

ride, and the resultant solution was refluxed for 15 hours. The solution was then cooled, diluted with 100 ml. of ice-water, and neutralized with 10% aqueous sodium carbonate, which caused 310 mg. of gray solid to precipitate. Sublimation of the gray solid at 100–115° (0.5 mm.) followed by recrystallization of the sublimate from methanol gave 164 mg. (16% yield) of methyl 4-dimethylaminocinnamate. The ester had the same melting point (137–138°) and X-ray diffraction pattern as an authentic sample.<sup>16</sup>

**Basic Hydrolysis of 4-(4-Dimethylaminophenyl)-1,3-butadiene-1,1,2-tricarbonitrile (XI).**—A 0.000342 *M* solution of 4-(4-dimethylaminophenyl)-1,3-butadiene-1,1,2-tricarbonitrile in methanol was prepared;  $\lambda_{\max}$  582  $m\mu$  ( $k$  258), 355  $m\mu$  ( $k$  26). Fifty milliliters of this solution was mixed with 50 ml. of 0.12 *N* methanolic sodium hydroxide. The deep blue color of the tricarbonitrile was instantly replaced by a brownish-yellow color;  $\lambda_{\max}$  462  $m\mu$  ( $k$  19). In the course of five hours, the maximum at 462  $m\mu$  gradually disappeared and a new one appeared at 400  $m\mu$  ( $k$  31). At timed intervals a 5-ml. portion of the basic mixture was diluted to 25 ml. with a 0.21 *N* solution of acetic acid in methanol, and the spectrum of the acidic solution was determined. The tricarbonitrile was partially regenerated by the acid, as shown by reappearance of blue color and a

corresponding absorption maximum at 582  $m\mu$ . Except for diminished absorption at 582  $m\mu$ , the treatment with base caused no marked spectral change. From the optical density at 582  $m\mu$ , it was possible to estimate the extent of hydrolysis of the tricarbonitrile for the following times in minutes. The percentages were: 1.5 min., 2.7%; 10, 9.3%; 20, 13.9%; 40, 25.2%; 80, 43%; 160, 67%; 320, 87%. These figures correspond to a rate of hydrolysis approximately first order in tricarbonitrile concentration.

**Semi-quantitative Determination of Tetracyanoethylene.**—A weighed 10-mg. sample of material believed to contain tetracyanoethylene is dissolved in 100 ml. of *N,N*-dimethylaniline by shaking the mixture at room temperature for a few minutes. The solution is allowed to stand for 15 to 20 hours at room temperature to ensure complete conversion of tetracyanoethylene to 4-tricyanovinyl-*N,N*-dimethylaniline. A 5-ml. portion is diluted to 100 ml. with acetone, and the visible absorption spectrum of the solution is determined. A maximum near 515  $m\mu$  indicates that the original material contains tetracyanoethylene. The percentage, *P*, of tetracyanoethylene can be estimated within a few per cent. from the corresponding specific extinction coefficient,  $k_{\max}$ . With pure tetracyanoethylene the coefficient determined in this way is 246, so that  $P = 100k_{\max} \div 246$ .

(16) P. Pfeiffer and G. Haefelin, *Ber.*, **55**, 1769 (1922).

WILMINGTON, DELAWARE

[CONTRIBUTION NO. 441 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO.]

## Cyanocarbon Chemistry. VII.<sup>1</sup> Tricyanoethylenes

BY G. N. SAUSEN, V. A. ENGELHARDT AND W. J. MIDDLETON

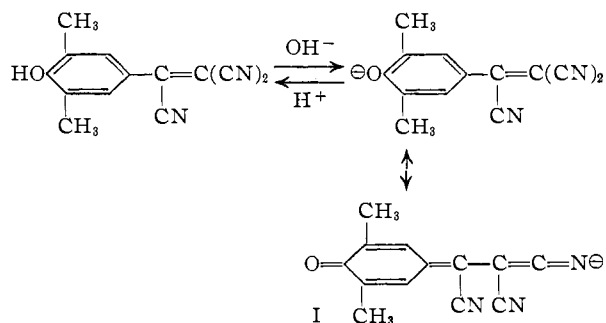
RECEIVED NOVEMBER 14, 1957

Routes to tricyanoethylenes include direct alkylation of an aromatic or heterocyclic nucleus with tetracyanoethylene, condensation of an aldehyde with malononitrile followed by the addition of hydrogen cyanide and subsequent dehydrogenation, and condensation of an acyl cyanide with malononitrile. The tricyanovinyl group undergoes a variety of chemical reactions including replacement of the 1-cyano group by reaction with nucleophilic reagents such as alcohols, hydroxide ion, amines and malononitrile anion. It serves as the dienophilic group in Diels-Alder reactions, and is converted to substituted pyrroles and substituted thiophenes by reaction with mercaptans and with hydrogen sulfide, respectively.

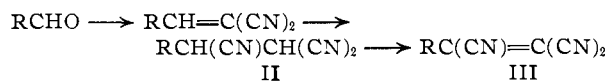
Tetracyanoethylene (TCNE) reacts with most primary and some secondary aromatic amines with elimination of hydrogen cyanide to give *N*-tricyanovinylamines, and it reacts readily with both tertiary and secondary aromatic amines to give the corresponding 4-tricyanovinylarylamines.<sup>1</sup> This paper describes the preparation and chemistry of tricyanovinyl hydrocarbons, tricyanovinyl phenols and tricyanovinyl heterocyclic compounds.

**Syntheses of Tricyanoethylenes. A. Alkylation with Tetracyanoethylene.**—Tetracyanoethylene reacts readily with selected aromatic and heterocyclic nuclei with elimination of the elements of hydrogen cyanide to give the corresponding C-tricyanovinyl compounds. For example, reaction with phenanthrene gives a mono-(tricyanovinyl)-phenanthrene, probably the 9-derivative, and reaction of TCNE with pyrrole and *N*-methylpyrrole gives the corresponding tricyanovinyl heterocycles, probably substituted in the 2-position. These reactions are carried out at room temperature in solvents such as acetone and tetrahydrofuran. Reaction of TCNE with 2,6-dimethylphenol occurs in the presence of pyridine, and 4-(tricyanovinyl)-2,6-dimethylphenol is obtained as an orange solid. In the absence of a basic catalyst lower yields of product are obtained. The phenol serves as an in-

dicator becoming bright yellow in dilute acid solution and deep burgundy in alkaline solution (I).



**B. Aldehyde Route.**—An alternate route to tricyanovinyl compounds involves condensation of an aldehyde with malononitrile followed by the addition of hydrogen cyanide to give the 1,2,2-tricyanoethyl compound II. Dehydrogenation of II to the corresponding tricyanovinyl derivative III completes the synthesis.

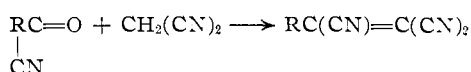


The application of this route to the preparation of tricyanovinylarylamines was described in a previous paper.<sup>1</sup> In the present study tricyanovinyl-

(1) Paper VI, B. C. McKusick, R. E. Heckert, T. L. Cairns, D. D. Coffman and H. F. Mower, *THIS JOURNAL*, **80**, 2806 (1958).

benzene (III, R = C<sub>6</sub>H<sub>5</sub>) and 4-(tricyanovinyl)-anisole (III, R = *p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>) have been synthesized by this route. In the conversion of II to III (R = C<sub>6</sub>H<sub>5</sub>) the use of lead tetraacetate gives low yields of impure tricyanovinyl compound, but yields are improved markedly when N-bromosuccinimide is employed as the oxidizing agent. The use of one equivalent of N-bromosuccinimide gives an intermediate monobromo substitution compound. Dehydrobromination to the tricyanovinyl derivative proceeds readily in the presence of pyridine. Alternatively, the use of two equivalents of N-bromosuccinimide gives the tricyanovinyl compound directly. Over-all yields of tricyanovinylbenzene of 40–52% from benzaldehyde have been obtained.

**C. Acyl Cyanide Route.**—In a new approach to the tricyanovinyl structure the condensation of a suitable acyl cyanide with malonitrile gives the corresponding tricyanovinyl compound directly. The condensation reaction



is catalyzed by a salt of an amine with an organic or mineral acid in the presence of excess acid. Typical catalyst systems are piperidine–acetic acid,  $\beta$ -alanine–acetic acid and piperidine–sulfuric acid. The use of excess acyl cyanide gives increased yields of product, and 35–40% yields of tricyanovinylbenzene have been obtained in the presence of a large excess of benzoyl cyanide. Other tricyanovinyl compounds prepared by this route include 4-(tricyanovinyl)-anisole from *p*-anisoyl cyanide, 2-(tricyanovinyl)-furan from 2-furoyl cyanide, and 2-(tricyanovinyl)-2-methylpropane from trimethylacetyl cyanide.

In a previous paper<sup>1</sup> the bathochromic effect obtained by introduction of a 1-cyano group into an aminoarylidene malonitrile was described. The same effect is noted with the tricyanovinyl compounds which do not contain an amino group. In Table I the ultraviolet spectra of several tri-

TABLE I  
ULTRAVIOLET ABSORPTION SPECTRA OF 2,2-DICYANOVINYL AND 1,2,2-TRICYANOVINYL COMPOUNDS

2,2-Dicyanovinyl compd., RCH=C(CN) <sub>2</sub> , R =	$\lambda_{\text{max}}$ , m $\mu$	$\epsilon_{\text{max}} \times 10^{-2}$
C <sub>6</sub> H <sub>5</sub>	307 <sup>a</sup>	216
<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	348 <sup>a</sup>	293
	352 <sup>b</sup>	312
C <sub>4</sub> H <sub>9</sub> O	339 <sup>a</sup>	255
1,2,2-Tricyanovinyl compd., RC(CN)=C(CN) <sub>2</sub> , R =		
C <sub>6</sub> H <sub>5</sub>	335 <sup>a</sup>	59.5 <sup>c</sup>
	343 <sup>b</sup>	166
<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	396 <sup>a</sup>	105 <sup>c</sup>
	407 <sup>b</sup>	254
C <sub>4</sub> H <sub>9</sub> O	379 <sup>a</sup>	219
	383 <sup>b</sup>	252
C <sub>4</sub> H <sub>9</sub>	251 <sup>a</sup>	113

<sup>a</sup> Ethyl alcohol solvent. <sup>b</sup> Chloroform solvent. <sup>c</sup> Decreased value apparently caused by complexing with solvent.

cyanovinyl compounds are compared with the spectra of the corresponding 2,2-dicyanovinyl derivatives. With tricyanovinylbenzene and 4-(tri-

cyanovinyl)-anisole the molar extinction coefficients are markedly depressed in ethyl alcohol solution, probably because of complex formation with the solvent. In chloroform solution no such interaction is observed. With 2-(tricyanovinyl)-furan and 2-(tricyanovinyl)-2-methylpropane solvent interaction with ethyl alcohol is not detected in the time required for determination of the ultraviolet spectra.

**Chemistry of Tricyanoethylenes.**—A previous paper in this series<sup>2</sup> describes the facile reaction of TCNE with a variety of 1,3-dienes at room temperature to give high yields of the corresponding Diels–Alder adducts. Although the tricyanovinyl compounds fail to react with 1,3-dienes at room temperature, high yields of adducts are obtained at elevated temperatures. Thus, 2,3-dimethylbutadiene and butadiene readily add to tricyanovinylbenzene, 2-(tricyanovinyl)-2-methylpropane and 4-(tricyanovinyl)-N,N-dimethylaniline<sup>1</sup> at 175° to give the corresponding adducts in good yields.<sup>3</sup>

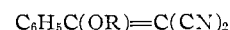
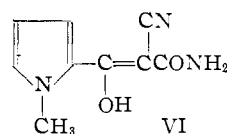
Reaction of 1,2,2-tricyanovinyl compounds with nucleophilic reagents generally results in replacement of the 1-cyano group. In reactions of this type tricyanovinyl compounds may be considered as analogs of acyl cyanides (IV).<sup>4</sup>



The mild basic hydrolysis of tricyanovinylarylamines to 1-hydroxy-2,2-dicyanovinyl compounds was described in an earlier paper.<sup>1</sup> In the present study tricyanovinylbenzene, 2-(tricyanovinyl)-N-methylpyrrole and 4-(tricyanovinyl)-2,6-dimethylphenol have been converted to the corresponding 1-hydroxy-2,2-dicyanovinyl compounds. The hydrolysis products are soluble in 5% sodium bicarbonate solution and in this way resemble the analogous carboxylic acids V. Further hydrolysis of 2-(1-hydroxy-2,2-dicyanovinyl)-N-methylpyrrole



gives the corresponding carbamoyl compound VI.



VII

Replacement of the 1-cyano group of a tricyanovinyl compound with an alkoxy group readily is achieved by reaction with an alcohol in the presence of a suitable catalyst. In this way 1-methoxy- and (1-ethoxy-2,2-dicyanovinyl)-benzene (VII) are obtained by alcoholysis with methanol and ethyl alcohol, respectively. Suitable catalysts include urea, zinc chloride and alkoxide ion. The sample of (1-methoxy-2,2-dicyanovinyl)-benzene prepared in this way is identical with a sample prepared by condensation of methyl orthobenzoate with malonitrile.<sup>5</sup>

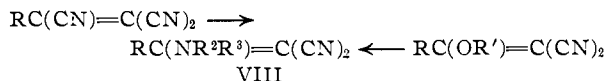
(2) Paper III, W. J. Middleton, R. E. Heckert, E. L. Little and C. G. Krespan, *THIS JOURNAL*, **80**, 2783 (1958).

(3) K. Alder and H. F. Rickert, U. S. Patent 2,264,354 (1941). describe the Diels–Alder addition of 1,3-dienes to activated olefins such as benzylidenemalonitrile and ethyl ethylideneacetate.

(4) For a recent review of the chemistry of acyl cyanides see J. Thiesing and D. Witzel, *Angew. Chem.*, **68**, 425 (1956).

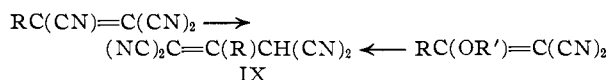
(5) J. Pascual and R. Granados, *Anales fis. y quim. (Madrid)*, **40**, 946 (1944), describe the preparation, in 31% yield, of (1-ethoxy-2,2-

Although tricyanovinyl compounds do not react with tertiary amines, they react readily with ammonia and primary and secondary amines to give the corresponding 1-amino-2,2-dicyanovinyl derivatives VIII.



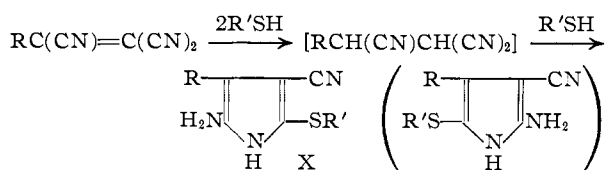
The same derivatives are obtained by ammonolysis of the corresponding 1-alkoxy intermediates.<sup>6</sup> In this manner tricyanovinylbenzene and 4-(tricyanovinyl)-N,N-dimethylaniline have been converted to the corresponding amino derivatives by reaction with ammonia, aniline, *p*-chloroaniline, diethylamine and dimethylamine. The amino derivatives obtained are neutral and similar in this respect to the analogous carboxylic acid amides.

Reaction of tricyanovinyl compounds with sodiomalonitrile in ethanolic or inert (tetrahydrofuran) media gives the corresponding 2-substituted-1,1,3,3-tetracyanopropenes (IX).



In this way tricyanovinylbenzene and 4-(tricyanovinyl)-N,N-dimethylaniline are converted to the corresponding tetracyanopropenes, isolated as the sodium salts.<sup>7</sup> The intermediate 1-alkoxy compounds can be converted similarly to the tetracyanopropenes by reaction with sodiomalonitrile.<sup>8</sup> Other salts, such as the less soluble tetramethylammonium salts, are prepared by metathetical reaction in aqueous solution. The free "acids" (R = C<sub>6</sub>H<sub>5</sub>, *pK*<sub>a</sub> 2.3) can be isolated by reaction of the salts with strong mineral acid or better by acidification of the salts with an acidic ion-exchange resin.

Tricyanovinyl compounds react readily with mercaptans, but the corresponding  $\alpha$ -thiol derivatives are not obtained. Instead reduction of the double bond appears to be the first step of the reaction, and the product actually isolated is a substituted pyrrole (X).



Thus tricyanovinylbenzene (R = C<sub>6</sub>H<sub>5</sub>) is converted to the corresponding pyrroles (R' = C<sub>2</sub>H<sub>5</sub>, HOC<sub>2</sub>H<sub>4</sub>) by reaction with ethyl mercaptan and 2-mercaptoethanol, respectively, in pyridine solution. The intermediate (1,2,2-tricyanoethyl)-benzene is

dicyanovinyl)-benzene by condensation of ethyl orthobenzoate with malonitrile.

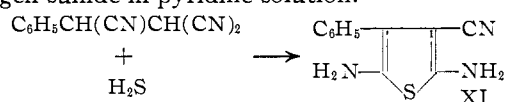
(6) C. C. Price and V. Boekelheide, *THIS JOURNAL*, **68**, 1246 (1946), describe the reaction of ethoxymethylenemalonitrile with aromatic amines to give the corresponding arylaminomethylenemalonitriles.

(7) For other examples of cyanocarbon acids see Paper V, W. J. Middleton, E. L. Little, D. D. Coffman and V. A. Engelhardt, *ibid.*, **80**, 2795 (1958).

(8) Y. Urushibara and M. Takebayashi, *Bull. Chem. Soc. Japan*, **11**, 557 (1936), describe the reaction of  $\alpha$ -ethoxyethylidenemalonitrile with sodiomalonitrile to give the corresponding tetracyanopropene (IX, R = CH<sub>3</sub>).

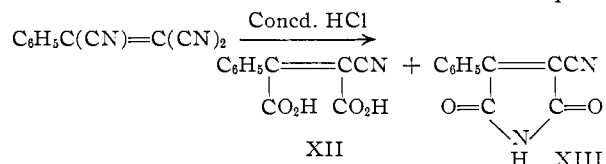
also readily converted to the same pyrroles.<sup>9</sup> The exact positions of the substituents on the pyrrole rings are not known with certainty. The physical and analytical data accommodate either formulation. The pyrrole structures have been assigned on the basis of elemental analysis and ultraviolet and infrared spectral analysis. The ultraviolet spectra ( $\lambda_{\text{max}}$  280–285 m $\mu$ ,  $\epsilon \sim 14,000$ ) indicate the presence of a conjugated ethylenic system, and the infrared spectra show the presence of an amino group, conjugated nitrile group and aromatic groups. The cyclic (pyrrole) structure fits these data better than an alternative open-chain formulation. From the reaction of (1-methoxy-2,2-dicyanovinyl)-benzene with 2-mercaptoethanol, bis-(2-hydroxyethyl) disulfide is isolated. This indicates that reduction of the double bond rather than replacement of the methoxy group is the preferred reaction.

The novel diaminothiophene (XI) is obtained by reaction of (1,2,2-tricyanoethyl)-benzene with hydrogen sulfide in pyridine solution.



The purified product is contaminated with a small amount of a blue impurity ( $\lambda_{\text{max}}$  560 m $\mu$ ) which is not readily removed by crystallization or chromatography. The thiophene structure has been assigned on the basis of physical and analytical data as well as chemical evidence. The infrared spectrum (conjugated CN, -NH<sub>2</sub> and aromatic bands) is consistent with the proposed structure, and no chemical evidence for the presence of a free mercaptan group has been obtained (negative iodine test). Condensation of the diaminothiophene with *p*-dimethylaminobenzaldehyde gives a deep red bis-arylidene derivative ( $\lambda_{\text{max}}$  509 m $\mu$ ). The formation of a bis-derivative shows the presence of two amino groups in the original compound.

Mild alkaline hydrolysis of the tricyanovinyl group causes replacement of the  $\alpha$ -cyano group as previously discussed. However, hydrolysis of tricyanovinylbenzene with concentrated hydrochloric acid gives products (XII, XIII) in which the original carbon skeleton is retained. In this respect



tricyanovinylbenzene resembles benzoyl cyanide, for hydrolysis of this acyl cyanide with acid gives benzoylformamide and benzoylformic acid. Mild heating of 2-phenyl-3-cyanomaleic acid gives the corresponding anhydride as previously described.<sup>10</sup>

## Experimental

**Tricyanoethylenes: Alkylation with TCNE.**—The tricyanoethylenes listed in Table II were prepared by reaction

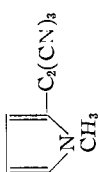
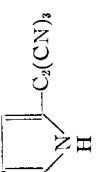
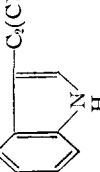
(9) Paper VIII, W. J. Middleton, V. A. Engelhardt and B. S. Fisher, *THIS JOURNAL*, **80**, 2822 (1958), describes a like reaction of TCNE with mercaptans to give substituted pyrroles.

(10) E. P. Kohler and B. B. Corson, *ibid.*, **45**, 1975 (1923).

of aromatic compounds with TCNE and include 9-(tricyanovinyl)-phenanthrene, 2-(tricyanovinyl)-N-methylpyrrole,<sup>11</sup> 2-(tricyanovinyl)-pyrrole,<sup>11</sup> 3-(tricyanovinyl)-indole<sup>11</sup> and 4-(tricyanovinyl)-2,6-dimethylphenol.<sup>12</sup>

In a typical preparation, a solution of 12.8 g. (0.1 mole) of tetracyanoethylene and 8.9 g. (0.11 mole) of N-methylpyrrole in 60 ml. of acetone was allowed to stand at room temperature for 30 minutes and was then poured into 250 ml. of water. After the black oil which precipitated had solidified, it was separated by filtration. The solid was dissolved in acetic acid, treated with decolorizing charcoal and filtered. The filtrate was diluted with water, and the greenish-yellow precipitate was recrystallized from dimethylformamide and washed with ether. There was obtained 13 g. (71% yield) of bright yellow, crystalline 2-(tricyanovinyl)-N-methylpyrrole, m.p. 182-183°.

TABLE II  
PROPERTIES OF TRICYANOETHYLENES, RC(CN)<sub>2</sub>=C(CN)<sub>2</sub>, PREPARED FROM TCNE

Tricyanoethylene	Solvent	Yield, %	M.p., °C.	Crystn. solvent	$\lambda_{max}$ , $\mu$	$\epsilon_{max} \times 10^{-3}$	Formula	Carbon, % Calcd. Found	Hydrogen, % Calcd. Found	Nitrogen, % Calcd. Found
9-C <sub>14</sub> H <sub>9</sub> C <sub>3</sub> (CN) <sub>3</sub>	THF <sup>a</sup>	24	Dec. 225	EtOH			C <sub>19</sub> H <sub>9</sub> N <sub>3</sub>	81.71 81.62	3.25 3.38	15.05 15.07
	Acetone	71	182-183	EtOH	338 <sup>a</sup>	182	C <sub>10</sub> H <sub>6</sub> N <sub>4</sub>	65.92 65.89	3.32 3.33	30.76 30.89
	Acetone	45	211-213 <sup>b</sup> d.	EtOH	428 <sup>a</sup>	257	C <sub>9</sub> H <sub>4</sub> N <sub>4</sub>	64.28 64.33	2.40 2.52	33.32 33.33
	Pyridine	76	275-276 <sup>d,e</sup>	HOAc	453 <sup>a</sup>	207	C <sub>13</sub> H <sub>6</sub> N <sub>4</sub>	71.55 71.40	2.77 2.85	25.68 25.50
4-HOC <sub>6</sub> H <sub>2</sub> (CH <sub>2</sub> ) <sub>2</sub> C <sub>2</sub> (CN) <sub>2</sub>	THF + pyridine	34	182-183 d. <sup>d</sup>	HOAc-H <sub>2</sub> O	538 <sup>f</sup> 426 <sup>g</sup>	490 212	C <sub>13</sub> H <sub>6</sub> N <sub>3</sub> O C <sub>12</sub> H <sub>6</sub> N <sub>3</sub>	69.94 70.02	4.06 4.12	18.83 18.73

<sup>a</sup> Absorption measured in acetone solution. <sup>b</sup> Infrared spectrum showed absorption at 3.0  $\mu$  (-NH). <sup>c</sup> The authors are indebted to Dr. R. E. Heckert for this preparation. <sup>d</sup> The melting point was determined on a preheated block. <sup>e</sup> Infrared spectrum showed absorption at 3.05  $\mu$  (-NH), 4.5  $\mu$  (-CN). <sup>f</sup> Solvent, ethyl alcohol + 5% triethylamine. <sup>g</sup> Solvent, ethyl alcohol + 1% acetic acid. <sup>h</sup> THF = tetrahydrofuran.

Tricyanovinylbenzene. Aldehyde Route.—Benzylidene-malonitrile was prepared by the method of Corson and Stoughton<sup>13</sup> in 92-93% yield, m.p. 84.5-85° (reported 96% yield, m.p. 83.5-84°).

- (11) R. E. Heckert, U. S. Patent 2,762,810 (1956).  
 (12) R. E. Heckert, U. S. Patent 2,762,833 (1956).  
 (13) B. B. Corson and R. W. Stoughton, THIS JOURNAL, 50, 2825 (1928).

TABLE III  
PROPERTIES OF 1-AMINO-2,2-DICYANOVINYL COMPOUNDS, RC(NR<sup>2</sup>R<sup>3</sup>)=C(CN)<sub>2</sub>

1-Amino derivative	Prepn. solvent	Yield, %	M.p., °C.	Crystn. solvent	$\lambda_{max}$ , $\mu$	$\epsilon_{max} \times 10^{-3}$	Formula	Carbon, % Calcd. Found	Hydrogen, % Calcd. Found	Nitrogen, % Calcd. Found
C <sub>6</sub> H <sub>5</sub> C(NHC <sub>6</sub> H <sub>5</sub> )C(CN) <sub>2</sub>	Pyridine	69	182-184	EtOH	322 <sup>a,b</sup>	148.5	C <sub>16</sub> H <sub>11</sub> N <sub>3</sub>	78.35 78.47	4.43 4.52	17.13 17.14 <sup>c</sup>
C <sub>6</sub> H <sub>5</sub> C(NH <sub>2</sub> )C(CN) <sub>2</sub>	Liq. NH <sub>3</sub>	36 <sup>d</sup>	182.5-184	EtOAc-C <sub>6</sub> H <sub>6</sub>	294 <sup>a,e</sup>	120.5	C <sub>10</sub> H <sub>7</sub> N <sub>3</sub>	70.99 70.76	4.17 4.30	24.84 24.75 <sup>f</sup>
C <sub>6</sub> H <sub>5</sub> C(N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> )C(CN) <sub>2</sub>	Pyridine	82	101.5-102.5	MeOH-H <sub>2</sub> O <sup>m</sup>	294 <sup>a</sup>	148	C <sub>14</sub> H <sub>16</sub> N <sub>3</sub>	74.64 74.49	6.71 6.68	18.65 18.70 <sup>g</sup>
C <sub>6</sub> H <sub>5</sub> C(NHC <sub>6</sub> H <sub>4</sub> Cl-)C(CN) <sub>2</sub>	Pyridine	55	193-196	CHCl <sub>3</sub> -hexane <sup>m</sup>	325 <sup>a</sup>	173.5	C <sub>16</sub> H <sub>10</sub> N <sub>3</sub> Cl	68.70 68.27	3.60 3.81	15.02 15.08 <sup>h</sup>
4-(CH <sub>3</sub> ) <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> (NH <sub>2</sub> )C(CN) <sub>2</sub> <sup>i</sup>	HCON(CH <sub>3</sub> ) <sub>2</sub>	62	243-244	HOAc	346, 295, 236 <sup>j</sup>	229, 106, 76	C <sub>12</sub> H <sub>12</sub> N <sub>4</sub>	67.90 66.6	5.70 5.7	26.40 25.9
4-(CH <sub>3</sub> ) <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> (N(CH <sub>3</sub> ) <sub>2</sub> )C(CN) <sub>2</sub> <sup>i</sup>	HCON(CH <sub>3</sub> ) <sub>2</sub>	62	145-145.5	EtOH	347 <sup>k</sup>	176	C <sub>14</sub> H <sub>16</sub> N <sub>4</sub>	69.97 69.9	6.71 6.7	23.32 23.3 <sup>l</sup>

<sup>a</sup> Absorption measured in chloroform solution. <sup>b</sup> Infrared spectrum showed bands at 3.1  $\mu$  (-NH) and 4.55  $\mu$  (conjugated -CN). <sup>c</sup> Mol. wt., calcd. 240. <sup>d</sup> Reaction was carried out with a solution of 0.5 mole of sodium in liquid ammonia per mole of tricyanovinylbenzene. Use of excess sodium would undoubtedly give a better yield of product. <sup>e</sup> Reaction of (1-methoxy-2,2-dicyanovinyl)-benzene with aqueous ammonia in methanol gave a quantitative yield of product. <sup>f</sup> Infrared spectrum showed bands at 2.9, 3.0, 3.1 and 6.05  $\mu$  indicative of the presence of an amino group. <sup>g</sup> Mol. wt., calcd. 169; found 170. <sup>h</sup> Chlorine, calcd. 12.68; found 12.71. <sup>i</sup> The authors are indebted to Dr. B. C. McKusick for this experiment. <sup>j</sup> Absorption measured in ethyl alcohol solution. <sup>k</sup> Absorption measured in acetone solution. <sup>l</sup> Mol. wt., calcd. 240; found 218 (neutral equivalent with perchloric acid in acetic acid). <sup>m</sup> Recrystallization followed by sublimation.

To a stirred suspension of 500 g. (3.25 moles) of benzylidenemalononitrile and 5 g. of potassium cyanide in 2 l. of anhydrous ether was added 750 ml. (19.3 moles) of commercial hydrogen cyanide. After the addition had been completed (30 minutes) the solution was homogeneous. Addition of 1 ml. of piperidine and slight warming for 3 hours were required to initiate the reaction. The solution was stirred 1.5 hours at room temperature with cooling of the reaction flask, cooled to 5° and the precipitate was filtered. The crude product was washed with cold ether, with water and dried to give 362 g. (62% yield) of (1,2,2-tricyanoethyl)-benzene, m.p. 122.5–123.5° (with previous softening) (reported<sup>13</sup> m.p. 124.5–125°). Attempts to prepare the compound from potassium cyanide<sup>13</sup> gave an impure product in low yield.

A solution of 3.00 g. (0.0165 mole) of (1,2,2-tricyanoethyl)-benzene in 40 ml. of carbon tetrachloride was heated to 50° under nitrogen and a total of 3.08 g. (0.0173 mole) of *N*-bromosuccinimide was added portionwise with stirring over a 35-minute period. The solution was stirred an additional 40 minutes, cooled to room temperature and the succinimide was separated by filtration; yield 1.77 g. The filtrate was concentrated to dryness at reduced pressure (35°) to give 4.9 g. of crude semi-solid (2-bromo-1,2,2-tricyanoethyl)-benzene. This crude product was dissolved in 50 ml. of anhydrous ether, the solution was cooled to –20°, and a solution of 1.37 g. (0.0173 mole) of pyridine in 30 ml. of ether was added dropwise with stirring over a 12-minute period. The solution was stirred an additional 5 minutes at –15 to –20° and then allowed to warm up to room temperature. The pyridine hydrobromide was removed by filtration, and the filtrate extracted twice with cold 1 *N* hydrochloric acid, with water and dried over anhydrous magnesium sulfate. Evaporation of the solvent on a steam-bath left 2.7 g. (91% yield) of crude tricyanovinylbenzene, m.p. 95.5–97.5° (with previous softening). Repeated recrystallizations from cyclohexane gave yellow prisms, m.p. 98.5–99°;  $\lambda_{\text{max}}^{\text{CHCl}_3}$  343 m $\mu$  ( $\epsilon$  16,580), 244 m $\mu$  ( $\epsilon$  5940),  $\lambda_{\text{max}}^{\text{EtOH}}$  335 m $\mu$  ( $\epsilon$  5950).

*Anal.* Calcd. for  $\text{C}_{11}\text{H}_5\text{N}_3$ : C, 73.73; H, 2.81; N, 23.45; mol. wt., 179. Found: C, 73.02, 73.35; H, 2.84, 2.98; N, 23.64, 23.44; mol. wt., 192, 188.

The conversion of (1,2,2-tricyanoethyl)-benzene to tricyanovinylbenzene directly with two equivalents of *N*-bromosuccinimide was carried out essentially as described by Miller<sup>14</sup> for the dehydrogenation of phenylsuccinic anhydride. From 3.00 g. of (1,2,2-tricyanoethyl)-benzene there was obtained 3.2 g. of crude product, m.p. 65–93°. Recrystallization from methylcyclohexane with decolorizing charcoal gave 2.32 g. (78% yield) of tricyanovinylbenzene, m.p. 96–99°.

Scale-up of these dehydrogenation reactions (100–150 g. of tricyanoethylbenzene) gave less pure product. Purification was achieved by filtration of a benzene solution of the crude product through a column of XXF Florex and elution with benzene. Yields of 55–75% of purified product were obtained.

**Tricyanovinylbenzene. Acyl Cyanide Route.**—A solution of 149 g. (1.14 moles) of benzoyl cyanide,<sup>15</sup> 5.00 g. (0.076 mole) of malononitrile, 0.66 g. of piperidine and 2.36 g. of acetic acid in 50 ml. of benzene was heated under reflux and the water formed was removed by azeotropic distillation through a continuous water separator. After 40 hours a total of 0.9 ml. of water had been collected. The solution was cooled, washed with water, and dried over anhydrous magnesium sulfate. The solvent was evaporated and the residue distilled at reduced pressure to give a recovery of 117 g. (0.89 mole) of benzoyl cyanide. The undistilled residue was recrystallized twice from cyclohexane (decolorizing charcoal was used) to give 5.63 g. (42% yield) of crude tricyanovinylbenzene, m.p. 90–96°. Another recrystallization raised the melting point to 97–99.5° (37% yield). In a reaction in which equimolar amounts of benzoyl cyanide and malononitrile were used with a reaction time of 63 hours a 21% yield of purified product was obtained.

**4-(Tricyanovinyl)-anisole.**—Condensation of *p*-anisoyl cyanide<sup>15</sup> with malononitrile was carried out in toluene solution for 19 hours. From an equimolar mixture of acyl cyanide and malononitrile, there was obtained a 6.3%

yield of crude product, m.p. 106–115°. Recrystallization from cyclohexane followed by sublimation gave deep yellow prisms, m.p. 122.5–123.5° (with previous softening);  $\lambda_{\text{max}}^{\text{CHCl}_3}$  407 m $\mu$  ( $\epsilon$  25,400), 258 m $\mu$  ( $\epsilon$  9000),  $\lambda_{\text{max}}^{\text{EtOH}}$  396 m $\mu$  ( $\epsilon$  10,500), and minor peaks at lower wave lengths.

*Anal.* Calcd. for  $\text{C}_{12}\text{H}_7\text{N}_3\text{O}$ : C, 68.89; H, 3.37; N, 20.09; mol. wt., 209. Found: C, 69.56; H, 3.36; N, 20.24, 19.94; mol. wt., 215, 210.

The tricyanovinyl compound also was obtained in low yield (~1%) by oxidation of 4-(1,2,2-tricyanoethyl)-anisole<sup>13</sup> with an equimolar quantity of lead tetraacetate in glacial acetic acid at 35–40° for 1.5 hours.

**2-(Tricyanovinyl)-furan.**—Condensation of 2-furoyl cyanide (b.p. 84–85° (11 mm.)),  $n_D^{25}$  1.5429<sup>16</sup> with malononitrile was carried out in benzene solution with a  $\beta$ -alanine-acetic acid catalyst for 31 hours. From an equimolar mixture of acyl cyanide and malononitrile, there was obtained a 6.7% yield of 2-(tricyanovinyl)-furan, m.p. 143–146°. Recrystallization from carbon tetrachloride followed by sublimation gave deep yellow needles, m.p. 145–146°;  $\lambda_{\text{max}}^{\text{CHCl}_3}$  383 m $\mu$  ( $\epsilon$  25,150), 273 m $\mu$  ( $\epsilon$  4120);  $\lambda_{\text{max}}^{\text{EtOH}}$  379 m $\mu$  ( $\epsilon$  21,900), 270 m $\mu$  ( $\epsilon$  4260), 215 m $\mu$  ( $\epsilon$  9090).

*Anal.* Calcd. for  $\text{C}_9\text{H}_5\text{N}_3\text{O}$ : C, 63.91; H, 1.79; N, 24.84; mol. wt., 169. Found: C, 63.98; H, 1.98; N, 24.56; mol. wt., 168, 169.

**2-(Tricyanovinyl)-2-methylpropane.**—Condensation of trimethylacetyl cyanide<sup>17</sup> (1.4 moles) with malononitrile (1.20 moles) was carried out in benzene solution for 54 hours. A 13% yield of crude product, m.p. 77–78°, was realized. Recrystallization from hexane gave white platelets, m.p. 78–79°,  $\lambda_{\text{max}}^{\text{EtOH}}$  251 m $\mu$  ( $\epsilon$  11,280).

*Anal.* Calcd. for  $\text{C}_9\text{H}_9\text{N}_3$ : C, 67.90; H, 5.70; N, 26.40; mol. wt., 159. Found: C, 67.91; H, 5.73; N, 26.47, 26.21; mol. wt., 172, 177.

**Diels-Alder Addition to Tricyanoethylenes. 1,2-Dimethyl-4,4,5-tricyano-5-*t*-butylcyclohexene.**—A solution of 1.00 g. (6.3 millimoles) of 2-(tricyanovinyl)-2-methylpropane and 0.015 g. of hydroquinone in 3.2 ml. (28 millimoles) of 2,3-dimethylbutadiene was heated under nitrogen in a sealed glass tube for 17 hours at 125° and finally for 12 hours at 175°. Evaporation of the solvent and recrystallization of the residue from carbon tetrachloride-hexane gave 1.23 g. (81% yield) of white prisms, m.p. 127–128°. White prisms, m.p. 128–128.5°, were obtained by an additional recrystallization from carbon tetrachloride-hexane.

*Anal.* Calcd. for  $\text{C}_{18}\text{H}_{19}\text{N}_3$ : C, 74.65; H, 7.94; N, 17.41; mol. wt., 241. Found: C, 74.93; H, 8.00; N, 17.05, 16.99; mol. wt., 220, 230.

The reaction of 14.8 g. of 2-(tricyanovinyl)-2-methylpropane with 2,3-dimethylbutadiene at 175° for 20 hours gave 19.9 g. (89% yield) of recrystallized adduct.

**1,2-Dimethyl-4,4,5-tricyano-5-phenylcyclohexene** was similarly obtained from 2,3-dimethylbutadiene and tricyanovinylbenzene in 77% yield as white prisms, m.p. 181–181.5°.

*Anal.* Calcd. for  $\text{C}_{17}\text{H}_{15}\text{N}_3$ : C, 78.13; H, 5.79; N, 16.08; mol. wt., 261. Found: C, 78.21; H, 5.66; N, 15.89, 15.82; mol. wt., 260, 255.

**4,4,5-Tricyano-5-phenylcyclohexene** was obtained from butadiene and tricyanovinylbenzene in 43% yield as a colorless solid, m.p. 122.5–126°;  $\lambda_{\text{max}}$  3.4  $\mu$  (–CH), 4.43  $\mu$  (unconjugated –CN), 5.97  $\mu$  (unconjugated C=C).

*Anal.* Calcd. for  $\text{C}_{16}\text{H}_{11}\text{N}_3$ : C, 77.23; H, 4.75; N, 18.02; mol. wt., 233. Found: C, 76.14; H, 4.73; N, 18.04, 18.08; mol. wt., 228, 235.

**1,2-Dimethyl-4,4,5-tricyano-5-(4-dimethylaminophenyl)-cyclohexene** was obtained from 2,3-dimethylbutadiene and 4-(tricyanovinyl)-*N,N*-dimethylaniline<sup>1</sup> in 71% yield. The visible spectrum showed that the crude product contained tricyanovinyl compound.<sup>1</sup> Repeated recrystallization from carbon tetrachloride of a sample which contained approximately 2% of tricyanovinyl compound gave a pale pink solid, m.p. 162–163.5°. The spectrum indicated the presence of a trace (0.02%) of tricyanovinyl compound.

*Anal.* Calcd. for  $\text{C}_{19}\text{H}_{20}\text{N}_4$ : C, 74.97; H, 6.62; N, 18.41; mol. wt., 304. Found: C, 73.56; H, 6.48; N, 18.11, 18.49; mol. wt., 315, 315.

(14) L. E. Miller, H. B. Staley and D. J. Mann, *THIS JOURNAL*, **71**, 374 (1949).

(15) J. T. Marsh and H. Stephcn, *J. Chem. Soc.*, 1633 (1925).

(16) E. Fischer and F. Brauns, *Ber.*, **46**, 892 (1913).

(17) N. Sperber and R. Pricano, *THIS JOURNAL*, **72**, 2792 (1950).

An attempt was made to regenerate 4-(tricyanovinyl)-*N,N*-dimethylaniline by pyrolysis of the Diels-Alder adduct.<sup>18</sup> At 375–400° the characteristic red color of the tricyanovinyl dye appeared, but the dye was so unstable at these temperatures that the color quickly faded.

**Alkaline Hydrolysis of Tricyanoethylenes.** 2-(1-Hydroxy-2,2-dicyanovinyl)-*N*-methylpyrrole.<sup>19</sup>—A suspension of 2.5 g. (0.014 mole) of 2-(tricyanovinyl)-*N*-methylpyrrole in 25 ml. of 10% sodium hydroxide solution was warmed until solution was complete. The pale yellow solution was cooled and acidified with hydrochloric acid. The white precipitate which formed was separated by filtration, washed with water, and recrystallized twice from water (decolorizing charcoal was used) to give 1.0 g. (42% yield) of matted, white needles, m.p. 158–159°,  $\lambda_{\text{max}}^{\text{EtOH}}$  315 m $\mu$  ( $\epsilon$  15,540).

*Anal.* Calcd. for  $\text{C}_9\text{H}_7\text{N}_3\text{O}$ : C, 62.42; H, 4.07; N, 24.27; neut. equiv., 173.2. Found: C, 62.19, 62.09; H, 4.34, 4.38; N, 24.23, 24.08; neut. equiv., 170.3, 171.5.

The product was soluble in 5% sodium bicarbonate solution. The infrared spectrum showed absorption at 2.9  $\mu$  (–OH), but no carbonyl group absorption was detected. The 1-hydroxy structure is assigned by analogy with the other base-catalyzed reactions of tricyanovinyl compounds.

2-(1-Hydroxy-2-cyano-2-carbamoyl)-*N*-methylpyrrole.—A solution of 2.0 g. (0.012 mole) of 2-(1-hydroxy-2,2-dicyanovinyl)-*N*-methylpyrrole in 50 ml. of 10% sodium hydroxide solution was heated under reflux for 18 hours. The solution was cooled and acidified with hydrochloric acid. The white precipitate which formed was separated by filtration and recrystallized from water to give 0.5 g. (23% of product in the form of white needles, m.p. 158–160°. The infrared spectrum showed absorption at 3.03, 3.15, 4.55  $\mu$ , a weak band at 5.95  $\mu$  and a stronger band at 6.2  $\mu$ . The spectrum is consistent with the proposed formulation.

*Anal.* Calcd. for  $\text{C}_9\text{H}_9\text{N}_3\text{O}_2$ : C, 56.54; H, 4.75; N, 21.98; neut. equiv., 191.2. Found: C, 56.29, 56.45; H, 4.71, 4.60; N, 22.05, 22.25; neut. equiv., 195.2, 194.8.

4-(1-Hydroxy-2,2-dicyanovinyl)-2,6-dimethylphenol<sup>19</sup> was obtained similarly from the corresponding tricyanovinyl compound in 52% yield as pale pink, matted needles, m.p. 236–238°;  $\lambda_{\text{max}}^{\text{EtOH}}$  312 m $\mu$  ( $\epsilon$  14,350), 240 m $\mu$  ( $\epsilon$  8150);  $pK_a$  2.55.

*Anal.* Calcd. for  $\text{C}_{12}\text{H}_{10}\text{N}_2\text{O}_2$ : C, 67.28; H, 4.71; N, 13.08; neut. equiv., 214.2. Found: C, 66.93, 66.84; H, 4.74, 4.71; N, 13.10, 12.95; neut. equiv., 216.4.

(1-Hydroxy-2,2-dicyanovinyl)-benzene, m.p. 75–100°, was obtained by aqueous alkaline hydrolysis of tricyanovinylbenzene. The crude product was not purified readily by crystallization, and it was converted to benzoic acid by acid-catalyzed ethanolysis followed by hydrolysis of the intermediate ester.<sup>1</sup>

**Controlled Hydrolysis of Tricyanoethylenes.**<sup>18</sup>—The rates of hydrolysis of tricyanovinylbenzene, 4-(tricyanovinyl)-*N,N*-dimethylaniline and 2-(tricyanovinyl)-2-methylpropane in boiling water at pH 4 were compared. Comparative half-lives were 5.5 hours for 4-(tricyanovinyl)-*N,N*-dimethylaniline and 0.4 hour for tricyanovinylbenzene. The rate of hydrolysis of 2-(tricyanovinyl)-2-methylpropane was too rapid to measure.

(1-Methoxy-2,2-dicyanovinyl)-benzene.—A solution of 1.98 g. (0.011 mole) of tricyanovinylbenzene and 2.50 g. (0.018 mole) of freshly fused zinc chloride in 35 ml. of methanol was heated under reflux in a system protected from atmospheric moisture with a drying tube. After 16 hours the purple solution was concentrated at reduced pressure (35°), the residue was poured into water and the aqueous solution was extracted with ether. The combined ether extracts were washed with water and dried, and the solvent was evaporated to leave a blue, semi-solid residue. Trituration of the product with cold ether gave 0.64 g. (32% yield) of crude (1-methoxy-2,2-dicyanovinyl)-benzene, m.p. 84.5–90.5°. Two recrystallizations from carbon tetrachloride-hexane (decolorizing charcoal was used) gave the purified product in the form of white prisms, m.p. 91–92°,  $\lambda_{\text{max}}^{\text{CHCl}_3}$  277 m $\mu$  ( $\epsilon$  13,100). The melting point of the product was not depressed on admixture with an authentic sample of (1-methoxy-2,2-dicyanovinyl)-benzene, m.p. 93–93.5°, pre-

pared in 54% yield from methyl orthobenzoate<sup>20</sup> and malononitrile.

*Anal.* Calcd. for  $\text{C}_{11}\text{H}_8\text{N}_2\text{O}$ : C, 71.72; H, 4.38; N, 15.21; mol. wt., 184. Found: C, 71.49; H, 4.53; N, 15.09, 15.16; mol. wt., 188, 189.

Reaction of tricyanovinylbenzene with methanol in the presence of urea as a catalyst also gave (1-methoxy-2,2-dicyanovinyl)-benzene, but the product was contaminated with starting material. Reaction in the absence of a catalyst was very slight; after 69 hours 84% of the tricyanovinylbenzene was recovered unchanged.

Reaction of tricyanovinylbenzene with an equimolar amount of sodium methoxide in methanol at 0° (2.5 hours) gave a yellow solution which was acidified with aqueous ammonium chloride and allowed to stand at room temperature overnight. From the organic extract of the reaction mixture, a crude solid was isolated by crystallization, m.p. 160–175°. A lower-melting solid was isolated from the filtrate. Sublimation of this lower-melting material gave slightly impure (1-methoxy-2,2-dicyanovinyl)-benzene, m.p. 84–88°, which was undepressed on admixture with an authentic sample. Sublimation of the higher-melting solid gave a colorless product, m.p. 182–183.5°, which was undepressed on admixture with an authentic sample of (1-amino-2,2-dicyanovinyl)-benzene prepared directly from (1-methoxy-2,2-dicyanovinyl)-benzene (see below). This product apparently was formed by ammonolysis of (1-methoxy-2,2-dicyanovinyl)-benzene during the work-up of the reaction mixture.

Similarly, (1-ethoxy-2,2-dicyanovinyl)-benzene was obtained by reaction of tricyanovinylbenzene with ethyl alcohol in the presence of urea. The product was obtained as white plates, m.p. 85.5–87.5°,  $\lambda_{\text{max}}^{\text{CHCl}_3}$  278 m $\mu$  ( $\epsilon$  13,500) (reported<sup>5</sup> m.p. 89.5–91.5°).

*Anal.* Calcd. for  $\text{C}_{12}\text{H}_{10}\text{N}_2\text{O}$ : C, 72.71; H, 5.09; N, 14.13; mol. wt., 198. Found: C, 72.63; H, 4.96; N, 13.73, 13.96; mol. wt., 200, 205.

**1-Amino-2,2-dicyanovinyl Derivatives.**—Reaction of a tricyanovinyl compound or the corresponding 1-alkoxy-2,2-dicyanovinyl derivative with ammonia or primary or secondary amines has given the corresponding 1-amino-2,2-dicyanovinyl compound. Table III summarizes the properties of the amino compounds, and a typical preparation follows.

(1-Anilino-2,2-dicyanovinyl)-benzene.—To a solution of 1.86 g. (0.02 mole) of freshly distilled aniline in 5 ml. of pyridine was added 2.01 g. (0.011 mole) of tricyanovinylbenzene in portions over a 5-minute period. The red solution was heated 1 hour on the steam-bath, poured into ice-water, and the red precipitate separated by filtration. The crude solid was triturated with cold ether and recrystallized from ethyl alcohol-water to give 1.91 g. (69%) of colorless (1-anilino-2,2-dicyanovinyl)-benzene, m.p. 182–184°. An analytical sample was obtained after repeated recrystallizations from ethyl alcohol and a final sublimation, m.p. 182–184°,  $\lambda_{\text{max}}^{\text{CHCl}_3}$  322 m $\mu$  ( $\epsilon$  14,850);  $\lambda_{\text{max}}$  3.1  $\mu$  (–NH), 4.55  $\mu$  (conjugated –CN).

A solution of 0.256 g. of 4-(1-dimethylamino-2,2-dicyanovinyl)-*N,N*-dimethylaniline in 10 ml. of methyl iodide was heated under reflux for 2 hours.<sup>18</sup> A total of 0.278 g. (68% yield) of colorless methiodide, 4-(1-dimethylamino-2,2-dicyanovinyl)-*N,N,N*-trimethylanilinium iodide, separated from solution. The methiodide was recrystallized twice from ethyl alcohol to give an analytical sample as colorless needles, m.p. 167–168°.

*Anal.* Calcd. for  $\text{C}_{13}\text{H}_{13}\text{N}_4\text{I}$ : C, 47.13; H, 5.01; N, 14.66. Found: C, 47.3; H, 4.9; N, 14.9.

The absence of color in the methiodide indicates that the quaternary nitrogen is on the benzene ring. If the quaternary nitrogen were on the side chain the product would probably be colored.

**2-Phenyl-1,1,3,3-tetracyanopropene.**—A suspension of sodiomalononitrile in ethyl alcohol (nitrogen atmosphere) was prepared by the addition of 10.3 g. (0.156 mole) of malononitrile in 16 ml. of ethyl alcohol to a solution of sodium ethoxide (from 3.57 g. of sodium) in 63 ml. of ethyl alcohol. An additional 15 ml. of ethyl alcohol was added, the suspension was cooled to 5°, and a solution of 27.8 g. (0.155 mole) of tricyanovinylbenzene in 105 ml. of benzene

(18) The authors are indebted to Dr. B. C. McKusick for this experiment.

(19) W. J. Middleton, U. S. Patent 2,726,219 (1955)

(20) S. M. McElvain and J. T. Venetable, THIS JOURNAL, 72, 1661 (1950).

was added dropwise with stirring over a 50-minute period. The homogeneous solution was stirred an additional hour at 5°, and the solvent was removed at reduced pressure (35°). The residue was triturated with benzene to leave 36.4 g. (98% yield) of crude sodium salt, m.p. >300°. Recrystallization of a sample several times from acetone-ether gave white needles, m.p. >300° (slight "yellowing" above 250°).

*Anal.* Calcd. for C<sub>13</sub>H<sub>5</sub>N<sub>4</sub>Na: C, 65.00; H, 2.10; N, 23.33; Na, 9.57. Found: C, 65.41; H, 2.33; N, 24.26, 24.31; Na, 9.5.

Reaction of sodiomalononitrile with tricyanovinylbenzene in the absence of alcohol (tetrahydrofuran as solvent) gave high yields of the sodium salt of 2-phenyl-1,1,3,3-tetracyanopropene. The salt also was obtained (in 94% yield) by reaction of (1-methoxy-2,2-dicyanovinyl)-benzene with sodiomalononitrile in ethyl alcohol.

The tetramethylammonium salt was obtained by reaction of an aqueous solution of the sodium salt with tetramethylammonium chloride. Recrystallization of the crude salt from water (with decolorizing charcoal) gave pale yellow needles having two melting points, 113.5–115° and 141.5–142.5°. After prolonged drying at 125–130° (0.1 mm.) the salt was obtained as colorless needles, m.p. 141–142.5°. The infrared spectrum showed absorption at 4.55 μ (conjugated -CN group) and a very strong band at 6.75 μ (highly resonating -C=C-).

*Anal.* Calcd. for C<sub>17</sub>H<sub>17</sub>N<sub>5</sub>: C, 70.08; H, 5.88; N, 24.04. Found: C, 69.84; H, 5.92; N, 24.06, 24.41.

An acetone solution of the tetramethylammonium salt (4.06 g.) was filtered through a 2.5 × 11 cm. column of Amberlite IR-120-H ion-exchange resin (40 g.). The column had been prepared with water and washed with 15 ml. of acetone prior to use. The column was eluted with additional acetone, and the filtrate was evaporated under a jet of nitrogen. The residue was triturated with benzene to give 3.32 g. (94% yield) of 2-phenyl-1,1,3,3-tetracyanopropene as a yellow solid, m.p. dec. 88°; λ<sub>max</sub><sup>EtOH</sup> 357 mμ (ε 22,800), 254 mμ (ε 10,550); p*K*<sub>a</sub> 2.3.

*Anal.* Calcd. for C<sub>13</sub>H<sub>5</sub>N<sub>4</sub>·2H<sub>2</sub>O: C, 61.41; H, 3.96; N, 22.04. Found: C, 62.42; H, 4.22; N, 22.01.

The acid could be dried for short periods (~1 hour) under vacuum but prolonged drying caused some decomposition. The infrared spectrum showed broad absorption in the region of 3 μ (water of crystallization), but no bond for the -NH<sub>2</sub> group of an amide was present near 6 μ. Hence all the combined water appeared to be water of crystallization.

Similarly, the sodium salt of 2-(4-dimethylaminophenyl)-1,1,3,3-tetracyanopropene was obtained by reaction of sodiomalononitrile with 4-(tricyanovinyl)-N,N-dimethylaniline. The crude sodium salt, m.p. >300°, was converted to the tetramethylammonium salt for characterization. This crude salt, m.p. 182.5° dec., was recrystallized from ethyl alcohol to give violet plates, m.p. 233–238° dec.; λ<sub>max</sub><sup>acetone</sup> 360 mμ (ε 32,300), slight hump in 500–520 mμ region.

*Anal.* Calcd. for C<sub>19</sub>H<sub>22</sub>N<sub>6</sub>: C, 68.24; H, 6.63; N, 25.13. Found: C, 67.93; H, 6.69; N, 24.91, 25.00.

**2-Amino-3(or 4)-cyano-4(or 3)-phenyl-5-ethylthiopyrrole.**—To a solution of 5 ml. (0.068 mole) of ethyl mercaptan in 10 ml. of pyridine was added 3.00 g. (0.017 mole) of tricyanovinylbenzene in portions over a 10-minute period. The solution was stoppered and allowed to stand for 3 days at room temperature. The deep red solution was poured onto ice and the aqueous solution extracted with ether. From the ether extract 0.84 g. of product, m.p. 136–139° (with previous softening), precipitated from solution. An additional 0.92 g. of product was obtained from the filtrate to give a total of 1.76 g. (43%). Recrystallization from ethyl acetate-benzene (decolorizing charcoal was used) gave a colorless solid, m.p. 132.5–135° (with previous softening), λ<sub>max</sub><sup>CHCl<sub>3</sub></sup> 281 mμ (ε 14,550). The precise melting point was dependent upon the rate of heating of the sample. An attempt to further purify the product by vacuum sublimation resulted in extensive decomposition.

*Anal.* Calcd. for C<sub>13</sub>H<sub>13</sub>N<sub>3</sub>S: C, 64.17; H, 5.38; N, 17.27; S, 13.18; mol. wt., 243. Found: C, 64.51; H, 5.43; N, 17.69, 17.45; S, 13.30; mol. wt., 245, 245.

The infrared spectrum showed bands at 2.9, 3.0, 3.1 and 6.0 μ (-NH<sub>2</sub>), 4.45 and 4.55 μ (-CN) and 6.2, 6.55 and 6.7 μ (aromatic group). Proton magnetic resonance failed to

further define the structure because of interference bands of the solvents (dioxane and dimethylformamide). The pyrrole was too weak an acid to titrate with alkali. The available data support a pyrrole structure although the exact positions of the substituents are uncertain.

The same pyrrole was obtained in 77% yield by reaction of (1,2,2-tricyanoethyl)-benzene with ethyl mercaptan in pyridine solution.

**2-Amino-3(or 4)-cyano-4(or 3)-phenyl-5-(2-hydroxyethylthio)-pyrrole.**—To a solution of 2.34 g. (0.03 mole) of 2-mercaptoethanol in 5 ml. of pyridine was added 2.50 g. (0.014 mole) of (1,2,2-tricyanoethyl)-benzene in portions over a 5-minute period. The solution was heated for 10 minutes on the steam-bath and the deep red solution poured onto ice. The oily solution was extracted with ether and the combined ether extracts washed with water and dried over anhydrous magnesium sulfate. Evaporation of the solvent left an oil which solidified after standing at 5° overnight in carbon tetrachloride solution. The solid was separated, triturated with cold ether and dried to give 2.42 g. (68% yield) of crude pyrrole, m.p. 115–121.5° (with previous softening). Recrystallization twice from chloroform (decolorizing charcoal was used) gave white needles, m.p. 118–121°, λ<sub>max</sub><sup>CHCl<sub>3</sub></sup> 283 mμ (ε 13,950).

*Anal.* Calcd. for C<sub>13</sub>H<sub>13</sub>N<sub>3</sub>OS: C, 60.21; H, 5.05; N, 16.20; S, 12.36; mol. wt., 259. Found: C, 60.08; H, 5.04; N, 15.59, 15.79; S, 12.60, 12.82; mol. wt., 230, 235.

The infrared spectrum showed the presence of an amino group (2.9, 2.95, 3.1, 6.0 μ), nitrile group (4.4, 4.5 μ), and aromatic nucleus (6.2, 6.3, 6.45, 6.7 μ).

The same product was obtained in lower yield by reaction of tricyanovinylbenzene with excess 2-mercaptoethanol.

**2,5-Diamino-3-cyano-4-phenylthiophene.**<sup>21</sup>—To 20 ml. of pyridine saturated with hydrogen sulfide was added rapidly 5.00 g. (0.028 mole) of (1,2,2-tricyanoethyl)-benzene. Hydrogen sulfide gas was passed through this solution for 8 minutes while the temperature was held below 55° by intermittent cooling. The solution was poured onto ice, the aqueous solution extracted with ether and the combined ether extracts dried over anhydrous magnesium sulfate. Evaporation of most of the solvent on a steam-bath and addition of carbon tetrachloride to the residue produced 3.78 g. (64% yield) of pale green, crude product, m.p. 84–99° (with previous softening). An alcoholic solution of the compound failed to decolorize an aqueous 0.1 *N* iodine solution, indicating the absence of a free mercaptan group. The product was partially purified by recrystallization from benzene. Final purification was achieved by filtration of an ether solution of the product through a column of XXF Florex followed by elution with ether. The product obtained was a blue-gray solid, m.p. 100–105° dec.; λ<sub>max</sub><sup>CHCl<sub>3</sub></sup> 560 mμ (ε 57.9), 300 mμ (ε 5790).

*Anal.* Calcd. for C<sub>11</sub>H<sub>9</sub>N<sub>3</sub>S: C, 61.37; H, 4.21; N, 19.52; S, 14.89; mol. wt., 215. Found: C, 62.18, 62.05; H, 4.66, 4.54; N, 18.90, 19.23; S, 14.51; mol. wt., 235, 230.

The infrared spectrum was consistent with the thiophene structure. Principal bands were present at 2.9 μ (shoulder), 2.95 μ (shoulder), 3.05 μ (-NH<sub>2</sub> or -NH), 4.55 μ (conjugated -CN) and 6.2, 6.3, 6.4, 6.5, 6.6 and 6.7 μ.

**Condensation of 2,5-Diamino-3-cyano-4-phenylthiophene with *p*-Dimethylaminobenzaldehyde.**—A solution of 1.07 g. (5.0 millimoles) of 2,5-diamino-3-cyano-4-phenylthiophene and 1.49 g. (10.0 millimoles) of *p*-dimethylaminobenzaldehyde in 10 ml. of ethyl alcohol was heated under reflux for 21 hours (nitrogen atmosphere). The solution was cooled and 1.91 g. (80% yield) of crude 2,5-bis-(4-dimethylaminobenzylideneamino)-3-cyano-4-phenylthiophene, m.p. 213–220°, was separated by filtration. The product was recrystallized twice from tetrahydrofuran to give a deep red microcrystalline solid, m.p. 239.5–241°; λ<sub>max</sub><sup>acetone</sup> 509 mμ (ε 54,900), 395 mμ (ε 24,300).

*Anal.* Calcd. for C<sub>29</sub>H<sub>27</sub>N<sub>5</sub>S: C, 72.92; H, 5.70; N, 14.67; S, 6.71. Found: C, 71.39; H, 5.85; N, 13.81, 13.76; S, 6.41.

**Hydrolysis of Tricyanovinylbenzene with Hydrochloric Acid.**—A suspension of 3.00 g. (0.017 mole) of tricyanovinylbenzene in 25 ml. of concentrated hydrochloric acid was stirred at room temperature for 6 days and then allowed to stand an additional 3 days. The suspension was poured

(21) W. J. Middleton, U. S. Patent 2,801,908 (1957).

into water, and the yellow solid was separated by filtration, washed with water and dried to give 1.2 g. (36%) of 2-phenyl-3-cyanomaleimide, m.p. 216–217.5°. Recrystallization from methanol–water gave yellow needles, m.p. 218–219°;  $\lambda_{\text{max}}^{\text{CHCl}_3}$  360 m $\mu$  ( $\epsilon$  8840), 278 m $\mu$  ( $\epsilon$  5710).

*Anal.* Calcd. for  $\text{C}_{11}\text{H}_8\text{N}_2\text{O}_2$ : C, 66.66; H, 3.05; N, 14.14; mol. wt., 198. Found: C, 66.62; H, 3.16; N, 14.27, 14.25; mol. wt., 204, 195.

The infrared spectrum showed bands at 5.6 and 5.85  $\mu$  (cyclic –CONHCO–), 3.0  $\mu$  (–NH), 4.50  $\mu$  (conjugated –CN) and 6.22, 6.27, 6.39  $\mu$  (aromatic and olefinic carbon–carbon double bonds). The proton magnetic resonance spectrum showed a peak, probably assignable to the imide hydrogen, which was displaced from the normal frequency for the hydrogen atom of a carboxyl group. These results suggest the imide formulation rather than the isomeric (1-carboxy-2,2-dicyanovinyl)-benzene. The compound showed

good thermal stability; unchanged imide was recovered after pyrolysis in the presence of “basic” lead carbonate at 300°.

Concentration of the filtrate gave 0.9 g. (25%) of crude 2-phenyl-3-cyanomaleic acid, m.p. 137–150°. The crude maleic acid was purified by recrystallization from dilute hydrochloric acid and obtained as an off-white solid, m.p. 144–148° (with previous softening),  $\lambda_{\text{max}}^{\text{EtOH}}$  292 m $\mu$  ( $\epsilon$  10,730),  $\lambda_{\text{hump}}$  220–225 m $\mu$  (reported<sup>10</sup> m.p. 145–146°).

*Anal.* Calcd. for  $\text{C}_{11}\text{H}_7\text{NO}_4$ : C, 60.83; H, 3.25; N, 6.45. Found: C, 60.24; H, 3.56; N, 6.60, 6.73.

Mild heating of 2-phenyl-3-cyanomaleic acid readily converted it to the anhydride, obtained as a deep yellow solid, m.p. 144.5–146°. Anhydride formation occurred even below the melting point of the diacid and the melting point observed for the acid is actually that of the anhydride.<sup>10</sup>

WILMINGTON, DELAWARE

[CONTRIBUTION NO. 442 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND Co.]

## Cyanocarbon Chemistry. VIII.<sup>1</sup> Heterocyclic Compounds from Tetracyanoethylene

BY W. J. MIDDLETON, V. A. ENGELHARDT AND B. S. FISHER

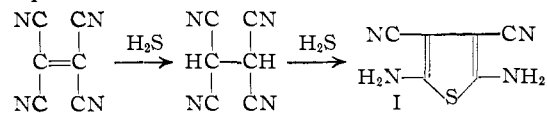
RECEIVED NOVEMBER 14, 1957

2,5-Diamino-3,4-dicyanothiophene has been prepared by the reaction of tetracyanoethylene with hydrogen sulfide. Sodium hydroxide catalyzes the rearrangement of this thiophene to 2-amino-3,4-dicyano-5-mercaptopyrrole. Thiols react with tetracyanoethylene to give 1,4-bis-(alkylthio)-1,4-diamino-2,3-dicyanobutadienes. These butadienes cyclize under acidic conditions to give either 2-amino-3,4-dicyano-5-alkylthiopyrroles or 2,5-bis-(alkylthio)-3,4-dicyanopyrroles. Reaction of tetracyanoethane with hydrogen bromide produces 2-amino-5-bromo-3,4-dicyanopyrrole, and reaction of sodium bisulfite with tetracyanoethane yields 5-amino-3,4-dicyanopyrrole-5-sulfonic acid. A number of acyl, alkyl and benzylidene derivatives of these heterocyclic compounds have been prepared and characterized.

Thiophenes and pyrroles that contain electron-donating substituents such as amino and thio groups are generally difficult to prepare and quite unstable, and consequently not much is known of their chemistry. If electron-withdrawing substituents, such as cyano groups, were also present, the resulting heterocyclic compounds would be expected to be much more stable. The discovery of a facile synthesis for tetracyanoethylene<sup>2</sup> has made readily available an intermediate which can be converted easily to 3,4-dicyanothiophenes and pyrroles that also contain amino and/or thio substituents. This paper deals with the syntheses and properties of a number of these substituted thiophenes and pyrroles.

**2,5-Diamino-3,4-dicyanothiophene.**—2,5-Diamino-3,4-dicyanothiophene was prepared by the reaction of tetracyanoethylene with sodium sulfide or hydrogen sulfide in the presence of a basic catalyst. The reaction proceeds in two steps. First, tetracyanoethylene is reduced to tetracyanoethane by the sulfide ion, and then the elements of hydrogen sulfide add to the tetracyanoethane under the influence of a basic catalyst. The stepwise nature of this reaction was demonstrated by first preparing and isolating tetracyanoethane<sup>3</sup> and then converting it to the thiophene I by treating it with sodium sulfide. When sodium sulfide was used to convert tetracyanoethylene to I, no added cat-

alyst was needed; but if hydrogen sulfide was used instead of sodium sulfide, the reaction stopped with the formation of tetracyanoethane and sulfur, and it was necessary to add a basic catalyst, such as pyridine, triethylamine or sodium hydroxide to complete the reaction.



2,5-Diamino-3,4-dicyanothiophene is almost completely insoluble in most common organic solvents with the exception of dimethylformamide. The thiophene is also high melting, and is stable up to its melting point of 240°. Molecular weight determinations in dimethylformamide indicate that the thiophene is monomeric. The basicity of the amino groups is reduced to a considerable extent, for 2,5-diamino-3,4-dicyanothiophene is insoluble in dilute mineral acids. However, the amino groups still retain some basic character. The aminothiophene was acylated easily by acetic anhydride and by benzoyl chloride in pyridine.

Stable anils were prepared from 2,5-diamino-3,4-dicyanothiophene and aromatic aldehydes. Dianils (II) were prepared from benzaldehyde, *p*-nitrobenzaldehyde, *p*-dimethylaminobenzaldehyde and *p*-bis-(2-cyanoethyl)-aminobenzaldehyde by heating the thiophene and aldehyde together at a temperature sufficient to distil the water formed in the condensation.

Under the same conditions, the monoanil was formed by reaction of the thiophene with 2,4-di-

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(3) Paper III, W. J. Middleton, R. E. Heckerl, E. L. Little and C. G. Krespan, *ibid.*, **80**, 2783 (1958).