and product were deduced from the optical densities at three or four wavelengths, and an average of these values was calculated and used in the following expression (*a* and *b* are the initial concentrations of the starting ketone and amine, respectively; *x* is the concentration of the product). The kinetic constants were determined by the least-squares method.

$$1/(b - a) \ln [a(b - x)/b(a - x)]$$

Registry No.—**2a**, 15982-76-0; **2b**, 5387-51-9; **2c**, 16096-94-9; **3b**, 16031-03-1; **3c**, 15982-88-4; **3e**, 16096-36-9; **4a**, 5386-20-9; **4b**, 16003-61-5; **4c**, 16096-39-2.

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Reactions of 1,3-Diphenyl-4-(phenylimino)-2-uretidinone

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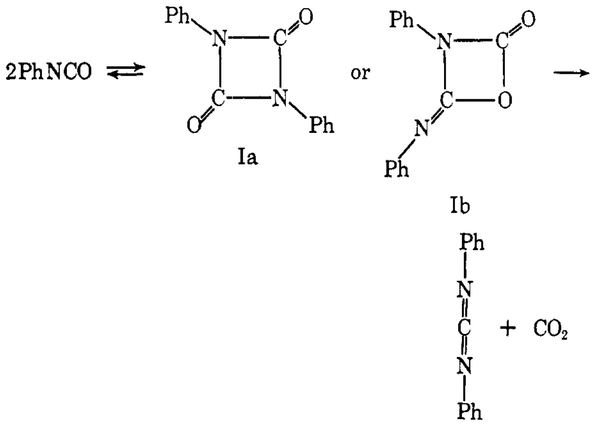
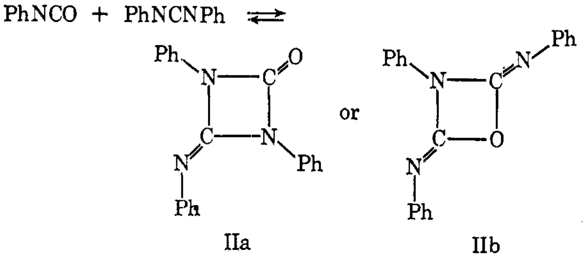
1,3-Diphenyl-4-(phenylimino)-2-uretidinone (IIa) reacts with nucleophiles to give triphenylguanidinecarboxylic acid derivatives. The isolation of the guanidine derivatives confirms the iminouretidinone structure for the isocyanate–carbodiimide adducts. At 80–100°, IIa dissociates reversibly to phenyl isocyanate and diphenylcarbodiimide, with an equilibrium constant of 1.2 at 80° and 4.2 at 100°. The rate constants and activation parameters for the dissociation are described.

Although cycloaddition reactions of isocyanates, particularly dimerization, have been known for some time, they are incompletely understood and still the object of lively interest.[1] The kinetics of the catalyzed dimerization and dedimerization of phenyl isocyanate have been described recently and the equilibrium nature of the reaction well documented.[2] An uncatalyzed dimerization is also possible, and appears more prevalent with difunctional isocyanates.[3] The structure of the phenyl isocyanate dimer by X-ray diffraction,[4] and the assumed one for all the rest is the symmetrical uretidinedione, Ia, although Ib derives chemical support from the conversion of dimer into carbodiimide with loss of carbon dioxide at 180–200°[5] (eq 1).



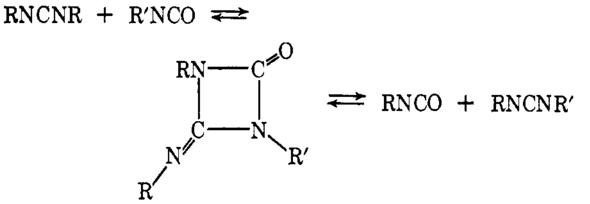
(1)

A similar uncatalyzed cycloaddition occurs between isocyanate and carbodiimide to give an adduct which by analogy is accorded the iminouretidinone[5] structure, IIa (eq 2).



(2)

The ready reversibility of this reaction (eq 3) has prompted its use in the synthesis of mixed carbodiimides.[5] Although either structure (IIa or IIb)



(3)

would accommodate the facile interchange reaction, IIa is preferred on the basis of its infrared spectrum, as discussed below.

It was the object of this research to investigate the kinetics of formation and dissociation of II and its chemical reactions. From the results of nucleophilic attack on II, chemical support for structure IIa was obtained.

Results

When equimolar quantities of diphenylcarbodiimide and phenyl isocyanate are heated, with or without cuprous chloride as catalyst,[5] there is obtained II, a white solid, in *ca.* 30% yield. The infrared spectrum of recrystallized II exhibits a carbonyl band at 5.78 μ (1730 cm^{-1}) with a weaker band at 5.88 μ (1700 cm^{-1}). For a four-membered-ring amide carbonyl, the value of 5.73 μ (1745 cm^{-1}) is reported,[6] and the cyclobutaneimine C=N is recorded[7] as 5.76–5.80 μ (1720–1740 cm^{-1}). If one assigns the weaker absorption at 5.88 μ to the C=N group and the 5.78-μ band to the C=O function, then the infrared spectrum is in accord with IIa, and does not support the symmetrical structure IIb.

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(1) H. Ulrich, "Cycloaddition Reactions of Heterocumulenes," Academic Press Inc., New York, N. Y., 1967.

(2) R. E. Buckles and L. A. McGrew, *J. Amer. Chem. Soc.*, **88**, 3582 (1966).

(3) J. H. Saunders and R. J. Slocombe, *Chem. Rev.*, **43**, 203 (1948).

(4) C. J. Brown, *J. Chem. Soc.*, 2931 (1955).

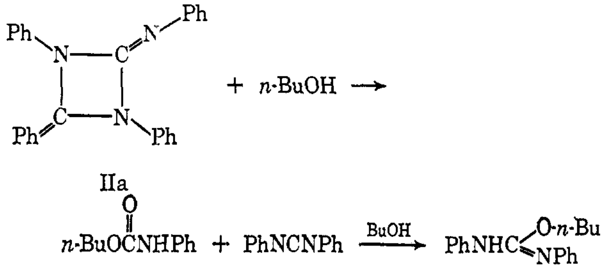
(5) W. Neumann and P. Fischer, *Angew. Chem. Intern Ed. Engl.*, **1**, 621 (1962).

(6) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962, p 47.

(7) L. A. Singer and P. D. Bartlett, *Tetrahedron Lett.* 1887 (1964).

When II was heated in solvent to 80–120°, the infrared spectrum showed the appearance of isocyanate and carbodiimide bands indicating dissociation of II to its components. When a solution of II in chloroform was examined by vapor phase chromatography, only peaks for phenyl isocyanate and diphenylcarbodiimide could be detected in the area ratio of 0.58:1. Since II contains phenyl isocyanate and diphenylcarbodiimide in the weight ratio of 0.61:1, the vpc results suggest the quantitative dissociation of II to its constituents on heating.

The reaction of IIa with nucleophiles such as *n*-butyl alcohol does not occur readily except at elevated temperatures. When a solution of IIa in tetrachloroethane is heated with *n*-butyl alcohol at 90–110°, the IIa is consumed with the formation of *n*-butyl N-phenylcarbamate and diphenylcarbodiimide (eq 4).


IIa

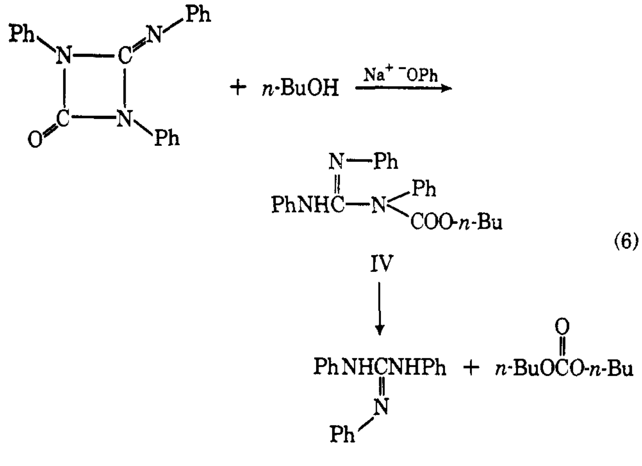
III

(4)

With further heating, some of the carbodiimide is converted into the pseudourea III. Complete reaction of IIa is achieved in about 4–5 hr. The usual urethan catalysts were without effect on this reaction, except in that carbodiimide consumption was variously influenced. When cuprous chloride (a reported catalyst for formation of iminouretidinones[5] and for reaction of nucleophiles with carbodiimides)[8] was employed, the over-all reaction time was inappreciably affected, but the level of carbodiimide detectable was greatly reduced. Since the reaction with *n*-butyl alcohol occurs at about the same rate as the dissociation in the absence of nucleophiles, it seems reasonable to suggest that IIa is reacting by prior dissociation to its components, followed by reaction of these with *n*-butyl alcohol (eq 5). Since the carbodiimide is much slower reacting unless properly catalyzed, its concentration builds up to detectable levels. The highly reactive isocyanate, on the other hand, is consumed too rapidly to be discernible.

$$\text{IIa} \rightleftharpoons \text{PhNCO} + \text{PhNCNPh} \xrightarrow{n\text{-BuOH}} \text{products} \qquad (5)$$

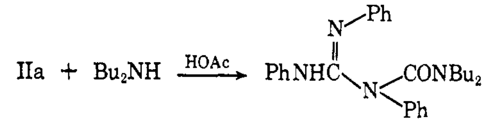
Quite a different reaction (eq 6) occurs when the reaction of IIa with *n*-butyl alcohol is catalyzed by bases such as sodium phenoxide, sodium methoxide, or sodium *n*-butoxide. Here, the reaction is exothermic and is complete in 15–60 min at room temperature. The initial product, in greater than 80% yield is the carbobutoxytriphenylguanidine IV. If the reaction mixture is heated, or allowed to stand for too long, especially with the stronger bases methoxide and butoxide, some triphenylguanidine is produced. The identity of IV


IV

(6)

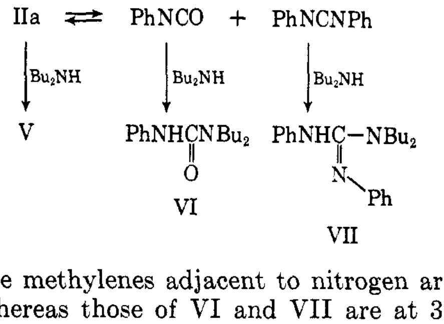
was determined from its infrared spectrum [N—H at 2.90 μ (3450 cm^{-1}), C=O at 5.80 μ (1725 cm^{-1}), C=N at 6.02 μ (1660 cm^{-1})], its nmr spectrum which showed aromatic, N—H, CH$_2$—O, and —CH$_2$CH$_2$CH$_3$ groups in the proper ratio, molecular weight, and analysis. In addition, IV could be hydrolyzed with aqueous caustic to triphenylguanidine. In keeping with its guanidine structure, IV is slightly less basic than triphenylguanidine, and is about equivalent to dibutylamine. Methanol and phenol could be used as nucleophiles in phace of *n*-butyl alcohol.

The addition of amines, such as di-*n*-butylamine, could not be accomplished cleanly with the same catalysts, or without catalyst. At 60°, di-*n*-butylamine could be added to IIa with formation of the carboxamide derivative in the presence of acetic acid (eq 7). The carboxamide V, a viscous oil, was purified as the hydrochloride salt, mp 156–157°, and characterized by nmr and elemental analysis.


V

(7)

It was found subsequently that di-*n*-butylamine, although unreactive at 60°, could be added to IIa in the absence of catalyst at higher temperatures (eq 8). Thus, in refluxing toluene, the reaction of IIa with di-*n*-butylamine affords a mixture of products which includes V. The components of the mixture besides V were identified by thin layer chromatography as the urea VI and the guanidine VII. In the nmr spectrum


VII

(8)

of V, the methylenes adjacent to nitrogen are at 2.80 ppm, whereas those of VI and VII are at 3.28 ppm. The mixture was analyzed for its components thereby and shown to be composed of 4.6 parts of VI and VII to 1 part of V. Since VI and VII are produced in equal amounts from the dissociation process, the ratio of

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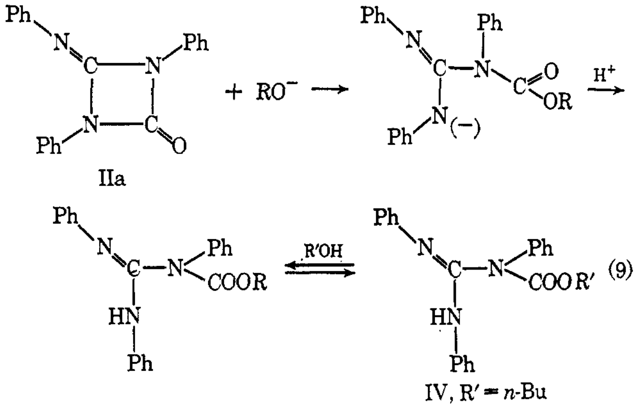
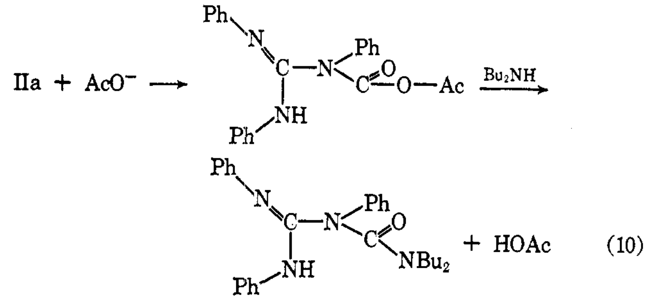
(8) Farbenfabriken Bayer, A. G., British Patent 795,720 (1958).

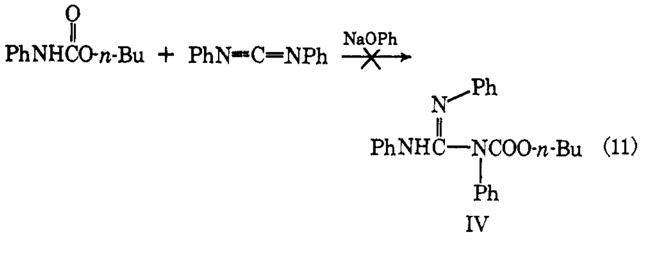
dissociation to direct ring attack was 2.3:1 under these conditions.

A possible explanation for the types of catalysts effective in opening the ring of IIa may lie in the nucleophilicity of the attacking reagent. With alcohols this attacking species is probably an alkoxide or phenoxide ion, with the resultant product determined by ester interchange with the solvent alcohol, present in large excess (eq 9). For the amine–acetic acid reaction, acetate ion may be the nucleophile, with the product determined by attack of the amine on the mixed anhydride (eq 10). In agreement with this scheme, ring opening by *n*-butyl alcohol to IV could be achieved with acetic acid–sodium acetate catalysis, whereas acetic acid alone was ineffective.





It must be emphasized that the formation of the carboxyguanidine derivatives from II presents excellent chemical evidence for IIa as the proper structure. Of the possible structures for a dipolar addition product between an isocyanate and a carbodiimide only IIa can satisfy the infrared spectrum, the ready interchange of isocyanate–carbodiimide, and the ring opening to guanidine derivatives. Structure IIa is the only one with three nitrogens attached to carbon. It should be pointed out here that the guanidine derivatives observed could not be prepared from any combination of products derivable from IIa by thermal dissociation and subsequent reactions. For example, *n*-butyl N-phenylcarbamate and diphenylcarbodiimide gave no detectable IV when heated with sodium phenoxide (eq 11).



$$\mathrm{PhNHC(=O)O\text{-}}n\text{-}\mathrm{Bu} + \mathrm{PhN{=}C{=}NPh} \xrightarrow{\mathrm{NaOPh}} \mathrm{PhNHC(=NPh)N(Ph)COO\text{-}}n\text{-}\mathrm{Bu} \quad (11)$$

IV

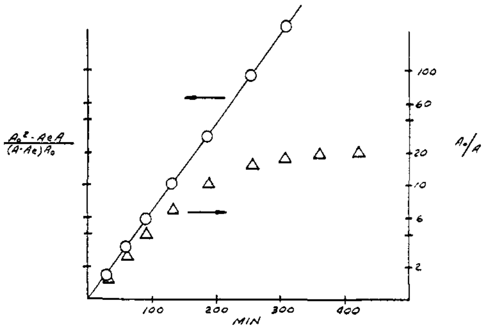


Figure 1.—Dissociation of 0.32 *M* II at 100°.

Kinetics.—Determination of the rate of dissociation of IIa was attempted, utilizing the absorbance values of the infrared band at 5.78 μ as a measure of the concentration of IIa. When IIa was heated in solvent at 80–100°, it was found that the 5.78-μ band did decrease considerably and eventually reached a constant value. A plot of the log of the absorbance values for this peak with time showed a marked curvature beyond 30–40% reaction (Figure 1), indicating, as expected, that the dissociation is not a simple first-order process. If an equilibrium process is assumed, in which a first-order forward reaction is opposed by a second-order reverse reaction, then a rate equation can be derived[9] (eq 12)

$$\ln\left[\frac{A_0^2 - A_eA}{(A - A_e)A_0}\right] = k\left(\frac{A_0 + A_e}{A_0 - A_e}\right)t \qquad (12)$$

where the A's relate to the concentration of IIa. In this case, the absorbance data was used directly and A_0 is the initial absorbance of the 5.78-μ band, A_e is the equilibrium value, and A is the value at time t. When the left-hand side of eq 12 was plotted against time, a reasonably good straight line was obtained (Figure 1) of slope k_d, the rate constant for dissociation. The equilibrium constant K can be calculated from eq 13

$$K = \frac{[\mathrm{NCN}][\mathrm{NCO}]}{[\mathrm{IIa}]} = \left[\left(\frac{A_0 - A_e}{A_0}\mathrm{Co}\right)\right]^2 \bigg/ \frac{A_e}{A_0}\mathrm{Co} \qquad (13)$$

where [NCN] = [NCO] = $A_0 - A_e$, [IIa] = A_e. The values for k_d, K, and % dissociation for IIa at 80 and 100° and at two concentrations are shown in Table I.

TABLE I

KINETIC AND EQUILIBRIUM DATA FOR DISSOCIATION OF II

Concn, mol/l.	$k_d \times 10^{-5}$ sec^{-1}	K_{equil}	% dissociation	Temperature, °C
0.64	2.67 ± 0.07	1.2 ± 0.1	72	80 ± 0.3
0.32	2.85 ± 0.12	1.2	83	80 ± 0.3
0.32	23.0 ± 0.3	4.4	94	100 ± 0.3
0.32	23.3 ± 0.3	4.0	93[a]	100 ± 0.3
0.64[b]		0.9		80 ± 0.3

[a] Cuprous chloride (1%) added. [b] Reverse reaction, 0.64 *M* in phenyl isocyanate and diphenylcarbodiimide.

The equilibrium data are in accord with the assumed reaction process. A decrease in concentration of IIa results in a greater degree of dissociation, since the reverse reaction is a second-order one whose rate is more concentration dependent. Higher temperatures favor dissociation also (83% at 80°, 94% at 100°). Roughly the same equilibrium constant was obtained when

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[9] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1961, p 187.

equilibrium was approached from the opposite direction, although the accuracy of the analytical determinations was somewhat reduced.

The activation parameters calculated from the rate and equilibrium data are shown in Table II. These data can be accommodated to the equilibrium in question. Higher temperatures will favor the higher activation energy process, namely dissociation. Comparison of these activation parameters with those obtained for the catalyzed dimerization[2] of phenyl isocyanate is given in Table II also. The catalyzed dimerization process requires much less activation energy and a more highly ordered transition state compared with the reassociation process for IIa. When the equilibrium data are compared, however, one finds more comparable values: for IIa dissociation, $\Delta H^\circ = 15.7$ kcal mol^{-1}, $\Delta S^\circ = 45$ cal deg^{-1}, $\Delta F^\circ = -1.08$ kcal mol^{-1}; for phenyl isocyanate dimerization, $\Delta H^\circ = -10.2$ kcal mol^{-1}, $\Delta S^\circ = -37.6$ cal deg^{-1}, $\Delta F^\circ = 1.02$ kcal mol^{-1}. The opposite signs reflect the different directions for which the reactions were studied.

Table II

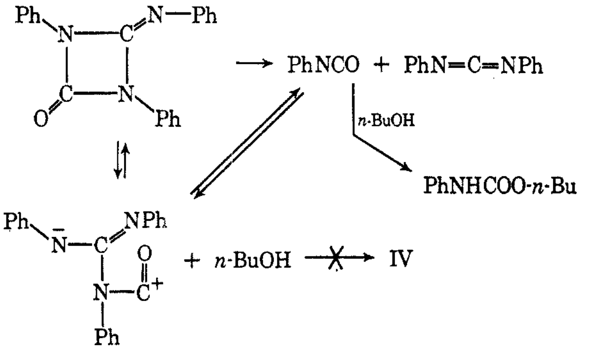
Activation Parameters for the Dissociation of IIa

	Dissociation	Reassociation	PhNCO-catalyzed[a] dimerization
E_a	28.2 kcal/mol	12.2 kcal/mol	1.1 kcal
$\Delta F^{\ddagger}$	29.0 kcal/mol	29.5 kcal/mol	21.5 kcal
$\Delta H^{\ddagger}$	27.5 kcal/mol	11.5 kcal/mol	0.5 kcal
$\Delta S^{\ddagger}$	−2.4 cal/deg	−48.4 cal/deg	−70 cal/deg

[a] See ref 2.

These comparisons suggest similar initial and final states for the two systems; substitution of carbodiimide for isocyanate does not appreciably affect the relative energies of the initial and final states. The rather different values for the activation parameters in the catalyzed and uncatalyzed processes reflect a dissimilarity in transition states. These data support the contention that the equilibrium being measured is truly uncatalyzed.

The details of the steps in the dissociation process are not known. It can be claimed, however, that, if the dissociation is a stepwise process, the intermediates are short lived and untrappable with alcohols. This is shown by the absence of the carboxyguanidine derivatives from thermal cleavage of IIa in *n*-butyl alcohol (eq 14).



(14)

Experimental Section

Synthesis of Diphenyl Carbodiimide.[10]—Into a 500-ml flask equipped with a mechanical stirrer, thermometer, condenser, and nitrogen inlet tube were charged 359.9 g of phenyl isocyanate and 0.4 g of 1-phenyl-3-methylphospholene oxide. The mixture was heated at 120–200° for 3 hr and distilled. There was obtained 170.8 g of light yellow liquid, bp 132–135° (1.5 mm).

1,3-Diphenyl-4-(phenylimino)-2-uretidinone (II).—A mixture of 80 g (0.41 mol) of diphenylcarbodiimide and 49 g (0.41 mol) of phenyl isocyanate was heated at 100–120° for 1.5 hr. On cooling, there was obtained 33 g (25%) of white solid, which after repeated crystallization from carbon tetrachloride had mp 139–140° (with decomposition)[11] and showed only a single spot on thin layer chromatography. No isocyanate or carbodiimide bands were present in the infrared spectrum. The adduct had strong infrared absorption at 5.8 and 7.32 μ.

Anal. Calcd for $C_{20}H_{15}N_3O$: C, 76.60; H, 4.83; N, 13.40; mol wt, 313.4. Found: C, 76.5; H, 5.0; N, 13.5; mol wt, 316.

A similar reaction of 97 g of diphenylcarbodiimide and 60 g of phenyl isocyanate with 0.2 g of cuprous chloride was conducted at 70–85° for 4 hr. On cooling, a pale yellow solid was collected and recrystallized from carbon tetrachloride. The yield of once recrystallized product was 43.5 g, 28%.

Vpc Analysis.—A solution of II in carbon tetrachloride was injected into an F & M 720 vapor phase chromatograph (Carbowax column, 100–300° at 15°/min). Two peaks were observed corresponding in retention time to phenyl isocyanate and diphenylcarbodiimide. The ratio of the peak areas 1.03/1.77 = 0.58 was close to the ratio of weights of phenyl isocyanate and diphenylcarbodiimide in IIa, 119/194 = 0.61.

***n*-Butyl N-phenylcarbamate** was prepared from *n*-butyl alcohol and phenyl isocyanate, mp 60–61°.[12]

Methyl N-phenylcarbamate, mp 45°,[13] was prepared similarly.

2-Butyl-1,3-diphenylpseudourea was prepared from the cuprous chloride catalyzed addition of *n*-butyl alcohol to diphenyl carbodiimide and had mp 48–58°; ir ($CHCl_3$), 2.93 (NH), 6.02 (C=N) (lit.[14] 6.00 C=N); nmr ($CDCl_3$), δ 7.09 (m, 10, ArH), 5.84 (s, 1, NH), 4.38 (t, 2, OCH_2), 0.84–1.9 (m, 7).

2-Methyl-1,3-diphenylpseudourea, mp 62°, was prepared similarly: ir ($CHCl_3$), 2.91 (NH), 6.00 (C=N); nmr ($CDCl_3$), δ 6.93 (m, 10, ArH), 5.85 (s, 1, NH), 3.87 (s, OCH_3).

Table III

Catalyzed Reaction of IIa with *n*-Butyl Alcohol

Catalyst	Time, hr (temperature, °C)	Major products
None	5 (100)	PhNHCOOBu, III, PhNCNPh
Cu_2Cl_2	4 (100)	PhNHCOOBu, III
T-9[a]	3 (100)	PhNHCOOBu, III, PhNCNPh
DABCO[b]	5 (100)	PhNHCOOBu, III, PhNCNPh
$Bu_4N^+Br^-$		PhNHCOOBu, III, PhNCNPh
NaOBu	0.25[c]	IV + triphenylguanidine
NaOPh	0.5	IV
NaOAc–HOAc	48[d]	Methyl ester of IV
Bu_2NH–HOAc	24 (60)[e]	V
H_2O	12 days[f]	Triphenylguanidine, PhNHCONHPh, $PhNH_2$

[a] Stannous octoate, M and T Chemicals, Inc. [b] Triethylenediamine, Houdry Process and Chemical Co. [c] At 25–95°; reaction nearly complete in 15 min at 25°. [d] In methanol solution. [e] No *n*-butyl alcohol. [f] At 70°; hydrolysis incomplete.

Reaction of Iminouretidinone with Nucleophiles (Table III). Reaction with *n*-Butyl Alcohol.—A solution of 6 g of II in 75 g of dried *n*-butyl alcohol and 225 g of *sym*-tetrachloroethane was heated in an oil bath for 6 hr at 98–102° under nitrogen. Samples were withdrawn periodically and examined by infrared and thin layer chromatogaphy. As the sample was heated, the infrared spectrum revealed the appearance of a carbodiimide band at 4.67 μ (2140 cm^{-1}) and a slight decrease in the 5.78-μ carbonyl absorption. As the heating was continued, the carbonyl di-

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(10) T. W. Campbell, J. J. Monagle, and V. S. Foldi, *J. Amer. Chem. Soc.*, **84**, 3673 (1962).

(11) Farbenfabriken Bayer, A. G., British Patent 959,997 (June 3, 1964).

(12) H. Tiecklmann and H. W. Post [*J. Org. Chem.*, **13**, 268 (1948)] report mp 58–60°.

(13) J. W. Baker and J. B. Holdsworth [*J. Chem. Soc.*, 713 (1947)] report mp 48°.

(14) S. E. Forman, C. A. Erickson, and H. Adelman, *J. Org. Chem.*, **28**, 2653 (1963).

minished to a constant value, about one-third its original intensity. The residual carbonyl band is due to the *n*-butyl N-phenylcarbamate formed during the reaction. No isocyanate band was detected. If the solvent were not dried carefully, carbanilide was also detected as the reaction product. This could have been derived from either the isocyanate or carbodiimide.

The parallel thin layer chromatography record indicated the onset of adduct disassociation with heat. The first products were carbodiimide and *n*-butyl N-phenylcarbamate. Carbodiimide was slowly consumed in formation of 2-*n*-butyl-1,3-diphenylpseudourea. The thin layer record was confirmed by vpc data. The carbamate, carbodiimide, and pseudourea were established by comparison of their retention times with those of authentic samples.

Dissociation of the adduct in the presence of cuprous chloride, a known catalyst for addition of nucleophiles to carbodiimides,[8] yielded only a trace of carbodiimide; the pseudourea content increased at the same rate as the carbamate.

Reaction with Di-*n*-butylamine.—A solution of 6.0 g of II in 225 g of benzene was heated with 20 g of di-*n*-butylamine for 18 hr at 50-60°. At the end of this time, no reaction could be detected in the infrared spectrum. Glacial acetic acid (1.0 g) was added and the heating continued. It was apparent from the infrared spectrum that a reaction was occurring, which was nearly complete after 9 hr. After 24 hr, the heating was stopped. A portion of the reaction mixture was stripped of solvent and washed with dilute hydrochloric acid to remove excess di-*n*-butylamine. There remained a yellow resinous oil which did not crystallize. Trituration of the oil with hexane yielded a white solid, mp 156-157, the hydrochloride of V.

Anal. Calcd for $C_{28}H_{35}N_4OCl$: C, 70.20; H, 7.36; N, 11.70. Found: C, 70.08; H, 7.39; N, 11.86.

Evaporation of the hexane gave an oil (V): ir ($CHCl_3$), 2.91 (N-H), 6.04 (C=N); nmr ($CDCl_3$), δ 7.15 (m, 15, ArH), 6.01 (s, 1, NH), 2.84 (t, 4, CH_2N), 0.85-1.3 (m, 14).

Synthesis of Carbobutoxytriphenylguanidine.—A 6.0-g (0.019 mol) sample of II was dissolved in 300 g of a 75:25 mixture of dried tribromomethane and *n*-butyl alcohol. To this was added, with stirring under dry nitrogen, 0.1 g of sodium phenoxide. After 15 min at 25°, a sample was taken and the reaction mixture heated to 96° over 0.5 hr, when another sample was removed. The infrared spectra and thin layer chromatography of these samples showed the absence of starting material and were nearly identical, indicating that the bulk of the reaction was completed before the heating was begun. The reaction mixture was cooled to room temperature. The products of the uncatalyzed reactions (carbamate, pseudourea, carbodiimide) were absent. Evaporation of the solvent on a rotary evaporation gave 6.1 g (82% yield) of a white solid (IV) which, after several recrystallizations from petroleum ether (30-60°), had mp 114-115°.

Anal. Calcd for $C_{24}H_{25}N_3O_2$: C, 74.39; H, 6.5; N, 10.85; mol wt, 387.46. Found: C, 74.6; H, 6.8; N, 11.1; mol wt, 400.

The nmr spectrum of IV in deuteriochloroform showed 15 aromatic protons at 7.1 ppm, a triplet of 2 protons at 4.0 ppm ($-CH_2-O-$), a single sharp proton resonance (N-H) at 2.3 ppm, and a complex multiplet of 7 protons at 1.4 ppm ($-CH_2-$ groups) and 0.8 ppm (CH_3 triplet). The infrared spectrum of IV in chloroform showed a sharp N-H at 2.90 μ (3450 cm^{-1}), C=O at 5.80 μ (1725 cm^{-1}), and C=N at 6.02 μ (1660 cm^{-1}).

Hydrolysis of IV in 1 *N* sodium hydroxide proceeded slowly at 100° to yield triphenyl guanidine, mp 140-145° (identified by infrared analysis and tlc), carbanilide (by infrared analysis and tlc), and aniline (vpc); the last two products were produced from hydrolysis of the triphenyl guanidine.

When the sodium phenoxide ring opening was carried out in methanol solution, the corresponding carbomethoxytriphenylguanidine was prepared, mp 117-118°, and with phenol, the carbophenoxy derivative, a white solid, was prepared, mp 125-127°.

Anal. Calcd for $C_{26}H_{21}N_3O_2$: C, 76.64; H, 5.19; N, 10.31. Found: C, 76.6; H, 5.1; N, 10.1.

Kinetic Runs.—Solutions of IIa were prepared in 1,2,3-trichloropropane solvent and placed into 2-ml ampoules. The ampoules were sealed and placed in an oil bath regulated to ±0.3°. At appropriate times, the ampoules were withdrawn from the bath and quickly chilled in ice water, and a 1-ml sample was withdrawn and diluted to volume with additional solvent. The infrared spectrum of the diluted samples were then examined in matched 0.1-mm cells with 1,2,3-trichloropropane in the reference cell. A Perkin-Elmer 237 grating instrument was used. At least two separate determinations were made for the initial (A_0) and final (A_e) points. The absorbance of the 5.78-μ band was determined for each sample using the base-line density method.[15] The base line was essentially constant, and this correction was small. Control experiments indicated no measurable shift in the equilibrium during the sampling, dilution, and infrared measurement procedure. Measurements were continued until equilibrium was established as evidenced by a constant infrared spectrum, including, of course, a constant absorbance at 5.78 μ.

By plotting the data as an equilibrium process involving a first-order forward reaction opposed by a second-order reverse reaction, a good straight line for the log [concn] *vs.* time plot was obtained, where the concentration was represented by eq 12.

$$2.303 \log \frac{{A_0}^2 - A_eA}{(A - A_e)A_0} = k_d\left(\frac{A_0 + A_e}{A_0 - A_e}\right)t \qquad (12)$$

The instantaneous rate constants for each sample were calculated from eq 12 and the average rate constant determined from these. No drift in these instantaneous rate constants was noticed, even at 70-90% reaction to equilibrium.

The equilibrium constants were calculated from the absorbance data at equilibrium using eq 13.

$$K = \frac{[\mathrm{NCO}][\mathrm{NCN}]}{[\mathrm{IIa}]} = \left[\left(\frac{A_0 - A_e}{A_0}\right)\mathrm{Co}\right]^2 \Big/ \frac{A_e}{A_0}\mathrm{Co} \qquad (13)$$

Registry No.—IIa, 14124-22-2; IV, 16005-53-1; IV carbomethoxy derivative, 16031-08-6; IV carbophenoxy derivative, 16005-54-2; V, 16005-55-3; V HCl, 16005-56-4; 2-butyl-1,3-diphenylpseudourea, 16005-57-5; 2-methyl-1,3-diphenylpseudourea, 16005-58-6; triphenylguanidine, 101-01-9.

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(15) R. G. White, "Handbook of Industrial Infrared Analyses," Plenum Press, New York, N. Y., 1964, p 241.