[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY[1]]

Fatty Acid Amides. III.[2a] N-Alkenyl and N,N-Dialkenyl Amides[2b]

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In attempting to extend the utility of long-chain amides as chemical intermediates fifteen N-alkenyl and N,N-dialkenyl amides have been prepared in good yield from allylamine, diallylamine, methallylamine and dimethallylamine and caprylic, capric, lauric, myristic, stearic and oleic acids. Several of the amides, notably those of myristic and stearic acids, are excellent derivatives for the characterization of the unsaturated amines. Alkenyl amides of the long-chain saturated acids are readily sulfated in high yield with sulfuric acid containing from about 2–22% of free sulfur trioxide. The sodium salts of sulfated alkenyl amides show good surface-active properties in neutral, acidic and salt solutions, but not in alkaline solutions. The N-methallyl-, N,N-diallyl-, and N,N-dimethallyl amides can be polymerized at 125° in the presence of 1–4% of di-*t*-butyl peroxide as initiator. The polymers are solids melting below 45°.

In general, unsubstituted and N-alkyl amides of long-chain fatty acids are comparatively stable and unreactive compounds. Various attempts have been made to increase the reactivity and potential utility of amides by the introduction of reactive functional groups on the nitrogen atom, the most important of which are probably the hydroxymethyl and hydroxyethyl groups.[3] In attempting to extend the utility of long-chain amides as intermediates, we have prepared a series of N-alkenyl and N,N-dialkenyl amides of several long-chain acids, namely, caprylic, capric, lauric, myristic, stearic and oleic acids. These compounds were obtained in high yield (Table I) by the reaction of the appropriate acyl chlorides with monoalkenyl and dialkenyl amines, namely, allylamine, methallylamine, diallylamine and dimethallylamine. This reaction is probably the most convenient laboratory method for the preparation in high yields of amides from volatile amines.

The alkenyl and dialkenyl amides are either white crystalline solids or colorless liquids. They are insoluble in water and soluble in the common organic solvents at or above 25°. The liquid alkenyl amides are very soluble in organic solvents, in some cases even at −40°.

Crude, unrecrystallized alkenyl amides, isolated by acid-washing and evaporating the reaction mixtures, or once-crystallized products were obtained in excellent yields (86–100%) and their purity was high. Their melting points were only slightly lower than those of analytically pure specimens which had been recrystallized several times. Since long-chain saturated fatty acids of high purity are readily available from chemical supply houses and the preparation of the amides is simple, selected alkenyl amides are excellent derivatives for the identification of alkenyl and dialkenyl amines. The best derivatives are N-allylmyristamide, N-allylstearamide, N-methallylstearamide, N,N-diallylstearamide and N,N-dimethallylstearamide.

Brief reference has been made in the patent literature[4,5] to the preparation of surface-active agents by sulfation of some alkenyl amides of long-chain saturated fatty acids. Data on the preparation or surface-active efficiency of such products are usually lacking. N-Allylmyristamide was selected as a typical compound of this series, and it was found that it could be readily sulfated in high yield with sulfuric acid containing from about 2 to 22% sulfur trioxide. The sodium salt of sulfated N-allylmyristamide showed good surface-active characteristics in neutral, acidic and salt solutions, and was a good detergent for cotton in a washing test.[6]

Preliminary investigation of the polymerizability of alkenyl amides indicated that the N,N-diallyl-, N,N-dimethallyl- and N-methallylamides polymerized at about 125° in the presence of di-*t*-butyl peroxide as initiator. Large amounts of catalyst (1–4%) were required, however, as would be expected.[7] The polymers were low-melting solids. Benzoyl peroxide at 90° was unsatisfactory as an initiator.

Experimental[8]

Starting Materials.—Pure saturated fatty acids were prepared as described in a previous paper.[9] Oleic acid was prepared from olive oil fatty acids by multiple low-temperature crystallization and fractional distillation under vacuum.[10] Pure allylamine, diallylamine, methallylamine and dimethallylamine were obtained from the best commercial grades by multiple fractional distillation through efficient columns.

Preparation of Amides.—The preparation of N-allylstearamide is typical: 60.6 g. (0.2 mole) of undistilled stearyl chloride, prepared by the reaction of stearic acid with oxalyl chloride in benzene solution,[11] was added dropwise from a separatory funnel equipped with a drying tube, to a stirred solution of 23.1 g. (0.4 mole) of allylamine in 1300 ml. of petroleum naphtha (hexane fraction) at 0°. The reaction mixture was acidified with 3 *N* aqueous hydrochloric acid, and the multiphase system was filtered. The precipitate was washed with water until acid-free, and then dried under vacuum at 45°. A quantitative yield of N-allylstearamide, m.p. 82.2–83.1°, was obtained. Recrystallization from 95% ethanol (9 ml. of solvent per gram) at room temperature gave the analytically pure product in about 80% yield, m.p. 83.5–84.1° (Table I).

The amides which melted below 45° precipitated incompletely or did not precipitate from the hexane reaction solutions. After discarding the aqueous acid layer and washing the hexane solutions several times with water, they were cooled to −20 or −40°. The precipitates were washed with cold solvent and recrystallized to constant melting point.

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[2] (a) For paper II, see THIS JOURNAL, **71**, 3017 (1949). (b) This paper was presented at the Spring Meeting of the American Chemical Society held in Boston, Mass., April, 1951. Also at the Meeting-in-Miniature of the American Chemical Society held at Philadelphia, Pa., in January, 1951.

[3] Ralston, "Fatty Acids and Their Derivatives," John Wiley and Sons, Inc., New York, N. Y., 1948, pp. 581–610, 924–926.

[4] Davis, Price and Milligan, U. S. Patent 2,367,010 (1945).

[5] I. G. Farbenindustrie, German Patent 677,601 (1939).

[6] American Association of Textile Chemists and Colorists, *Technical Manual and Yearbook*, **24**, 98 (1947–1948).

[7] Bartlett and Nozaki, *J. Polymer Sci.*, **3**, 216 (1948); THIS JOURNAL, **68**, 1495 (1946); *ibid.*, **67**, 812, 817 (1945).

[8] All distillations and amide preparations were conducted in a nitrogen atmosphere.

[9] Swern and Jordan, THIS JOURNAL, **70**, 2334 (1948).

[10] Swern, Knight and Findley, *Oil and Soap*, **21**, 133 (1944); Brown and Sinowara, THIS JOURNAL, **59**, 6 (1937).

[11] Bauer, *Oil and Soap*, **23**, 1 (1946).

TABLE I

N-ALKENYL AND N,N-DIALKENYL AMIDES OF LONG-CHAIN FATTY ACIDS

	Reaction product		Recrystallized product										
Amide	Yield, %	M.p., °C.	Solvent[a]	Yield, %	M.p., °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	Double bonds[b] Calcd.	Double bonds[b] Found
N-Allylcapryl-	92[c]	21.0–21.8	H	90	27.1–27.6	72.1	71.6	11.6	11.7	7.64	7.44	1.00	1.00
N-Allylmyrist-	98	68.0–68.5	E	74	70.2–70.9	76.3	76.5	12.4	12.6	5.24	5.17	1.00	1.01
N-Allylstear-	100	82.2–83.1	E	79	83.5–84.1	78.0	78.2	12.8	12.7	4.33	4.32	1.00	1.01
N-Allylole-	87	37.1–37.7	H	84	37.7–38.1	78.4	78.4	12.2	12.1	4.36	4.32	2.00	2.00
N-Methallylcapr-	97[c]	42.8–43.6	H	94	42.8–43.6	74.6	74.8	12.1	12.0	6.22	6.19	1.00	1.01[e]
N-Methyallylmyrist-	97	67.8–68.2	A	72	68.5–69.0	76.8	76.8	12.5	12.4	4.98	4.94	1.00	1.01
N-Methallylstear-	100	81.7–82.6	E	71	82.1–82.6	78.3	77.8	12.8	12.9	4.15	4.32	1.00	1.01
N-Methallylole-	90[c]	28.1–28.6	H	88	29.6–30.1	78.7	79.0	12.3	12.4	4.17	4.13	2.00	2.05
N,N-Diallyllaur-	94[c]	10.8–11.6	A	66	11.6–12.1	77.4	77.6	11.9	12.1	5.01	4.89	2.00	1.98
N,N-Diallylmyrist-	91[c]	20.0–20.7	H	67	22.9–23.6	78.1	78.2	12.1	12.2	4.56	4.42	2.00	2.00
N,N-Diallylstear-	92[c]	42.4–42.8	H	63	43.3–43.8	79.3	79.4	12.5	12.4	3.85	3.82	2.00	2.01
N,N-Diallylole-[d]	97	<0	..	..	....	79.7	80.4	12.0	12.4	3.87	3.62	3.00	2.94
N,N-Dimethallylmyrist-	86[c]	14.6–15.6	H	74	15.1–15.6	78.7	78.8	12.3	12.4	4.20	4.24	2.00	1.99[e]
N,N-Dimethallylstear-	91[c]	34.7–35.2	H	86	34.8–35.4	79.7	79.8	12.6	12.7	3.58	3.49	2.00	2.05[e]
N,N-Dimethallylole-[d]	100	<0	..	..	....	80.1	79.5	12.2	12.1	3.59	3.30	3.00	3.00[e]

[a] Recrystallizing solvents: H = petroleum naphtha, hexane fraction; E = 95% ethanol; A = acetone. [b] Determined by semi-micro quantitative hydrogenation [Ogg and Cooper, *Anal. Chem.*, **21**, 1400 (1949)]. [c] Yield given is that of once-crystallized products. [d] Analytical data obtained on crude reaction product. [e] Determined by the modified Rosenmund–Kuhnhenn method [Benham and Klee, *J. Am. Oil Chem. Soc.*, **27**, 127, 130 (1950)].

N,N-Diallyl- and N,N-dimethallyloleamide did not crystallize even at −40°. The crude reaction products obtained by evaporation of the washed hexane solutions in these two cases were almost analytically pure, however (Table I).

Sulfation of N-Alkenyl Amides.—The sulfation of N-allylmyristamide is described: 2.67 g. (0.01 mole) of N-allylmyristamide was added in one portion to 3.92 g. (0.04 mole) of sulfuric acid (containing 1.8% free sulfur trioxide) at 0°. The mixture was stirred for a few minutes until it became homogeneous and it was then allowed to stand at room temperature for 24 hours. Ice and ice-water were added to the reaction mixture and the clear solution was neutralized with 0.5 *N* aqueous sodium hydroxide. The neutralized solution was evaporated to dryness first on the steam-bath and then under vacuum, yielding a white solid as a residue. This was finely ground, extracted with boiling anhydrous methanol and filtered. Evaporation of the methanol solution yielded 3.4 g. (88%) of the sodium salt of sulfated N-allylmyristamide.

Anal. Calcd. for $C_{17}H_{34}NO_5SNa$: S, 8.27. Found: S, 8.24.

Sulfur analyses ranged from about 6% to the calculated value. Satisfactory results were obtained with sulfuric acid containing from 2–22% free sulfur trioxide. The final product was much darker in color when the higher contents of free sulfur trioxide were employed.

The surface tension of a 0.1% solution of the sodium salt of sulfated N-allylmyristamide (S, 5.9%) was 24.4 dynes/cm. at 25°, and that of a 0.00156% solution was 34.1 dynes/cm. Sinking times (cotton skein)[12] for a 0.2% solution in distilled water were 19–25 seconds. In 5% aqueous sulfuric acid, the sinking times were 9–13 seconds, a considerable improvement. In 5% aqueous sodium sulfate the sinking times were 20–45 seconds. In 5% aqueous sodium hydroxide, however, the sinking time was 55 seconds after 10 minutes contact between the surface-active agent and the alkaline solution. After 1 hour of contact the sinking time was about 2 minutes, and after 5 hours the surface-active agent was destroyed. In neutral, acidic and salt solutions, no significant change in sinking time was observed even after the solutions had been allowed to stand for 24 hours.

In a washing test[6] 0.25% aqueous solution of the sodium salt of sulfated N-allylmyristamide (S, 5.9%) was slightly superior in detergency to a commercial sulfated amide of a long-chain acid, a commercial alkylarylsulfonate and a commercial sulfated monoglyceride, but inferior to a commercial long-chain alkyl sulfate (all sodium salts). The content of active ingredient in the sulfated N-allylmyristamide, however, was about 70% whereas in the commercial samples it was probably about 40%.

Polymerizability of Alkenyl Amides.—Little polymerization occurred when the amides were heated for as long as 48 hours at 90° in a nitrogen atmosphere with 1–4% of benzoyl peroxide as initiator. At 125°, however, and in the presence of 1–4% di-*t*-butyl peroxide as initiator, polymerization occurred in 16–48 hours with N-methallyl-, N,N-diallyl- and N,N-dimethallylamides. Substantial decrease in unsaturation and increase in refractive index were noted. All the polymers were solids melting below 45°. Polymerized diallylmyristamide was soluble in benzene, carbon tetrachloride, chloroform and ether, and insoluble in acetic acid, acetone and ethanol.

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[12] American Association of Textile Chemists and Colorists, *Technical Manual and Yearbook*, **24**, 151 (1947–1948).