[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NEW YORK UNIVERSITY]

A New Reaction of Nitriles. VI. Unsaturated Amides[1]

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The amide synthesis from nitriles and alcohols or olefins has been extended to include unsaturated nitriles and aldo-cyanhydrins. A number of N-alkyl acrylamides, methacrylamides, cinnamamides and lactamides are described.

Previous publications in this series[3] have described the reaction of nitriles with olefins or alcohols to yield N-substituted amides and the application of this synthesis to form *t*-carbinamines and N-benzoylamino acids. This paper records the extension of this novel synthesis to produce N-alkyl unsaturated amides. For example

$$CH_2{=}CH{-}CN + HOC{-}(CH_3)_3 \xrightarrow{H^+} CH_2{=}CH{-}\overset{\overset{O}{\|}}{C}{-}NH{-}C(CH_3)_3$$

Table I lists the reactants used and the products obtained, together with yields, physical properties, analyses and the melting points of the dibromo-derivatives.

One of us, with another collaborator, has previously reported the reaction of acrylonitrile and *t*-amyl alcohol[3a] but the subject was not then further investigated.

The N-alkyl acrylamides and methacrylamides are of interest as components of polymeric systems. None of the cinnamamides prepared in this study, however, could be made to polymerize or copolymerize with other acrylic monomers in the presence of peroxides. The study of the polymerization of these materials is under investigation in this Laboratory.

An alternative preparation of these N-alkyl acrylamides by the pyrolysis of the respective α-acetoxy N-alkyl propionamides as made through the amide synthesis from lactonitrile was investigated; the products were identical with those derived from acrylonitrile *via* the amide synthesis. Table II lists the data relative to the reactions of lactonitrile. The various relationships are shown in Fig. 1.

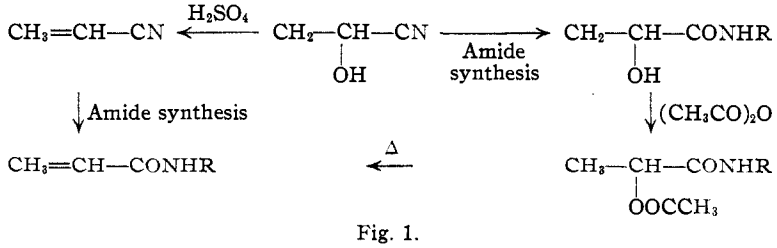


Fig. 1.

Acetone cyanhydrin could not be made to react under the same conditions in the amide synthesis.

The possibility of reaction of the nitrile with itself was considered and found to go when the time of reaction was extended to one week. As no case of addition to the terminal carbon has ever been found in this type of reaction, the polymer is represented as propagating through the α-carbon; no experimental evidence is available.

$$CH_2{=}CH{-}CN \longrightarrow CH_2{=}CH{-}CO{-}\left[NH{-}\underset{\underset{CH_3}{|}}{CH}{-}CO\right]_x NH{-}\underset{\underset{CH_3}{|}}{CH}{-}CN$$

Reaction of the N-alkyl acrylamides with nitriles could not be achieved; even under the most drastic conditions only the original N-alkyl acrylamides were recovered unchanged.

Experimental

Preparation of Materials.—Certain of the tertiary and secondary alcohols were obtained by Grignard reactions. Acrylonitrile and lactonitrile were kindly supplied by the American Cyanamid Corporation and used without further purification. Methacrylonitrile was prepared by pyrolysis of acetone cyanhydrin acetate. The preparation of cinnamonitrile is described below.

The reactions with olefins and tertiary alcohols were carried out in glacial acetic acid. Concentrated sulfuric acid was the solvent employed for the condensations of the secondary alcohols. Liquid products were distilled *in vacuo* after neutralization, ether extraction and drying. Traces of acid caused violent polymerization on heating. Solid products were recrystallized from benzene, hexane or combinations of the two. Some cinnamamides required preliminary recrystallization from aqueous methanol.

Analyses were performed in the Laboratory of Micro Chemistry at New York University. Nitrogen determinations were by the Kjeldahl method.

Cinnamonitrile.[4]—A warm solution of 66 g. (0.5 mole) of freshly distilled cinnamaldehyde in 200 ml. of 95% ethanol was mixed with a solution of 41.7 g. (0.6 mole) of hydroxylamine hydrochloride in 50 ml. of water. Sodium hydroxide, 30 g. (0.75 mole), in 40 ml. of water was then added with agitation. The solution was set aside for 3 hours after which the oxime was precipitated by adding 250 g. of crushed ice and rapidly saturating with CO_2. Filtered and air-dried, the yield was 71 g., 97%.

The oxime was mixed with 100 ml. of acetic anhydride and gently warmed to initiate the dehydration, the mixture refluxed for 0.5 hour after the violent reaction subsided, quenched in 300 g. of ice, the oil layer separated, washed free of acid, dried (Na_2SO_4) and distilled, b.p. 134–136° (12 mm.); yield 45 g., 70%, based on aldehyde.

Reaction of Nitriles with Olefins and Tertiary Alcohols.—The following procedure is typical of that used throughout the work. A solution of 5.3 g. (0.1 mole) of acrylonitrile, 50 ml. of acetic acid and 7.4 g. (0.1 mole) of *t*-butyl alcohol cooled in an ice-bath was treated with 10.1 g. (0.1 mole) of concd. sulfuric acid with stirring so as to keep the temperature below 40° during the addition and subsequent reaction (1 hour). The reaction mixture was poured onto 200 g. of ice, the product filtered and air-dried; yield 10 g. (80%), m.p. 124°. An additional 0.7 g. could be obtained by neutralization and ether extraction of the filtrate. The analytical sample (from benzene) melted at 126.8°.

(1) Based in part on the thesis submitted by Herman Plaut in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

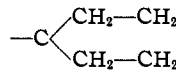
(2) Vegetable Oil Products Company, Inc., Los Angeles, Calif.

(3) (a) J. J. Ritter and P. Paul Minieri, THIS JOURNAL, **70**, 4045 (1948); (b) J. J. Ritter and Joseph Kalish, *ibid.*, **70**, 4048 (1948); (c) F. R. Benson and J. J. Ritter, *ibid.*, **71**, 4128 (1949); (d) L. W. Hartzel and J. J. Ritter, *ibid.*, **71**, 4130 (1949); (e) R. M. Lusskin and J. J. Ritter, *ibid.*, **72**, 5577 (1950).

(4) Posner, *Ann.*, **389**, 117 (1912).

TABLE I

AMIDES FROM ACRYLONITRILE CH_2=CH—CO—NHR

R	Alcohol or olefin	M.p., °C.[a]	Crude yield, %	Formula	Nitrogen, % Calcd.	Found	Dibromo-derivative, m.p., °C.[b]
$-C(CH_3)_2CH_2C(CH_3)_3$	Diisobutylene	83[c]	71	$C_{11}H_{21}NO$	7.64	7.56	132 dec.
$-C(CH_3)_2C_2H_5$	*t*-Amyl alcohol	91–92[d]	78	$C_8H_{15}NO$	9.92	9.87	171
$-C(CH_3)_3$	*t*-Butyl alcohol	126–128	80	$C_7H_{13}NO$	11.02	10.94	174–175 dec.
$-C(CH_3)(C_2H_5)_2$	3-Pentanol	63	77	$C_9H_{17}NO$	9.02	8.94	165–166 dec.
$-CH(CH_3)_2$	Isopropanol	62[e]	45	$C_6H_{11}NO$	12.38	12.29	119–120
$-C(CH_3)_2$-*n*-C_4H_9	2-Methylhexanol-2	60	70	$C_{10}H_{19}NO$	8.28	8.18	105–106
	Cyclohexanol[f]	112–113	72	$C_9H_{15}NO$	9.14	9.19	170
$-C(CH_3)(C_2H_5)$-iso-C_4H_9[g]	2,4-Dimethylhexanol-4	88–89	57	$C_{11}H_{21}NO$	7.64	7.62	119 dec.
$-C(CH_3)(C_2H_5)(n\text{-}C_3H_7)$	3-Methylhexanol-3	71–72	82	$C_{10}H_{19}NO$	8.28	8.23	193–194 dec.
$-C(CH_3)_2$(iso-C_3H_7)	2,3-Dimethylbutanol-2	91–92	71	$C_9H_{17}NO$	9.02	9.08	158–159 dec.
$-C(CH_3)(n\text{-}C_4H_9)$(iso-$C_4H_9$)[h]	2,4-Dimethyloctanol-4	79–80	36	$C_{13}H_{25}NO$	6.63	6.72	.....
$-C(CH_3)_2(n\text{-}C_3H_7)$	2-Methylpentanol-2	56–57	71	$C_9H_{17}NO$	9.02	8.91	124
$-C(CH_3)(C_2H_5)$	*s*-Butyl alcohol	26[i]	76	$C_7H_{13}NO$	11.02	11.12	133 dec.
$-C(CH_3)_2CH_2Cl$	Methallyl chloride	93–94	92	$C_7H_{12}NOCl$	8.67	8.71	149 dec.
	Amides from cinnamonitrile C_6H_5—CH=CH—CONHR						
$-C(CH_3)_2C_2H_5$	*t*-Amyl alcohol	141	73	$C_{14}H_{19}NO$	6.45	6.31	188 dec.
$-C(CH_3)_3$	*t*-Butyl alcohol	143	70	$C_{13}H_{17}NO$	6.89	6.79	187 dec.
$-C(CH_3)_2CH_2C(CH_3)_3$	Diisobutylene	118–120	77	$C_{17}H_{25}NO$	5.28	5.23	168–169 dec.
$-C(CH_3)_2(n\text{-}C_4H_9)$	2-Methylhexanol-2	125–126	96	$C_{16}H_{23}NO$	5.71	5.78	167 dec.
$-C(CH_3)(C_2H_5)$(iso-C_4H_9)	2,4-Dimethylhexanol-2	137–138	73	$C_{17}H_{25}NO$	5.28	5.38	.....
$-C(CH_3)(C_2H_5)(n\text{-}C_3H_7)$	3-Methylhexanol-3	140–141	61	$C_{16}H_{23}NO$	5.71	5.74	193–194 dec.
$-C(CH_3)(n\text{-}C_4H_9)$(iso-$C_4H_9$)	2,4-Dimethyloctanol-4	108–109	67	$C_{19}H_{29}NO$	4.87	5.02	186–187 dec.
$-C(CH_3)_2$(iso-C_3H_7)	2,3-Dimethylbutanol-2	122–123	86	$C_{15}H_{21}NO$	6.06	6.11	181 dec.
$-C(CH_3)_2(n\text{-}C_3H_7)$	2-Methylpentanol-2	151–152	69	$C_{15}H_{21}NO$	6.06	5.95	175 dec.
$-C(CH_3)(n\text{-}C_4H_7)(n\text{-}C_4H_9)$[h]	4-Methyloctanol-4	90–91[j]	74	$C_{18}H_{27}NO$	5.12	5.17	158–159 dec.
$-C(CH_3)(n\text{-}C_3H_7)$(iso-$C_3H_7$)	2,3-Dimethylhexanol-3	97	69	$C_{17}H_{25}NO$	5.28	5.39	... .
$-C(CH_3)(n\text{-}C_4H_9)(n\text{-}C_6H_{13})$[h]	4-Methylundecanol-4	89	79	$C_{21}H_{33}NO$	4.48	4.33	161 dec.
	Amides from methacrylonitrile CH_2=C(CH_3)—CO—NHR						B.p., °C. Mm.
$-C(CH_3)_3$[k]	*t*-Butyl alcohol	57.5	55	$C_8H_{15}NO$	9.92	9.92	87 15
$-C(CH_3)_2C_2H_5$	*t*-Amyl alcohol	26	78	$C_9H_{17}NO$	9.03	8.95	106–108 15
$-C(CH_3)_2CH_2C(CH_3)_3$	Diisobutylene	44	60	$C_{12}H_{23}NO$	7.10	6.98	120–123 14

[a] All melting points uncorrected. [b] M.p. in sealed tube. [c] B.p. 140–142° (20 mm.). [d] Ritter and Minieri; 3a reported 93°. [e] B.p. 110–115° (15 mm.). [f] From cyclohexene the yield was 66%. [g] Reaction run at 60° for 1 hour. [h] Reaction run at 70° for 1 hour. [i] B.p. 125–130° (20 mm.). [j] Recrystallize from 70% ethanol below 70°. Above 70° an oil separates. [k] Heyboer and Steveman, *Rec. trav. chim.*, **69**, 787 (1950), give b.p. 111–112° (43 mm.), m.p. 59°.

TABLE II

AMIDES FROM LACTONITRILE $CH_3CH(OH)CONHR$

R	M.p., °C.	B.p., °C.	Mm.	Yield, %	Formula	Nitrogen, % Calcd.	Found	M.p., °C. benzoate	M.p., °C. acetate
$-C(CH_3)_3$	53	114–122	15	40	$C_7H_{15}NO_2$	9.65	9.63	143	84–85
$-C(CH_3)_2C_2H_5$	23	128–135	13	35	$C_6H_{17}NO_2$	8.80	8.87	121–122	77–78
$-C(CH_3)_2CH_2C(CH_3)_3$	88	.....	..	65	$C_{11}H_{23}NO_2$	6.96	7.03	.....	74

Anal. Calcd. for $C_7H_{13}NO$: N, 11.02. Found: N, 10.94.

The dibromo-derivative was prepared by addition of bromine to a carbon tetrachloride suspension of the air-dried amide to a permanent excess of bromine. The carbon tetrachloride and excess bromine were removed by evaporation and an analytical sample obtained by recrystallization (charcoal) from hexane, m.p. 174–175° dec. in a sealed tube.

Anal. Calcd. for $C_7H_{13}Br_2NO$: N, 4.88. Found: N, 4.85.

Secondary alcohols were treated in the same way except that 20–25 ml. of concd. sulfuric acid was substituted for the acetic acid.

The self condensation of acrylonitrile was accomplished in a mixture of 1:1 acetic acid; concd. sulfuric acid at 30° for 7 days. The product is a pasty resinous mass that swells in water alkaline to litmus. No analysis was obtained.

Preparation of N-*t*-Butylacrylamide from the Lactamide.—N-*t*-Butyl lactamide was prepared from lactonitrile and *t*-butyl alcohol in acetic acid solution as described above. The oil formed on hydrolysis was taken up in ether, dried (Na_2SO_4), the ether removed and the residue refluxed for 1 hour with twice its volume of acetic anhydride. The acetate crystallized on dilution with H_2O; recrystallized from hexane, m.p. 84–85°. It was pyrolyzed by dropping an ether solution of the acetate into a flask kept at 500–550° by a Wood's metal-bath. The distillate was recrystallized from hexane, m.p. 126°. Mixed m.p. with an authentic sample of N-*t*-butylacrylamide showed no depression.

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