

Urethanes. II. The Effect of Amine Bases on the Thermal Degradation of Carbanilates

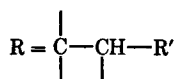
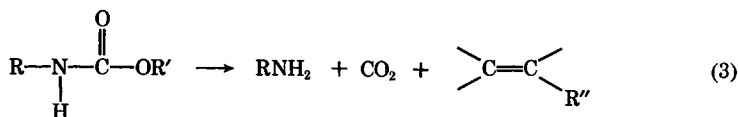
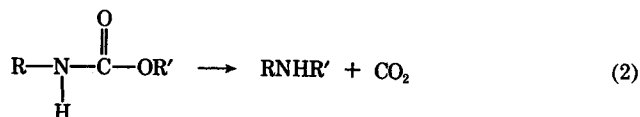
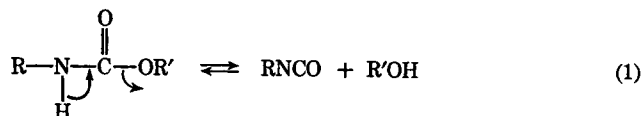
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Synopsis

The amine-catalyzed, low-temperature (<200°C) thermal degradation of aromatic urethanes, specifically carbanilates, was studied to determine the primary reactions responsible for the loss of starting material and the resultant products. The primary degradation reactions are (1) the reversible dissociation of the urethane to isocyanate and alcohol and (2) the nonreversible nucleophilic attack by a basic species on the carbon attached to the carbamate oxygen to yield amine, carbon dioxide, and an alkylated base. Secondary products fall into two categories, neutral and basic species. The neutral components consist of carbanilide, dialkyl carbonate, isocyanurate, and N-alkylated carbamates. The basic components, derived from starting materials, are pseudoureas and guanidines. Their formation depends solely on the presence of carbanilide in the reaction mixture. When the amine catalyst is 1,4-diaza[2.2.2]bicyclooctane, novel piperazine compounds are formed. In general, quarternized triethylenediamine species undergo nucleophilic displacement reactions to form N-alkyl-N'-ethylpiperazine derivatives.

INTRODUCTION

Interest in the chemistry of urethanes has increased with the rapid growth in the use of polyurethanes. The most common type of urethanes, mono-substituted on nitrogen, exhibit three primary paths of decomposition:



Reaction (1) is known to occur very slowly at 150°C and to increase in rate rapidly as the temperature is increased.¹⁻⁵ Reactions (2)^{6,7} and (3)^{8,9} have been shown to occur intramolecularly. They are, however, unimolecular high-energy transformations requiring temperatures in excess of 230°C.

We had reason to believe that extensive degradation of an urethane would occur below 200°C especially in the presence of an amine catalyst such as 1,4-diaza[2.2.2]bicyclooctane (triethylenediamine). Since at temperatures below 200°C reactions (2) and (3) are slow, we wished to determine those reactions which were causing loss of urethane.

EXPERIMENTAL

Procedure

Equipment and Analysis. Infrared spectra were recorded on a Perkin-Elmer 237B spectrograph. Nuclear magnetic resonance spectra were recorded on a Varian A-60 using tetramethylsilane as an internal standard. Mass spectral analysis were done at the University of Connecticut on a MS 12. Melting points were taken either on a Thomas-Hoover or a Fisher-Johns melting point apparatus and are uncorrected. Elemental analyses were determined at the Clark Microanalytical Laboratory, Urbana, Illinois.

Gas Chromatography. Gas chromatographs were made on a F & M Model 720 dual column programmed temperature apparatus. The column was aluminum, 6 ft long, $\frac{3}{16}$ in. in diameter and packed with 15% GP 53B (Dow Corning Silicone 11) on Anakrom ABS 60/70 mesh (Analabs). The flow rate was 60 ml/min (He). The injector temperature was 240°C; detector, 300°C at 130 mA. The column was kept at 70°C for 4 min after the sample was injected, then programmed at 10°C/min up to 280°C. All compounds were detectable except for the following: Carbanilide and triphenyl isocyanurate were not eluted; all simple carbanilates always showed a small peak due to phenyl isocyanate. The allophanates yielded peaks due to its constituent isocyanate and carbanilate. 1,2,3-Triphenylguanidine broke down to yield aniline and diphenylcarbodiimide, while 1,3,5-triphenylbiuret yielded only isocyanate. The pseudoureas were detectable only as broad peaks of which one shoulder corresponds to diphenylcarbodiimide, triphenyl uretidoneimine was used as a standard to yield the peaks for phenyl isocyanate and diphenylcarbodiimide.

Standard Materials

Dimethyl and dibutyl carbonates, triethylamine, and dimethylaniline were redistilled before use. Chlorobenzene and *o*-dichlorobenzene were distilled from tosyl isocyanate and stored over molecular sieves; bp 130-131°C and 180-181°C, respectively. All standard materials, preparations, and properties are listed in Table I.

TABLE I
 Standard Materials

Compound	Recrystallization solvent	mp, °C	bp, °C	IR (CCl ₄)		NMR (DMSO-d ₆) Hz	Analysis found	
				NH	C=O		%C	%H
Methyl carbanilate ^a	Ether-hexane	48-49	80-83 (0.07-0.10 mm)	2.9	5.70	578		
Butyl carbanilate ^a	Ether-hexane	63-64	—	2.9	5.74	578		
Neopentyl carbanilate ^a	Benzene-ligroin	114.5-115.5	—	2.9	5.74	570		
1,2,3-Triphenylguanidine	Ether-hexane	146.5-148	—	2.90 (doublet)	6.02	495		
2-Methyl-1,3-diphenylpseudourea ^b	Ether-hexane	64-65	—		6.0	770	74.31	6.01
2-Butyl-1,3-diphenylpseudourea ^b	Hexane	52.5-53.5	—		6.0	469	76.28	7.85
1,2,3-Triphenylbiuret ^c	Chloroform-ether	150-151	—	2.92(C ₆ H ₆)	5.78(C ₆ H ₆)			10.63
Methyl 2,4-diphenylallophanate ^d	Ether-hexane	130.5-131.5	—	302	5.74	570		
<i>n</i> -Butyl 2,4-diphenylallophanate ^d	Ether-hexane	87.5-88.5	—	(broad)	5.88	645		
Methyl <i>N</i> -methylcarbanilate ^e		—	85 (0.7-0.9 mm)	302	5.74	648	69.35	6.62
<i>n</i> -Butyl <i>N</i> - <i>n</i> -butylcarbanilate ^e		—	60 (0.15 mm) 122-123 (0.7 mm)	(broad)	5.88			9.18
<i>N</i> -Methylcarbanilide ^f		85.5-90.0	—					
							192(N-CH ₃)	65.60
							222(t,N-CH ₃)	6.71
							247(t,OCH ₃)	8.57
								72.48
								9.16
								5.79

^a Prepared by the reaction of phenyl isocyanate with excess alcohol with no added catalyst.

^b Prepared by the addition of diphenylcarbodiimide to an excess of the desired alcohol, saturated with copper(I) chloride at room temperature. An exothermic reaction.

^c Prepared by the reaction of phenyl isocyanate in carbonilide in toluene at 100°C.

^d Prepared by the reaction of phenyl isocyanate with the desired carbanilate at 100°C with cobalt naphthenate as catalyst.

^e Prepared by the reaction of the desired alkyl chloroformate on *N*-methylaniline.

^f Prepared from phenyl isocyanate and *N*-methylaniline.

Reactions

Pyrolysis

The procedures used for the pyrolysis of methyl carbanilate are exemplary of those used for all pyrolysis experiments.

The methyl carbanilate, 15.1 g (100 mmoles), was placed in a three-necked round-bottomed flask equipped with a nitrogen inlet, outlet, and a magnetic stirrer. The outlet tube was connected to a series of three gas traps set in a Dry Ice-acetone bath, an ascarite tube, and finally a bubble counter. The nitrogen was set to allow a steady flow of discrete bubbles. The carbanilate was then heated for 20 hr at 110°C to remove all traces of water. The carbanilate was then cooled, and triethylenediamine, 168 mg (1.5 mmoles), purified by sublimation, then dried by freeze drying from benzene at 10–13 mm, was added and stirred in. The mixture was then placed in an oil bath at 130°C, and stirred rapidly under a stream of nitrogen for 4 hr.

After this time the heating bath was removed and the traps were sealed off. The ascarite trap gained 270 mg of weight, representing 6.15 mmoles of carbon dioxide. The cold traps were washed out with chlorobenzene, diluted to 10 ml, and analyzed via VPC. The amounts of methanol (6.63 mmoles) and dimethylcarbonate (6.76 mmoles) were estimated from peak heights which were compared to those of standard solutions of the same materials.

The reaction mixture was taken up in benzene, filtered, and washed with chloroform to leave carbanilide, which was identified by infrared analysis (KBr), mp, and mixed mp with an authentic sample. The mother liquor was then diluted with ether and extracted with 10% hydrochloric acid. The acidic aqueous phase was then washed with ether. The organic phases were combined, washed with one small portion of 10% hydrochloric acid, washed to neutrality with saturated salt solution, and dried (MgSO_4).

The original aqueous acid phase was made basic with dilute sodium hydroxide; extracted continuously with ether overnight; and, dried, (Na_2SO_4).

The neutral phase, on evaporation of the solvent, was taken up in a small amount of chloroform and filtered to yield additional small amounts of carbanilide. The residue was then percolated through 100 g of Fisher alumina with 250 ml of ether. The column was then washed with chloroform to yield triphenylisocyanurate, 40 mg, 0.13 mmoles, identified by IR (CHCl_3), mp, and mixed mp with an authentic sample. The total yield of carbanilide was 2.60 g (12.3 mmoles). The residue, 10.2 g, was determined to contain, by VPC and NMR (DMSO-d_6) analysis, starting material and methyl N-methylcarbanilate, 0.34 g (2.4 mmoles). The crude basic phase was chromatographed on 70 g of Fisher alumina using 500-ml portions of petroleum ether-ether mixtures. Elution with 10% ether-petroleum ether yielded the methyl pseudourea, compound VIII, 268 mg (1.1 mmoles). Elution with ether yielded first triphenylguanidine, IX, 115 mg (0.40 mmoles) and the piperazine compound, X, 83 mg (0.30

TABLE II
Products of Pyrolysis of 100 mmoles of Methyl Carbanilate at 130°C^a

Product	Yield, mmoles		
	dried ^b	undried ^b	in solution
CO ₂	6.2	10.3	—
CH ₃ OH	6.6	19.0	—
(CH ₃ O) ₂ C=O	6.8	12.5	—
(C ₆ H ₅ NH) ₂ C=O	12.4	17.6	6.6
C ₆ H ₅ N(CH ₃)CO ₂ CH ₃	2.0	— ^c	trace
(C ₆ H ₅ NCO) ₃	0.12	0.14	—
C ₆ H ₅ N=COCH ₃	1.1	3.9	0.22
$\begin{array}{c} \\ \text{NHC}_6\text{H}_5 \\ \\ \text{C}_6\text{H}_5\text{N}=\text{CNHC}_6\text{H}_5 \\ \\ \text{NHC}_6\text{H}_5 \end{array}$	0.51	0.81	1.5
$\begin{array}{c} \text{CH}_3\text{N} \begin{array}{c} \diagup \quad \diagdown \\ \text{---} \quad \text{---} \\ \diagdown \quad \diagup \end{array} \text{NCH}_2\text{CH}_2\text{NCO}_2\text{CH}_3 \\ \\ \text{C}_6\text{H}_5 \end{array}$	0.28	— ^c	1.0

^a Average of two runs, triethylenediamine catalyst.

^b Dried refers to heating under flow of nitrogen at 110°C before addition of catalyst.

^c Unmeasured.

TABLE III
Products of Pyrolysis of 100 mmoles of Butyl Carbanilate at 150°C^a

Product	Yield, mmoles	
	dried ^b	undried
CO ₂	0.57	1.8
CH ₃ CH ₂ CH ₂ CH ₂ OH	2.7	3.2
(C ₆ H ₅ NH) ₂ C=O	0.40	0.71
(C ₆ H ₅ NCO) ₃	0.29	0.33
$\begin{array}{c} \text{C}_6\text{H}_5\text{N}=\text{C}-\text{NHC}_6\text{H}_5 \\ \\ \text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \end{array}$	°	°
$\begin{array}{c} \text{C}_6\text{H}_5\text{N}=\text{C}-\text{NHC}_6\text{H}_5 \\ \\ \text{NHC}_6\text{H}_5 \end{array}$	0.22	0.30
$\begin{array}{c} n\text{-C}_4\text{H}_9\text{N} \begin{array}{c} \diagup \quad \diagdown \\ \text{---} \quad \text{---} \\ \diagdown \quad \diagup \end{array} \text{NCH}_2\text{CH}_2 \\ \\ \text{C}_6\text{H}_5\text{N} \\ \\ n\text{-C}_4\text{H}_9\text{O}-\text{C}=\text{O} \end{array}$	0.40	0.56

^a Average of two runs.

^b Heated under flow of nitrogen at 110° for 20 hr.

^c Trace.

TABLE IV
The Pyrolysis of 100 mmoles of Butyl Carbanilate at 200°C

Product	Yield, mmoles			
	Catalyzed		Uncatalyzed	
	dried ^a	undried	dried ^a	undried
CO ₂	8.2	12.9	0.14	0.24
CH ₂ CH ₂ CH ₂ CH ₂ OH	2.7	10.5	2.0	3.5
(C ₆ H ₅ NH) ₂ C=O	2.6	2.3	0.8	0.8
C ₆ H ₅ N=C(NHC ₆ H ₅) ₂	1.1	1.0		
C ₆ H ₅ N=CNHC ₆ H ₅	1.8	0.52	0.3	0.4
$\begin{array}{c} \\ \text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \\ \\ \text{n-C}_4\text{H}_9\text{N} \begin{array}{c} \diagup \quad \diagdown \\ \text{---} \quad \text{---} \\ \diagdown \quad \diagup \\ \text{NCH}_2\text{CH}_2 \\ \\ \text{n-C}_4\text{H}_9\text{O}_2\text{C} - \text{N} \\ \\ \text{C}_6\text{H}_5 \end{array} \end{array}$	3.7	3.5		

^a Heated under nitrogen flow 110°C for 20 hr.

mmoles). All compounds were identified by comparison of IR and NMR spectra with authentic samples, and by mp and mixed mp where possible.

A complete listing of yields for methyl carbanilate is given in Table II; for butyl carbanilate, in Tables III and IV.

The following compounds were looked for but were not detected: triphenyl biuret, the allophanate, and the alkylated carbanilide.

Neopentyl carbanilate is completely stable to heat at 130°C, in the presence of triethylenediamine. At 200°C for 4 hr in the presence of triethylenediamine, only 1.4% of carbon dioxide and 3.4% of the alcohol and a trace of carbanilide were found.

Pyrolysis of Methyl Carbanilate in Solution A. To methyl carbanilate, 7.5 g (49.6 mmoles), dissolved in 100 ml chlorobenzene was added triethylene diamine, 0.28 g (2.5 mmoles), and the mixture was refluxed for 24 hr. The reaction mixture was then worked up into neutral and basic phases. The neutral phase consisted of carbanilide, 0.14 g (6.6 mmoles) and 5.4 g of unreacted starting material (72%) contaminated with only trace amounts of methyl N-methylcarbanilate. The basic phase consisted of methyl pseudourea (VIII) 50 mg (0.22 mmoles); triphenylguanidine (IX), 0.43 g (1.5 mmoles); and the piperazine compound X, 0.29 g (1.0 mmoles). When methyl carbanilate was subject to 130°C temperature either in solution or neat for 4 hr without a catalyst, no products were found and only starting material was recovered.

Pyrolysis of Methyl Carbanilate in Solution B. When a mixture of methyl carbanilate, 15.1 g (100 mmoles), triethylamine, 5.1 g (50 mmoles), 10 ml dimethyl carbonate, and 90 ml chlorobenzene was refluxed for 20 hr, the neutral phase yielded 2.1 g triphenyl isocyanurate and 10.8 g of a mixture of starting material and compound VII. The basic mixture, 0.81 g,

consisted mainly of the pseudourea (VIII) with approximately 10–15% of triphenylguanidine (IX).

Pyrolysis of Methyl Carbanilate in Solution C. In this case the methyl carbanilate, 15.1 g (100 mmoles), and N,N-dimethylaniline, 0.12 g (1.0 mmoles), were heated at 200°C for 24 hr. The neutral materials consisted of 1.21 g carbanilide and 4.2 g of an approximately equal mixture of starting material and compound VII. The basic phase contained at least six components. Three low-boiling components were distilled off at water vacuum pressures. This fraction consisted of a mixture of aniline, N-methylaniline, and N,N-dimethylaniline. The amount of dimethylaniline present was estimated by VPC to be far greater than that initially present. The higher boiling residue was chromatographed on Fisher alumina to yield 0.64 g pseudourea (VIII), 2.3 g triphenylguanidine (IX), and 0.1 g of an unidentified oil.

Reaction of Neopentyl Carbanilate with Triethylenediamine in o-Dichlorobenzene

The urethane, 10.35 g, (50 mmoles), and triethylenediamine, 1.0 g (10 wt-%), were dissolved in 100 ml *o*-dichlorobenzene and refluxed for 24 hr. The mixture was then worked up by extraction procedures to yield the neutral and basic components. The neutral phase yielded 0.10 g carbanilide and 9.60 g of recovered starting material. The NMR spectrum (DMSO- d_6) could detect no impurities in this phase.

The basic mixture contained a gelatin which could not be extracted with ether. This material, 0.8 g, was insoluble in DMSO and trifluoroacetic acid. The ether extract of this material yielded only 0.10 g of materials which could not be identified.

Reaction of Methyl Carbanilate with Triethylenediamine

Methyl carbanilate, 15.2 g (0.1 mole), triethylenediamine, 5.6 g (0.05 mole), dimethyl carbonate, 10 ml, and chlorobenzene, 90 ml, were mixed and refluxed for 6 hr. The basic fraction, after work-up, was nearly pure compound X, 11.3 g (82%). The neutral fraction was a mixture of starting material and VII.

The piperazine compound was distilled, bp 156–158°C (0.5 mm); IR (CCl₄) 3.4 μ (s), 3.56 μ (s), 5.85 μ (s, C=O); NMR (C₆D₆) 7.2 δ (5, C₆H₅), 3.8 δ (2, t, J = 6.5, C₆H₅N(CO)CH₂), 3.5 δ (3, s, OCH₃), 2.1 δ (3, s, N—CH₃); mass spectrum (70 eV) m/e (rel intensity) 277 (5), 120 (5), 114 (7.5), 113 (100), 104 (6.5), 98 (5), 91 (6), 77 (13), 70 (59), 56 (12), 43 (15), 42 (18.5).

ANAL. Calcd for C₁₅H₂₃N₃O₂: C, 64.95%; H, 8.36%; N, 15.15%; Found: C, 65.14%; H, 8.42%; N, 15.22%.

When the reaction was run without the dimethyl carbonate, the basic fraction consisted mostly of a mixture of triphenylguanidine (IX) and methyl pseudourea (VIII). The neutral fraction yielded carbanilide in addition to starting material and VII.

Reaction of Butyl Carbanilate with Triethylenediamine

A mixture of butyl carbanilate, 19.3 g (100 mmoles), and triethylenediamine, 5.6 g (50 mmoles), was heated neat at 150°C for 20 hr. The reaction mixture was then separated into its neutral and basic components. The neutral phase yielded 1.0 g of carbanilide and 14 g starting material. The basic phase contained 0.10 g of the pseudourea XVI and 2.7 g of the piperazine compound XVII.

When a mixture of butyl carbanilate, 38.7 g (200 mmoles), triethylenediamine, 22.5 g (200 mmoles), and dibutyl carbonate, 35 ml, were heated at 150°C for 20 hr, the neutral phase contained only 0.21 g carbanilide and 19.7 g starting material. The basic phase consisted of 32.9 g crude piperazine compound XVII: bp 185–87°C (0.4 mm); IR (CCl₄) 3.36 μ (s), 3.54 μ (s), 5.85 μ (C=O), 8.55 μ (s); NMR (CDCl₃) 7.2 δ (s, 5, C₆H₅), 4.0 δ (t, 2, CH₂O), 3.8 δ (t, 2, CH₂N), 2.4 δ (m, 12), 0.8–1.8 δ (m, 14).

ANAL. Calcd for C₂₁H₃₅N₃O₂: C, 69.77%; H, 9.76%; N, 11.62%; Found: C, 69.39%; H, 9.70%; N, 11.81%.

Condensation of Methyl N-Methylcarbanilate with Triethylenediamine

The carbanilate, 6.7 g (40.5 mmoles), and triethylenediamine, 4.6 g (41 mmoles), were dissolved in 50 ml chlorobenzene and refluxed for 24 hr. The mixture was worked up into neutral and basic fractions. The neutral fraction contained only 2.74 g of unreacted starting material, while the basic fraction contained N-methylaniline and 5.16 g of the piperazine compound XXVIII: yield 78%; bp 165°C (0.12 mm); IR (CCl₄) 5.82 μ (C=O); NMR (CDCl₃) 7.2 δ (s, 5, C₆H₅), 4.1 δ (t, 2, COOCH₂), 3.2 δ (s, 3, CON—CH₃), 2.4–2.6 δ (m, 10), 2.2 δ (s, 3, NCH₃).

ANAL. Calcd for C₁₅H₂₃N₃O₂: N, 15.15%. Found: N, 15.23, 15.39%.

Reaction of Butyl Carbanilate with Dimethyl Carbonate

Butyl carbanilate, 3.90 g (20.0 mmoles), and triethylenediamine, 0.39 g (3.5 mmoles), were dissolved in a mixture of 25 ml chlorobenzene and 2 ml dimethyl carbonate and refluxed for 24 hr. The mixture was then separated into basic and neutral fractions. The neutral phase was then distilled to remove all liquids boiling below 125°C. The remaining low-boiling materials were removed by vacuum distillation and were proved to be a mixture of chlorobenzene and butylmethyl carbonate. The residue, analyzed by VPC, showed four materials; butyl carbanilate, methyl carbanilate, methyl N-methylcarbanilate and butyl N-methylcarbanilate.

The basic fraction, 1.2 g, consisted mainly of the piperazine derivative XXIX, plus piperazine compound X.

Reaction of Butyl Carbanilate with Methyl Acetate

The butyl carbanilate, 3.86 g (20.0 mmoles), and triethylenediamine, 2.24 g (20.0 mmoles), were dissolved in a mixture of 25 ml chlorobenzene

and 3 ml methyl acetate. This solution was refluxed for 20 hr, then worked up by extraction techniques into its neutral and basic components. The neutral phase yielded carbanilide, 0.16 g, on filtration. The remainder, analyzed by VPC, contained butyl acetate and 2.41 g of a mixture of butyl and methyl carbanilates. The basic fraction consisted of 0.96 of XXIX contaminated with X.

*Reaction of Butyl Carbanilate with Methyl
Hexanoate and Triethylenediamine*

A mixture of butyl carbanilate, 38.6 g (0.20 mole), triethylenediamine: 12.4 g (0.11 mole), and methyl hexanoate 13.0 g (0.10 mole), was heated at 150°C for 24 hr. The mixture was then separated into basic and neutral fractions. The neutral fraction yielded 4.1 g carbanilide by filtration; 11.3 g butyl hexanoate by distillation, bp 62°C (0.3 mm); and the residue on chromatography yielded 10.5 g of the starting carbanilate and 2.1 g phenylhexamide, and a trace of *n*-butyl *N*-methylcarbanilate, identified by NMR.

The basic fraction on distillation yielded 4 g aniline and 0.7 g of the piperazine compound XXX: bp 101°C (0.7 mm); IR (CCl₄) 2.92 μ (N—H), 3.38 μ, 3.54 μ, 6.2 μ, 6.62 μ; NMR (DMSO-d₆) 6.4–7.2 δ (m, 5), 5.2 δ (t, 1, NH—CH₂, J = 5.5), 3.0 δ (t, 2, NHCH₂ J = 6.0), 2.4 δ (m, 10), 2.05 δ (s, 3, NCH₃).

ANAL. Calcd for C₁₃H₂₁N₃: C, 71.19%; H, 9.65%; N, 19.16%. Found: C, 70.66%; H, 9.68%; N, 18.63%.

The residue, 8 g, proved to be the piperazine compound XXIX.

When this reaction was run with dibutyl carbonate added to the reaction mixture, the basic fraction, 10.1 g crude, was nearly pure piperazine compound XXIX; bp 180–1°C (0.7 mm); (CCl₄) 3.38 μ (s), 3.56 μ (s), 5.85 μ (C=O). 7.1 μ, 8.5 μ; NMR (C₆D₆) 7.1 δ (m, 5), 4.0 δ (t, 2, J = 6.5, OCH₂), 3.88 δ (t, 2, J = 6.0, CH₂N(C₆H₅)CO₂), 2.3 δ (m, 10), 2.05 δ (s, 3, NCH₃), 0.6–1.6 δ (m, 7).

ANAL. Calcd for C₁₅H₂₅N₃O₂: C, 67.67%; H, 9.15%; N, 13.16%. Found C, 67.20%; H, 9.04%; N, 13.50%.

Reaction of Triethylenediamine with Methyl Hexanoate

Triethylenediamine, 11.2 g (0.100 mole), was dissolved in 25 ml methyl hexanoate and the mixture was then heated at 150°C for 20 hr. The red reaction mixture was worked up to isolate the basic material. Most of the color was left in the aqueous basic phase. The basic material, an oil, bp 111–112°C (0.6 mm), was 7 g, 29%, of piperazine compound XXVII: IR (CCl₄) 3.38 μ (s), 3.54 μ (s), 5.72 μ (C=O), 8.48 μ (s), NMR (CDCl₃) 4.2 δ (t, 2, J = 6, OCH₂), 2.4 δ (m, 12), 2.15 δ (s, 3, NCH₃), 0.80–2.0 δ (m, 9).

ANAL. Calcd for C₁₃H₂₃N₃O₂: C, 64.42%; H, 10.81%; N, 11.56%. Found: C, 64.20%; H, 10.63%; N, 11.61%.

Reaction of Carbanilide with Dimethyl Carbonate—A

Carbanilide, 2.0 g (4.7 mmoles), was slurried with 1.5 ml dimethyl carbonate and 25 ml chlorobenzene. To this mixture was added 200 mg triethylenediamine and the mixture was refluxed for 3 hr, after which time the reaction mixture was a clear solution. A VPC analysis of the reaction mixture indicated the same array of reaction products as in the thermal degradation of methyl carbanilate. The mixture was separated into basic and neutral components. The basic fraction, 1.8 g crude, consisted of a mixture of triphenylguanidine (IX), pseudourea (VIII), and piperazine compound X. The neutral fraction yielded 1.13 g of unreacted starting material and 3.3 g methyl carbanilate, 97% based on reacting carbanilide, and a trace amount of compound VII.

Reaction of Carbanilide with Dimethyl Carbonate—B

Carbanilide, 21.2 g (100 mmoles), was slurried in a mixture of 5 ml triethylamine, 10 ml dimethyl carbonate, and 100 ml chlorobenzene and the mixture was refluxed for 8 hr. Filtration of the cooled reaction mixture returned 1.1 g unreacted carbanilide. The residue separated into neutral and basic fractions yielded, in the neutral phase, 25 g of a 92/8 mixture of methyl carbanilate (VII). The basic fraction, 1.7 g, consisted mainly of the pseudourea VIII contaminated with small amount of triphenylguanidine (IX).

When carbanilide, dimethyl carbonate, and chlorobenzene were refluxed for 24 hr without a tertiary amine catalyst, only starting material is recovered from the reaction mixture.

When dimethyl carbonate, 9 g, was heated at 135°C for 24 hr in a mixture of 25 ml aniline, 25 ml chlorobenzene, and 0.1 g triethylamine, no methyl carbanilate was detected in the reaction mixture.

Reaction of Carbanilide with Dibutyl Carbonate

This reaction was run in the same manner as above using 4.2 g carbanilide, 7.7 ml dibutyl carbonate, and 0.24 g triethylenediamine. This mixture was heated at 180°C for 4 hr. The neutral reaction mixture yielded 1.35 g unreacted carbanilide and 3.25 g butyl carbanilate (63% based on reacted carbanilide). The basic fraction was not analyzed.

Reaction of Carbanilide with Methanol

The carbanilide, 2.12 g (10 mmoles), was refluxed for 24 hr in a mixture of 15 ml methanol and 200 mg triethylenediamine. The reaction mixture showed traces of methyl carbanilate (VPC).

*Reaction of Carbanilide with *n*-Butanol*

The carbanilide, 2.0 g, was refluxed overnight in a mixture of 40 ml *n*-butanol and 190 mg triethylenediamine. The mixture was separated into

neutral and basic fractions. The neutral fraction contained 1.7 g (95%) butyl carbanilate. The basic fraction contained only aniline.

Carbanilide Condensation

Carbanilide, 1.53 g, was slurried in 25 ml dried toluene. A sliver of sodium was added and the mixture was then refluxed for 24 hr. Work-up of the reaction mixture yielded 1.22 g starting material and 0.26 g triphenylguanidine

Reaction of Aniline with 2-Methyl-1,3-diphenylpseudourea (VIII)

A mixture of the pseudourea VIII, 2.26 g (10 mmoles), aniline, 0.95 g (10 mmoles), triethylamine, 0.25 ml, and chlorobenzene, 25 ml, was refluxed for 4 hours. The cooled reaction mixture was filtered to yield 70 mg carbanilide. The residue on chromatography yielded 1.57 g of the starting material and 0.43 g triphenylguanidine. No triphenylguanidine was found when the reaction was run without the added catalyst.

RESULTS

Methyl Carbanilate

Methyl carbanilate (I) is stable at 130°C under a nitrogen sweep. No volatile materials such as methanol or phenyl isocyanate were detected in traps set up to catch volatile materials. When approximately 1 wt-% trimethylenediamine was added at this temperature, degradation products were visible in a few minutes. The reaction products are shown in Scheme 1 (Fig. 1) and Table II.

Volatile products II, III, and IV were swept out of the reaction mixture by the nitrogen. Removal of the methanol (III) and dimethyl carbonate (IV) allowed the reaction to proceed with increased formation of secondary degradation products. If the formation of III and IV was monitored each hour, carbonate formation was initially much slower than methanol formation and increased steadily while methanol production remained relatively constant. Carbanilide (V), is visible (solid) in the reaction mixture after the first hour. At the end of 4 hr, the reaction mixture was slushy. The infrared spectrum of the reaction mixture in benzene showed no detectable amounts of isocyanate or carbodiimide.

The cooled reaction mixture was then filtered to remove the carbanilide and the residue was separated into basic and neutral components. The neutral phase yielded additional carbanilide and triphenylisocyanurate (VI). Analysis of the liquid residue via VPC, NMR and IR spectra indicated the presence of the starting material, methyl carbanilate, and a lower-boiling species, methyl N-methylcarbanilate (VII). The structure of VII was defined by comparisons of VPC, NMR, and IR spectra of an authentic mixture of I with VII (prepared from N-methylaniline and methyl chloroformate). A sample of this mixture was successfully separated on a spin-

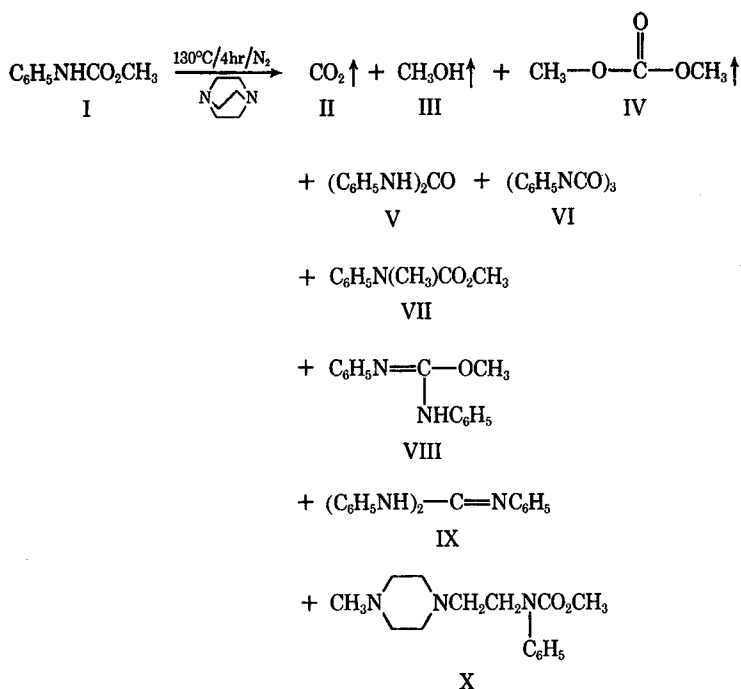


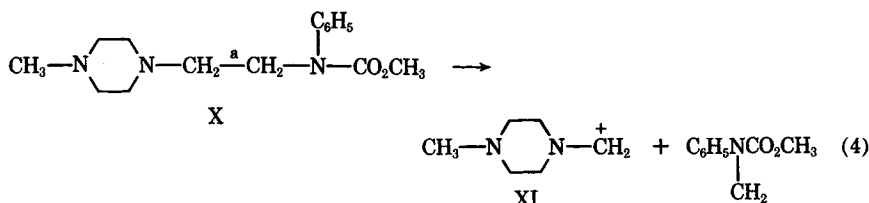
Fig. 1. Scheme 1, showing the products formed in the triethylenediamine-catalyzed pyrolysis of methyl carbanilate.

ning band column. The lower-boiling species was identical in all respects to the independently synthesized sample of VII.

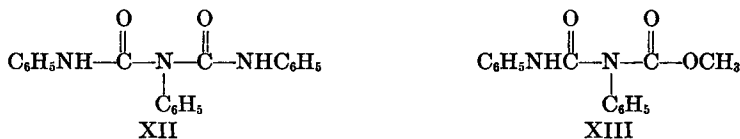
The basic fraction contained the methyl pseudourea VIII, triphenylguanidine, IX, and, the piperazine derivative X, all of which were separable via column chromatography. Both VIII and IX were identical in all respects to authentic samples. The structure of the piperazine derivative X was deduced from the following facts. Since X was found in the basic phase, it was assumed to contain at least one basic nitrogen atom. The IR spectrum exhibited no N—H band and a carbonyl absorption at 5.85μ , indicating that any nitrogen was trisubstituted and that an ester-type grouping was present. The NMR spectrum clearly defined a phenyl group, 7.2δ ; an O—CH₃ group, 4.5δ ; a piperazine ring, 2.3δ ; and a N—CH₃ group, 2.15δ . The C(O)—N—CH₂—CH₂—N grouping was also defined by a set of triplets centered at 3.7δ and 2.4δ with equivalent J values. These triplets were shifted downfield to 3.8δ and 2.5δ , respectively, when the NMR solvent was switched from deuteriochloroform to perdeuterobenzene owing to the interaction of the aromatic solvent with the urethane group.¹⁰

The mass spectrum provided further evidence for the structure of X. The parent peak, with P + 1 and P + 2 peaks, clearly defined the molecular weight and molecular formula of X. The predominant mode of cleavage of this system was, as expected, the rupture of the C—C bond α, β to both the

nitrogen of the piperazine ring and the nitrogen of the urethane group to yield the dehydromethylpiperazine species XI, mass 113, reaction (4).¹¹ Compound X was easily prepared by refluxing stoichiometric amounts of triethylenediamine with methyl carbanilate in a mixture of chlorobenzene and dimethyl carbonate:



Both triphenylbiuret, XII and the allophanate, XIII although stable to the work-up procedures, were not detected in the reaction mixture:



Methyl carbanilate yielded the same products, V-X, on refluxing in chlorobenzene for 25 hr with a catalytic amount of triethylenediamine (Table II). As expected, since neither methanol nor dimethyl carbonate were removed from the reaction mixture, total degradation was less, and 72% of the starting material was recovered in this case, compared to 52% for the neat pyrolysis. The basic fraction in this case was noted to contain more guanidine (IX) than pseudourea (VIII).

Similar degradation products were found when either triethylamine or dimethylaniline was used as catalyst. In these cases, compounds of type X were not found.

Butyl Carbanilate

At the temperature at which methyl carbanilate underwent extensive base-catalyzed degradation, 130°C, butyl carbanilate (XIV) did so only to a very small extent. At 150°C, the uncatalyzed pyrolysis yielded less than 1% butyl alcohol over a 4-hr period. When triethylenediamine was added to butyl carbanilate at this temperature, degradation was evident. The products are shown in Scheme 2 (Fig. 2), and the yields are given in Table III. Carbon dioxide accounts for only 0.6% of the degradation, at 150°, while *n*-butyl alcohol accounts for 2.7%. Again, both carbanilide (V) and the isocyanurate (VI) were isolated from the neutral reaction mixture. However, no *N*-*n*-butyl carbanilate was detected by VPC analysis. The basic components again were triphenylguanidine, IX, the butyl pseudourea XVI, and the piperazine derivative XVII.

Table IV gives the results of pyrolysis of butyl carbanilate at 198–200°C. At this temperature, the uncatalyzed reaction occurs yielding a very small

amount of carbon dioxide and up to 2% of butyl alcohol. The only other compounds detected were the carbanilide from the neutral phase and a trace of pseudourea from the basic phase. When triethylenediamine was added to butyl carbanilate at 200°, extensive decomposition took place (Table IV). At these temperatures no triphenyl isocyanurate nor *N-n*-butyl carbanilate was found; neither was the butyl allophanate nor triphenylbiuret detected.

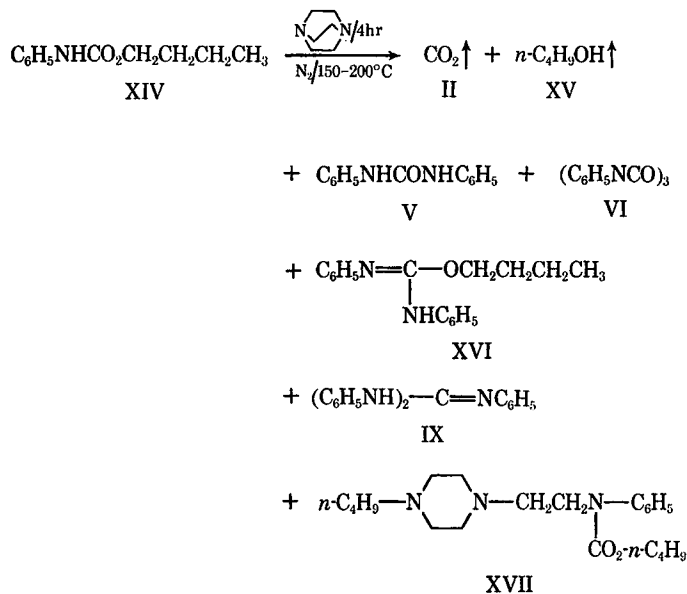


Fig. 2. Scheme 2, showing the products formed in the triethylenediamine-catalyzed pyrolysis of butyl carbanilate.

The piperazine compound, XVII, was also made in large yields by condensing butyl carbanilate with triethylenediamine in the presence of dibutyl carbonate. Comparison of the IR and NMR spectra of compounds XVII and X showed that these two compounds were of the same type, differing only in the alkyl group present in the molecule.

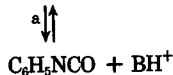
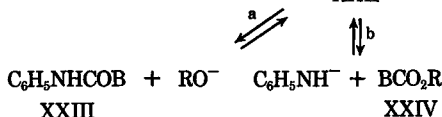
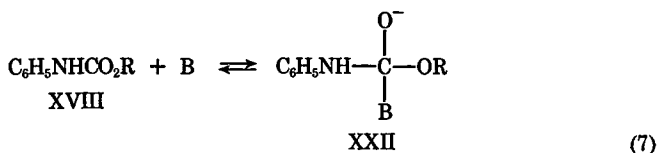
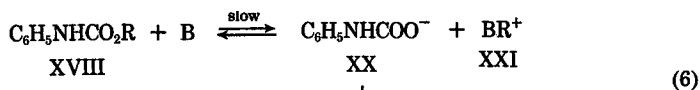
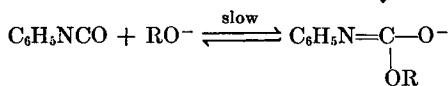
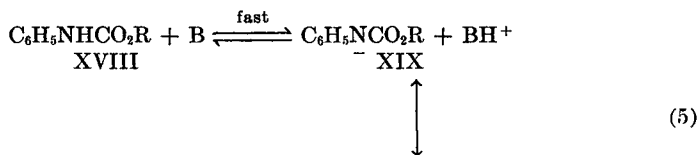
Neopentyl Carbanilate

When neopentyl carbanilate was heated for 4 hr at 200°C with triethylenediamine as catalyst, there was detected in the volatiles only 1.4% carbon dioxide and 3.4% neopentyl alcohol. The residue, however, contained no basic materials! The neutral phase yielded only the starting material from which only a small amount of carbanilide was isolated. Refluxing the neopentyl carbanilate with triethylenediamine in *o*-dichlorobenzene for 24 hr produced the same results, i.e., no basic materials and only a trace of carbanilide.

DISCUSSION

Primary Degradation Processes

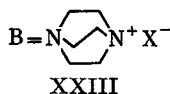
The primary reactions which one can visualize leading to the catalyzed degradation of carbanilates are listed in reactions (5), (6), and (7):



The primary products one can envision being produced from these reactions are the isocyanate and alcohol which make up the starting material, reactions (5) and (7a); carbon dioxide, aniline, an alkylated base, reaction (6); and an ester (XXIV) via reaction (7b). Reaction (5) is undoubtedly faster than the uncatalyzed decomposition of XVIII. When the starting carbanilate was not put through a drying cycle, the amount of alcohol produced was seen to increase in all cases, (Tables II, III, and IV). Increased amounts of alcohol are also known to be produced when amines or other basic materials are added to carbamates. Obviously, these bases facilitate alcohol formation via rapid establishment of equilibrium, reaction (5), and increase carbon dioxide formed by the reaction of isocyanate with water present. Water may also hydrolyze any carbonate formed, thus contributing further to the alcohol and carbon dioxide totals. Under basic conditions, the first step of reaction (5) has been shown to be extremely fast, and it has been demonstrated that the anion XIX has a finite lifetime.^{12,13}

Another primary mode of degradation of a urethane (XVIII) is reaction (6). This S_{N2} displacement of an acid anion from an ester by an amine is well documented.¹⁴⁻¹⁷ Dyer and Wright⁶ have presented evidence proving that reaction (6) was occurring during the high-temperature thermal degradation of carbanilates along with the intramolecular rearrangement (2). In this case, initial first-order degradation is reported to be autocatalytic, while added amines were shown to vary the ratio of basic products in a manner such as could be explained only by reaction (6).⁶ Reaction mechanism (6) must also account for the product differences encountered by Duthie and Plant¹⁸ and Fletcher et al.¹⁹ for the noncatalyzed and the catalyzed degradations of carbamates.

The third degradation route (7a) yields alcohol and carbanilide, B = 1° or 2° amine. Hence, when the amine is aniline or substituted aniline, carbanilide and substituted carbanilides are the expected products. Previous work has demonstrated that this mode of degradation is unfavorable.^{6,20-22} Also, when triethylenediamine is used as a catalyst, products of intermediate XXIII could be expected.²³ In our case, we could find no evidence of the formation of derivatives of triethylenediamine derived from intermediate XXIII,



however, triethylenediamine derivatives of intermediate XXI are insoluble (vide infra).

Further evidence pointing out the fact that N-monosubstituted carbamates prefer to lose a proton to a base rather than undergo substitution via compounds XXII to XXIII is that hydrolysis of N-monosubstituted carbamates occurs many times faster than does the hydrolysis of N,N-disubstituted carbamates.²⁴ Kinetic evidence demonstrated that reaction (5)¹² occurred in preference to reaction (7a), with the slow step being the decomposition of the intermediate anion XIX.

Reaction path (7b) is a possible route to carbonates when the base is an alkoxide. This reaction is known, but only for carbamates whose leaving amine is a very weak base, i.e., diarylamines²⁵ or imidazole.²⁶ Reaction (7b), therefore, cannot be considered a favorable route for carbonate formation. Thus, neither of the pathways of reaction (7) appears as possible route for the degradation of carbanilates at temperatures below 200°C.

Lastly, formation of some of the carbon dioxide is a primary process, a direct result of reaction (6).

It is apparent then that the S_{N2} displacement reaction (6) is a primary reaction leading to degradation of urethanes. To demonstrate the importance of the S_{N2} displacement reaction (6) on initiating the thermal degradation of carbanilates, neopentyl carbanilate was studied. The neopentyl group was chosen because its steric bulk should hinder any nucleophilic attack on the methylene oxygen bond. Thus, any process dependent upon

reaction (6) should be slowed considerably. When the neopentyl carbanilate was subjected to temperatures of 200°C in the presence of triethylenediamine, only very small amounts of carbon dioxide, carbanilide, and alcohol were found. Refluxing a mixture of neopentyl carbanilate and triethylenediamine for 24 hr in *o*-dichlorobenzene also failed to produce any noticeable changes. In either case, no allophanate or biuret was found. Triphenyl isocyanurate and carbanilide must account for the balance of the reaction. We were, however, unable to isolate these small amounts of compounds from the reaction mixture. No basic derivatives of phenyl isocyanate were found in the reaction mixture.

Therefore, the primary degradation processes of carbamates, specifically carbanilates catalyzed by amines below 200°C, are (1) dissociation of the carbamate to isocyanate and alcohol and (2) nucleophilic attack by the base on the carbon attached to the carbamate oxygen to yield an amine, carbon dioxide, and alkylated base. The former case is essentially a reversible reaction and will only lead to degradation when either species can be removed from the equilibrium, either by distillation or by a subsequent reaction of either isocyanate or alcohol with other species present in the reaction mixture. In the latter case, reaction (6), the reaction is irreversible once the carbanilic acid loses carbon dioxide. Then the aniline produced is free to act as a base catalyst, or as a reactant. Similarly, the alkylated catalyst is also now free to react further.

Secondary Reaction Processes: Formation of Neutral Products

Most of the reaction products found in the degradation mixtures arise out of secondary reactions. Carbanilide formation arises partially from the reaction (8) of an isocyanate with aniline produced directly by reaction (6), or by other secondary reactions. Carbanilide can also be formed concurrently with dialkyl carbonates:



Formation of carbonates as reaction products from thermal degradation of urethanes has been noted before.^{7,25-27} This phenomenon has been considered to be minor. This does not appear to be the case especially when alcohol forming the ester linkage is a primary alcohol free of steric hindrance.

When the carbonate formed is volatile, such as methyl or ethyl carbonate, it is easily removed from the reaction mixture as was done during the degradation of methyl carbanilate. Any other alcohol will form a carbonate whose boiling point is too high to cause it to be removed from the reaction mixture at the reaction temperatures used in this study.

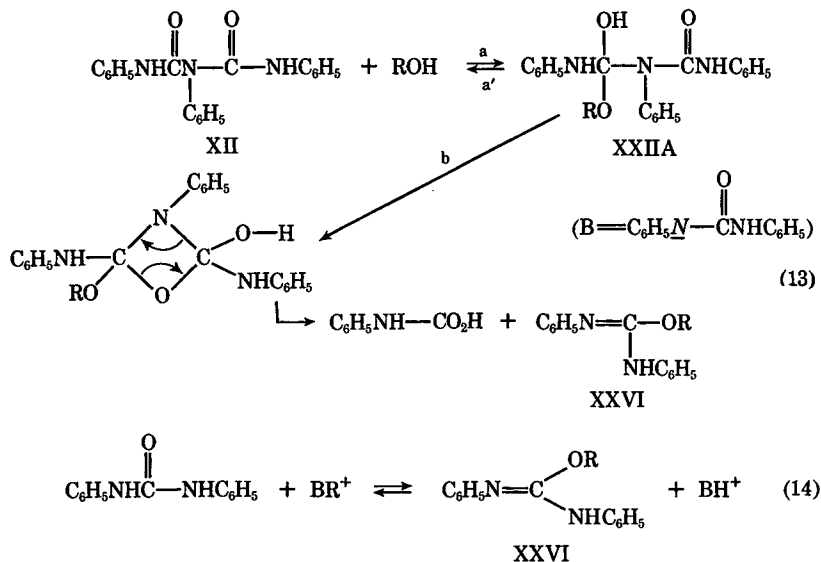
Since it has been demonstrated that reaction (7b) does not account for carbonate production, one must look for an alternate pathway to explain its formation. We propose that carbonate formation occurs via reaction (9), with concurrent formation of carbanilide. Removal of the volatile carbonate species allowed accumulation of product from an otherwise un-

Reaction (11) is a simple alkylation reaction between alkylated base formed in reaction (6) with the starting carbamate. It is suggested that the intermolecular reaction (12) is also responsible for the formation of VII. This reaction is analogous to reaction (6), with the urethane anion XIX also known to be a strong nucleophile, acting as the base.³⁰ The stability of the base XIX has been noted previously,¹³ so it is not unexpected that it is present in sufficient amounts to be a reactant. Also, it will be shown later that XIX is indeed a nucleophilic species capable of an intermolecular displacement reaction (*vide infra*).

Secondary Reaction Processes Formation of Basic Materials

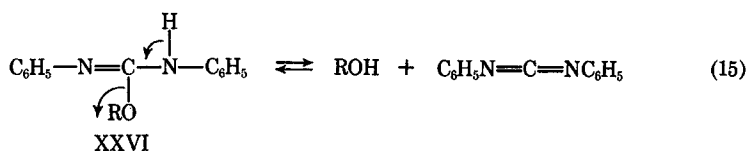
The basic materials, pseudoureas and triphenylguanidine, are definitely secondary products. Their presence depends solely on carbanilide being present in the reaction media. We have demonstrated that carbanilide reacts with carbonates to produce carbanilates in the presence of strong bases. Thus reaction (9) is reversible. When the degradation of a carbanilate is run with an added excess of carbonate so that carbanilide does not accumulate, formation of pseudourea and guanidine are repressed. High temperatures and longer reaction times increased the amount of triphenylguanidine formed.

Since the addition of carbonates to the reaction mixture effectively eliminated the formation of pseudourea and triphenylguanidine, the formation of these products through the intermediacy of diphenylcarbodiimide, formed by the self-condensation of phenyl isocyanate, must be negligible. In addition, the temperatures and catalysts used argue against the intermediacy of carbodiimide. We postulate that these products are formed either through the intermediacy of triphenylbiuret, reaction (13), or via an intermolecular alkylation such as in reaction (11), with the carbanilide acting as an oxygen nucleophile, reaction (14):

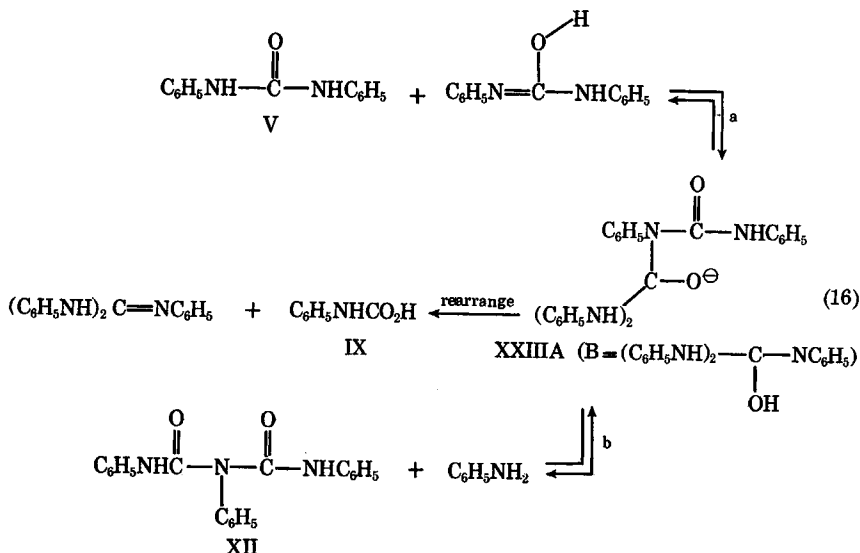


The formation of XXIIA is analogous to the formation of XXIVA from allophanate and alcohol (9). Equilibrium (13a) is unproductive; however, if XXIIA rearranges through a four-centered pathway, reaction (13b), the pseudourea XXVI is formed with concurrent elimination of carbanilic acid. Formation of intermediate XXIIA may also be thought of as occurring via a base-catalyzed condensation of carbanilide with carbanilate.

Diphenylcarbodiimide may be produced from pseudourea by the base elimination of alcohol, reaction (15). Triphenylguanidine, IX, may then be formed by the reaction of aniline with the carbodiimide so formed. Such a reaction sequence would explain the increased production of triphenylguanidine with longer reaction times and higher reaction temperatures and why aniline reacts with pseudourea to form triphenylguanidine at low temperatures in the presence of a strong base:

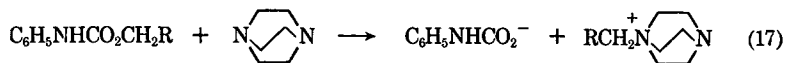


Since carbanilide reacts to form guanidine in the presence of a catalytic amount of sodium, an alternate pathway to guanidine formation may be the direct condensation of carbanilide with itself, reaction (16a); or, as in the case of pseudourea formation (13), intermediate XXIIIA may be thought of as being formed by the reaction of aniline with triphenyl biuret, XII, reaction (16b):

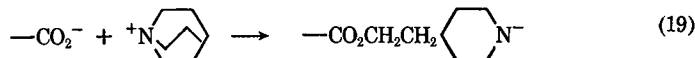


Secondary Reaction Processes: Formation of Piperazine Derivatives

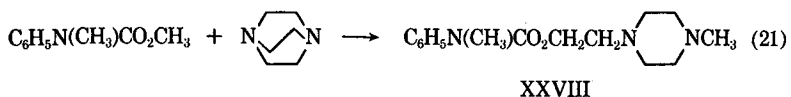
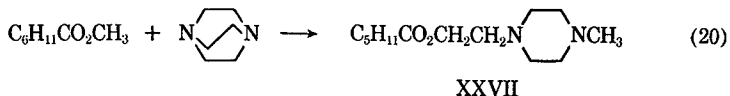
The formation of piperazine compounds X and XVII must have occurred by reaction sequences (17) and (18):



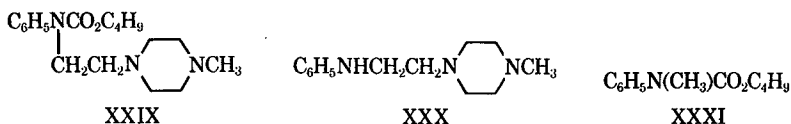
Reaction (17) is simple reaction (6) with the base being triethylenediamine. The stability of the urethane anion has already been discussed as well as the possibility of the nucleophilicity of the carbanilate anion. This reaction sequence is, to our knowledge, the first definitive case of the carbanilate anion acting as a nucleophile in an intermolecular reaction. It also illustrates the ease with which the triethylenediamine species can be converted to piperazine derivatives. A similar type of reaction (19) has recently been reported by Wilson and Beamann.³¹



The quarternary triethylenediamine species has a finite lifetime, and the formation of piperazine compounds is facile and depends only on the anions present in the reaction mixture. For example, when methyl hexanoate was reacted with triethylenediamine, reaction (20), only the ester, XXVII was isolated from the reaction mixture. Similarly when VII was reacted with triethylenediamine, the ester XXVIII was found, reaction (21):



Furthermore, when butyl carbanilate was reacted with triethylenediamine in the presence of methyl hexanoate, not only was product XXVII formed, but the major product turned out to be XXIX. A small amount of compound XXX was also isolated. These reaction products give further evidence of the ease with which an alkylated triethylenediamine species opens to an ethylpiperazine derivative. In this last-mentioned reaction, butyl N-methylcarbanilate, XXXI, was also identified in the neutral reaction mixture:



The reaction mechanisms discussed were based on the product distributions in Tables I, II, and III, as well as on observations noted in the experimental section. In conclusion, secondary neutral products are formed from the allophanate (carbanilide, carbonate, isocyanurate) by the reaction of isocyanate with aniline generated during the reaction process and, in the case of methyl carbanilate, by the action of the carbanilate anion as a base in reaction (6). The base compounds are formed from carbanilide, possibly by means of a biuret intermediate. The use of triethylenediamine as a catalyst leads to formation of novel piperazine compounds. All the bases formed by the thermal degradation of carbanilates are themselves strong bases capable of catalyzing the further degradation of the starting urethane.

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