covered glycol. The acid was also obtained in 36% yield by oxidation of 1-methyl-1-cyclopentene following the procedure given above for the diol.

6-Ketoheptanoic Acid.[19]—This acid, b. p. 154–158° (2 mm.), (neut. equiv. 142, calcd. 144) was obtained in 57% yield, or 84% if allowance is made for recovered glycol, by the oxidation of 1-methyl-1,2-cyclohexanediol (13 g.) with permanganate in acetone as described for 5-ketohexanoic acid. The acid gave a semicarbazone, m. p. 144°,[20] a 2,4-dinitrophenylhydrazone, m. p. 82–83°, and a *p*-nitrophenylhydrazone, m. p. 112°.

4-Methyl-5-ketocaproic Acid.—This acid (neut. equiv. 145, calcd. 144), b. p. 120–130 (1 mm.), was obtained in 43–46% yield from 1,2-dimethyl-2,3-cyclopentene and from 1,2-dimethyl-2,3-cyclopentenediol using the permanganate in acetone procedure described above. The acid gave a semicarbazone, m. p. 168–169°.[21]

Oxidation of 1,2-Dimethyl-1-cyclopentene.—The application of the permanganate in acetone procedure to 1,2-dimethyl-1-cyclopentene (19.2 g.) gave a small amount of acids (2.4 g.) and neutral products (11.1 g.), b. p. 58–72°. The neutral product gave a *p*-nitrophenylhydrazone, m. p. 158–160°, and a 2,4-dinitrophenylhydrazone, m. p. 196–198°.

α-Methylglutaric Acid.—1-Methyl-2,3-cyclopentanediol (11.6 g.) in a mixture of 16 ml. of sulfuric acid and 200 ml. of water, was oxidized at about 0° with chromic acid. Chromic anhydride (20 g.) was added in 1–2 g. portions, allowing time for the decolorization of one portion before the next was added. The reaction mixture was warmed up to 40° after the addition of the last portion of the oxidizing agent and extracted with a liter of ethyl acetate in five portions. The ethyl acetate was distilled and the residue extracted with a solution containing 8 g. of sodium hydroxide in 60 ml. of water. The unoxidized glycol (4 g.) was extracted with ethyl acetate. The alkaline solution was made acid with sulfuric acid and the organic acid extracted with ethyl acetate. After distillation of ethyl acetate the acids were distilled at 150–180° (2 mm.). The distillate crystallized in part when stored at about 0°. After recrystallization from ethyl acetate 0.6 g. of α-methylglutaric acid, m. p. 75–76°, neut. equiv. 74 (calcd. 73) was obtained.[22]

β-Methyladipic Acid.—1-Methyl-3,4-cyclohexanediol (13 g.) was oxidized in the manner described above with chromic acid to give 8.5 g. of crude β-methyladipic acid, m. p. 88°; after recrystallization, 4 g. of acid, m. p. 93–94°, (neut. equiv. 81, calcd. 80) was obtained.[23]

Oxidation of 1-Methyl-2,3-cyclohexanediol.—The oxidation of the isomeric glycols by the chromic acid procedure just described, gave dibasic acids of different properties. The solid isomer gave an acid, m. p. 51–52°, while the liquid isomer gave an acid, m. p. 75–76°. Each of the acids showed a molecular weight of 166 as compared with a calculated value of 160 for a seven carbon atom saturated dibasic acid. The yield of solid acids was only about 10% of the theoretical but the loss in obtaining the crystalline acids was considerable.

Summary

Cyclohexene is isomerized over pure alumina at 470–480° to methylcyclopentene-1 and -2. Methylcyclohexene-1 is isomerized over pure alumina to 1,2-dimethyl- and ethyl-cyclopentenes as indicated in formulas V to VIII, inclusive. The four cyclopentenes have all been isolated in yields which make them available for synthesis. The method of oxidation using hydrogen peroxide in formic acid has been used quite effectively for the conversion of cyclohexene, three isomeric methylcyclohexenes and four cyclopentenes to the corresponding glycols. These glycols have been oxidized further with potassium permanganate or chromic acid to various dibasic and keto acids.

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[19] Perkin, *J. Chem. Soc.*, **57**, 229 (1890).

[20] Wallach, *Ann.*, **329**, 377 (1903).

[21] Chiurdoglu, *Bull. soc. chim. Belg.*, **47**, 363 (1938); *Chem. Abstr.*, **32**, 9052 (1938).

[22] Mulliken, "Identification of Organic Compounds," Vol. I, p. 41.

[23] Heilbron, "Dictionary of Organic Compounds," Vol. II, p. 608.

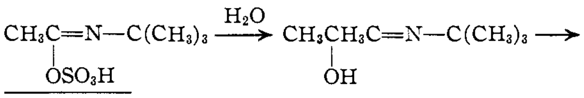
MADISON, WISCONSIN RECEIVED JUNE 14, 1948

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NEW YORK UNIVERSITY]

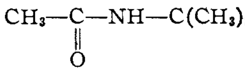
A New Reaction of Nitriles. I. Amides from Alkenes and Mononitriles[1]

BY JOHN J. RITTER AND P. PAUL MINIERI

It has been found in this Laboratory that interaction of alkenes with nitriles occurs in the presence of concentrated sulfuric acid. Hydrolysis of the reaction product by simple dilution with water yields an amide, I. This reaction has been accomplished with nitriles generally and a number of active alkenes, and appears to be of wide applicability. Amide formation from these reactants seems explainable as follows, formulated for acetonitrile, isobutene and sulfuric acid:



$$(CH_3)_2C{=}CH_2 + H_2SO_4 \longrightarrow (CH_3)_3C{-}OSO_3H$$
$$(CH_3)_3C{-}OSO_3H + CH_3C{\equiv}N \longrightarrow$$
$$\underset{\substack{|\\ OSO_3H}}{CH_3C}{=}N{-}C(CH_3)_3 \xrightarrow{H_2O} \underset{\substack{|\\ OH}}{CH_3CH_3C}{=}N{-}C(CH_3)_3 \longrightarrow$$



$$\underset{\substack{\|\\ O}}{CH_3{-}C}{-}NH{-}C(CH_3)_3 \qquad I$$

Experiments under identical conditions with substitution of acetamide for acetonitrile gave no reaction product, setting aside the possibility of addition of an amide, or its equivalent in sulfuric acid solution, to the olefinic double bond.

Confirmation of the identities of these compounds was reached through synthesis of N-*t*-butyl acetamide by an authentic method as well as by hydrolysis of N-*t*-amyl acetamide and N-*t*-octyl acetamide (Tables II, III) to *t*-amylamine and *t*-octylamine, respectively. N-*t*-butyl acetamide was obtained previously[2] by Beckmann rearrangement of pinacolone oxime; the product of the acetonitrile–isobutene reaction was identical with this compound, thus establishing the reac-

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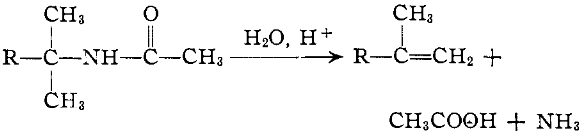
[1] Based in part upon the thesis submitted by P. Paul Minieri in May, 1948, to the Graduate School of New York University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] R. Scholl, *Ann.*, **338**, 16 (1905).

tion pattern definitely. Scholl noted that N-*t*-butyl acetamide is difficult to hydrolyze with alkalies; a similar difficulty was found by us in the alkaline hydrolysis of N-*t*-amyl- and N-*t*-octyl acetamide, which required prolonged treatment under drastic conditions. Acid hydrolysis occurred rapidly, accompanied by complete loss of ammonia, and yielded the corresponding olefin instead of the expected amine:



$$\text{R—C(CH}_3)_2\text{—NH—CO—CH}_3 \xrightarrow{H_2O,\ H^+} \text{R—C(CH}_3)\text{=CH}_2 + \text{CH}_3\text{COOH} + \text{NH}_3$$

TABLE I

N-*t*-BUTYL AMIDES R—CO—NH$(CH_3)_3$

R	M. p., °C.	Yield, %[b]	Formula	Nitrogen, % Calcd.	Nitrogen, % Found
CH_3–	97–98, b. p. 194	85	$C_6H_{13}ON$	..	..
C_6H_5–	134–134.5	90	$C_{11}H_{15}ON$	7.91	7.82
$C_6H_5CH_2$–	115–116	80	$C_{12}H_{17}ON$	7.33	7.27
n-C_9H_{19}–	B. p. 156–159 (2 mm.)	75	$C_{14}H_{29}ON$	6.16	6.40
n-$C_{13}H_{27}$–	57–58	70	$C_{16}H_{37}ON$[a]	4.95	5.06
n-$C_{17}H_{35}$–	73–73.5	85	$C_{22}H_{45}ON$	4.13	3.99

[a] Recrystallized from 70% isopropanol. [b] Yields are reported throughout on amounts isolated and subjected to analysis. Lower yields in some cases were due to incomplete reaction or mechanical losses in isolation and purification.

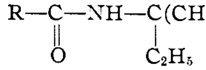
The general applicability of this hitherto unreported reaction is indicated in Tables I–IV. It occurs spontaneously with most active alkenes investigated, accompanied by some rise in temperature, and is as a rule substantially complete in about two hours. It is suggested that the reaction might serve as a convenient source of solid derivatives for the identification of a number of olefinic compounds and nitriles.

The N-*t*-alkyl amides (except formamides) are quite inert toward common reagents. In addition to being difficult to hydrolyze, those examined failed to react with methylmagnesium iodide, sodium and ethanol, alkylating agents, and hydrogen at high temperature and pressure in the presence of a copper chromite catalyst. Three members were decomposed by boiling at ordinary pressure to yield the parent nitrile, alkene and water.

This reaction has already been explored over a considerable area and will be the subject of further reports in THIS JOURNAL.

The authors wish to express their thanks to the Armour Company, Chicago, Ill., for providing the high molecular weight aliphatic nitriles used in this work and also to the American Cyanamid Company for supplying a quantity of cyanamide.

TABLE II

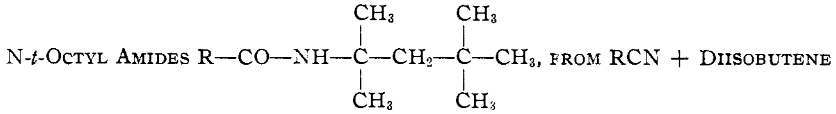


N-*t*-AMYL AMIDES $\text{R—C(=O)—NH—C(CH}_3)_2(\text{C}_2\text{H}_5)$, FROM RCN + 2-METHYLBUTENE-2

R	M. p., °C.	Yield, %	Formula	Nitrogen, % Calcd.	Nitrogen, % Found
H_2N–	160	10	$C_6H_{14}ON_2$[a]	...	...
$ClCH_2$–	B. p. 62–63 (1 mm.)	21	$C_7H_{14}ONCl$[b]	21.67	21.68
CH_3–	78–79	70	$C_7H_{15}ON$[c]	10.85	10.81
H_2NCONH–	149–150	75	$C_7H_{15}O_2N_3$[d]	24.30	24.25
CH_2=CH–	92–93	75	$C_8H_{15}ON$	9.93	10.06
H_2NCOCH_2–	143–144	63	$C_8H_{16}O_2N_2$	16.28	16.18
C_2H_5–	B. p. 110–112 (19 mm.)	50	$C_8H_{17}ON$	9.75	9.10
CH_2=C(CH_3)–	B. p. 86–87 (12 mm.)	65	$C_9H_{17}ON$	9.03	9.03
CH_3O—$COCH_2$–	B. p. 141–143 (16 mm.)	57	$C_9H_{17}O_3N$	7.48	7.53
n-C_3H_7–	B. p. 123–125 (23 mm.)	50	$C_9H_{19}ON$	8.85	8.63
$(CH_3)_2C(Cl)$–	B. p. 87–88 (17 mm.)	35	$C_9H_{18}ONCl$	7.31	7.29
C_2H_5O—$COCH_2$–	B. p. 130–131 (8 mm.)	45	$C_{10}H_{19}O_3N$	6.96	7.05
CH_3CO—OC(CH_3)H–	80–80.5	56	$C_{10}H_{19}O_3N$	6.96	6.92
CH_3CO—OCH_2CH_2–	B. p. 150–153 (10 mm.)	76	$C_{10}H_{19}O_3N$	6.96	7.13
n-C_4H_9–	B. p. 129–130 (16 mm.)	58	$C_{10}H_{21}ON$	8.18	8.31
C_6H_5–	81–82	70	$C_{12}H_{17}ON$	7.33	7.30
p-NO_2—$C_6H_4CH_2$–	143–144	89	$C_{13}H_{18}O_3N_2$	11.20	11.06[e]
$C_6H_5CH_2$–	96.5	70	$C_{13}H_{19}ON$[f]	6.82	6.81
o-CH_3—C_6H_4–	86–87	35	$C_{13}H_{19}ON$	6.82	6.71
p-CH_3—C_6H_4–	83.5	45	$C_{13}H_{19}ON$	6.82	6.85
n-C_7H_{15}–	B. p. 154–156 (14 mm.)	52	$C_{13}H_{27}ON$	6.57	6.58
C_6H_5CH=CH–	141–141.5	70	$C_{14}H_{19}ON$	6.45	6.34
n-C_9H_{19}–	B. p. 171–174 (14 mm.)	45	$C_{15}H_{31}ON$	5.81	5.78
n-$C_{11}H_{23}$–	B. p. 167–170 (4 mm.)	30	$C_{17}H_{35}ON$	5.20	5.20
n-$C_{13}H_{27}$–	B. p. 180–186 (4 mm.)	25	$C_{19}H_{39}ON$	4.71	4.84
n-$C_{17}H_{35}$–	68.5	22	$C_{23}H_{47}ON$	3.93	3.92

[a] Prepared by Frederic R. Benson, Ph.D. thesis, 1947. [b] Prepared by Francis X. Murphy. [c] Obtained also in about the same yield from 2-methylbutene-1 and acetonitrile. [d] From dicyandiamide. [e] Dumas. [f] Obtained also in 90% yield from benzyl cyanide and 2-methylbutene-1.

TABLE III



N-*t*-OCTYL AMIDES $R—CO—NH—C(CH_3)_2—CH_2—C(CH_3)_2—CH_3$, FROM RCN + DIISOBUTENE

R	M. p., °C.	Yield, %	Formula	Nitrogen, % Calcd.	Nitrogen, % Found
H-	B. p. 110 (2 mm.)	50	$C_9H_{19}ON$	8.85	8.77
CH_3-	97–98; b. p. *ca.* 240	85	$C_{10}H_{21}ON$	8.18	8.23
H_2NCONH-	189–190	50	$C_{10}H_{21}O_2N_3$[a]	19.53	19.91
H_2NCOCH_2-	120–121	65	$C_{11}H_{22}O_2N_2$	13.08	12.78
$HOCH_2CH_2$-	B. p. 163–164 (3 mm.)	85	$C_{11}H_{23}O_2N$	6.96	6.03
C_2H_5O-$COCH_2$-	64–65	70	$C_{13}H_{25}O_3N$[b]	5.30	5.02
C_6H_5-	70–71	90	$C_{15}H_{23}ON$	6.01	6.11
$C_6H_5CH_2$-	85–86	75	$C_{16}H_{25}ON$	5.42	5.76
n-C_7H_{15}-	B. p. 159–161 (2 mm.)	70	$C_{16}H_{33}ON$	5.49	5.37
n-C_9H_{19}-	B. p. 171–173 (2 mm.)	70	$C_{18}H_{37}ON$	4.94	5.56
n-$C_{11}H_{23}$-	B. p. 188–190 (3 mm.)	60	$C_{20}H_{41}ON$	4.50	4.39
n-$C_{13}H_{27}$-	B. p. 192–193 (2 mm.)	50	$C_{22}H_{45}ON$	4.13	4.58

[a] From dicyandiamide. [b] M. w. calcd., 243; found (in camphor), 235.

TABLE IV

AMIDES FROM NITRILES AND MISCELLANEOUS ALKENES, $R—CN + \text{ALKENE} \xrightarrow{H_2SO_4,\ H_2O} R—CO—NHR'$

R	Alkene	R'	M. p., °C.	Yield, %	Formula	Nitrogen, % Calcd.	Nitrogen, % Found
H_2N-	$(CH_3)_2C{=}CHC_3H_7$-*n*	$(CH_3)_2C—C_4H_9$	102	12	$C_8H_{18}ON_2$[a]	18.20	18.31
CH_3-	$C_6H_5CH{=}CH_2$	$C_6H_5CHCH_3$	72–73	43	$C_{10}H_{13}ON$[b]	8.59	8.47
CH_3-	$C_6H_5—C(CH_3){=}CH_2$	$C_6H_5—C(CH_3)_2$	96–97	28	$C_{11}H_{15}ON$[b]	7.91	7.85
H-	$C_{10}H_{16}$ (camphene)	$C_{10}H_{17}$ (*i*-bornyl)-	72–73	40	$C_{11}H_{19}ON$[c]	7.73	7.82
CH_3-	*p*-$CH_3—C_6H_4—C(CH_3){=}CH_2$	*p*-$CH_3—C_6H_4—C(CH_3)_2$	137–138	39	$C_{12}H_{17}ON$[b]	7.33	7.16
CH_3-	$C_{10}H_{16}$ (camphene)	$C_{10}H_{17}$ (*i*-bornyl)-	142–143[d]	75	$C_{12}H_{21}ON$	7.18	7.19
$C_6H_5CH_2$-	$(CH_3)_2C{=}CHC_2H_5$	$(CH_3)_2CC_3H_7$	93–94	69	$C_{14}H_{21}ON$	6.39	6.34
C_6H_5-	$C_{10}H_{16}$ (camphene)	$C_{10}H_{17}$ (*i*-bornyl)-	130	90	$C_{17}H_{23}ON$	5.45	5.59
$C_6H_5CH_2$-	$C_{10}H_{16}$ (camphene)	$C_{10}H_{17}$ (*i*-bornyl)-	127–128	67	$C_{18}H_{25}ON$	5.16	5.01

[a] Prepared by Frederic R. Benson, Ph.D. thesis, 1947. [b] Benzenesulfonic acid used in place of sulfuric acid (Elmar V. Piel, M.S. thesis, 1945; Jack Swerdloff, M.S. thesis, 1948. [c] The preparation of a series of N-*t*-alkyl formamides by this reaction has been completed by one of us with another collaborator. [d] Forster and Hart-Smith, *J. Chem. Soc.*, **77**, 1157 (1900), reported m. p. 144°.

Experimental

The same general procedures were followed in most cases; detailed directions are given for only a few typical preparations. Reactions were carried out generally in glacial acetic acid solution; more recently, dibutyl ether as solvent has been found to give equally good results. Concentrated sulfuric acid alone was necessary to effect reaction of certain less active alkenes. Most of the products were crystallized from hexane or diisobutene, a few from benzene, and high molecular weight aliphatic members from methanol. Liquid products were distilled *in vacuo* after neutralization, ether extraction and drying.

Analyses were performed in the Laboratory of Microchemistry at New York University. Nitrogen determinations were carried out by the Kjeldahl method unless otherwise indicated.

N-*t*-Butyl Acetamide.—Gaseous isobutene (12 g.) was led into a solution of 4.5 g. (0.11 mole) of acetonitrile in 50 ml. of glacial acetic acid containing 10 g. (0.1 mole) of concentrated sulfuric acid while the temperature was maintained at about 20°. The reaction vessel was then stoppered loosely and allowed to stand overnight. The product was poured into 200 ml. of water, neutralized with sodium carbonate, and extracted with five 50-ml. portions of ether. The combined extracts were dried (anhydrous potassium carbonate), and most of the ether was removed at 50°, and the rest evaporated at room temperature. The residue (11 g., 85%) was recrystallized from hexane as needles, b. p. 194° (cor.), m. p. 97–98° alone or when mixed with an authentic specimen made from pinacolone oxime.

N-*t*-Octyl Acetamide.—To a solution of 100 g. (1 mole) of concentrated sulfuric acid in 500 ml. of glacial acetic acid was added 45 g. (1.1 mole) of acetonitrile portionwise at about 20°. Diisobutene (112 g., 1.0 mole) was then added and the mixture was stirred mechanically, keeping the temperature below 50°. After about one-half hour the hydrocarbon, immiscible at first, was completely dissolved. The resulting colorless or slightly yellow solution was allowed to stand overnight, then diluted in four volumes of water to yield an oil which solidified in a few minutes to a crystalline mass. This was filtered, washed with water and air dried (122 g.). After twenty-four hours the filtrate deposited an additional 15 g. as long needles; combined yield, 137 g. (80%), m. p. 97–98°. Recrystallization from diisobutene yielded needles, m. p. 97–98°.

Anal. Calcd. for $C_{10}H_{21}ON$: C, 70.17; H, 12.28; N, 8.18; mol. wt., 171. Found: C, 70.87; H, 12.12; N, 8.23; mol. wt., 159.

N-*t*-Octylamine.—A mixture of 34.2 g. (0.2 mole) of N-*t*-octyl acetamide and 400 ml. of 0.4 molar potassium hydroxide in ethylene glycol was refluxed for forty-eight hours, then distilled through a six-inch Vigreux column collecting a fraction boiling up to 180° (27 g.). This was dissolved in ether (75 ml.), the solution was dried over potassium hydroxide, the ether was removed and the amine was distilled at ordinary pressure; yield 16 g. (74.5% based on reacting material), b. p. 138°, $n^{27}D$ 1.4222.

Anal. Calcd. for $C_8H_{19}N$: N, 10.84. Found: N, 10.51.

Hydrochloride (by treatment of 1 g. of amine in 10 ml. of anhydrous ether with dry hydrogen chloride), crystals which did not melt at 210°.

Anal. Calcd. for $C_8H_{20}NCl$: C, 58.1; H, 12.2; N, 8.47; Cl, 21.5. Found: C, 58.2; H, 12.2; N, 8.70; Cl, 21.5.

Acetyl derivative, m. p. 98–99° alone or when mixed with N-*t*-octyl acetamide prepared above.

The ethylene glycol residue from the hydrolysis was diluted with water (800 ml.) and yielded, after twenty-four hours, unhydrolyzed N-*t*-octyl acetamide (5.7 g., 16.6%).

***t*-Amylamine.**—Hydrolysis of N-*t*-amyl acetamide (Table II) in the same manner yielded *t*-amylamine, b. p. 77–78° (27%). Acetylation of the amine reformed N-*t*-amyl acetamide, m. p. 78–79° alone or mixed with the starting material.

Acid Decomposition of N-*t*-Octyl Acetamide.—N-*t*-Octyl acetamide (5 g.) was boiled with 15% hydrochloric acid in a distilling flask with condenser affixed for distillation. Diisobutene (3 g., calcd. 3.3 g.) was obtained and identified by recondensation with acetonitrile to form N-*t*-octyl acetamide, m. p. 97–98°.

N-*t*-Amyl Biuret.—To a mixture of 8.4 g. (0.1 mole) of dicyandiamide and 7.0 g. (0.1 mole) of trimethylethene was added portionwise over one hour, and with mechanical stirring and external ice cooling, a solution of 10 g. (0.1 mole) sulfuric acid in 20 ml. glacial acetic acid. After one additional hour in the ice-bath the mixture, containing solid material, was heated at 60° for four hours during which the solids dissolved. The cooled solution was then poured on cracked ice and neutralized with ammonia. An oil separated, which crystallized on standing overnight. The crystals (9.8 g.) were filtered, washed with ice-water, and air dried. Recrystallization from water yielded 7.0 g. (53.8%), m. p. 148.5–149°, after drying *in vacuo* at 75°.

Anal. Calcd. for $C_7H_{11}O_2N_3$: N, 24.30. Found: N, 24.25.

N-*t*-Amyl Urea.—A mixture of 42 g. (1.0 mole) of cyanamide, 70 g. (1.0 mole) of trimethylethene and 300 ml. of glacial acetic acid was stirred mechanically while 205 g. (2.0 mole) of sulfuric acid was added dropwise at 30–40°. The reaction mixture was poured into water (3500 ml.), neutralized with sodium carbonate, and allowed to stand for several hours. A solid separated; it was filtered, dissolved in hot methanol and refiltered to separate inorganic matter, and the filtrate was evaporated to dryness under reduced pressure. The crude product remaining was recrystallized from water; yield 14 g. (10%), m. p. 160° in agreement with J. S. Buck and A. M. Hjort.[3] By the same procedure, substituting one mole of *t*-amyl alcohol for the trimethylethene used above, the same product was obtained in 30% yield.

N-α-Phenethyl Acetamide.—Styrene (10.4 g., 0.1 mole) and acetonitrile (6.1 g., 0.15 mole) were mixed and added to a solution of 17.1 g. (0.1 mole) of benzenesulfonic acid (94.5%, sulfuric acid-free) in 50 ml. of glacial acetic acid. The resulting solution was allowed to stand for fifteen hours, then poured on 200 g. of cracked ice and neutralized with ammonia. A viscous oil separated; this was extracted with three 100-ml. portions of ether, the combined extracts were dried over anhydrous potassium carbonate, the ether was removed, and the amide was distilled at 7 mm. Seven grams (43%), b. p. 175–180°, was obtained and recrystallized from petroleum ether. Analogous products from acetonitrile and α-methylstyrene, and from acetonitrile and α-methyl-*p*-methylstyrene were obtained by the same procedure (Table IV).

Pyrolysis of N-*t*-Octyl Acetamide.—Fifty grams (0.29 mole) of the amide was distilled through a short unpacked steam-jacketed column at a rate to permit a distillate to come over at 50–60° (one hour). The distillate (43.3 g.) consisted of an oil (29.5 g.) and a lower aqueous layer. The oil was removed, washed with water, dried (anhydrous sodium sulfate) and distilled, yielding 21.3 g. boiling at 100–101°. This was identified as diisobutene through its physical constants and by condensation with acetonitrile to reform the original amide. The aqueous layer was saturated with sodium chloride, extracted with ether, and the extract dried and distilled to yield 3.0 g. of acetonitrile, identified by condensation with diisobutene to yield the original amide.

Summary

The interaction of nitriles and alkenes in the presence of concentrated sulfuric acid has been shown to result in N-alkyl amides. A series of such amides has been prepared and characterized, and the structures of typical members have been verified by hydrolysis to the corresponding amines.

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(3) J. S. Buck and A. M. Hjort, THIS JOURNAL, **59**, 2567 (1937).

WASHINGTON SQUARE
NEW YORK, N. Y.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NEW YORK UNIVERSITY]

A New Reaction of Nitriles. II. Synthesis of *t*-Carbinamines

BY JOHN J. RITTER AND JOSEPH KALISH(1)

The synthesis of *t*-carbinamines R_3CNH_2 has occupied the attention of several investigators[2] but up to the present no simple general method of synthesis has been reported. In an earlier publication[3] was reported the reaction of hydrogen cyanide with diisobutene and with camphene to form N-*t*-alkyl formamides. The ease of hydrolysis of formic acid derivatives in general suggested to the present authors the use of N-*t*-alkyl formamides as a source of *t*-carbinamines. The formamides already reported[3] were obtained by addition of hydrogen cyanide to alkene-sulfuric acid–acetic acid mixtures. The present procedure employs a tertiary alcohol or an alkene in acetic acid solution to which one equivalent of sodium cyanide has been added; the reaction occurs spontaneously when sulfuric acid is added, as follows[4]:

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(1) Based upon a part of the thesis to be presented by Joseph Kalish to the Graduate Faculty of New York University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) (a) Linnemann, *Ann.*, **192**, 72 (1878); (b) Klages, *et al.*, *ibid.*, **347**, 24 (1941); (c) C. Mentzer, *et al.*, *Bull. soc. chim.*, **9**, 813–818 (1942); (d) H. R. Henze, B. B. Allen and W. B. Leslie, THIS JOURNAL, **65**, 87–89 (1943); (e) J. V. Karabinos and K. T. Serijan, *ibid.*, **67**, 1856 (1945); (f) L. I. Smith and O. H. Emerson, *ibid.*, **67**, 1862 (1945); (g) K. N. Campbell, A. H. Sommers and B. K. Campbell, *ibid.*, **68**, 140 (1946); (h) R. Brown and W. E. Jones, *J. Chem. Soc.*, 781–782 (1946).

(3) J. J. Ritter and P. P. Minieri, THIS JOURNAL, **70**, 4045 (1948).

(4) The use of alcohols in place of alkenes in this method of amide synthesis was developed in collaboration with others (Frederic R. Benson, Ph.D. thesis, 1947; Robert M. Lusskin, research in progress).