

Thermal degradation of Ethylene bis-(N-phenylcarbamate) (*)

by

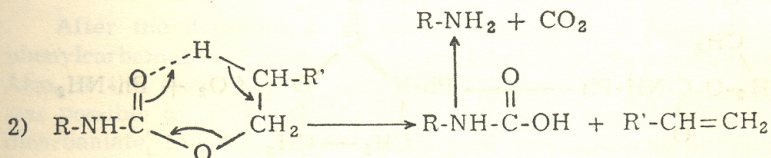
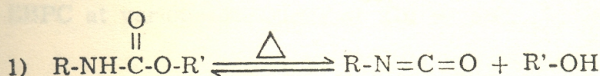
CHU-PHẠM NGỌC-SƠN

ABSTRACT. — The study of this dicarbamate was undertaken to uncover the mechanism of the degradation of certain types of polyurethanes under drastic conditions of heat or ultraviolet radiations. The degradation of Ethylene bis-(N-phenylcarbamate) occurs by a double process of decomposition. The final products are carbon dioxide, aniline, 3-phenyl-2-oxazolidone, ethylene oxide, N,N'-diphenylurea, N,N'-diphenylethylenediamine, 1,3-diphenyl-2-imidazolidone.

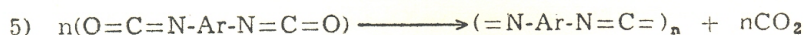
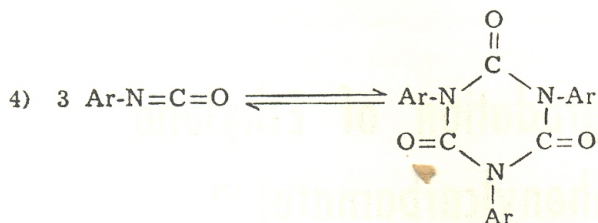
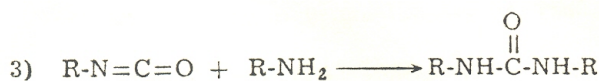
INTRODUCTION

Several investigations have been carried out on the thermal degradation of urethanes (1-10), as polyurethanes become more and more important in industry.

In general, the first step of degradation was a dissociation of the urethane into the corresponding alcohol and isocyanate, or the formation of amine, olefin and carbon dioxide by a cyclic intramolecular process. Further reactions can occur, such as the formation of the disubstituted urea, the allophanate, the polymerization of isocyanates, the obtaining of polycarbo-diimide in the case of a diisocyanate and its subsequent numerous derivatives.



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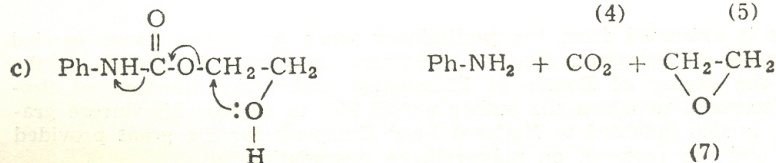
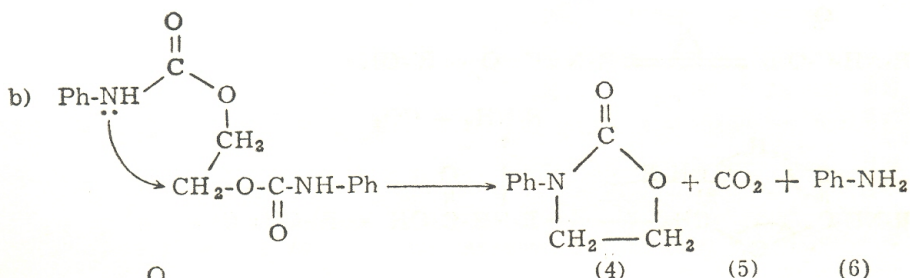
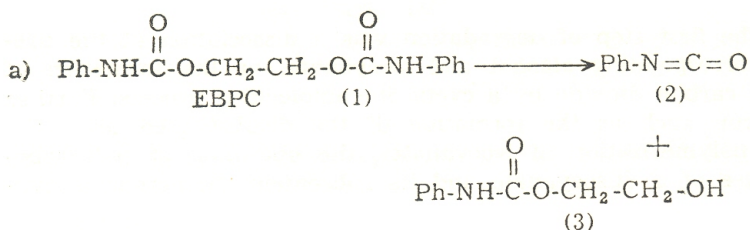
The study of the pyrolysis of Ethylene bis-(N-phenylcarbamate) (EBPC) is of great interest owing to its unusual decomposition leading to the formation of heterocyclic compounds.

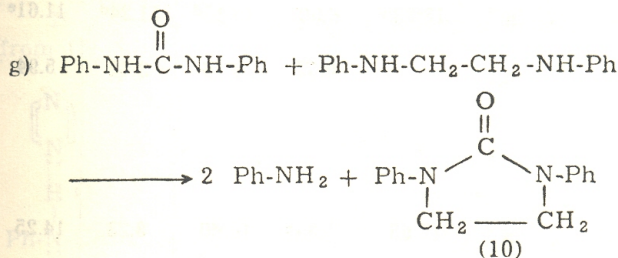
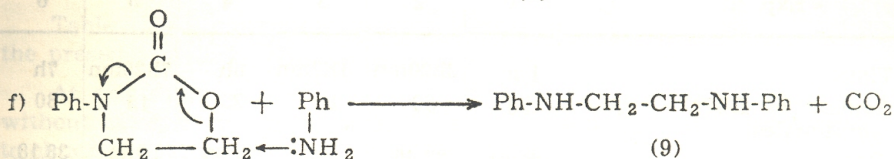
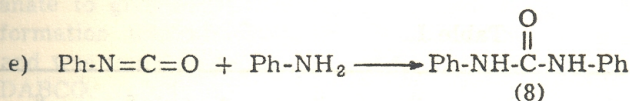
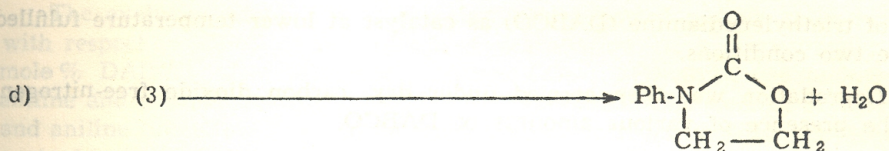
RESULTS AND DISCUSSION

A. — MECHANISM OF PYROLYSIS.

EBPC was pyrolysed under nitrogen at various temperatures from 180° to 215°C. The products of decomposition were identified by elemental analysis, and comparison with authentic samples (infrared spectra, physical constants, derivatives).

Investigations of the process of pyrolysis of EBPC lead us to propose the following mechanism of decomposition :





EBPC (1) is partially dissociated into phenyl isocyanate (2) and β -hydroxyethyl-N-phenylcarbamate (3). Also, by a simultaneous process of decomposition, it gives 3-phenyl-2-oxazolidone (4), carbon dioxide (5) and aniline (6). β -hydroxyethyl-N-phenylcarbamate decomposes and gives (4), (5), (6) and ethylene oxide (7), the latter is recognized by infrared spectrum or by a very sensitive reaction with potassium thiocyanate (11). Aniline liberated from the previous reactions reacts with phenyl isocyanate to give the symmetrical diphenylurea (SPDU) (8). Further decomposition produces N,N'-diphenylethylenediamine (9) by the reaction of (6) with 3-phenyl-2-oxazolidone, and 1,3-diphenyl-2-imidazolidone by the reaction of (8) and (9).

B. — EVIDENCE SUPPORTING THIS MECHANISM.

Table I summarizes the experimental data obtained from the pyrolysis of EBPC at various durations at $210 \pm 5^\circ\text{C}$.

1. — Process a)

After the degradation of EBPC from 1 to 2 hours, β -hydroxyethyl-N-phenylcarbamate (3) was isolated by adsorption chromatography on alumina. Also, if the residue after pyrolysis was treated with p-tolyl isocyanate, it was possible to isolate by the same technique ethylene-(N-phenyl-N'-p-tolyl)-dicarbamate, this compound was formed from the reaction of p-tolyl isocyanate on (3).

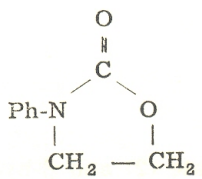
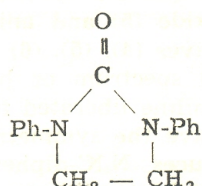
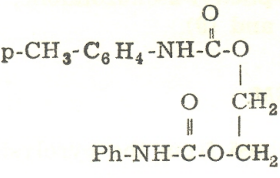
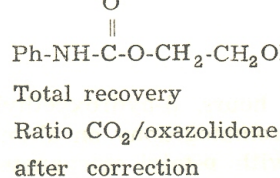
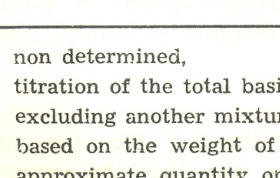
2. — Process b)

In order to detect more precisely the process of the first step of degradation it was obvious to carry the reaction in such a way that the extent of the degradation was large without having appreciable side reactions. The

use of triethylenediamine (DABCO) as catalyst at lower temperature fulfilled these two conditions.

Degradation was then carried under dry, carbon dioxide free-nitrogen, in the presence of various amounts of DABCO.

Table I

| Exp. n° | 1 | 2 | 3 | 4 | 5 | 6 |
|--|-------|--------------------|-------------------|--------------------|--------------------|--------------------|
| Time | 1 h | 2h20mn | 1h7mn | 6h | 7h20mn | 7h |
| Amount of EBPC (millimoles) | 30 | 30 | 10 | 22 | 15 | 30 |
| CO ₂ | 26.61 | 27.40 | 8.45 | 31.90 | 19.60 | 38.18 |
| Ph-NH ₂ | a | 13.33 ^b | 6.50 | 15.17 ^d | 11.24 ^d | 11.61 ^e |
| Ph-NH-CH ₂ Ph-NH-CH ₂ | a | | 0.57 | 5.18 | 3.42 | 5.94 |
|  | a | 17.65 | 5.34 ^c | 10.60 | 8.23 | 14.25 |
| SPDU  | a | 6.56 | 1.65 | 0 | 0.10 | 0.37 |
|  | a | | 0 | 1,2 | 0,44 | 2,14 |
|  | 5.43 | | | | | |
|  | | 2.63 | | | | |
| Total recovery | | | 34 % | 90 % | 91 % | 80 % |
| Ratio CO ₂ /oxazolidone after correction | | | | 1.58 | 1.35 | 1.44 |

a) non determined,

b) titration of the total basic amines by HClO₄ in glacial acetic acid.

c) excluding another mixture of oxazolidone and unidentified product, weighing 0.251 g.

d) based on the weight of aniline hydrochloride.

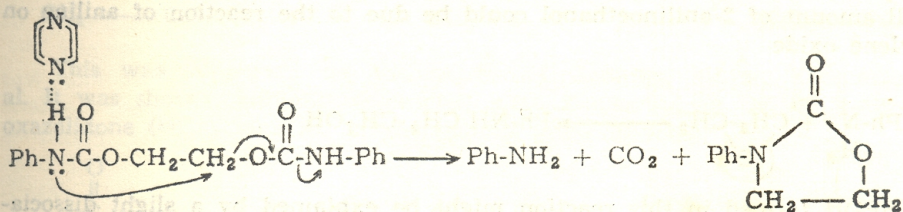
e) approximate quantity obtained from recovery from the mixture of amine hydrochlorides with 3 N NaOH.

The evolution of CO_2 was very fast and followed a first order kinetics with respect to EBPC up to 50-60% of degradation. At a concentration of 3 mole % DABCO, after 20 to 25 minutes CO_2 , 3-phenyl-2-oxazolidone (4), aniline and a small quantity of SPDU were isolated. The amount of CO_2 , (4), and aniline (including free aniline and the aniline reacting with phenyl isocyanate to give SPDU) were approximately equal. The rate constant of CO_2 formation was almost proportional in the present experimental conditions and was found to be respectively 4.27, 3.00, $1.80 \times 10^{-2} \text{ sec}^{-1}$ at 3,2,1 mole % DABCO.

Table (II) summarizes the data found in the degradation of EBPC in the presence of 3 % DABCO.

At the same temperature or at $210^\circ\text{-}212^\circ\text{C}$, the degradation of EBPC without catalyst was very slow. It took 5 hours at 183° or 1 hour at 212° to obtain the same amount of CO_2 .

It is presumed then that DABCO probably helps to pull out the proton from the nitrogen, making it more nucleophile.



The fact that CO_2 was given off at the first beginning of the decomposition was observed by the precipitation of BaCO_3 from a saturated solution of $\text{Ba}(\text{OH})_2$ which was almost simultaneous with the bubbling observed in the flask of reaction.

The small amount of SPDU suggests a slight dissociation according to the process a), this slight dissociation takes place only at the end of the reaction as judged by the color of the aqueous solution of KSCN .

Table II

| Exp. | 1 | 2 | 3 |
|----------------------------------|-------------------|-------------------|-------------------------|
| Time (minutes) | 20 | 21 | 25 |
| Temperature | $183 \pm 1^\circ$ | $182 \pm 1^\circ$ | $182^\circ \pm 1^\circ$ |
| Amount of EBPC (millimoles) | 10 | 10 | 10 |
| CO_2 (millimoles) | 3.21 | 8.50 | 8.72 |
| Aniline (millimoles) | 7 ^a | 6.0 ^b | 6.64 ^a |
| Oxazolidone (millimoles) | 7.60 | non determined | 7.90 |
| SPDU (millimoles) | 1.02 | 1.44 | 0.95 |
| Ratio CO_2 /oxazolidone | 1.08 | | 1.10 |
| Total recovery | 82 % | | 83 % |

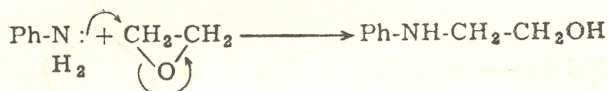
a) weight as $\text{C}_6\text{H}_5\text{NH}_2$, HCl .

b) titration with HCIO_4 after extraction with ether.
the error would be due to incomplete extraction.

3. — Processes c) and d) — Degradation of β -hydroxyethyl-N-phenylcarbamate (3)

The above experiments have shown the simultaneous mechanism of decomposition of EBPC. However in the absence of DABCO, β -hydroxyethyl-N-phenylcarbamate was isolated in small amount. This was a proof of the existence of the process a).

The question arose naturally: What were the products of the degradation of (3) in the same experimental conditions? The pyrolysis of (3) was then carried at various temperatures from 180° to 205°C. In every case, 3-phenyl-2-oxazolidone, ethylene oxide, aniline, CO₂ were obtained with a small amount of SPDU and in certain experiments some 2-anilinoethanol. The amounts of CO₂ and aniline were large and approximately equal. The formation of CO₂ increased with increasing the temperature or the amount of DABCO. The quantity of 3-phenyl-2-oxazolidone increased also with the amount of DABCO. These experimental results fitted with the previous equations c) and d). Decomposition by the reaction c) was predominant. The small amount of 2-anilinoethanol could be due to the reaction of aniline on ethylene oxide



SPDU formed in this reaction might be explained by a slight dissociation of (3) into phenyl isocyanate and ethylene glycol, the former reacted with aniline to give SPDU according to the reaction e).

The experimental data were recorded in the table III:

Table III

| Experiments : | 1 | 2 | 3 | 4 |
|---|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| Amount of III in grams ^a | 5.104 (~ 28.2 mmoles) | 5.833 (~ 32.2 mmoles) | 5.025 (~ 27.7 mmoles) | 3.900 (~ 21.5 mmoles) |
| Time (hrs) | 5 | 3.5 | 1 | 35 min |
| Temperature | 183 ± 1° | 202 ± 2° | 182 ± 1° | 183° ± 1 |
| DABCO (mole %) | 0 | 0 | 1 | 3 |
| CO ₂ (mmoles) | 11.57 | 17.75 | 10.60 | 10.67 |
| Amines ^b (mmoles) | 10.70 | 16.36 | non deter- mined | 8.75 |
| 3-phenyl- 2-oxazolidone (mmoles) | 2.46 | 2.80 | 4.55 | 6.01 |
| SPDU (mmoles) | 0.37 | 0.52 | 0.52 | 0.38 |
| Ratio CO ₂ /oxazo- lidone | 4.7 | 6.3 | 2.4 | 1.8 |

a) assumed to be pure.

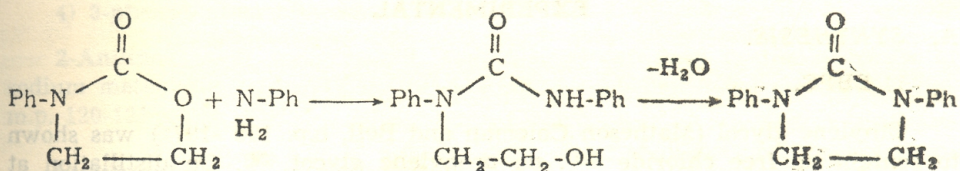
b) from titration by perchloric acid in glacial acetic acid.

Without any DABCO, the ratio of CO_2 to oxazolidone was much larger in the pyrolysis of (3) than in EBPC.

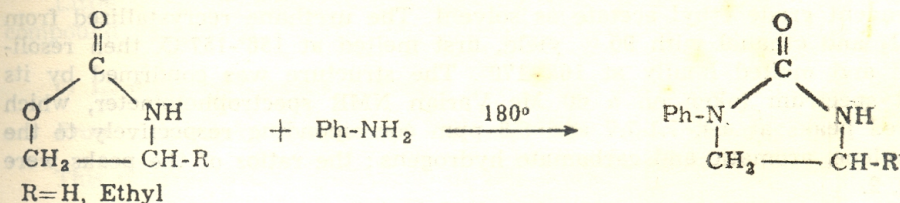
Thus it is impossible to attribute the formation of oxazolidone to the process d) only, this again supports the existence of the process b).

4. — Reaction f) : formation of N,N'-diphenylethylenediamine.

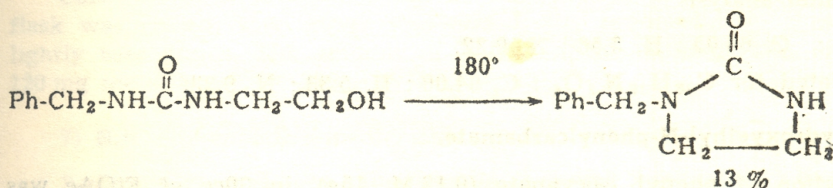
This is due to the nucleophilic attack of aniline on 3-phenyl-2-oxazolidone. This type of displacement on carbon was observed by DYER and SCOTT (12). It was presumed that this attack would be directed at the carbonyl site and would give 1,3-diphenyl-2-imidazolidone.



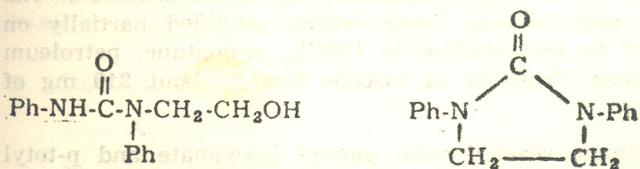
This was supported by the works of GABRIEL, NAJER, CHABRIER et al. It was shown that aniline reacted with 2-oxazolidone (13) or 4-ethyl-2-oxazolidone (14) to give the corresponding imidazolidones



Also N-benzyl-N'-(β -hydroxyethyl) urea was shown to cyclize to 1-benzyl-2-imidazolidone (15).



However, we could not isolate (10) from the reaction of aniline on 3-phenyl-2-oxazolidone. Also no 1,3-diphenyl-2-imidazolidone was found from N-(β -hydroxyethyl)-N,N'-diphenylurea.



The attack of aniline on the carbon seems to be governed by the steric effect which decreases very much the reactivity of the carbonyl in a five-membered-ring compound.

This fact was shown by BROWN and coworkers (16, 17, 18). Furthermore the phenyl ring attached to the nitrogen seems to give more hindrance.

5) — Reaction g) : formation of 1,3-diphenyl-2-imidazolidone (10).

Table I shows that the degradation of EBPC for a short time did not give any imidazolidone. Instead, a large amount of SPDU was obtained. The quantity of SPDU decreased while that of the imidazolidone increased on longer heating. Thus SPDU seemed to be an intermediate for the formation of (10). Effectively, it was found that N,N-diphenylethylenediamine reacted with SPDU to give (10) with a yield of 15 %.

EXPERIMENTAL

A. SYNTHESIS.

1) EBPC.

Ethylene glycol (Matheson Coleman and Bell, b.p. 195°-197°) was shown to contain no free chloride (19), no propylene glycol (20). On distillation at 67°C under 6-7 mm Hg, it gave a single peak on gas chromatography (21). Phenyl isocyanate (Matheson Coleman and Bell b.p. 60°-62°C/20 mm) was purified by distillation under suction at 53°C, the heart cut was used. Ethylene glycol was allowed to react with phenyl isocyanate in equimolar quantities in reagent grade ethyl acetate as solvent. The urethane recrystallized from CHCl_3 and ethanol with 90 % yield, first melted at 156°-157°C, then resolidified and melted finally at 168°-170°. The structure was confirmed by its NMR spectrum taken on a 60 Mc Varian NMR spectrophotometer, which showed peaks at 4.4, 7.1-7.7 and 8.8 ppm corresponding respectively to the methylene, aromatic and carbamate hydrogens; the ratios of the peaks were 4, 10, 2.

Infrared spectrum showed the NH stretching at 3333 cm^{-1} , a C=O stretching at 1695 cm^{-1} and a C=O deformation at 1235-1220 cm^{-1} .

Elemental analysis:

Found: C, 64.05; H, 5.56; N, 9.32.

Calculated for $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_4$: C, 64.00; H, 5.33; N, 9.33.

2) β -hydroxyethyl-N-phenylcarbamate.

A solution of phenyl isocyanate (0.12 M, 15g), in 30cc of EtOAc was added dropwise very slowly at reflux to a solution of ethylene glycol (1 M, 62g) in 60cc EtOAc and refluxed for 8 hours. Ethylacetate was evaporated and the excess of ethylene glycol was distilled off at 80°C under vacuum. Overheating in vacuo caused the decomposition of the monocarbamate. The latter was obtained as a very viscous liquid which solidified partially on standing, and which failed to recrystallise in CHCl_3 , n-pentane, petroleum ether, alcohol-water solutions. From 8g of viscous liquid, about 210 mg of EBPC (3 %) was collected.

The above monocarbamate reacted with phenyl isocyanate and p-tolyl isocyanate and gave respectively EBPC (87 % yield) and ethylene-(N-phenyl-N'-p-tolyl) dicarbamate (86 % yield), the latter melted at 134°-136°.

Elemental analysis of the latter dicarbamate.

Found: C, 65.18; H, 5.88; N, 8.68.

Calculated for $C_{17}H_8N_2O_4$: C, 64.96; H, 5.73; N, 8.91.

3) N-(β -hydroxyethyl)-N,N'-diphenylurea.

This compound was obtained by a slight excess of 2-anilino-ethanol on phenyl isocyanate in ethyl acetate as solvent.

The urea recrystallized from a mixture of ether, petroleum ether, melting at 82-83° was obtained with a 93 % yield. Infrared spectrum showed a large OH band at 3448-3333 cm^{-1} and an urea band at 1639 cm^{-1} , no urethane band was observed.

4) 3-phenyl-2-oxazolidone.

2-Anilinoethanol was reacted with diethylcarbonate in the presence of sodium methoxide according to the procedure of CALDWELL (22), (yield 80 % m.p. 120-121°). Lit. 121°.

5) 1,3-diphenyl-2-imidazolidone.

By the reaction of phosgene on N,N'-diphenylethylenediamine (23, 24, 25). Yield 12 %, m.p. 210°, Lit. 209°.

Little or no depression of melting point was observed when the authentic compound was mixed with the corresponding product from degradation.

6) 1,3-diphenyl-2-imidazolidone.

From N,N'-diphenylurea and N,N'-diphenylethylenediamine.

This procedure was discovered in this work.

The diamine (2g) was allowed to react with 1g of SPDU at 205°-210° in 100cc 3-neck flask, completely immersed in an oil bath for 6 hours.

Care had to be taken to avoid the sublimation of the urea. The reaction flask was cooled, then ether was added, the imidazolidone crystallized in lightly rose plates. The amount of imidazolidone isolated was from 190 to 120 mg melting at 208°-210° (10-18 % yield).

7) N,N'-diphenylethylenediamine.

3-phenyl-2-oxazolidone (18.4 mmole, 3g) and 3cc aniline were heated at 210° for 8 hours with an oil bath. The mixture of amines was obtained then by their hydrochlorides. The hydrochlorides were then dissolved in water and the amines were precipitated by 3N NaOH. The solid diamine was then filtered, dried, recrystallized from ether, petroleum ether (yield: 58 %, m.p. 61-63°, mixed m.p. with a sample from Eastman Kodak 61°).

B. DEGRADATION OF THE URETHANES.

1 — Apparatus.

The degradation was carried out in a 100 cc 3-neck flask. The carrier gas was dry, CO_2 -free nitrogen obtained by passing nitrogen through a washing bottle of concentrated sulfuric acid, a tower of calcium chloride, a tower of ascarite and finally a tower of molecular sieves. The nitrogen swept at a

rate 20 cc/minute the whole apparatus composed of the reaction flask, a receiver flask then a trap cooled by dry ice in acetone, an U tube filled with CaCl_2 ; the latter was connected to a three-way stopcock, each of the other two ends of which carried an ascarite tube. By turning the stopcock in a suitable direction, it was possible to measure without any loss the amount of CO_2 evolved as a function of time.

2 — Isolation of the products.

After pyrolysis, the residue was dissolved in a small amount of cold dry ether and filtered. The amines were precipitated by their hydrochlorides. They were then separated by dissolution in water and reprecipitation by 3N NaOH.

The aniline was then calculated by difference and characterized by its hydrochloride (mp 193-195°, mixed m.p. 194°), 3-phenyl-2-oxazolidone was separated from the solid residue by extraction with a mixture of ether and chloroform (ratio 4/1). After recrystallisation in ether, n-pentane, it melted at 118°-119° (mixed m.p. 119°). The imidazolidone was recrystallised from alcohol (m.p. 207-214°). After sublimation it melted at 209-210°. If the imidazolidone and SPDU were present, the first one was separated from the latter by partial extraction with a mixture of equal volume of ether and chloroform.

In some experiments, the amines were titrated by perchloric acid in glacial acetic acid in presence of crystal violet as indicator (26). The change of color was checked first by potentiometric titration.

Elemental analysis of the oxazolidone and imidazolidone found from degradation.

α) 3-phenyl-2-oxazolidone.

Found : C, 66.71 ; H, 5.73 ; N, 8.57

Calculated for $\text{C}_9\text{H}_9\text{NO}_2$: C, 66.25 ; H, 5.52 ; N, 8.58.

β) 1,3-diphenyl-2-imidazolidone.

Found : C, 75.56 ; H, 5.64 ; N, 7.03.

Calculated for $\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}$: C, 75.63 ; H, 5.88 ; N, 6.73.

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