The α-benzyldesoxybenzoin required in the above synthesis was prepared by alkylation of desoxybenzoin with benzyl chloride in the presence of sodamide in liquid ammonia using the general procedure developed by Hauser[9] for such alkylations.

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(9) C. R. Hauser and T. M. Harris, *J. Am. Chem. Soc.*, **81**, 1161 (1959).

Diels-Alder Reactions with Dihydronaphthalenes[1]

N. C. DENO AND HARRY CHAFETZ

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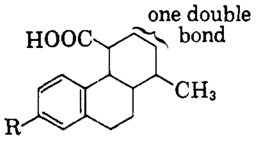
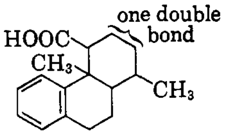
It had been shown that 1,2-dihydronaphthalene reacts with 2,4-hexadienoic acid (sorbic acid) to give a phenanthrene derivative I in 18% yield.[2] This reaction has now been extended to 7-methoxy-1,2-dihydronaphthalene and 1-methyl-3,4-dihydronaphthalene. In both cases the Diels-Alder reaction with 2,4-hexadienoic acid gave low yields of noncrystalline gums. These two products were shown to be primarily structures II and III respectively by degradation of II to 1-methyl-7-methoxyphenanthrene and III to 1-methylphenanthrene. The crude products may have been mixtures of isomers. The position of the double bond was not determined.



I. R = H
II. R = CH3O



III

The structural isomer formed in these reactions is analogous to that formed when 2,4-hexadienoic acid reacts with styrene and its derivatives.[2] In all of these reactions, the number two carbon atom of 2,4-hexadienoic acid bonds to the α-carbon of the phenylolefin system and the number five carbon atom bonds to the β-carbon of the phenylolefin.

EXPERIMENTAL

7-Methoxy-1,2-dihydronaphthalene plus 2,4-hexadienoic acid. 7-Methoxy-1,2-dihydronaphthalene was prepared by the following sequence: β-Naphthol was hydrogenated to 1,2,3,4-tetrahydro-6-hydroxynaphthalene by the method of Stork.[3] The conversion to the methyl ether was effected with methyl sulfate.[4] Oxidation with lead tetraacetate and thermal removal of acetic acid gave 7-methoxy-1,2-dihydronaphthalene.[5]

7-Methoxy-1,2-dihydronaphthalene was treated with 2,4-hexadienoic acid in a manner similar to that used with 1,2-dihydronaphthalene.[2] Dimethylaniline was added to the extent of one-fourth the total weight of the reactants and 2% by weight of hydroquinone was also added. An atmosphere of carbon dioxide was employed. Variation in the ratio of reactants from equimolar to 1:2 and 2:1 seemed to have little effect. Raising the temperature of the reaction from 140° to 190° increased the yield of distillable product from 6 to 12.5% and lowered the yield of acidic copolymer from 35 to 12%. The runs were held at these temperatures for 100 to 150 hr.

The product II was collected as a hard, yellow gum, b.p. 150–200° (1 mm.). The neutral equivalent was 274, which agrees with 272 which is that calculated for $C_{17}H_{20}O_3$.

The carbon skeleton of the adduct was indicated by its degradation to 1-methyl-7-methoxyphenanthrene. A mixture of 0.95 g. of adduct and 0.4 g. of 10% palladium-carbon catalyst was heated for 20 min. at 300–315° in a carbon dioxide atmosphere. The crude product was dissolved in acetone and the catalyst was removed by filtration. The acetone was replaced by benzene and the solution washed with aqueous alkali. After evaporative distillation and recrystallization of the distillate from methanol, 40 mg. (5%) of white plates, m.p. 134–135°, were isolated. The melting point was not depressed when mixed with an authentic sample of 1-methyl-7-methoxyphenanthrene.[6]

1-Methyl-3,4-dihydronaphthalene plus 2,4-hexadienoic acid. 1-Methyl-3,4-dihydronaphthalene was prepared by the method of English and Cavaglieri.[7]

A mixture of 35 g. of this compound, 22.4 g. of 2,4-hexandienoic acid, 5 ml. of dimethylaniline, and 1.5 g. of hydroquinone was heated at 190° for 100 hr. in a carbon dioxide atmosphere. An ether solution of the reaction mixture was extracted with 5% potassium hydroxide solution and the aqueous extract precipitated with dilute hydrochloric acid. Evaporative distillation of the precipitated acid at 170–210° (1 mm.) gave 6.2 g. (12%) of distillate and 6.4 g. (12.5%) of acidic copolymer. The distillate was a hard yellow, acidic gum and is believed to possess structure III. The position of the double bond is uncertain.

The carbon skeleton of III was indicated by its degradation to 1-methylphenanthrene. The experimental conditions were identical with those used in the degradation of II to 1-methyl-7-methoxyphenanthrene. The yield of 1-methylphenanthrene, m.p. 117–119°, was 30%. The melting point was not depressed when mixed with an authentic sample of 1-methylphenanthrene and the identity was further checked by preparation of the picrate, m.p. 134–137°.

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(1) Grateful acknowledgment is made for the support of this research by the Bristol Laboratories Inc., Syracuse, N. Y.

(2) N. Deno, *J. Am. Chem. Soc.*, **72**, 4057 (1950).

(3) G. Stork, *J. Am. Chem. Soc.*, **69**, 576 (1947).

(4) V. C. Burnop, G. M. Elliot, and R. P. Linstead, *J. Chem. Soc.*, 727 (1940).

(5) W. S. Johnson, J. M. Anderson, and W. E. Shelberg, *J. Am. Chem. Soc.*, **66**, 218 (1944).

(6) This sample was kindly supplied by Dr. Andre S. Dreiding of the Detroit Institute for Cancer Research.

(7) J. English, Jr., and G. Cavaglieri, *J. Am. Chem. Soc.*, **65**, 1085 (1943).

Preparation of Some Bicyclic Nitriles by the Diels-Alder Reaction

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As part of a program to relate the dielectric properties of some nitriles to their structures it became necessary to prepare some bicyclic nitriles of established configuration.

Alder and co-workers[1] have recently reported that acrylonitrile and cyclopentadiene react to give a mixture that is 60% 5-*endo*-cyano-2-norbornene and 40% 5-*exo*-cyano-2-norbornene. They found that this ratio of isomers was not greatly affected by changing the temperature of the reaction. They also found that the reaction between acrylonitrile and 1,3-cyclohexadiene gave about equal amounts of the 5-*exo*-cyano- and 5-*endo*-cyano-bicyclo[2.2.2]oct-2-ene. Thus, their results showed that the cyano group has little or no directing influence in the Diels-Alder reaction.

Gillois-Doucet[2], Yashunskii *et al.*[3] and Trapp[4] prepared the adduct of methacrylonitrile and cyclopentadiene without assigning a structure to it. Trapp hydrolyzed the adduct to an amide which was identical with the amide prepared from 5-*endo*-methyl-2-norbornene-5-*exo*-carboxylic acid.[5] A suggestion that this adduct is principally the *endo*-methyl *exo*-nitrile was made by Boehme *et al.*[6]

We dehydrated the amide obtained from hydrolysis of the adduct of methacrylonitrile and cyclopentadiene to yield 5-*exo*-cyano-5-*endo*-methyl-2-norbornene. The infrared spectrum of this latter compound was identical with that of the nitrile prepared directly by the Diels-Alder reaction, indicating that there was no *endo*-cyano isomer formed in this reaction.

The adduct from ethacrylonitrile and cyclopentadiene was shown to be 5-*exo*-cyano-5-*endo*-ethyl-2-norbornene since hydrolysis yielded only one amide, which proved to be identical with 5-*endo*-ethyl-2-norbornene-5-*exo*-carboxamide identified by Boehme and co-workers[6] after preparation from the corresponding acid.

When methacrylonitrile and 1,3-cyclohexadiene reacted, the adduct could not be separated from cyclohexadiene dimer by distillation. The reaction mixture was hydrolyzed to yield, exclusively, 5-*endo*-methylbicyclo[2.2.2]oct-2-ene-5-carboxamide which has been prepared by Boehme *et al.*[6] from the acid chloride of known configuration. Dehydration of the amide with phosphorous pentoxide yielded pure 5-*exo*-cyano-5-*endo*-methylbicyclo[2.2.2]oct-2-ene.

Similarly, when ethacrylonitrile and 1,3-cyclohexadiene reacted, the adduct was contaminated with cyclohexadiene dimer. Upon hydrolysis, only one amide was isolated; it was dehydrated to give a pure nitrile. Since methacrylonitrile gave the *exo*-cyano adducts with both cyclopentadiene and cyclohexadiene, and since ethacrylonitrile gave the *exo*-cyano adduct with cyclopentadiene, the adduct of ethacrylonitrile and cyclohexadiene probably also has the *exo*-cyano structure.

Chemical proof is lacking because the corresponding *endo*- and *exo*-acids are not available. The amide proved to be extremely resistant to hydrolysis, preventing proof of structure *via* the iodo lactone method.

These results indicate that alkyl groups must have considerable directing influence in Diels-Alder reactions. While it was shown by Alder *et al.*[1] that acrylonitrile reacted with cyclopentadiene to yield an adduct of a three to two *endo*-*exo* ratio, the present experiments showed that α-methacrylonitrile and α-ethacrylonitrile yielded the *exo*-cyano form exclusively.

The same conclusion can be drawn from the preparation of the adducts of 1,3-cyclohexadiene. In the acrylonitrile -1,3-cyclohexadiene adduct prepared by Alder *et al.*[1], the *endo*-*exo* ratio was about one to one. However, the adduct formed from methacrylonitrile and 1,3-cyclohexadiene was the *exo*-cyano derivative. Since only one amide could be isolated from the adduct of ethyl acrylonitrile and 1,3-cyclohexadiene, the *exo*-cyano structure has been assigned to it.

This same directing influence of alkyl groups has been observed in the reaction of α-substituted acrylic acids with cyclopentadiene. The acrylic acid–cyclopentadiene adduct has been shown to comprise a three to one mixture of *endo*- and *exo*-isomers[7], the α-methacrylic acid–cyclopentadiene adduct a one to three *endo*-*exo* mixture[5], and the α-ethacrylic acid–cyclopentadiene adduct almost exclusively the *exo* acid.[6]

The unsaturated nitriles were reduced catalytically to the corresponding saturated compounds.

The infrared spectra of the bicylic nitriles showed certain properties in common. The nitrile absorption was found at 4.5 μ, and the unsaturated nitriles exhibited maxima at 6.1 and 6.2–6.4 μ. Both 2-cyano-2-methylbicyclo-octane and 2-cyano-2-ethyl bicyclo-octane had maxima at 3.8 μ.[8] This maximum was absent in the corresponding bicyclo-octenes.

EXPERIMENTAL

5-exo-Cyano-5-endo-methyl-2-norbornene. A mixture of 377 g. (5.7 moles) of cyclopentadiene and 377 g. (5.7 moles) of methylacrylonitrile was refluxed for 8 hr. until the temperature reached 120°. The mixture was then distilled. After methacrylonitrile and cyclopentadiene dimer were removed, there was obtained 178 g., 22%, of 5-*exo*-cyano-5-*endo*-methyl-2-norbornene, b.p. 98–100°/30 mm., m.p. 61–63°

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(1) K. Alder, K. Heimbach, and R. Reubke, *Chem. Ber.*, **91**, 1516 (1958).

(2) J. Gillois-Doucet, *Ann. Chim. (Paris)*, **10**, 497 (1955).

(3) V. G. Yashunskii, A. P. Terent'ev, and Ya. G. Neklin, *Zhur. Obshcheĭ Khim.*, **26**, 723 (1956).

(4) W. B. Trapp, Thesis, University of Colorado, 1952.

(5) J. S. Meek and W. B. Trapp, *J. Am. Chem. Soc.*, **79**, 3909 (1957).

(6) W. R. Boehme, E. Schipper, W. G. Scharpf, and J. Nichols, *J. Am. Chem. Soc.*, **80**, 5488 (1958).

(7) C. D. VerNooy and C. S. Rondestvedt, Jr., *J. Am. Chem. Soc.*, **77**, 3583 (1955).

(8) J. Hine, J. A. Brown, L. H. Zalkow, W. E. Gardner, and M. Hine, *J. Am. Chem. Soc.*, **77**, 597 (1955).

(lit.[3] m.p. 55° and 30–32°[4]). Infrared absorption maxima: 10.25(s), 10.58(s), 10.62(s), 10.88(s), 11.05(s), 11.65(s), 11.78(s), 11.81(m), 12.22(s), 13.00(s), 13.75(s), 14.30(s) μ.

Anal. Calcd. for $C_9H_{11}N$: C, 81.16; H, 8.33. Found: C, 81.0; H, 8.5.

In order to prove the configuration of the nitrile, it was first hydrolyzed in alcoholic potassium hydroxide to 5-*endo*-methyl-2-norbornene-5-*exo*-carboxamide which after recrystallization from benzene melted at 157° (lit.[5] m.p. 157.5–158.5°). The infrared spectrum of this amide was identical with that of an authentic sample of 5-*endo*-methyl-2-norbornene-5-*exo*-carboxamide.[9] The amide obtained by hydrolysis was dehydrated with phosphorus pentoxide by the method of Boehme *et al.*[6] to give a 45% yield of 5-*exo*-cyano-5-*endo*-methyl-2-norbornene, b.p. 98°/28 mm., m.p. 63–64°. The spectrum of this nitrile was identical with the spectrum of the original adduct.

2-exo-Cyano-2-endo-methylnorbornane. 5-*exo*-Cyano-5-*endo*-methyl-2-norbornene (23.8 g., 0.18 mole) in 200 ml. of ethanol was hydrogenated in the presence of platinum oxide catalyst under about 20 lb. pressure at room temperature. After removal of catalyst and solvent, the residue was distilled, to yield 15 g., 62%, of 2-*exo*-cyano-2-*endo*-methylnorbornane, b.p. 116–117°/45 mm., m.p. 47–48°.

Anal. Calcd. for $C_9H_{13}N$: C, 79.95; H, 9.69. Found: C, 80.2; H, 9.6.

5-exo-Cyano-5-endo-ethyl-2-norbornene. A mixture of 84 g. (1.04 moles) ethacrylonitrile and 135 g. (2.05 moles) of cyclopentadiene was refluxed about 3.5 hr. until its temperature had risen to 140°. The product was distilled to yield 62 g., 40.5%, of 5-*exo*-cyano-5-*endo*-ethyl-2-norbornene, b.p. 101°/15 mm., n_D 1.4775, m.p. 9.5–12°. Infrared absorption maxima: 10.0(s), 10.5(s), 10.9(s), 11.32(s), 11.75(s), 12.2(s), 12.8(s), 13.75(s), 14.3(s) μ.

Anal. Calcd. for $C_{10}H_{13}N$: C, 81.58; H, 8.90. Found: C, 81.23; H, 8.6.

This nitrile was hydrolyzed in alcoholic potassium hydroxide to yield 5-*endo*-ethyl-2-norbornene-5-*exo*-carboxamide, which on recrystallization from benzene-*n*-heptane melted at 94–95° (lit.[6] 97–98°).

2-exo-Cyano-2-endo-ethylnorbornane. A solution of 30 g. (0.22 mole) of 5-*exo*-cyano-5-*endo*-ethyl-2-norbornene in 50 ml. of alcohol was hydrogenated at 40 lb. pressure at room temperature in the presence of platinum oxide catalyst. After removal of catalyst and solvent the residue was distilled to yield 26 g., 79%, of 2-*exo*-cyano-2-*endo*-ethylnorbornane b.p. 103–104°/13 mm. The analytical sample was redistilled, b.p. 96°/10 mm., $n_D^{25.5}$ 1.4708. Infrared absorption maxima: 10.0(w), 10.45(s), 10.6(m), 10.7(m), 11.45(s), 11.9(s), 12.7(s), 12.98(m), 13.12(m) μ.

Anal. Calcd. for $C_{10}H_{15}N$: C, 80.48; H, 10.13. Found: C, 80.8; H, 10.3.

5-endo-Methylbicyclo[2.2.2]oct-2-ene-5-exo-carboxamide. A mixture of 44.5 g. (0.55 mole) of 1,3-cyclohexadiene and 38 g. (0.58 mole) of methacrylonitrile was placed in a steel bomb and heated in an oil bath at 190° for 6.5 hr. Distillation of the reaction mixture gave some unchanged methacrylonitrile and 37.0 g. of crude adduct b.p. 95–100°/10 mm. The product thus obtained solidified at room temperature, but on standing overnight some liquid separated from it. It is assumed that at this stage the adduct was contaminated with some bicyclohexadiene which has nearly the same soiling point. Several attempts to purify this adduct by distillation failed to give a sample that had a satisfactory analysis.

The crude adduct was hydrolyzed with alcoholic potassium hydroxide to yield 5-*endo*-methylbicyclo[2.2.2]oct-2-ene-5-*exo*-carboxamide, which on recrystallization from ethanol-water, melted at 127–128° (lit.[6] m.p. 125–126°).

5-exo-Cyano-5-endo-methylbicyclo[2.2.2]oct-2-ene. The above amide was dehydrated by the procedure of McElvain.[10] A mixture of 62.0 g. (0.38 mole) of 5-*endo*-methylbicyclo[2.2.2]oct-2-ene-5-*exo*-carboxamide, 175 ml. of benzene, 102 g. of triethylamine, and 95 g. of phosphorus pentoxide was heated with stirring until the reaction began. After the initial exothermic reaction had subsided, the mixture was refluxed for an additional 0.5 hr. The liquid was decanted from the inorganic layer and the residue washed several times with benzene. The combined organic extracts were distilled yielding 35 g., 63% of 5-*exo*-cyano-5-*endo*-methylbicyclo[2.2.2]oct-2-ene, b.p. 127–129°/50 mm. A sample for analysis was sublimed *in vacuo* and melted at 98–99°. Infrared absorption maxima: 9.98(w), 10.22(s), 10.48(s), 10.72(s), 10.88(s), 11.49(s), 11.83(s), 12.3(s), 13.95(s), 14.2(s) μ.

Anal. Calcd. for $C_{10}H_{13}N$: C, 81.58; H, 8.90. Found: C, 81.6; H, 9.1.

2-Cyano-2-methylbicyclo[2.2.2]octane. A mixture of 15 g. (0.1 mole) of 5-*exo*-cyano-5-*endo*-methylbicyclo[2.2.2]oct-2-ene, 100 ml. of alcohol, and 0.1 g. of platinum oxide was hydrogenated under 20 lb. pressure. After removal of the catalyst, the solution was poured into water, precipitating the product which was dried over phosphorus pentoxide, yielding 13 g., 87%, of 2-cyano-2-methylbicyclo[2.2.2]octane melting at 108–109°. A sample for analysis was sublimed *in vacuo*, m.p. 108–109°. Infrared absorption maxima: 3.8(m), 9.85(w), 10.10(s), 10.29(w), 10.53(m), 10.69(m), 11.1(s), 11.35(s), 11.62(m), 11.96(m), 12.8(s), 12.48(m), 12.85(m), 14.8(m) μ.

Anal. Calcd. for $C_{10}H_{15}N$: C, 80.48; H, 10.13. Found: C, 80.4; H, 10.2.

5-endo-Ethylbicyclo[2.2.2]oct-2-ene-5-exo-carboxamide. A mixture of 50 g. (0.63 mole) of 1,3-cyclohexadiene and 40 g. (0.5 mole) of ethacrylonitrile was heated in a steel bomb to 190° for 8 hr. The reaction mixture was distilled and after a forerun of unchanged starting material there was obtained 14.5 g. of crude adduct, b.p. 133–140°/35 mm. Fractionation of this product failed to yield a pure sample of nitrile.

A mixture of 39 g. of the crude adduct, 50 g. of potassium hydroxide, 100 ml. of ethylene glycol, and 10 ml. of water was refluxed 8 hr. The cooled reaction mixture was dissolved in water and extracted with benzene. The extract was steam-distilled to remove the benzene and most of the unhydrolyzed starting material. The residual aqueous mixture was kept at 0° overnight and the solid collected by filtering. Several recrystallizations from methanol-water yielded 5-*endo*-ethylbicyclo[2.2.2]oct-2-ene-5-*exo*-carboxamide, m.p. 92°.

Anal. Calcd. for $C_{11}H_{17}NO$: C, 73.70; H, 9.56. Found: C, 74.0; H, 9.6.

5-exo-Cyano-5-endo-ethylbicyclo[2.2.2]oct-2-ene. A mixture of 28 g. (0.15 mole) of 5-*endo*-ethylbicyclo[2,2,2]oct-2-ene-5-*exo*-carboxamide, 400 ml. of benzene, 100 g. of triethylamine, and 50 g. of phosphorus pentoxide was stirred and refluxed for 1.5 hr. The cooled mixture was extracted several times with benzene. The combined benzene extracts were dried and distilled to yield 19.5 g., 77.5%, of 5-*exo*-cyano-5-*endo*-ethylbicyclo[2.2.2]oct-2-ene, b.p. 75–80°/3 mm., $n_D^{22.4}$ 1.4876. Infrared absorption maxima: 10.08(w), 10.35(s), 11.01(w), 11.6(s), 12.4(s), 12.75(s), 12.95(s) μ.

Anal. Calcd. for $C_{11}H_{15}N$: C, 81.94; H, 9.36. Found: C, 81.9; H, 9.4.

2-Cyano-2-ethylbicyclo[2.2.2]octane. The unsaturated nitrile was reduced in alcohol with hydrogen in the presence of platinum oxide under 25 lb. pressure to yield 2-cyano-2-ethylbicyclo[2.2.2]octane, b.p. 105°/8 mm., n_D^{25} 1.4824. Infrared absorption maxima: 3.81(w), 10.1(w), 10.39(s), 10.72(m), 11.0(w), 11.32(w), 11.7(s), 12.15(s), 12.48(w), 12.8(m), 12.98(m) μ.

Anal. Calcd. for $C_{11}H_{17}N$: N, 8.58. Found: N, 8.3.

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(9) The authors are indebted to Dr. J. S. Meek for this spectrum.

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

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Reaction of Cyanogen with Organic Compounds. XIV. Compounds Containing Hydrogen Activated by Neighboring Groups[1]

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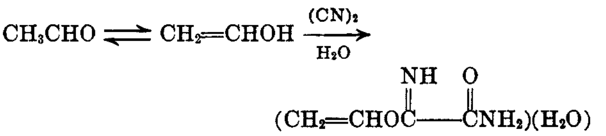
Received March 11, 1959

Previous papers in this series[3] have described many reactions of cyanogen with the hydrogen of functional groups. However, little has been done with the cyanogen reactions of hydrogen activated by neighboring groups. Traube[4] has reported on malonic ester, acetoacetic ester, and acetylacetone and Langenbeck[5] showed that acetaldehyde reacts with cyanogen. However, the structure of the product indicates that hydrolysis was an accompanying step:



$$CH_3CHO \rightleftharpoons CH_2{=}CHOH \xrightarrow[H_2O]{(CN)_2} (CH_2{=}CHO\overset{NH}{\overset{\|}{C}}{-}{-}\overset{O}{\overset{\|}{C}}NH_2)(H_2O)$$

TABLE I

REACTION OF CYANOGEN WITH COMPOUNDS CONTAINING ACTIVE HYDROGEN

Reagent	Product	M.P.	Yield, %	Analysis Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
$C_2H_5NO_2$	$CH_3CHNO_2C(=NH)CN$	117–119	7.5	37.8	4.0	33.1	37.9	4.4	33.3
$C_2H_5CH_2NO_2$	$C_2H_5CHNO_2C(=NH)CN$	67–69	4.7	42.6	5.0	29.8	42.6	4.9	30.4
C_6H_5NHCO | CH_2COCH_3	$C_6H_5NHCOCHC(=NH)CN$ | $COCH_3$	204–205	43.0	62.0	4.8	18.3	62.4	5.1	18.1
$CH_2CNCO_2C_2H_5$	$CHCNCO_2C_2H_5$ | $C(=NH)CN$	168–170	2.4	50.9	4.3	25.4	50.7	4.5	25.2
$CH_2(CN)_2$	$(CN)_2CHC(=NH)CN$	171	6.5	50.8	1.7	47.5	50.4	2.2	47.2
$(CH_3)_2CHCHO$	$(CH_3)_2C=CHOC(=NH)$ | $CONH_2 \cdot H_2O$	108–110	22.7	45.0	7.6	17.5	45.2	7.5	17.0
C_3H_7CHO	Gummy product			Infrared spectrum closely resembled that from isobutyraldehyde product					

The present study was undertaken to discover other active hydrogen compounds which would react with cyanogen. Table I lists the compounds with which some measure of success was obtained. In every case the product consisted of a substance in which one molecule of the organic reagent had added to one molecule of cyanogen.

Other compounds which were studied but were recovered unchanged were nitromethane, 2-nitropropane, 1-nitrobutane, phenylacetonitrile, succinonitrile, benzaldehyde, and cyclopentadiene.

Attempts were made without success to add a second molecule of cyanogen to the condensation products of cyanogen with acetylacetone and with acetoacetanilide. In addition the following compounds, all of which contain but one active hydrogen, failed to react: ethyl butylmalonate, 3-chloroacetylacetone, ethyl α-acetylacetoacetate, triphenylmethane, and 4-pyridyldiphenylmethane.

In no case was it possible to obtain products in which the ratio of organic reagent to cyanogen was 2:1 instead of 1:1

EXPERIMENTAL

Pure, compressed cyanogen in cylinders was supplied by the American Cyanamid Company. The gas was led from the cylinder into a trap cooled by Dry-Ice–acetone where it became solid and permitted the tube to be weighed before and after a reaction. The rate of vaporization was easily controlled by warming or cooling the tube.

Except for nitroparaffins and aldehydes where the nature and strength of a basic solvent appeared to be critical, all the successful reactions took place in the presence of alcohol and a small amount of sodium. Three procedures illustrative of the above are given.

Reaction with nitroethane. A solution of 22.1 g. (0.29 mole) of nitroethane was prepared in 200 ml. of 1*N* aqueous sodium hydroxide and cooled to 0°. Three-tenths of a mole (15.6 g.) of cyanogen was bubbled into the solution. The mixture darkened quite rapidly and after a short time a small amount of crystalline material formed. When all the cyanogen had been added, the dark mixture was extracted immediately with 200 ml. of ether and the extract dried over anhydrous magnesium sulfate while standing in the ice chest. Evaporation of the ether left 2.8 g. (7.5% yield) of yellow solid. Recrystallization from ether with decolorizing carbon present gave pure material forming yellow needles which melted at 117–119°.

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(3) Paper No. 1 of this series appeared in *J. Org. Chem.*, **14**, 555 (1949).

(4) W. Traube, *Ber.*, **31**, 2938 (1898).

(5) W. Lagenbeck, *Ann.*, **469**, 16 (1929).