NOTES

Synthesis of N-Vinylsuccinamides

By Kiyoshi KATO

(Received February 19, 1962)

In 1959 Yanagi¹⁾ reported a reaction of Nvinylsuccinimide with amines at room temperature. Under his experimental conditions, a white precipitate was given as an addition product, and he presumed the addition of amines to occur on the vinyl double bond. CH2C However, the reaction of N-vinylsuccinimide with amines may take place in two ways, to yield either an addition product to the double bond or N-vinylamide by the opening reaction of the imide ring.

Therefore, the present author has tried to prepare N-vinylamide derivatives through the latter reaction. When N-vinylsuccinimide (I) was treated with benzylamine at room temperature, a reaction occurred immediately and gave a solid flake (II), m. p. 172~173°C (decomp.). II was converted into N-benzylsuccinimide by the thermal decomposition. The infrared spectrum of II (Fig. 1) showed the absorption bands²⁾ at 3.02, 6.10 and 6.50 μ which suggested the existence of an amide radical. The existence of a double bond in the product was recognized by the Baeyer test and by bromination. Thus, II was concluded to be N-vinyl-N'-benzylsuccinamide.

Similarly, N-vinylsuccinimide reacted with various primary and secondary aliphatic, aromatic and heterocyclic amines and gave the respective vinyl compounds (see Table I).

N-Vinylsuccinamide copolymerized readily with such a monomer as methyl methacrylate or acrylonitrile.



Experimental

Only a few typical procedure are described in detail.

The physical properties and analyses of products are collected in Table I.

Preparation of N-Vinyl-N'-benzylsuccinamide.-A mixture of 1.1 g. of N-vinyl succinimide and 1.25 g. of benzylamide was kept at room temperature for thirty minutes. The purified sample melted at 172~173°C (decomp.) and weighed 2.21 g. (95.2%).

15.21 15.02

12.06 12.20

15.05 14.87

16.46 16.45

13.32 13.33

N-VINYISUCCINALINGES KOCCH2CH2CONHCH=CH2							
	M. p. (decomp.) °C	Yield	Crystn. ^{a)} solvent	Formula	Analyses		
					C, %	H, %	N, %
					Calcd. Found	Calcd. Found	Calcd. Found
	153.5~154.5	94.8	Ε	$C_7H_{12}O_2N_2$	53.83 53.88	7.75 7.91	17.94 18.12
	180 ~181	87.0	Ε	$C_8H_{14}O_2N_2$	56.45 56.30	8.30 8.34	16.46 16.46
	158.5~159.5	93.0	Μ	$C_9H_{14}O_2N_2$	59.32 59.51	7.75 7.68	15.37 15.33
Н	$168 \sim 168.5$	94.2	Ε	$C_9H_{16}O_2N_2$	58.67 58.94	8.75 9.12	15.21 15.20

 $C_9H_{16}O_2N_2$

 $C_{13}H_{16}O_2N_2$

 $C_8H_{14}O_3N_2$

 $C_8H_{14}O_2N_2$

 $C_{11}H_{18}O_2N_2$

58.67 58.91

67.18 67.23

51.60 51.62

56.45 56.58

62.82 63.01

·	TABLE I
N-Vinylsuccinamides	ROCCH ₂ CH ₂ CONHCH=CH ₂

a) AE, Ethyl acetate; BE, Benzene-ethanol; E, Ethanol; M, Methanol

Ε

Е

BE

Ε

AE

1) K. Yanagi, J. Org. Chem., 24, 1121 (1959).

164.5~165.5

134.5~135.5

172 ~173

132.5~133

 $86 \sim 87$

R

CH₃NH

 C_2H_5NH

C₃H₅NH

 $n-C_3H_7N$

C7H7NH

C₂H₆N

 $C_5H_{10}N$

i-C₃H₇NH

C₂H₅ONH

90.2

95.2

94.8

62.9

91.9

8.75 8.85

6.94 7.21

7.59 7.64

8.30 8.42

8.64 8.72

²⁾ L. J. Bellamy, "The Infrared Spectra of Complex

Molecules", John Wiley and Sons, Inc., New York (1954), p. 176.



Fig. 1. Infrared spectrum of II (Nujol).

Thermal Decomposition of N-Vinyl-N'-benzylsuccinamide.—When II was heated at about 180° C for a few minutes, a red liquid was obtained. After recrystallization of the product from methanol, crystals were obtained; m. p. $98 \sim 99^{\circ}$ C, undepressed by admixture with an authentic compound (Found : N, 7.28%).

Synthesis of N-Vinyl-N'-2-hydroxyethylsuccinamide.—A mixture of 1.25 g. of N-vinylsuccinimide and 0.6 g. of monoethanolamine in 2 ml. of benzene was kept at room temperature for few minutes. The precipitate was then filtered and dried. The product was recrystallized from benzene-ethanol. The purified sample melted at $134.5 \sim 135.5^{\circ}$ C (decomp.); the yield was 1.75 g. (94.8%).

Reaction of N-Vinylsuccinimide with Morphorine.—N-Vinylamide was expected to be produced in this run, too, but it was not obtained in an analytically pure state. In the infrared spectrum of the crude material, absorption bands were observed at 3.02, 6.58 and 10.06μ ; these were assigned to the NH stretching vibration of a secondary amide and to CH out-of-plane deformation.

Copolymerization of N-Vinyl-N'-n-propylsuccinamide with Methyl Methacrylate.—A solution of 0.2 g. of N-vinyl-N'-n-propylsuccinamide, 1.8 g. of methyl methacrylate and 0.02 g. of benzoyl peroxide in 7 ml. of dioxane was heated at $65\sim 66^\circ C$ in a water bath for 6 hr. The polymer solution was poured into 70 ml. of methanol. After filtration and drying, the polymer weighed 0.41 g. (N, 1.69%). It was soluble in acetone, tetrahydrofurane, dioxane, benzene, toluene, chloroform, tetrachloroethane and ethyl acetate.

The author is indebted to Professor Niro Murata of the University of Osaka Prefecture for his invaluable advice and encouragement. Thanks are also due to Dr. Seibei Yoshikawa for his encouragement.

> Government Industrial Research Institute, Osaka Oyodo-ku, Osaka