temperature for 24 hr. The solvent was decanted from the dried mixed catalyst, which readily catalyzed the acylation of toluene (in excess) with benzoyl chloride, 4.20 g., 0.03 mole, giving *p*-methylbenzophenone in 60% yield.

Hydrolysis of 1,1,1-trichloroethane. A mixture of 21 g. of ferric chloride (0.13 mole) containing 3 g. (0.028 mole) of water and 72 g. (0.54 mole) of 1,1,1-trichloroethane was warmed gently until hydrogen chloride began to evolve. As reaction progressed, 3.0 g. of water was added over a period of 4 hr. while maintaining a temperature of 30° by water bath. When gas evolution had ceased, the reaction mixture consisted of an organic layer and a heavier layer containing the catalyst as a black oil. The organic layer was combined with several milliliters of product distilled under reduced pressure from the catalyst oil, and then fractionated, giving 6.3 g. of acetic acid (70% yield based on water added), 5.5 g. of vinylidene chloride, and 22 g. of methylchloroform. The inorganic residue was triturated with water which turned a deep violet color, leaving out of solution a tarry oil which eventually partially crystallized. The mixture was extracted with ether, decolorized and dried. Evaporation of the ether left a crystalline deposit which when recrystallized from hexane yielded 4.9 g. of white needlelike crystals, m.p. 85–6.

Anal. Calcd. for $C_6H_5ClO_2$: C, 49.84; H, 3.49; Cl, 24.53. Found: C, 50.10; H, 3.63; Cl, 24.36.

Infrared analysis in carbon tetrachloride gave an extremely intense absorption at 1744 cm.$^{-1}$ In methanol solution, maximum absorption occurred at 300 mμ, log ϵ = 3.38. Qualitative organic analytical tests for carbonyl and active chlorine were negative; bromine would not add; hydrolysis by acid solution was negative.

SILVER SPRING, MD.

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

O-Alkyl- and Aryl-*N*,*N*-ethyleneurethanes. I. Preparation and Reaction with Amines[1]

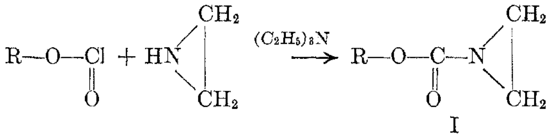
YOSHIO IWAKURA AND AIKO NABEYA

Received December 1, 1959

Several *O*-alkyl- or aryl-*N*,*N*-ethyleneurethanes were prepared, and the reactions of these urethanes with some aromatic amines were investigated. *O*-Alkyl-*N*,*N*-ethyleneurethanes gave only O-alkyl-*N*-(β-substituted ethyl)urethanes as the reaction products with amines. In the case of *O*-phenyl-*N*,*N*-ethyleneurethane, however, 1-substituted imidazolidinones-2 were obtained in addition to *O*-phenyl-*N*-(β-substituted ethyl)urethanes. This unexpected result was also observed in the reaction of other *O*-aryl-*N*,*N*-ethyleneurethanes with amines.

In our previous paper,[2] we reported the reaction of *N*-thiocarbamyl- and carbamyl derivatives of ethylenimine with several nucleophilic reagents. The results obtained there are summarized as follows: (1) *N*-phenyl- or cyclohexyl-*N'*,*N'*-ethylenethiourea is isomerized to thiazoline derivatives by heating in a high boiling solvent such as decalin or more smoothly in acids such as hydrochloric[3] or acetic. (2) The derivatives react with thiophenol giving *N*-phenyl- or cyclohexyl-*N'*-(β-phenylthioethyl)thiourea in good yields, and (3) in all cases, they show a strong tendency to polymerize by ring opening. In the case of *N*-phenyl-*N'*,*N'*-ethyleneurea, however, (1) the tendency to polymerize is not marked, and (2) isomerization to the oxazoline derivative is only observed in the reaction with picric acid, but (3) it reacts with thiophenol, hydrochloric acid, benzoic acid, and *p*-nitrobenzoic acid to give *N*-phenyl-*N'*-(β-substituted ethyl)-urea. Summarizing these results, it may be said that the substituent groups on the nitrogen of ethylenimine exert a strong influence upon the ring opening reaction of ethylenimine compounds.

We have extended the study to *N* - alkoxycarbonyl- or aryloxycarbonylethylenimine. The preparation of *O*-ethyl-*N*,*N*-ethyleneurethane (Ia) was described by Bestian.[4] In the same manner, we prepared several *O*-alkyl- and aryl-*N*,*N*-ethyleneurethanes from chloroformic acid esters and ethylenimine.



I

R = alkyl or aryl

O-Alkyl-*N*,*N*-ethyleneurethanes of lower molecular weight, in general, can be isolated by distillation and stored in a sealed tube for years without any appreciable change. But, the *O*-phenyl derivative (Id) seemed to be very unstable, especially on heating, and our attempts to isolate it by distillation under high vacuum were unsuccessful. Moreover, Id could not be crystallized by strong cooling in a Dry Ice–acetone bath. Accordingly, the purification of Id was only performed by extracting impurities with petroleum ether. *O*-*p*-substituted phenyl derivatives (Ie–Ih) were re-

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(1) Presented at the annual meetings of the Chemical Society of Japan, April 1957 and April 1958, and at the symposium of Organic Synthetic Chemistry of Japan, November 1958.

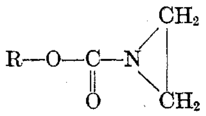
(2) Y. Iwakura and A. Nabeya, in part in the paper, J. *Chem. Soc. Japan, Pure Chem. Sect,* **77**, 773 (1956), and in part presented at the symposium of Organic Synthetic Chemistry of Japan, November 1958.

(3) Reported by S. Gabriel and R. Stelzner, *Ber.*, **28**, 2929 (1895).

(4) H. Bestian, *Ann.*, **566**, 210 (1950).

TABLE I

O-Alkyl- or Aryl-*N*,*N*-ethyleneurethanes (I)

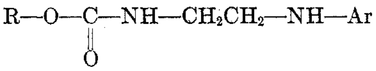


	R	B.P., °	Mm.	M.P., °	Formula	Analyses Calcd. C	H	N	Found C	H	N
Ia	Ethyl	67–68[a]	27		$C_5H_9NO_2$						
Ib	*n*-Butyl	49–51.5	2		$C_7H_{13}NO_2$	58.72	9.15		58.81	9.31	
Ic	Cyclohexyl	80–82	2.5		$C_9H_{15}NO_2$	63.88	8.94		63.68	8.99	
Id	Phenyl				$C_9H_9NO_2$	66.24	5.56		65.80	5.77	
Ie	*p*-Tolyl			46–48	$C_{10}H_{11}NO_2$			7.91			8.00
If	*p*-Ethoxyphenyl			47–49	$C_{11}H_{13}NO_3$			6.76			6.97
Ig	*p*-Nitrophenyl			125	$C_9H_8N_4O_2$	51.92	3.87	13.46	51.52	4.06	13.66
Ih	*p*-Chlorophenyl			50–51.5	$C_9H_8ClNO_2$			7.10			7.32

[a] Lit.,[4] b.p. 60–63°/21 mm.

TABLE II

Reaction Products Obtained by the Reaction of *O*-Alkyl-*N*,*N*-ethyleneurethanes with Aromatic Amines



$$R—O—\underset{\underset{O}{\|}}{C}—NH—CH_2CH_2—NH—Ar$$

II

	R	Ar	M.P., °	Yield, %	Formula	N Analyses Calcd.	Found
IIc	Cyclohexyl	Phenyl[a]	74–75	30	$C_{15}H_{22}N_2O_2$	10.68	10.82[b]
IIa′	Ethyl	*p*-Ethoxyphenyl	80–81.5	40	$C_{13}H_{20}N_2O_3$	11.10	11.10[b]
IIb′	*n*-Butyl	*p*-Ethoxyphenyl	68–69.5	30	$C_{15}H_{24}N_2O_3$	9.99	10.14
IIc′	Cyclohexyl	*p*-Ethoxyphenyl	82.5–83.5	55[c]	$C_{17}H_{26}N_2O_3$	9.14	9.36

[a] When the reaction was carried out at 75°, a small amount of higher melting compound (IVc), m.p. 127–128°, was obtained in addition to IIc. *Anal.* Calcd. for $C_{24}H_{37}N_3O_4$: C, 66.74; H, 8.64; N, 9.79. Found: C, 67.02; H, 8.58; N, 9.82. From the analytical data, IVc is considered to be *N*,*N*-bis(β-cyclohexyloxycarbonylamino)ethylaniline. [b] Phenyl isocyanate adducts were made as a proof of existence of amino group. From IIc: R = cyclohexyl and Ar = phenyl, m.p. 142–143°.

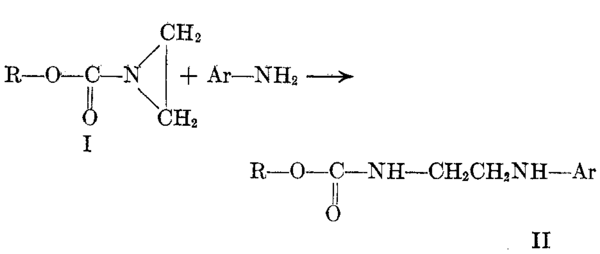
$$R—O_2C—NH—CH_2CH_2—N(Ar)CONHC_6H_5$$

Anal. Calcd. for $C_{22}H_{27}N_3O_3$: N, 11.02. Found: 10.90. From IIa′: R = ethyl and Ar = *p*-ethoxyphenyl, m.p. 129–130°. *Anal.* Calcd. for $C_{20}H_{25}N_3O_4$: N, 11.31. Found: 11.72. [c] By reaction at 75° the yield was 36% after 24 hr.

crystallized from ether or alcohol (in the case of Ig).

It was said that amines did not add to ethylenimine in an anhydrous state and without a catalyst,[5] while thiophenol[6] and phenol[7] did, giving β-substituted ethylamines. In our previous study,[2] no addition reactions of amines to the ethylenimine ring of ethylenethiourea or urea were observed.

O-Cyclohexyl-*N*,*N*-ethyleneurethane (Ic) gave, after standing two months with aniline at room temperature, *O*-cyclohexyl-*N*-(β-anilinoethyl)urethane (IIc) in 30% yield, while the other two *O*-alkyl urethanes (Ia and Ib) failed to give such a product under the same conditions even after one year. *p*-Phenetidine reacted with all of the three *O*-alkyl derivatives (Ia–Ic) giving *O*-alkyl-*N*-(β-*p*-phenetidinoethyl)urethanes (IIa′–IIc′) after standing one week at room temperature.



II

where R = alkyl and Ar = aryl

In the case of *O*-phenyl-*N*,*N*-ethyleneurethane (Id), the reaction proceeded rather differently. A few hours after Id was mixed with aniline at room temperature, white crystals began to separate, and soon the whole contents grew to a white mass. The melting point of the crude product ranged from 90° to 160° showing that it was a mixture. Recrystallization from alcohol gave 1-phenylimidazolidinone-2 (III), m.p. 163–164° (lit.,[3]

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(5) G. I. Braz and V. A. Skorodumov, *Compt. rend. acad. sci. U.R.S.S.* **55**, 315 (1947); *Chem. Abstr.*, **41**, 6527 (1947).

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

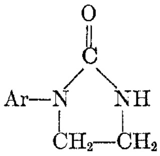
(7) L. B. Clapp, *J. Am. Chem. Soc.*, **73**, 2584 (1951).

TABLE III

RESULTS OBTAINED BY THE REACTION OF *O*-ARYL-*N*,*N*-ETHYLENEURETHANES WITH AROMATIC AMINES

$ArNHCH_2CH_2NHCO_2Ar$

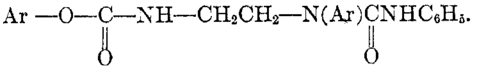
II



III

I	Ar′	Ar	React. Temp., °	Product	M.P., °	Yield, %	Formula	N Analyses, % Calcd.	N Analyses, % Found
Id	Phenyl	Phenyl	0	(IId)[a]					
				III	163–164		$C_9H_{10}N_2O$	17.27	17.17
		p-Ethoxyphenyl	0	IId′	89–91	17	$C_{17}H_{20}N_2O_3$	9.33	9.39[b]
				III′	210–211	15	$C_{11}H_{14}N_2O_2$	13.58	13.42
Ie	*p*-Tolyl	*p*-Ethoxyphenyl	0	IIe′	120–122	80	$C_{18}H_{22}N_2O_3$	8.91	9.27[b]
			35	[c] IIe′		56			
				IVe′	141–142	16	$C_{28}H_{33}N_3O_5$	8.55	8.43[d]
			75	IIe′		10			
				III′		19			
				IVe′		6			
If	*p*-Ethoxyphenyl	*p*-Ethoxyphenyl	0		120–140[e]				
Ih	*p*-Chlorophenyl	*p*-Ethoxyphenyl	0	IIh′	118–120	30	$C_{17}H_{19}ClN_2O_3$	8.37	8.70
				III′		20			
			35	IIh′		20			
				III′		30			
			75	III′		73			
Ig	*p*-Nitrophenyl[f]	Phenyl	0	IIg	107–109	40	$C_{15}H_{15}N_3O_4$	13.95	13.95[b]
			35	IIg		7			
				III		>0			
		p-Tolyl	0	IIg″	108–110	20	$C_{16}H_{17}N_3O_4$	13.33	13.65[b]
			35	IIg″		6			
				III″	193–194	17	$C_{10}H_{12}N_2O$	15.90	15.91
		p-Ethoxyphenyl	0	IIg′	115–117	18	$C_{17}H_{19}N_3O_5$	12.17	12.56
			35	III′		39			

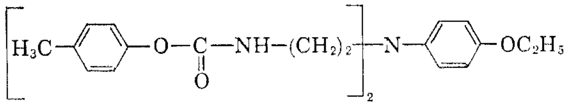
[a] II or III refers to aniline, II′ or III′ to *p*-phenetidine, and II″ or III″ refers to *p*-toluidine. [b] Phenyl isocyanate adducts were prepared.



$Ar{-}O{-}\underset{\underset{O}{\|}}{C}{-}NH{-}CH_2CH_2{-}N(Ar)\underset{\underset{O}{\|}}{C}NHC_6H_5.$

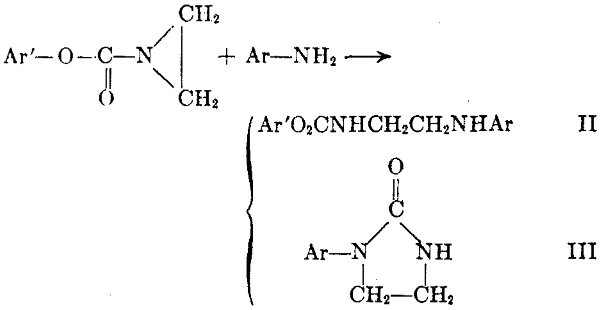
Ar′	Ar	M.P., °	Formula	N Analyses, % Calcd.	N Analyses, % Found
Phenyl	*p*-Ethoxyphenyl	101–102	$C_{24}H_{25}N_3O_4$	10.02	9.98
p-Tolyl	*p*-Ethoxyphenyl	106–108	$C_{25}H_{27}N_3O_4$	9.69	9.81
p-Nitrophenyl	Phenyl	122–124	$C_{22}H_{20}N_4O_5$	13.33	13.52
p-Nitrophenyl	*p*-Tolyl	110 *ca.*	$C_{23}H_{22}N_4O_5$	12.90	12.86

[c] In the presence of 1% of triethylaminehydrochloride, III′ was produced in 24% yield along with IIe′ and IVe′. From this fact it may be said that a small amount of triethylaminehydrochloride which might be contained in Id as an impurity has a catalytic action on the formation of type III compounds. Accordingly, further study on the reaction of Id was abandoned. [d] IVe is considered to be *N*,*N*-bis(β-*p*-methylphenoxycarbonylamino)ethyl-*p*-phenetidine,



It will be discussed in the Experimental. [e] The separation was unsuccessful. [f] Toluene was used as a solvent.

m.p. 160–161°), which was identified with an authentic sample prepared from *N*-phenyl-*N*′-(β-chloroethyl)urea and alcoholic potassium hydroxide. We failed, after some efforts, to isolate another compound, presumably *O*-phenyl-*N*-(β-anilinoethyl)urethane (IId). By the reaction of Id with *p*-phenetidine at 0°, 1-*p*-ethoxyphenylimidazolidinone-2 (III′), m.p. 210–211° (lit.,[8] m.p. 211–212°), and *O*-phenyl-*N*-(β-*p*-phenetidinoethyl)-urethane (IId′), m.p. 89–91°, were obtained in 15% and 17% yield respectively.



where Ar′ = aryl

To confirm these unexpected results encountered in the case of Id, we tried the same reaction using crystalline *O*-arylurethanes such as Ie–Ih, at various temperatures. The results are summarized in Table III.

These results support the general observation that the higher the reaction temperature and the greater the basicity of amine, the more type III compounds are formed (from the results of Ig, >0% for aniline, 17% for *p*-toluidine, and 39% for *p*-phenetidine at 35°), and that the greater the electron-attracting power of the substituent on the phenyl group of the urethanes the more type III compounds produced. It is a matter of interest by what mechanism type III compounds are formed under the experimental conditions. First, it may be considered that type II compounds once formed will be converted to III by the condensation reaction initiated by the intramolecular attack of nitrogen on the carbonyl carbon.

To confirm this hypothetical mechanism, we investigated the conversion of II to III. First, we heated the former in pyridine for one hour and compared the percentages of conversion with the yields of III by the reaction of ethyleneurethanes and amines in dioxane at 55°. The results are summarized in Table IV.

It is noted from Table IV that the order of conversion percentages from II to III is the same as the order of yields of III by the reaction of ethyleneurethanes and amines (NO_2 > Cl > CH_3, with respect to *p*-phenetidine).

TABLE IV

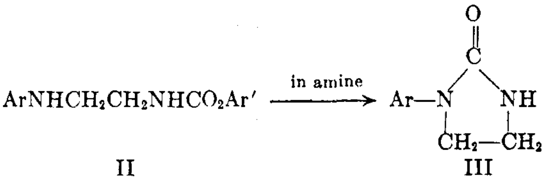
COMPARISON OF THE PERCENTAGES OF CONVERSION FROM II TO III WITH THE YIELDS OF TYPE III COMPOUNDS FROM ETHYLENEURETHANES AND AMINES

Yield of III from I and Amine[a]			Conversion from II to III[d]	
I	Amine	Yield of III(II), %	II	Conversion, %
Ic	Aniline	0(34)[b]	IIc	0
Ic	*p*-Phenetidine	0(26)	IIc′	0
Ie	*p*-Phenetidine	18(17)	IIe′	0
Ih	*p*-Phenetidine	31(32)	IIh′	32
Ig	Aniline[c]	10	IIg	74
Ig	*p*-Phenetidine[c]	43	IIg′	83

[a] A 0.005-mole sample of I and 0.005 mole of amine in 10 ml. of dioxane (in the case of Ic, dioxane was not added) were allowed to stand at 55° for 48 hr. [b] A small amount of IVc, m.p. 127–128°, was obtained. [c] An appreciable amount of Ig was polymerized. [d] II was heated in pyridine at reflux temperature for 1 hr.

TABLE V

CONVERSION OF TYPE II COMPOUNDS TO TYPE III COMPOUNDS



Ar′	Ar	Amine	React. Temp., °	Conversion
Phenyl	*p*-Ethoxyphenyl	*p*-Phenetidine	35	0
p-Tolyl	*p*-Ethoxyphenyl	*p*-Phenetidine	35	0
p-Tolyl	*p*-Ethoxyphenyl	*p*-Phenetidine	75	0
p-Chlorophenyl	*p*-Ethoxyphenyl	*p*-Phenetidine	35	0
p-Chlorophenyl	*p*-Ethoxyphenyl	*p*-Phenetidine	75	76
p-Nitrophenyl	Phenyl	Aniline[a]	35	>0
p-Nitrophenyl	*p*-Ethoxyphenyl	*p*-Phenetidine[a]	35	83

[a] Toluene was used as a solvent.

We next investigated the conversion of II to III under nearly the same experimental conditions (of Table III). The results are summarized in Table V.

These results suggest that in some cases, type III compounds might be formed *via* type II (from Ig and aniline and from Ig and *p*-phenetidine at 35°, and from Ih and *p*-phenetidine at 75°). But this fact does not entirely support the previous mechanism. (At 75°, Ie and *p*-phenetidine gave III′ in 19% yield, but IIe′ did not give III′ at 75° in the presence of excess *p*-phenetidine. At 0°, Ih and *p*-phenetidine gave III′ in 20% yield, but IIh′ did not give III′ at a temperature lower than 35° in the presence of excess *p*-phenetidine.)

The second hypothetical mechanism in which *N*-aryl-*N*′,*N*′-ethyleneurea is taken as an intermediate of the reaction, must be discarded, be-

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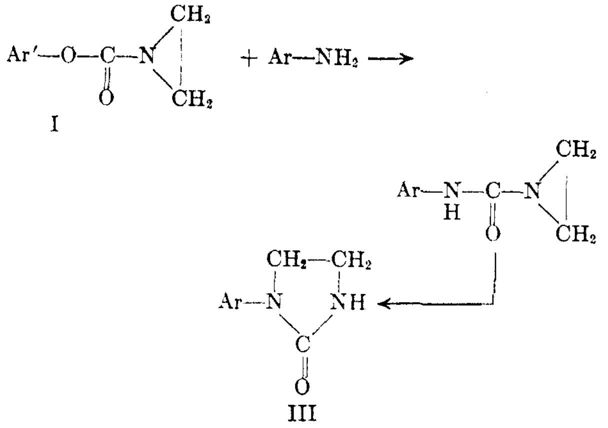
(8) A. F. McKay, W. R. R. Park, and S. J. Viron, *J. Am. Chem. Soc.*, **72**, 3660 (1950).



cause N-phenyl-N',N'-ethyleneurea and p-phenetidine gave N-phenyl-N'-p-ethoxyphenylurea at 35°.

EXPERIMENTAL

All boiling points and melting points are uncorrected. Microanalyses were done by Mr. 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.

Chloroformic acid esters. Chloroformic acid esters were prepared by the usual method[9] from phosgene and alcohols or phenols. (Commercially available ethyl chloroformate was distilled; b.p. 92–93°.) The following esters, ROCOCl, were prepared: R = *n*-Butyl, b.p. 50°/32 mm., yield: 80% (lit.,[10] b.p. 137.8°/734.5 mm.; lit.,[11] b.p. 142°, yield: 35%; lit.,[12] b.p. 40–47°/16 mm., 138°/756 mm.); R = Cyclohexyl, b.p. 46–47°/2–3 mm., yield: 82% (lit.,[13] b.p. 78–83°/12 mm.; lit.,[14] b.p. 38–44°/2 mm., yield: 73%); R = phenyl, b.p. 80°/22 mm., yield: 70% (lit.,[15] b.p. 95°/20 mm.); R = *p*-tolyl, b.p. 55–56°/4 mm., yield: 82% (lit.,[16] b.p. 108°/30 mm., yield: 78–80%); R = *p*-ethoxyphenyl, b.p. 99°/5 mm., yield: 65%; R = *p*-Nitrophenyl, m.p. 80–81°, yield: 80% (lit.,[17] m.p. 81–82°); R = *p*-Chlorophenyl, b.p. 79–80°/5 mm., yield: 82% (lit.,[9a] b.p. 114°/20 mm.).

An example of the preparation of N-alkoxycarbonylethylenimine. O-Cyclohexyl-N,N-ethyleneurethane (Ic). To a solution of 10.7 g. (0.250 mole) of ethylenimine and 24.4 g. (0.241 mole) of triethylamine in 100 ml. of ether, a solution of 37.7 g. (0.232 mole) of cyclohexyl chloroformate in 20 ml. of ether was added dropwise under cooling in an ice-salt bath and with vigorous stirring. After the addition was complete, stirring was continued for 1 hr., then triethylamine hydrochloride was removed by filtration. After the ether was evaporated, the residual liquid was distilled under vacuum. The yield was 72% (28 g.).

The yield of Ia was 74%, of Ib 78%. Ib and Ic were almost unchanged after storage in a sealed tube for 2.5 years at room temperature.

Examples of the preparation of N-aryloxycarbonylethylenimine. (a) *O-Phenyl-N,N-ethyleneurethane* (Id). A 23.5-g. sample (0.150 mole) of phenyl chloroformate, 6.6 g. (0.153 mole) of ethylenimine and 15.5 g. (0.153 mole) of triethylamine were mixed by the above method keeping the temperature below −5°. After removing triethylamine hydrochloride by filtration and ether by distillation under reduced pressure, the residual liquid was submitted to distillation at 0.06 mm. When the temperature of the bath reached 60°, the liquid became very viscous. Even by strong cooling in a Dry Ice–acetone bath, it failed to crystallize. Thus the isolation of Id was unsuccessful. Washing the above liquid twice with petroleum ether, followed by distillation of the low boiling substances under reduced pressure left 13.5 g. of viscous liquid, which on standing at room temperature, solidified to a polymer-like mass.

(b) *O-p-Tolyl-N,N-ethyleneurethane* (Ie). An 8.5-g. sample (0.050 mole) of *p*-tolyl chloroformate 2.2 g. (0.051 mole) of ethylenimine, and 5.2 g. (0.051 mole) of triethylamine were brought to reaction in the preceding way. After removal of the triethylamine hydrochloride, the ethereal solution was immersed in a Dry Ice–acetone bath. White crystals precipitated. Thus 6.4 g. (72%) of Ie, melting at 45–47°, was obtained. After washing with cold water and recrystallization from ether, it melted at 46–48°. Infrared absorption spectra showed a strong absorption band at 1743 cm.$^{-1}$ (C═O).

If (yield 69%) and Ih (yield 70%) were prepared in the same manner.

(c) *O-p-Nitrophenyl-N,N-ethyleneurethane* (Ig). When a solution of *p*-nitrophenyl chloroformate was added to a solution of ethylenimine and triethylamine, in the same method mentioned in the preparation of Ic, *p,p′*-dinitrophenyl carbonate was obtained instead of ethyleneurethane, (m.p. 138–140°,[18] after recrystallization from chloroform and petroleum ether).

Anal. Calcd. for $C_{13}H_8N_2O_7$: N, 9.21. Found: N, 9.37. As the same substance was obtained by the reaction of *p*-nitrophenyl chloroformate with triethylamine, the preceding method of mixing was considered to be inadequate to the preparation of ethyleneurethane. (At the beginning of the reaction, *p*-nitrophenyl chloroformate was surrounded by a large amount of amine). Therefore, a solution of amines was slowly added to a solution of chloroformate.

To a solution of 15.0 g. (0.075 mole) of *p*-nitrophenyl chloroformate in 200 ml. of ether was added a solution of 3.3 g. (0.075 mole) of ethylenimine and 7.6 g. (0.075 mole) of triethylamine in 50 ml. of ether, keeping the temperature at about −10°. The precipitate was filtered and extracted with 200 ml. of acetone. By cooling the acetone solution in a Dry Ice–acetone bath, colorless crystals were obtained. Additional yield was obtained by treating the above residue with ice water. The combined product after being washed several times with ice water and dried, weighed 10 g. (65%), and melted at about 125°. Recrystallization from alcohol did not raise the melting point. Infrared absorption spectra of Ig showed a strong carbonyl absorption band at 1737 cm.$^{-1}$

Examples of reaction of ethyleneurethane with aromatic amines. (a) *Reaction of O-ethyl-N,N-ethyleneurethane* (Ia) *with p-phenetidine.* A 1.2-g. sample (0.01 mole) of Ia and 1.4 g. (0.01 mole) of *p*-phenetidine were allowed to stand at room temperature. After a week, crystals began separating. By adding petroleum ether (b.p. 40°–65°), the crude product was obtained. After recrystallization from ether and petroleum ether (b.p. 40°–65°) 1.0 g. (40%) of IIa′ was obtained.

IIb′ and IIc′ were obtained in the similar way.

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By refluxing IIa′ with phenyl isocyanate in benzene for 2 hr. the adduct was obtained.

(b) *Reaction of O-p-tolyl-N,N-ethyleneurethane* (Ie) *with p-phenetidine at 0°.* A 1.77-g. sample (0.010 mole) of Ie and 1.37 g. (0.010 mole) of *p*-phenetidine were mixed together at 0°, and stored in a refrigerator for a week. By recrystallization of the product from ether and alcohol, 2.5 g. (80%) of IIe′, melting at 120–122°, was obtained. Infrared absorption spectra of IIe′ showed a strong carbonyl absorption band at 1701 cm.$^{-1}$, and NH band at 3349 cm.$^{-1}$.

At 35°. A 1.77-g. sample of Ie and 1.37 g. of *p*-phenetidine were mixed at 35° and stored in a thermostat kept at 35°. After 4 days, the crude product was recrystallized from alcohol. Fine needles, melting at about 140° (IVe′), were obtained, weighing 0.8 g. From the alcoholic filtrate, 1.8 g. (56%) of IIe′, melting at about 120°, was obtained.

IVe′ was recrystallized from alcohol and melted at 141–142°. Infrared absorption spectra of IVe′ showed a strong absorption band at 1695 cm.$^{-1}$, (C=O), and of NH at 3311 cm.$^{-1}$.

Anal. Calcd. for $C_{28}H_{33}N_3O_5$: C, 68.41; H, 6.79. Found: C, 67.71; H, 6.70. Molecular weight determined by Akiya's method[19] was nearly 490. (Calcd.: 491.)

By the reaction of 220 mg. of Ie and 400 mg. of IIe′ in toluene at 35°, 450 mg. of IVe′ was obtained. IVe′ reacted with diethylamine to give presumably *N,N*-bis(β-diethylureido)ethyl-*p*-phenetidine, m.p. 124–125°.

Anal. Calcd. for $C_{22}H_{39}N_5O_3$: C, 62.68; H, 9.33; N, 16.61. Found: C, 62.50; H, 9.39; N, 17.06.

At 75°. A 1.77-g. sample of Ie and 1.37 g. of *p*-phenetidine were mixed at 75°, and stored in a thermostat kept at 75°. After an hour, crystals began separating. After 24 hr., the sticky crude product (presumably polymerization of Ie took place in part) was recrystallized from alcohol. Glittering flakes, melting at 210° (III′), were obtained first. After filtration of III′, the alcoholic solution was concentrated gradually, and an additional crop of III′ was filtered, and the filtrate was again concentrated. As soon as fine needle crystals began separating, the solution was cooled gradually. IVe′ was thus obtained. After removing IVe′ and evaporating the alcohol, the residue was recrystallized from ether. Thus IIe′ was obtained.

III′ weighed 0.4 g. (19%) and melted at 210°. IVe′ weighed 0.3 g. (6%) and melted at 140°. IIe′ weighed 0.3 g. (10%) and melted at 120°.

(c) *Reaction of O-p-nitrophenyl-N,N-ethyleneurethane* (Ig) *with p-toluidine, at 0°.* To a solution of 0.54 g. (0.005 mole) of *p*-toluidine in 2 ml. of toluene, 1.04 g. (0.005 mole) of finely powdered Ig was added at 0°. Ig remained undissolved in part. The mixture was then stored in a refrigerator. After a month, ether was added to the sticky contents, when 0.2 g. of Ig was recovered unchanged. Evaporation of the solvent gave a yellow polymer-like residue from which 0.3 g. (20%) of IIg″, melting at 108–109° with brown coloration, was extracted with ether.

At 35°. To a solution of 1.07 g. (0.010 mole) of *p*-toluidine in 1 ml. of toluene, 2.08 g. (0.010 mole) of Ig was added at 35°. Ig gradually dissolved. After the mixture had stood at 35° for 4 days, the contents were recrystallized from alcohol. III″, 0.3 g. (17%) melting at 193° was obtained as flakes, and then from the filtrate, about 0.2 g. (6%) of IIg″, melting at 108° with brown coloration, was obtained.

An example of the reaction of ethyleneurethane with amine in dioxane at 55°. Reaction of O-p-nitrophenyl-N,N-ethyleneurethane (Ig) *with p-phenetidine.* A 1.04-g. sample (0.005 mole) of Ig and 0.69 g. (0.005 mole) of *p*-phenetidine in 10 ml. of dioxane were allowed to stand at 55° for 48 hr. Fine flakes, melting at 210° (III′), were filtered, and the filtrate was concentrated under reduced pressure. An additional crop of III′ was filtered and the filtrate was again concentrated to dryness. The residue was a polymer-like substance from which pure compound was not obtained by extraction with ether. The yield of III′ was 440 mg. (43%).

An example of conversion of a type II *compound to a type* III *in refluxing pyridine. O-p-Chlorophenyl-N-(β-p-phenetidinoethyl)-urethane* (IIh′). A 100-mg. sample of IIh′ was refluxed in 1 ml. of pyridine for 1 hr. After the pyridine was removed by distillation under reduced pressure, the residue was recrystallized from alcohol. A 20-mg. sample (32%) of III′, melting at 210°, was obtained first. From the filtrate, 50 mg. (50%) of IIh′ was recovered.

Conversion of IIh′ *in p-phenetidine.* A 100-mg. sample of IIh′ was allowed to stand in *p*-phenetidine, at 35° for 3 days, at 55° for 2 days, and at 65° for a day. In all cases, IIh′ was recovered unchanged. But at 70°, after a day, a small quantity of III′ was obtained with 70 mg. of IIh′.

A 340-mg. sample of IIh′ was allowed to stand in *p*-phenetidine at 75° for 24 hr. By addition of ether and alcohol, 160 mg. (76%) of III′, melting at 210°, was obtained. Attempts to recover IIh′ were unsuccessful.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE PAINT DIVISION, PITTSBURGH PLATE GLASS COMPANY]

Reaction of Acrylamide and Pyridinium Chloride

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Acrylamide and pyridinium chloride react to give *N*-(2-carbamylethyl)pyridinium chloride, II, whose structure was proved by hydrogenation of it to the piperidinium analog which was synthesized independently. The reaction was extended to several other heterocyclic base salts and α,β-unsaturated amides.

Some time ago it was disclosed in a patent[1] that aliphatic amides, formaldehyde (or *N*-hydroxymethylamides) and salts of the tertiary heterocyclic bases react to form *N*-amidomethyl inium salts (I). More recently, Weaver and coworkers[2] investigated this reaction in more detail

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