel, and a gas inlet tube, 30 ml of AcOEt was placed and it was saturated with phosgene under reflux. Enaminonitrile **1d** (4.3 g, 25 mmol) in 20 ml of AcOEt was added to the solution in 15 min; then the reaction mixture was heated under reflux with stirring for an additional 35 min. The introduction of phosgene was continued throughout these procedures. After phosgene was purged with dry N<sub>2</sub>, the solvent was removed under reduced pressure to give a yellow solid, which was washed with a small amount of CCl<sub>4</sub> and dried *in vacuo*, giving a yellow powder of **2d** (5.2 g, 88%). The acid chloride was recrystallized from C<sub>6</sub>H<sub>6</sub>-CCl<sub>4</sub> (2:1, v/v) to give colorless needles.

The solvent was removed from the CCl<sub>4</sub> washings to give a viscous liquid, which was extracted with hexane to give benzyl isocyanate (**12**) (0.12 g) after removal of the solvent. The isocyanate was treated with aniline (0.3 g) in CCl<sub>4</sub> to give *N*-benzyl-*N'*-phenylurea (0.18 g, 3%).

Crystallizations of all the acid chlorides were carried out in a dry atmosphere.

**Reaction of Acid Chloride **2** with EtOH.**—A typical procedure is as follows. EtOH (5.1 g) was rapidly added to a solution of acid chloride **2b** (0.5 g, 2.4 mmol) in 10 ml of AcOEt at room temperature; then the mixture was stirred for 1 hr. After evaporation of the solvent under reduced pressure, the resulting residue was washed with water and dried *in vacuo*, giving a yellow powder of **3b** (0.5 g, 95%).

**Reaction of **1g** with Phosgene. Isolation of **5** and **6**.**—Treatment of nitrile **1g** (3.0 g, 27 mmol) with phosgene in AcOEt gave 3.3 g of a reddish viscous liquid (**2g**). The product was dissolved in 20 ml of CH<sub>2</sub>Cl<sub>2</sub> and was added to a solution of aniline (5.3 g, 57 mmol) in 20 ml of CH<sub>2</sub>Cl<sub>2</sub> in 30 min at room temperature; then the mixture was allowed to stand overnight at room temperature. The aniline hydrochloride formed was filtered off and the solvent was removed under reduced pressure, giving a viscous liquid. A small amount of CCl<sub>4</sub> was added to it and the solution was allowed to stand overnight in a refrigerator. The precipitates formed were filtered, washed with water, and dried *in vacuo*, giving a yellow powder of **5** (0.52 g), which was recrystallized from *i*-PrOH to give yellow prisms, mp 141–142° dec. After

evaporation of CCl<sub>4</sub> from the filtrate, the residue was dissolved in a small amount of AcOEt, the solution being allowed to stand overnight in a refrigerator. The precipitates formed were filtered and dried *in vacuo*, giving 2.3 g of a mixture of **5** and **6** (content of **5**, 0.46 g, content of **6**, 1.84 g) (determined by nmr), which was crystallized from *i*-PrOH to give yellow prisms of **6**, mp 139–142° dec.

Anilide **5** had ir (Nujol) 2170 (C≡N), 1663 (C=O), 1598, 1563, and 1526 cm<sup>-1</sup>; nmr (CDCl<sub>3</sub>) δ 2.42 (s, 3 H), 3.13 (s, 6 H), 7.0–7.6 (m, 5 H), and 7.7 (br s, 1 H); mass spectrum (70 eV) *m/e* (rel intensity) 229 (21, M<sup>+</sup>), 212 (10), 61 (100), and 56 (15).

*Anal.* Calcd for C<sub>13</sub>H<sub>15</sub>N<sub>3</sub>O: C, 68.10; H, 6.59; N, 18.33. Found: C, 68.15; H, 6.66; N, 18.63.

Anilide **6** had ir (Nujol) 2185 (C≡N), 1635 (C=O), 1592, 1573, and 1523 cm<sup>-1</sup>; nmr (CDCl<sub>3</sub>) δ 2.28 (s, 3 H), 6.9–7.1 (m, 10 H), 7.65 (br s, 1 H), and 12.42 (br s, 1 H); mass spectrum (70 eV) *m/e* (rel intensity) 277 (48, M<sup>+</sup>), 185 (64), 118 (16), 93 (100), and 77 (19).

*Anal.* Calcd for C<sub>17</sub>H<sub>15</sub>N<sub>3</sub>O: C, 73.63; H, 5.45; N, 15.15. Found: C, 73.77; H, 5.41; N, 15.17.

**Reaction of **1h** with Phosgene.**—Treatment of **1h** (3.7 g, 20 mmol) with phosgene in AcOEt gave 5.3 g of a reddish, viscous liquid (**2h**).

**3-Isocyanato-2,2,3-trichlorobutyronitrile (**8**).**—Enaminonitrile **1e** (11.7 g, 100 mmol) was treated with phosgene in AcOEt by the same method as described above. On removal of the solvent from the reaction mixture was obtained a yellow, moist solid, which was washed with 50 ml of CCl<sub>4</sub> and dried *in vacuo*, giving a yellow powder of **2a** (6.0 g, 48%). The solvent was removed from the CCl<sub>4</sub> washings to give a yellow liquid, which was distilled under reduced pressure to give isocyanate **8** (colorless liquid) (3.9 g, 18%); bp 80–82° (20 mm); ir (liquid film) 2260 cm<sup>-1</sup> (NCO); nmr (CCl<sub>4</sub>) δ 2.25 (s); mass spectrum (70 eV) *m/e* (rel intensity) 178 (8, M<sup>+</sup> + 2 - HCl), 176 (22, M<sup>+</sup> - HCl), 142 (49, M<sup>+</sup> - Cl<sub>2</sub>), and 141 (100, M<sup>+</sup> - HCl - Cl).

*Anal.* Calcd for C<sub>5</sub>H<sub>3</sub>N<sub>2</sub>OCl<sub>3</sub>: C, 28.13; H, 1.42; N, 13.12; Cl, 49.83. Found: C, 28.46; H, 1.26; N, 13.44; Cl, 49.60.

***N*-Phenyl-*N'*-phenylcarbamoylacetamide (**10**).**—A solution of aniline (1.3 g, 14 mmol) in 5 ml of CCl<sub>4</sub> was added to a solution of isocyanate **8** (0.94 g, 4.4 mmol) in 20 ml of CCl<sub>4</sub> in 5 min under ice cooling and the solution was stirred for 30 min. Then the reaction mixture was allowed to stand overnight at room temperature. The precipitates formed were filtered, washed with CCl<sub>4</sub>, and water successively, and dried *in vacuo*, giving a tan powder of **10** (0.79 g, 77%), which was recrystallized from CH<sub>3</sub>CN and MeOH successively, giving colorless needles: mp 186–189°; ir (Nujol) 1715, 1650, 1600, and 1565 cm<sup>-1</sup>; nmr (DMSO-*d*<sub>6</sub>) δ 2.07 (s, 3 H), 6.2–7.8 (m, 10 H), and ca. 9.5 (br, 1 H); mass spectrum (70 eV) *m/e* (rel intensity) 253 (8, M<sup>+</sup>), 134 (39), 119 (100), 93 (64), 91 (11), and 77 (36).

*Anal.* Calcd for C<sub>15</sub>H<sub>15</sub>N<sub>3</sub>O: C, 71.13; H, 5.99; N, 16.59. Found: C, 71.14; H, 5.80; N, 16.62.

**Preparation of Amidine **10** from *N*-Phenylacetamide and Phenyl Isocyanate.**<sup>12</sup>—A solution of phenyl isocyanate (0.6 g, 5.0 mmol) in 2 ml of ether was added to a solution of *N*-phenylacetamide<sup>18</sup> (0.7 g, 5.2 mmol) in 10 ml of ether in 5 min at room temperature; then the reaction mixture was stirred for 30 min. The precipitates formed were filtered, washed with ether, and dried *in vacuo* to give 1.2 g (94% based on phenyl isocyanate) of **10**, mp 189–190° (from MeOH).

**Registry No.**—**1a**, 1118-61-2; **1b**, 1823-99-0; **1c**, 25354-49-8; **1d**, 39603-75-3; **1e**, 39603-76-4; **1f**, 39603-77-5; **1g**, 39603-78-6; **1h**, 39603-79-7; **2a**, 39603-80-0; **2b**, 39603-81-1; **2c**, 39603-82-2; **2d**, 39603-83-3; **2g**, 39603-84-4; **2h**, 39603-85-5; **3a**, 39603-86-6; **3b**, 3336-69-4; **3c**, 22990-46-1; **5**, 39603-89-9; **6**, 39603-90-2; **8**, 39603-91-3; **10**, 32772-96-6; phosgene, 75-44-5; ethanol, 64-17-5.

(18) *N*-Phenylacetamide was prepared by the method of Oxley and Short: P. Oxley and W. F. Short, *J. Chem. Soc.*, 147 (1946).

(15) Melting points were determined on a Yanagimoto micromelting point apparatus and were corrected. Boiling points were uncorrected. Nmr spectra were obtained using a JNM-G-60 spectrometer (Japan Electronic Optics Laboratory Co.) with tetramethylsilane as an internal reference. Ir spectra were recorded on a Japan Electroscopic IR-E spectrophotometer or on a Hitachi 225 spectrophotometer equipped with gratings. Mass spectra were recorded on a Hitachi RMU-6E spectrometer. Uv spectra were recorded on a Shimadzu UV-200 spectrometer.

(16) H. Adkins and G. M. Whitman, *J. Amer. Chem. Soc.*, **64**, 150 (1942).

(17) J. Kuthan, V. Jehlička, and E. Hakr, *Collect. Czech. Chem. Commun.*, **32**, 4309 (1967).