Reactions of Nitriles. I. Synthesis of Propiolonitrile from Acetylene and Hydrocyanic Acid

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A new synthesis of propiolonitrile is described. At 770 to 975° and in the absence of added catalysts, acetylene and hydrocyanic acid react to form propiolonitrile, acrylonitrile, cyanogen, and hydrogen. The specificity of the reaction for propiolonitrile increases with temperature in the range studied. Pyrolysis of acrylonitrile at 770 to 935° gave low yields of propiolonitrile.

Of the many examples of vapor phase reactions of acetylene with hydrocyanic acid and other nitriles, most concern the addition of hydrocyanic acid to acetylene at 300–800° over solid catalysts to give acrylonitrile.[1] None of these mentions any formation of acetylenic nitriles under any conditions but several workers concede unattractive yields of acrylonitrile in the range of 700–900° in the absence of catalysts. Earlier, it was reported that acetylene, hydrocyanic acid, and hydrogen at 950° gave some pyridines and numerous condensed aromatic compounds.[2] Under conditions of higher pressure, lower temperature, and basic catalysis, pyridines and pyrimidines are formed.[3] Recently it was stated that substantially no nitriles were produced from alkynes and cyanogen or hydrocyanic acid above 800° in the absence of catalysts.[4] In contrast, Comp has obtained propiolonitrile in yields up to 95% based on converted acetylene by the uncatalyzed reaction of cyanogen and acetylene at 800–900°.[5] The good yield may be attributed to the high dilution of acetylene in cyanogen or inert gas. The over-all reaction is illustrated by the equation

$$HC\equiv CH + NC{-}CN \longrightarrow HC\equiv C{-}CN + HCN \qquad (1)$$

Another relevant thermal route to acetylenic nitriles is the dehydrogenation of propionitrile and β-phenylpropionitrile over metal oxide catalysts at 600–800° to give propiolonitrile and phenylpropiolonitrile, respectively, in unstated yields.[6]

Because cyanogen was not readily available, it seemed desirable to investigate the reaction of acetylene and hydrocyanic acid under conditions similar to those of Comp. It has been found that propiolonitrile as well as acrylonitrile and cyanogen are produced by the thermal reaction of acetylene with excess hydrocyanic acid in the range of 770–975°.[7]

Hydrocyanic acid and acetylene with argon as the diluent were reacted at four temperatures from 770–975° at an approximately constant mole ratio of 4:1:7 ± 1. The mole ratios were also varied at an approximately constant temperature of 900–925°. Reaction times were maintained at 0.34 ± 0.05 sec except at 975°. At this temperature, soot plugged the reactor before an effluent sample could be taken. Sampling was possible at a contact time of 0.25 sec. The results are summarized in Table I.

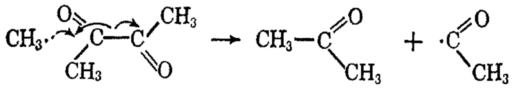
As the temperature is increased the yield of propiolonitrile increases while the yield of acrylonitrile decreases. In an attempt to establish whether or not acrylonitrile is an intermediate in the formation of propiolonitrile as this inverse relationship suggested, acrylonitrile was pyrolyzed in argon between 770 and 935° (Table II). Under conditions similar to the acetylene–hydrocyanic acid reaction, yields of propiolonitrile are lower than would be expected if acrylonitrile were an intermediate. Such a simple reaction, therefore, can perhaps be best explained by one or both of the simple metathetical primary steps

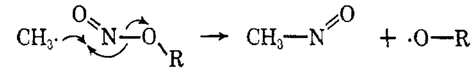
$$HC\equiv C\cdot + HC\equiv N \longrightarrow HC\equiv C{-}C\equiv N + H\cdot \qquad (2)$$

and/or

$$N\equiv C\cdot + HC\equiv CH \longrightarrow HC\equiv C{-}C\equiv N + H\cdot \qquad (3)$$

The similarity of the carbon–hydrogen bond energies of acetylene and hydrocyanic acid does not allow a preference between the acetylide or cyanide radicals as the attacking species. When compared with precedent metathetical reactions it can be seen that geometries and electric fields are similar. Apparently extended π-bonded systems are not shielded by hydrogen atoms and attack of a central atom with abstraction of a large moiety is favored over hydrogen atom abstraction, *viz*


(4)[8]


(5)[9,10]

Initiation may have been provided by 0.04% acetonitrile present as an impurity in the hydrocyanic acid. The 78-kcal α-carbon–hydrogen bond would be expected to dissociate completely above 800°. Less

$$CH_3{-}C\equiv N \longrightarrow H\cdot + \cdot CH_2C\equiv N \qquad (6)$$

$$H\cdot + HC\equiv CH \longrightarrow HC\equiv C\cdot + H_2 \qquad (7)$$

than detectable amounts of propylene or acetone in the acetylene would have served similarly.

The formation of cyanogen is unusual in the light of the equilibrium

$$2HCN \rightleftharpoons (CN)_2 + H_2 \qquad (8)$$

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[1] Too numerous to list but see, for example, C. R. Harris, U. S. Patent 2,413,623 (1946), and A. Kianpour and D. W. McDonald, U. S. Patent 2,998,443 (1961).

[2] R. Meyer and A. Tanzen, *Ber.*, **46**, 3183 (1913).

[3] T. L. Cairns, J. C. Sauer, and W. K. Wilkinson, *J. Am. Chem. Soc.*, **74**, 3989 (1952).

[4] W. L. Fierce and W. J. Sandner, U. S. Patent 3,056,826 (1962).

[5] J. L. Comp, U. S. Patent 3,079,423 (1963).

[6] I. G. Farbenind., A.-G., French Patent 790,262 (1935).

[7] L. J. Krebaum, U. S. Patent 3,079,424 (1963).

[8] F. E. Blacet and W. E. Bell, *Discussions Faraday Soc.*, **14**, 70 (1953).

[9] B. Jest and L. Phillips, *Proc. Chem. Soc.*, 73 (1960).

[10] P. Gray and P. Rathbone, *ibid.*, 316 (1960).

TABLE I

THERMAL CYANATION OF ACETYLENE WITH HYDROCYANIC ACID

Run no.	1	2	3	4	5	6	7	8
Temp, °C	770	820	875	975	920	925	900	900
Reaction time, sec	0.36	0.39	0.38	0.25	0.34	0.38	0.30	0.31
Mole ratio, HCN:C_2H_2:argon	4:1:8	4:1:7	4:1:7	4:1:6	5.5:1:2.5	6.5:1:0.6	14.1:1:0.5	15.0:1:40.4
Conversion, %								
C_2H_2	17	25	40	76	84	89	70	73
HCN	2	3	4	4	4	3	3	4
Yields on C_2H_2 converted, %								
Propiolonitrile	2	4	6	8	8	7	21	31
Acrylonitrile	22	29	20	4	8	8	16	21
Acetonitrile	7	1	2	1	1	2	3	2
Methane	2	1	1	1	1	2	1	1
Ethylene	Trace	0	0	Trace	7	9	22	24
Benzene	24	29	23	3	1	5	10	10
Tars	11	13	28	73	68	68	24	11
Yields on HCN, converted, %								
Propiolonitrile	4	9	14	37	34	29	35	41
Acrylonitrile	39	71	43	19	33	31	27	27
Acetonitrile	12	6	9	9	11	13	9	6
Cyanogen	11	6	6	16	19	25	28	26

TABLE II

PYROLYSIS OF ACRYLONITRILE

Run no.	1	2	3	4
Temp, °C	770	830	885	935
Reaction time, sec	1.17	0.63	0.55	0.43
Mole ratio, acrylonitrile: argon	1:4.3	1:11.2	1:14.2	1:12.9
Acrylonitrile converted, %	23	46	80	98
Yields on acrylonitrile converted				
Propiolonitrile	11	12	8	3
Hydrocyanic Acid	35	65	80	93
Acetylene	11	21	28	23
Tars	3	13	24	58

which is generally considered to lie essentially to the left below 1000° and because hydrogen produced by the other reactions should force the reaction further to the left. One possibility is oxidation by acetylene.

$$\mathrm{HC{\equiv}CH + 2HCN \longrightarrow NC{-}CN + H_2C{=}CH_2} \tag{9}$$

More cyanogen than ethylene is formed but ethylene cannot be expected to survive under the conditions of the reactions. Their yield trends are comparable (Table I). Propiolonitrile could be an oxidant also.

$$\mathrm{2HCN + HC{\equiv}C{-}C{\equiv}N \longrightarrow NC{-}CN + H_2C{=}CH{-}CN} \tag{10}$$

Of practical interest is the fact that cyanogen could be recycled and propiolonitrile yields improved to the range of Comp's yields from cyanogen.[5]

Benzene yields were erratic. Tar formation increased with temperature and decreased with dilution by argon or hydrocyanic acid. It appears by interpolation that dilution with hydrocyanic acid is more effective than with argon. In addition to the products listed in Table I, trace amounts of ethane, butadiene, vinylacetylene, biacetylene, toluene, styrene, naphthalene, acenaphthalene, anthracene, malononitrile, succinonitrile, fumaronitrile, dicyanoacetylene, crotononitrile, 1-cyanobutadiene, isomeric cyanovinylacetylenes, benzonitrile, tolunitrile, and cyanonaphthalenes were detected by mass spectroscopy. They totaled less than 1.0 mole % of the products and no quantitatively significant trends were discernable among them. Some qualitative observations of significance were that succinonitrile was detected only at the two lowest temperatures whereas fumaronitrile and dicyanoacetylene were observed only at the higher temperatures.

Experimental Section

Apparatus.—The reaction vessels were unpacked silica "Vycor" tubes mounted horizontally in a radiant furnace. The effective reactor length was 20 cm defined by a temperature variance of less than ±20°. Vessels of inside diameters from 0.50 to 2.00 cm were used to extend the range of reaction times (0.10 to 10.0 sec) beyond the limitations of the feed system. Preceding the reactor was an electrically heated, 25-cc spherical mixing chamber with a sampling outlet and an intake manifold for eight feeder lines. The mixing chamber was maintained at 120° for most experiments. Gases were introduced from cylinders *via* pressure regulators, Fisher–Porter floating-ball flowmeters, and Moore Products Co. Type 63SU upstream pressure controllers into the mixing chamber. Liquids were introduced from pressured reservoirs *via* steam or electrically heated vaporizers, electrically heated lines, jacketed electrically heated flowmeters, and similarly heated pressure controllers into the mixing chamber.

The sampling devices at the end of the reactor and at the mixing chamber consisted of electrically heated, 100-cc bulbs in the effluent streams fitted with quick couplings to evacuated 1.7-l. bombs and valves which simultaneously by-passed and blocked in the bulbs. The bulbs were heated to 180° in most experiments and bombs were evacuated to 10^{-4} mm resulting in samples at *ca.* 50 mm.

Samples were analyzed by a modified Consolidated Electrodynamics Model 21-103B mass spectrometer from the bombs heated to 200° through an inlet system heated to 140°. The instrument was calibrated with synthetic samples of hydrocarbons from methane to methylnaphthalenes, nitriles from hydrocyanic acid to cyanonaphthalenes, and other gases used as diluents or catalysts. Mixtures of up to 30 compounds could be analyzed to ±0.1 mole %.

General Procedure.—The temperature of the furnace was allowed to stabilize while an inert gas was passed through. The reactants were then introduced rapidly in order of decreasing thermal stability and after 1 min the mixing chamber was sampled. The gas was allowed to flush the bulb for 15 sec, and then the bulb was blocked in and bypassed. The contents of the bulb were then evacuated into the sample bomb. After again stabilizing the system for 1 min, the reactor effluent was sampled in the same way. The reactant compositions calculated by flowmeter calibration, inlet sampling, and back calculation from the products were in excellent agreement.

Yields and conversions were calculated from the stoichiometric equations in the Discussion and checked for hydrogen balance. Tars were determined gravimetrically and analyzed from 93 to 95% C, 5 to 8% H, and less than 0.3 % N.

Specific reaction conditions are summarized in Table I.

Acknowledgments.—The author is indebted to K. Allen Pinkerton for the calibration and interpretations of the mass spectra and to Dr. Keith M. Taylor for his invaluable advice.

Reaction of Heterocyclic Polycarbonyl Compounds with Phosphite Esters. Alloxan and Parabanic Acid[1,2]

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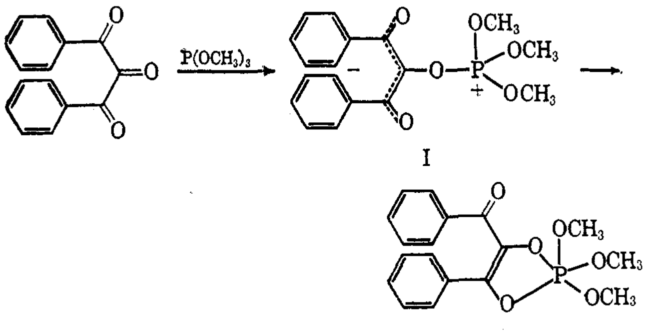
Trimethyl phosphite reacted with anhydrous alloxan at 22° and gave 5-hydroxy-6-methoxyuracil 5-dimethyl phosphate (XIII) in 92% yield. The reaction of the phosphite with alloxan monohydrate afforded the same enediol phosphate XIII in 30% yield, plus 5-hydroxybarbituric acid 5-dimethyl phosphate (XIX) in 40% yield. The two phosphates, XIII and XIX were converted into the same 5-hydroxy-2,4,6-trimethoxypyrimidine 5-dimethyl phosphate (XIV) by diazomethane. Alkylation of XIII with dimethyl sulfate gave the pyrimidine phosphate XIV in 20% yield, plus 1-methyl-2,4-dimethoxy-5-hydroxy-6(1)-pyrimidone 5-dimethyl phosphate (XXII) in 40% yield. Dimethyl phosphite converted alloxan or its monohydrate into 5-hydroxybarbituric acid 5-dimethyl phosphate (XIX) in 75% yield. Parabanic acid failed to react with trimethyl phosphite and with dimethyl phosphite. N,N′-Dimethylparabanic acid was converted into N-tetramethylbiparabanyl (XXV) in 91% yield by boiling triethyl phosphite. The biparabanyl XXV was hydrogenated to a mixture (80:20) of diastereomeric dihydrobiparabanyls (XXVI and XXVII).

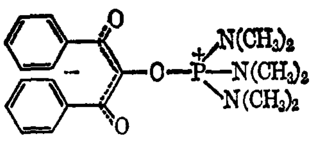
The reaction of trimethyl phosphite with 1,3-diphenylpropanetrione gave a 1,3,2-dioxaphospholene (II) with pentacovalent phosphorus.[3] The suspected dipolar intermediate I could not be detected.



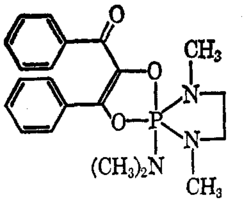
I

II, $\delta_{P^{31}} = +49.3$ ppm *vs.* H_3PO_4

The product of the reaction of trisdimethylaminophosphine with 1,3-diphenylpropanetrione was the crystalline dipolar adduct III, which showed no tendency to form a phosphorane.[4] However, when the carbon atoms of the aminophosphine were linked in the form of a five-membered ring, the resulting adduct had, again, a dioxaphospholene structure IV.[5]

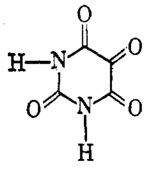


III, $\delta_{P^{31}} = -35.9$ ppm

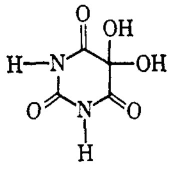


IV, $\delta_{P^{31}} = +31.9$ ppm

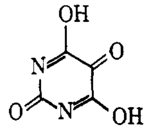
This paper is concerned with the reaction of heterocyclic polycarbonyl compounds with trialkyl phosphites. We have studied the behavior of alloxan (V) and of its monohydrate[6] (VI). This acidic (pK = 6.6) cyclic ureide can exist in several tautomeric forms like Va and Vb, which have quinonoid character.



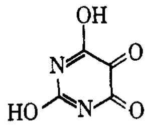
V



VI



Va



Vb

It is known[7] that trialkyl phosphites convert *p*-benzoquinone into an alkyl ether of a *p*-quinol phosphate (VIII); *i.e.*, the intermediate dipolar adduct VII underwent an alkyl group translocation. On the other hand, the reaction of the phosphite with an *o*-quinone[8] led to the dioxaphospholene IX as in the case of the triketone II.

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[1] Organic Compounds with Pentavalent Phosphorus. Part XXIV Supported by Public Health Service Research Grant No. CA-04769-07 from the National Cancer Institute, and by the National Science Foundation GP-3341.

[2] Part XXIII: F. Ramirez, A. V. Patwardhan, and C. P. Smith, *J. Org. Chem.*, **31**, 3159 (1966).

[3] F. Ramirez, A. V. Patwardhan, and C. P. Smith, *ibid.*, **30**, 2575 (1965).

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[5] F. Ramirez, A. V. Patwardhan, H. J. Kugler, and C. P. Smith, *Tetrahedron Letters*, **No. 26**, 3053 (1966).

[6] H. Biltz, *Ber.*, **45**, 3659 (1912).

[7] (a) F. Ramirez and S. Dershowitz, *J. Org. Chem.*, **22**, 856 (1957); (b) *ibid.*, **23**, 778 (1958); (c) *J. Am. Chem. Soc.*, **81**, 587 (1959); (d) F. Ramirez, C. H. Chen, and S. Dershowitz, *ibid.*, **81**, 4338 (1959).

[8] For documentation see: (a) F. Ramirez, *Pure Appl. Chem.*, **9**, 337 (1964); (b) F. Ramirez, C. P. Smith, A. S. Gulati, and A. V. Patwardhan, *Tetrahedron Letters*, **No. 19**, 2151 (1966).