

## Cyanation and Hydrocyanation of Unsaturated Hydrocarbons. I. Reaction of 4a-Methyl-1,3,9-triphenyl-4aH-fluorene with Sodium Cyanide<sup>1</sup>

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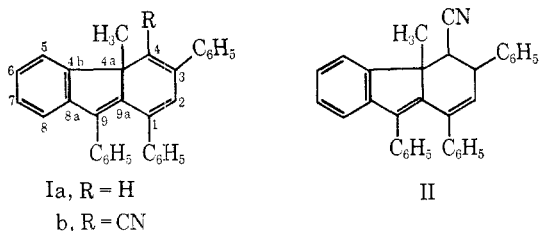
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Solutions of the heavily arylated conjugated triene, 4a-methyl-1,3,9-triphenyl-4aH-fluorene (Ia), in dipolar aprotic solvents rapidly develop an intense green color when sodium cyanide is added. Treatment of the colored solutions with air or oxygen results in the formation of 4-cyano-4a-methyl-1,3,9-triphenyl-4aH-fluorene (Ib), a cyanation product of the original hydrocarbon. Treatment of the solutions with hydrogen cyanide, hydrogen chloride, or water results in the formation of 4-cyano-4a-methyl-1,3,9-triphenyl-3,4-dihydro-4aH-fluorene (II), a hydrocyanation product of the original hydrocarbon. The occurrence of the cyanation and hydrocyanation is attributed to the presence in the solutions of the carbanion (IIIa), formed by addition of cyanide ion to the hydrocarbon (Ia).

In earlier papers,<sup>2-5</sup> it was shown that 4a-methyl-1,3,9-triphenyl-4aH-fluorene (Ia) is one of the isomeric yellow hydrocarbons obtained from the polyphosphoric acid-catalyzed condensation of acetophenone. Electrophilic attack of the hydrocarbon Ia was shown to occur at the 4 position in both protonation and substitution reactions.<sup>3,4</sup> Protonation gives a carbonium ion, solutions of which possess a characteristic intense green color. Salts of this highly stable carbonium ion have been isolated. Intensely green solutions are also obtained when the hydrocarbon is treated with strongly nucleophilic reagents.<sup>5,6</sup>

Further investigation of the reactions of hydrocarbon Ia with nucleophiles has led to the discovery of a facile reaction between sodium cyanide and the hydrocarbon. Mixtures of sodium cyanide and the hydrocarbon in



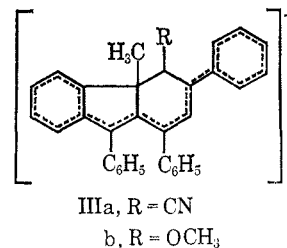
dimethylformamide, dimethyl sulfoxide, and other dipolar aprotic solvents give intensely green solutions within a few minutes at room temperature. Dilution with water of such a solution in dimethyl sulfoxide, prepared and handled under air, yielded 4-cyano-4a-methyl-1,3,9-triphenyl-4aH-fluorene (Ib). In a similar experiment using as solvent as 8:1 mixture of dimethylformamide and water, the same nitrile was isolated in a yield of 55%. The yield of the nitrile was 63% when an intensely green mixture of the hydrocarbon and sodium cyanide, prepared under nitrogen in dimethylformamide, was treated with oxygen prior to dilution with water. The structure of nitrile Ib was assigned on the basis of its infrared and nmr spectra, elemental analysis, and molecular weight. Synthesis of the nitrile from 4-formyl-4a-methyl-1,3,9-

triphenyl-4aH-fluorene<sup>4</sup> by the method of Hunt<sup>7</sup> confirmed the assigned structure.

When the hydrocarbon (Ia) was treated with sodium cyanide in dimethylformamide under nitrogen and the resulting intensely green solution was treated with an excess of gaseous hydrogen cyanide, 4-cyano-4a-methyl-1,3,9-triphenyl-3,4-dihydro-4aH-fluorene (II) was isolated in a yield of 61%. The yield of nitrile II was 48% when the reaction of hydrocarbon Ia and sodium cyanide was carried out in the presence of an excess of hydrogen cyanide. In this experiment, with both hydrogen cyanide and sodium cyanide present at the time of the addition of the hydrocarbon, no green color was observed. In a similar experiment in which the hydrocarbon was treated with hydrogen cyanide in the absence of sodium cyanide, only the unchanged hydrocarbon Ia was recovered. Treatment of an intensely green solution of the hydrocarbon and sodium cyanide in dimethylformamide with either gaseous hydrogen chloride or water also gave nitrile II, in lower yields.

The structure of nitrile II was assigned on the basis of its infrared and nmr spectra, elemental analysis, and molecular weight. The nmr spectrum of the compound in dimethylformamide-*d*<sub>7</sub> shows an ABX pattern consisting of a doublet at  $\tau$  3.88 with a coupling constant of 3 cps and a complex multiplet centered at 5.56. The ratio of the area of the doublet to that of the multiplet is 1:2. This pattern is in agreement with the assigned structure (II) of the nitrile, the doublet being due to the vinyl proton at the 2 position and the multiplet to the methine protons at the 3 and 4 positions.

The intense green color of the above reaction solutions is attributed to the presence of the carbanion IIIa. An analogous species (IIIb) was proposed by Moore<sup>6</sup>



to explain the intense green color observed when hydrocarbon Ia was treated with sodium methoxide in either dimethylformamide or dimethyl sulfoxide. Oxidation of carbanion IIIa by molecular oxygen and loss of a

(1) Grateful acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation (Grants PRF-2042-A1 and NSF (G6223) for the partial support of this work.

(2) H. W. Moore and H. R. Snyder, *J. Org. Chem.*, **28**, 535 (1963).

(3) H. W. Moore and H. R. Snyder, *ibid.*, **28**, 297 (1963).

(4) H. W. Moore and H. R. Snyder, *ibid.*, **29**, 97 (1964).

(5) R. W. Roeske, D. B. Bright, R. L. Johnson, W. J. DeJarlais, R. W. Bush, and H. R. Snyder, *J. Am. Chem. Soc.*, **82**, 3128 (1960).

(6) H. W. Moore, Ph.D. Thesis, University of Illinois, 1962.

(7) J. H. Hunt, *Chem. Ind. (London)*, 1873 (1961).

hydrogen atom from the 4 position of the resulting radical could account for the formation of nitrile Ib. Nitrile II, of course, could be produced by protonation of the carbanion.

When carbonation of the intensely green intermediate in the reaction of hydrocarbon Ia with sodium cyanide was attempted, nitrile II was isolated in 44% yield. Neutralization of the solution as the result of the reaction of cyanide ion with carbon dioxide to give cyanofornate, followed by protonation of carbanion IIIa may account for the formation of the observed product (II). Although cyanofornic acid and its salts seem not to have been reported in the literature, sodium cyanide is known to react readily with carbon disulfide in dimethylformamide to give the analogous sodium cyanodithioformate.<sup>8</sup> The free acid has been isolated from this salt.<sup>9</sup> Evidence that sodium cyanide does react with carbon dioxide in dimethylformamide was obtained by rough measurement of the volume of carbon dioxide consumed when sodium cyanide was added to a saturated solution of carbon dioxide in dimethylformamide in an atmosphere of carbon dioxide. The molar ratio of the amount of carbon dioxide consumed to the amount of sodium cyanide added was approximately 3:4. When hydrocarbon Ia was added to this mixture, no green color was observed and only the unchanged hydrocarbon was recovered.

Addition of benzene to an intensely green mixture of the hydrocarbon (Ia) and sodium cyanide in dimethylformamide, prepared under nitrogen, resulted in the precipitation of sodium cyanide and the recovery of 66% of unchanged hydrocarbon. In contrast, when a similar intensely green mixture was treated with hydrogen cyanide, only 1% of the unchanged hydrocarbon was recovered. These observations suggest that the addition of sodium cyanide to hydrocarbon Ia is reversible. The failure of attempts to trap the carbanion IIIa by treating the colored solutions with trimethylchlorosilane or phenyl isocyanate is attributed to the reaction of these reagents with sodium cyanide and the consequent reversal of the reaction by which the carbanion is formed. The use of trimethylchlorosilane to trap carbanions has recently been reported.<sup>10</sup>

Nitrile II also reacted with sodium cyanide in dimethylformamide under nitrogen to give an intensely green solution, treatment of which with oxygen gave a 49% yield of nitrile Ib. Abstraction of a proton from the 3 position of the nitrile (II) by cyanide ion to give carbanion IIIa, followed by reaction of this intermediate with oxygen, could account for the formation of the observed product (Ib). Other reactions in dimethylformamide or dimethyl sulfoxide in which cyanide ion apparently effects the removal of a proton attached to a carbon atom have been reported,<sup>11,12</sup> although the hydrogen atoms involved are probably more highly acidic than any in II.

The reaction of hydrocarbon Ia with sodium cyanide is believed to be the first reported attack of a carbon-carbon double bond in a hydrocarbon by cyanide ion. This ion is known to react with acrylonitrile to form

polymers<sup>13</sup> and with 1,1-difluoro olefins to form amides and acids, presumably the products of hydrolysis of the intermediate nitriles.<sup>14</sup> Middleton<sup>15</sup> reported the isolation of a salt formed by the addition of sodium cyanide to the highly reactive 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene. When we attempted a similar isolation procedure with an intensely green mixture of hydrocarbon Ia and sodium cyanide in dimethylformamide, the green color disappeared when the solvent had been removed and only unchanged hydrocarbon was recovered.

The reaction of unsaturated hydrocarbons with sodium cyanide to give nitriles has been extended to include reaction of sodium cyanide with 9-benzylidene-fluorene and 9-(4-bromobenzylidene)fluorene.<sup>16</sup> A variety of other compounds gave intensely colored solutions when treated with sodium cyanide in dipolar aprotic solvents. Some of these reactions are presently being investigated in this laboratory.

### Experimental Section<sup>17</sup>

**Purification of Materials.**—Commercial dimethylformamide was distilled at atmospheric pressure from barium oxide.<sup>18</sup> The distillate, bp 149–151° (lit.<sup>18</sup> bp 153°), was collected and stored over Linde Type 4A Molecular Sieves.<sup>19</sup> Commercial sodium cyanide (98%) was powdered, dried overnight at 110° in a vacuum oven, and stored in a tightly closed container.<sup>20</sup>

**Preparation of 4a-Methyl-1,3,9-triphenyl-4aH-fluorene (Ia).**—The procedure described by Moore<sup>6</sup> for preparing hydrocarbon Ia by treating acetophenone with polyphosphoric acid was used with the following modification. The yellow solid obtained from the benzene extract of the hydrolysis mixture was dissolved in benzene and the solution was chromatographed through a column of neutral alumina. Elution with a 1:1 mixture of benzene and cyclohexane, evaporation of the solvent *in vacuo*, and recrystallization of the residue from a 1:1 mixture of benzene and cyclohexane gave yellow crystals of 4a-methyl-1,3,9-triphenyl-4aH-fluorene (Ia), mp 182–184° (lit.<sup>6</sup> mp 180–181°).

**Reaction of Hydrocarbon Ia with Sodium Cyanide in Dimethyl Sulfoxide. Preparation of 4-Cyano-4a-methyl-1,3,9-triphenyl-4aH-fluorene (Ib).**—A mixture of 0.49 g (0.010 mole) of sodium cyanide and 50 ml of dimethyl sulfoxide was stirred for 10 min at room temperature in a 50-ml erlenmeyer flask equipped with a magnetic stirrer and a reflux condenser fitted with a calcium sulfate drying tube. To the mixture was added 0.41 g (0.001 mole) of hydrocarbon Ia and heating was begun. Within 5 min the mixture became intensely green. Heating was stopped and stirring was continued for 22 hr. The dark mixture was poured into 180 ml of a mixture of ice and water. After the ice had melted, the mixture was extracted twice with 100-ml portions of cyclohexane and twice with 100-ml portions of low-boiling petroleum ether. The extracts were combined and washed with water and the solvent was evaporated *in vacuo* to give a dark, oily residue. Treatment of the residue with ethanol gave a yellow solid which was recrystallized from ethanol to give orange crystals (0.11 g, 26%) of 4-cyano-4a-methyl-1,3,9-triphenyl-4aH-fluorene (Ib), mp 194–196°. A second recrystallization from ethanol produced an analytically pure sample, mp 195–196°.

(13) A. J. Parker, *Quart. Rev. (London)*, **16**, 163 (1962).

(14) D. C. England, R. V. Lindsay, Jr., and L. R. Melby, *J. Am. Chem. Soc.*, **80**, 6442 (1958).

(15) W. J. Middleton, *J. Org. Chem.*, **30**, 1402 (1965).

(16) B. E. Galbraith, Ph.D. Thesis, University of Illinois, 1966.

(17) Melting points are uncorrected. Microanalyses were performed by Mr. J. Nemeth and his associates, University of Illinois. Infrared and nuclear magnetic resonance spectra were recorded by Mr. O. W. Norton and his associates, University of Illinois. Evaporations done *in vacuo* were carried out in a rotary evaporator.

(18) K. B. Wiberg, "Laboratory Technique in Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p 251.

(19) G. R. Pettit, M. V. Kalnins, T. M. H. Liu, E. G. Thomas, and K. Parent, *J. Org. Chem.*, **26**, 2563 (1961), footnote 9.

(20) R. A. Smiley and C. Arnold, *ibid.*, **25**, 257 (1960).

(8) G. Bahr and G. Schleitzer, *Chem. Ber.*, **88**, 1771 (1955).

(9) G. Bahr and G. Schleitzer, *ibid.*, **90**, 438 (1957).

(10) D. R. Weyenberg, L. H. Toporcer, and A. E. Bey, *J. Org. Chem.*, **30**, 4096 (1965).

(11) G. E. Ham and J. Stevens, *ibid.*, **27**, 4638 (1962).

(12) B. B. Molloy, D. H. Reid, and F. S. Skelton, *J. Chem. Soc.*, 65 (1965).

*Anal.* Calcd for  $C_{23}H_{23}N$ : C, 91.40; H, 5.34; N, 3.23; mol wt, 433. Found: C, 91.21; H, 5.47; N, 3.40; mol wt (mass spectrum), 433.

The infrared spectrum in a potassium bromide disk shows strong nitrile absorption at  $2190\text{ cm}^{-1}$ . The nmr spectrum in deuteriochloroform shows the absorption of only one vinyl proton, at  $\tau$  3.50 (singlet).

When hydrocarbon Ia was treated with sodium cyanide in an 8:1 mixture of dimethylformamide and water, the yield of nitrile Ib was 55%. No pure compounds were isolated when this reaction was carried out under strenuous conditions using dimethylformamide as solvent.

**Reaction of Hydrocarbon Ia with Sodium Cyanide in Dimethylformamide Followed by Treatment with Oxygen. Preparation of Nitrile Ib.**—A mixture of 0.10 g (0.002 mole) of sodium cyanide and 20 ml of dimethylformamide was stirred at room temperature under nitrogen in a 50-ml, three-necked, round-bottomed flask equipped with a magnetic stirrer, a calcium sulfate drying tube, and two gas inlet tubes. One of the inlet tubes was connected to a mercury manometer system which had been closed off from the flask and filled with oxygen. After 15 min, 0.41 g (0.001 mole) of hydrocarbon Ia was added to the reaction mixture. It became intensely green within 5 min and was stirred under nitrogen for 15 min longer. Then the flask was stoppered and oxygen was admitted. The mixture was stirred for 5.5 hr (it became intensely red after about 2.5 hr). About 24 ml of oxygen was absorbed. The mixture was poured into 35 ml of water and 2 ml of 5% hydrochloric acid solution was added. The yellow precipitate was collected by filtration, washed with water, dried, and dissolved in cyclohexane. The solution was chromatographed through a column of silica gel. Elution with benzene, evaporation of the solvent *in vacuo*, and recrystallization of the residue from cyclohexane gave 0.27 g (63%) of nitrile Ib, mp 194–196°. The identity of the product was confirmed by comparison of its infrared spectrum with that of an authentic sample.

When hydrocarbon Ia was treated with sodium cyanide in dimethylformamide in an oxygen atmosphere, a 42% yield of nitrile Ib was obtained.

**Reaction of Hydrocarbon Ia with Sodium Cyanide in Dimethylformamide Followed by Treatment with Carbon Dioxide. Preparation of 4-Cyano-4a-methyl-1,3,9-triphenyl-3,4-dihydro-4aH-fluorene (II).**—One-half of a gram (0.010 mole) of sodium cyanide, 0.82 g (0.002 mole) of hydrocarbon Ia, and 20 ml of dimethylformamide were stirred at room temperature under nitrogen in a 50-ml, three-necked, round-bottomed flask equipped with a magnetic stirrer, a gas inlet tube, and a calcium sulfate drying tube. The mixture became intensely green within 3 min. After 2.5 hr stirring was interrupted and a mercury manometer system was connected to the flask. The entire system was swept with carbon dioxide (dried by bubbling it through concentrated sulfuric acid). When stirring was resumed, the mixture became yellow-orange within 2 min. After 10 min the flask was swept with nitrogen and the mixture was stirred for 2.5 hr. During this period the intense green color reappeared. Carbon dioxide was readmitted to the flask and the mixture became orange within 20 min. After 10 min more the manometer system was closed off from the flask, the flask was swept with nitrogen, and the mixture was stirred for 4.5 hr. The orange mixture was poured into 50 ml of water and the resulting yellow precipitate was collected by filtration, washed with water, and dried. Acidification of the colorless, slightly basic filtrate gave no precipitate. The yellow solid was recrystallized from benzene to give colorless crystals (0.38 g, 44%) of 4-cyano-4a-methyl-1,3,9-triphenyl-3,4-dihydro-4aH-fluorene (II), mp 274–276°. Two further recrystallizations from benzene gave an analytically pure sample, mp 277–278°.

*Anal.* Calcd for  $C_{33}H_{25}N$ : C, 90.98; H, 5.78; N, 3.21; mol. wt, 435. Found: C, 90.69; H, 5.89; N, 3.00; mol wt (mass spectrum), 435.

The infrared spectrum of the compound in a potassium bromide disk shows weak nitrile absorption at  $2230\text{ cm}^{-1}$ . The nmr spectrum of the compound in dimethylformamide-*d*<sub>7</sub> showed absorption for one vinyl proton, at  $\tau$  3.88 (a doublet with a coupling constant of 3 cps) and absorption for two methine protons, centered at 5.56 (complex multiplet).

**Reaction of Hydrocarbon Ia with Sodium Cyanide in Dimethylformamide Followed by Treatment with Hydrogen Cyanide. Preparation of Nitrile II.**—Twenty milliliters of dimethylformamide and 0.49 g (0.010 mole) of sodium cyanide

were stirred at room temperature with nitrogen bubbling into the liquid in a 100-ml, three-necked, round-bottomed flask equipped with a magnetic stirrer, a gas inlet tube extending into the liquid, and a gas outlet tube connected to a trap containing 10% sodium hydroxide solution. After 20 min 0.82 g (0.002 mole) of hydrocarbon Ia was added to the mixture, which became intensely green within 2 min. It was stirred under nitrogen for 3 hr. Then the nitrogen inlet tube was replaced by an inlet tube connected to a hydrogen cyanide generator.<sup>21</sup> The generator consisted of a 50-ml, round-bottomed flask fitted with a distilling adapter, the side arm of which was connected successively to a calcium chloride drying tube, a side-arm test tube cooled by an ice-water bath, and finally to the reaction flask. The generator flask was charged with 11 ml of 50% sulfuric acid solution (0.10 mole of sulfuric acid), and the adapter was fitted with a serum cap. Hydrogen cyanide was generated by injecting a solution of 4.9 g (0.10 mole) of sodium cyanide in 10 ml of water into the sulfuric acid solution. Vigorous evolution of hydrogen cyanide occurred and about 0.5 ml condensed in the trap. Both the generator flask and the trap were warmed to drive over as much hydrogen cyanide as possible. Generation of hydrogen cyanide resulted in the reaction mixture becoming red immediately and gradually turning orange. The generating system was disconnected and the reaction mixture was stirred at room temperature for 3 hr. It was then poured into 80 ml of water and 20 ml of 10% sodium hydroxide solution was added. The yellow precipitate was collected by filtration, washed with water, dried, and recrystallized from a 1:2 mixture of benzene and cyclohexane to give 0.53 g (61%) of the colorless 4-cyano-4a-methyl-1,3,9-triphenyl-3,4-dihydro-4aH-fluorene (II), mp 272–275°. The mother liquor was chromatographed through a column of neutral alumina. Elution with cyclohexane and evaporation of the solvent *in vacuo* gave 0.01 g (1%) of unchanged hydrocarbon Ia, mp 180–183°. The material obtained by elution with benzene was recrystallized from ethanol to give 0.06 g (7%) of nitrile Ib, mp 192–195°. Each of the compounds was identified by comparison of its infrared spectrum with that of an authentic sample.

When hydrocarbon Ia was treated with sodium cyanide in dimethylformamide in the presence of hydrogen cyanide, a 48% yield of nitrile II was obtained. A quantitative yield of unchanged hydrocarbon Ia was obtained when the hydrocarbon was treated with hydrogen cyanide in dimethylformamide in the absence of sodium cyanide.

In an experiment similar to the one described in detail above, the intensely green reaction mixture was treated with gaseous hydrogen chloride (instead of hydrogen cyanide). Nitrile II was isolated in a yield of 25%.

**Reaction of Hydrocarbon Ia with Sodium Cyanide in Dimethylformamide Followed by Treatment with Water. Preparation of Nitrile II.**—A mixture of 0.82 g (0.002 mole) of hydrocarbon Ia, 0.49 g (0.010 mole) of sodium cyanide, and 20 ml of dimethylformamide was stirred at room temperature under nitrogen in a 50-ml, three-necked, round-bottomed flask equipped with a magnetic stirrer, a calcium sulfate drying tube, a gas inlet tube, and a serum cap. The mixture became intensely green within 2 min. After 2 hr, 2 ml of water was added by syringe over a 10-min period. The mixture remained deep green and was stirred for 15 min longer. Then 8 ml of water was added slowly by syringe. The mixture gradually turned yellow-orange. It was poured into 50 ml of water, and the resulting yellow precipitate was collected by filtration, washed with water, dried, and recrystallized from benzene to give 0.12 g (14%) of nitrile II, mp 275–276°. The identity of the product was confirmed by comparison of its infrared spectrum with that of an authentic sample. No other pure compounds were obtained.

**Reaction of Hydrocarbon Ia with Sodium Cyanide in Dimethylformamide Followed by Treatment with Benzene.**—One-half of a gram (0.010 mole) of sodium cyanide and 20 ml of dimethylformamide were stirred at room temperature with nitrogen bubbling into the liquid in a 200-ml, three-necked, round-bottomed flask equipped with a magnetic stirrer, a nitrogen inlet tube extending into the liquid, and a 250-ml pressure-equalizing dropping funnel fitted with a calcium sulfate drying tube. After 10 min 0.82 g (0.002 mole) of hydrocarbon Ia was added. The mixture became green immediately and intensely green within 1 min. It was stirred under nitrogen for 2.5 hr. Then 160 ml of benzene

(21) The procedure used for hydrogen cyanide generation is adapted from that of W. W. Hartman, in "Organic Syntheses," Coll. Vol. I, H. Gilman, Ed., 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1941, p 316.

was added over a 25-min period. The brown mixture was poured into 100 ml of water, and the two layers were thoroughly mixed and separated. The aqueous layer was extracted with 40 ml of benzene. The yellow benzene solutions were combined, washed with water, dried over sodium sulfate, and concentrated to a volume of about 50 ml. Addition of 150 ml of cyclohexane and concentration of the solution gave 0.02 g (2%) of nitrile II, mp 274–278°. The mother liquor was chromatographed through a column of neutral alumina. Elution with a 1:1 mixture of benzene and cyclohexane and evaporation of the solvent *in vacuo* gave 0.54 g (66%) of unchanged hydrocarbon (Ia), mp 179–183°. Elution with benzene gave a material which was recrystallized from a mixture of chloroform and ethanol to give 0.16 g (18%) of nitrile Ib, mp 190–193°. The identification of each compound was confirmed by comparison of its infrared spectrum with that of an authentic sample.

**Reaction of Nitrile II with Sodium Cyanide in Dimethylformamide Followed by Treatment with Oxygen. Preparation of Nitrile Ib.**—A mixture of 0.50 g (0.010 mole) of sodium cyanide and 20 ml of dimethylformamide was stirred at room temperature with nitrogen bubbling into the liquid in a 50-ml, three-necked, round-bottomed flask equipped with a magnetic stirrer, a calcium sulfate drying tube, and a gas inlet tube extending into the liquid. After 20 min 0.44 g (0.001 mole) of nitrile II was added. The mixture became intensely green within 1 min and was stirred under nitrogen for 3 hr. Oxygen was passed into the flask and the mixture became yellow-brown in about 45 min. Nitrogen was again bubbled into the liquid while it was being stirred at room temperature. After 45 min the red-orange mixture was poured into 100 ml of water, 20 ml of 10% sodium hydroxide solution was added, and the mixture was extracted twice with 100-ml portions of benzene. The yellow benzene extracts were combined, washed with 5% sodium hydroxide solution and

with water, dried over sodium sulfate, and concentrated to a volume of about 15 ml. Addition of 30 ml of cyclohexane and concentration of the solution was followed by chromatography of the solution through a column of neutral alumina. Elution with benzene, evaporation of the solvent *in vacuo*, and recrystallization of the orange residue from ethanol gave 0.21 g (49%) of nitrile Ib, mp 190–194°. The product was identified by comparison of its infrared spectrum with that of an authentic sample.

**Distillation of the Solvent from a Mixture of Hydrocarbon Ia and Sodium Cyanide in Dimethylformamide.**—A mixture of 0.16 g (0.0004 mole) of hydrocarbon Ia, 0.002 g (0.0004 mole) of sodium cyanide, and 4 ml of dimethylformamide was placed in a 10-ml, round-bottomed flask. The flask was evacuated by means of a vacuum pump and allowed to stand at room temperature. The mixture became intensely green within 15 min. After 5 hr at room temperature, the solvent was removed under reduced pressure by heating the mixture to about 85° (oil-bath temperature). The green color disappeared when the solvent had been distilled. The yellow-orange residue was washed with benzene, the benzene was evaporated, and the residue was recrystallized from cyclohexane to give 0.06 g (38%) of unchanged hydrocarbon (Ia), mp 182–84°, identified by comparison of its infrared spectrum with that of an authentic sample.

**Nuclear Magnetic Resonance Spectroscopy.**—The nmr spectra were recorded with a Varian Associates Model A-60 nmr spectrometer and, in the case of nitrile II, with a Varian Associates Model A-56/60A analytical nmr spectrometer, using tetramethylsilane as an internal standard. Chemical shifts are expressed in parts per million as shielding values ( $\tau$ ), defined by Tiers.<sup>22</sup>

(22) G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1959).

## Reactions of Isocyanates with Cyanohydrins. The Synthesis of 2,4-Oxazolidinediones and 1,3-Disubstituted Parabanic Acids

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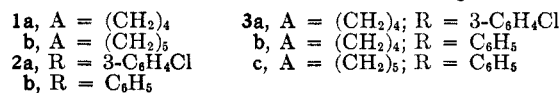
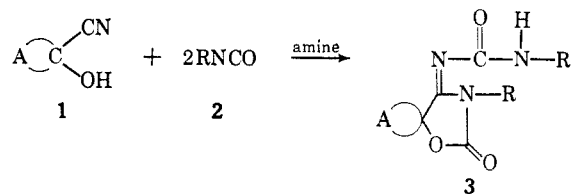
Isocyanates react with cyanohydrins to form substituted 4-carbamoylimino-2-oxazolidinones which hydrolyze to 2,4-oxazolidinediones. Acetone cyanohydrin reacts with 3-chlorophenyl isocyanate to form two products: 3-(3-chlorophenyl)-4-(3-chlorophenylcarbamoylimino)-5,5-dimethyl-2-oxazolidinone and 1,3-di(3-chlorophenyl)-4-imino-2,5-imidazolidinedione. The latter product arises from the reaction of the isocyanate with hydrogen cyanide which is formed when the cyanohydrin dissociates. Reaction conditions necessary to produce either product in high yield with the exclusion of the other are reported. Acid hydrolysis of the 4-imino-2,5-imidazolidinediones produces 1,3-disubstituted parabanic acids.

Many methods are available for the synthesis of 2,4-oxazolidinediones.<sup>2–7</sup> 3-Substituted 2,4-oxazolidinediones have been prepared by the reaction of N-substituted carbamates with  $\alpha$ -chloroacetyl chlorides<sup>6</sup> and by cyclization of the urethans formed by the reaction of  $\alpha$ -hydroxy esters with isocyanates.<sup>7</sup>

It has now been found that cyanohydrins can be used for the synthesis of 2,4-oxazolidinediones without first converting them into the corresponding  $\alpha$ -hydroxy esters. This paper describes the base-catalyzed reaction of isocyanates with cyanohydrins to form labile 1-cyanoalkyl carbamates which immediately cyclize

to 3-substituted 4-imino-2-oxazolidinones. These products then react with 1 additional mole of isocyanate to form stable 3-substituted 4-carbamoylimino-2-oxazolidinones which readily hydrolyze in the presence of acid to form the corresponding 3-substituted 2,4-oxazolidinediones quantitatively.

When a benzene solution of equimolar quantities of 1-cyanocyclopentanol (1a) and 3-chlorophenyl isocyanate (2a) was heated in the presence of DABCO (triethylenediamine), a 42% yield of 3-(3-chloro-



(1) (a) Esso Research and Engineering Co., Baytown, Texas. (b) Spencer Chemical Co. is now named Gulf Research and Development Co., Kansas City Division.

(2) J. W. Clark-Lewis, *Chem. Rev.*, **58**, 63 (1958).

(3) K. Gulbins, M. Roth, and K. Hamann, *Angew. Chem.*, **73**, 434 (1961).

(4) J. W. Cornforth, "Heterocyclic Compounds," Vol. 5, R. C. Elderfield, Ed., John Wiley and Sons, Inc., New York, N. Y., 1957, p 411.

(5) E. Schmidt and W. Carl, *Ann.*, **639**, 24 (1961).

(6) M. Pianka and D. J. Polton, *J. Chem. Soc.*, 983 (1960).

(7) R. F. Rekker, A. C. Faber, D. H. E. Tom, H. Verleur, and W. Th. Nauta, *Rec. Trav. Chim.*, **70**, 113 (1951).