the liquid under reduced pressure, the residue was separated into two parts: ether insoluble part (III) and soluble part (II).

Reaction of *O-p*-chlorophenyl-*N*,*N*-ethyleneurethan with nucleophilic reagents in the presence of triethylamine and water (Table IV) were carried out in a similar way.

N,N'-Diethyleneurea (IV). *N,N'*-Diethyleneurea was prepared in a way similar to that described by Bestian.[5] (Ether was used as a solvent in this case.) The yield was not good (29%), because of the polymerization during distillation, b.p. 42–43°/0.06 mm., m.p. 38–41°.

Reaction of N,N'-diethyleneurea. (a) *With thiophenol.* To a solution of 1.2 g. of thiophenol in 5 ml. of benzene, 0.6 g. of IV was added at room temperature. The crystals began separating in 2 hr. After standing overnight, they were collected, and recrystallized from alcohol. *N,N'*-Bis(β-phenylthioethyl)urea weighed 1.0 g. (60%).

Reactions of IV with other nucleophilic reagents were carried out in a similar manner. The yield was 22% with benzoic acid, and 55% in the case of *p*-nitrobenzoic acid.

(b) *With hydrochloric acid.* To 1 g. of concd. hydrochloric acid, 0.6 g. of IV was added portionwise. Reaction took place vigorously. The crystals were washed with water and dried, yield 0.6 g. (65%), m.p. 124–126°. (lit.,[5] m.p. 127°).

Conversion of O-p-chlorophenyl-N-(β-substituted ethyl)-urethans to N,N'-bis(β-substituted ethyl)ureas (III) *in the presence of triethylamine and water in dioxane.* To 5 ml. of a solution of 0.2 mole/l. of triethylamine and 40 g./l. of water in dioxane, 0.005 mole of *O-p*-chlorophenyl-*N*-(β-substituted ethyl)urethan was added, and the reaction mixture was allowed to stand for 24 hr. at 35°. After distillation of the liquid substances, the residue was recrystallized.

O-p-Chlorophenyl-N-n-butylurethan, O-p-chlorophenyl-N-(β-chloroethyl)urethan and O-p-chlorophenyl-N-(β-picrylethyl)urethan were recovered.

In the case of *O-p*-chlorophenyl-*N*-(β-bromoethyl)urethan, m.p. 105–106° (*Anal.* Calcd. for $C_9H_9BrClNO_2$: N, 5.03. Found: N, 5.21) and *O-p*-chlorophenyl-*N*-(β-iodoethyl)urethan, m.p. 116–118° (*Anal.* Calcd. for $C_9H_9ClINO_2$: N, 4.30. Found: N, 4.35.), urethans were recovered in lower yield and the formation of Br^- or I^- was observed under these conditions.

In the following examples, III was obtained: In the case of *O-p*-chlorophenyl-*N*-(β-phenylthioethyl)urethan, *N,N'*-bis-(β-phenylthioethyl)urea in 30% yield; in the case of *O-p*-chlorophenyl-*N*-(β-phenyloxyethyl)urethan (this urethan was prepared from *p*-chlorophenyl chloroformate and β-phenyloxyethylamine, m.p. 73–75°).

Anal. Calcd. for $C_{15}H_{14}ClNO_3$: N, 4.80. Found: N, 4.84.), *N,N'*-bis(β-phenyloxyethyl)urea, m.p. 159–160°, in 10% yield; and with *O-p*-chlorophenyl-*N*-(β-benzoyloxyethyl)-urethan, *N,N'*-bis(β-benzoyloxyethyl)urea (Table IV) in 30% yield, were obtained respectively.

Conversion of O-p-chlorophenyl-N-(β-substituted ethyl)-urethans to N,N'-bis(β-substituted ethyl)ureas in dimethylformamide in the presence of water. In 1 ml. of dimethylformamide containing 0.2 g. of water, 310 mg. of *O-p*-chlorophenyl-*N*-(β-phenylthioethyl)urethan was added, and the solution allowed to stand at 35°. After 24 hr., the reaction mixture was poured into a large amount of cold water. The precipitate was filtered off, and dried. Extraction with ether gave 140 mg. of unchanged urethan. The residue was recrystallized from alcohol to give 80 mg. (48%) of *N,N'*-bis-(β-phenylthioethyl)urea.

In the same manner, 240 mg. of *O-p*-chlorophenyl-*N*-(β-chloroethyl)urethan was treated. The recovered urethan weighed 220 mg.

Acknowledgment. We wish to express our appreciation to Dr. A. Kondo of our institute for analyses, and also to Miss Y. Kada for infrared spectral data.

OOKAYAMA, MEGURO-KU, TOKYO, JAPAN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF DELAWARE]

Thermal Degradation of *O*-1-Hexadecyl *N*-1-Naphthylcarbamates and Related Compounds

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The products from pyrolysis of *O*-1-hexadecyl *N*-1-naphthylcarbamate at 255–275° were carbon dioxide, *N*-1-hexadecyl *N*-1-naphthylamine, 1-hexadecanol, and the trimer of 1-naphthyl isocyanate. At 137°, the lowest temperature at which carbon dioxide was evolved, small amounts of di-1-hexadecyl carbonate and 1,3-di-1-naphthylurea were formed. The pyrolysis of *O*-1-hexadecyl *N*-1-propyl-*N*-1-naphthylcarbamate at 265–280° gave carbon dioxide, 1-hexadecene, and *N*-1-naphyl-*N*-1-propylamine. Mechanisms of degradation of both carbamates are considered with reference to the products, to the kinetics of evolution of carbon dioxide, and to the species of carbon dioxide formed on pyrolysis of samples containing an O^{18}-enriched 1-hexadecanol moiety.

Previous work[2,3] on the pyrolysis of carbamates showed that two major paths were (a) dissociation to isocyanate and alcohol and (b) breakdown (probably cyclic) giving olefin, amine, and carbon dioxide. Subsequent reactions included the decomposition of the isocyanate to carbodiimide[2] and the attack of the amine product on the carbamate,[3] giving substituted amines. The purpose of the present investigation was to secure further information on the relative importance of various pyrolysis routes, using *O*-1-hexadecyl *N*-1-naphthylcarbamate, and *O*-1-hexadecyl *N*-1-propyl-*N*-1-naphthylcarbamate. The former carbamate was chosen to approximate in physical properties the bisurethans studied previously.[2] The latter carbamate is an example of an *N*-disubstituted carbamate in which dissociation by path (a) is excluded.

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(1) From the Ph.D. thesis, University of Delaware, of Robert E. Read, Armstrong Cork Co. Research Fellow, 1957–60.

(2) E. Dyer and G. E. Newborn, *J. Am. Chem. Soc.*, **80**, 5495 (1958).

(3) E. Dyer and G. C. Wright, *J. Am. Chem. Soc.*, **82**, 2138 (1959).

TABLE I

PYROLYSIS PRODUCTS OF *N*-1-NAPHTHYLCARBAMATES

Run No.	Carbamate	Moles	Temp.	Time, Hr.	CO_2, Mole %	Amine Name	Amine Mole %	Other Products Name	Other Products Mole %
1	HNC[a]	0.0539	275	48	45	HNA[b]	22	Cetyl alc.[c]	31
								$(NI)_3$[d]	17
2	HNC	0.0598	275	110	41	HNA	39	Cetyl alc.	51
								$(NI)_3$	9
								DNU[e]	0.5
3	HNC[f]	0.0514	275	6	59	HNA	20	DNU	2
4	HNC[f,g]	0.0188	137	54	27			DHC[h]	1
								DNU	34
5	HNC	0.0189	255	2					
			137	90	25			DHC	2
6	HNC	0.0233	255	8	10			DHC	10
								DNU	1
7	HNC[g,i]	0.0042	137	118	24			Pseudourea[j]	76[k]
8	HNC[f,g,l]	0.0097	137	171	95[n]			Pseudourea[j]	95[m]
9	HPNC[n]	0.0066	275	44	76	NPA[o]	50	1-Hexadecene	50
10	HPNC	0.0111	275	8	16	NPA[o]	10	1-Hexadecene	10

[a] *O*-1-Hexadecyl *N*-1-naphthylcarbamate. [b] *N*-1-Hexadecyl *N*-1-naphthylamine. [c] 1-Hexadecanol. Yield includes less than 1% di-1-hexadecyl ether. [d] 1-Naphthyl isocyanate trimer. [e] 1,3-Di-1-naphthylurea. [f] With 0.31 g. of manganese naphthenate per mole of carbamate. [g] Run in 50–100 ml. of dry xylene. [h] Di-1-hexadecyl carbonate. [i] In the presence of 50 mole % di-1-naphthylcarbodiimide. [j] 1,3 Di-1-naphthyl-2-hexadecyl pesudourea. [k] Yield based on added carbodiimide. [l] In the presence of 61 mole % 1-naphthyl isocyanate. [m] Yield based on isocyanate added. [n] *O*-1-Hexadecyl *N*-1-naphthyl-*N*-1-propylcarbamate. [o] *N*-1-Naphthyl-*N*-1-propylamine; no tertiary amine found.

The pyrolyses were followed by determining the rates of evolution of carbon dioxide and by separating the other products. At high temperatures secondary amines were major products of decomposition of both carbamates. Efforts were made to trace the origin of the secondary amine obtained from *O*-1-hexadecyl *N*-1-naphthylcarbamate.

Pyrolysis of O-1-hexadecyl N-1-naphthylcarbamate at high temperatures. The products obtained from heating *O*-1-hexadecyl *N*-1-naphthylcarbamate at 275° under dry nitrogen are listed in Table I (Runs 1, 2, 3). In addition to 1-hexadecanol and the isocyanate trimer, *N*-1-hexadecyl *N*-1-naphthylamine was obtained in yields close to those of the carbon dioxide.

Hence the process leading to the formation of *N*-1-hexadecyl *N*-1-naphthylamine probably also gave rise to much of the evolved carbon dioxide. Found in trace amounts were 1,3-di-1-naphthylurea and di-1-hexadecyl ether. The product balance accounts for 90% of the 1-hexadecyl moiety of the hexadecyl *N*-1-naphthylcarbamate and for only 70% of the 1-naphthyl isocyanate moiety, probably due to the high affinity of the alumina chromatography columns for the pyrolysis products.

The evolution of carbon dioxide by heating *O*-1-hexadecyl *N*-1-naphthylcarbamate at 255–275° under dry nitrogen followed a first-order rate law to 20–25% completion (Table II). At greater extents of reaction the rate decreased markedly. This could be attributed to the conversion of the carbamate (none of which was found in the pyrolysis residue) to 1-hexadecanol and the very stable isocyanate trimer, triphenylisocyanurate).

TABLE II

RATES OF CARBON DIOXIDE EVOLUTION FROM PYROLYSIS OF *N*-1-NAPHTHYLCARBAMATES AND 1-NAPHTHYL ISOCYANATE

Cpd.	Temp.[a]	Rate Constants[b,c] $k_1 \times 10^6$	Rate Constants[b,c] $k_2 \times 10^7$	CO_2,[d] Mole %	ΔH*, Kcal.[e]
HNC[f]	255	4.6		20	34
	265	5.9		22	
	275	13[g]		21	
NI[h]	255[i]		0.55	4	49
	265		1.3	6	
	268		1.7	6	
	273		3.5		
HPNC[j]	265	1.8		8[k]	62
	275	6.1		21[k]	
	280	7.4		30[k]	

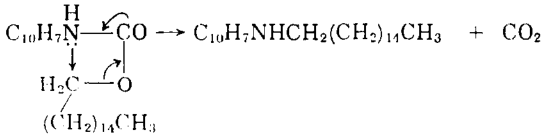
[a] Held to 0.5°, except for NI at 265° where rate data are an average of results at 266° and 265°. The over-all accuracy of the k values is ±4–5%; accuracy of ΔH is ±5% for HNC, ±8% for NI and ±7% for HPNC. [b] The k_1 values are in sec.$^{-1}$; the k_2 values in l. mole^{-1} sec.$^{-1}$ [c] Usually averages of two or three determinations in which the average deviation was 1–3%. [d] Per cent completion of reaction following a linear plot. [e] Approx. values, due to small temp. intervals. Estimated values of ΔS*, for HNC at 255°, −3.1 e.u.; for NI at 265°, −23 e.u.; for HPNC at 265°, −45 e.u. [f] *O*-1-Hexadecyl *N*-1-naphthylcarbamate, 0.004–0.06 mole. [g] Average deviation, 6%. [h] 1-Naphthyl isocyanate, 0.03–0.04 mole. [i] 1-Methoxynaphthalene as solvent. [j] *O*-1-Hexadecyl *N*-1-propyl-*N*-1-naphthylcarbamate, 0.0066–0.011 mole. [k] Measurement stopped, but plot of reaction still linear.

It is of interest to compare the above results with those reported for the pyrolysis of the carbanilates.[3] The rate of carbon dioxide formation from the carbanilates was also found to obey a first-order law at low extents of pyrolysis. But, in contrast to the present study, the deviation from first-order kinetics was the result of a marked increase in rate. It was shown that this increase in rate was due to the effect of the aniline and secondary amines related to aniline that were major components of the carbanilate pyrolysis residues. The secondary amine, hexadecyl naphthylamine of the present study, appears unable to engage in those reactions which, in the carbanilate series, lead to enhanced rates of carbon dioxide evolution and perhaps contribute to the formation of such products as olefin and primary and tertiary amines. The failure of the hexadecyl naphthylamine to increase the rate of pyrolysis of the naphthylcarbamate might be attributed to a steric effect due to the large groups on nitrogen. In accord with this supposition is the sluggish reactivity of this amine toward methyl iodide under alkylation conditions. A similar steric hindrance might account for the previously observed[3] lack of rate enhancement of the pyrolysis of benzyl carbanilate by dibenzylaniline, whereas benzylaniline increased the rate markedly.

A further comparison of the pyrolysis products from the naphthylcarbamate and the carbanilates concerns the formation of olefins. With both ethyl carbanilate[3] and hexadecyl *N*-1-naphthylcarbamate, no olefin was produced on pyrolysis, although in both cases it was looked for. Therefore, it appears that olefin formation is not a necessary accompaniment of carbon dioxide formation in carbamates derived from primary alcohols containing a free beta hydrogen.

This observation, together with the fact that the yields of secondary amine and carbon dioxide were nearly equal in the pyrolysis of the hexadecyl naphthylcarbamate, indicates that this carbamate decomposes by a mechanism different from that of the carbanilate of the secondary alcohol previously studied[3] which gave large quantities of olefin. (The latter compound was assumed to decompose by an initial intramolecular degradation to carbamic acid and olefin, followed by amine displacements.)

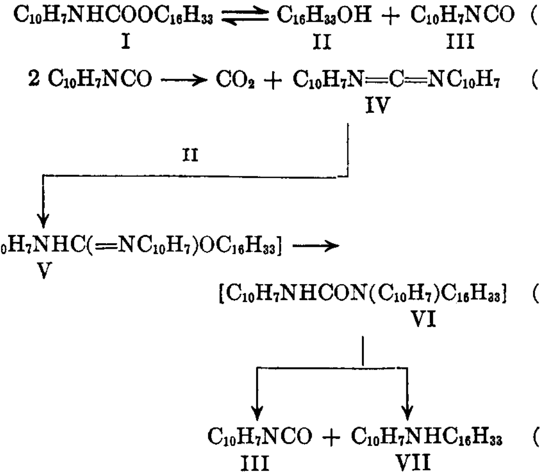
It is suggested that the hexadecyl naphthylcarbamate decomposes chiefly by a concerted intramolecular displacement of the following type:



$$C_{10}H_7\overset{H}{N}—CO \longrightarrow C_{10}H_7NHCH_2(CH_2)_{14}CH_3 + CO_2 \quad (1)$$

Degradation by an intramolecular route would be in accord with the observed first-order kinetics of the carbon dioxide evolution. Moreover, the negative entropy of activation (Table II) suggests a four-center reaction,[4] and the energy of activation is similar in magnitude to that of several cyclic degradation reactions.[5]

An alternative route for the pyrolysis of the hexadecyl naphthylcarbamate (I) would give initially 1-hexadecanol (II) and naphthyl isocyanate (III). Two moles of the latter could condense to give carbon dioxide and di-1-naphthylcarbodiimide (IV).[6] Reaction of the carbodiimide (IV) with 1-hexadecanol (II) would yield the pseudourea (V). In view of the reported thermal isomerization[7] of *N*-disubstituted *O*-alkylpseudoureas to trisubstituted ureas, compound V would be expected to rearrange to the trisubstituted urea (VI). This urea should split thermally to the secondary amine (VII) and the isocyanate (III).[8] The isocyanate could then be recycled with the further formation of carbon dioxide and secondary amine.



$$\underset{I}{C_{10}H_7NHCOOC_{16}H_{33}} \rightleftharpoons \underset{II}{C_{16}H_{33}OH} + \underset{III}{C_{10}H_7NCO} \quad (2)$$

$$2\,C_{10}H_7NCO \longrightarrow CO_2 + \underset{IV}{C_{10}H_7N{=}C{=}NC_{10}H_7} \quad (3)$$

$$\xrightarrow{II} \underset{V}{[C_{10}H_7NHC({=}NC_{10}H_7)OC_{16}H_{33}]} \longrightarrow \underset{VI}{[C_{10}H_7NHCON(C_{10}H_7)C_{16}H_{33}]} \quad (4)$$

$$\longrightarrow \underset{III}{C_{10}H_7NCO} + \underset{VII}{C_{10}H_7NHC_{16}H_{33}} \quad (5)$$

The potential importance of the isocyanate in this degradation scheme prompted studies of the pyrolysis of the isocyanate alone, a test of the pseudourea (V) as a possible intermediate, and pyrolysis of an isotopically labeled variety of the carbamate.

Pyrolysis of 1-naphthyl isocyanate. When heated without solvent at 255–275°, 1-naphthyl isocyanate gave off carbon dioxide in a yield of 90% or greater. The carbon dioxide evolution followed a second-order rate law up to about 6% completion (Table II) and then the rate was greatly increased, as typical of an autocatalytic reaction.

Examination of the products of the pyrolysis after about 4% completion showed a high content of carbodiimide (by infrared absorption). The catalytic effect of the carbodiimide was indicated by the greatly increased rate of carbon dioxide evolution in a pyrolysis of naphthyl isocyanate carried on in the presence of 0.99 mole % of the carbodiimide. A graph of a pyrolysis reaction containing 0.3 mole % of added carbodiimide when

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(4) J. Hine, *Physical Organic Chemistry*, McGraw-Hill Book Co., New York, N. Y., 1956, pp. 453–465.

(5) C. H. DePuy and R. W. King, *Chem. Revs.*, **60**, 431 (1960).

(6) H. G. Khorana, *Chem. Revs.*, **53**, 145 (1953).

(7) J. R. Robinson and W. H. Brown, *Can. J. Chem.*, **29**, 1069 (1951); J. R. Robinson, *Can. J. Chem.*, **32**, 557 (1954).

(8) W. B. Bennet, J. H. Saunders, and E. E. Hardy, *J. Am. Chem. Soc.*, **75**, 2101 (1953).

plotted as a third-order autocatalytic reaction showed linearity to at least 21% completion. These results suggest that the accelerating action of the carbodiimide is due to the formation of a complex with the isocyanate. 1,3-Dinaphthylurea also acted as a catalyst for the decomposition of the isocyanate.

Although carbodiimide was present during the early stages of the pyrolysis of the 1-naphthyl isocyanate, it could not be detected by spectral methods in the reaction mixtures of runs carried to 80–90% conversions. Instead, several yellow compounds were present. The major one, comprising over 40% of most of these mixtures, appeared to be a dimer of the carbodiimide, easily converted to a trimer.

These data indicate that the carbodiimide could be formed as a possible intermediate under the pyrolysis conditions used for the carbamate, *O*-1-hexadecyl *N*-1-naphthylcarbamate.

Test of 1,3-Di(1-naphthyl)-2-hexadecylpseudourea as a source of secondary amine in the degradation of hexadecyl N-1-naphthylcarbamate. 1-Hexadecanol (II) was found to react with dinaphthylcarbodiimide (IV) at 265° to give a high yield of the pseudourea (V). In an attempt to induce the thermal rearrangement of V to give first the urea (VI) and subsequently the amine (VII) and 1-naphthyl isocyanate, the pseudourea (V) was heated from six to forty-eight hours at various temperatures ranging between 133 and 275°. The products included carbon dioxide in up to 50% yield, about 17% 1-hexadecanol, traces of dinaphthylurea and 1-hexadecene, and a variety of bright yellow, nitrogenous residues. Heating of V in the presence of equivalent amounts of 1-hexadecanol or 1-naphthylamine gave similar products. It is to be noted that neither the secondary amine VII nor the trisubstituted urea VI was a product of the pyrolysis of the pseudourea under conditions duplicating those encountered in the pyrolysis of the hexadecyl naphthylcarbamate (II). Therefore, the pseudourea V does not seem to be a satisfactory source of the observed amine VII, although it could be one source of the evolved carbon dioxide.

Pyrolysis of O^{18}-enriched O-1-hexadecyl N-1-naphthyl carbamates. 1-Hexadecanol enriched with O^{18} was used to prepare *O**-1-hexadecyl-*N*-1-naphthylcarbamate, which was alkylated to give *O**-1-hexadecyl *N*-1-naphthyl-*N*-1-propylcarbamate. The two carbamates were pyrolyzed under identical conditions and the species of carbon dioxide produced were determined by a mass spectrometer.

TABLE III

CARBON DIOXIDE FROM PYROLYSIS OF O^{18}-ENRICHED *O*-1-HEXADECYL *N*-1-NAPHTHYLCARBAMATES

	Relative % of Total CO_2		
Carbamates[a]	$O^{18}CO^{18}$	$O^{18}CO$	OCO
HNC	0.3	3.4	96.3
HPNC	0	7.9	92.1

[a] Degraded at 275° under helium, using 0.0060 mole of HNC and 0.0065 mole of HPNC and carrying the pyrolysis to the same amount of evolved CO_2.

Table III shows that 7.9% of the carbon dioxide from the *N*,*N*-disubstituted carbamate was of the tagged variety. Since both carbamates were prepared from the same batch of O^{18}-enriched 1-hexadecanol, the total O^{18} content should be the same in both. The absence of doubly tagged carbon dioxide in the gases from the *N*,*N*-disubstituted carbamate indicates that no exchange reactions occurred during the pyrolysis of this carbamate. Under these conditions there is no tendency for the alkyl group to migrate to the carbonyl oxygen.

As shown in Table III, the pyrolysis of the O^{18}-enriched, monosubstituted carbamate furnished a small but significant amount of doubly tagged carbon dioxide and gave different amounts of the other species than came from the *N*,*N*-disubstituted carbamate. Also, a considerable percentage of O^{18} remained in the pyrolysis residues. The doubly tagged carbon dioxide could not have resulted from the simple intramolecular decomposition of Equation 1, but must have come from the isocyanate, which cannot be formed from the disubstituted carbamate. The conversion of the isocyanate to the carbodiimide (IV) and of the carbodiimide to an O^{18}-containing pseudourea (V) (Equations 2–5) followed by the reactions 6 and 7 below could explain the origin of the doubly tagged carbon dioxide.

$$C_{10}H_7NHC({=}NC_{10}H_7)O^*C_{16}H_{33} \longrightarrow C_{10}H_7NCO^* + \text{other products} \quad (6)$$

$$2\ C_{10}H_7NCO^* \longrightarrow {}^*OCO^* + C_{10}H_7N{=}C{=}NC_{10}H_7 \quad (7)$$

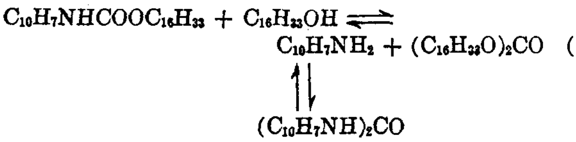
Thus, the thermal degradation of *O*-1-hexadecyl *N*-1-naphthylcarbamate involves not only a major intramolecular decarboxylation leading to the concomitant formation of the secondary amine (VII) and carbon dioxide, but also a minor side reaction in which additional carbon dioxide is postulated to be formed through the conversion of isocyanate to carbodiimide and subsequent reactions leading to the formation of doubly tagged carbon dioxide.

Further evidence that the secondary amine and some of the carbon dioxide are produced by different routes on pyrolysis of *O*-1-hexadecyl *N*-1-naphthylcarbamate is given by the data of Experiment 3 in Table I. When *O*-1-hexadecyl *N*-1-naphthylcarbamate was pyrolyzed at 275° in the presence of manganese naphthenate as catalyst, the yield of carbon dioxide after a short time was much greater than that of an uncatalyzed reaction, but the yield of the secondary amine was the same as might have been expected for an uncatalyzed reaction. Had both the amine and carbon dioxide been formed as the result of the same reaction or within the same point in a series of reactions, their yields should have shared a common enhancement.

It is of interest that recent work on pyrolysis of polythiolcarbamates[9] shows that two types of degradation occur, a decomposition involving isocyanate leading to carbon dioxide and an elimination reaction giving carbonyl sulfide and olefins.

Pyrolysis of O-hexadecyl N-1-naphthylcarbamate under mild conditions. Di-1-hexadecyl carbonate and 1,3-di-1-naphthylurea were formed when the carbamate was heated at 137° with a catalyst for a long time or at 255° for a short time, as shown in Table I (Runs 4–6). Carbonate formation from heating carbamates in the presence of catalysts was previously reported by Gaylord[10] and by Laakso and Reynolds.[11]

The carbonate could arise from dissociation of the carbamate to alcohol and isocyanate, followed by attack of the free alcohol on the carbamate[10] to give naphthylamine and the carbonate. The amine would react at once with isocyanate to form the urea.[12]

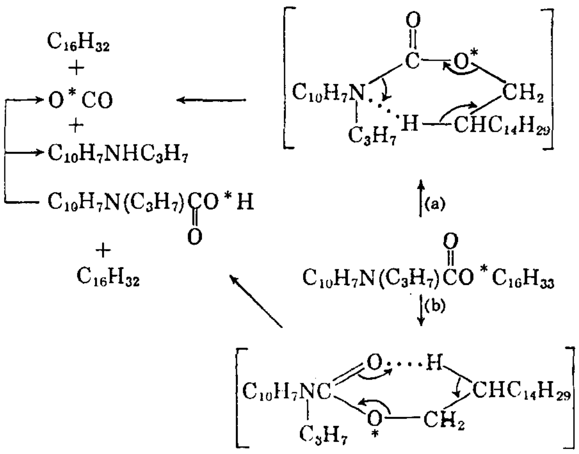


$$\begin{array}{l} C_{10}H_7NHCOOC_{16}H_{33} + C_{16}H_{33}OH \rightleftharpoons \\ \qquad\qquad C_{10}H_7NH_2 + (C_{16}H_{33}O)_2CO \quad (8) \\ \qquad\qquad\quad \upharpoonleft\downharpoonright \\ \qquad\qquad (C_{10}H_7NH)_2CO \end{array}$$

Evidence of the formation of the necessary hexadecanol by dissociation of the carbamate at 133° was obtained by heating the carbamate I in the presence of a trap for the alcohol, *N,N′*-di-1-naphthylcarbodiimide. Under these conditions 1,3-di-1-naphthyl-2-hexadecyl pseudourea was formed (Table I, runs 7 and 8). The carbodiimide was both added to the reaction as such and generated *in situ* through the catalyzed condensation[13] of 1-naphthyl isocyanate.

At 275° reaction 8 was shown to be easily reversible. Moreover, the pyrolysis residues from heating *O*-hexadecyl *N*-1-naphthylcarbamate for long times at 275° included none of the carbonate, only small amounts of the urea, traces of di-1-hexadecyl ether and no 1-hexadecene. (The ether and olefin would be logical degradation products of the carbonate.) Hence at high temperatures the carbonate could be a source of only small amounts of the evolved carbon dioxide. The carbonate and urea are not plausible intermediates for the formation of the major degradation product, the secondary amine.

Pyrolysis of O-1-hexadecyl N-1-propyl-N-1-naphthylcarbamate. When this *N*-disubstituted carbamate was subjected to pyrolysis under nitrogen at 265–280°, carbon dioxide was evolved according to a first-order rate law during at least 30% of reaction (Table II). An examination of the pyrolysis products by vapor phase chromatography showed that 1-hexadecene and *N*-1-propyl-*N*-1-naphthylamine were formed in equal amounts (Table I, runs 9 and 10). No tertiary amine was found. The pyrolysis of the O^{18}-labeled *N*-disubstituted carbamate (Table III) gave only those species of carbon dioxide expected for a simple intramolecular displacement reaction. The reaction could proceed by path (a) or path[5] (b) shown below. The present data do not discriminate between these two possibilities.



CONCLUSIONS

The *N*-disubstituted carbamate decomposed at 275° by a simple, intramolecular elimination reaction to give carbon dioxide and equal quantities of olefin and secondary amine.

The decomposition of the *N*-monosubstituted carbamate at 275° was complex, with carbon dioxide formed by at least two different paths. The major reaction was the formation of carbon dioxide and *N*-1-hexadecyl *N*-1-naphthylamine probably by an intramolecular displacement. A minor route to carbon dioxide involved the initial decomposition of the carbamate to alcohol and isocyanate, followed by formation of carbodiimide and pseudourea ether. The latter compound, however, was not a satisfactory source of the observed hexadecyl naphthylamine.

Under milder conditions other minor products from the *N*-monosubstituted carbamate were di-1-hexadecyl carbonate and di-1-naphthylurea, also originating from dissociation of the carbamate to isocyanate and alcohol. These substances are not considered to be intermediates for the major products of degradation at 275°.

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EXPERIMENTAL

Carbamates. O-1-Hexadecyl N-1-naphthylcarbamate[14] was prepared in 82% yield from a dry ether solution of equivalent quantities (0.504 mole) of distilled 1-naphthyl isocyanate and recrystallized 1-hexadecanol in the presence of 0.05 g. of 1,4-diaza[2.2.2]bicyclooctane.[15] *O*-Ethyl *N*-1-naphthylcarbamate[16] was prepared similarly (in 86% yield).

O-1-Hexadecyl N-1-propyl-N-1-naphthylcarbamate was prepared from *O*-1-hexadecyl *N*-1-naphthylcarbamate by alkylation with *n*-propyl bromide and sodium hydride, using the technique of Dannley and Lukin.[17] The product, obtained in 91% yield after chromatography of a benzene solution on alumina and distillation under nitrogen, boiled at 240–242° at 2–3 mm.

Anal. Calcd. for $C_{30}H_{47}NO_2$: C, 79.42; H, 10.44; N, 3.09. Found: C, 79.29; H, 10.32; N, 2.92.

O-Ethyl N-1-propyl-N-1-naphthylcarbamate was obtained in 81% yield by the same alkylation procedure.[17] It was distilled at 143–144° at 0.6 mm.; m.p. 47.5–48° (from *n*-hexane).

Anal. Calcd. for $C_{16}H_{19}NO_2$: C, 74.68; H, 7.44; N, 5.45. Found: C, 74.82; H, 7.33; N, 5.52.

An exploratory pyrolysis of this compound gave a linear first-order plot to at least 20% completion at 265°; the k value was 2.02×10^{-6} sec.$^{-1}$

N-1-Hexadecyl N-1-naphthylamine was prepared by alkylation of 1-naphthylamine with 1-bromohexadecane[18] in xylene with sodium hydride dispersion. The product, obtained in 72% yield after recrystallization from 1-butanol, melted at 53°. After chromatography on alumina with benzene as eluent, the m.p. was 55–57°.

Anal. Calcd. for $C_{26}H_{41}N$: C, 84.95; H, 11.24; N, 3.81. Found: C, 84.39; H, 11.27; N, 4.00.

This amine did not react with 1-bromohexadecane or with methyl iodide under alkylation conditions.

Di-1-hexadecyl carbonate. A mixture of 50.0 g. (0.234 mole) of diphenyl carbonate, 113.4 g. (0.468 mole) of 1-hexadecanol and 0.2 g. of aluminum isopropoxide was heated in a bath at 230° first at atmospheric pressure and then under reduced pressure to remove most of the phenol formed. The residue was dissolved in benzene, washed five times with 20% sodium hydroxide, and the benzene layer was dried and the solvent evaporated. The product consisted of 96.0 g. (81% yield) of crystals, m.p. 43° (from 2-propanol), which showed strong infrared absorption at 5.74 μ.

Anal. Calcd. for $C_{33}H_{66}O_3$: C, 77.68; H, 13.02. Found: C, 77.77; H, 13.15.

N,N',N''-Tri-1-naphthylguanidine. This guanidine, prepared as a reference compound, was obtained in 98% yield from di-1-naphthyl carbodiimide and 1-naphthylamine in refluxing xylene. It was recrystallized from methanol or chloroform to give fine needles, m.p. 186°. The melting point, unchanged by chromatography of the compound on activated alumina, was appreciably higher than that reported[19] (178°) for the guanidine made through the thiourea synthesis.

Anal. Calcd. for $C_{31}H_{23}N_3$: C, 85.10; H, 5.30; N, 9.60. Found: C, 85.19; H, 5.38; N, 9.71.

Low polymers of di-1-naphthylcarbodiimide. When the pyrolysis of 1-naphthyl isocyanate at 255–280° was carried to 90% completion (as indicated by evolution of carbon dioxide), the residue contained a mixture of yellow substances. By chromatography on activated alumina the major component was separated (about 40% of the whole), as a compound melting at 167–169°. This was not di-1-naphthylcarbodiimide (m.p. 91°)[20] or 1-naphthylcarbostyryl[21] but appeared to be an unstable dimer of the carbodiimide.

Anal. Calcd. for $(C_{21}H_{14}N_2)_2$: C, 85.70; H, 4.75; N, 9.52; mol. wt., 588. Found: C, 85.48; H, 5.21; N, 9.59; mol. wt. (ebullioscopic in benzene), 520.

When the dimer, m.p. 167–169°, was refluxed with methanol, it was converted to a trimer, melting at 218–219°. The latter substance was changed by chromatography on alumina to the dimer. The infrared absorption spectrum of the trimer had a strong band at 6.1 μ and in general resembled the spectra of *N,N',N''*-triarylguanidines.

Anal. Calcd. for $(C_{21}H_{14}N_2)_3$: C, 85.70; H, 4.75; N, 9.52; mol. wt., 882. Found: C, 85.52; H, 4.74; N, 9.42; mol. wt., 840 (ebullioscopic in carbon tetrachloride).

1,3-Di(1-naphthyl)-2-hexadecyl pseudourea. This new compound, m.p. 65–66° after recrystallization from methanol was prepared in 97% yield (crude) from di-1-naphthylcarbodiimide, 1-hexadecanol, and sodium by the method of Khorana,[22] using xylene-dimethylformamide solution. The compound was also formed at 265° without catalyst or solvent (88% yield in 35 min.).

Anal. Calcd. for $C_{37}H_{48}N_2O$: C, 82.84; H, 8.96; N, 5.22. Found: C, 82.37; H, 9.13; N, 5.20.

1,3-Di(1-naphthyl)-1-propylurea. The *N*- and *O*-propyl derivatives of di-1-naphthylurea were prepared for comparative purposes. Treatment of di-1-naphthylurea with 1-bromopropane and sodium hydride in a mixture of dimethylformamide and xylene gave a 60% yield of the crude *N*-alkylation product, m.p. 142–143° after chromatography on alumina and recrystallization from ether.

Anal. Calcd. for $C_{24}H_{22}N_2O$: C, 81.32; H, 6.26; N, 7.91. Found: C, 81.05; H, 6.20; N, 8.04.

1,3-Di(1-naphthyl)-2-propylurea. To a solution of sodium in 30 ml. of 1-propanol was added 0.0034 mole of di-1-naphthylcarbodiimide and the mixture refluxed for 30 min. On addition of 5 ml. of water and 3 ml. of methanol, 1.18 g. of product separated (98% yield). Recrystallization from 2-propanol gave needles, m.p. 113–113.5°.

Anal. Calcd. for $C_{24}H_{22}N_2O$: C, 81.32; H, 6.26; N, 7.91. Found: C, 81.14; H, 6.17; N, 8.11.

Pyrolysis of 1,3-di(1-naphthyl)-2-hexadecyl pseudourea. This compound was undecomposed by heating in xylene at 133° and only slightly affected by heating without solvent up to 182°. By heating at 275° under nitrogen for 4.5 hr., 0.0187 mole of the pseudourea gave 0.0031 mole of carbon dioxide (33%), and an orange-yellow residue which was chromatographed on alumina to give thirteen fractions (with 91% recovery of solids). These included 0.0031 mole of 1-hexadecanol and unidentified yellow substances. No *N*-1-hexadecyl-*N*-1-naphthylamine was present.

Three experiments on pyrolysis of the pseudourea at temperatures of 255–275° (under nitrogen) in the presence of equimolar amounts of 1-hexadecanol gave none of the secondary amine. In a typical experiment 0.0418 mole of pseudourea and 0.418 mole of 1-hexadecanol gave in 6.75 hr. at 275° 0.0064 mole of carbon dioxide, 0.0120 mole of 1-1-naphthylamine, 0.0007 mole of di-1-naphthylurea, and 0.0002 mole of 1-hexadecene. Extensive chromatography of the solids gave no other identifiable amines. Similar results were obtained from heating a mixture of di-1-naphthylcarbodiimide (0.0418 mole) and 1-hexadecanol (0.0836 mole), which were shown to form the pseudourea at this temperature.

The pseudourea was largely undecomposed by heating at reflux in xylene or tetralin in the presence of 1-naphthylamine. When a mixture of 0.0147 mole of the pseudourea and 0.029 mole of 1-naphthylamine was heated at 265° un-

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der nitrogen for 4 days, the products were carbon dioxide (44%), di-1-naphthylurea (1%), and four unidentified substances, none of which was the expected secondary amine.

Pyrolysis procedure. Thermal degradations performed in the presence of solvent were carried out in flamed ground-glass equipment. All the solvents were dried by use of Linde 5A molecular sieves. The reaction flasks were swept by a stream of Linde high purity nitrogen free from carbon dioxide and dried by passing through a tower of molecular sieves. After the reaction vessel, the gas stream was cooled to −78° to remove organic vapors and monitored for carbon dioxide with Ascarite-filled absorption tubes.

Degradations done in the absence of solvent were carried out in a 2.5 × 30 cm. Pyrex test tube that was flame dried before use. The test tube had provision for a thermometer, thermocouple, a nitrogen sweep stream, and a reflux condenser. The test tube was heated in an aluminum block,[23] a cylinder 6 in. in diameter and 12 in. high, insulated by 4 in. of rock wool. The block was heated by a 500-watt cylindrical heater operated through a relay-controlled Variac and a 120-watt heater operated through a Fenwal, bimetallic thermoregulator. Temperature fluctuations within the pyrolysis tube were held to a ±0.3° range.

In a typical pyrolysis the sample (5–20 g.) was placed in the pyrolysis tube, the system flushed with nitrogen for 15 min., the tube placed in the heating bath and allowed to equilibrate for 10–15 min. (while collecting evolved carbon dioxide which was used as a correction factor). After constant temperature had been reached by the pyrolysis mixture, reaction rates were followed by collecting carbon dioxide in Ascarite-filled weighing tubes. In the case of pyrolysis of the O^{18}-enriched carbamates, helium was used as a sweep stream and the evolved carbon dioxide was frozen out in traps cooled to −168° (liquid nitrogen). The carbon dioxide was transferred to evacuated gas sampling bulbs and analyzed for variously tagged species of tagged carbon dioxide.

Solid degradation residues were separated by solubility differences and chromatography on activated alumina. Liquid degradation residues were separated by distillation or vapor phase chromatography.

All vapor phase chromatography was carried out with an F and M Scientific Corp., Model 202 programmed gas phase chromatograph, using helium as a carrier gas and 10- to 12-ft. silicon-oil packed columns. Quantitative analyses were done by the techniques of both internal normalization of peak area and internal standardization. Qualitative work was carried out using authentic samples.[24]

Autocatalysis in the formation of carbon dioxide from 1-naphthyl isocyanate. The equation for autocatalysis $dC/dt = k(a - x)^2 (b + x)$ was integrated by partial fractions to give

$$k_3't = \frac{2}{(2a + b)^2}\left[\frac{(2a + b)x}{(a - x)a} + \ln\frac{a(b + x)}{b(a - x)}\right]$$

A plot of the right-hand side of the equation *vs.* time was linear to at least 21% of reaction, when 1-naphthyl isocyanate was pyrolyzed at 268° with 0.3 mole % of added *N,N′*-di-1-naphthylcarbodiimide.

O^{18}-Enriched 1-hexadecanol. By a slight modification of the method of Boschan,[25] O^{18}-enriched 1-hexadecanol was prepared in an over-all yield of 52%.

To 5.000 g. (0.270 mole) of O^{18}-enriched water, containing 32.08% O^{18} and 0.965% O^{17} (from the Weizmann Institute, Rehovoth, Israel) and 30 ml. of dry xylene was slowly added 27.6 g. (0.270 mole) of freshly distilled acetic anhydride. The mixture stood for 1 hr. at room temperature followed by warming to 60° for 11.5 hr. The resulting mixture of xylene and O^{18}-enriched acetic acid was slowly added to 24.65 g. (0.542 mole) of a 52.7% mineral oil dispersion of sodium hydride (Metal Hydrides Corp.) in 80 ml. of dry xylene. After completion of the dropwise addition, the mixture was warmed to gentle reflux, cooled, and the O^{18}-enriched sodium acetate filtered off as 44.15 g. (0.537 mole) of white solid (dried).

Using the method of Drahowzal and Klamann[26] the new compound, 1-hexadecyl *p*-toluenesulfonate, was prepared in 83.4% yield as a white solid, m.p. 48–49° (recrystallized from ether).

Anal. Calcd. for $C_{23}H_{40}O_3S$: C, 69.65; H, 10.17; S, 8.09. Found: C, 69.71; H, 10.02; S, 8.85.

Following the procedure of Boschan,[25] the O^{18}-enriched sodium acetate was treated with 1-hexadecyl *p*-toluenesulfonate to give a 55.2% yield of O^{18}-enriched 1-hexadecyl acetate, and the acetate was reduced to O^{18}-enriched 1-hexadecanol, m.p. 49–50°, in 95% yield. The latter substance was used to prepared the O^{18}-enriched O-hexadecyl *N*-1-naphthylcarbamates.

Based on the procedure of synthesis, the O^{18} content of the alcohol should have been 8%. The data of Table III indicate that the actual content was 7.9%.

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[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DIVISION, SMITH KLINE AND FRENCH LABORATORIES]

Sulfolane Derivatives

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A number of 3- and 3,4-substituted sulfolanes, prepared for biological screening, are described.

The marked chemical reactivity of sulfolene-3 made it an attractive starting material for the synthesis of sulfone-containing analogs of a variety of known biologically active compounds. A number of 3- and 3,4-substituted sulfolanes were prepared and are tabulated in Tables I and II.

The 3-substituted sulfolanes, compounds 1 through 11, were readily prepared by alkali-cat-