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AND CO.]

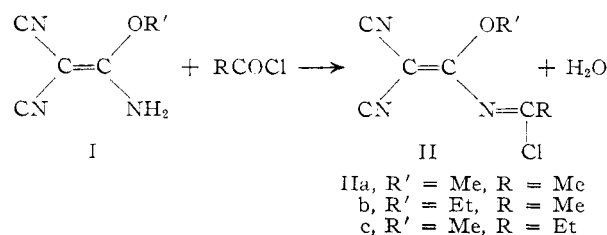
Cyanocarbon Chemistry. XIII.¹ N-(2,2-Dicyano-1-alkoxyvinyl)-imidoyl Chlorides and their Reactions

BY H. F. MOWER AND C. L. DICKINSON

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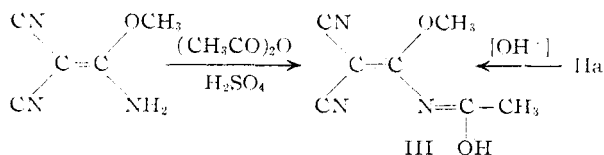
The amino moiety of 1-amino-1-alkoxy-2,2-dicyanoethylenes has been found to condense with the carbonyl group of aliphatic acid chlorides to give, with the loss of water, N-(2,2-dicyano-1-alkoxyvinyl)-imidoyl chlorides. The imidoyl chlorides easily react with amines and alcohols to form amides and esters of the corresponding imidic acids.

The reaction of a primary amine with an acyl chloride usually yields an amide. However, there are certain exceptions, such as the reaction of primary amines with the tautomeric forms of succinoyl² and phthaloyl chlorides,³ which can yield the *gem*-diamino derivatives of the corresponding anhydride. Another exception now has been found in the reaction of the amino group of 1-amino-1-alkoxy-2,2-dicyanoethylene (I)⁴ with aliphatic acid chlorides to form N-(2,2-dicyano-1-alkoxyvinyl)-imidoyl chlorides (II).



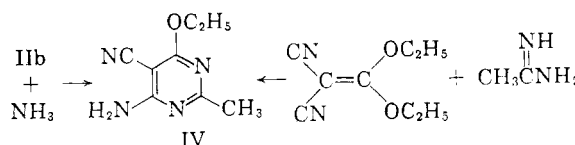
This reaction is carried out by boiling an acetone solution of the amino dicyanoethylene with a large excess of the acid chloride. The product is obtained by evaporation of the reaction medium.

The structures of the imidoyl chlorides were established by infrared spectroscopy and by syntheses of some of their derivatives by known procedures. The infrared absorption spectra of the imidoyl chlorides have strong absorption in the region of 6.30 and 6.55 μ which is indicative of the conjugated C=C and C=N structures, and the spectra are otherwise in agreement with the assigned structures. Further confirmation of the structure of the imidoyl chlorides was obtained by their facile reaction with anionic reagents to form derivatives of the corresponding imidic acids. For example, hydrolysis of IIa gave the free imidic acid III; independently, this compound was synthesized by the reaction of acetic anhydride with 1-amino-1-methoxy-2,2-dicyanoethylene.



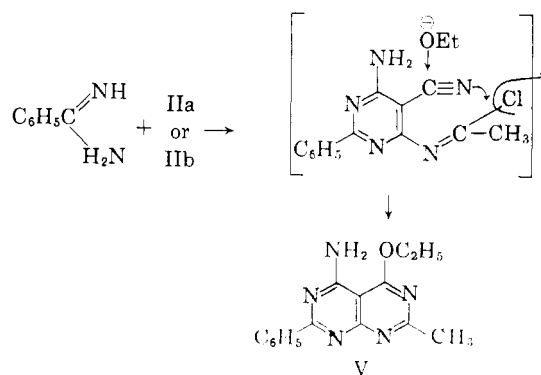
Additional evidence for the imidoyl chloride structure was furnished by the reaction of ammonia

with IIb to form the pyrimidine IV, probably *via* intermediate formation of the amide of the imidic acid. The pyrimidine was independently synthesized by condensing dicyanoketene diethyl acetal with acetamidine, a known type of reaction.⁵



Amide and ester derivatives of the parent imidic acid III can be formed easily by nucleophilic displacement reactions of the imidoyl chlorides with amines and alcohols. Some of these compounds are listed in Table I.

In addition to the simple displacement reaction of the imidoyl chlorine atom, nucleophilic attack also can take place at other centers of the molecule. For example, when IIa or b is treated in ethanol solution with benzamidine, the dipyrimidine V is formed.



It is believed that the course of the reaction involves an intermediate pyrimidine which is formed in an analogous manner to the way in which IV is formed from the dicyanoketene acetal, that is, by initial attack at the ketal carbon atom (resulting in displacement of the alkoxy group), followed by cyclization with one of the nitrile groups. The bipyrimidine V then is envisioned as arising by a concerted ring-closing reaction initiated by solvent attack upon the nitrile carbon atom.

The mechanism of the formation of II from the aminoalkoxydicyanoethylenes and acid chlorides is unknown. Two possible reaction sequences for the formation of II, both involving the intermediate

(1) For previous papers in this series see *THIS JOURNAL*, **80**, 2775 (1958).

(2) G. F. Morrell, *J. Chem. Soc.*, **105**, 1732 (1914).

(3) J. Scheiber, *Ber.*, **46**, 2366 (1913).

(4) Paper IV, W. J. Middleton and V. A. Engelhardt, *THIS JOURNAL*, **80**, 2788 (1958).

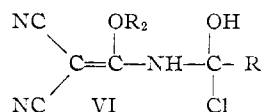
(5) Paper IX, W. J. Middleton and V. A. Engelhardt, *ibid.*, **80**, 2829 (1958).

TABLE I
 N-(2,2-Dicyano-1-alkoxyvinyl)-imidic Esters and Amides $(NC)_2C=C-N=CR$

Imidic acid R	R'	Derivative X	Yield, %	M.p., °C.	Empirical formula	Carbon, %		Hydrogen, %		Nitrogen, %	
						Calcd.	Found	Calcd.	Found	Calcd.	Found
CH ₃	CH ₃	OCH ₃	25	132	C ₈ H ₉ N ₃ O ₂	53.85	53.63	5.10	5.03	22.98	23.45
CH ₃	CH ₃	OC ₄ H _{9-n}	60	109-110	C ₁₁ H ₁₅ N ₃ O ₂	60.00	59.70	6.80	6.40	18.00	18.50
CH ₃	CH ₃	OC ₆ H ₅	75	133	C ₁₃ H ₁₁ N ₃ O ₂	64.70	65.07	4.56	4.76	17.41	17.38
C ₂ H ₅	C ₂ H ₅	OC ₂ H ₅	92	160-161	C ₁₁ H ₁₅ N ₃ O ₂	59.97	58.14	6.28	6.39	22.92	22.47
CH ₃	CH ₃	OC ₆ H ₄ Cl _{2-2,4}	82	94-95	C ₁₃ H ₉ N ₃ O ₂ Cl ₂	50.32	49.78	2.90	2.96	13.55	13.48
CH ₃	CH ₃	N(C ₂ H ₅) ₂	85	40-41	C ₁₁ H ₁₅ N ₄ O	60.00	60.30	7.27	7.17	25.42	25.51

formation of acylated product III, were suggested. In one it was supposed that HCl present in the reaction mixture might react with III to form the imidoyl chloride, and in an alternate mechanism the imidoyl chloride was thought to arise from a possible reaction of III with the excess acid chloride in the manner of an acid anhydride-acid chloride interconversion. These hypotheses were tested and shown to be invalid when the imidic acid III did not react with dry hydrogen chloride gas or with acetyl chloride under conditions used in the formation of II.

In consequence of these negative results, it is supposed that the product II arises by the direct combination of reactants to give the intermediate VI which loses water to form II.⁶



Experimental

N-(2,2-Dicyano-1-ethoxyvinyl)-acetimidoyl Chloride (IIb).—Three grams (0.022 mole) of 1-amino-1-ethoxy-2,2-dicyanoethylene³ was dissolved in 200 ml. of boiling acetone. Acetyl chloride (100 ml., 1.4 moles) was added and the reaction mixture was heated under reflux for 2 hours. After cooling, the reaction mixture was poured into a large crystallizing dish and evaporated under a stream of air to obtain the crude crystalline product. Purification was accomplished by recrystallization from petroleum ether; yield 1.3 g. (25%), m.p. 69-70°.

Anal. Calcd. for C₈H₉N₃OCl: C, 48.60; H, 4.05; N, 21.25; Cl, 17.95. Found: C, 49.18; H, 4.31; N, 20.95; Cl, 18.04.

In like manner N-(2,2-dicyano-1-methoxyvinyl)-acetimidoyl chloride (IIa) was formed by the reaction of acetyl chloride and 1-amino-1-methoxy-2,2-dicyanoethylene; yield 22%, m.p. 88°.

Anal. Calcd. for C₇H₇N₃OCl: C, 45.80; H, 3.27; N, 22.90. Found: C, 46.05; H, 3.35; N, 23.41.

N-(2,2-Dicyano-1-methoxyvinyl)-propionimidoyl Chloride (IIc).—One gram (0.009 mole) of 1-amino-1-methoxy-2,2-dicyanoethylene was dissolved in 30 ml. of dry acetone and heated to boiling. Propionyl chloride (20 ml., 0.325 mole) was added and the solution was heated under reflux for two hours. The solution then was cooled and evaporated in a stream of air to obtain a thick red oil. This oil was triturated with water to obtain a crystalline mass, which was extracted with ethyl acetate. The resulting solution was evaporated to dryness to give N-(2,2-dicyano-

1-methoxyvinyl)-propionimidoyl chloride. Recrystallization from petroleum ether gave colorless crystals melting at 44-45°, yield 50%.

Anal. Calcd. for C₈H₉N₃OCl: C, 48.60; H, 4.05; N, 21.25; Cl, 17.95. Found: C, 48.74; H, 4.18; N, 21.40; Cl, 17.48.

N-(2,2-Dicyano-1-methoxyvinyl)-acetimidic Acid (III).

A. By Hydrolysis of N-(2,2-Dicyano-1-methoxyvinyl)-acetimidoyl Chloride.—N-(2,2-Dicyano-1-methoxyvinyl)-acetimidoyl chloride (0.7 g., 0.0035 mole) was dissolved in a solution consisting of 8 ml. of water, 12 ml. of methyl alcohol and 1.1 g. of potassium carbonate. The mixture was heated under reflux for 0.5 hour and cooled and the volume of the solution diminished by half by evaporation under a stream of air to obtain a white crystalline precipitate. This material was removed by filtration and recrystallized from ethyl alcohol. It was identified as the methyl ester of N-(2,2-dicyano-1-methoxyvinyl)-acetimidic acid; yield 0.16 g. (25%), m.p. 132°.

Anal. Calcd. for C₈H₉N₃O₂: C, 53.85; H, 5.10; N, 22.98. Found: C, 53.65; H, 5.03; N, 23.45.

The filtrate from above was acidified to give a second compound. This compound was recrystallized from water and identified as N-(2,2-dicyano-1-methoxyvinyl)-acetimidic acid; yield 0.17 g. (30%), m.p. 239-241° dec.

Anal. Calcd. for C₇H₇N₃O₂: C, 50.90; H, 4.25; N, 24.45. Found: C, 51.20; H, 4.22; N, 24.95.

The compound is acidic, being soluble in cold potassium carbonate and insoluble in cold dilute acids. Its infrared spectrum shows broad absorption in the region of 5.5 μ and sharp peaks at 6.05, 6.25, 6.40 and 6.70 μ , indicating the presence of both carbonyl and hydrogen-bonded hydroxyl groups, and suggesting a tautomeric mixture of the keto and enol forms.

N-(2,2-Dicyano-1-methoxyvinyl)-acetimidic Acid (III).

B. By Acetylation of 1-Amino-1-methoxy-2,2-dicyanoethylene.—1-Amino-1-methoxy-2,2-dicyanoethylene (2.0 g., 0.018 mole) was dissolved in 15 ml. of acetic anhydride and heated to reflux. One drop of concentrated sulfuric acid was added and refluxing continued for 10 minutes. The dark-red reaction mixture was cooled slowly and then allowed to evaporate to dryness in an air draft. The solid residue was recrystallized from water and from ethyl alcohol; yield 0.89 g. (40%), m.p. 243-244° dec. A mixed melting point with the sample prepared in procedure A was 241-242°.

Anal. Calcd. for C₇H₇N₃O₂: C, 50.90; H, 4.25; N, 24.45. Found: C, 51.34; H, 4.65; N, 25.02.

4-Amino-5-cyano-6-ethoxy-2-methylpyrimidine (IV) from Dicyanoketene Acetal.—To a solution of 0.71 g. (0.031 g.-atom) of sodium in 20 ml. of ethanol was added 5.95 g. (0.036 mole) of dicyanoketene diethyl acetal and 3.45 g. (0.03 mole) of acetamide hydrochloride. After 30 minutes, 50 ml. of water was added and 4.40 g. (82% yield) of 4-amino-5-cyano-6-ethoxy-2-methylpyrimidine was collected. The sample was recrystallized from ethanol for analysis. The melting point in a sealed capillary tube was 233.5-235°.

Anal. Calcd. for C₈H₁₀N₄O: C, 53.93; H, 5.62; N, 31.46. Found: C, 54.06; H, 5.58; N, 31.57.

4-Amino-5-cyano-6-ethoxy-2-methylpyrimidine (IV) from N-(2,2-Dicyano-1-ethoxyvinyl)-acetimidoyl Chloride and Ammonia.—Ten ml. of ethanol saturated with ammonia was added to 0.99 g. (0.005 mole) of N-(2,2-dicyano-1-ethoxyvinyl)-acetimidoyl chloride and the resulting solution was allowed to stand overnight; 10 ml. of water was added,

(6) The referee made some helpful suggestions concerning the mechanism. He pointed out that the loss of water from VI may be facilitated by the decreased basicity of the nitrogen atom, which in this case is much lower than in usual amides.⁷ The stability of the product is increased by formation of a conjugated system in the imidoyl chloride. The loss of HCl from VI would result in the formation of an amide with a less stable, cross-conjugated system.

(7) The basicity of the 1-amino-1-alkoxy-2,2-dicyanoethylenes is discussed in Paper IV of this series: W. J. Middleton and V. A. Engelhardt, *This Journal*, **80**, 2790 (1958).

causing 0.55 g. (51% yield) of 4-amino-5-cyano-6-ethoxy-2-methylpyrimidine to precipitate. The infrared spectrum of this sample was identical with the spectrum of the material prepared from acetamidine and dicyanoketene acetal.

Preparation of Amide and Ester Derivatives of the N-(2,2-Dicyano-1-alkoxyvinyl)-imidic Acids.—The same general procedure was used to obtain all the ester and amide derivatives listed in Table I. To illustrate the procedure the preparation of the phenyl ester is described in detail.

Phenol (2.82 g., 0.029 mole) was dissolved in 20 ml. of dry tetrahydrofuran and 0.69 g. (0.03 g.-atom) of sodium was added. The solution was stirred until the sodium had dissolved. N-(2,2-Dicyano-1-methoxyvinyl)-acetimidoyl chloride (5.0 g., 0.027 mole) was added and the solution was stirred for 0.5 hour and then heated to boiling and evaporated to one-half of its original volume. Anhydrous ethyl ether (25 ml.) was added and the mixture was cooled and filtered. The filtrate was evaporated to dryness to obtain a crystalline solid. This material was recrystallized from ether. The physical properties of the phenyl ester of N-(2,2-dicyano-1-methoxyvinyl)-acetimidic acid are reported in Table I.

5-Amino-4-ethoxy-2-methyl-7-phenylpyrimido[4,5-d]pyrimidine (V).—To a solution of 0.70 g. (0.03 g.-atom) of sodium in 25 ml. of ethanol was added 7.61 g. (0.634 mole) of benzamidinium hydrochloride trihydrate followed by 3.96 g. (0.02 mole) of N-(2,2-dicyano-1-ethoxyvinyl)-acetimidoyl chloride. The mixture was stirred for two hours at room temperature and then filtered. The solid was collected and washed with water to yield 1.25 g. (22%) of the crude dipyrimidine. Further purification was accomplished by recrystallization from dimethylformamide; m.p. 264.5°.

Anal. Calcd. for $C_{15}H_{15}N_5O$: C, 64.13; H, 5.33; N, 24.91. Found: C, 64.58; H, 5.64; N, 25.03.

The same results were obtained by using N-(2,2-dicyano-1-methoxyvinyl)-acetimidoyl chloride as the starting mate-

rial. The infrared spectrum is in agreement with the above structure, indicating the presence of all the functional groups.

The ethanol filtrate from above was evaporated almost to dryness, treated with water and filtered. The solid that was collected was identified as the ethyl ester of N-(2,2-dicyano-1-ethoxyvinyl)-acetimidic acid; yield 2.70 g. (65%). This latter compound is formed by a competing reaction and is not an intermediate leading to the dipyrimidine. This point was established when it was shown that the ethyl ester of III did not react with benzamidinium under the conditions used in formation of the dipyrimidine.

Attempted Preparation of N-(2,2-Dicyano-1-methoxyvinyl)-acetimidoyl Chloride from the Imidic Acid II and Hydrogen Chloride.—N-(2,2-Dicyano-1-methoxyvinyl)-acetimidic acid (2.0 g.) was dissolved in 50 ml. of boiling acetone. The solution was saturated slowly with dry hydrogen chloride. After the solution was cooled and allowed to stand overnight, a crystalline precipitate was obtained (m.p. 148–149°). This solid dissolved rapidly in water to form solutions which gave an immediate precipitate with silver nitrate. Upon careful neutralization of the cold aqueous solution, 1.8 g. of the starting material was obtained and identified by the mixed melting point method.

Attempted Preparation of N-(2,2-Dicyano-1-methoxyvinyl)-acetimidoyl Chloride from the Imidic Acid II and Acetyl Chloride.—N-(2,2-Dicyano-1-methoxyvinyl)-acetimidic acid (1.0 g.) was dissolved in 20 ml. of boiling acetone. Acetyl chloride (15 ml.) was added and the mixture was heated under refluxing conditions for 8 hours. The solution was cooled and allowed to evaporate under a stream of air. The residue weighed 0.93 g. and was identified as the starting material II by mixed melting points and infrared analysis.

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[CONTRIBUTION NO. 518 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO.]

Cyanocarbon Chemistry. XIV.¹ Formation of a Bicyclo[2.2.0]hexane from Tetracyanoethylene

By J. K. WILLIAMS

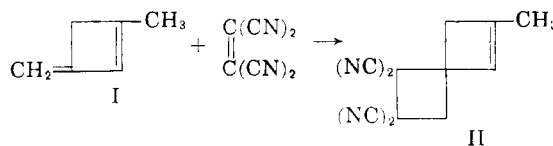
RECEIVED JANUARY 22, 1959

Cyclobutane ring formation occurs when tetracyanoethylene reacts with certain dienes, and in one case a bicyclo[2.2.0]-hexane has been obtained.

Recent reports from this Laboratory have described the chemistry of tetracyanoethylene and have discussed its high reactivity as a dienophile in the Diels-Alder reaction.² Blomquist and Meinwald^{3a,b} have shown that tetracyanoethylene in the presence of a diene that is incapable of forming a Diels-Alder adduct may react by cycloaddition to form a cyclobutane.

We have found that 1-methyl-3-methylenecyclobutene (I)^{4,5} reacts with tetracyanoethylene to give 2-methyl-5,5,6,6-tetracyanospiro[3.3]hept-1-ene (II) in a manner analogous to the formation of 1-methyl-2,3-diphenyl-5,5,6,6-tetracyanospiro[3.3]hept-1-ene from 1-methyl-2,3-diphenyl-4-methyl-

enecyclobutene and tetracyanoethylene reported by Blomquist and Meinwald.^{3b} The structure of II is based largely upon infrared and nuclear magnetic



resonance (n.m.r.) spectra. The double bond stretching vibration in the infrared occurs at $6.10\ \mu$, a position consistent with an isolated, monosubstituted double bond in a four-membered ring.⁶ The n.m.r. spectrum⁷ of II showed resonance peaks

(1) Paper XIII, H. F. Mower and C. L. Dickinson, *THIS JOURNAL*, **81**, 4011 (1959).

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

(3) (a) A. T. Blomquist and Y. C. Meinwald, *ibid.*, **79**, 5316 (1957); (b) A. T. Blomquist and Y. C. Meinwald, Abstracts of Papers, 133rd Meeting of A.C.S., San Francisco, Calif., 1958, p. 77-N.

(4) J. K. Williams and W. H. Sharkey, *ibid.*, **81**, in press (1959).

(5) F. F. Caserio, S. H. Parker, R. Piccolini and J. D. Roberts, *ibid.*, **80**, 5507 (1958).

(6) F. F. Cleveland, M. J. Murray and W. S. Gallaway, *J. Chem. Phys.*, **15**, 742 (1947); **16**, 158 (1948).

(7) N.m.r. spectra were obtained by means of a high resolution nuclear magnetic resonance spectrometer and associated electromagnet, both manufactured by Varian Associates, Palo Alto, Calif., operating at 40 Mc. and approximately 10,000 gauss. Spectra were calibrated in terms of displacements in cycles per second (c.p.s.) from the proton resonance of H₂O. Negative frequency displacements indicate resonances occurring at higher fields relative to the reference.