Reaction of 9-*exo*-Hydroxy-2-thiatetrahydro-*endo*-dicyclopentadiene (XIX) with Hydrobromic Acid.—To 1 g. of XIX in absolute ethanol was added excess 48% hydrobromic acid. The mixture was held under reflux for 8 hr. on a steam bath and was stirred overnight. After excess HBr and the solvent were removed by evaporation, a solid residue remained which, after recrystallization, was identified as the sulfonium salt XVIII.

Acknowledgment.—The authors are indebted to Mrs. Rosita B. Feliu for valuable technical assistance.

The Preparation of 4-Pentenenitriles and 3,4-Pentadienenitriles from N-(2-Alkenyl)- and N-(2-Alkynyl)amides

KENT C. BRANNOCK AND ROBERT D. BURPITT

Research Laboratories, Tennessee Eastman Company, Division of Eastman Kodak Company, Kingsport, Tennessee

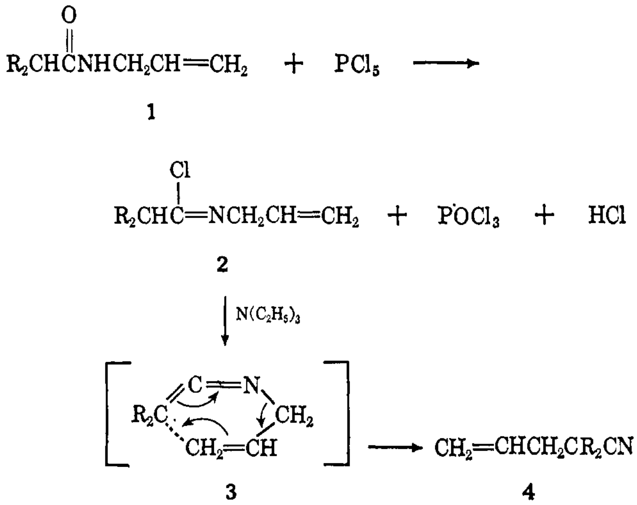
Received March 3, 1965

N-(2-Alkenyl)amides are converted to imino chlorides or imino chloride hydrochlorides with phosphorus(V) chloride or phosgene, respectively. These products, on treatment with a tertiary amine, give 4-pentenenitriles *via* a Claisen-type rearrangement. Since intermediates have not been isolated, it is not known whether the reaction proceeds through the formation of a discrete ketenimine or whether the process is a concerted one. The reaction appears to be intramolecular, however, since N-(2-butenyl)isobutyramide gives 2,2,3-trimethyl-4-pentenenitrile instead of 2,2-dimethyl-4-hexenenitrile. N-(2-Propynyl)butyramide gives 2-ethyl-3,4-pentadienenitrile. This reaction represents a new example of the Claisen-type rearrangement and provides a synthetic route to 4-pentenenitriles and 3,4-pentadienenitriles.

We should like to add an example to the already considerable list of systems which undergo Claisen-type rearrangements. It appeared of interest, despite expectations to the contrary, to determine whether N-(2-alkenyl)ketenimines, which had not been reported, would undergo such a rearrangement, leading to 4-pentenenitriles. Since the cumulative double-bond system is linear, one would not expect the ketenimines to lend themselves to six-membered, cyclic transition states.

Ketenimines themselves have been known for some time, but comparatively little work has been done with them. A classical route to ketenimines is analogous to the preparation of ketene from acid chlorides and a tertiary amine. An imino chloride is used in place of the acid chloride, and treatment with a base such as triethylamine leads, in most cases, to the formation of a ketenimine.[1] Imino chlorides, in turn, may be prepared from secondary amides by treatment with phosphorus(V) chloride or phosgene.

We found that when the amide possessed only one α-hydrogen atom, phosphorus(V) chloride was the preferred reagent. The mixture of amide 1 and phosphorus(V) chloride was heated in a solvent until hydrogen chloride evolution ceased. The phosphoryl chloride was removed by distillation under reduced pressure, and the imino chloride 2 was then distilled. Treatment of 2 with triethylamine in refluxing benzene gave the substituted 4-pentenenitriles 4. The isolation of the ketenimine 3 was never accomplished.



$$R_2CH\overset{O}{\overset{\|}{C}}NHCH_2CH{=}CH_2 + PCl_5 \longrightarrow$$

1

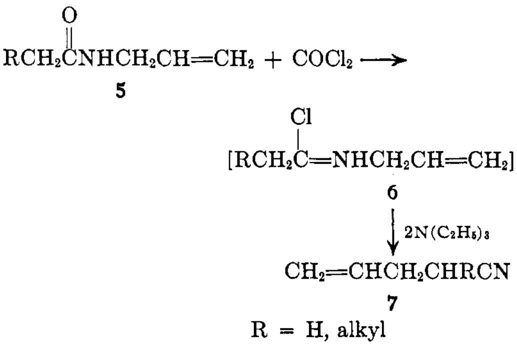
$$R_2CH\overset{Cl}{\overset{|}{C}}{=}NCH_2CH{=}CH_2 + POCl_3 + HCl$$

2

$$\downarrow N(C_2H_5)_3$$

3 → $CH_2{=}CHCH_2CR_2CN$ 4

When the starting amide 5 possessed more than one α-hydrogen atom, phosgene was found to be the preferred reagent. The reaction of 5 with phosgene was carried out in a solvent such as ether or tetrahydrofuran, and carbon dioxide was evolved. There resulted, presumably, the hydrochloride 6 of the imino chloride. Treatment of the crude salt with 2 moles of tertiary amine gave the nitrile 7.



$$RCH_2\overset{O}{\overset{\|}{C}}NHCH_2CH{=}CH_2 + COCl_2 \longrightarrow$$

5

$$[RCH_2\overset{Cl}{\overset{|}{C}}{=}NHCH_2CH{=}CH_2]^+Cl^- + CO_2$$

6

$$\downarrow 2N(C_2H_5)_3$$

$$CH_2{=}CHCH_2CHRCN$$

7

R = H, alkyl

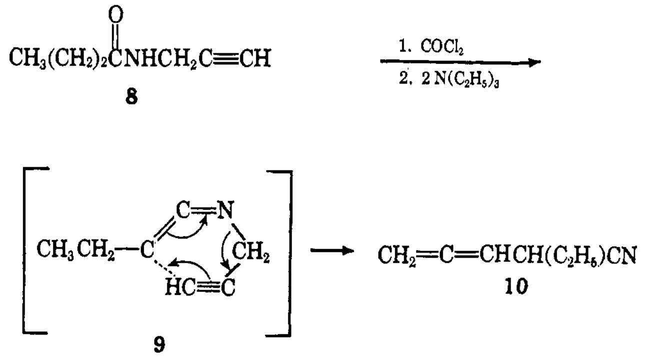
It is not known whether the formation of the unsaturated nitrile proceeds through the formation of a discrete ketenimine or whether the reaction is a concerted one. It appears to be intramolecular, however, since N-(2-butenyl)isobutyramide was converted, with inversion of the 2-butenyl group, to 2,2,3-trimethyl-4-pentenenitrile.

N-(2-Propynyl)butyramide (8) was converted, although in poor yield, to 2-ethyl-3,4-pentadienenitrile (10). This result is indeed striking, for, if the ketenimine intermediate 9 is involved, it contains two linear groups. Even if a concerted process is operative, the intermediate still contains the linear propynyl group.

Our crude nitriles sometimes contained small amounts of chlorine-containing impurities which were usually removed by washing with dilute acid. In one case we obtained evidence that the impurity was diethyl-

---

[1] C. L. Stevens and J. C. French, *J. Am. Chem. Soc.*, **76**, 4398 (1954).



carbamoyl chloride, which is known to result from the reaction of triethylamine with phosgene.[2,3] The over-all yields of the nitriles obtained in this investigation are summarized in Table I.

Table I

Preparation of Nitriles from Amides

Amide	Product	Reagent	Yield, %
N-Allylacetamide	4-Pentenenitrile	COCl$_2$	50
N-Allylbutyramide	2-Ethyl-4-pentenenitrile	COCl$_2$	77
N-(2-Propynyl)butyramide	2-Ethyl-3,4-pentadienenitrile	COCl$_2$	26
N-Allylisobutyramide	2,2-Dimethyl-4-pentenenitrile	PCl$_5$	45
N-(2-Butenyl)isobutyramide	2,2,3-Trimethyl-4-pentenenitrile	PCl$_5$	34

Experimental[4]

Starting Materials.—The following new amides were prepared by standard methods from the appropriate acid chloride and amine: N-(2-propynyl)butyramide, b.p. 78–79° (1 mm.), m.p. 28° (*Anal.* Calcd. for $C_7H_{11}NO$: C, 67.1; H, 8.8. Found: C, 66.7; H, 8.6.); N-allylisobutyramide, b.p. 60° (*ca.* 0.5 mm.) (*Anal.* Calcd. for $C_7H_{13}NO$: N, 11.0. Found: N, 11.1.); N-(2-butenyl)isobutyramide, b.p. 93–95° (1.0–1.1 mm.), $n^{20}\text{D}$ 1.4597 (*Anal.* Calcd. for $C_8H_{15}NO$: C, 68.0; H, 10.7. Found: C, 67.5; N, 10.6.).

2,2-Dimethyl-4-pentenenitrile.—N-Allylisobutyramide (95.3 g., 0.75 mole) was dissolved in benzene (100 ml.) and added to a slurry of phosphorus(V) chloride (156 g., 0.75 mole) in benzene (200 ml.) over a 2-hr. period. The resulting clear solution was refluxed for 2.5 hr. and then distilled through a 17-in. glass ring packed column. Most of the benzene was removed at atmospheric pressure and then the phosphoryl chloride was removed at 100 mm. The residue, on continued distillation, gave 81 g. of the crude imino chloride, b.p. 63–78° (85–65 mm.), which was redistilled to give 65.5 g. (60%) of N-(1-chloro-2-methylpropylidene)allylamine, b.p. 79–82° (79 mm.), $n^{20}\text{D}$ 1.4543, infrared absorptions 5.93 (>C=N–) and 6.12 μ (>C=C<).

Anal. Calcd. for $C_7H_{12}ClN$: N, 9.6. Found: N, 9.4.

N-(1-Chloro-2-methylpropylidene)allylamine (65 g., 0.45 mole) was combined with dry triethylamine (101 g., 1 mole) and benzene (300 ml.), and the mixture was refluxed for 17 hr. The solid was removed by filtration and washed with ether. The combined filtrate and washings were then washed several times with water and subjected to distillation. After removal of the ether and benzene, 36.7 g. (74%) of 2,2-dimethyl-4-pentenenitrile, b.p. 147–149°, $n^{20}\text{D}$ 1.4198 (lit.[5] b.p. 147–148.5°, $n^{20}\text{D}$ 1.4180), was obtained. The infrared spectrum was identical with that of authentic 2,2-dimethyl-4-pentenenitrile.[5]

2,2,3-Trimethyl-4-pentenenitrile.—The phosphorus(V) chloride procedure was used with N-(2-butenyl)isobutyramide to give 2,2,3-trimethyl-4-pentenenitrile in 33% over-all yield: b.p. 113–116° (155 mm.); $n^{20}\text{D}$ 1.4294; n.m.r. spectrum, peaks at 1.27 and 1.29 (*gem*-dimethyl group), doublet at 1.15 (3-methyl group), multiplet centered at 2.24 (tertiary proton, C-3), multiplet centered at 5.23 (terminal methylene, C-5), and quintuplet centered at 5.85 p.p.m. (single olefinic proton, C-4).

Anal. Calcd. for $C_8H_{13}N$: C, 77.9; H, 10.6. Found: C, 78.2; H, 10.6.

4-Pentenenitrile.—A 1-l. three-necked reaction flask was equipped with a stirrer, thermometer, Dry Ice–acetone condenser, drying tube, and gas inlet tube. A solution of N-allylacetamide (69 g., 0.7 mole) in tetrahydrofuran (400 ml.) was introduced into the flask and the contents were cooled to $-5 \pm 5°$ by means of a Dry Ice–acetone bath. Phosgene (73 g., 0.74 mole) was passed into the mixture over a 1.5-hr. period while the temperature was maintained at $-5 \pm 5°$. The mixture was stirred for an additional 20 min. and was then added rapidly with cooling to a solution of triethylamine (212 g., 2.1 moles) in tetrahydrofuran (750 ml.). The resulting slurry was stirred and refluxed for 4 hr. and then allowed to stand overnight. The mixture was filtered and the filtrate was distilled to a base temperature of 110°. The distillation residue was then dissolved in ether and the solution was washed with water. Distillation of the ethereal layer gave, after removal of ether and a small forerun, 28 g. (50%) of 4-pentenenitrile: b.p. 144–147°; $n^{20}\text{D}$ 1.4223 (lit.[6] b.p. 146–147°, $n^{19.5}\text{D}$ 1.4233); n.m.r. spectrum (consistent with the assigned structure), unresolved peaks centered at 2.37 (two methylene groups), multiplet centered at 5.13 (terminal methylene protons), and multiplet centered at 5.70 p.p.m. (single olefinic proton). Infrared absorptions of the residue from distillation of one run were 5.79, 8.05, 8.3, 8.95, 9.15 w, 9.33 w, and 11.9 μ. Comparison of this spectrum with a spectrum of diethylcarbamoyl chloride indicated the residue to be a mixture of 4-pentenenitrile and diethylcarbamoyl chloride. This was also confirmed by n.m.r. spectra.

2-Ethyl-4-pentenenitrile.—The phosgene method was used to prepare this nitrile from N-allylbutyramide in 73% yield, b.p. 162–163°, $n^{20}\text{D}$ 1.4273. A sample for analysis was purified further by being dissolved in ether, washed with 10% hydrochloric acid solution, and redistilled. N.m.r. spectrum showed a triplet centered at 1.04 (methyl protons), triplet centered at 2.30 (methylene protons, C-3), quintet centered at 1.58 (methylene protons of the ethyl group), quintet centered at 2.62 (tertiary proton), multiplet centered at 5.16 (single olefinic proton), and multiplet centered at 5.74 p.p.m. (terminal olefinic protons).

Anal. Calcd. for $C_7H_{11}N$: C, 76.9; H, 10.2. Found: C, 76.3; H, 10.1.

2-Ethyl-3,4-pentadienenitrile.—The phosgene method was used to prepare this nitrile from N-(2-propynyl)butyramide in 28% yield: b.p. 88–90° (39–40 mm.); $n^{20}\text{D}$ 1.4603; infrared absorptions 4.5 (–C≡N), 5.15 (>C=C=C<), and 6.01 w μ (possibly an amide impurity). A sample for analysis was purified by preparative-scale gas chromatography. N.m.r. spectrum showed a triplet centered at 1.07 (methyl protons), quintet centered at 1.76 (methylene protons), closely spaced multiplet centered at 3.23 (tertiary proton), and multiplet centered at 5.03 p.p.m. (three olefinic protons).

Anal. Calcd. for C_7H_9N: C, 78.5; H, 8.5. Found: C, 77.8; H, 8.6.

Acknowledgment.—The authors wish to acknowledge the assistance of Dr. V. W. Goodlett for determining the n.m.r. spectra and interpreting them.

---

(2) V. A. Rudenko, A. Ya. Yakubovitch, and T. Ya. Nikiforova, *J. Gen. Chem. USSR*, **17**, 2256 (1947); *Chem. Abstr.*, **42**, 4918 (1948).

(3) E. Stein and O. Bayer, U. S. Patent 2,698,343 (1954).

(4) Melting points were determined using a calibrated Fisher-Johns melting point apparatus. N.m.r. spectra were recorded on a Varian A-60 spectrometer with tetramethylsilane as an internal standard.

(5) R. H. Hasek, E. U. Elam, and J. C. Martin, *J. Org. Chem.*, **26**, 1822 (1961).

(6) R. Paul and S. Tchelitcheff, *Bull. soc. chim. France*, 470 (1949).