Hydrolysis of 1-(1-Cyclohexen-1-yl)-3-(3,4-dichlorophenyl)-1-methylurea (3b).—**3b** (5 g) was placed in 20 ml of water and 20 ml of 10% hydrochloric acid added. The material was permitted to stand overnight with occasional stirring. The solid which formed was filtered off, washed with water, and recrystallized from benzene, mp 157–159°. The material proved to be 1-(3,4-dichlorophenyl)-3-methylurea as determined by ir and mixture melting point with an authentic sample.

Hydrolysis of 3′,4′-Dichloro-2-(*p*-chloroanilino)-1-cyclohexene-1-carboxanilide (4).—Approximately 2 g of **4** was heated on a steam bath with 20 ml of 18% hydrochloric acid for 2–3 hr, cooled, filtered, washed with water, and recrystallized from aqueous ethanol, followed by a second recrystallization from methylcyclohexane, mp 138–140°. The structure of 3′,4′-dichloro-2-oxocyclohexanecarboxanilide was assigned to this material from consideration of the following data: ir (CCl_4) 3.0 (NH), 5.9 (ketone C=O), and 6.0 μ (amide C=O).

Anal. Calcd for $C_{13}H_{13}Cl_2NO_2$: Cl, 24.8; N, 4.9. Found: Cl, 24.6; N, 4.9.

Hydrolysis of 1-(Cyclohexen-1-yl)-3-(3,4-dichlorophenyl)-1-methyl-2-thiourea (5b).—**5b** (*ca.* 2 g) was placed in 30 ml of 10% hydrochloric acid, and the mixture was allowed to stand overnight with occasional stirring. Upon filtering, the resulting solid was recrystallized from chloroform, mp 150–152°. The material proved to be 1-(3,4-dichlorophenyl)-3-methyl-2-thiourea as determined by ir and mixture melting point comparison with an authentic sample.

Hydrolysis of 3′,4′-Dichloro-2-(methylamino)thio-1-cyclohexene-1-carboxanilide (6a).—**6a** (*ca.* 1 g) was placed in 20 ml of 18% hydrochloric acid and heated gently on a steam bath for 10–15 min. The aqueous portion was decanted, and the residual tacky solid recrystallized from aqueous ethanol to give crystals, mp 112–114°. The structure of 3′,4′-dichloro-2-oxothiocyclohexanecarboxanilide was assigned this material from consideration of the following data: ir (CCl_4) 3.0 (NH), and 5.95 μ (C=O); nmr showed nine aliphatic hydrogens, one NH, and three aromatic hydrogens.

Anal. Calcd for $C_{13}H_{13}Cl_2NOS$: Cl, 23.60; N, 4.63; S, 10.6. Found: Cl, 23.97; N, 4.70; S, 10.6.

Hydrolysis of [2-(3,4-Dichlorocarbaniloyl)-2-methylpropylidene](2-methylpropenyl)amine (9a).—**9a** (*ca.* 5 g) was placed in 20 ml of 18% hydrochloric acid and heated on a steam bath for 15 min. The acid was decanted, and the residue heated further with water on the steam bath. The mixture was decanted again and the residual solid air dried, then recrystallized from methylcyclohexane, mp 102–104°. The structure of 3′,4′-dichloro-2,2-dimethylmalonaldehydanilide (**10**) was assigned to this material from consideration of the following data: ir (CCl_4) 3.0 (N–H), 5.85 (aldehyde C=O), and 5.96 μ (amide C=O); nmr spectra were consistent, showing six identical methyl protons, one aldehydic proton, one NH, and three aromatic protons.

Anal. Calcd for $C_{11}H_{11}Cl_2NO_2$: Cl, 27.4; N, 5.4. Found: Cl, 27.7; N, 5.5.

Hydrolysis of 2-(*p*-Chlorophenyl)-1-methyl-1-(2-methylpropenyl)urea (12a).—**12a** (*ca.* 1 g) was placed in 20 ml of 20% hydrochloric acid solution, and the mixture was refluxed for 15 min. The cooled solution was decanted and diluted with water. The resulting precipitate was separated and recrystallized from aqueous methanol to give 0.5 g of *p*-chlorophenyl-3-methylurea as identified by ir spectra and mixture melting point.

Registry No.—**2a**, 16241-20-6; **2b**, 16241-21-7; **3a**, 16240-17-8; **3b**, 16240-18-9; **3c**, 16240-19-0; **4**, 16286-17-2; **5a**, 16240-20-3; **5b**, 16240-21-4; **5c**, 16240-22-5; **6a**, 16240-23-6; **6b**, 16240-24-7; **6c**, 16240-25-8; **8**, 16240-26-9; **9a**, 16240-27-0; **9b**, 16240-28-1; **10**, 16240-29-2; **11a**, 16240-30-5; **11b**, 16240-31-6; **12a**, 2572-41-0; **12b**, 16240-33-8; **12c**, 16240-34-9; 3′,4′-dichloro-2-oxocyclohexanecarboxanilide, 16240-35-0; 3′,4′-dichloro-2-oxothiocyclohexanecarboxanilide, 16240-36-1; cyclohexanone, 108-94-1; isobutyraldehyde, 78-84-2.

The Reaction of 2-Phenyl-1-pyrroline with Phenyl Isocyanate

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The reaction of phenyl isocyanate with 2-phenyl-1-pyrroline at 25° leads to 2-phenyl-1-phenylcarbamoyl-2-pyrroline (**2**). At higher temperatures the 3-substituted 2-pyrroline **4** is formed, and loss of isocyanate from **4** gives the 1-pyrroline-3-carboxanilide **5**. The 1-carbamoylpyrroline **2** undergoes rapid thermal elimination of phenyl isocyanate at 40°.

Although 2 + 2 cycloaddition reactions of isocyanates and olefins or of ketenes and azomethines are well-established preparative methods for azetidinones,[2] the cycloaddition of isocyanates and azomethines to form uretidinones have been reported on only a few occasions,[3,4] and the structural evidence for these products was extremely limited by contemporary standards. With a view to the possibility of obtaining a 1,6-diazabicyclo[3.2.0]heptane derivative by this cycloaddition process, we have studied the reaction of phenyl isocyanate with 2-phenyl-1-pyrroline (**1**). In previous work, a "well-defined" product was reported from the reaction of 2,5-dimethyl-1-pyrroline with phenyl isocyanate,[5] but the composition and structure of the compound were not specified.

The reaction of equimolar amounts of 2-phenyl-1-pyrroline and phenyl isocyanate at room temperature in hydrocarbon solution gave an unstable 1:1 product in 75% yield. The 1-phenylcarbamoyl-Δ^2-pyrroline structure **2** was indicated by the shift in the ultraviolet maximum from 243 mμ in **1** to 255 mμ **2**, a triplet nmr peak due to H-3 at δ 5.31, and acid hydrolysis to the ureido ketone **3**. Hydrolysis of **2** resulted in a significant amount of the original pyrroline as well.

At 110°, equimolar condensation led to a different 1:1 product and a compound containing one pyrroline and two isocyanate units, together with unreacted pyrroline and a trace of the hydrolysis product, **3**. The 1:1 and 1:2 products were obtained in a combined yield of about 40% (based on phenyl isocyanate), with the latter predominating in a ratio of about 3:1.

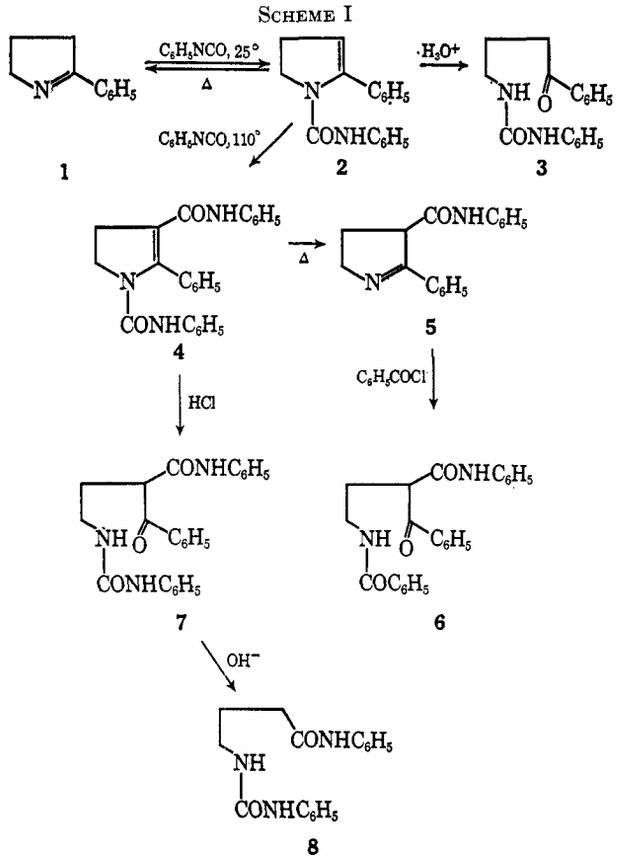
The minor (1:1) product was a base with ultraviolet absorption very similar to that of the pyrroline **1**; the pK_a' was 1.8 units lower than that of **2**. Schotten–Baumann benzoylation of the compound gave a product whose properties were consistent with the benzamido ketone **6**. These data suggest the Δ^1-pyrroline-3-carboxanilide structure **5** for the condensation product. Dickinson and Lang quite recently reported the

(1) National Science Foundation Predoctoral Fellow, 1965–1967.
(2) H. Ulrich, "Cycloaddition Reactions of Heterocumulenes," Academic Press Inc., New York, N. Y., 1967.
(3) A. Seiner and F. G. Shepheard, *J. Chem. Soc.*, 494 (1909).
(4) W. J. Hale and N. A. Lange, *J. Amer. Chem. Soc.*, **41**, 379 (1919).
(5) G. G. Evans, *ibid.*, **73**, 5230 (1951).

formation of another 2-substituted Δ^1-pyrroline-3-carboxamide and commented on the point that the nonconjugated tautomer is the stable form.[6]

The 1:2 adduct, formed in larger amount at 110°, was a neutral compound with λ_{max} 316 mμ, indicative of a conjugated system. It was shown to be the 1-carbamoyl-2-pyrroline-3-carboxanilide **4** by acid hydrolysis to the ureido ketoanilide **7** and cleavage of the β-keto anilide system in **7** with base to benzoic acid and the anilide **8** (Scheme I). An authentic sample of **8** was prepared for comparison from γ-aminobutyric acid.

SCHEME I



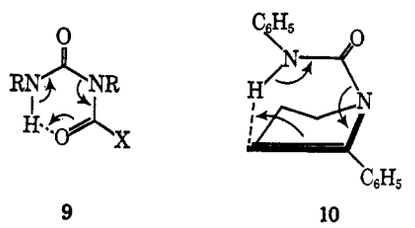
At 170°, the Δ^1-3-carboxanilide (**5**) was the only product isolated from the reaction of **1** and isocyanate. The product distribution at various temperatures indicates that the initial attack of phenyl isocyanate on **1** occurs at N-1, and that the 3-substituted products **4** and **5** arise sequentially at higher temperatures. The conversion of **4** to **5** occurred in low yield on heating the former at 180° under reduced pressure; a more practical procedure is the treatment of **4** with aniline, which led cleanly to an easily separable mixture of **5** and diphenylurea.

Conversion of the primary 2-pyrroline **2** or the 3-carboxanilide **5** to the disubstituted product **4** with excess phenyl isocyanate could be demonstrated, but these reactions did not provide an improved preparation of **4** because the presence of excess isocyanate seriously complicated the product isolation. In the reaction of **5** with isocyanate, it appeared from thin layer chromatography that the amount of the disubstitution product increased on cooling the reaction solution from 80° to room temperature.

(6) W. B. Dickinson and P. C. Lang, *Tetrahedron Lett.*, 3035 (1967).

Perhaps the most significant point among these transformations is the exceptional facility with which the 1-carbamoylpyrroline **2** undergoes loss of phenyl isocyanate. This reaction was followed by measurement of the characteristic isocyanate band in the infrared at 2250 cm^{-1}. The dissociation of a 0.017 *M* solution of **2** in chloroform at 40° is shown in Figure 1; under these conditions about 20% of the compound dissociated in 3 hr. On longer standing the isocyanate concentration eventually dropped, presumably owing to further reaction with **1** and/or oligomerization. The acceleration in rate of isocyanate release evidently reflects catalysis of the reaction by the product pyrroline.

The pyrroline **2** is a vinylurea, a system which seems not to have been described heretofore.[7] The thermal decomposition of ureas normally requires temperatures above 200°, although biurets and allophanates dissociate smoothly at 130°,[8] presumably to a cyclic elimination (**9**) similar to the decarboxylation of a β-keto acid. The dissociation of **2** can also be envisioned as a cyclic process (**10**), recalling the facile decarboxylation of β,γ-unsaturated acids.[9,10] The only isocyanate elimination comparable with that of **2** of which we are aware is the dissociation of 1-phenylcarbamoylimidazole and -benzimidazole reported by Staab and others.[11,12]



9 **10**

The second stage in the reactions of **1** with phenyl isocyanate at higher temperatures is evidently electrophilic attack on the vinylurea system of **2** by another mole of isocyanate, and subsequent loss of the 1-carbamoyl group by elimination as in the case of **2**. The dissociation of **4** was not studied in detail. The compound does not decompose at a detectable rate at moderate temperatures, but, from the appearance of **5** at 110°, dissociation must become appreciable at 80–100°. The greater stability of **4**, compared with **2**, is consistent with the conjugated enamide system.

Since the present work was completed, the reaction of phenyl isocyanate with cyclic azomethine systems has been reported by Huisgen and coworkers in connection with the general phenomenon of "1,4-dipolar cycloaddition."[13] With dihydroisoquinoline, a dipolar intermediate is obtained which combines with a second mole of the azomethine to given an oxotriazine; combination of the dipolar intermediate with a second mole of isocyanate was not observed, nor were uretidinones reported. In another recent related study, attack of phenyl isocyanate on 2-methyl-2-oxazoline has been

(7) Compounds of this type have also been obtained by J. P. Chupp and E. R. Weiss, *J. Org. Chem.*, **33**, 2357 (1968).

(8) I. C. Kogon, *ibid.*, **23**, 1594 (1958).

(9) R. T. Arnold, O. C. Elmer, and R. M. Dodson, *J. Amer. Chem. Soc.*, **72**, 4359 (1950).

(10) R. B. Woodward and E. C. Kornfeld, *ibid.*, **70**, 2508 (1948).

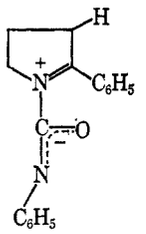
(11) H. A. Staab and W. Benz, *Angew. Chem.*, **73**, 66 (1961); H. A. Staab and G. Seel, *Ann. Chim.*, **612**, 187 (1958).

(12) J. Derkosch, K. Schlogl, and H. Woidich, *Monatsh. Chem.*, **88**, 35 (1957).

(13) R. Huisgen, K. Herbig, and M. Morikawa, *Chem. Ber.*, **100**, 1107 (1967).

reported to occur at the exocyclic methyl group rather than at the annular nitrogen,[14] a result which presents an interesting contrast to the behavior of the pyrroline 1. 2-Phenyl-2-oxazoline was unreactive. In the present work, an attempt was made to bring about reaction of 2-phenyl-1-*p*-toluenesulfonyl-2-imidazoline with phenyl isocyanate; again, no reaction occurred.

The dipolar adduct 11, corresponding to that proposed in 1,4-dipolar cycloadditions,[13] is assumed to be the intermediate in the formation of the carbamoylpyrroline 2. Unlike the previous cases studied, further addition of a second pyrroline molecule can be interdicted by deprotonation. The steric effect of the phenyl group may also be an interfering factor in the 1,4-dipolar addition reaction of 1 and the 2-phenylimidazoline or -oxazoline.



11

Experimental Section[15]

2-Phenyl-1-pyrroline (1) was prepared by the procedure of Starr:[16] bp 95–97° (0.5 mm); mp ~30°; nmr, δ^{CCl_4} 1.85 (apparent quintet of triplets, 2, J = ~7.5 and ~2 Hz; H_4), 2.77 (triplet of quintets, 2, J = 8 and ~2 Hz; H_3), 3.92 (triplet of triplets, 2, J = 7 and 2 Hz; H_5), 7.24 (m, 3 H; H_{meta} and H_{para}), 7.73 ppm (m, 2 H; H_{ortho}).[17]

2-Phenyl-1-phenylcarbamoyl-2-pyrroline (2).—A solution of 1.14 g (7.9 mmol) of 2-phenyl-1-pyrroline and 0.94 g (7.9 mmol) of phenyl isocyanate in 10 ml of *n*-decane was allowed to stand at 25°. A white solid began to separate after 1 hr; after 24 hr, the mixture was diluted with hexane and the solid was collected; 1.55 g (75%) of white crystals, mp 98–102° and 102–108°, was obtained in two crops. After recrystallization from methanol, the melting point was 116–117°, but analytical data were unsatisfactory. In a subsequent preparation, polar solvents were avoided; several recrystallizations from methylene chloride–hexane gave 2 as white needle clusters: mp 116–118°; λ_{max}^{MeOH} 255 mμ (ε 23,000); ν_{Nujol} 3300 (w), 1650 (s), 1625 (w), 1600 (s), 1540 (s), cm^{-1}; δ^{CDCl_3} 2.3–3.1 (m, 2; H_4), 4.22 (t, 2, J = 9 Hz; H_5), 5.31 (t, 1, J = 3 Hz; H_3), 6.20 (s, br; NH), 7.0–7.4 ppm (m, 9–10; aryl).

Anal. Calcd for $C_{17}H_{16}N_2O$: C, 77.25; H, 6.10; N, 10.60. Found: C, 76.87; H, 5.99; N, 10.51.

Hydrolysis of 2 was carried out by warming a solution of 100 mg of 2 in 1.5 ml of dioxane and 1.5 ml of 6 *N* HCl for 1 hr. After addition of water and chilling, a pale tan solid, 25 mg, mp 136–138°, separated. The infrared spectrum corresponded in all peaks with that of a specimen of the urea 3 characterized as described below. The acidic filtrate was basified, and the ether-soluble base was converted into the picrate of 2-phenyl-1-pyrroline, 69 mg, mp 202° dec.

Dissociation of 2-Phenyl-1-phenylcarbamoyl-2-pyrroline (2).—The infrared measurements were recorded on a Perkin-Elmer Model 337 spectrophotometer using a 2.5-mm cavity cell. The integrated absorption intensity of the isocyanate band was obtained by cutting out and weighing the peak. A calibration curve with known concentrations of phenyl isocyanate (0.5–5.0 × 10^{-3} *M*) was used to obtain concentrations; this curve was not linear (negative slope).

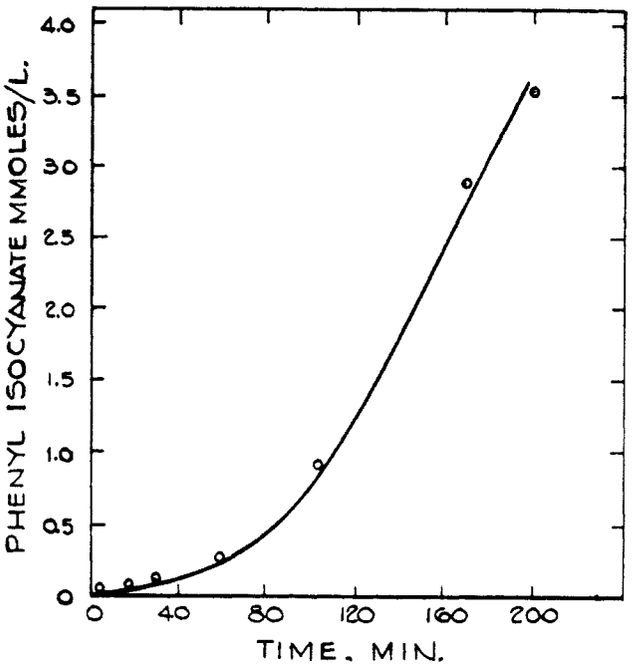


Figure 1.—Loss of phenyl isocyanate from 2 at 40° in0. 017 *M* $CHCl_3$ solution.

Reaction of 2-Phenyl-1-pyrroline and Phenyl Isocyanate at 110°.—A solution of 5.02 g (0.035 mol) of freshly distilled 2-phenylpyrroline and 4.13 g (0.035 mol) of phenyl isocyanate in 75 ml of toluene was refluxed for 21 hr. An orange color developed but faded on cooling. Distillation of the toluene gave a semisolid residue which was dissolved in warm CCl_4. Addition of hexane gave a pale brown gum (A).

Evaporation of the hexane solution gave an oil which contained phenyl isocyanate (odor) and a basic substance. A methylene chloride solution of the oil was extracted with 5 *N* HCl; basification of the aqueous phase gave a yellow oil which was treated with picric acid to give 4.0 g (0.011 mol, 31%) of 2-phenylpyrroline picrate, mp 200° dec (lit.[16] 198° dec).

The residue from the methylene chloride phase was partially crystalline; after trituration with warm ethyl acetate, the solid was collected to give 0.3 g, mp 138–140°. Recrystallization from isopropyl alcohol–hexane gave colorless crystals of **1-phenyl-3-[1-(3-benzoyl)propyl]urea** (3): mp 141–142°; ν_{Nujol} 3380, 1690, 1650 cm^{-1}; δ (pyr-d_5) 1.35 (q, 2, J = 6 Hz), 2.33 (t, 2, J = 6 Hz), 2.83 ppm (q, 2, J = 6 Hz).

Anal. Calcd for $C_{17}H_{18}N_2O_2$: C, 72.32; H, 6.43; 0, 11.33. Found: C, 72.71; H, 6.50; O, 11.31.

The gum (A) precipitated with hexane was crystallized by digesting with ether; a total of 3.6 g of crystalline solid was obtained. The melting point was very broad and thin layer chromatography showed a mixture of two compounds, with the less polar (faster moving) one in larger amount. The ratio of the two products was about 3:1 based on thin layer chromatography and the amounts finally isolated. The actual yields cannot be stated because of large losses on recrystallization.

Crystallization from methanol–water and then 2-propanol–water gave the major component, mp 168–170°. Further recrystallization from benzene–hexane furnished a pure sample of **2-phenyl-1-phenylcarbamoyl-2-pyrroline-3-carboxanilide** (4): mp 170–171°; $\lambda_{max}^{CH_2Cl_2}$ 316 mμ (ε 18,000); ν_{Nujol} 3400, 1680, 1650 cm^{-1}; δ^{CDCl_3} 3.00 (t, 2, J = 9 Hz; H_4), 4.11 (t, 2, J = 9 Hz; H_5), 6.19 (s, NH), 6.72 (s, NH), 7.1–7.6 ppm (m, aryl).

Anal. Calcd for $C_{24}H_{21}N_3O_2$: C, 75.17; H, 5.52; O, 8.35. Found: C, 74.89; H, 5.74; O, 8.32.

The aqueous methanol mother liquors from the initial crystallization of 4 were concentrated to give crystals, mp 180–183°, corresponding to the slower moving component on thin layer chromatography. Further crystallization from aqueous ethanol gave 2-phenyl-1-pyrroline-3-carboxanilide (5): mp 183–184°;

(14) R. Nehring and W. Seeliger, *Ann. Chim.*, **698**, 167 (1966).

(15) Melting points were determined with a Fisher-Johns block. Infrared spectra were obtained, except where otherwise stated, with a Perkin-Elmer Model 137 spectrophotometer. Nmr spectra were obtained with a Varian A-60A instrument.

(16) D. F. Starr, H. Bulbrook, and R. M. Hixon, *J. Amer. Chem. Soc.*, **54**, 3971 (1932).

(17) In nmr descriptions, s = singlet, d = doublet, t = triplet, q = quintet, m = multiplet; the numeral following the multiplicity is the whole number of protons by integration.

λ_{max}^{MeOH} 243 mμ (ε 28,000); ν_{Nujol} 3300, 1655; pK_a' (50% MeOH) 4.1[18] [pK_a' (50% MeOH) of 2-phenyl-1-pyrroline was 5.9].

Anal. Calcd for $C_{17}H_{16}N_2O$: C, 77.25; H, 6.10; N, 10.60. Found: C, 76.82; H, 5.82; N, 10.49.

2-Benzoyl-4(N'-phenylureido)butananilide (7).—A suspension of 200 mg of **4** in 6 ml of 6 *N* HCl was warmed on the steam bath. After a few minutes the solid **4** became gummy and, on further heating and stirring, the gum crystallized. The solid was collected, washed with water, and air-dried to give 187 mg, mp 195–198°. Recrystallization from pyridine–water gave colorless crystals of **7**: mp 201–202°; ν_{Nujol} 3400, 1695, 1680, 1650 cm^{-1}.

Anal. Calcd for $C_{24}H_{23}N_3O_3$: C, 71.80; H, 5.78; N, 10.47. Found: C, 72.37; H, 5.97; N, 10.68.

4-(N'-Phenylureido)butananilide (8).—A mixture of 181 mg of the 2-benzoylanilide **7**, 5 ml of 15% NaOH, and 4 ml of ethanol was stirred at 80° for 6 hr. The solid changed in appearance during this treatment from a fine powder to larger crystals. After addition of water the solid was collected, washed with water, and air-dried to give 85 mg (63%), mp 238°. Recrystallization from pyridine–water gave colorless crystals of **8**: mp 240–241°; ν_{Nujol} 3400, 1650 cm^{-1}.

Anal. Calcd for $C_{17}H_{19}N_3O_2$: C, 68.66; H, 6.44; N, 14.13. Found: C, 68.77; H, 6.74; N, 14.10.

The alkaline filtrate from above was partially neutralized (pH 10) and evaporated to dryness. The solid residue of sodium benzoate and inorganic salt was treated with thionyl chloride, evaporated, and treated with excess aniline. After acidification the solid product was collected; the melting point was 150–160°. Recrystallization from ethanol gave a sample of benzanilide whose ir spectrum corresponded to that of an authentic sample.

Synthesis of 8 from 4-Aminobutanoic Acid.—4-(N'-Phenylureido)butanoic acid was prepared by dropwise addition of 4.7 ml (0.043 mol) of phenyl isocyanate, with vigorous stirring over a 30-min period, to a solution of 4.10 g (0.04 mol) of 4-aminobutanoic acid in 20 ml of 2 *N* NaOH. After stirring for an additional 12 hr, a small amount of insoluble solid was removed and the solution was acidified; the ureido acid was collected, washed with water, and dried to give 8.0 g of colorless crystals, mp 127–128° (lit.[19] mp 126°).

To a solution of 2.2 g of this acid in 20 ml of 1,2-dimethoxyethane (glyme) was added 0.95 ml of oxalyl chloride. After a transient yellow color had faded and a small amount of solid separated, the mixture was stirred for 1 hr and evaporated *in vacuo* to a white solid residue (minimal conditions were used to suppress cyclization of the acid chloride). A solution of 0.9 ml of aniline in 15 ml of glyme was then added, and after stirring for 30 min, the mixture was diluted with water. The resulting voluminous solid precipitate was collected. Much of this solid was soluble in aqueous alkali and was presumably unreacted ureido acid. The alkali-insoluble material was collected, washed, and air-dried to give 250 mg of solid of indefinite melting point. This solid was warmed in pyridine, some insoluble material was removed, and the pyridine was evaporated to give colorless crystals of **8**, mp 238°; the infrared spectrum corresponded, in position and relative intensities of 17 peaks, with that of a sample obtained by hydrolysis of **7**.

(18) We thank Dr. J. M. Vandenbelt and Mrs. C. Spurlock, Parke, Davis and Co., for the pK_a' measurements.

(19) German Patent 929,191 (June 20, 1955); *Chem. Abstr.*, **52**, 5457*f* (1958).

2-Benzoyl-4-benzamidobutananilide (6).—A mixture of 150 mg of the 1-pyrroline-3-carboxanlide (**5**), 0.24 g of benzoyl chloride, and 1 ml of 10% aqueous NaOH was shaken vigorously in a stoppered tube until the solid had become gummy and then resolidified. The aqueous solution was decanted, and the residue dissolved in ethanol. The solution was treated with charcoal, filtered, and diluted with water, and the resulting poorly formed crystals were collected to give 73 mg of off-white solid, mp 187–193°; thin layer chromatography showed the presence of a small amount of unreacted **5**. Recrystallization from ethanol and then chloroform–hexane gave colorless prisms of **6**: mp 198–199°; ν_{Nujol} 3300, 1690, 1660, 1645 cm^{-1}; δ (pyr) 2.73 (m, 2), 3.90 (m, 2), 5.00 ppm (t, 1, J = 7 Hz; H_2).

Anal. Calcd for $C_{24}H_{22}N_2O_3$: C, 74.59; H, 5.74; N, 7.25. Found: C, 74.78; H, 5.96; N, 6.97.

Reaction of 2-Phenyl-1-pyrroline and Phenyl Isocyanate at 170°.—A solution of 3.68 g (25 mmol) of pyrroline and 2.74 ml (25 mmol) of isocyanate in 25 ml of decane was refluxed with stirring for 2 hr. A dark oil which separated during the heating period solidified on cooling. Tlc showed four components, with **5** as the major spot. The solid was slowly crystallized from methanol at 0°, giving 1.9 g of pale yellow crystals which was largely **5** (thin layer chromatography). Recrystallization from tetrahydrofuran gave 1.3 g of **5**, mp 184–185°.

2-Phenyl-1-pyrroline-3-carboxanilide (5) from 4.—A solution of 765 mg of **4** in 7 ml of xylene containing 180 mg of aniline was refluxed for several hours, during which time a white precipitate of diphenylurea separated. The hot mixture was filtered, and 340 mg (80%) of urea was collected; on cooling, the filtrate deposited 436 mg (83%) of crystals of **5**, mp 173–175°; the infrared spectrum was identical with that of the sample of **5** described above.

2-Phenyl-1-*p*-toluenesulfonyl-2-imidazoline.—To a solution of 5.0 g of 2-phenylimidazoline[20] in 20 ml of pyridine containing 3.46 g of triethylamine was added during 30 min a solution of 6.5 g of *p*-toluenesulfonyl chloride in 30 ml of methylene chloride. After several hours, ether was added and the precipitated triethylamine hydrochloride was collected. The filtrate was washed thoroughly with water, dried, and evaporated to an oil which crystallized at 0°. Recrystallization of the crude solid (9.9 g, mp 74–78°) from methanol–water and then carbon tetrachloride–hexane gave white needles, mp 86–87°.

Anal. Calcd for $C_{16}H_{16}N_2O_2S$: C, 63.99; H, 5.37; N, 9.33. Found: C, 63.80; H, 5.19; N, 9.04.

A solution of 1.5 g (5 mmol) of the tosylimidazoline and 0.6 g (5 mmol) of phenyl isocyanate in 5 ml of benzene was stored at 25° overnight. Thin layer chromatography showed no indication of reaction. After 12-hr reflux there was still no evidence of reaction; after adding aniline at this point, diphenylurea and unchanged imidazoline were recovered in 90% yields.

Registry No.—**1**, 700-91-4; **2**, 16054-51-6; **3**, 16054-56-1; **4**, 16054-52-7; **5**, 16109-69-6; **6**, 16054-57-2; **7**, 16054-53-8; **8**, 16054-54-9; 2-phenyl-1-*p*-toluenesulfonyl-2-imidazoline, 16054-55-0; phenyl isocyanate, 103-71-9.

(20) R. Forsyth, V. K. Nimkar, and F. L. Pyman, *J. Chem. Soc.*, 800 (1926).