1.8 g. of aniline hydrochloride and 0.6 g. of *sym*-diphenylurea, which is equivalent to 0.3 g. of phosgene (0.003 mole), were obtained. One and one-half grams of a mixture of phenyl isocyanate and benzonitrile was obtained by distillation (b.p., 50–74°/18 mm.), from which 0.4 g. of *sym*-diphenylurea was precipitated by addition of aniline (equivalent to 0.2 g. (9%) of phenyl isocyanate).

Acknowledgment. The authors wish to express their hearty thanks to Mr. Asaji Kondo for the microanalyses and to Dainippon Celluloid Co. Ltd. for the gift of ketene dimer.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF RESOURCES UTILIZATION, TOKYO INSTITUTE OF TECHNOLOGY]

O-Alkyl- and Aryl-*N*,*N*-ethyleneurethans. II. Reaction with Thiophenol, Acids, and Phenols

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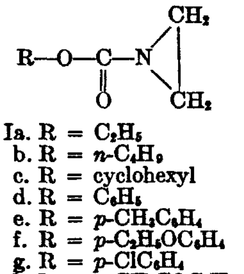
Received February 2, 1961

Reactions of *O*-alkyl- and aryl-*N*,*N*-ethyleneurethans with several nucleophilic reagents were investigated. *O*-Alkyl- and aryl-*N*,*N*-ethyleneurethans reacted with thiophenol or benzoic acid to give the addition products: *O*-alkyl- and aryl-*N*-(β-substituted ethyl)urethans. When a small amount of triethylamine and water was present in these reactions, *O*-aryl-*N*,*N*-ethyleneurethans gave *N*,*N'*-bis(β-substituted ethyl)ureas along with urethans. This urea formation was explained as proceeded *via* *O*-aryl-*N*-(β-substituted ethyl)urethans.

Ethylenimines are known to react with several nucleophilic reagents such as thiophenol,[1] phenols,[2] and acids[3] to give β-substituted ethylamines. We extended these studies to *N*-substituted ethylenimines such as *N*-alkoxycarbonyl and *N*-aryloxycarbonyl (I).

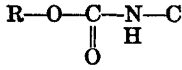


(I)

Ia. R = C_2H_5
b. R = $n\text{-}C_4H_9$
c. R = cyclohexyl
d. R = C_6H_5
e. R = $p\text{-}CH_3C_6H_4$
f. R = $p\text{-}C_2H_5OC_6H_4$
g. R = $p\text{-}ClC_6H_4$
h. R = $p\text{-}CH_3COC_6H_4$
i. R = $p\text{-}NO_2C_6H_4$

TABLE I

O-ALKYL- and ARYL-*N*-(β-PHENYLTHIOETHYL)URETHANS



$$R{-}O{-}\underset{\underset{O}{\|}}{C}{-}\underset{H}{N}{-}CH_2CH_2{-}SC_6H_5$$

R	M.P.	Formula	Nitrogen, % Calcd.	Nitrogen, % Found
Ethyl	41–42.5	$C_{11}H_{15}NO_2S$	6.22	6.45
n-Butyl	49–50	$C_{13}H_{19}NO_2S$	5.61	5.68
Cyclohexyl	58–59	$C_{15}H_{21}NO_2S$	5.01	5.25
Phenyl	56–58	$C_{15}H_{15}NO_2S$	5.12	5.18
p-Tolyl	66–68	$C_{16}H_{17}NO_2S$	4.88	5.07
p-Ethoxyphenyl	83.5–84.5	$C_{17}H_{19}NO_3S$	4.41	4.18
p-Chlorophenyl	83–84	$C_{15}H_{14}ClNO_2S$	4.55	4.72
p-Acetophenyl	80–81	$C_{17}H_{17}NO_3S$	4.44	4.60
p-Nitrophenyl	85–87	$C_{15}H_{14}N_2O_4S$	8.80	8.68

TABLE II

O-ALKYL- AND ARYL-*N*-(β-BENZOYLOXYETHYL)URETHANS

$$R{-}O{-}\underset{\underset{O}{\|}}{C}{-}\underset{H}{N}{-}CH_2CH_2{-}O{-}\underset{\underset{O}{\|}}{C}{-}C_6H_5$$

R	M.P.	Yield, %	Formula	Nitrogen, % Calcd.	Nitrogen, % Found
Ethyl	83–85	46[a]	$C_{12}H_{15}NO_4$	5.90	6.20
n-Butyl	50–51	50[a]	$C_{14}H_{19}NO_4$	5.28	5.40
Cyclohexyl	117–119	70[a]	$C_{16}H_{21}NO_4$	4.81	4.97
Phenyl	116–117	30[b]	$C_{16}H_{15}NO_4$	4.91	5.13

[a] After standing for about a year at room temperature and without a solvent. [b] After standing for 5 days at room temperature and without a solvent.

Thiophenol reacted with all these ethylenimino compounds at room temperature to give the addition products (Table I) in less than a day with good yields. Benzoic acid also reacted with these derivatives, but prolonged standing was required to give the products (Table II) at room temperature. Phenol, on the other hand, was found to be much less reactive. *O*-Cyclohexyl-*N*,*N*-ethyleneurethan (Ic) and phenol did not react after standing for a year at room temperature without a solvent, or by heating at 100° in excess phenol for four hours.

In the presence of a small quantity of water, thiophenol and crude *O*-phenyl-*N*,*N*-ethyleneurethan (Id) gave *N*,*N'*-bis(β-phenylthioethyl)urea in addition to *O*-phenyl-*N*-(β-phenylthioethyl)urethan. Reaction of Id with other nucleophilic reagents in the presence of water gave more complicated results. Benzoic acid and *p*-nitrobenzoic acid reacted with Id to give *N*,*N'*-bis(β-substituted ethyl)ureas along with *O*-phenyl-*N*-(β-substituted ethyl)urethans, while hydrochloric acid and picric acid gave only *O*-phenyl-*N*-(β-substituted ethyl)-

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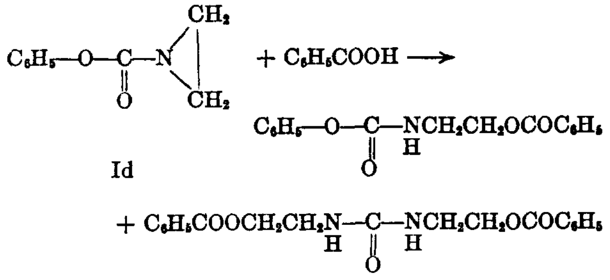
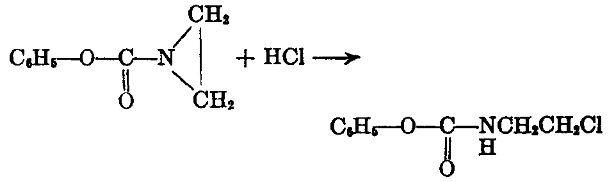
(1) G. Meguerian and L. B. Clapp, *J. Am. Chem. Soc.*, 73, 2121 (1951).

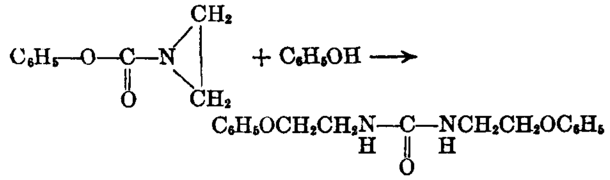
(2) L. B. Clapp, *J. Am. Chem. Soc.*, 73, 2584 (1951).

(3) S. Gabriel and R. Stelzner, *Ber.*, 21, 1053 (1888).

urethans. With Id phenol, alcohols and diphenylamine gave *N*,*N*′-bis(β-phenyloxyethyl)urea.

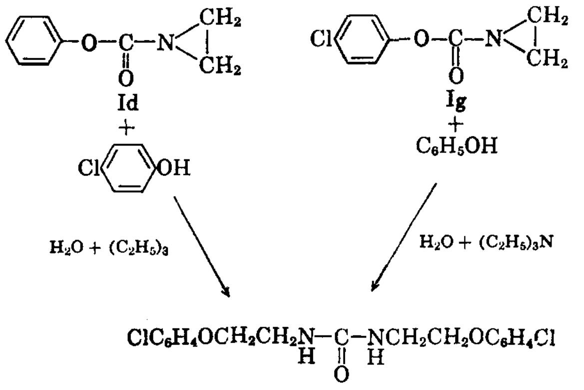






Thiophenol reacted with purified *O*-alkyl- and aryl-*N*,*N*-ethyleneurethans to give *O*-alkyl- and aryl-*N*-(β-phenylthioethyl)urethans in good yields without formation of *N*,*N*′-bis(β-phenylthioethyl)-urea in the presence of water. The urea formation was considered to be induced catalytically by some impurity contained in crude Id. Triethylamine was shown to have this effect, because *O*-aryl-*N*,*N*-ethyleneurethans (Ie, Ig, Ih, and Ii) and thiophenol gave *N*,*N*′-bis(β-phenylthioethyl)urea along with *O*-aryl-*N*-(β-phenylthioethyl)urethans in the presence of triethylamine and water (Table III). Reactions of several nucleophilic reagents with *O*-*p*-chlorophenyl-*N*,*N*-ethyleneurethan (Ig) were tried in the presence of triethylamine and water, using dioxane as a solvent (Table IV). Hydrochloric and picric acids gave only urethans. In the case of the reaction with phenols, the phenol produced from I by hydrolysis also took part in attacking ethylenimine ring. Phenol and Ig gave *N*,*N*′-bis(β-*p*-chlorophenyloxyethyl)urea and not *N*,*N*′-bis(β-phenyloxyethyl)-urea or *O*-*p*-chlorophenyl-*N*-(β-phenyloxyethyl)urethan. It was further observed that when *O*-phenyl-*N*,*N*-ethyleneurethan (Id) or Ig was allowed to stand with triethylamine and water in dioxane for a long time, *N*,*N*′-bis(β-phenyloxyethyl)urea and *N*,*N*′-bis(β-*p*-chlorophenyloxyethyl)urea were produced respectively. The latter compound was also obtained from *p*-chlorophenol and Id.

These facts may be explained as follows: Of the two phenols present—the one added at the beginning and the other produced from I by hydrolysis—the more reactive one will attack the ethylenimine ring. *p*-Ethoxyphenol was expected to be more reactive than *p*-chlorophenol, and in fact, *O*-*p*-chlorophenyl-*N*-(β-*p*-ethoxyphenyloxyethyl)-urethan was obtained by the reaction of Ig with *p*-ethoxyphenol under the same conditions, more reactive *p*-ethoxyphenol participating in the ring-opening reaction.



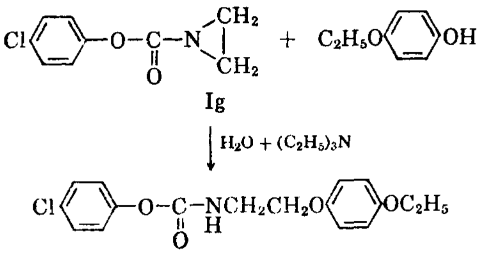
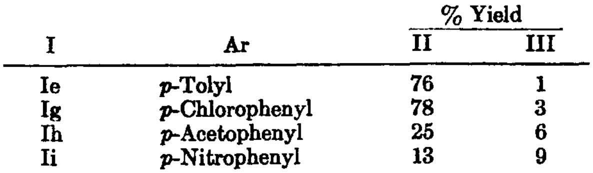


TABLE III

Results Obtained by the Reaction of *O*-Aryl-*N*,*N*-ethyleneurethans (I) with Thiophenol in the Presence of Triethylamine and Water in Dioxane at 15°[a]



I	Ar	% Yield II	% Yield III
Ie	*p*-Tolyl	76	1
Ig	*p*-Chlorophenyl	78	3
Ih	*p*-Acetophenyl	25	6
Ii	*p*-Nitrophenyl	13	9

[a] When the reaction was carried out at 35°, polymerization of Ih and of Ii took place appreciably.

T. Mukaiyama *et al.*[4] stated that in basic media, *O*-arylurethans were much more easily dissociated than *O*-alkylurethans. If in the course of the formation of *N*,*N*′-bis(β-substituted ethyl)urea (III),

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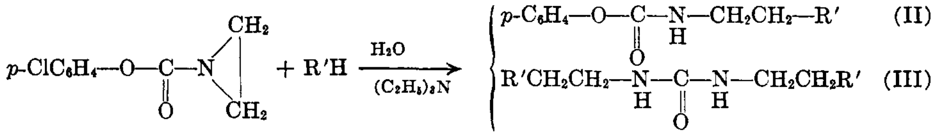
(4) T. Mukaiyama, T. Akiba, and T. Asahi, *Bull. chem. soc., Japan*, **33**, 1137 (1960).

TABLE IV

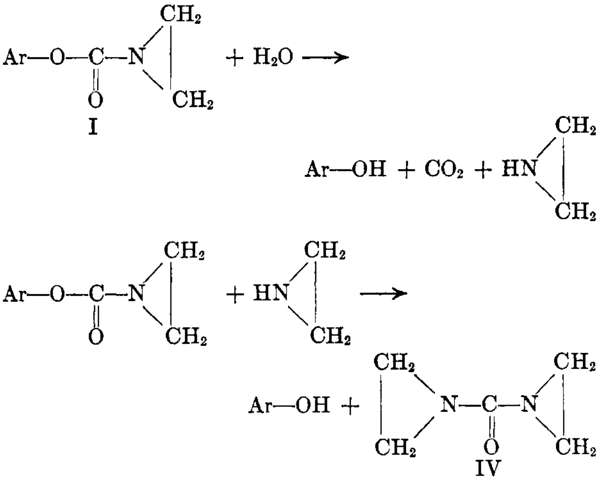
RESULTS OBTAINED BY THE REACTION OF Ig WITH SOME NUCLEOPHILIC REAGENTS (R'H) IN THE PRESENCE OF TRIETHYLAMINE AND WATER IN DIOXANE AT 35°



R'H	Product	M.P.	Yield, %	Formula	Nitrogen, % Calcd.	Nitrogen, % Found
Thiophenol	II	83–84	32			
	III	149–150	55	$C_{17}H_{20}N_2OS_2$	8.43	8.60
Benzoic acid	II	108–110	25	$C_{16}H_{14}ClNO_4$	4.38	4.58
	III	204–206	4	$C_{19}H_{20}N_2O_5$	7.86	7.98
p-Nitrobenzoic acid[a]	II	132–133		$C_{16}H_{13}ClN_2O_6$	7.68	7.70
	III	193–194		$C_{19}H_{18}N_4O_9$	12.55	12.73
Hydrochloric acid	II	100–102	67	$C_9H_9Cl_2NO_2$	5.98	6.21
Picric acid	II	135 ca	42	$C_{15}H_{11}ClN_4O_9$	13.12	13.36
Phenol[b]	III[c]	175–177	Little	$C_{17}H_{18}Cl_2N_2O_3$	7.64	7.81
p-Chlorophenol[b]	III		Little			
p-Ethoxyphenol	II	115–117	30[d]	$C_{17}H_{18}ClNO_4$	4.17	4.03

[a] II and III were each identified, but the quantitative separation of these two compounds was unsuccessful. [b] The reaction mixture was allowed to stand at room temperature for a month. [c] The product was *N,N'*-bis(β-*p*-chlorophenyloxyethyl)urea. [d] After two weeks. After a month a small amount of a higher melting substance, m.p. *ca.* 150°, was obtained, but the separation of the latter was unsuccessful.

I is assumed to be hydrolyzed before the attack by a nucleophilic reagent, *N,N'*-diethyleneurea (IV) may be the intermediate:



IV was prepared from phosgene and ethylenimine using triethylamine as an acid acceptor as Bestian described.[5] IV reacted with thiophenol vigorously and gave *N,N'*-bis(β-phenylthioethyl)urea in 60% yield. With benzoic, *p*-nitrobenzoic and hydrochloric acid IV gave III in 22%, 55%, and 65% yield respectively. With phenol, *p*-chlorophenol and picric acid, polymerization of IV took place.

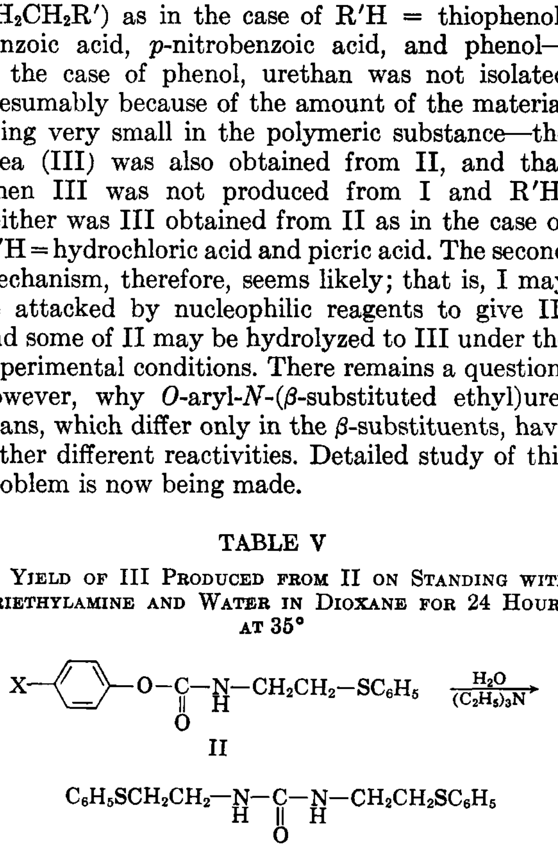
If the above mechanism is valid, IV must be formed from I in the presence of triethylamine and water before the addition of a nucleophilic reagent. If hydrochloric acid is added to this solution, *N,N'*-bis(β-chloroethyl)urea should be formed. But it was not the case, and IV is therefore not an intermediate.

The possibility that *O*-aryl-*N*-(β-substituted ethyl)urethan (II) is an intermediate to III was considered and in order to prove this, II was allowed to stand with water in basic media (Table V). From Table V it may be said that more III is produced when X is more electron attractive. Under the same conditions, several *O*-*p*-chlorophenyl-*N*-(β-substituted ethyl)urethans (ClC_6H_4-$OCONHCH_2CH_2$—R') and *O*-*p*-chlorophenyl-*N*-*n*-butylurethan were allowed to stand for twenty-four hours for comparison. Unexpectedly, no ureas were produced in the case of *O*-*p*-chlorophenyl-*N*-(β-chloroethyl)urethan, *O*-*p*-chlorophenyl-*N*-(β-picrylethyl)urethan, and *O*-*p*-chlorophenyl-*N*-*n*-butylurethan; while ureas were produced from *O*-*p*-chlorophenyl-*N*-(β-phenylthioethyl)urethan, *O*-*p*-chlorophenyl-*N*-(β-benzoyloxyethyl)urethan, *O*-*p*-chlorophenyl-*N*-(β-*p*-nitrobenzoyloxyethyl)urethan, and *O*-*p*-chlorophenyl-*N*-(β-phenyloxyethyl)urethan. In the case of *O*-*p*-chlorophenyl-*N*-(β-chloroethyl)urethan, formation of the quarternary ammonium salt with triethylamine must be taken into consideration. Actually, when R' was bromine or iodine, the formation of Br^- or I^- was observed under the same conditions. In such cases, the catalytic action of triethylamine on the hydrolysis of urethan must be diminished. To exclude the problem of salt formation, *O*-*p*-chlorophenyl-*N*-(β-chloroethyl)urethan (R' = Cl) and *O*-*p*-chlorophenyl-*N*-(β-phenylthioethyl)-urethan (R' = SC_6H_5) were allowed to stand with water in dimethylformamide. About 50% of *N,N'*-bis(β-phenylthioethyl)urea was produced from the latter (R' = SC_6H_5), while the former (R' = Cl) was recovered quantitatively. Comparing these results with Table IV, it can be seen that when *O*-

aryl-*N*,*N*-ethyleneurethan (I) gave *N*,*N'*-bis(β-substituted ethyl)urea (III. $R'CH_2CH_2NHCONHCH_2CH_2R'$) in the reaction with a certain nucleophilic reagent (R'H), along with *O*-aryl-*N*-(β-substituted ethyl)urethan (II. $ArOCONHCH_2CH_2R'$) as in the case of R'H = thiophenol, benzoic acid, *p*-nitrobenzoic acid, and phenol—in the case of phenol, urethan was not isolated presumably because of the amount of the material being very small in the polymeric substance—the urea (III) was also obtained from II, and that when III was not produced from I and R'H, neither was III obtained from II as in the case of R'H = hydrochloric acid and picric acid. The second mechanism, therefore, seems likely; that is, I may be attacked by nucleophilic reagents to give II, and some of II may be hydrolyzed to III under the experimental conditions. There remains a question, however, why *O*-aryl-*N*-(β-substituted ethyl)urethans, which differ only in the β-substituents, have rather different reactivities. Detailed study of this problem is now being made.

TABLE V

% YIELD OF III PRODUCED FROM II ON STANDING WITH TRIETHYLAMINE AND WATER IN DIOXANE FOR 24 HOURS AT 35°



II

$C_6H_5SCH_2CH_2-NH-CO-NH-CH_2CH_2SC_6H_5$

III

X	% Yield of III
CH_3	<6
H	6
Cl	12
Ac	24
NO_2	60

EXPERIMENTAL

All boiling points and melting points are uncorrected. Microanalyses were done by Dr. A. Kondo of Tokyo Institute of Technology. Infrared absorption spectra were determined by Miss Y. Kada of Tokyo Institute of Technology, using a Perkin-Elmer Spectrometer Model 112.

Preparation of chloroformic acid esters and of *O*-alkyl- and aryl-*N*,*N*-ethyleneurethans (I, except Ih) was described in the previous paper.[6]

p-Acetophenyl chloroformate. To a solution of 30 g. (0.30 mole) of chlorine-free phosgene in 100 ml. of benzene, a solution of 15.3 g. (0.113 mole) of *p*-hydroxyacetophenone and 14 g. (0.113 mole) of *N*,*N*-dimethylaniline in 100 ml. of ether was added under cooling and with stirring. The precipitated dimethylaniline hydrochloride was filtered off, and the filtrate was washed several times with cold, dilute hydrochloric acid, and dried over calcium chloride. After the solvent was distilled under reduced pressure, the residue was submitted to vacuum distillation. Thus 15 g. (67 %) of colorless liquid, boiling at 97–98°/0.1 mm., which solidified later (m.p. 32–34°), was obtained.

Anal. Calcd. for $C_9H_7ClO_3$: C, 54.93; H, 3.56. Found: C, 54.69; H, 3.80.

The chloroformate obtained became purple after storage overnight in the cold.

O-p-Acetophenyl-N,N-ethyleneurethan (Ih). To a solution of 10 g. (0.05 mole) of *p*-acetophenyl chloroformate in 100 ml. of ether, a solution of 2.2 g. (0.05 mole) of ethylenimine and 5.1 g. (0.05 mole) of triethylamine in 20 ml. of ether was added under cooling with an ice-salt bath and with vigorous stirring. After the addition was complete, stirring was continued for 1 hr. under cooling. The precipitate was filtered off, and washed with dry ether. The ethereal solution was immersed in a Dry Ice–acetone bath. The crystals were filtered, washed with water and dried. Thus 8 g. (78 %) of crude Ih, melting at about 80°, was obtained. Two recrystallizations from dry ether raised the m.p. to 85–86°.

Anal. Calcd. for $C_{11}H_{11}NO_3$: N, 6.83. Found: N, 6.60.

Reaction of O-alkyl- and aryl-N,N-ethyleneurethans (I) *with thiophenol* (Table I). Thiophenol (1.2 g.) was added to 1.7 g. of *O*-cyclohexyl-*N*,*N*-ethyleneurethan, and the mixture was allowed to stand at room temperature. After a day, the reaction mixture grew to a white mass. By recrystallizing from petroleum ether (b.p. 40–65°), 2.7 g. (96 %) of *O*-cyclohexyl-*N*-(β-phenylthioethyl)urethan, m.p. 58–59°, was obtained.

Reactions of *O*-ethyl- and *O*-*n*-butyl-*N*,*N*-ethyleneurethans with thiophenol proceeded similarly, and yields were quantitative in both cases.

To 0.6 g. of thiophenol, 1.0 g. of *O*-*p*-chlorophenyl-*N*,*N*-ethyleneurethan was added at room temperature. After a while, crystals began separating, and the reaction seemed complete within several hours. Recrystallization from ether gave 1.3 g. (84%) of *O*-*p*-chlorophenyl-*N*-(β-phenylthioethyl)urethan, which melted at 82–83°.

Infrared absorption spectra showed a strong carbonyl absorption band at 1752 cm.$^{-1}$, and —NH band at 3459 cm.$^{-1}$

The same product (m.p. 83–84°) was obtained from *p*-chlorophenyl chloroformate and β-phenylthioethylamine using triethylamine as an acid acceptor.

Reaction of O-phenyl-N,N-ethyleneurethan (Id). (a) *With thiophenol.* When crude Id and thiophenol were mixed together without a solvent at room temperature, reaction took place too vigorously and Id polymerized. It was found that triethylamine catalyzed the reaction of *N*,*N'*-polymethylene bisethyleneurethans with mercaptans.[7]

To a solution of 1.2 g. of thiophenol in 10 ml. of benzene 1.6 g. of crude Id was added at room temperature. After standing overnight, petroleum ether (b.p. 40–65°) was added to the reaction mixture and the crystals were filtered. By recrystallizing from ether, 2.0 g. (74%) of *O*-phenyl-*N*-(β-phenylthioethyl)urethan was obtained.

When a small quantity of water was present in the above reaction, 0.2 g. of a higher melting substance was isolated. Recrystallization from alcohol gave *N*,*N'*-bis(β-phenylthioethyl)urea (Table IV).

(b) *With benzoic acid.* Quite similar result was obtained by the reaction of 1.6 g. of Id with 1.3 g. of benzoic acid in the presence of water. Yield of *O*-*p*-chlorophenyl-*N*-(β-benzoyloxyethyl)urethan was 28%, and that of *N*,*N'*-bis(β-benzoyloxyethyl)urea was 8.5%.

Reaction of O-aryl-N,N-ethyleneurethans (I) *with thiophenol in the presence of triethylamine and water* (Table III). 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 I and 0.55 g. (0.005 mole) of thiophenol were added, and the reaction mixture was allowed to stand at 15° for 24 hr. After distilling

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(5) H. Bestian, *Ann.*, **556**, 210 (1950).

(6) Y. Iwakura and A. Nabeya, *J. Org. Chem.*, **25**, 1118 (1960).

(7) Y. Iwakura and M. Sakamoto, *J. Polym. Sci.*, **47**, 277 (1960).

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.

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[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-naphthyl-*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).