bromo-3,3,3-trifluoro-1-propene for 13 days gave 52.3 g. (0.14 mole, 38% yield) of 1:1 adduct (XV), b.p. 86–88° (12 mm.), and 19.4 g. (0.035 mole, 10% yield) of 1:2 adduct (XVI), b.p. 86–89° (1 mm.).

Dehydrobromination of 1,3-Dibromo-5,5,5-trichloro-3,4,4-trifluoropentane (IX).—In a 300-ml. three-necked flask with a stirrer and reflux condenser was placed 81.5 g. (0.21 mole) of the halopentane. A solution of 34 g. (0.61 mole) of potassium hydroxide in 150 ml. of absolute ethanol was added dropwise for 40 min. and kept stirring for an additional 10 min. The cooled reaction mixture was suction filtered to remove the potassium bromide and water was added to the solution. The organic layer was separated, dried, and distilled to give 11 g. (0.036 mole, 17% yield) of a mixture of $CH_2BrCH{=}CHCF_2CCl_3$ (II) and $CH_2{=}CHCFBrCF_2CCl_3$, b.p. 88–90° (17 mm.), and 27.6 g. (0.10 mole, 48% yield) of $C_2H_5OCH_2CH{=}CFCF_2CCl_3$ (XVII), b.p. 93–94° (16 mm.), and viscous liquid residue, 9.8 g.

In the same procedure, a reaction of 99 g. (0.26 mole) of the halopentane with 21 g. (0.37 mole) of potassium hydroxide in 60 ml. of absolute ethanol gave 3.7 g. (0.01 mole, 5% yield) of $CH_2{=}CHCFBrCF_2CCl_3$, 37.4 g. (0.12 mole, 47% yield) of II, 6.3 g. (0.02 mole, 9% yield) of XVII, and 20.5 g. of unchanged halopentane.

Dehydrobromination of 1,2,4-Tribromo-1,1,2-trifluorobutane.—A reaction of 92 g. (0.26 mole) of the halobutane with 19 g. (0.34 mole) of potassium hydroxide in 100 ml. of absolute ethanol gave 31.6 g. (0.12 mole, 46% yield) of $CH_2BrCH{=}CFCF_2Br$, b.p. 51–52° (70 mm.), 10.6 g. of a mixture of two compounds, b.p. 70–72° (67 mm.), and 8 g. of unchanged halobutane.

Dehalogenation of 1,3-Dibromo-2,5,5,5-tetrachloro-1,1,2-trifluoropentane.—To 15 g. (0.23 mole) of zinc dust in 100 ml. ethanol was added dropwise 49 g. (0.12 mole) of the halopentane for 1 hr. The reaction mixture was filtered and diluted hydrochloric acid was added to the filtrate. The organic layer was separated and dried. Fractionation gave 4 g. (0.013 mole, 11% yield) of $CF_2{=}CFCHBrCH_2CCl_3$, 9.4 g. (0.031 mole, 26% yield) of $CF_2BrCF{=}CHCH_2CCl_3$, b.p. 74–78° (14 mm.), and 14.6 g. of unchanged halopentane.

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The Synthesis and Reactions of β-Chloroacrylonitrile

F. SCOTTI AND E. J. FRAZZA

Stamford Research Laboratories, American Cyanamid Company, Stamford, Connecticut

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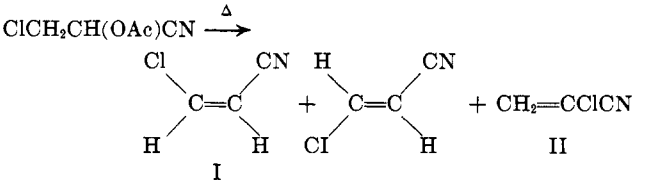
A mixture of *cis* and *trans* isomers of β-chloroacrylonitrile and α-chloroacrylonitrile is obtained by the pyrolysis of α-acetoxy-β-chloropropionitrile. The chlorine of β-chloroacrylonitrile is easily displaced by nucleophilic reagents enabling the compound to be used successfully as a cyanovinylating reagent. Reactions involving compounds containing nitrogen, sulfur, phosphorus, and carbon as the nucleophilic ceuters are described. Ethoxide ion and *p*-toluene sulfide ion react with *cis*- or *trans*-β-chloroacrylonitrile to give products of the same steric configuration as the starting material. In contrast, only one product, the *trans*-β-cyanovinylpiperidine, is obtained on cyanovinylation of piperidine with either the *cis*- or *trans*-β-chloroacrylonitrile. The mechanism of the cyanovinylation reaction is discussed.

In the last few years several investigators have shown increasing interest in the reactivity of vinyl halides both from a mechanistic and practical synthetic point of view. Vinyl halides which have β-electron-attracting substituents have been of particular interest because of the ease of replacement of the halogen atom by nucleophilic reagents.[1] The reactions of β-chloroacrylonitrile (I), a material of this structural type, have not been described in the literature.

Two methods for the preparation of I have been published. Dutcher[2] reported its synthesis by the addition of cyanogen chloride to acetylene; however, no physical or chemical properties were described. Gryszkiewicz-Trochimowski[3] described the synthesis of the *trans* isomer from the corresponding *trans* amide. A brief investigation of Dutcher's procedure revealed that only a very low yield of the hitherto unknown *cis* isomer was produced. We have found that I can be conveniently obtained by the pyrolysis of α-acetoxy-β-chloropropionitrile at 535°. Fractionation of the



pyrolysate gave equivalent amounts of the *cis* (b.p. 145–146°) and *trans* (b.p. 118°) isomers in 33% total yield along with a 28% yield of α-chloroacrylonitrile (II). The large amount of II obtained in the reaction is surprising. Acetate pyrolyses of this type are generally considered to proceed through an uncharged cyclic transition state; the chlorine rearrangement observed here suggests a unique mechanism involving charged species in the vapor phase.

The physical properties of *trans*-I obtained by pyrolysis were identical with those previously reported.[3] The *cis*-I obtained by the pyrolysis route was identical with the product of the cyanogen chloride–acetylene reaction.[2] In addition, the above assignments of configuration were substantiated by both infrared and nuclear magnetic resonance spectra (Table VI). The *trans* isomer exhibits a band at 935 cm.$^{-1}$ in the infrared which has been assigned to the *trans* in-phase, out-of-plane, carbon–hydrogen bending vibration.[4] The isomer to which we assign the *cis* configuration exhibits this vibrational band at 740 cm.$^{-1}$ as expected. The hydrogen–hydrogen coupling constants, 7.7 c.p.s.

(1) (a) D. E. Jones, R. O. Morris, C. A. Vernon, and R. F. M. White, *J. Chem. Soc.*, 2349 (1960); D. E. Jones and C. A. Vernon, *Nature*, **176**, 791 (1955); D. E. Jones, C. A. Vernon, and R. F. M. White, *Proc. Chem. Soc.*, 303 (1958); (b) F. Montanari, *Boll. Sci. Fac. chim. ind. Bologna*, **16**, 31, 140 (1958); (c) G. Modena, *et al.*, *Ric. sci. Suppl.*, **28**, 341 (1958); G. Modena, *et al.*, *Gazz. chim. ital.*, **89**, 854, 866, 878 (1959); (d) M. K. Kochetkov, *Usp. Khim.*, **24**, 32 (1955); (e) S. I. Miller and P. K. Yonan, *J. Am. Chem. Soc.*, **79**, 5831 (1957); (f) J. Erickson, U. S. Patent 2,433,742 (1947); (g) P. B. D. de LaMare, "Progress in Stereochemistry," Vol. 2, Academic Press, Inc., New York, N. Y., 1958, p. 90; (h) W. E. Truce, *et al.*, *J. Am. Chem. Soc.*, **78**, 2743, 2748, 2752, 2756 (1949); (i) C. L. Dickenson, Jr., D. W. Wiley, and B. C. McKusick, *ibid.*, **82**, 6132 (1960).

(2) H. A. Dutcher, U. S. Patent 2,419,488 (1947).

(3) Gryszkiewicz-Trochimowski, *et al.*, *Bull. soc. chim. France*, 593 (1948).

(4) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 45.

TABLE I

NITROGEN CYANOVINYLATIONS

Nitrogen compound	β-Chloro-acrylonitrile	Yield, %	B.p. (m.m.) or [m.p.], °C. $n^{25}D$	Formula	Calcd., % / Found, % C	H	N
n-Butylamine[a,b]	*trans*	80	121 (0.2–0.25)	$C_7H_{12}N_2$	67.70	9.74	22.56
	cis	78	1.5085[j]		67.42	9.95	22.43
Di-*n*-propylamine[a]	*cis*	93	107–109° (0.3)	$C_9H_{12}N_2$	71.00	10.59	18.40
			1.5065		70.60	10.51	18.32
Diethylamine[a]	*trans*	90	85–87° (0.5)	$C_7H_{12}N_2$	67.70	9.74	22.56
	cis	90	1.5160		67.98	10.07	22.35
Dimethylamine[a]	*cis*	77	93–99° (0.6–1)	$C_5H_8N_2$	62.47	8.38	
			1.5308		62.40	8.54	
Piperidine[a]	*trans*	90	118–20° (0.5)	$C_8H_{12}N_2$	70.54	8.88	20.57
	cis[c]	88	[57–58°]		70.76	8.93	20.29
Cyclohexylamine[a,d]	*cis*	60	[164–166°]	$C_8H_{14}N_2$	72.03	9.39	18.65
					72.03	9.50	18.95
Aniline[e]	*trans*	78	[138–140°]	$C_{17}H_9N_3$	73.83	4.55	21.53
	cis	70			73.74	4.50	21.24
N-Ethylaniline[f]	*trans*	78	125–140° (0.1–0.2)	$C_{11}H_{12}N_2$			16.39
			1.6120				16.39
Phenylhydrazine[g]	*trans*	60	[80–85°]	$C_9H_9N_3$	67.90	5.69	26.39
					67.61	5.65	26.13
Pyridone[h]	*trans*	53	[55–56°]	$C_8H_6N_2O$	65.74	4.14	19.17
					65.56	4.40	19.22
Pyrrolidone[h]	*trans*	5	[54–55°]	$C_7H_9N_2O$	61.75	5.92	25.58
					61.69	6.04	25.33
Succinimide[i]	*cis*	25	[155–156.4°]	$C_7H_6N_2O_2$	55.99	4.03	18.66
					55.93	4.16	18.48

[a] Ether used as solvent for reaction; temp. 0–20°. [b] Yield and analyses on undistilled material; distillation accompanied by decomposition. [c] Recrystallized from ethylacetate–ligroin. Also obtained a 5% yield of 4-(piperidinomethylene)glutaconononitrile. *Anal.* Calcd. for $C_{11}H_{13}N_3$: C, 70.46; H, 7.00; N, 22.44. Found: C, 70.41; H, 7.03; N, 22.65. [d] Recrystallized from benzene. [e] Ethanol was used as solvent for reaction; temp. 70°; product obtained was 4-(anilinomethylene)glutaconononitrile. [f] Ethanol used as solvent. [g] Benzene used as solvent. [h] Reacted as sodium salt in 9:1 benzene–DMF solution. [i] Acetone used as solvent. [j] $n^{27}D$.

for *cis*-I and 14 c.p.s. for *trans*-I, observed in the n.m.r. spectra are also consistent with the proposed structures.[5]

Addition reactions at the nitrile and ethylenic linkages of I are comparable to those of acrylonitrile. For instance, *cis*-I was readily hydrolyzed with 85% sulfuric acid to the previously unknown *cis*-β-chloroacrylamide; however, an attempt at complete hydrolysis with 58% sulfuric acid gave only a low yield of *trans*-β-chloroacrylic acid.[6] The activity of I as a dienophile was demonstrated by the preparation of Diels–Alder adducts of *cis*-I with cyclopentadiene and hexachlorocyclopentadiene. Chlorination of β-chloroacrylonitrile has previously been shown to give 2,2,3,3-tetrachloropropionitrile.[7]

The facile displacement of halogen from I by nucleophilic reagents provides a method for the introduction of a cyanovinyl moiety. The reaction has wide applicability, as evidenced by cyanovinylations[8] of alcohols, phenols, thiols, amines, amides, imides, sulfinates, and active methylene compounds. The general reaction can be represented by the following, where BH is the nucleophilic reagent.

$$BH + ClCH{=}CHCN \longrightarrow BCH{=}CHCN + HCl$$

Nitrogen Cyanovinylations.—Both primary and secondary alkyl amines react rapidly with *cis*- and *trans*-I at relatively low temperatures (0–20°) to give cyanovinylamines (III) in good yields (Table I).

$$2R_1R_2NH + Cl{-}CH{=}CHCN \longrightarrow R_1R_2N{-}CH{=}CHCN + R_1R_2NH_2Cl$$

III

$R_1 = R_2$ = alkyl or H

These weakly basic enamines dissolve in cold 5% hydrochloric acid solution with the evolution of heat. This is undoubtedly due to the hydrolysis to cyanoacetaldehyde[9] rather than simple salt formation, since the acidic solutions give a positive enol test with ferric chloride.[10] This test was negative with aqueous solutions even upon heating. Further, under the usual acidic conditions, the enamine was converted easily to the 2,4-dinitrophenylhydrazone of cyanoacetaldehyde. The N–H band at 3350 cm.$^{-1}$ shown by the secondary cyanovinylamines and their spectral similarities with the tertiary cyanovinylamines clearly indicate the absence of any of the tautomeric Schiff base form, $RN{=}CHCH_2CN$.

The reaction temperature required for the formation of quaternary cyanovinylammonium chlorides from tertiary amines varies to a considerable extent (Table II) depending on the structure of the amine. For instance, trimethylamine reacts readily at 0°, whereas triethylamine requires heating to 50° before reaction occurs at an appreciable rate. At reaction temperatures above 90°, the triethylcyanovinylammonium chloride (IV) initially produced decomposes *via* a Hoffmann-type degradation to form diethyl β-cyanovinylammonium chloride (V), the free amine (VI), and ethylene.

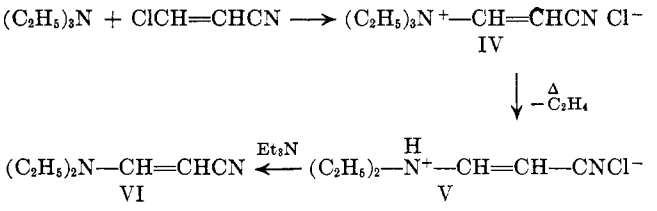
(5) C. N. Banwell and N. Sheppard, *Mol. Phys.*, **3**, 351 (1960).
(6) H. J. Backer and A. E. Beute, *Rec. trav. chim.*, **54**, 167 (1935).
(7) W. H. Jura and R. J. Gaul, *J. Am. Chem. Soc.*, **80**, 5402 (1958).
(8) By analogy with the term "cyanoethylation" for the incorporation of a cyanoethyl moiety, the incorporation of the cyanovinyl moiety can be called "cyanovinylation."
(9) C. Moureau and I. Lazannec, *Bull. soc. chim. France*, [3]**35**, 1179 (1906).
(10) R .L. Shriner and R. C. Fuson, "Identification of Organic Compounds," 3rd Ed., John Wiley and Sons, New York, N. Y., 1958, p. 98.

TABLE II

REACTIONS OF TERTIARY AMINES AND β-CHLOROACRYLONITRILE

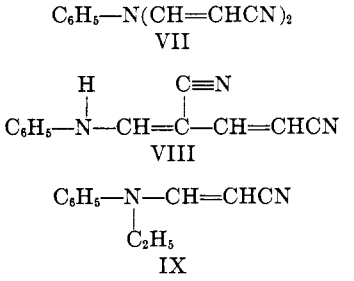
$R_3N + ClCH{=}CHCN \rightarrow (R_3NCH{=}CHCN)^+Cl^-$

Amine	β-ClAN	Temp., °C.	M.p., °C.	Yield, %	Formula	Calcd., % / Found, % C	H	N
Triethylamine	*cis*	50	138	90	$C_9H_{17}N_2Cl$	57.28	9.08	14.85
						57.09	9.27	15.03
Triethylamine	*cis*	0	158	90	$C_6H_{11}N_2Cl$			19.10
								19.18
Pyridine	*cis*	80	150–152	90	$C_8H_7N_2Cl$	57.67	4.24	16.82
						57.42	4.40	16.79



This elimination was first encountered in some of our earlier experiments in which triethylamine was used as a hydrogen chloride acceptor in an attempt to cyanovinylate nucleophiles of low reactivity at elevated temperatures. Distillation of the reaction mixtures afforded small amounts of VI, formed no doubt by the neutralization of V with unchanged triethylamine.

Aniline is much less reactive than the aliphatic amines and only a diadduct was obtained under various reaction conditions. There are two possible structures (VII and VIII), other than those which involve ring substitution, that can be written for this diadduct.

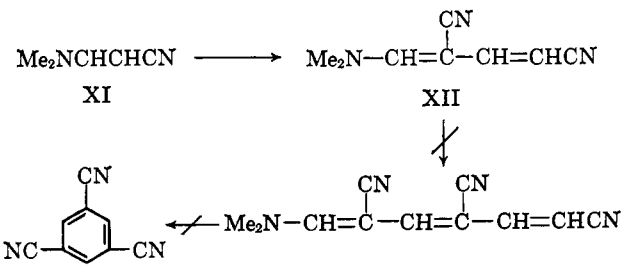


The infrared spectrum exhibited an N–H vibration (3300 cm.$^{-1}$) which is consistent with structure VIII. Efforts to obtain a similar diadduct with N-ethylaniline, where only one hydrogen is replaceable, were unsuccessful; only the monoadduct IX was formed. A comparison of the ultraviolet spectrum of IX (λ_{max} 285 mμ) with that of the diaddition product (λ_{max} 351 mμ) is revealing, since structures such as VII would be expected to have an absorption maximum near that of IX.

Interestingly, a small yield of a diadduct similar in structure to VIII, 4-(N-piperidinomethylene)glutacononitrile (X), was obtained along with the major product, β-cyanovinylpiperidine, when piperidine reacted with *cis*-I. However, compound X could be obtained much more conveniently from N-β-cyanovinylpiperidine by a procedure which appears to be of a general nature. This reaction was discovered in an attempt to prepare 1,3,5-tricyanobenzene from β-cyanovinyldimethylamine (XI) *via* Kochetkov's[11] procedure for obtaining 1,3,5-triacetylbenzene from β-aminovinyl methyl ketones.[12] These reactions may be mechanistically similar to the conversion of 1-butyne-3-one to 1,3,5-triacetylbenzene at room temperature in the presence of dimethylamine or pyridine acetate.[12]

When XI was heated in glacial acetic acid, a 45% yield of a yellow solid (XII) was obtained which decolorized both 2% aqueous permanganate solution and bromine in carbon tetrachloride. Dissolution in a large excess of 5% hydrochloric acid at 25° was slow.

In addition to its molecular weight and elemental analysis the spectral properties exhibited by the yellow solid are consistent with those of the previously unreported 4-(dimethylaminomethylene)glutacononitrile (XII). Catalytic hydrogenation indicated an equivalent weight of 48, in good agreement with the theoretical value of 49 based on the absorption of 3 moles of hydrogen (2 for the carbon double bond reduction and 1 for hydrogenolysis of the amino nitrogen–carbon bond). This diene could be considered as the first intermediate in the anticipated condensation leading to 1,3,5-tricyanobenzene.



This reaction path could also be proposed for Kochetkov's synthesis of triacetylbenzene; however, it is not readily apparent why our reaction did not lead to the aromatic structure.

Phenylhydrazine was monocyanovinylated in good yield; however, the position of cyanovinylation has not been established. Hydrazine reacted readily with I at 0° as evidenced by the formation of hydrazine hydrochloride in high yield; however, several attempts at isolation of the cyanovinyl product afforded only tars or led to explosive decomposition of the reaction mixture.

Succinimide was successfully cyanovinylated as its sodium salt or by the use of triethylamine as a hydrogen chloride acceptor. Amides, however, proved to be very difficult to cyanovinylate; tertiary amines did not catalyze the reaction, and treatment of the amide sodium salts with I led to the formation of tars. Only

(11) N. K. Kochetkov, *Izv. Akad. Nauk SSSR*, 991 (1953).

(12) R. A. Raphael, "Acetylenic Compounds in Organic Synthesis," New York Academic Press, New York, N. Y., 1953, p. 159.

TABLE III

OXYGEN CYANOVINYLATIONS

Alcohol	β-Chloro-acrylonitrile	Yield, %	B.p., °C. (mm.)	M.p., °C.	$n^{25}D$	Formula	Calcd., % / Found, % C	H	N
CH_3OH	*cis*	85	92–94 (27)		1.4540	C_4H_5NO	57.82	6.07	
							58.09	6.14	
C_2H_5OH	*cis*	90	85–87 (15)		1.4530	C_5H_7NO	61.84	7.22	14.42
							61.91	7.04	14.77
C_2H_5OH	*trans*	91	76–78 (15)		1.4510	C_5H_7NO	60.84	7.27	14.42
							61.64	7.21	14.49
C_6H_5OH[a]	*cis*	60	87–89 (2)	27–28		C_9H_7NO	74.46	4.86	9.55
							73.99	4.81	9.47
$C_{10}H_5OH$[a]	*cis*	67		73–74		$C_{13}H_9NO$	80.00	4.65	7.19
							79.98	4.88	7.25

[a] Dioxane used as solvent.

TABLE IV

ACETAL FORMATION FROM β-CHLOROACRYLONITRILE

$$RONa + Cl{-}CH{=}CH{-}CN \xrightarrow{ROH} (RO)_2CH{-}CH_2CN$$

Alcohol	β-Chloro-acrylonitrile	B.p. (mm.), °C. $n^{25}D$	Yield, %	Formula	Calcd., % / Found, % C	H	N
CH_3OH	*cis* or *trans*	94–98 (25)	56	$C_5H_9NO_2$	52.17	7.82	12.17
		1.4124			52.43	7.86	12.28
C_2H_5OH	*cis* or *trans*	57° (1)	87	$C_7H_{13}NO_2$	58.72	9.15	9.78
		1.4142			59.95	9.01	9.84

cyclic amides such as 2-pyrrolidone or 2-pyridone appear to undergo cyanovinylation. Again tertiary amines were ineffective as catalyst and these amides were cyanovinylated as their sodium salts. A 5% yield of N-β-cyanovinylpyrrolidone and a 50% yield of N-β-cyanovinylpyridone were obtained. The strong basicity of the amide salts apparently limits this reaction, by favoring dehydrohalogenation of I to cyanoacetylene, which then can polymerize under the reaction conditions.[13]

Oxygen Cyanovinylations.—Cyanovinyl ethers were readily obtained in good yields on treatment of sodium alkoxides or phenoxides with an equivalent of I (Table III). Use of more than an equivalent of alkoxide will catalyze the addition of a second molecule of alcohol with acetal formation. This is a convenient method for making acetals of β-cyanoacetaldehyde (XIII, Table IV).[14]

$$RONa + Cl{-}CH{=}CH{-}CN \longrightarrow ROCH{=}CHCN + NaCl$$

$$ROCH{=}CHCN \xrightarrow{ROH,\ base} (RO)_2CHCH_2CN \quad \text{XIII}$$

Sulfur Cyanovinylations.—Alkyl and aryl mercaptans were readily cyanovinylated in the presence of triethylamine to yield the corresponding β-cyanovinyl thioethers. Ether was used as solvent so that the amine hydrochloride could be easily removed. β-Cyanovinyl aryl sulfones were easily obtained by the cyanovinylation of sodium aryl sulfinates. In general, these reactions required a higher temperature than those with the corresponding mercaptans. Sodium sulfide was dicyanovinylated as a suspension in ethano to yield β-cyanovinyl thioether.

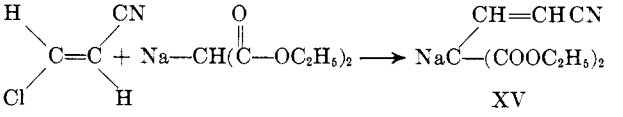
$$Na_2S + 2ClCH{=}CHCN \longrightarrow S(CH{=}CHCN)_2 + 2NaCl$$

Reaction of sodium bisulfite with I yielded the disodium salt XIV.

$$3NaHSO_3 + ClCH{=}CHCN \longrightarrow (NaSO_3)_2CHCH_2CN + NaCl + H_2O + SO_2 \quad \text{XIV}$$

Undoubtedly, the product resulted from addition of sodium bisulfite to the intermediate cyanovinyl compound. Attempts to isolate the mono sulfato intermediate were unsuccessful.

Carbon and Phosphorus Cyanovinylation.—The cyanovinylation of activated methylene compounds appears to be quite general as evidenced by the ease of reaction of diethyl sodiomalonate with I. The substitution product XV was easily isolated as its sodium salt when equivalent amounts of reactants were used.



XV

Cyanovinylphosphonates were easily obtained by the Arbuzov reaction of either *cis*- or *trans*-I with trialkyl phosphites; diethyl β-cyanovinyl phosphonate was also prepared from *cis*-I and diethyl phosphite in the presence of triethylamine, but this reaction proved difficult to repeat.

$$(RO)_3P + ClCH{=}CHCN \longrightarrow (RO)_2\overset{O}{\overset{\|}{P}}{-}CH{=}CHCN + RCl \quad (R = \text{alkyl})$$

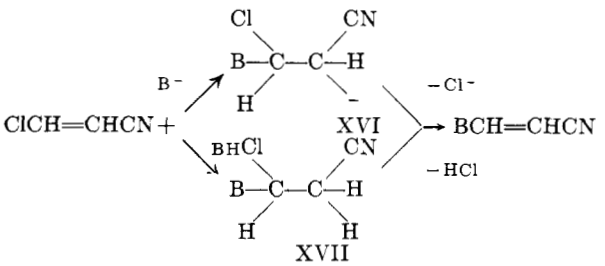
Mechanism.—The possible reaction mechanisms for substitution of halogen on a vinyl group containing an electron withdrawing moiety at the β-position have recently been examined by Vernon[1a] and may be assigned to either of two fundamental types: one, an "elimination–addition" mechanism

(13) S. Murahashi, *et al.*, *J. Chem. Soc. Japan*, **77**, 1689 (1956); **78**, 324, 327, 330 (1957).

(14) S. M. McElvain and R. L. Clarke, *J. Am. Chem. Soc.*, **69**, 2657 (1947).

$$ClCH{=}CHCN + B^- \longrightarrow HC{\equiv}C{-}CN + HB + Cl^- \longrightarrow BCH{=}CHCN$$

involving cyanoacetylene as a free intermediate (above), the other an addition–elimination mechanism.



With regard to this second mechanism, the nature of the addition product may vary from a carbanionic intermediate such as XVI to that of the uncharged adduct (XVII). If the reaction proceeded by an elimination–addition mechanism, with the production of cyanoacetylene, one would expect by the rule of *trans* addition that the product of the reaction would have the *cis* configuration.[15] If, on the other hand the reaction proceeds by an addition–elimination mechanism, the product or products would depend on the nature of the primary addition product. Vernon[1a] has shown by the use of deuterated solvent that the reaction of phenyl sulfide ion with *cis*- or *trans*-β-chlorocrotonates does not involve an intermediate such as XVII. The nature of the intermediate complex (XVI) may vary from one involving simultaneous bond formation of the nucleophile and bond breaking of the halogen (concerted mechanism), to one involving a true carbanion intermediate. The nature of the products will therefore depend on the degree of formation of the incipient carbanion. The more stable the carbanion or the greater its life, the greater the probability of rotation around the carbon–carbon bond. Elimination from such an intermediate can produce initially either a mixture of *cis* or *trans* isomers or a single isomer, which would be the thermodynamically more stable one. On the other hand, if the life is extremely short, retention of configuration would be expected.[1a] Thus, examination of the stereochemistry of the reaction products of β-chloroacrylonitrile might indicate which mechanism is operative. An investigation of I with several nucleophilic agents was made and the results are compiled in Table V.

TABLE V

REACTIONS OF VARIOUS NUCLEOPHILES WITH *cis*- AND *trans*-β-CHLOROACRYLONITRILE AT 0°

Isomer of I	Nucleophile	Isomer content of products, % *cis*	*trans*
cis	EtO^-	95	<5
trans	EtO^-	<5	95
cis	$p\text{-}CH_3C_6H_4S^-$	95	<5
trans	$p\text{-}CH_3C_6H_4S^-$	10	90
cis	$C_5H_{11}N$	0	100
trans	$C_5H_{11}N$	0	100

Nucleophilic displacements by ethoxide or *p*-toluene sulfide ion resulted in a high retention of geometric configuration, but the reactions were not completely stereospecific. The configurations of the products were established by both infrared and n.m.r. spectra. The ratio of isomers was established by infrared analysis. It is interesting to note that the *cis*-β-cyanovinyl-*p*-tolyl thioether reaction proceeds with a higher degree of stereospecificity than that of its *trans* isomer. It is difficult to say with certainty that the *trans* thioether is formed in a lesser degree of stereospecificity than the *cis*, since the *trans* thioether may be the thermodynamically unstable isomer.[1a] It is clear with both ethoxide and *p*-toluene sulfide ion, because of high degree of retention of configuration of the products, that the reaction proceeds by the addition–elimination mechanism. Furthermore, the intermediate complex (XVI) must have an extremely short half life. Montanari[1b] recently showed that nucleophilic displacement by alkoxides and phenyl sulfide ion on β-chlorocrotonates proceeds by an addition–elimination mechanism; however, retention of configuration was only observed when phenyl sulfide ion was the nucleophile.

Only one product was obtained when piperidine was used as the nucleophilic reagent. Since our mechanism is solely based on the nature of the product, it was essential that we determine its structure. It is more difficult to assign structure on the basis of physical methods, as was done with the cyanovinyl ethers and cyanovinyl thioethers, when only one of the isomers is at hand. The infrared spectra of the cyanovinylamines have bands in the 960- and 720-cm.$^{-1}$ region. These two bands are very similar in intensity and wave length of absorption to those of the *trans*- and *cis*-β-ethoxyacrylonitriles, suggesting that a mixture was obtained. However, n.m.r. spectra and vapor-phase chromatographic analysis indicated that only one product was obtained. In addition, the vinyl hydrogen coupling constant in the n.m.r. spectrum[7] indicated that only the *trans* product was obtained (Table VI).

N-β-Cyanovinylpiperidine has been reported[13] and was prepared by the addition of piperidine to cyanoacetylene. This procedure was repeated and the product was identical with that obtained from either *cis*- or *trans*-I. If the rule of *trans* addition is applicable, the product should have the *cis* configuration; however, this extension of the *trans* rule might not necessarily be valid when the nucleophile is an amine.[16] We are inclined to favor the n.m.r. data, but cannot give adequate explanation for the 720-cm.$^{-1}$ band in the infrared spectrum.

Not only can the structure of the product shed light on the mechanism which is involved, but the relative reaction rates of the *cis*- and *trans*-β-chloroacrylonitrile should indicate which mechanism is operative. The rates of reaction of *cis*- and *trans*-I with piperidine were therefore determined (Table VII).

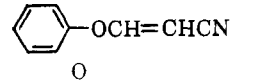
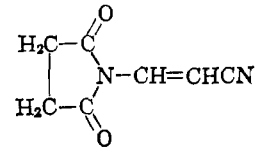
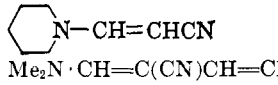
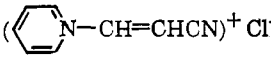
These kinetic results indicate that the elimination–addition mechanism is not in effect since, if it were, the *cis* isomer should undergo elimination much more rapidly than the *trans*.[15] It therefore may be concluded that, at least with neutral (uncharged) reagents, the reaction proceeds essentially in the same manner as that of anionic nucleophiles (addition–elimination). It is evident, moreover, particularly from the steric course of the reaction, that a difference exists in the

(15) W. E. Truce, *et al.*, *J. Am. Chem. Soc.*, **78**, 2743, 2748, 2752, 2756 (1949); A. Michael, *Ber.*, **34**, 4215 (1901); *J. prakt. chem.*, **52**, 344 (1895).

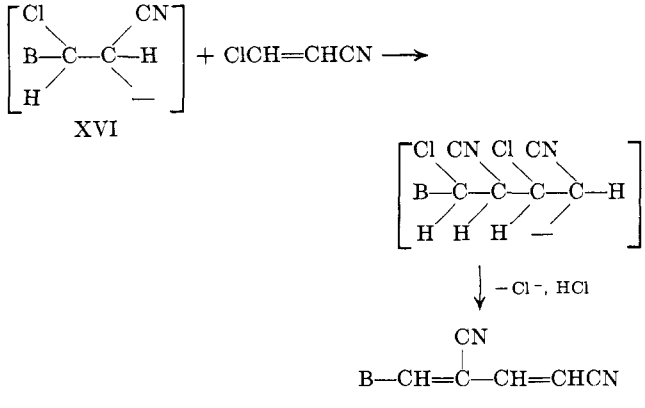
(16) E. A. Braude, *et al.*, *J. Chem. Soc.*, **45**, 948 (1946).

TABLE VI

SPECTRAL CHARACTERISTICS OF β-CYANOVINYL COMPOUNDS

	Product	β-Chloro-acrylonitrile	Infrared spectra, cm.$^{-1}$ CN	C=C	C-H	Ultraviolet spectra mμ	ϵ_{max}	N.m.r. proton coupling constants, J_{HH}, c.p.s.
1	CH_3—S—CH=CHCN	*cis*	2235	1572	692	274	11,980	
2	*cis*-*p*-$CH_3C_6H_5S$—CH=CHCN	*cis*	2210	1555	715	281	16,700	11
3	*trans*-*p*-$CH_3C_6H_4S$—CH=CHCN	*trans*	2220	1590	935	273	28,700	14.8
				1585		218	shoulder	
4	$S(CH{=}CH{-}CN)_2$	*cis*	2210	1555		292	20,890	
5	*cis*-CH_3OCH=CHCN	*cis*	2235	1637	718	224	13,600	6.4
6	*cis*-C_2H_5OCH=CHCN	*cis*	2220	1637	725			6.5
7	*trans*-C_2H_5OCH=CHCN	*trans*	2220	1637	956	222	14,200	11.5
8		*cis*	2230	1650		240	15,700	
9	$(EtO)_2P(O)$—CH=CHCN	*cis*	2250	1615				
10	*cis*-*p*-CH_3—C_6H_5—SO_2CH=CHCN	*cis*	2235	1605				
11	*trans*-*p*-CH_3—C_6H_5—SO_2CH=CHCN	*trans*	2235	1605	958	205		
12	*cis*-ClCH=CHCN		2230	1610	740			7.7
13	*trans*-ClCH=CHCN		2230	1610	935			14.0
14		*cis*	2230	1640				
15	BuNHCH=CHCN	*cis*	2200	1635				
16	Me_2N—CH=CHCN	*cis*	2200	1640		258	20,160	
17	Et_2N—CH=CHCN	*cis* or *trans*	2200	1640				13.6
18	*n*-Pr_2N—CH=CHCN	*cis*	2200	1640				13.8
19		*cis* or *trans*	2200	1640				11.5
20	$Me_2N \cdot CH{=}C(CN)CH{=}CHCN$		2200	1657		320	41,200	
				1605				
21	C_6H_5—NHCH=C(CN)CH=CHCN	*cis* or *trans*	2200	1665		351	43,500	
				1605				
22	$(Et_2NHCH{=}CHCN)^+Cl$	*cis*	2245	1655				
23		*cis*	2235	1635				
24	$(Me_3NCH{=}CHCN)^+Cl^-$	*cis*	2245	1650				
25	$(Et_3NCCH{=}CHCN)^+Cl^-$	*cis*	2245	1650				
26	C_6H_5—$N(C_2H_5)$CH=CHCN	*trans*	2200	1665		285		16
				1605				

half-life of the carbanion of the primary addition product (see preceding discussion). This is further exemplified in the case where aniline is the nucleophile and only a diadduct is obtained. Apparently here the carbanion (XVI) is stable enough to react further with another molecule of I as shown by the following.



XVI

The question arises as to a reason for the observed differences in the stability of the intermediate when amines are used as the nucleophiles. To determine whether the difference of the stereochemical course of the reaction with amines has any relation to the ionic charge of the nucleophilic species, the lithium salt of piperidine was treated with *trans*-I. Less than 1% of a product was obtained, which proved to be *trans*-β-cyanovinylpiperidine. Apparently the basicity of the material was too great, causing dehydrohalogenation and subsequent polymerization of the intermediate cyanoacetylene. However, Vernon[18a] has shown that nucleophilic atttack by a charged species such as ethoxide ion on *cis*- and *trans*-chlorocrotonates yields exclusively the *trans* product. From this we may conclude that the stability of the activated complex depends on the nucleophilic species as well as the activating group.

TABLE VII

REACTION OF β-CHLOROACRYLONITRILE AND PIPERIDINE IN METHANOL AT 0°

Reaction	Rate constant
cis-I + piperidine	2.00×10^{-2} sec.$^{-1}$ mole^{-1} l.
trans-I + piperidine	2.67×10^{-2} sec.$^{-1}$ mole^{-1} l.

Spectra.—Perhaps the most significant feature in the infrared spectra of the β-cyanovinylamines is the lowering of the nitrile band to 2200 cm.$^{-1}$ compared to the bands obtained with saturated nitriles (2250 cm.$^{-1}$) and with simple α,β-unsaturated[17] nitriles (*ca.* 2228 cm.$^{-1}$). This displacement is associated with a reduction in the triple bond character of the nitrile group and may be attributed to the contribution of the ionic resonance structure (XVIII) for the ground state of these molecules.[18-20] This pronounced frequency shift, which would not be expected to be operative in

$$>N-CH=CH-CN \longleftrightarrow \overset{+}{N}=CH-CH=C=\overset{-}{N}$$
XVIII

the case of α-cyanovinylamines, is compatible with the observed low basicity of these materials. The p electrons of the amino nitrogen, which are the seat of amine basicities, are here tied up by interaction within the system and are not readily available for coordination with acids.

Another characteristic of the spectra of the cyanovinylamines was the marked intensity of the double-bond vibration,[20] an effect which was encountered in most of the other cyanovinyl compounds, with the exception of the phosphonate ester. The ethylenic stretching frequencies for the amines were higher than those reported by Baldwin[20] for compounds which were similar except for the fact that the double bonds were tri- or tetrasubstituted. The ethylenic stretching frequency for the cyanovinyl thioethers was lowered considerably.

It is interesting that, in compounds in which the β-carbon of the carbon–carbon double bond is joined to an electron-attracting group, the nitrile group behaves spectroscopically like a simple unconjugated nitrile. This may be due to complete inhibition of resonance of the type shown in structure XVIII. The large bathochromic effects in the ultraviolet exerted by the amino, thio, and oxy auxochromes in conjugation with an α,β-unsaturated nitrile are readily apparent.[16] In this series of compounds the auxochromic power increases in the order O < N < S.

Experimental[21]

α-Acetoxy-β-chloropropionitrile.[22,23]—To 8000 g. of an aqueous solution of chloroacetaldehyde (pH adjusted to 7.5 ± 0.5 with solid sodium bicarbonate) was added 1580 g. of liquid hydrogen cyanide at a temperature of 0–9°. After the addition had been completed (2 hr.), the reaction mixture was allowed to stand overnight. Stabilization of the cyanohydrin for further treatment was accomplished by adjusting the pH to 2.5 or below with concentrated phosphoric acid. The hydrocyanic acid was removed *in vacuo* at 25° and the water was removed by continuous stripping (50° at 15 mm.). This procedure gave a 95% aqueous solution of chloroacetaldehyde cyanohydrin. Distillation of a 215-g. aliquot gave 193 g. (94%) of a colorless oil, b.p. 110° (3 mm.). Distillation of this material is hazardous since slight overheating may result in explosive decomposition of the cyanohydrin to chloroacetaldehyde and hydrogen cyanide.

A mixture of 1530 g. of acetic anhydride and 970 g. of a 95% aqueous solution of α-hydroxy-β-chloropropionitrile was held at 40° for 2 hr. and then at 100° for 3 hr. (n^{25}D remained constant). The acetic acid was removed *in vacuo*. The acetic anhydride was stripped under 5-mm. pressure. Distillation of the residue gave 1200 g. (90%) of a colorless oil, b.p. 70° (215 mm.), n^{25}D 1.4458.

β-Chloroacrylonitrile.—Into a glass tube packed with glass beads, heated to 535°, was fed 77 g. of α-acetoxy-β-chloropropionitrile over a 2-hr. interval (contact time = 10 sec.). Seventy grams of liquid product was collected in a trap at 25°. The crude product was poured into 100 ml. of water and sodium bicarbonate was added until the pH was 7.0. The mixture was extracted with 200 ml. of ether, the ether layer was dried over sodium sulfate, and the solvent was removed. Distillation of the residue gave 13 g. (28%) of α-chloroacrylonitrile and 15 g. (33%) of a 50:50 mixture of *cis*- and *trans*-β-chloroacrylonitrile. Distillation of the mixture provided pure *cis*- and *trans*-β-chloroacrylonitrile and α-chloroacrylonitrile. These compounds are potent lachrymators and vesicants, and should be handled accordingly. *cis*-I boiled at 145–146°, n^{25}D 1.4560.

Anal. Calcd. for C_3H_2ClN: C, 41.17; H, 2.31. Found: C, 41.37; H, 2.60.

trans-I boiled at 118° and melted at 45°, n^{25}D 1.4520.

Anal. Calcd. for C_3H_2ClN: C, 41.17; H, 2.31. Found: C, 41.27; H, 2.61.

α-Chloroacrylonitrile boiled at 88°, n^{20}D 1.4297, n^{25}D 1.4303.

***cis*-β-Chloroacrylamide.**—*cis*-β-Chloroacrylonitrile (87.5 g.) was added to 113.2 g. of 95.4% sulfuric acid and 14.6 g. of water. The reaction mixture was maintained at 85–90° during the addition and for an additional 90 min., first with an ice bath, and then with heating as the reaction subsided. The mixture was cooled to about 40° and poured into a stirred mixture of 400 g. of ice and 145 ml. of concentrated ammonium hydroxide. The temperature was held below 35° with external cooling. The precipitate was filtered, air-dried, and triturated with four 15-ml. portions of hot acetone. Evaporation of the acetone and recrystallization of the solid residue (67.5 g.) from ethyl acetate gave 51.5 g. of *cis*-β-chloroacrylamide, m.p. 111–112°.

Anal. Calcd. for C_3H_4ClNO: N, 13.27. Found: N, 13.11.

The known *trans* isomer melts at 143.5–145°.[3]

***trans*-β-Chloroacrylic Acid.**—Aqueous sulfuric acid (58%) was heated to 95° and *cis*-I was added over 35 min. The two-phase mixture was then heated under reflux for 11 hr., during which time hydrogen chloride was steadily evolved. The reaction mixture was cooled and shaken with 100 ml. of water and 100 ml. of chloroform. The organic phase was separated and extracted with a solution of 73 g. of potassium carbonate and 250 ml. of water. The alkaline solution was stirred with carbon black, filtered, acidified with hydrochloric acid, and extracted with four 50-ml. portions of chloroform. After drying with calcium sulfate, the chloroform was evaporated; recrystallization of the residue (12 g.) from 40 ml. of hexane gave 6.7 g. (13%) of *trans*-β-chloroacrylic acid melting at 84–86°, lit.[6] m.p. 85–86°.

2,2,3,3-Tetrachloropropionitrile.—*cis*-I (43.9 g., 0.5 mole) was placed in a 250-ml. three-necked flask equipped with a stirrer, thermometer, and Y-tube connected to a condenser and a gas dispersion tube. Benzoyl peroxide (0.1 g.) was added to the mixture and chlorine was passed through. A self-sustaining reaction ensued, with vigorous evolution of hydrogen chloride, which carried the temperature to 83°. The total gain in weight was 42.2 g. (theory 35.5 g.). The crude product was dissolved in ether and washed with water and 0.1 *M* sodium thiosulfate. After drying over calcium sulfate, the ethereal solution was vacuum stripped to give 66.7 g. (69.2%) of crude product. Fractional distillation afforded pure 2,2,3,3-tetrachloropropionitrile, b.p. 64–65° (10 mm.).

Anal. Calcd. for C_3HCl_4N: C, 18.68; H, 0.52; Cl, 73.54. Found: C, 18.65; H, 0.83; Cl, 73.56.

Cyanovinylation of Primary and Secondary Alkyl Amines (Table I).—The cyanovinylations of the amines in Table I were carried out according to the following procedure. β-Chloroacrylonitrile (0.1 mole) was added to a stirred solution of the amine (0.2 mole) in ether or in benzene. A precipitate formed almost immediately after the addition was started. The reaction mixture was allowed to stand until the reaction was completed. The mixture was then filtered to remove the amine hydrochloride, and the product was isolated by distillation or recrystallization.

Cyanovinylation of Tertiary Amines (Table II).—A solution comprising 0.1 mole each of β-chloroacrylonitrile and a tertiary amine was heated in an inert solvent such as anhydrous toluene

(17) J. Felton, *et al.*, *J. Chem Soc.*, 2120 (1955).
(18) J. Weinstein and G. M. Wyman, *J. Org. Chem.*, **23**, 1519 (1958).
(19) J. P. Freeman and W. D. Emmons, *J. Am. Chem. Soc.*, **78**, 3405 (1956).
(20) S. Baldwin, *J. Org. Chem.*, **26**, 3288 (1961).
(21) Melting points are uncorrected.
(22) R. M. Nowak, U. S. Patent 2,915,549 (1959).
(23) J. Houben and E. Pfankuch, *Ber.*, **59B**, 2397 (1926).

or anhydrous ether. Upon cooling, the salt precipitated and was isolated by filtration and recrystallized from ethanol.

4-(Anilinomethylene)glutaconitrile.—In a flask equipped with a reflux condenser, 18.6 g. of aniline and 8.75 g. of *cis*- or *trans*-I were dissolved in ethanol. After heating for 24 hr. in refluxing ethanol, a yellow precipitate formed. The reaction mixture was slurried with 100 ml. of water and filtered to give 7.5 g. of a mustard-yellow product. Recrystallization of the solid from acetonitrile yielded 5.2 g. of material, m.p. 138–140°.

N-β-Cyanovinyl-N-ethylaniline.—N-Ethylaniline (36 g.) and 13.1 g. of *trans*-I were dissolved in 100 ml. of absolute ethanol. The mixture was heated for 24 hr. at 78°. Upon cooling, crystals of the amine hydrochloride formed. The solution was poured into 200 ml. of cold water and the organic phase was separated. The organic layer was removed, dried, and distilled. A forerun of N-ethylaniline was obtained (6.48 g.) before the cyanovinylamine fraction distilled. A total of 10.6 g. of the cyanovinylated amine was collected at 125–140° (0.1–0.2 mm.) as a viscous, clear liquid.

N-β-Cyanovinylsuccinimide (Table I).—To a solution consisting of 19.8 g. (0.2 mole) of succinimide and 20.2 g. (0.2 mole) of triethylamine in 100 ml. of acetone was added 17.5 g. (0.2 mole) of *cis*-I. After standing for several hours, the orange solution was filtered and the filtrate evaporated. A slushy residue remained, which was triturated with 150 ml. of water and then recrystallized from 175 ml. of ethanol, affording 5.5 g. (18.3%) of N-β-cyanovinyl succinimide, m.p. 155–156.4°.

N-β-Cyanovinylpyridone.—The sodium salt of 2-pyridone was prepared by the addition of 9.8 g. of 2-pyridone dissolved in a 10% solution of DMF in benzene to a mixture of 4.55 g. of sodium hydride dispersion in the 10% DMF–benzene solution. The salt was then added to a stirred solution of 8.75 g. of *trans*-I in 500 ml. of benzene. The addition was complete in 2 hr., and the resulting black solution was filtered to remove the sodium chloride, washed with 200 ml. of water, and dried over magnesium sulfate. Evaporation of the solvents left a brown crystalline material which was recrystallized from a water–acetone solution. Another recrystallization from methanol yielded 7.7 g. of the substitution product (53%), m.p. 55–56°.

N-β-Cyanovinylpyrrolidine.—The reaction was performed essentially as described above, yielding 5% of material, m.p. 54–55°.

β-Cyanovinyldiethylammonium Chloride (Table II).—*cis*-β-Chloroacrylonitrile (0.2 mole) and triethylamine were heated in a 70° oil bath. The temperature rose within a few minutes to 90°, and vigorous boiling started. The bath was removed and, when the boiling subsided, heat was reapplied (90°) for an additional 25 min., during which time the mixture became semisolid. After cooling, the liquid portion was decanted and the solid was washed repeatedly with acetone and ether. The light residue (15 g.) was dissolved in 300 ml. of anhydrous ethanol, decolorized, and reprecipitated into ether as fine off-white needles (5 g.). The purification was repeated and, after drying under vacuum (0.3 mm.), the product was submitted for analysis. The material was extremely hygroscopic.

Anal. Calcd. for $C_7H_{13}ClN_2$: N, 17.44. Found: N, 17.64.

β-Cyanovinylphenylhydrazine.—Into a suitable reaction vessel equipped with stirrer, reflux condenser, and thermometer were introduced 9.8 g. of phenylhydrazine and 50 g. of benzene. Subsequently, 8.7 g. of β-chloroacrylonitrile was added slowly over a period of 30 min., while the temperature of the reaction was held at 60° with stirring. The reaction mixture was held at this temperature for another 6 hr. At the end of this time, the reaction mixture was cooled, and phenylhydrazine hydrochloride was filtered off. Approximately one-half of the benzene was evaporated under reduced pressure. Crystallization of β-cyanovinylphenylhydrazine was induced by cooling. Filtration of the solid product from the benzene mother liquor resulted in a recovery of 6.5 g. of pale orange needles, m.p. 80–85°.

Oxygen Cyanovinylation (Table III).—The following procedure was used for cyanovinylation of alcohols and phenols. Phenols were cyanovinylated in ethanol.

A solution of 1.0 mole of the alkoxide in 100 ml. of the corresponding alcohol was added to a similar solution of 1.1 moles of the *cis*- or *trans*-I. The temperature of the reaction was kept below 20° by external cooling. On completion of addition, the contents of the flask were allowed to warm to room temperature and then neutralized with glacial acetic acid to a phenolphthalein end point. The sodium chloride which formed during the course of the reaction was removed by filtration. The solvents were stripped and the residue was distilled.

Acetal Formation (Table IV).—Example given is for the formation of β,β-diethoxypropionitrile from *trans*-I. This procedure was followed for other examples given in Table IV.

A solution of 17.4 g. of sodium ethoxide in 550 ml. of ethanol was added to a stirred solution of 21.9 g. of *trans*-I in 150 ml. of ethanol. The addition was complete in 45 min. and the reaction mixture was stirred for an additional 4 hr. The mixture was then neutralized with glacial acetic acid to a phenolphthalein end point. The precipitated sodium chloride was removed by filtration, and evaporation of the ethanol followed by distillation of the residual liquid yielded 28 g. of β,β-diethoxypropionitrile, b.p. 57° (1 mm.), $n^{25}D$ 1.4142.[14]

***cis*-β-Cyanovinyl Methyl Thioether.**—A benzene solution of *cis*-I (29.2 g.) and triethylamine (33.8 g.) was cooled to 0° and methyl mercaptan (16 g.) was bubbled in over a period of 75 min. After standing overnight at room temperature, the precipitate (41.3 g.) was removed by filtration and the filtrate was distilled, yielding 27.8 g. (84%) of β-cyanovinyl methyl thioether, b.p. 92–93° (10 mm.), $n^{25}D$ 1.5371.

Anal. Calcd. for C_4H_5NS: C, 48.45; H, 5.08; N, 14.13. Found: C, 48.67; H, 5.25; N, 13.89.

***trans*-β-Cyanovinyl *p*-Tolyl Thioether.**—*trans*-I (8.75 g.) was added to a stirred solution of *p*-thiocresol (12.4 g.) and triethylamine (10.1 g.) in 300 ml. of anhydrous ether. The temperature of the solution was kept below 20° during addition. Stirring was continued for 1 hr. after the addition was complete. The triethylamine hydrochloride was removed by filtration and the ether solution was washed successively with water, cold 2% sodium hydroxide, and a saturated sodium chloride solution. The solution was dried over anhydrous magnesium sulfate, and the ether was evaporated. Low-temperature recrystallization from petroleum ether (b.p. 30–60°)–ethanol mixture yielded 16.5 g. (94%) of *trans*-β-cyanovinyl *p*-tolyl thioether as a white low-melting solid, $n^{25}D$ 1.6065. This material contained 10% of the *cis* isomer, as indicated by its infrared spectrum. Distillation resulted in additional isomerization; the product had b.p. 115° (1 mm.).

Anal. Calcd. for $C_{10}H_9NS$: C, 68.57; H, 5.14; N, 8.00. Found: C, 68.88; H, 5.03; N, 8.16.

***cis*-β-Cyanovinyl *p*-Tolyl Thioether.**—Use of *cis*-I in the above procedure gave the corresponding *cis* product, b.p. 116–120° (2 mm.).

Anal. Calcd. for $C_{10}H_9NS$: C, 68.57; H, 5.14; N, 8.00. Found: C, 68.40; H, 5.07; N, 7.71.

β,β-Dicyanovinyl Thioether.—A solution of sodium sulfide monohydrate (48 g., 0.2 mole) in 350 ml. of 95% ethanol was added to a stirred ethanolic solution of β-chloroacrylonitrile (35 g., 0.4 mole). After standing overnight, the solution was filtered to remove sodium chloride (21 g.). The filtrate was concentrated to about 225 ml. and diluted to 900 ml. with ice–water. Filtration gave 15 g. (55%) of light yellow product which, after recrystallization from ethyl acetate–cyclohexane, melted at 141–142°. An additional recrystallization raised the melting point to 142.4–143.2°.

Anal. Calcd. for $C_6H_4N_2S$: C, 52.92; H, 2.96; N, 20.58. Found: C, 52.73; H, 2.95; N, 20.54.

2-Benzothiazolyl β-Cyanovinyl Thioether.—To a solution of 33.4 g. of mercaptobenzothiazole and 20.2 g. of triethylamine in 120 ml. of acetone, was added 17.5 g. of *cis*-I at 25–30°. Filtration, evaporation of the filtrate, and recrystallization of the residue from methylene chloride gave 36 g. (82%) of 2-benzothiazolyl β-cyanovinyl thioether, m.p. 105–107°.

Anal. Calcd. for $C_{10}H_6N_2S_2$: C, 55.05; H, 2.77; N, 12.83. Found: C, 55.03; H, 2.93; N, 13.07.

1,1-Ethanedisulfuric Acid 2-Cyano Disodium Salt.—A solution of 20.8 g. of sodium bisulfite in 400 ml. of water was added to a reaction vessel equipped with a reflux condenser and stirrer. To this solution, 8.75 g. of *cis*-I was added. The reaction mixture was heated to 80° and kept at this temperature for 24 hr. During the course of the reaction, the mixture became homogeneous. On cooling, the disodium salt precipitated with the addition of methanol. On filtration, the product was obtained in 92.5% yield.

Anal. Calcd. for $C_3H_3NNa_2O_6S_2$; C, 13.90; H, 1.17; N, 5.40. Found: C, 13.44; H, 1.47; N, 5.17.

β-Cyanovinyl *p*-Tolyl Sulfone.—A solution of *trans*-β-chloroacrylonitrile (17.5 g., 0.2 mole) in 50 ml. of ethanol was added to a stirred alcoholic solution of the sodium *p*-tolyl sulfinate (43 g., 0.2 mole) at reflux temperature in 15 min. After heating for an

additional hour, the mixture was cooled and filtered. The filtrate was concentrated to about 125 ml. on a rotary evaporator and crystallization was induced by cooling. Filtration gave 37 g. (89%) of the substitution product. This material was recrystallized from isobutyl alcohol for analysis; the product had m.p. 135–136°.

Anal. Calcd. for $C_{10}H_9NO_2S$: C, 58.10; H, 4.38; N, 6.77. Found: C, 58.28; H, 4.40; N, 6.61.

Use of the *cis*-I in the above procedure gave a 26% yield of solid, m.p. 73–85°. This was presumed to be a mixture of the *cis* and *trans* isomers.

Anal. Calcd. for $C_{10}H_9NO_2S$: C, 58.10; H, 4.38; N, 6.77. Found: C, 57.76; H, 4.41; N, 6.73.

O,O-Diethyl-β-cyanovinyl Phosphonate.—A solution of 24.9 g. of triethyl phosphite and 13.1 g. of a 50:50 mixture of *cis*- and *trans*-I was heated in an oil bath at 120. Ethyl chloride was evolved, and the heating was continued for 4 hr. Distillation yielded 18.7 g. (66%) of O,O-diethyl-β-cyanovinyl phosphonate boiling at 106° (1.5 mm.), $n^{25}D$ 1.4510.

Anal. Calcd. for $C_7H_{12}NO_3P$: C, 44.44; H, 6.40; N, 7.41. Found: C, 44.30; H, 6.53; N, 7.47.

O,O-Dibutyl-β-cyanovinyl Phosphonate.—A solution of 12.5 g. of tributyl phosphite and 5.36 g. of *cis*-I was placed in an oil bath. When the reaction mixture reached 127°, a volatile liquid distilled. Heating was continued until the temperature reached 154°, at which point the reaction was essentially complete, with 2.8 g. of butyl chloride distilled. Two redistillations of the residue gave 6.56 g. of O,O-dibutyl-β-cyanovinyl phosphonate, b.p. 119–120° (3 mm.), $n^{25}D$ 1.4505.

Anal. Calcd. for $C_{11}H_2ONO_3P$: C, 53.87; H, 8.22; N, 5.71. Found: C, 54.05; H, 8.30; N, 5.44.

Carbon Cyanovinylation.—Sodium diethyl malonate (0.1 mole) made from 16 g. of diethyl malonate and 2.3 g. of sodium in ethanol was added slowly to 8.75 g. of *trans*-β-chloroacrylonitrile in ethanol. The temperature of the reaction flask was kept below 50°. During the course of the reaction, a solid material precipitated from solution. The solid was filtered, washed with water, and dried in an oven, yielding 12 g. of the sodium salt of the addition product (XV).

Anal. Calcd. for $C_{12}H_{12}NNaO_4$: C, 51.50; H, 5.19. Found: C, 51.33; H, 5.15.

5-Chlorobicyclo[2.2.1]hept-1-ene-4-carbonitrile.—Dicyclopentadiene (7.2 g.) and *cis*-I (0.5 g.) were sealed in a glass tube. The tube was kept at 150° for 24 hr. The contents were dissolved in hexane and the mixture was filtered. Crystallization occurred on cooling, and the precipitate was filtered, yielding 4.1 g. (24.5%) of the addition product, m.p. 96–97°.

Anal. Calcd. for C_8H_8ClN: C, 62.55; H, 5.25; N, 9.12. Found: C, 62.87; H, 5.51; N, 8.91.

1,3,4,5,6,7,7-Heptachloro-5-norbornene-2-carbonitrile.—Hexachlorocyclopentadiene (27.3 g.) and *cis*-β-chloroacrylonitrile (8.75 g.) were sealed in a glass tube. The tube was immersed in in an oil bath and kept at 180° for 24 hr. After opening the tube, the contents were slurried in petroleum ether (b.p. 30–60°) and filtered to remove any carbonaceous material. Crystallization, followed by filtration, yielded 18.6 g. (52%) of the addition product.

Anal. Calcd. for $C_8H_2Cl_7N$: Cl, 68.93; N, 3.88. Found: Cl, 68.62; N, 3.91.

4-Dialkyl Aminomethylene Glutacononitriles.—A solution of 0.1 mole of the β-cyanovinylalkylamine in 100 ml. of glacial acetic acid was heated at reflux for 30 min. The solution, on cooling, was poured into 100 ml. of water. The solid was filtered, dried, and recrystallized.

4-Piperidinomethylene glutacononitrile was obtained in 73% yield after crystallization from acetonitrile; it melted at 146–147° alone and when mixed with the product obtained from I and piperidine (*cf.* Table I, footnote *c*).

4-Dimethylaminomethyleneglutacononitrile was obtained in 40% yield after crystallization from methanol and had m.p. 121.5–122.5°.

Anal. Calcd. for $C_8H_9N_3$: C, 65.28; H, 6.16; N, 28.55. Found: C, 65.61; H, 6.01; N, 28.17.

Kinetics.—Kinetic measurements were carried out in an ice–water bath provided with an efficient stirrer. The solutions were precooled to 0° before mixing. Ten-milliliter aliquots were withdrawn at suitable intervals and rapidly poured into a dilute nitric acid solution. The reaction was followed by determining the amount of chloride ion present, using the Volhard method. The concentration of the piperidine was made double that of the β-chloroacrylonitrile. The concentrations of the various solutions were *trans*-I, 0.01995 mole/l.; *cis*-I, 0.01997 mole/l.; KCNS, 0.01 mole/l.; piperidine, 0.1003 mole/l.; and $AgNO_3$, 0.005 mole/l.

The analytical data then were used to calculate the kinetic constants by graphical methods, using the customary formulas.[24]

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