14 was dehydrated and purified to produce 17 in the same manner used for the preparation of 16 from 13.

Anal. Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 91.09; H, 8.82.

Registry No.—3, 573-57-9; 9, 4453-90-1; 10, 30953-00-5; 11, 30882-79-2; 12, 30882-80-5; 13, 30882-81-6; 14, 30882-82-7; 15, 30882-83-8; 16, 2876-35-9; 17, 1134-62-9.

Acknowledgment.—We are indebted to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.

Synthetic Reactions by Complex Catalysts. XX. Copper(I)-Catalyzed Formimidation of Amine, Alcohol, and Amide by Vinyl Isocyanide

TAKEO SAEGUSA,* ICHIKI MURASE, AND YOSHIHIKO ITO

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan

Received November 30, 1970

In the presence of cuprous oxide catalyst, vinyl isocyanide (VIC) easily reacts with amine, alcohol, thiol, and several *N*-alkyl derivatives of carboxylic amide, carbamate, urea, and thiourea. The reaction with primary amine occurs in two courses according to the VIC–amine feed ratio; the one leads to **4** by the twofold formimidation and the other to the production of a mixture of **6** and **7**. The reaction of VIC with *N*-alkylamide produces the formimidation product **11**. Similarly, the reactions of VIC with *N*-alkyl derivatives of carbamate, urea, and thiourea proceed at room temperature to give the corresponding *N*-vinylformimidate derivatives (eq 5). In the reaction with alcohol, two consecutive reactions take place. The first reaction is formimidation and the second one is the 1,4 addition of alcohol to the formimidation product (eq 9). The product is determined by the VIC–alcohol feed ratio and the reaction temperature. The reaction with thiol is similar to that with alcohol.

In previous papers[1-5] we have described the copper-catalyzed reactions of various $R_{n-1}YH$ compounds with isocyanide to give α-addition products (eq 1).

$$R_{n-1}YH + R'N{\equiv}C: \longrightarrow R_{n-1}YCH{=}NR' \quad (1)$$

(1)

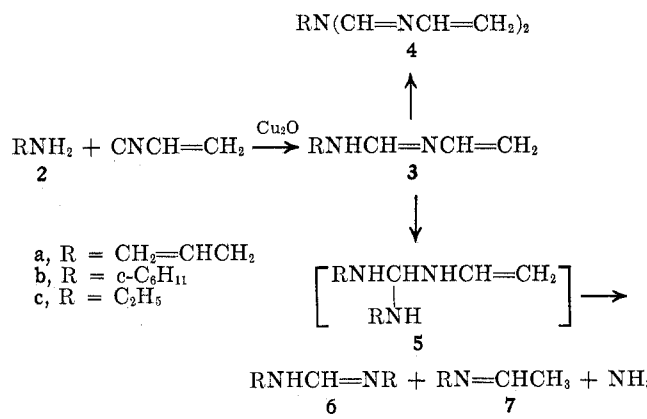
Y = N, P, O, S, Si

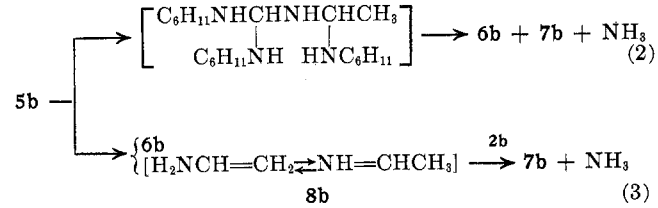
The products of these reactions can be regarded as the derivatives of a hypothetical species of formimidic acid, HOC(=NR)H. We wish to propose a general name of "formimidation" for these reactions. In this paper we report the extension of these reactions to vinyl isocyanide (VIC).

Results and Discussion

Reaction with Amines.—In the combination of VIC–secondary amine, (*e.g.*, piperidine), the usual formimidation takes place at room temperature to produce *N*-vinylformamidine in quantitative yields (Table I).

The Cu_2O-catalyzed reactions of VIC with primary amines, however, give three products (**4**, **6**, and **7**) depending upon the VIC–amine feed ratio and the nature of the amine. The equimolecular reaction of VIC with cyclohexylamine (**2b**) produces three products, **4b**, **6b**, and **7b**, in a ratio of 0.4:1:1.3. The reaction of 2:1 VIC–**2b** gives only **4b**, whereas that of 1:4 VIC–**2b** affords **6b** and **7b**. The formation of **4b** is explained by the secondary reaction of the normal formimidation product **3b**, *i.e.*, the insertion of VIC into >NH of **3b**. The formations of **6b** and **7b** are rationalized by a scheme of the reaction of **3b** with amine. The addition of **2b** to the >C=N– bond of **3b** leads to an unstable triamine **5b**, whose decomposition produces **6b** and **7b**. The decomposition of **5b** may possibly take either of the following two courses. The one is the addition of amine to **5b**, which is followed by the cleavages of an unstable polyamino compound (eq 2). The other is the cleavage of **5b**, producing **6b** and aldimine (**8b**), which is followed by the reaction of **8b** with **2b** (eq 3).





It is important that the transient product of **3b** is not isolated even in the system of an equimolecular reaction of VIC with primary amine. The same result was obtained with ethylamine; *i.e.*, the reaction of excess VIC with ethylamine afforded **4c** in a high yield. The

(1) T. Saegusa, Y. Ito, S. Kobayashi, K. Hirota, and H. Yoshioka, *Tetrahedron Lett.*, 6121 (1966).

(2) T. Saegusa, Y. Ito, and S. Kobayashi, *ibid.*, 935 (1968).

(3) T. Saegusa, Y. Ito, S. Kobayashi, N. Takeda, and K. Hirota, *ibid.*, 1273 (1967).

(4) T. Saegusa, S. Kobayashi, K. Hirota, Y. Okumura, and Y. Ito, *Bull. Chem. Soc. Jap.*, **41**, 1638 (1968).

(5) T. Saegusa, Y. Ito, S. Kobayashi, and K. Hirota, *J. Amer. Chem. Soc.*, **89**, 2240 (1967).

TABLE I

FORMIMIDATION OF AMINES AND FORMAMIDINES BY VINYL ISOCYANIDE (VIC)[a]

Amine or formamidine	Concn, mmol	VIC, mmol	Cu_2O, mmol	Solvent (ml)	Time, hr	Product	Yield, %
Piperidine	60	45	0.75	Benzene (5)	12	**3**	~100[b]
CH_2=$CHCH_2NH_2$	30	30	0.75	Benzene (5)	15	**4a**	~100[b]
c-$C_6H_{11}NH_2$	15	40	0.35	Toluene (8)	24	**4b**	~100[b]
c-$C_6H_{11}NH_2$	60	15	0.35	Toluene (8)	24	**6b**	80[c]
						7b	61[c]
$EtNH_2$	20	60	0.75	Toluene (8)	12	**4c**	95[c]
EtNHCH=N-c-C_6H_{11}	13	10	0.35	Toluene (4)[d] CH_2Cl_2 (4)	12	**10a**	71[c]
EtNHCH=NEt	10	7.5	0.35	Toluene (4)	18	**10b**	85[c]

[a] All the reactions were carried out at room temperature. [b] Yields were determined by glpc analysis. [c] Yields were determined by vacuum distillation. [d] Mixed solvent was used.

equimolecular reaction VIC with allylamine produces **4a** alone (Table I).

The scheme of the formation of **4** *via* **3** has been substantiated by a reference experiment, in which a formamidine **9** was first prepared from a primary amine and a saturated alkyl isocyanide and was then subjected to the Cu_2O-catalyzed reaction with VIC. The

$$\underset{\mathbf{9}}{RNHCH{=}NR'} + CNCH{=}CH_2 \xrightarrow{Cu_2O} RN\begin{matrix}\diagup CH{=}NR' \\ \diagdown CH{=}NCH{=}CH_2 \\ \mathbf{10}\end{matrix} \quad (4)$$

a, R = Et; R′ = c-C_6H_{11}
b, R = Et; R′ = Et

formimidation of **9** with VIC under the same reaction conditions (Cu_2O catalyst and room temperature) gave **10** in a high yield (Table I). Saturated alkyl isocyanides do not react with the >NH group of formamidine **9** under the conditions of the present study. Thus, a higher reactivity of VIC has been demonstrated.

Reaction with Amide.—In the presence of Cu_2O catalyst, VIC reacts also with the >NH group of *N*-alkylamide at room temperature (eq 5, Table II). Saturated alkyl isocyanides did not react with *N*-alkylamide even at 80°. The formimidations of *N*-allyl-

$$RCONHR' + CNCH{=}CH_2 \longrightarrow RCON\begin{matrix}\diagup R' \\ \diagdown CH{=}NCH{=}CH_2 \\ \mathbf{11}\end{matrix} \quad (5)$$

formamide and *N*-methylacetamide with VIC are rapid at room temperature, whereas the formimidation of ε-caprolactam is slow at room temperature (conversion 5–10% after 24 hr) and becomes fairly fast at 80°. Without catalyst, the VIC–*N*-alkylamide reaction did not take place. Among the catalysts examined, Cu_2O gave the best results. CuCl, Ag_2O, CH_3COOAg, and AgCl were inactive. Unsubstituted amides such as formamide and acetamide as well as succinimide did not react with VIC even in the presence of Cu_2O.

Interestingly, phenyl isocyanide also reacts with monosubstituted amides at 80° (eq 6). The results are incorporated in Table II.

$$RCONHR' + CNPh \longrightarrow RCON\begin{matrix}\diagup R' \\ \diagdown CH{=}NPh \\ \mathbf{12}\end{matrix} \quad (6)$$

TABLE II

FORMIMIDATION OF AMIDES BY VIC AND PHENYL ISOCYANIDE[a]

Amide	Concn, mmol[a]	Cu_2O, mmol	Time, hr	Temp, °C	Yield,[c] %
		Vinyl Isocyanide			
CH_2=$CHCH_2NHCHO$	15	0.35	12	Room	60
$CH_3NHCOCH_3$	15	0.35	12	Room	71
ε-Caprolactam	30[b]	0.75	6	80	75[d]
		Phenyl Isocyanide			
CH_2=$CHCH_2NHCHO$	10	0.35	12	80	69
$CH_3NHCOCH_3$	10	0.35	12	80	81
ε-Caprolactam	20	0.35	12	80	83

[a] An equimolar mixture of isocyanide and amide was subjected to the Cu_2O-catalyzed reaction in 5 ml of toluene. [b] As the reaction solvent, 10 ml of toluene was used. [c] Yields were determined by distillation. [d] By glpc analysis, the reaction at room temperature for 24 hr gave a yield of 5–10%.

Probably the distinctive reactivities of VIC and phenyl isocyanide in the Cu_2O-catalyzed reaction with amides may be ascribed to strong electron deficiency at the terminal carbon atom of these isocyanides. The ir stretching vibrations of isocyanide groups of VIC and phenyl isocyanide are at lower frequencies compared with those of saturated isocyanides (ν_{NC}, cm^{-1}).

CH_2=$CHNC$	C_6H_5NC	C_4H_9NC	c-$C_6H_{11}NC$	CH_3NC
(2128)	(2129)	(2147)	(2144)	(2163)

The ν_{NC} band at a lower frequency is taken to suggest that the contribution of the canonical form of **13** is more enhanced in VIC and phenyl isocyanide than in the usual alkyl isocyanides.

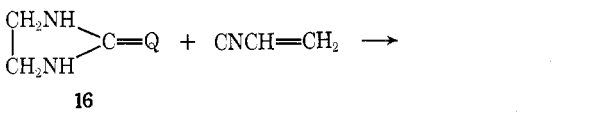
$$\underset{\mathbf{13}}{R{-}\ddot{N}{=}C:} \longleftrightarrow \underset{\mathbf{14}}{R{-}\overset{+}{N}{\equiv}\bar{C}:}$$

Reaction with Urethane, Urea, and Thiourea.—In the presence of Cu_2O catalyst, *N*-alkyl derivatives of urethane (eq 7), urea, and thiourea (eq 8) reacted successfully with VIC at room temperature. Under the conditions of the present study, species having no alkyl substituent at amino group did not react. Ethyl carbamate and urea were recovered unchanged from the reaction mixture of formimidation. In the reactions of ethyleneurea (**16a**) and ethylenethiourea (**16b**) with equimolar amount of VIC, monoformimidated (**17a** and **17b**) and bisformimidated (**18a** and **18b**) products were formed. The relative ratios of these two products depend upon the feed ratios of VIC–urea and

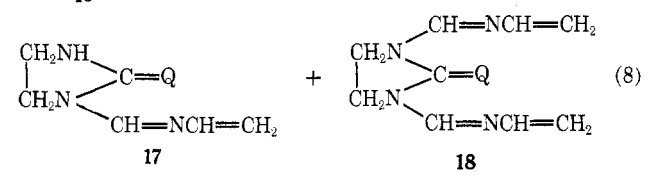
$$RNHCO_2R' + CNCH{=}CH_2 \longrightarrow \underset{\displaystyle CH{=}NCH{=}CH_2}{\overset{\displaystyle |}{RNCO_2R'}} \quad (7)$$

15

a, R = R′ = Me
b, R = Et; R′ = Me
c, R = Me; R′ = c-C_6H_{11}



16



17 18 (8)

a, Q = O
b, Q = S

VIC–thiourea, respectively. The VIC–urea and VIC–thiourea reactions were quantitative (Table III).

TABLE III
FORMIMIDATION OF CARBAMATES, UREAS, AND THIOUREAS BY VIC[a]

Reagent	Concn, mmol	VIC, mmol	Cu_2O, mmol		Yield, %
		Carbamate[b]			
CH_3NHCOO-c-C_6H_{11}	7	7	0.35		73[c]
$CH_3NHCOOCH_3$	15	15	0.35		75[c]
$C_2H_5NHCOOCH_3$	15	15	0.35		70[c]
		Urea, Thiourea[d]			
Ethyleneurea	20	15	0.35	17a	100[e]
Ethyleneurea	10	25	0.35	18a	100[e]
Ethylenethiourea	20	15	0.35	17b	100[e]
Ethylenethiourea	10	25	0.35	18b	100[e]

[a] All the reactions were carried out at room temperature for 12 hr. [b] The reaction was carried out in 4 ml of toluene. [c] By distillation. [d] The reaction was carried out in 10 ml of pyridine. [e] Quantitative.

Reaction with Alcohol and Thiol.—In the Cu_2O-catalyzed reaction of VIC with alcohol, the normal formimidation takes place, which is sometimes followed by the addition of a second alcohol molecule to the product formimidate (**19**) (Table IV). These are

$$ROH + CNCH{=}CH_2 \xrightarrow[\text{step 1}]{Cu_2O} \underset{\displaystyle 19}{ROCH{=}NCH{=}CH_2} \xrightarrow[\text{step 2}]{ROH} (RO)_2CHN{=}CHCH_3 \quad (9)$$

20

a, R = Me
b, R = Et
c, R = c-C_6H_{11}
d, R = $CH_2CH{=}CH_2$
e, R = isopropyl
f, R = *tert*-butyl

consecutive reactions, and the relative rates of steps 1 and 2 of reactions determine the product ratio of **19** and **20**. For example, the VIC–methanol reaction at a molar ratio of 3:5 at room temperature produced **20a** in a quantitative yield, whereas the reaction at a ratio of 5:1 gave only **19a** quantitatively. The VIC–ethanol reaction at a ratio of 1:1.1 produced **20b** quantitatively. Furthermore, the VIC–cyclohexanol ratio of 1:3 at room temperature produced **19c**, but the reaction of the same feed ratio of 1:3 carried out at 80° gave **20c**. The equimolecular reactions of VIC with isopropyl alcohol and VIC with *tert*-butyl alcohol produced only **19d** and **19e**, respectively, in decreased yields.

The mechanism of the consecutive reactions has been supported by a reference experiment in which **19c** was isolated and subjected to the reaction with cyclohexanol at 80°. The reaction of **19c** with cyclohexanol proceeded without Cu_2O catalyst. The addition of alcohol to **19c** is of the mode of a 1,4 addition.

The Cu_2O-catalyzed VIC–ethanethiol (1.1:1) reaction produced two products, **21a** and **22a** adducts.

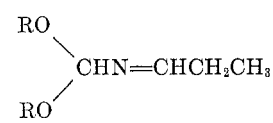
$$RSH + CNCH{=}CH_2 \longrightarrow \underset{\displaystyle 21a}{RSCH{=}NCH{=}CH_2} \longrightarrow (RS)_2CHN{=}CHCH_3 \quad (10)$$

22a

a, R = Et

The analogous type of product **24** was obtained by the formimidation of alcohol with a kind of α,β-unsaturated isocyanide and propenyl isocyanide **23**. The 1,4 addition seems to be characteristic for the formimidation of alcohol with α,β-unsaturated isocyanide.

$$ROH + \underset{\displaystyle 23}{CH_3CH{=}CHNC} \xrightarrow{Cu_2O} ROCH{=}NCH{=}CHCH_3 \longrightarrow$$



24

a, R = CH_3

Experimental Section

Reagents.—VIC was prepared according to Matteson's procedure.[6] Cyclohexyl isocyanide[7] and phenyl isocyanide[8] were prepared according to Ugi's procedure. Allyl- and cyclohexylamines and piperidine were all commercial reagents and were purified by distillation after drying over potassium hydroxide. Anhydrous ethylamine was prepared by dehydrating aqueous ethylamine with potassium hydroxide.[9] *N*-cyclohexyl-*N*′-ethyl- and *N*,*N*′-diethylformamidine were prepared by the Cu_2O-catalyzed formimidation of ethylamine with cyclohexyl and ethyl isocyanides, respectively.[1] Allylformamide was prepared from allylamine and ethylformate. *N*-methylacetamide and ϵ-caprolactam were commercial reagents of extra pure grade. Methyl *N*-methylcarbamate and cyclohexyl *N*-methylcarbamate were prepared from methyl isocyanate with the corresponding alcohols. Methyl *N*-ethylcarbamate was prepared from ethylamine and chloroformate.[10] Ethyleneurea and ethylenethiourea were commercial reagents. Cuprous oxide was a commercial reagent of analytical reagent grade and was dried under nitrogen atmosphere prior to use.

Reaction of VIC with Amines. Reaction with Primary Amines.—The reaction was carried out in a sealed test tube under nitrogen. Most of the products were isolated by vacuum distillation and purified by preparative glpc. Some products were isolated and purified by recrystallization. The product structures were determined mostly by ir and nmr spectra and elemental analysis.

(6) (a) D. S. Matteson and R. A. Bailey, *Chem. Ind. (London)*, 191 (1967); (b) D. S. Matteson and R. A. Bailey, *J. Amer. Chem. Soc.*, **90**, 3762 (1968).
(7) I. Ugi and R. Meyer, *Chem. Ber.*, **93**, 239 (1960).
(8) I. Ugi, *Angew. Chem.*, **77**, 492 (1965).
(9) R. Mozingo and J. McCracken, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y. 1962, p 258.
(10) W. Hartman and M. Brethen, "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1961, p 278.

TABLE IV

REACTION OF ALCOHOL AND THIOL WITH VIC

Reagent	Concn, mmol	VIC, mmol	Cu_2O, mmol	Solvent (ml)	Time, hr	Temp, °C	Product	Yield, %
CH_3OH	5	45	0.75	Benzene (6)	24	Room	**20a**	~100[a]
CH_3OH	12.5	62.5	0.75	CH_2Cl_2 (8)	24	Room	**19a**	~100[a]
EtOH	17.3	15	0.75	Benzene (3)	24	Room	**20b**	~100[a]
c-$C_6H_{11}OH$	30	30	0.75	CH_2Cl_2 (8)	12	Room	**19c**	~76[b]
c-$C_6H_{11}OH$	90	30	0.75	Benzene (6)	12	Room	**19c**	~100[a]
c-$C_6H_{11}OH$	90	30	0.75	Benzene (6)	4	80	**20c**	~82[b]
Allyl OH	41	37.5	0.75	Benzene (5)	24	Room	**20d**	~100[a]
i-PrOH	30	30	0.75	(CH_2Cl_2 (5)	6	Room	**19e**	~60[b]
tert-BuOH	30	30	0.75		24	80	**19f**	~4–5[a]
EtSH	45	50	0.35	CH_2Cl_2 (10)	24	Room	**21:22**	~2:3 mixture[a]

[a] Yields were determined by glpc analysis. [b] Yields were determined by distillation.

Identification of Products.—*N*,*N*-Di(*N*′-vinylformimidoyl)-allylamine (**4a**): bp 72° (3 mm); ir (neat) 1640 and 1595 cm^{-1} (C=C, N=C); nmr ($CDCl_3$) τ 2.02 (2 H, singlet, CH=N), 3.27 (2 H, quartet, C**H**=CH_2), 4.83, 5.25 (4 H, two sets of doublets, CH=C**H**$_2$).

Anal. Calcd for $C_9H_{13}N_3$: C, 66.22; H, 8.03; N, 25.75. Found: C, 65.97; H, 8.46; N, 25.33.

N,*N*-Di(*N*′-vinylformimidoyl)cyclohexylamine (**4b**): bp 125–130° (1 mm); ir (neat) 1630 and 1950 (broad, C=C, N=C), 972 cm^{-1} (terminal olefin); nmr ($CDCl_3$) τ 1.76 (2 H, singlet, CH=N), 3.15 (2 H, quartet, C**H**=CH_2), 4.85, 5.27 (4 H, two sets of doublets, CH=C**H**$_2$).

Anal. Calcd for $C_{12}H_{19}N_3$: C, 70.20; H, 9.33; N, 20.47. Found: C, 69.57; H, 9.46; N, 20.13.

N,*N*-Di(*N*′-vinylformimidoyl)ethylamine (**4c**): bp 95–100° (2 mm); ir (neat) 1600 and 1580 cm^{-1} (broad, C=C, N=C); nmr ($CDCl_3$) τ 2.10 (2 H, singlet, CH=N), 3.18 (2 H, quartet, C**H**=CH_2), 4.84, 5.25 (4 H, two sets of doublets, CH=C**H**$_2$).

Anal. Calcd for $C_8H_{13}N_3$: C, 63.54; H, 8.67; N, 27.79. Found: C, 63.05; H, 8.57; N, 28.22.

N,*N*′-Dicyclohexylformamidine (**6b**): mp 101°. The identification was made by comparison of ir and nmr spectra and mixture melting point with the authentic sample.[1]

N-Ethylidenecyclohexylamine (**7b**): bp 65–72° (70 mm); mass spectrum *m*/*e* 125 (M^+); ir 1667 cm^{-1} (N=C); nmr ($CDCl_3$) τ 2.25 (1 H, quartet, N=CH), 8.25 (3 H, doublet, CHC**H**$_3$), *ca.* 10 (1 H, cyclohexyl proton).

Anal. Calcd for $C_8H_{15}N$: C, 76.74; H, 12.08; N, 11.19. Found: C, 75.87; H, 12.67; N, 11.42.

Reaction with Piperidine.—A mixture of 2.4 g (45 mmol) of VIC, 5.1 g (60 mmol) of piperidine, and 0.1 g (0.75 mmol) of Cu_2O in 5 cm^3 of benzene was kept still at room temperature in a sealed test tube under nitrogen for 12 hr. Then petroleum ether (bp 30–70°) (5 cm^3) was added, undissolved cuprous oxide and precipitated complex were separated by filtration, and the filtrate was subjected to vacuum distillation. The fraction boiling at 77° (1 mm) was obtained, 5.6 g (91%). The fraction was purified by means of preparative glpc.

N-Vinyl-*N*′,*N*′-pentamethyleneformamidine: ir (neat) 1640 and 1602 cm^{-1} (C=C, N=C); nmr ($CDCl_3$) τ 2.60 (1 H, singlet, CH=N), 3.25 (1 H, quartet, C**H**=CH_2), 5.18, 5.68 (2 H, two sets of doublets, CH=C**H**$_2$).

Anal. Calcd for $C_8H_{14}N_2$: C, 69.52; H, 10.21; N, 20.27. Found: C, 68.90; H, 10.28; N, 19.84.

Reaction with *N*-Alkylamide.—The reaction was carried out by a similar procedure to that of the reaction with amine under the conditions shown in Table II.

Identification of the Products (**11**).—*N*-(*N*′-Vinylformimidoyl)-*N*-allylformamide: bp 110° (12 mm); ir (neat) 1700 (C=O), 1630, 1600 cm^{-1} (C=C, N=C); nmr $CDCl_3$) τ 1.45 (1 H, singlet, CH=N), 1.91 (1 H, singlet, HCON<), 3.23 (1 H, quartet, C**H**=CH_2), 4.77, 5.18 (2 H, two sets of doublets, CH=C**H**$_2$).

Anal. Calcd for $C_7H_{10}N_2O$: C, 60.85; H, 7.30; N, 20.28. Found: C, 60.59; H, 7.07; N, 20.01.

N-(*N*′-Vinylformimidoyl)-*N*-methylacetamide: bp 80–90° (5 mm); ir (neat) 1690 (C=O), 1640, 1610 cm^{-1} (C=C, N=C); nmr ($CDCl_3$) τ 1.51 (1 H, singlet, CH=N), 3.10 (1 H, quartet, C**H**=CH_2), 4.76, 5.15 (2 H, two sets of doublet, CH=C**H**$_2$).

Anal. Calcd for $C_6H_{10}N_2O$: C, 57.11; H, 7.99; N, 22.21. Found: C, 56.52; H, 8.10; N, 21.96.

N-(*N*′-Vinylformimidoyl)caprolactam: bp 100° (3 mm); ir (neat) 1675 (C=O), 1625, 1602 cm^{-1} (C=C, N=C); nmr ($CDCl_3$) τ 1.31 (1 H, singlet, CH=N), 3.08 (1 H, quartet, C**H**=CH_2), 4.81, 5.18 (2 H, two sets of doublets, CH=C**H**$_2$).

Anal. Calcd for $C_9H_{14}N_2O$: C, 65.03; H, 8.49; N, 16.85. Found: C, 64.34; H, 8.74; N, 16.49.

Identification of Products (**12**).—*N*-(*N*′-Phenylformimidoyl)-*N*-allylformamide: bp 151° (5 mm); ir (neat) 1705 (C=O), 1635, 1625 cm^{-1} (C=C, N=C); nmr ($CDCl_3$) τ 1.35 (1 H, singlet, CH=N), *ca.* 2.8 (5 H, phenyl), 1.95 (1 H, singlet, HCON<), in addition of allyl group pattern.

Anal. Calcd for $C_{11}H_{12}N_2O$: C, 70.18; H, 6.43; N, 14.88. Found: C, 70.22; H, 6.66; N, 15.15.

N-(*N*′-Phenylformimidoyl)-*N*-methylacetamide: bp 162–165° (8 mm); ir (neat) 1682 (C=O), 1630, 1620 cm^{-1} (C=C, N=C); nmr ($CDCl_3$) 1.49 (1 H, singlet, CH=N), *ca.* 2.8 (5 H, phenyl), 6.66 (3 H, singlet, NCH_3), 7.70 (3 H, singlet, $COCH_3$).

Anal. Calcd for $C_{10}H_{12}N_2O$: C, 68.16; H, 6.86; N, 15.90. Found: C, 68.06; H, 6.96; N, 15.66.

N-(*N*′-Phenylformimidoyl)caprolactam: bp 152–160° (4 mm); ir (neat) 1682 (C=O), *ca.* 1629 cm^{-1} (C=C, C=N); nmr ($CDCl_3$) τ 0.1 (1 H, singlet, –CH=N–), *ca.* 2.85 (5 H, phenyl).

Anal. Calcd for $C_{13}H_{16}N_2O$: C, 72.19; H, 7.46; N, 12.95. Found: C, 71.50; H, 7.39; N, 12.86.

Reaction with Carbamate (Urethane).—Most of the reaction was carried out by a similar procedure to that of the reaction with amine under the conditions shown in Table III.

Identification of the Products (**15**).—Methyl *N*-(*N*′-vinylformimidoyl)-*N*-methylcarbamate (**15a**): bp 63° (13 mm); ir (neat) 1727 (C=O), 1635, 1610 cm^{-1} (C=C, N=C); nmr ($CDCl_3$) τ 1.50 (1 H, singlet, CH=N), 3.14 (1 H, quartet, C**H**CH_2), 4.79, 5.19 (2 H, two sets of doublets, CH=C**H**$_2$).

Anal. Calcd for $C_6H_{10}N_2O_2$: C, 50.69; H, 7.09; N, 19.71. Found: C, 50.41; H, 7.38; N, 19.99.

Methyl *N*-(*N*′-vinylformimidoyl)-*N*-ethylcarbamate (**15b**): bp 85° (15 mm); ir (neat) 1730 (C=O), 1630, 1608 cm^{-1} (C=C, N=C); nmr ($CDCl_3$) τ 1.51 (1 H, singlet, CH=N), 3.13 (1 H, quartet, C**H**=CH_2), 4.81, 5.23 (2 H, two sets of doublets), 6.11 (3 H, singlet, $COOCH_3$).

Anal. Calcd for $C_7H_{12}N_2O_2$: C, 53.83; H, 7.74; N, 17.94. Found: C, 53.80; H, 7.85; N, 17.83.

Cyclohexyl *N*-(*N*′-vinylformimidoyl)-*N*-methylcarbamate (**15c**): bp 147–150° (8 mm); ir (neat) 1715 (C=O), 1630, 1605 cm^{-1} (C=C, N=C); nmr ($CDCl_3$) τ 1.50 (1 H, singlet, CH=N), 3.12 (1 H, quartet, C**H**=CH_2), 4.82, 5.23 (2 H, two sets of doublets), 6.75 (3 H, singlet, NCH_3).

Anal. Calcd for $C_{11}H_{18}N_2O_2$: C, 62.83; H, 8.63; N, 13.32. Found: C, 62.60; H, 8.78; N, 13.16.

Reaction with Ethylene Urea and Thiourea.—The reaction was carried out by a similar procedure to the reaction with amine under conditions shown in Table III. Isolation of these products by glpc was unsuccessful because they were decomposed in column (silicons 200°). The products were isolated by fractional crystallization from a mixture of CH_2Cl_2–ether.

Identification of Products.—*N*-(*N*″-Vinylformimidoyl)ethyleneurea (**17a**): mp 158–159°; mass spectrum *m*/*e* 139 (M^+); ir (KBr) 3280 (NH broad), 1735 (C=O), 1638, 1610 cm^{-1} (C=C, N=C); nmr ($CDCl_3$) τ 1.70 (1 H, singlet, CH=N), 3.11 (1 H, quartet, C**H**=CH_2), *ca.* 4.6 (1 H, broad NH), 4.75, 5.14 (2 H,

two sets of doublets, CH=C**H**$_2$), 6.01 (2 H, singlet, C**H**$_2$NH), 6.45 (2 H, singlet, CH$_2$N<).

Anal. Calcd for $C_6H_9N_3O$: C, 51.78; H, 6.52; N, 30.20. Found: C, 52.56; H, 6.50; N, 29.58.

N,*N*′-Di(*N*″-vinylformimidoyl)ethyleneurea (**18a**): mp 148–150° subl; mass spectrum *m/e* 192 (M$^+$); ir (KBr) 1745 (C=O), 1638, 1610 cm^{-1} (C=C, N=C); nmr (CDCl$_3$) τ 1.70 (2 H, singlet, CH=N), 3.13 (2 H, quartet, C**H**=CH$_2$), 4.76, 5.16 (4 H, two sets of doublets), 6.04 (4 H, singlet, (CH$_2$)$_2$).

Anal. Calcd for $C_9H_{12}N_4O$: C, 56.23; H, 6.29; N, 29.15. Found: C, 55.17; H, 6.31; N, 28.47.

N-(*N*″-Vinylformimidoyl)ethylenethiourea (**17b**): mp 150–151°; ir (KBr) 3182 (NH), *ca.* 1605 cm^{-1} (C=C, N=C); nmr (CDCl$_3$) τ 1.06 (1 H, singlet, CH=N), 3.00 (1 H, quartet, C**H**=CH$_2$), 4.64, 5.09 (2 H, two sets of doublets, CH=C**H**$_2$), 5.87, 6.05 (4 H, singlet, (CH$_2$)$_2$).

Anal. Calcd for $C_6H_9N_3S$: C, 46.43; H, 5.84; N, 27.07. Found: C, 46.33; H, 5.72; N, 26.96.

N,*N*′-Di(*N*″-vinylformimidoyl)ethylenethiourea (**18b**): mp 165–170° subl; mass spectrum *m/e* 208 (M$^+$); ir (KBr) *ca.* 1600 cm^{-1} (C=C, N=C); nmr (CDCl$_3$) τ 1.06 (2 H, singlet, CH=N), 3.00 (2 H, quartet, C**H**=CH$_2$), 4.64, 5.09 (4 H, two sets of doublets, CH=C**H**$_2$), 5.85 [4 H, singlet, (CH$_2$)$_2$].

Anal. Calcd for $C_9H_{12}N_4S$: C, 51.90; H, 5.81; N, 26.90. Found: C, 51.67; H, 6.09; N, 26.97.

Formidation of Formamidine.—The reaction was carried out by a similar procedure to that of the reaction with amine under the conditions shown in Table I.

Identification of the Products (10).—*N*-Ethyl-*N*-(*N*″-vinylformimidoyl)-*N*′-cyclohexylformamidine (**10a**): bp 114° (3 mm); ir (neat) 1610 cm^{-1} (C=C, N=C); nmr (CDCl$_3$) τ 2.19 (2 H, broad, N=CH), 3.21 (1 H, quartet, C**H**=CH$_2$), 4.94, 5.35 (2 H, two sets of doublets). In addition, ethyl and cyclohexyl patterns were observed.

Anal. Calcd for $C_{12}H_{21}N_3$: C, 69.52; H, 10.21; N, 20.27. Found: C, 69.22; H, 10.29; N, 20.56.

N,*N*′-Diethyl-*N*-(*N*″-vinylformimidoyl)formamidine (**10b**): bp 90–91° (3.5 mm); ir (neat) 1640 and 1610 cm^{-1} (C=C, N=C); nmr (CDCl$_3$) τ 2.2 (2 H, broad, N=CH), 3.22 (1 H, quartet, C**H**=CH$_2$), 4.94, 5.35 (2 H, two sets of doublets, CH=C**H**$_2$).

Anal. Calcd for $C_8H_{15}N_3$: C, 62.71; H, 9.87; N, 27.43. Found: C, 62.40; H, 9.79; N, 27.36.

Reaction of VIC with Alcohols and Thiols.—The reactions were carried out in sealed test tubes under nitrogen under the conditions shown in Table IV. The products were isolated by vacuum distillation and purified by preparative glpc. The product structures were determined mostly by ir and nmr spectra and elemental analysis.

Identification of the Products.—*N*-Ethylidene-*N*-dimethoxymethylamine (**20a**): bp 53° (4 mm); mass spectrum *m/e* 117 (M$^+$); ir (neat) 1661 cm^{-1} (N=C); nmr (CDCl$_3$) τ 2.34 (1 H, singlet, (O–)$_2$CHN=), 5.50 (1 H, quartet, =C**H**CH$_3$), 8.65 (3 H, doublet, =CHC**H**$_3$), 6.22 (3 H), 6.75 (3 H, singlet, OCH$_3$).

Anal. Calcd for $C_5H_{11}NO_2$: C, 51.26; H, 9.46; N, 11.96. Found: C, 50.11; H, 9.55; N, 11.99.

N-Ethylidene-*N*-diethoxymethylamine (**20b**): bp 60° (4 mm); mass spectrum *m/e* 145 (M$^+$); ir (neat) 1645 cm^{-1} (N=C); nmr (CDCl$_3$) τ 2.33 (1 H, singlet, (O–)$_2$CHN=), 5.4 (1 H, quartet, =C**H**CH$_3$).

Anal. Calcd for $C_7H_{15}NO_2$: C, 57.90; H, 10.41; N, 9.65. Found: C, 57.70; H, 10.28; N, 9.47.

N-Ethylidene-*N*-dicyclohexyloxymethylamine (**20c**): bp 125° (8 mm); ir (neat) 1648 cm^{-1} (N=C); nmr (CDCl$_3$) τ 2.31 (1 H, singlet, (O–)$_2$CHN=), 5.20 (1 H, quartet, =C**H**CH$_3$), 8.68 (3 H, doublet, =CHC**H**$_3$).

Anal. Calcd for $C_{15}H_{27}NO$: C, 71.10; H, 10.74; N, 5.53. Found: C, 70.88; H, 10.99; N, 5.81.

N-Ethylidene-*N*-diallyloxymethylamine (**20d**): bp 50° (5 mm); ir (neat) 1645–1655 cm^{-1} (N=C); nmr (CDCl$_3$) τ 2.33 (1 H, singlet, (O–)$_2$CHN=), 8.65 (3 H, doublet, =CHC**H**$_3$).

Anal. Calcd for $C_9H_{15}NO_2$: C, 63.88; H, 8.94; N, 8.28. Found: C, 63.16; H, 9.23; N, 8.84.

Methyl *N*-vinylformimidate (**19a**): ir (neat) 1640, 1619 (C=C, N=C), 1225 cm^{-1} (–O–); nmr (CDCl$_3$) τ 2.25 (1 H, singlet, C**H**=N), 3.25 (1 H, quartet, C**H**CH$_2$), 4.90, 5.30 (2 H, two sets of doublets, CH=C**H**$_2$), 6.17 (3 H, singlet, OCH$_3$).

Anal. Calcd for C_4H_7NO: C, 56.45; H, 8.29; N, 16.40. Found: C, 55.91; H, 8.36; N, 16.13.

Cyclohexyl *N*-vinylformimidate (**19c**): ir (neat) 1639, 1618 (C=C, N=C), 1225 cm^{-1} (–O–); nmr (CDCl$_3$) τ 2.28 (1 H, singlet, CH=N), 3.24 (1 H, quartet, C**H**=CH$_2$), 4.94, 5.34 (2 H, two sets of doublets, CH=C**H**$_2$).

Anal. Calcd for $C_9H_{15}NO$: C, 70.55; H, 9.87; N, 9.14. Found: C, 70.72; H, 10.08; N, 8.96.

Isopropyl *N*-vinylformimidate (**19e**): ir (neat) 1638, 1615 (C=C, N=C), 1225 cm^{-1} (–O–); nmr (CDCl$_3$) τ 2.30 (1 H, singlet, CH=N), 3.23 (1 H, quartet, C**H**=CH$_2$), 4.92, 5.33 (2 H, two sets of doublets, CH=C**H**$_2$).

Anal. Calcd for $C_6H_{11}NO$: C, 63.68; H, 9.80; N, 12.39. Found: C, 63.89; H, 9.96; N, 12.66.

tert-Butyl *N*-vinylformimidate (**19f**): ir (neat) 1638, 1615 (C=C, N=C), 1225 cm^{-1} (–O–); nmr (CDCl$_3$) 2.30 (1 H, singlet, CH=N), 3.25 (1 H, quartet, C**H**=CH$_2$), 4.88, 5.30 (2 H, two sets of doublets, CH=C**H**$_2$), 8.52 (9 H singlet, *tert*-Bu).

Ethyl *N*-vinylthioformimidate (**21a**): bp 45° (23 mm); mass spectrum *m/e* 115 (M$^+$); ir (neat) 1620, 1552 cm^{-1} (C=C, N=C); nmr (CDCl$_3$) τ 1.74 (1 H, singlet, >CHN=), 3.22 (1 H, quartet, C**H**=CH$_2$), 4.28, 5.20 (2 H, two sets of doublets, CH=C**H**$_2$).

N-Ethylidene-*N*-di(ethylthio)methylamine (**22a**): bp 84° (4 mm); mass spectrum *m/e* 177 (M$^+$); ir (neat) 1580 cm^{-1} (N=C); nmr (CDCl$_3$) τ 1.64, 1.87 (1 H, (S–)$_2$C**H**N=), 5.35 (1 H, quartet, =C**H**CH$_3$), 8.52, 8.72 (3 H, two sets of doublets, =CHC**H**$_3$).

Anal. Calcd for $C_7H_{15}S_2N$: C, 47.41; H, 8.52; N, 7.89. Found: C, 47.43; H, 8.81; N, 7.94.

Conversion of 19c to 20c.—A mixture of 0.327 mmol of **19c**, 1.94 mmol of cyclohexanol, and 0.5 cm^3 of toluene was heated at 80° for 6 hr and subjected to glpc analysis. The structure of **20c** was established by comparison of the glpc retention time and ir spectrum with that of the authentic sample. In the reaction with 0.01 mmol of Cu$_2$O as catalyst the same result was obtained.

Registry No.—VIC, 14668-82-7; **4a**, 30698-67-0; **4b**, 30698-68-1; **4c**, 30698-69-2; **7b**, 1193-93-7; **10a**, 30698-70-5; **10b**, 30698-71-6; **15a**, 30698-72-7; **15b**, 30698-73-8; **15c**, 30698-74-9; **17a**, 30698-75-0; **17b**, 30689-85-1; **18a**, 30689-86-2; **18b**, 30689-87-3; **19a**, 30689-88-4; **19c**, 30689-89-5; **19e**, 30689-90-8; **19f**, 30689-91-9; **20a**, 30689-92-0; **20b**, 30689-93-1; **20c**, 30689-94-2; **20d**, 30758-75-9; **21a**, 30698-08-9; **22a**, 30698-09-0; *N*-vinyl-*N*′,*N*′-pentamethyleneformamidine, 30698-10-3; *N*-(*N*′-vinylformimidoyl)-*N*-allylformamide, 30698-11-4; *N*-(*N*′-vinylformimidoyl)-*N*-methylacetamide, 30698-12-5; *N*-(*N*′-vinylformimidoyl)caprolactam, 30698-13-6; *N*-(*N*′-phenylformimidoyl)-*N*-allylformamide, 30698-14-7; *N*-(*N*′-phenylformimidoyl)-*N*-methylacetamide, 30698-15-8; *N*-(*N*′-phenylformimidoyl)caprolactam, 30698-16-9.