Reactions of *N*-Vinylimides with Amines

Kiyoshi Yanagi

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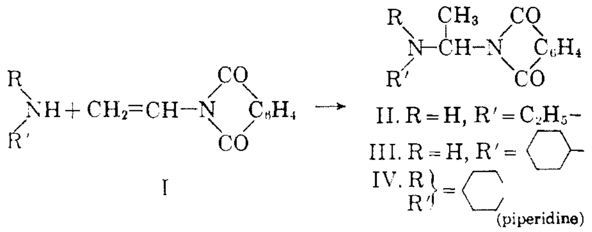
The reactions of *N*-vinylimides with inorganic compounds, such as halogen, hydrogen halide, and hydrogen are well known, but nothing is known about the reaction of *N*-vinylphthalimide, *N*-vinylsuccinimide and *N*-vinylsulfobenzimide with organic compounds. I have studied the reactions of *N*-vinylimides, described above, with amines, and addition reactions and imido interchange reactions were found.

Amines whose dissociation constants are larger than 10^{-4}, such as ethylamine[1] ($K = 5.6 \times 10^{-4}$), cyclohexylamine[2] ($K = 1.58 \times 10^{-4}$), piperidine[1] ($K = 1.6 \times 10^{-3}$) were allowed to react with *N*-vinylphthalimide (I) to yield the adducts, *N*-(1-ethylaminoethyl)phthalimide (II), *N*-(1-cyclohexylaminoethyl)phthalimide (III) and *N*-(1-piperidinoethyl)phthalimide (IV).



The position of the addition is presumed to be α in the vinyl group, because, for example, the melting point of *N*-(2-piperidinoethyl)phthalimide[3] is 91° but the melting point of the present adduct is 126–127°. The results are shown in Table I.

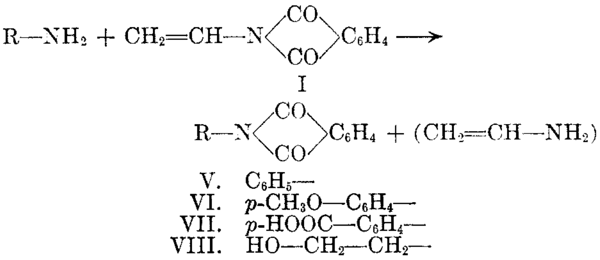
TABLE I

The Adducts of *N*-Vinylimides with Amines

				Analysis (%)					
				Carbon		Hydrogen		Nitrogen	
Adduct	M.P.	Yield, %	Formula	Calcd.	Found	Calcd.	Found	Calcd.	Found
II[a]	146–147	84	$C_{12}H_{14}N_2O_2$	66.03	66.22	6.47	6.28	12.84	12.84
III[b]	183–184	95	$C_{16}H_{20}N_2O_2$	70.56	70.25	7.40	7.27	10.29	9.98
IV[c]	126–127	96	$C_{15}H_{18}N_2O_2$	69.79	69.88	7.02	7.22	10.85	10.94
X[c]	187–188	70	$C_8H_{14}N_2O_2$	56.45	56.43	8.29	8.29	16.46	16.42
XI[d]	138.5–139.5	94	$C_8H_{14}N_2O_3$	51.60	51.71	7.58	7.78	15.04	15.06
XII[c]	202.5–203.5	90	$C_{12}H_{20}N_2O_2$	64.25	64.25	8.99	9.04	12.49	12.37
XIII[e]	88.5–89.5	93	$C_{11}H_{18}N_2O_2$	62.83	62.72	8.63	8.69	13.32	13.39

[a] Recrystallized from benzene. [b] Recrystallized from ethanol–water or ethanol–ethyl acetate. [c] Recrystallized from ethanol. [d] Recrystallized from ethanol–benzene. [e] Recrystallized from ethyl acetate–petroleum ether.

Amines whose dissociation constants are smaller than 10^{-5}, namely, aniline[1] ($K = 3.83 \times 10^{-10}$), *p*-anisidine[4] ($K = 1.47 \times 10^{-9}$), *p*-aminobenzoic acid[5] ($K = 3.6 \times 10^{-12}$) and ethanolamine[1] ($K = 2.77 \times 10^{-5}$) were allowed to react with *N*-vinylphthalimide to cause imido interchange reactions and yield *N*-phenylphthalimide (V), *N*-4-methoxyphenylphthalimide (VI), *N*-4-carboxyphenylphthalimide (VII), and *N*-2-hydroxyethylphthalimide (VIII). The reactions were accelerated by organic acids.



The effect of some organic acids in the reaction of *N*-vinylphthalimide with aniline are summarized in Table II. The yields were poor in the absence of organic acid but better in the presence of it.

TABLE II

The Effects of Organic Acids in the Reaction of *N*-Vinylphthalimide with Aniline

Organic Acid	Dissociation Constant (25°)	Yield, %
		3
Acetic acid	1.753×10^{-5}	85
Benzoic acid	6.30×10^{-5}	64
Phenol	1.3×10^{-10}	17
p-Toluene Sulfonic acid		19

N-vinylsuccinimide (IX) was allowed to react with ethylamine, ethanolamine, cyclohexylamine, and piperidine to yield *N*-(1-ethylaminoethyl)succinimide (X), *N*-(1,2-hydroxyethylaminoethyl)-

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[1] N. A. Lange, *Handbook of Chemistry*, 8th edition, Handbook Publishers, Inc., Sandusky, Ohio, 1952, p. 1229.

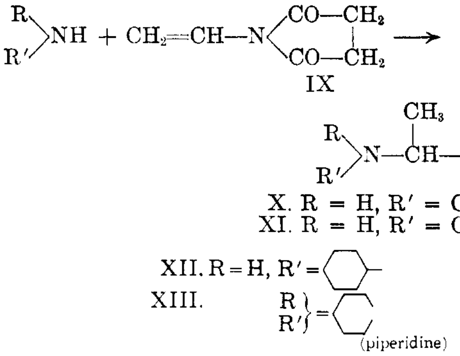
[2] A. Waksmundzki, *Roczniki Chem.*, **18**, 865 (1938); *Chem. Abstr.*, **33**, 6689 (1939).

[3] W. O. Kermack and J. F. Smith, *J. Chem. Soc.*, 3098 (1931).

[4] R. C. Farmer and F. J. Warth, *J. Chem. Soc.*, **85**, 1726 (1904).

[5] K. Winkelbleck, *Z. Ph. Chem.*, **36**, 546 (1901).

succinimide (XI), *N*-(1-cyclohexylaminoethyl)succinimide (XII) and *N*-(1-piperidinoethyl)succinimide (XIII) by the addition reaction. The results are shown in Table I.



N-vinylsulfobenzimide (XIV) was allowed to react with cyclohexylamine and aniline to yield products with empirical formula which correspond to *N*-cyclohexyl-*o*-sulfamoylbenzamide (XV) and *o*-sulfamoylbenzanilide (XVI), respectively. That is to say, neither addition reaction nor imido interchange reaction occurs in the case of *N*-vinylsulfobenzimide.

EXPERIMENTAL

Materials. *N*-vinylphthalimide,[6] *N*-vinylsuccinimide,[7] and *N*-vinylsulfobenzimide[8] were prepared by the pyrolysis of *N*-2-acetoxyethylphthalimide, *N*-2-acetoxyethylsuccinimide, and *N*-2-acetoxyethylsulfobenzimide, respectively.

Addition reactions of N-vinylphthalimide. A mixture of 5 g. of V.P.I. (*N*-vinylphthalimide) and 10 g. of ethylamine (33% water solution), a mixture of 5 g. of V.P.I. and 5.72 g. of cyclohexylamine, and a mixture of 4 g. of V.P.I. and 2.2 g. of piperidine in 15 ml. of benzene, were individually kept at room temperature for 3 hr. The precipitate was filtered and recrystallized. The results are summarized in Table I.

Imido interchange reactions of N-vinylphthalimide. A mixture of 5 g. of V.P.I., 3 g. of aniline, and 1 g. of acetic acid; a mixture of 5 g. of V.P.I., 3.56 g. of *p*-anisidine, and 1 g. of acetic acid; a mixture of 6 g. of V.P.I., 4.8 g. of *p*-aminobenzoic acid, and 1 g. of acetic acid; and a mixture of 4 g. of V.P.I., 1.6 g. of ethanolamine and 1 g. of acetic acid were individually heated at 100° for 4.5, 4, 5, and 10 hr., respectively. The resinous reaction products were rinsed with methanol and recrystallized from benzene and then *N*-phenylphthalimide, *N*-(4-methoxyphenyl)phthalimide, *N*-(4-carboxyphenyl)phthalimide, and *N*-(2-hydroxyethyl)-phthalimide were obtained.

N-phenylphthalimide: yield 85%, m.p. 209–210°.

Anal. Calcd. for $C_{14}H_9NO_2$: C, 75.32; H, 4.06; N, 6.28. Found: C, 75.61; H, 4.06; N, 6.54.

N-(4-methoxyphenyl)-phthalimide: yield 71%, m.p. 160–161°.

Anal. Calcd. for $C_{15}H_{11}NO_3$: C, 71.14; H, 4.37; N, 5.53. Found: C, 71.39; H, 4.55; N, 5.59.

N-(4-carboxyphenyl)-phthalimide: yield 80%, m.p. 261–262° (uncorr.).

Anal. Calcd. for $C_{15}H_9NO_4$: C, 67.41; H, 3.39; N, 5.24. Found: C, 67.18; H, 3.72; N, 5.13.

N-(2-hydroxyethyl)phthalimide: yield 70%, m.p. 128–129°.

Anal. Calcd. for $C_{10}H_9NO_3$: C, 62.82; H, 4.75; N, 7.33. Found: C, 63.06; H, 4.91; N, 7.12.

Addition reactions of N-vinylsuccinimide. A mixture of 6 g. of V.S.I. (*N*-vinylsuccinimide) and 12 g. of ethylamine (33% water solution), a mixture of 4 g. of V.S.I. and 2.2 g. of ethanolamine in 15 ml. of benzene, a mixture of 4 g. of V.S.I. and 7.5 g. of cyclohexylamine, and a mixture of 4 g. of V.S.I. and 3 g. of piperidine were individually kept at room temperature for 2, 0.5, 18 and 18 hr., respectively. The precipitates were filtered and recrystallized. The results are summarized in Table I.

N-cyclohexyl-o-sulfamoylbenzamide. A mixture of 4.5 g. of *N*-vinylsulfobenzimide and 6 g. of cyclohexylamine was stirred at room temperature. After 17 hr., the precipitate was rinsed with benzene to remove the resinous matter from it. Recrystallization from benzene gave *N*-cyclohexyl-*o*-sulfamoylbenzamide, yield 60%, m.p. 201–202.5°.

Anal. Calcd. for $C_{13}H_{18}N_2O_3S$: C, 55.31; H, 6.53; N, 9.93. Found: C, 55.23; H, 6.51; N, 9.81.

o-Sulfamoylbenzanilide. A mixture of 5.2 g. of *N*-vinylsulfobenzimide, 6 g. of aniline, and 2 ml. of acetic acid was heated at 100° for 3 hr. The reaction product was rinsed with benzene to remove the resinous matter. Recrystallization from ethanol gave 4.92 g. of *o*-sulfamoylbenzanilide, m.p. 189–190°.

Anal. Calcd. for $C_{13}H_9N_2O_3S$: C, 56.52; H, 4.83; N, 10.14. Found: C, 56.38; H, 4.51; N, 10.17.

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Department of Synthetic Chemistry
Faculty of Engineering, Kyushu University
Hakozaki Fukuoka, Japan

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[6] W. E. Hanford and H. B. Stevenson, U. S. Patent **2,276,840**; *Chem. Abstr.*, **36**, 4637 (1942).

[7] W. E. Hanford and H. B. Stevenson, U. S. Patent **2,231,905**; *Chem. Abstr.*, **35**, 3267 (1941).

[8] This is a new compound, m.p. 131–132° (from ethanol). *Anal.* Calcd. for $C_9H_7NO_3S$: C, 51.67; H, 3.37; N, 6.70. Found: C, 51.61; H, 3.36; N, 6.64.

Hydroxyethylation of Imides

Kiyoshi Yanagi and Saburo Akiyoshi

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Several methods of preparing *N*-2-hydroxyethylimides are known.[1–3] The present paper describes a new method of hydroxyethylation of imides by ethylene carbonate, which is used not only as solvent but also as reagent.[4–7]

Though monocarboxylic amides showed no reaction, dicarboxylic imides and saccharin were easily hydroxyethylated in good yield by heating the mixture of imide and ethylene carbonate. Aromatic dicarboxylic imides reacted easily with-

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