Nucleophilic Vinylic Substitution. I. The Synthesis and Reactions of 2-Substituted 3,3-Dichloroacrylonitriles

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Five 2-substituted 3,3-dichloroacrylonitriles (1 = 2-hydro, 2 = 2-chloro, 3 = 2-methyl, 4 = 2-cyano, and 5 = 2-phenyl) have been prepared and their reactions with methoxide and thiophenoxide studied. Spectral data and chemical reactivity indicate that 1–4 are coplanar molecules, whereas the phenyl group in 5 cannot lie in the same plane as the acrylonitrile system and does not activate the β-chlorine atoms. Nitrile 4 reacted exothermically with methanol to yield 3,3-dimethoxy-2-cyanoacrylimidyl chloride which hydrolyzed readily to the corresponding acrylamide. Nitriles 1, 2, 3, and 5 required the methoxide or thiophenoxide ion to substitute the vinylic chlorine atoms. Dichloromethylenetriphenylphosphorane, prepared from carbon tetrachloride and triphenylphosphorine, reacted with benzoyl cyanide to afford a 73% yield of nitrile 5.

With the exception of a few reports[1] the literature on nucleophilic substitution of activated vinylic chlorine atoms has dealt with systems which possessed only one activated halogen atom.[2]

A previous study on the cis and trans isomers of 3-chloroacrylonitrile showed that nucleophilic substitution of the vinyl halide proceeded in a straightforward manner.[3] Unfortunately, the literature on the substitution of two β-chlorine atoms from acrylonitriles is less clear. For example, Miller and Kalnins[1c] have reported that the reaction of 1 or 2,3-dichloroacrylonitrile with sodium p-toluenesulfinate resulted in shortening the acrylonitrile by one carbon to give p-toluenesulfonylacetonitrile. Others[1b] have reported that 2 reacted with sodium ethoxide in ethanol under all conditions to give only 3,3,3-triethoxy-2-chloropropionitrile. A more recent report showed that alkoxide reactions with 1 gave either ketene acetals or ortho esters depending upon the alkoxide/nitrile ratio.[1e] In this study we have found that the products from the reaction of substituted 3,3-dichloroacrylonitriles with methoxide or thiophenoxide depend on the molar ratio of the reactants and on the α substituent. The following nitriles were used in this study: 3,3-dichloroacrylonitrile (1), 2,3,3-trichloroacrylonitrile (2), 3,3-dichloro-2-methylacrylonitrile (3), 3,3-dichloro-2-cyanoacrylonitrile (4), and 3,3-dichloro-2-phenylacrylonitrile (5).

Preparation of the simplest member of this series (1) was first reported by Miller and Kalnins[1c] by the reaction of 2-acetoxy-3,3,3-trichloropropionitrile with zinc. More recently, 1 has been prepared in a 60% yield by the copyrolysis of carbon tetrachloride and acetonitrile.[1e] The procedure which we employed is outlined in Scheme I. The first three steps are similar to a procedure developed by Nesmeyanov[4] but avoids isolation of the intermediates. The oxime of 7 was obtained in a near-quantitative yield but underwent decomposition at room temperatures. Similarly unstable oximes have been reported for β-chlorovinyl aldehydes[5a] and an explosive decomposition was recorded during the distilla-

tion of 2-methylacrolein oxime.[5b] We found that mixing the oxime with an excess of cold acetic anhydride for at least 24 hr prior to distillation afforded a smooth dehydration to the nitrile.

2,3,3-Trichloroacrylonitrile (2) was prepared according to the procedure of Boeseken and Du Jardin;[6] however, by using a modification[7] for the hydrolysis of the trichloromethyl group, we were able to obtain 2 in a 59% yield starting from hexachloropropene.

3,3-Dichloro-2-methylacrylonitrile (3) has not been reported previously; however, it seemed reasonable to assume that the unknown 3,3-dichloro-2-methylacrylic acid (10) would be the most logical precursor (Scheme II). Morris and Kundiger[8] had previously shown that 3,3-dichloro-2-methylallyl alcohol (9) was unusually resistant to oxidation and required cold concentrated nitric acid or preferably hot chromic acid to convert 9 to the aldehyde 11. We have made a number of attempts to oxidize 9 to 10 using chromic acid or nitric acid under more severe conditions but without success. The only extractable material obtained from these reactions was varying amounts of 11 and small amounts of the very stable acetal 3,3-bis(3,3-dichloro-2-methyl-2-propenoxy)-1,1-dichloro-2-methyl-1-propene. Carbon dioxide was usually eliminated from these reactions indicating a surprisingly facile decarboxylation of the acid 10. A reinvestigation of the oxidation of 9 to 11 has revealed that dilute nitric acid containing vanadium pentoxide affords a more convenient synthesis and a slightly higher yield of 11.

The oxime of 11 was a stable white solid and was readily dried over phosphorus pentoxide without any noticeable decomposition. Dehydration of 12 with acetic anhydride proceeded quite smoothly giving 3 in 71% yield.

During one preparation of 12 the reaction mixture was heated and a stable yellow oil was obtained which has been identified as O-(3,3-dichloro-2-methyl-1-methoxyallyl)-3,3-dichloro-2-methylacrolein oxime (13). The appearance of three medium intensity bands in the 1600-cm^{-1} region, as well as a strong band at 914 cm^{-1} and shoulder at 880 cm^{-1}, strongly suggested the existence of a conjugated C=N and C=CCl$_2$ system and a nonconjugated C=CCl$_2$ group. The nmr spectrum consisted of five singlets with an integrated ratio

(1) For leading references, see (a) R. L. Soulen, D. G. Kundiger, S. Searles, Jr., and R. A. Sanchez, *J. Org. Chem.*, **32**, 2661 (1967); (b) A. Roedig, K. Grohe, and W. Mayer, *Chem. Ber.*, **100**, 2946 (1967); (c) B. Miller and M. V. Kalnins, *Tetrahedron*, **23**, 1145 (1967); (d) A. S. Gudkova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1248 (1962); (e) N. Hashimoto, Y. Kawano, and K. Morita, *J. Org. Chem.*, **35**, 828 (1970).

(2) Z. Rappoport, *Advan. Phys. Org. Chem.*, **7**, 1–114 (1969).

(3) F. Scotti and E. J. Frazza, *J. Org. Chem.*, **29**, 1800 (1964).

(4) A. N. Nesmeyanov, R. Kh. Freidlina, and L. I. Zakharkin, *Dokl. Akad. Nauk SSSR*, **99**, 781 (1954).

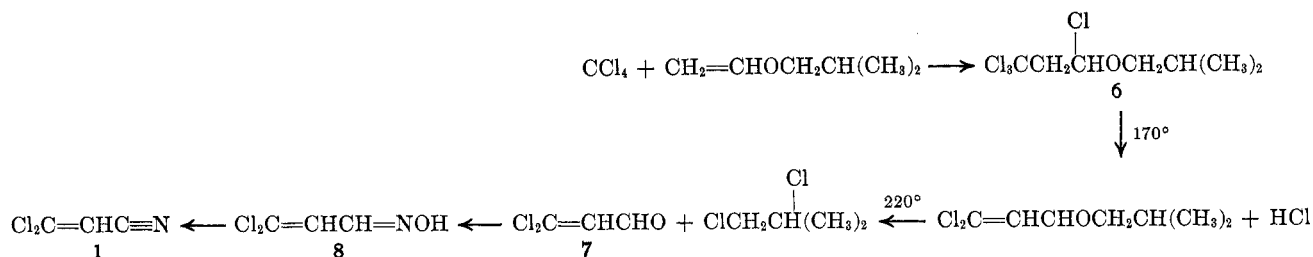(5) (a) W. R. Benson and A. E. Pohland, *J. Org. Chem.*, **30**, 1126 (1965); (b) D. T. Mowry and R. R. Morner, *J. Amer. Chem. Soc.*, **69**, 1831 (1947).

(6) J. Boeseken and P. Du Jardin, *Recl. Trav. Chim. Pays-Bas*, **32**, 97 (1913).
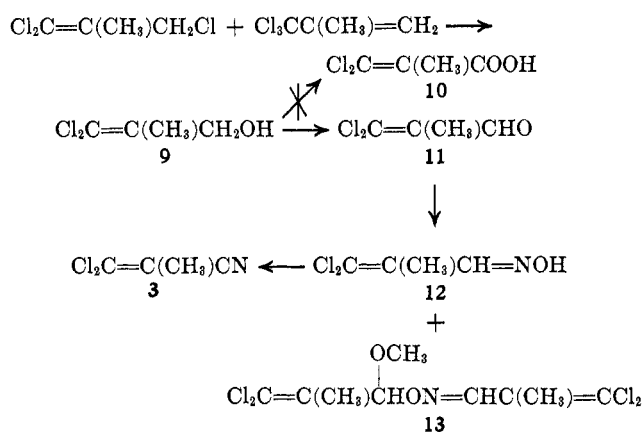
(7) F. Bergmann and L. Haskelberg, *J. Amer. Chem. Soc.*, **63**, 1437 (1941).

(8) D. G. Kundiger and G. F. Morris, *ibid.*, **80**, 5988 (1958).

SCHEME I

$$CCl_4 + CH_2=CHOCH_2CH(CH_3)_2 \longrightarrow Cl_3CCH_2\overset{\overset{\displaystyle Cl}{|}}{C}HOCH_2CH(CH_3)_2$$

6

$$\downarrow 170°$$

$$Cl_2C=CHC\equiv N \xleftarrow{\hspace{1cm}} Cl_2C=CHCH=NOH \xleftarrow{\hspace{1cm}} Cl_2C=CHCHO + ClCH_2\overset{\overset{\displaystyle Cl}{|}}{C}H(CH_3)_2 \xleftarrow{220°} Cl_2C=CHCHOCH_2CH(CH_3)_2 + HCl$$

1   **8**   **7**

SCHEME II

$$Cl_2C=C(CH_3)CH_2Cl + Cl_3CC(CH_3)=CH_2 \longrightarrow$$

$$Cl_2C=C(CH_3)COOH$$
10

$$Cl_2C=C(CH_3)CH_2OH \longrightarrow Cl_2C=C(CH_3)CHO$$
9   **11**

$$\downarrow$$

$$Cl_2C=C(CH_3)CN \xleftarrow{\hspace{1cm}} Cl_2C=C(CH_3)CH=NOH$$
3   **12**

$$+$$

$$Cl_2C=C(CH_3)\overset{\overset{\displaystyle OCH_3}{|}}{C}HON=CHC(CH_3)=CCl_2$$
13

of 3:3:3:1:1. Two of the methyl proton absorptions appeared at δ 1.90 and 2.00 corresponding to the nonconjugated and conjugated C=CCH₃ group. The OCH₃ absorption at δ 3.48, the CH=N absorption at δ 8.20, and the OCHO absorption at δ 5.93 fell well within the acceptable ranges for these proton absorptions.[9] This appears to be the first example of an acetal which employed an oxime as one of the alcohol groups.

We have used the method developed by Josey, *et al.*,[10] to prepare 3,3-dichloro-2-cyanoacrylonitrile (**4**) and would urge that special care be taken in working with this compound as it is a powerful irritant to the throat and lungs.

Previously unreported 3,3-dichloro-2-phenylacrylonitrile (**5**) was readily obtained in two steps from ben-

$$PhCOCl \xrightarrow{CuCN} PhCOCN \xrightarrow{(Ph)_3P=CCl_2} Cl_2C=C(Ph)CN$$
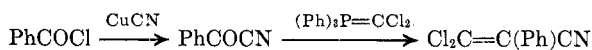
zoyl chloride. The first step is well known[11] and proceeds in good yields. The Wittig reagent employed in the second step was prepared by the direct reaction of triphenylphosphine and carbon tetrachloride at room temperature. Since most acyl cyanides are thermally unstable and decompose rapidly in basic media, this method appears to be ideally suited for the preparation of simple α alkyl and aryl acrylonitriles.

Spectra.—The infrared and ultraviolet spectra of the five 3,3-dichloroacrylonitriles used in this study are tabulated in Table I. As expected, the C≡N and C=C frequencies have been shifted to the longer wavelengths indicating good conjugation and coplanarity of the π electrons. The *gem*-dichlorovinyl stretching frequency

appeared as a strong absorption in the 920–975-cm⁻¹ region well above the region 900–930-cm⁻¹ suggested for nonconjugated dichlorovinyl absorption.[12] This rise in frequency is most likely due to a strengthening of the Cl–C bond due to election delocalization out of the β-chlorine atoms giving rise to resonance forms **14a** and **14b**.

14a   **14b**
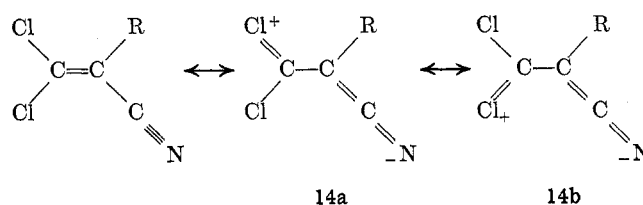
In a comparison of these chlorinated acrylonitriles with their corresponding hydrocarbon analogs it is apparent that the two β-chlorine atoms have very little if any effect on the nitrile absorption position. The α substituent, on the other hand, has a much more pronounced effect and exerted a shift of approximately 20 cm⁻¹ in passing from electron-donating to electron-withdrawing groups. This is twice the shift apparent in various para-substituted benzonitriles[13] and suggests that the nature of the α substituent and not the β-halogen atom will be a controlling factor in chemical reactivity. Kinetic data supports this contention quantitatively.[14]

The nitrile absorption in **2** appeared as a weak doublet of nearly equal intensity at 2240 and 2213 cm⁻¹. This doublet is likely the result of Fermi resonance with an overtone of a strong band appearing at approximately 1115 cm⁻¹. Similar splitting of the nitrile absorption by Fermi resonance has been reported by Evans and Lo[15] for acetonitrile complexes of zinc.

Replacing the two β-chlorine atoms in **1–4** by CH₃O or PhS groups increased the intensity of the nitrile absorption and lowered the position of this band to the 2220- and 2205-cm⁻¹ region. By contrast the nitrile absorptions in the ortho esters **17a**, **17b**, and **17c** and methyl phenylcyanoacetate appeared as a very weak absorption in the 2240–2250-cm⁻¹ region.

The most notable feature of the C=C stretching frequency was the pronounced bathochromic shift caused by the PhS group. Compared with the C=C band position in the hydrocarbon analogs of **1**, **2**, and **3** (1621, 1607 and 1624 cm⁻¹, respectively), two β PhS groups lowered this band approximately 90 cm⁻¹. Recent evidence from esr studies strongly suggests that

(9) L. M. Jackman and S. Sternhell, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, New York, N. Y., 1969, pp 163–192.

(10) A. D. Josey, C. L. Dickinson, K. C. Dewhirst, and B. C. McKusick, *J. Org. Chem.*, **32**, 1941 (1967).

(11) E. C. Horning, "Organic Syntheses," Collect Vol. III, Wiley, New York, N. Y., 1955, p 112.

(12) A. Fujino, Y. Nagata, and T. Sakan, *Bull. Chem. Soc., Jap.*, **38**, 295 (1965).

(13) L. J. Bellany, "Advances in Infrared Group Frequencies," Methuen and Co. Ltd., Great Britain, 1968, p 72.

(14) Unpublished work.

(15) J. C. Evans and G. Y.-S. Lo, *Spectrochim. Acta*, **21**, 1033 (1965).

TABLE I

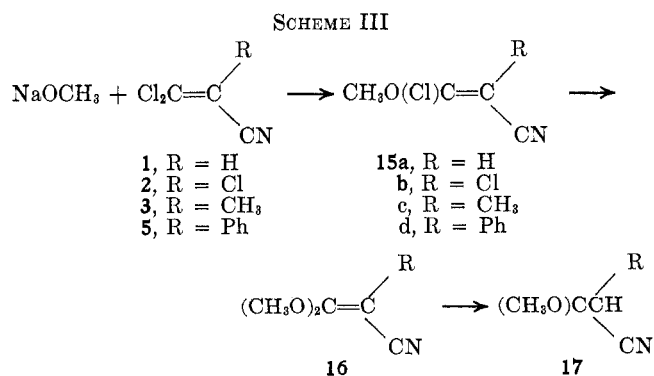IR AND UV SPECTRA OF SUBSTITUTED 3,3-DICHLOROACRYLONITRILES

Compd	CN	C=C	CCl$_2$	λ_{max}, nm	ϵ_{max}
Cl$_2$C=CHCN (1)	2232	1582	923	227.5	10,060
Cl$_2$C=CClCN (2)	2240, 2213	1562	952	238.5	10,820
Cl$_2$C=C(CH$_3$)CN (3)	2225	1596	937	228	11,960
Cl$_2$C=C(CN)$_2$ (4)	2240	1549	975	243[c]	11,270[c]
Cl$_2$C=C(Ph)CN (5)	2220	1560[d]	928	226	9,410
				269	9,840
H$_2$C=CHCN	2231[e]	1621[e]		203[f]	6,100[f]

In column header: ——Ir, cm^{-1} [a]—— and ——Uv[b]——

[a] Spectra were determined on neat liquid films except 4 which was run as a KBr pellet. [b] All spectra were obtained in 95% ethanol solvent. [c] Spectrum was started 3 min after addition of ethanol to nitrile 4. After 15 min the spectrum changed to λ_{max} 241 nm (ϵ 12,390). [d] The C=C stretching band and an aromatic absorption band overlapped in this band. [e] R. Heilmann and J. Bonnier, *C. R. Acad. Sci.*, **248**, 2595 (1959). [f] R. Heilmann, J. Bonnier, and G. de Gaudemaris, *ibid.*, **244**, 1787 (1957).

electronic factors due to the PhS group are not a result of electron donation,[16] but electron withdrawal through dπ–pπ bonding of sulfur and the phenyl ring.[17] Chemical evidence given below also support this view.

The role of the β-chlorine atoms in promoting resonance delocalization in the acrylonitrile system was also apparent from the uv spectra. A measured bathochromic shift of about 12 nm per β chlorine compared favorably with the value 15 nm per β chlorine found in β,β-dichlorovinyl ketones.[18] In contrast to the latter system, however, it was apparent from the extinction coefficients that nitriles 1-4 suffered no loss of coplanarity when the α substituent was increased in size from hydrogen to a methyl group. Some distortion and loss of conjugation must occur in nitrile 5 since the extinction coefficient and chemical reactivity were unusually low for a molecule which had two "activating" groups. Inspection of molecular models indicates that the minimum angle between the phenyl group and the double bond is about 45°. A closer approach to coplanarity is prevented by the ortho hydrogens and the β-chlorine atom. Crystallographic data on 2-bromo-1,1-di-p-tolylethylene show that the cis phenyl ring is distorted by 55°.[19]

Reactions with Methoxide.—The reaction of methoxide ion with acrylonitriles **1, 2, 3**, and **5** proceeded through three clearly defined steps depicted in Scheme III. Each step of the reaction was quite rapid and

SCHEME III

NaOCH$_3$ + Cl$_2$C=C(R)(CN) → CH$_3$O(Cl)C=C(R)(CN) →

1, R = H
2, R = Cl
3, R = CH$_3$
5, R = Ph

15a, R = H
b, R = Cl
c, R = CH$_3$
d, R = Ph

(CH$_3$O)$_2$C=C(R)(CN) → (CH$_3$O)CCH(R)(CN)

16   17

required anhydrous conditions to avoid hydrolysis of **15, 16,** or **17** to the methyl cyanoacetates.

The mechanism for nucleophilic substitution of activated vinylic halides is generally accepted to be an

"addition–elimination" type involving a stabilized carbanion intermediate.[2] Systems possessing only one β halogen have been shown to generally yield products which retained the configuration of the starting material. We are presently investigating the structure of monosubstituted products **15** as there exists some controversy in the literature as to whether the initial product has the incoming nucleophile cis,[1d] trans,[20a] or a mixture of isomers.[20b]

The monomethoxy **15** and dimethoxy **16** products were best prepared by very slowly adding methanolic sodium methoxide to a dilute solution of the acrylonitrile until the desired product reached maximum yield as indicated by vpc analysis. Nevertheless, ketene acetals **16** were produced in some of the reaction mixtures long before the CH$_3$O/acrylonitrile ratios reached one. Ortho esters did not appear in appreciable quantities, however, until this ratio was greater than two (Table II).

TABLE II[a]

REACTION OF SODIUM METHOXIDE WITH 2-SUBSTITUTED 3,3-DICHLOROACRYLONITRILES

Acrylonitrile	Ratio, MeO/CN	Product[b]	Bp (mm) or mp, °C	n^{25}D	Yield, %
1	1.15	15a	32.5–33[c]		
2	0.94	15b[d]	28–30[c]		60[e]
1	2.00	16a	61–62 (0.1), 38–39[f]		94
2	1.90	16b	124 (25)	1.4588	78
3	1.90	16c	46–48 (0.8)	1.4523	82
1	2.10	17a	c, g	1.4235	38
2	2.10	17b	65–57 (1.0)	1.4386	20
3	2.20	17c	c	1.4262	60[e]
4	1.90	h	c	1.5596	67

[a] Satisfactory analytical values (±0.4% for C, H, and N) were reported for all compounds except **15b** (calcd: C, 30.6; Cl, 46.6. Found: C, 31.33; Cl, 44.7) and **17c** (Calcd: C, 52.81. Found: C, 53.39). Satisfactory Cl analyses were reported for **15a, 16b,** and **17b**: Ed. [b] **15** = monomethoxy, **16** = ketene acetal, **17** = ortho ester. [c] Products were isolated by preparative vpc on a 20 ft × 0.25 in. column containing 25% SE-30 on Chromosorb W. [d] Due to decomposition good elemental analysis could not be obtained; however, the structure was strongly supported by ir spectra. [e] Yield estimated by vpc analysis of reaction mixture. [f] Lit. mp 41.5–42°, bp 127–128° (11 mm): S. M. McElvain and J. P. Schroeder, *J. Amer. Chem. Soc.*, **71**, 47 (1949). [g] Lit. bp 98–102° (13 mm), n^{25}D 1.4215: S. M. McElvain and J. P. Schroeder, *ibid.*, **71**, 40 (1949). [h] Methyl phenylcyanoacetate was isolated.

On slow addition of sodium methoxide to **3** only about 5% of the monomethoxy derivative **15c** was produced

(16) E. A. C. Lucken, *J. Chem. Soc.*, 4240 (1964).

(17) E. T. Strom and J. R. Norton, *J. Amer. Chem. Soc.*, **92**, 2327 (1970).

(18) S. Searles, Jr., R. A. Sanchez, R. L. Soulen, and D. G. Kundiger, *J. Org. Chem.*, **32**, 2655 (1967).

(19) P. Beltrame, P. L. Beltrame, and L. Bellotti, *J. Chem. Soc. B*, 932 (1969).

(20) (a) W. E. Truce and J. A. Simms, *J. Amer. Chem. Soc.*, **78**, 2756 (1965); (b) E. W. Cook, Ph.D. Thesis, University of Colorado, 1965.
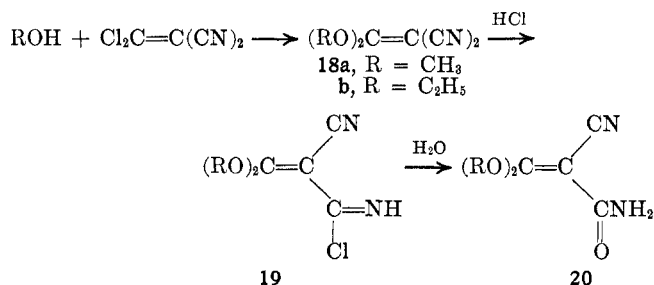
before the ketene acetal **16c** appeared. Further addition of methoxide gave more **16c** but did not increase **15c** concentration to a level where it could be isolated.

Using similar reaction conditions, sodium methoxide and **5** gave a 67% yield of methyl phenylcyanoacetate and two minor components in about 20 and 10% yield.

An infrared spectrum of the 20% components gave a strong absorption at 1600 and 2210 cm^{-1} indicative of the ketene acetal **16d**. A second scan of the same sample after 1 day gave a spectrum identical to the ester. The other minor component decomposed within a few minutes to the ester; hence, we suspect that it was the more reactive monosubstituted product **15d**. Since precautions had been taken to ensure anhydrous conditions in this reaction, the increased instability of the ketene acetal **16d** must have been due to steric strain caused by the bulky α phenyl group.

No reaction occurred between acrylonitriles **1, 2, 3, 5**, and methanol in the absence of base. The most reactive member of this group (**3**) and refluxing methanol showed no sign of reaction by vpc after 2 weeks.

It was expected that **4** would be the most reactive acrylonitrile of those studied since the vinylic chlorine atoms were activated by two cyano groups. We were surprised, however, to observe that **4** reacted cleanly and exothermically with anhydrous methanol without added base. The initial product of this reaction was undoubtedly 3,3-dimethoxy-2-cyanoacrylonitrile (**18a**) which subsequently reacted with 1 mol of hydrogen chloride yielding the acrylimidyl chloride **19a**.

$$\text{ROH} + \text{Cl}_2\text{C}=\text{C(CN)}_2 \longrightarrow (\text{RO})_2\text{C}=\text{C(CN)}_2 \xrightarrow{\text{HCl}}$$

18a, R = CH₃
b, R = C₂H₅

Similar findings have been reported by Middleton and Engelhardt[21] who observed that ether solutions of dicyanoketene acetals **18** reacted with excess hydrogen chloride to give products in which a cyano group was converted to CCl=NH and one ether bond broken.
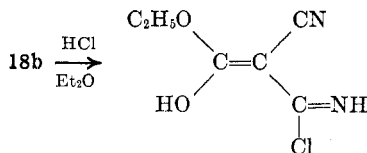
We have been unable to detect any alkyl chloride from the reaction of **4** with methyl or ethyl alcohol. Alcoholic ferric chloride tests for enols have also been negative indicating the absence of ether cleavage in these solvents. Hydrolysis of acrylimidyl chlorides (**19**) to the corresponding acrylamides (**20**) occurred readily in aqueous ethanol or dilute sodium carbonate.

Attempts to react **4** with sodium methoxide gave dark red resinous products confirming the unexpected base sensitive character of dicyanoketene acetals reported previously.[21]

(21) W. J. Middelton and V. A. Engelhardt, *J. Amer. Chem. Soc.*, **80**, 2788 (1958).

Reactions with Sodium Thiophenoxide.—Base-catalyzed reactions of thiophenol with nitriles **1, 3, 4**, and **5** proceeded in a straightforward manner to give good yields of 3,3-di(thiophenoxy)acrylonitriles (Table III).

TABLE III[a]
3,3-DI(THIOPHENOXY)-2-SUBSTITUTED ACRYLONITRILES

$$\underset{\underset{\text{(PhS)}_2\text{C}=\overset{|}{\text{C}}\text{CN}}{}}{\overset{\text{R}}{|}}$$

R	Registry no.	Yield, %	Bp (mm) or mp, °C
H	31413-70-4	53	210 (0.025)[b]
Cl	31413-71-5	63	110 (0.08)[c]
CH₃	31413-72-6	40	53.0–54.0
CN	31413-73-7	44	111.5–112.5
SPh	31413-74-8	8[d]	55–58
Ph	31413-75-9	60	104.0–105.0

[a] Satisfactory analytical values (±0.4% for C, H, N, and S) were reported for all compounds except R = Ph (Calcd: C, 73.01. Found: C, 72.39): Ed. [b] n^{20}D 1.665. [c] n^{20}D 1.6706. *Anal.* Calcd: Cl, 11.67. Found: Cl, 11.58. [d] Isolated from preparation of 2-chloro-3,3-di(thiophenoxy)acrylonitrile.

Nitrile **2** reacted with sodium thiophenoxide to give the disubstituted product **21** plus a small amount of a trisubstituted product **23** in which all three chlorine atoms had been replaced. Fortunately, the phenyl ketene thioacetals were quite stable and, if necessary, could be recrystallized from hot aqueous ethanol.

The ability of two β PhS groups to lower the C=C and C≡N stretching frequency in the acrylonitrile system has been discussed above. It becomes more reasonable to ascribe this effect to election withdrawal by the PhS group in view of the unexpected displacement of the α-chlorine atom in **21**.
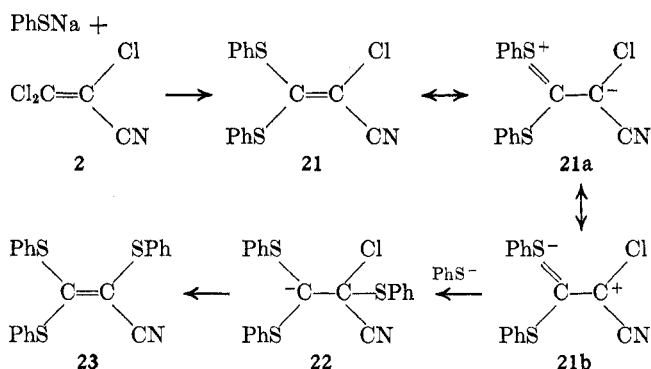
Three factors may be used in explaining the ability of the thiophenoxide anion to displace the normally inert α-chlorine atom: (a) the high nucleophilic character of the anion, (b) the increased positive charge on the α carbon of **21b**, and (c) the stabilization of the anion in **22** by the PhS group. The last two factors are possible only when the PhS group acts in an electron-withdrawing capacity and effectively competes with the nitrile group for the olefinic π electrons. Similar trisubstituted products of **2** have not been observed with oxygen nucleophiles such as alkoxides or phenoxide nor amines such as aniline or piperidine.[1b,22]

Experimental Section

All melting points were determined on a Fisher-Johns melting points apparatus and are uncorrected. A Varian A-60A spec-

(22) Unpublished reports, this laboratory.

trometer was used to obtain the nmr spectra and a Beckman IR-8 for the infrared spectra. Ultraviolet spectral analysis and elemental analysis were performed by Huffman Laboratories, Wheatridge, Colo., and by Galbraith Laboratories, Knoxville, Tenn.

3,3-Dichloroacrolein (7).—Carbon tetrachloride (2376 g, 15.44 mol) and isobutyl vinyl ether (227.6 g, 2.27 mol) were refluxed for 48 hr during which time 2.0 g of azobisisobutyronitrile was added in small portions. The excess carbon tetrachloride was removed by distillation and the residue heated to 170–180° where copious evolution of HCl occurred. Heating slowly to 220° under slight vacuum caused the dark residue to decompose and a crude mixture of isobutyl chloride and **7** distilled from 107–115°. Redistillation gave 70% yield of **7**, bp 54° (56 mm), $n^{24.0}$D 1.5062 [lit.[23] bp 124–125° (atm), $n^{17.5}$D 1.5090].

3,3-Dichloroacrylonitrile (1).—A solution of sodium acetate (123 g, 1.50 mol) in 500 ml of water was added dropwise over a period of 3 hr to an ice-cooled solution of 146.6 g (1.17 mol) of 3,3-dichloroacrolein and 104.3 g (1.50 mol) of hydroxylamine hydrochloride in 600 ml of methanol. The solution was stirred for an additional 2 hr and then concentrated under vacuum at room temperature to ca. 700 ml. The liquid oxime layer was removed and the aqueous layer extracted with three 100-ml portions of methylene chloride. The oil and extracts were combined, partially dried with MgSO₄, then added to 238 g (2.34 mol) of acetic anhydride, and cooled to 10° overnight. Slow distillation at atmospheric pressure brought about a smooth dehydration of the oxime yielding a mixture of mainly acetic acid and **1**. The fractions containing **1** (104–140°) were combined and slowly added to an ice-cooled mixture of 360 g of NaHCO₃ and 700 ml of water. The organic layer was separated and the aqueous layer extracted with CH₂Cl₂. The extracts and organic layer were combined, dried (MgSO₄), and distilled to give 114 g (74%) of **1**: bp 140–141° (745 mm); n^{25}D 1.4922; $d^{25}{}_{25}$ 1.349 [lit.^{c} bp 139–142° (atm)]. *Note:* It is possible to isolate the oxime of **7** as an unstable white solid (mp 38–39°) instead of an oil. Both the solid and the oil contain water of hydration and decompose readily at room temperature. Attempts to dry the solid oxime led to rapid and highly exothermic decomposition.

2,3,3-Trichloroacrylonitrile (2).—2,3,3-Trichloroacrylonitrile was prepared according to the procedure of Boeseken and Du Jardin[6] in an overall yield of 59% from 1,1,2,3,3,3-hexachloropropene. Physical properties for the pure compound (>99% by vpc) were bp 92° (127 mm), $d^{25}{}_{25}$ 1.5058, n^{25}D 1.5129 (lit.[6] $n^{20.5}$D 1.5100, mp 20°).

3,3-Dichloro-2-methylallyl Alcohol (9).—A mixture of 319 g (2.00 mol) of 1,1,3-trichloro-2-methyl-1-propene and 3,3,3-trichloro-2-methyl-1-propene[24] (80/20 wt % by vpc) and 217 g (2.05 mol) of sodium carbonate in 1500 ml of water was rapidly stirred at reflux temperature for 48 hr. The organic layer was separated and the aqueous layer neutralized with concentrated hydrochloric acid and then extracted with chloroform. The organic layer and chloroform were combined, dried (MgSO₄), and then distilled yielding 220.6 g (78% yield) of **9**: bp 93–94° (20–21 mm); $n^{25.2}$D 1.4990; ir (neat) prominent bands were 3310, 1624, 1010, and 80 cm⁻¹ [lit.[8] bp 91–92° (16 mm), n^{20}D 1.4998].

3,3-Dichloro-2-methylacrolein (11).—Under a slow N₂ purge, 92.0 g of 3,3-dichloro-2-methylallyl alcohol (0.66 mol) was added dropwise into 650 ml of gently boiling dilute nitric acid (16% HNO₃) containing 0.5 g of V₂O₅. The crude product (73.9 g, 81% yield) was collected in a Barrett trap as it distilled from the reaction mixture. After drying (MgSO₄) the light yellow liquid was distilled yielding 56 g (63%) of pure **11**: bp 68–69° (51 mm); n^{25}D 1.5006 [lit.[8] bp 65–66° (50 mm), n^{20}D 1.5045]; ir (neat) prominent bands were 1685, 1588, 1240, 1035, 907 and 705 cm⁻¹.

3,3-Dichloro-2-methylacrolein Oxime (12).—To a solution of 68.5 g (0.50 mol) of sodium acetate trihydrate and 35.8 g (0.50 mol) of hydroxylamine hydrochloride in 200 ml of methanol was added 56.6 g (0.41 mol) of **11**. The mixture was stirred overnight and then poured into 500 ml of ice water and the white precipitate was filtered and dried over phosphorus pentoxide. The crude oxime **12**, 55.8 g (91%), mp 81–82° (lit.[8] mp 84.5–85.5°), was used without further purification.

In a similar experiment the reaction mixture was heated to reflux for 2 hr and then poured into ice water. In addition to a much lower yield of the oxime (21%) there was also obtained a

16% yield of *O*-(3,3-dichloro-2-methyl-1-methoxyallyl)-3,3-dichloro-2-methylacrolein oxime as a stable yellow liquid: bp 108–110° (0.40 mm); n^{28}D 1.5318; ir (neat) prominent bands at 2935, 2840, 1628, 1598, 1570, 1105, 1050, 968, 914, and 900 cm⁻¹; nmr (neat) gave singlets at δ 1.90, 2.00, 3.48, 5.93 and 8.20 in the ratio 3:3:3:1:1.

Anal. Calcd for C₉H₁₁Cl₄NO₂: C, 35.21; H, 3.61; Cl, 46.19; N, 4.56. Found: C, 34.96; H, 3.67; Cl, 46.21; N, 4.64.

3,3-Dichloro-2-methylacrylonitrile (3).—A mixture of 26.5 g (0.26 mol) of acetic anhydride and 20.0 g (0.13 mol) of dry **12** was heated to gentle reflux for 3 hr and then 24.4 g of acetic acid and some acetic anhydride were removed by slow distillation. The light brown residue was washed with 100 ml of water containing 0.13 mol of sodium carbonate. The organic layer was removed by chloroform extraction, dried over calcium chloride, and then distilled to yield chloroform and 12.6 g (71%) of **3**, bp 65–67° (25 mm), n^{25}D 1.4873.

Anal. Calcd for C₄H₃Cl₂N: C, 35.33; H, 2.22; Cl, 52.14; N, 10.30. Found: C, 35.47; H, 2.31; Cl, 52.08; N, 10.23.

1,1-Dichloro-2,2-dicyanoethylene (4).—The procedure of Josey, *et al.*,[10] was used to prepare **4**, mp 61.0–61.5° (lit.[10] mp 61.5–62°).

3,3-Dichloro-2-phenylacrylonitrile (5).—A mixture of 178.0 g (0.680 mol) of triphenylphosphine, 45.0 g (0.343 mol) of benzoyl cyanide,[11] and 400 ml of dry carbon tetrachloride was stirred at room temperature overnight and then heated to gentle reflux for 4 hr. The mixture was cooled, 600 ml of ligroin added, and the precipitate of triphenylphosphine oxide collected. The filtrate was concentrated under reduced pressure and then vacuum distilled yielding 49.1 g (73%) of **5**, bp 101–104° (0.4 mm), $n^{25.0}$D 1.5866.

Anal. Calcd for C₉H₅Cl₂N: C, 54.58; H, 2.54; N, 7.07; Cl, 35.80. Found: C, 54.76; H, 2.74; N, 7.28; Cl, 35.84.

Reactions with Sodium Methoxide. General Procedure.— Anhydrous methanol was prepared by refluxing reagent grade methanol with calcium hydride for 24 hr and then collecting a center cut.

A solution of sodium methoxide in methanol was added slowly to an ice-cooled mixture of the acrylonitrile in methanol. Product formation was monitored by repeated vpc analysis of the reaction mixture. After addition of the methoxide the solution was stirred for a period (0.5–3.0 hr), then the methanol was removed by vacuum, and the residue filtered. The product was isolated from the filtrate by distillation through a micro distillation still or by vpc separation on a 20 ft × 0.25 in. column containing 25% SE-30 on Chromosorb W, 60–80 mesh. These reactions were usually carried out on a 0.05-mol scale. All products, especially the monosubstituted derivatives, were quite unstable and began decomposition within a few days at room temperature. The results are summarized in Table II.

2-Cyano-3,3-dimethoxyacrylamide (20a).—Anhydrous methanol (50 ml) was added to 3.00 g (0.0204 mol) of **4** under a N₂ atmosphere. After an initial exothermic reaction the mixture was heated to reflux for 3 days, concentrated under vacuum, and then the residue was poured into 100 ml of 5% sodium carbonate. The resulting light yellow precipitate was recrystallized from aqueous methanol to give 1.30 g (41%) of **20a**: mp 212–213°; ir (KBr pellet) prominent bands at 3300 and 3180 broad, 2210 sh, 1680 m, 1645 s, 1510 s, and 1125 cm⁻¹ s.

Anal. Calcd for C₆H₈N₂O₃: C, 46.15; H, 5.16; N, 17.94. Found: C, 46.51; H, 5.26; N, 17.84.

2-Cyano-3,3-diethoxyacrylamide (20b).—Anhydrous ethanol (30 ml) and 3.00 g (0.0204 mol) of **4** were heated to reflux for 3 days and then cooled and a light yellow precipitate was collected. The hygroscopic precipitate gave a positive alcoholic AgNO₃ test and a negative ferric chloride test for enols and decomposed at 240° in a sealed tube. The precipitate was recrystallized from 95% ethanol yielding 2.47 g (66%) of **20b** as white needles: mp 137.5–138.5°; ir (KBr pellet) prominent bands at 3290 broad, 3140 broad, 2210 sh, 1660 s, 1640 s, 1510 s, 1310 m, 1115 s, and 1080 cm⁻¹ m.

Anal. Calcd for C₈H₁₂N₂O₃: C, 52.17; H, 6.57; N, 15.21. Found: C, 51.87; H, 6.74; N, 15.18.

Reactions with Sodium Thiophenoxide. General Procedure. —A solution of sodium methoxide (1.9 equiv) and thiophenol (2.1 equiv) in methanol was added dropwise to an ice-cooled solution of the acrylonitrile (1.0 equiv) in methanol. The reaction mixture was stirred at room temperature for 24–48 hr and then filtered and evaporated to dryness. The residue was dis-

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tilled or recrystallized from benzene–ligroin mixtures. These reactions were carried out using 0.02–0.04 mol of the nitrile. The results are summarized in Table III.

Carbodiimide–Sulfoxide Reactions. XI.[1a] Reactions of Carboxylic Acids, Hydroxamic Acids, and Amides

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The mild acid-catalyzed reactions of DMSO and DCC with carboxylic acids, hydroxamic acids, and carboxamides have been examined. Reactions with carboxylic acids, or with the corresponding hydroxamic acids, lead to methylthiomethyl esters and to *N*-acylureas. In the case of hydroxamic acids, minor amounts of products arising from rearrangements of the Lossen type are also found. In the case of *N*-methoxy-*p*-nitrobenzamide, the major product is the *N*-(1,3-dicyclohexyl-1-ureidomethyl) derivative and lesser amounts of methylthiomethyl *N*-methoxy-*p*-nitrobenzimidates are also formed. Primary carboxamides in both the aromatic and aliphatic series react readily to form *N*-acylsulfilimines which can be oxidized to the corresponding *N*-acylsulfoximines. Nitriles are also formed in these reactions. Comparable reactions of amides with DMSO and phosphorus pentoxide or acetic anhydride gave only minor amounts of *N*-acylsulfilimines, the major products being *N*,*N*'-methylenebiscarboxamides. Photolysis of *N*-acylsulfilimines is shown to proceed primarily *via* formation of an acylnitrene which can either react with the solvent or rearrange to an isocyanate.

Previous papers in this series have shown that dimethyl sulfoxide (DMSO) and dicyclohexylcarbodiimide (DCC) react in the presence of a mild acidic catalyst to form the oxysulfonium intermediate **1**. This species can then be attacked by various nucleophiles such as alcohols,[2] phenols,[3] enols,[4] and oximes,[5] leading to dimethylsulfonium intermediates which can undergo oxidation, rearrangement, or a variety of other reactions. In the case of the reactions of alcohols, the mechanism of the oxidation reaction has been quite carefully studied using isotopes.[1,2b] In the present paper these studies have been extended to cover the acid-catalyzed reactions of DMSO and DCC with carboxylic acids, hydroxamic acids, and carboxamides. In view of the mechanistic similarities of these reactions to those using DMSO activated by acetic anhydride[6] or phosphorus pentoxide,[7] several comparable reactions have been studied using these reagent mixtures.

Our initial reactions were done using *p*-nitrobenzoic acid, which reacted exothermically with 3 molar equiv of DDC and 0.5 molar equiv of anhydrous orthophosphoric acid in a mixture of DMSO and benzene. Following destruction of excess DCC with oxalic acid,[8] two crystalline products were readily isolated and shown to be methylthiomethyl *p*-nitrobenzoate (**5a**) and 1-*p*-nitrobenzoyl-1,3-dicyclohexylurea (**7a**) in yields of 40 and 42%. The formation of methylthiomethyl esters has also been demonstrated by Onodera, *et al.*,[9] following reactions of carboxylic acids with DMSO and phosphorus pentoxide at 70° and can, in both cases, be considered as the products of Pummerer-type rearrangements[10] of the acyloxysulfonium ylide (**3**) according to Scheme I.

The ylide **3** is written as arising *via* the tetracovalent sulfur intermediate **2**, but, as has been discussed in our work on the oxidation of alcohols,[1] could also be formed by a concerted process without accumulation of **2**. Dissociation of the ylide into the methylene methylsulfonium ion **4** and recombination with the carboxylate anion to give **5** is typical of the Pummerer reaction[10] and is similar to what has been previously proposed for the reactions of oximes[5] and 2,6-disubstituted phenols.[3b] An alternative route involving initial reaction of the carboxylic acid with DCC to form the corresponding acid anhydride followed by a typical Pummerer reaction with DMSO cannot be excluded. Indeed, *p*-nitrobenzoic anhydride[11] has been found to react very rapidly with DMSO to form **5a**.

In our previous papers we have considered the direct product of the reaction of an oxygen nucleophile with the DMSO–DCC adduct **1** to be an oxysulfonium salt which subsequently readily loses a proton to form the sulfonium ylide (*e.g.*, **3**). Based upon our more recent results[1] on the mechanism of the DMSO–DCC oxidation of alcohols, however, direct formation of the ylide

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