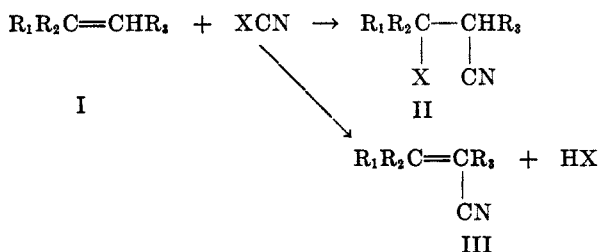# THE REACTIONS OF CYANOGEN CHLORIDE. I. ADDITION TO OLEFINS

F. M. COWEN

The successful addition of cyanogen halides to alkenes has recently been reported in the patent literature (1).[1] The reaction products were 3-halonitriles (II), 2-alkenenitriles (III), and hydrogen halides. This paper not only reviews the work on cyanogen chloride additions to olefins but also discusses proof of the direction of addition to the olefin double bond.

$$R_1R_2C{=}CHR_3 \; + \; XCN \; \rightarrow \; R_1R_2C{-}CHR_3$$

$$\underset{X \quad CN}{\underset{|\quad\;\;|}{}}$$

I II

$$R_1R_2C{=}CR_3 \; + \; HX$$

$$\underset{CN}{\underset{|}{}}$$

III

Outside of the cited reference above (1), there has been no previous report on the successful addition of cyanogen halides to simple alkenes. Dutcher (2) has claimed the catalyzed addition of cyanogen chloride to alkynes but Mooney and Reid (3) were unable to obtain the uncatalyzed addition of cyanogen halides to ethylene. Steinkopf (4) reported the addition of cyanogen bromide to indene and Klopp and Wright (5) obtained products from furan and cyanogen bromide which indicated an intermediate addition step.

Since it was assumed that any addition of this type would be ionic in nature (6), it was felt that the preparation of a suitable cyanogen halide complex, resulting in the formation of an ionic species, would favor addition reactions to olefins. It was thought that success might be achieved by the use of an intermediate complex of a Lewis Acid which would permit a ready transfer of the metal halide to the cyanogen halide in a homogeneous solution. Such liquid complexes have been reported (7) between aluminum chloride and nitroalkanes.

It was found that solutions of aluminum chloride or boron trifluoride in nitromethane or nitrobenzene promoted the addition of cyanogen chloride to propene, 1-butene, 2-butene (*cis* + *trans*), cyclohexene, 1-octene, and 1-dodecene. In all cases the products, as isolated, were mixtures of 3-chloronitriles (II) and 2-alkenenitriles (III) along with varying amounts of polymeric residues containing nitrile groups.

[1] *Chem. Abstr.*, **42**, 201 (1948) reports "I.G. Farbenind. A.-G., Belgium Patent 448,701, July 1943. CNCl is made to react under pressure at a temp. above atm. with unsatd. org. compds., particularly those contg. aliphatic double or triple bonds." Examination of a photostat of this patent revealed that reference was to nitryl chloride (NO_2Cl) and not cyanogen chloride (ClCN). The abstract is in error.
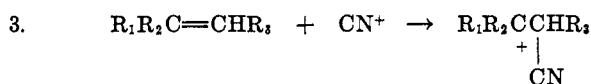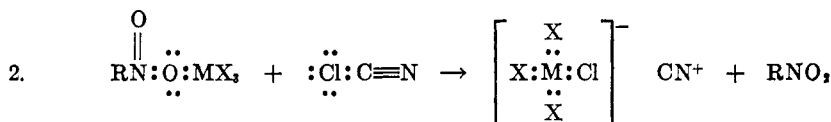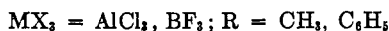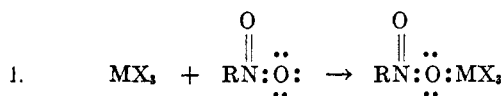
TABLE I

ADDITION OF CYANOGEN CHLORIDE TO OLEFINS

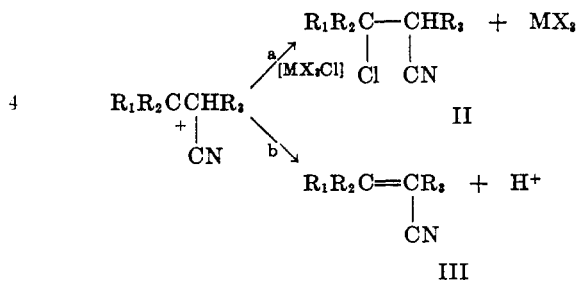| Olefin	No.	Method	Catalyst System	Yield, % 3-Chloro-nitrile	Yield, % 2-Alkene-nitrile[a]	Total Yield, % Nitriles
Propene	1	A	$CH_3NO_2–AlCl_3$[b]	6	1	7
Propene	2	B	$CH_3NO_2–AlCl_3$	15	6	21
1-Butene	3	A	$CH_3NO_2–AlCl_3$	18	7	25
2-Butene	4	A	$CH_3NO_2–AlCl_3$[b]	43	5	48
2-Butene	5	A	$\phi NO_2–AlCl_3$	37	20	57
2-Butene	6	A	$CH_3NO_2–BF_3$	2	7	9
2-Butene	7	A	$\phi NO_2–BF_3–BF_3 \cdot Et_2O$	<1	<1	<2
Cyclohexene	8	A	$CH_3NO_2–AlCl_3$[c]	30[d]	21	51
1-Octene	9	A	$CH_3NO_2–AlCl_3$[b]	9	15	24
1-Dodecene	10	A	$CH_3NO_2–AlCl_3$[b]	8	9	17

[a] Mixtures of *cis* and *trans* isomers except in the case of cyclohexene. [b] Carbon disulfide diluent. [c] Chlorobenzene diluent. [d] Approximately 50% *erythro* and 50% *threo*.

Although several other catalyst combinations or solutions were tried (*i.e.* $AlCl_3$ suspended in CS_2, $BF_3 \cdot (C_2H_5)_2O$, $BF_3 \cdot CH_3CO_2C_2H_5$, $AlCl_3 \cdot CH_3CN$) only those in which the aluminum chloride or boron trifluoride were dissolved in a nitrated hydrocarbon were effective (Table I).

The following equations, while they do not explain the unique role of the nitrated hydrocarbons, are proposed to account for the facts presented in this paper.

$$1. \quad MX_3 + RN\!\!:\!\!O: \ \rightarrow \ RN\!\!:\!\!O\!\!:\!\!MX_3$$

$$MX_3 = AlCl_3, BF_3; \ R = CH_3, C_6H_5$$

$$2. \quad RN\!\!:\!\!O\!\!:\!\!MX_3 + :\!Cl\!:\!C\!\!\equiv\!\!N \ \rightarrow \ \left[\begin{array}{c} X \\ X\!\!:\!\!M\!\!:\!\!Cl \\ X \end{array} \right]^- \ CN^+ + RNO_2$$

$$3. \quad R_1R_2C\!\!=\!\!CHR_3 + CN^+ \ \rightarrow \ R_1R_2\underset{\underset{CN}{+|}}{C}CHR_3$$

$$I$$

$$4. \quad R_1R_2\underset{\underset{CN}{+|}}{C}CHR_3 \ \overset{a}{\underset{[MX_3Cl]}{\nearrow}} \ R_1R_2\underset{\underset{Cl}{|}}{C}\!\!-\!\!\underset{\underset{CN}{|}}{C}HR_3 + MX_3$$
$$II$$
$$\underset{b}{\searrow} \ R_1R_2C\!\!=\!\!\underset{\underset{CN}{|}}{C}R_3 + H^+$$
$$III$$

It is assumed that the initial step is the formation of a complex between the electron-deficient metal halide and the nitrated hydrocarbon.

The contact of cyanogen chloride with the complex brings about either a complete transfer of the metal halide to the cyanogen chloride (equation 2) or an equilibrium between two complexes, one with the nitrated hydrocarbon and one with the cyanogen chloride.[2] Evidence for the existence of this latter type of complex is presented by Dilthey (8) and Fairbrother (9) for Friedel-Crafts acylations. Cyanogen halides show results analogous to acyl halides when reacted with aromatic ring structures in the presence of Lewis Acids (10). Thomas (11) has discussed the extensive literature on the addition of acyl halides to olefins.

Very strong evidence for the existence of the positive cyanide ion, especially when cyanogen chloride is complexed with gold chloride, boron chloride, aluminum chloride, ferric chloride, or platinum chloride, has recently been presented by Woolf (12). It is therefore assumed that the initial attack on the olefin is taken by the positive cyanide ion in what is probably the rate-determining step (equation 3).

The carbonium ion thus formed can conceivably do two things: react with the negative metallic ion $[MX_3Cl]^-$ and form a 3-chloronitrile (II) as in equation 4a, or expel a proton and be stabilized as a 2-alkenenitrile (III) as in equation 4b. Both of these reactions seem to occur simultaneously with 4a favored at lower temperatures and 4b at higher temperatures.

The resulting nitriles are then "tied-up" as complexes with the freed metal halide. These complexes can be readily destroyed by water. It is because of this complexing nature of the nitrile products that at least one mole of metal halide must be present per mole of cyanogen chloride added for maximum yields.

Polymeric nitriles and olefins result, of course, from the powerful polymerizing action of the metal halide on the unsaturated nitriles and olefins.

With terminal olefins such as 1-butene, the direction of addition follows the usual well-established rules (6). That is, the positive cyanide ion attacks the terminal carbon atom. The carbonium ion thus formed combines with a negative halogen ion or ejects a proton to produce a straight-chain nitrile. This direction of addition was firmly established by comparing the amines (as *p*-nitrobenzamides) obtained from the dehydrohalogenation and reduction of the addition products of cyanogen chloride with 1-butene (IVa) and 2-butene (IV).
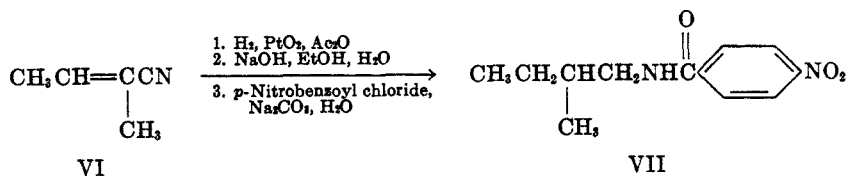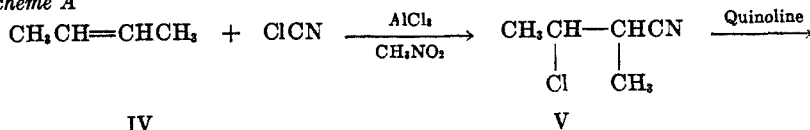
Comparison of the properties presented in the experimental section shows conclusively that VII and VIIa are different compounds with the same empirical formulae. If addition to IVa had been in reverse, the intermediate 2-ethylacrylonitrile produced by dehydrohalogenation would have been converted to the same *p*-nitrobenzamide as that obtained from IV.

Further proof of the direction of addition is obtained by an examination of the products listed in Table II. The isolation of *cis*- and *trans*-isomers of the by-product unsaturated nitriles from all terminal olefins indicates "normal" addition
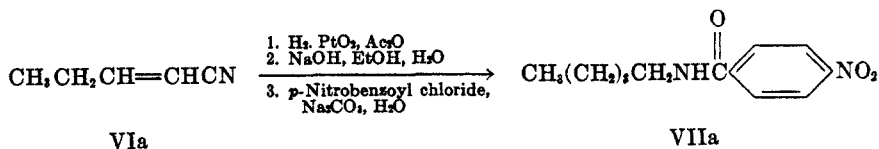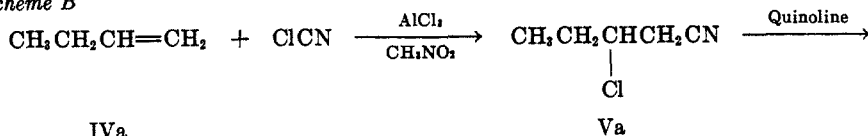
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[2] The nitrobenzene-aluminum chloride complex was a solid not readily soluble in excess nitrobenzene. Introduction of cyanogen chloride caused a phase change from solid-liquid to a homogeneous liquid.

(assuming no double bond isomerization). The physical properties of these isomers correspond reasonably closely to those which have been reported elsewhere.
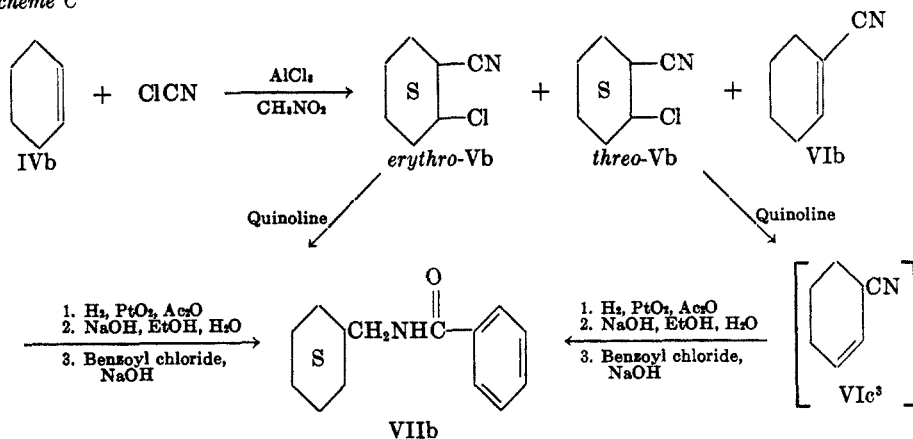
Scheme A

$$CH_3CH=CHCH_3 \;+\; ClCN \xrightarrow[CH_3NO_2]{AlCl_3} CH_3CH-CHCN \xrightarrow{Quinoline}$$

with Cl and CH$_3$ substituents below.

$$\underset{IV}{} \qquad\qquad \underset{V}{}$$

$$CH_3CH=CCN \xrightarrow[\substack{3.\ p\text{-Nitrobenzoyl chloride,}\\ Na_2CO_3,\ H_2O}]{\substack{1.\ H_2,\ PtO_2,\ Ac_2O\\ 2.\ NaOH,\ EtOH,\ H_2O}} CH_3CH_2CHCH_2NHC\!\!\begin{array}{c}O\\ \|\end{array}\!\!\langle\rangle NO_2$$

with CH$_3$ substituents.

$$\underset{VI}{} \qquad\qquad\qquad \underset{VII}{}$$

Scheme B

$$CH_3CH_2CH=CH_2 \;+\; ClCN \xrightarrow[CH_3NO_2]{AlCl_3} CH_3CH_2CHCH_2CN \xrightarrow{Quinoline}$$

with Cl substituent.

$$\underset{IVa}{} \qquad\qquad\qquad \underset{Va}{}$$

$$CH_3CH_2CH=CHCN \xrightarrow[\substack{3.\ p\text{-Nitrobenzoyl chloride,}\\ Na_2CO_3,\ H_2O}]{\substack{1.\ H_2,\ PtO_2,\ Ac_2O\\ 2.\ NaOH,\ EtOH,\ H_2O}} CH_3(CH_2)_3CH_2NHC\!\!\begin{array}{c}O\\ \|\end{array}\!\!\langle\rangle NO_2$$

$$\underset{VIa}{} \qquad\qquad\qquad \underset{VIIa}{}$$

Scheme C

Cyclohexene (IVb) produced approximately equal amounts of the reported (18) *erythro* and *threo* Vb plus considerable quantities of VIb. The products were all converted to the same benzamide by the methods outlined in Scheme C.

³ No attempt was made to determine the structure of VIc. It is assumed that *trans* elimination would result in the initial formation of 1-cyano-2-cyclohexene.

TABLE II

NITRILES PRODUCED BY THE ADDITION OF CYANOGEN CHLORIDE TO OLEFINS

Product[a]	Olefin Employed	B.P. °C./mm.	d_4/°C.	nD/°C.	Ref.
3-Chlorobutanenitrile	Propene	59–61/11.5	1.028/25	1.4315/24	(13)
2-Butenenitrile (cis + trans)	Propene	111–116	—	1.415/25	(14)
3-Chloropentanenitrile	1-Butene	59–59.5/5–6	1.018/25	1.4371/24	(15)
2-Pentenenitrile (cis + trans)	1-Butene	125–143	0.827/25	1.4212/25	(16)
3-Chloro-2-methylbutane-nitrile	2-Butene (cis + trans)	55/5–6	1.001/25	1.4338/25	(17)
2-Methylbutenenitrile (cis + trans)	2-Butene (cis + trans)	122–130	0.820/25	1.4224/25	(16)
erythro-2-Chloro-1-cyanocy-clohexane	Cyclohexene	90–92/3	1.078/26	1.4935/26	(18)
threo-2-Chloro-1-cyanocyclo-hexane	Cyclohexene	79/2–3	1.076/26	1.4382/25	(18)
1-Cyanocyclohexene	Cyclohexene	54/3	0.954/25	1.4818/25	(18)
3-Chlorononanenitrile[b]	1-Octene	88–89/1.5	0.944/25	1.4464/25	—
cis-2-Nonenenitrile	1-Octene	58/2	0.856/25	1.4371/25	(19)
trans-2-Nonenenitrile	1-Octene	68–70/2	0.867/25	1.4401/25	(19)
3-Chlorotridecanenitrile[c]	1-Dodecene	114–116/1	0.838/25	1.4493/25	—
cis-2-Tridecenenitrile	1-Dodecene	86–88/1	0.831/25	1.4444/25	—
trans-2-Tridecenenitrile	1-Dodecene	98–99/1	0.828/25	1.4464/25	—

[a] Infrared data and conversion to derivatives (see text) provide additional structural support.

[b] Calc'd for $C_9H_{16}ClN$: N, 8.07. Found: N, 7.74.

[c] Calc'd for $C_{13}H_{24}ClN$: N, 6.10. Found: N, 6.88.

In the early stages of this work carbon disulfide and chlorobenzene were employed as agents for suspending the aluminum chloride during the addition of the nitrated hydrocarbon and also to act as solvents for the olefins. It was later found that excess nitrated hydrocarbon was quite satisfactory for this purpose. No study was made of the solvent effect *per se*.

All additions, with one exception, were performed at room temperatures or lower and at atmospheric pressures. In this exception (Table I, No. 2, Method B) the use of an autoclave with propene increased the yield of nitriles with a greater proportion of unsaturated nitrile probably because of the higher temperatures of reaction. Since the propene was introduced in excess, considerable quantities were converted to polymer. The increased yield was presumably due to the higher concentrations of low-boiling propene maintained in the autoclave under pressure *vs.* the flask at atmospheric pressure.

Aluminum chloride was by far the catalyst of choice. Yields were poor with boron trifluoride (Table I) probably because of the less powerful complexing ability of the latter with the nitrated hydrocarbon.

In the experimental section, the general details are given for the various successful reactions listed in Table I. Reference should be made to Table II for

data on the specific products isolated. The products in all cases were analyzed as crude cuts from distillations through a 1″ x 12″ Stedman column.

Acknowledgments. The author wishes to express his thanks to Drs. J. K. Dixon and K. W. Saunders for helpful advice and criticism during the course of this work, to Mr. Ole Rörso for conducting the pressure reactions, to Dr. J. A. Kuck and Mr. R. P. Smith and members of their groups for chemical analyses, and to Dr. R. C. Gore and members of his group for infrared spectra.

EXPERIMENTAL

GENERAL PROCEDURES FOR THE ADDITION OF CYANOGEN CHLORIDE TO OLEFINS (TABLE I)

Boiling points. All boiling points given in Table II are corrected.

Yields. All yields given in Table I are based on added cyanogen chloride.

Olefins. Propylene, Matheson C.P. (99%); 1-Butene, Matheson C.P. (99%); 2-Butene (*cis* + *trans*), Phillips Petroleum (99%); Cyclohexene, Eastman Kodak, distilled before use; 1-Octene and 1-dodecene, Conn. Hard Rubber (>95%).

Nitromethane. Commercial Solvents nitromethane was purified by washing with dilute sodium bicarbonate and water, drying, and distilling.

Cyanogen chloride. American Cyanamid Company.

Method A. In those cases where anhydrous aluminum chloride (granular or sublimed C.P.) was employed as a catalyst, it was either dissolved in an excess of nitromethane (100 ml./1.35 moles of AlCl₃) or nitrobenzene (400 ml./1.35 of moles AlCl₃) or it was suspended in carbon disulfide (150–250 ml./1.35 moles of AlCl₃) or chlorobenzene (150 ml./1.35 moles of AlCl₃) and the suspension was treated with 1.35 moles of nitromethane. Ice-bath cooling and vigorous stirring were essential for rapid complex formation. The resulting mixture was then cooled to −10° and 52 ml. (1.0 mole) of cyanogen chloride was vaporized into it. The olefin (1.0 mole if liquid, 50–100% excess if gas at room temperature) was added to the stirred reaction mixture over a period of 1½ hours at *circa* 0°. Liquid olefins were added dropwise; gases, through a sintered-glass disc. The reaction mixture was allowed to stir overnight at room temperature. It then was poured on ice, acidified with concentrated hydrochloric acid, the product layer separated, and the aqueous layer extracted with ether. The combined organic layers were distilled at reduced pressures to give crude 3-chloronitriles and 2-alkenenitriles.

When boron trifluoride was the chosen catalyst, nitromethane (200 ml./mole of ClCN) was cooled to 10° and saturated with boron trifluoride (*circa* 70 g.) or nitrobenzene (100 g./mole of ClCN) was cooled to 10°, saturated with boron trifluoride (*circa* 10 g.), and mixed with 164 g. of boron trifluoride etherate. The rest of the procedure was the same as that outlined above.

Method B. The aluminum chloride-nitromethane-cyanogen chloride solution was prepared by Method *A* and charged to a cold rocking-type steel autoclave. Propene (120 g./ mole of ClCN) was gradually introduced so that the pressure remained in the limits of 20–120 p.s.i. and the temperature did not exceed 33°. After venting, the contents of the autoclave were worked up by Method *A*. When further excesses of propene were introduced, the yield of nitriles and the proportion of 3-chlorobutanenitrile were decreased. As with the residues from Method *A*, considerable polymeric nitrile was present. Because of its potential explosion hazard, Method *B* is not recommended.

GENERAL PROCEDURE FOR THE CONVERSION OF 3-CHLOROALKANENITRILES TO AMINE DERIVATIVES

Melting points. All melting points given below are corrected.

A. Dehydrohalogenation of 3-chloroalkanenitriles. The crude 3-chloroalkanenitrile was refluxed with excess quinoline for 2 hours. After standing overnight at room temperatures,

the nitrile was distilled out, dissolved in ether, and washed successively with dilute hydrochloric acid, water, dilute sodium hydroxide, and water. After drying, the solution was rectified through a small Vigreaux column and the water-white mixture of 2-alkenenitriles was collected. In those cases where they existed, no attempt was made to separate *cis* and *trans* forms.

B. Conversion of the 2-alkenenitriles to the corresponding benzamides of the saturated amines. The 2-alkenenitriles were reduced with hydrogen (3 atm.) in acetic anhydride employing a PtO_2 catalyst. When absorption of hydrogen was complete, the product was filtered free of catalyst and poured onto a mixture of dilute sodium hydroxide and ice. The resulting acetamide was extracted with ether and the ether was evaporated. The oily, colorless amide was hydrolyzed to the free amine by refluxing with 10% sodium hydroxide (1:1 ethanol-water). Acidification (excess hydrochloric acid) and steam-distillation to remove volatiles gave a solution which was filtered and made alkaline with dilute sodium hydroxide. The benzamides or *p*-nitrobenzamides of the amines were prepared from the solutions by the Schotten-Baumann (or modified) procedure employing the corresponding benzoyl chloride. The crude amides were purified by repeated recrystallizations from alcohol-water and heptane.

C. Derivatives prepared. p-Nitrobenzamide of 2-methyl-1-butylamine (VII). White fluffy needles, m.p. 76–77°. Mixed with VIIa, m.p. 63–72°.

Anal. Calc'd for $C_{12}H_{16}N_2O_3$: C, 61.00; H, 6.83.

Found: C, 61.21; H, 6.76.

p-Nitrobenzamide of 1-pentylamine (VIIa). White fluffy needles, m.p. 92–93°. Wenker (20) reported m.p. 92°.

Anal. Calc'd for $C_{12}H_{16}N_2O_3$: C, 61.00; H, 6.83.

Found: C, 60.96; H, 6.78.

Nitrobenzamide of cyclohexylmethylamine (VIIb). Flat white needles or plates, m.p. 106–107°. Gutt (21) reported m.p. 107–108°. No depression whether the amide was derived from *erythro* Vb, *threo* Vb, or VIb.

Anal. Calc'd for $C_{14}H_{19}NO$: C, 77.38; H, 8.81.

Found: C, 77.47; H, 8.64.

SUMMARY

1. The addition of cyanogen chloride to various olefins resulted in the formation of 3-chloroalkanenitriles and 2-alkenenitriles. Catalysts for this addition were aluminum chloride or boron trifluoride dissolved in nitromethane or nitrobenzene.

2. The direction of addition to unsymmetrical terminal olefins was found to proceed by the attachment of the cyano group to the terminal carbon atom.

STAMFORD, CONNECTICUT

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