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Syntheses of 4-(3-Cyano-1-triazeno)pyridines and Related Compounds

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4-(3-Cyano-1-triazeno)pyridines (III, IX) were synthesized by treating azides (I, VII) with potassium cyanide, followed by acidification with hydrochloric acid.

Cyanotriazene potassium salts (II, VIII) gave 4-[3-(N^2-hydroxyamidino)-1-triazeno]-pyridines (IVa, Xa) and 4-(3-thiocarbamoyl-1-triazeno)pyridines (IVb, Xb) on reaction with hydroxylamine hydrochloride and with hydrogen sulfide in the presence of ammonia, respectively. The reactions of II and VIII with dialkyl sulfates gave 4-(3-cyano-1-triazene)-1,4-dihydropyridines (Va, Vb, XIIa, XIIb), which were also derived from the quaternary azides (VIa, VIb, XIIIa, XIIIb).

An azourethan (XI) was obtained by treating VIII with ethanol containing a small amount of hydrochloric acid. The arylazo derivatives (XVa, XVb, XVc) were synthesized by treating VIII with a mixture of 2-naphthol or diphenylamine and ethanol containing hydrochloric acid.

The reaction of Va and XIIa with hydroxylamine hydrochloride gave 4-[3-(N^2-hydroxyamidino)-1-triazeno]-1,4-dihydropyridine hydrochlorides (XVI, XVII).

Keywords——4-azidopyridine; 4-azidopyridine 1-oxide; 4-azidopyridine quaternary salts; 4-(3-cyano-1-triazeno)pyridines potassium salts; 4-[3-(hydroxyamidino)-1-triazeno]-pyridines; 4-[3-(thioamidino)-1-triazeno]pyridines; 4-(3-cyano-1-triazeno)-1,4-dihydropyridines; azourethan; 4-[3-(ethoxycarbonyl)-1-triazeno]pyridine 1-oxide; 4-[3-(hydroxyamidino)-1-triazeno]-1,4-dihydropyridines

It is known[2] that azides react with dipolarophiles to give 1,3-dipolar cycloaddition products, whereas with nucleophilic reagents such as cyanide, sulfonyl anions, phosphines and some carbanions, they give open-chain addition products.

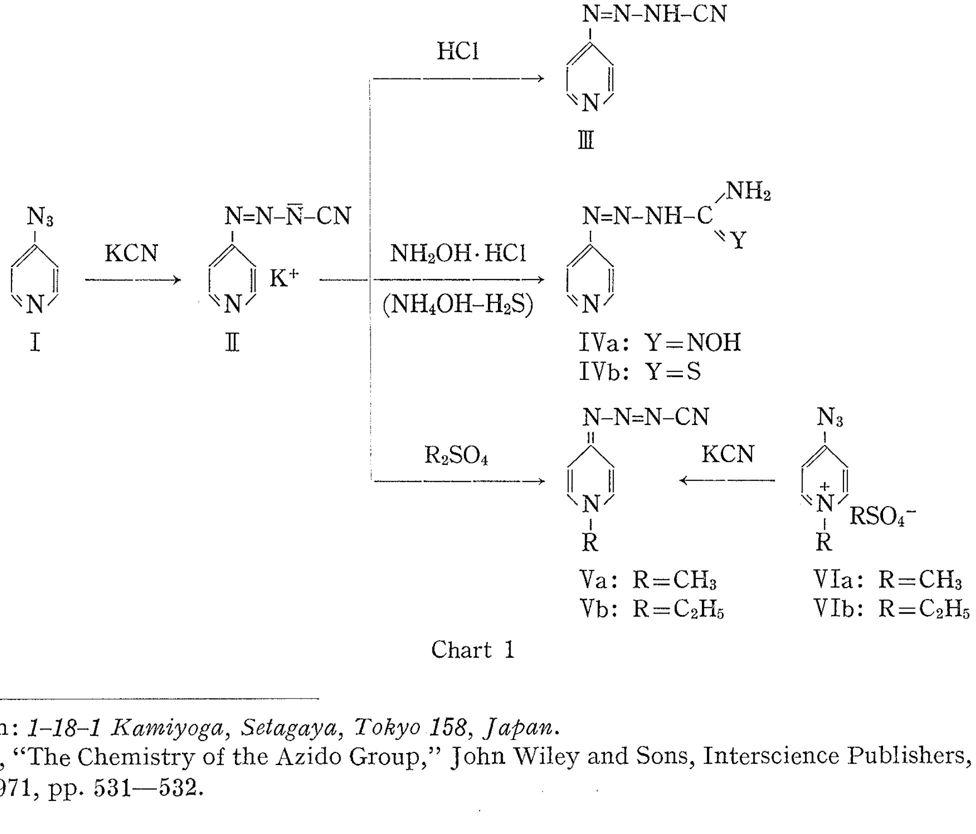

Chart 1

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[1] Location: *1-18-1 Kamiyoga, Setagaya, Tokyo 158, Japan.*

[2] S. Patai, "The Chemistry of the Azido Group," John Wiley and Sons, Interscience Publishers, Inc., New York, 1971, pp. 531—532.

We previously obtained an addition product in the reaction of 4-azidopyridine 1-oxide (VII) with potassium cyanide.[3] It was of interest to determine which nitrogen of the azido group reacted with cyanide because of the existence of several canonical formulae including the N-oxide group. The crystal structure of the potassium cyanide addition product was then determined by X-ray structure analysis to be 4-(3-cyano-1-triazeno)pyridine 1-oxide potassium salt (VIII), in which the cyano group is attached to the terminal nitrogen of the azido group.[4]

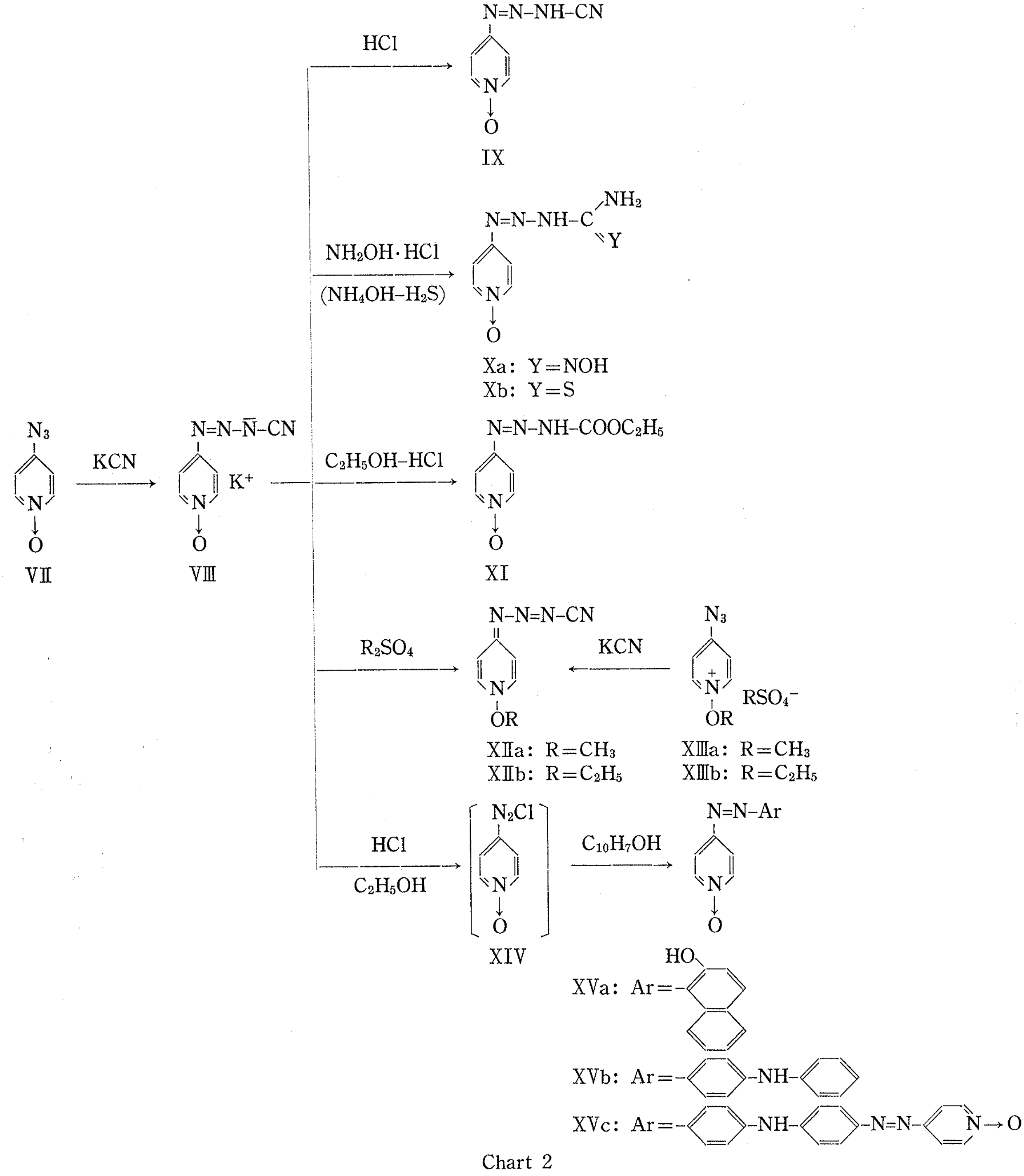

Chart 2

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3) S. Kamiya and M. Tanno, Annual Meeting of the Pharmaceutical Society of Japan, Nagoya, April 1976, Abstracts II-98.

4) T. Hata, S. Sato, K. Aiba, C. Tamura, M. Tanno, and S. Kamiya, Annual Meeting of the Chemical Society of Japan, Yokohama, April 1978, Abstracts I-588.

This paper describes the syntheses of 4-(3-cyano-1-triazeno)pyridines and related compounds.

The starting material, 4-azidopyridine (I) was prepared by the reaction of phosphorus trichloride and 4-azidopyridine 1-oxide, which was itself obtained by heating 4-nitropyridine 1-oxide and sodium azide in aqueous ethanol.

Treatment of I with potassium cyanide in aqueous dioxane, gave 4-(3-cyano-1-triazeno)-pyridine potassium salt (II) in 60% yield, and, on acidification with hydrochloric acid, this was converted to a free cyanotriazene (III), mp 156—157° (dec.). Its infrared spectrum in nujol showed the presence of a cyano group at 2180 cm^{-1}. The cyano group should be bound to the terminal nitrogen of the azido group by analogy with 4-(3-cyano-1-triazeno)pyridine 1-oxide potassium salt (VIII), whose structure has been determined by X-ray structure analysis.[4] Several reactions of this cyanotriazene also indicated that the cyano group was on the terminal nitrogen (Chart 1).

The reaction of II with hydroxylamine hydrochloride gave 4-[3-(N^2-hydroxyamidino)-1-triazeno]pyridine (IVa) in 87% yield, and that with hydrogen sulfide in the presence of ammonia gave 4-(3-thiocarbamoyl-1-triazeno)pyridine (IVb) in 72% yield.

The reaction of II with dialkyl sulfates gave 1-alkyl-4-(3-cyano-1-triazeno)-1,4-dihydropyridines, Va in 60% yield and Vb in 40% yield. They were also obtained by treating 1-methyl-4-azidopyridinium methosulfate (VIa) and 1-ethyl-4-azidopyridinium ethosulfate (VIb), respectively, with potassium cyanide.

The free cyanotriazene N-oxide (IX), mp 139—140° (dec.), was prepared analogously by treating 4-(3-cyano-1-triazeno)pyridine 1-oxide potassium salt (VIII) with hydrochloric acid (Chart 2).

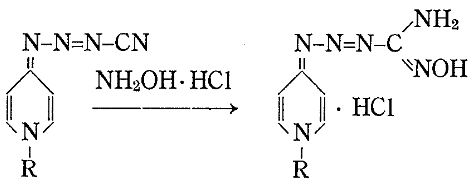
The reaction of VIII and hydroxylamine hydrochloride gave 4-[3-(N^2-hydroxyamidino)-1-triazeno]pyridine 1-oxide (Xa) in 70% yield, and that with hydrogen sulfide in the presence of ammonia gave 4-(3-thiocarbamoyl-1-triazeno)pyridine 1-oxide (Xb) in 96% yield.

When VIII was warmed with ethanol containing a small amount of hydrochloric acid, the product (isolated in 24% yield) was an azourethan, 4-(3-ethoxycarbonyl-1-triazeno)pyridine 1-oxide (XI).

Treatment of VIII with dialkyl sulfates gave 1-alkoxy-4-(3-cyano-1-triazeno)-1,4-dihydropyridines, XIIa and XIIb, which were also synthesized by treating 1-alkoxy-4-azidopyridinium salts, XIIIa and XIIIb, with potassium cyanide.

Attempts to methylate VIII with methyl iodide and to methylate IX with diazomethane under various conditions did not produce any of the presumable methylated compounds, and in most cases, the starting materials were at least partially recovered.

When a solution of VIII and 2-naphthol or diphenylamine in a mixture of ethanol and hydrochloric acid was warmed, 4-(2-hydroxy-1-naphthyl)azopyridine 1-oxide (XVa) and 4-[4-(phenylamino)phenyl]-azopyridine 1-oxide (XVb) were produced. The reaction of VIII and diphenylamine in a molar ratio of 2: 1, gave a bis-azo compound (XVc). Formation of these azo derivatives from the cyanotriazene suggested that a diazonium compound (XIV) was an intermediate of the reaction.



Va: R=CH_3 XVI: R=CH_3
XIIa: R=OCH_3 XVII: R=OCH_3

Chart 3

Hydrochlorides of 1-methyl- (XVI) and 1-methoxy-4-[3-(N^2-hydroxyamidino)-1-triazeno]-1,4-dihydropyridine (XVII) were synthesized by treating the corresponding cyanotriazenes (Va, XIIa) with hydroxylamine hydrochloride (Chart 3).

Although the nitrogen contents of some of these open-chain polynitrogen compounds (Charts 1, 2 and 3) reach 45—50%, they are surprisingly stable. They seem to exist as a strong resonance hybrid involving the pyridine ring and the polynitrogen residues.

The antitumor activities of the newly synthesized compounds (II, IVa, IVb, Va, VIII, Xa, Xb, XI, XIIa, XVI, XVII) were tested on rat ascites hepatoma, AH-13, but all were ineffective.[5]

Experimental[6]

4-Azidopyridine Hydrochloride (I)——A solution of 4-azidopyridine 1-oxide (VII) (4.7 g, 0.035 mol) and phosphorus trichloride (10.0 g) in $CHCl_3$ (150 ml) was refluxed on a water bath for 3 hr. The reaction mixture was evaporated to dryness under reduced pressure, the residue was treated with ice-water (100 ml), and the solution was extracted with $CHCl_3$. The $CHCl_3$ solution was dried over anhyd. Na_2SO_4, and the solvent was evaporated off. The residue was treated with a mixture of methanol and hydrochloric acid to prepare the hydrochloride. Colorless prisms (from methanol), mp 137—139° (dec.). IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1}: 2150, 2100 (N_3). *Anal.* Calcd. for $C_5H_4N_4 \cdot HCl$: C, 38.35; H, 3.22; N, 35.78. Found: C, 38.40; H, 3.16; N, 35.95.

4-(3-Cyano-1-triazeno)pyridine Potassium Salt (II)——A solution of potassium cyanide (0.65 g, 0.01 mol) in water (2 ml) was added to a solution of free I (1.2 g, 0.01 mol) in methanol, and the mixture was heated on a water bath for 30 min. The reaction mixture was evaporated down under reduced pressure, and the residue was recrystallized from methanol to give yellow plates, mp>300°. Yield, 1.2 g (60%). IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1}: 2175 (CN). NMR (DMSO-d_6, δ): 7.15 (2H, d, $J=6.5$, ring), 8.25 (2H, d, $J=6.5$, ring). *Anal.* Calcd. for $C_6H_4KN_5$: C, 38.90; H, 2.18; N, 37.81. Found: C, 38.92; H, 2.08; N, 38.08.

The free cyanotriazene (III) was prepared as follows. Hydrochloric acid (10%, 1 ml) was added to a solution of II (185 mg, 0.001 mol) in water (2 ml) under ice-cooling, and the reaction mixture was allowed to stand for 30 min. The crystals that separated were filtered off and washed with a small amount of cold water, then with methanol. Yellow powder, mp 156—157° (dec.). IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1}: 2180 (CN). *Anal.* Calcd. for $C_6H_5N_5$: C, 48.97; H, 3.43; N, 47.60. Found: C, 48.78; H, 3.33; N, 47.50.

4-[3-(N^2-Hydroxyamidino)-1-triazeno]pyridine (IVa)——Hydroxylamine hydrochloride (70 mg, 0.01 mol) was added to a solution of II (185 mg, 0.001 mol) in methanol (10 ml) and the reaction mixture was heated at 80° for 20 min. The crystals that separated were filtered off and recrystallized from aqueous methanol to give yellow needles, mp 193—194° (dec.). Yield, 106 mg (72%). IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1}; 945 (NOH). *Anal.* Calcd. for $C_6H_8N_6O \cdot 2H_2O$: C, 33.33; H, 5.59; N, 38.88. Found: C, 32.24; H, 5.59; N, 39.08.

4-(3-Thiocarbamoyl-1-triazeno)pyridine (IVb)——Hydrogen sulfide was passed into a mixture of II (0.75 g, 0.04 mol), water (10 ml) and 28% ammonia (5 ml) for 1 hr. The resulting crystals were filtered off and recrystallized from methanol to give yellow prisms, mp 136.5—137.5° (dec.). Yield, 0.46 g (63%). *Anal.* Calcd. for $C_6H_7N_5S$: C, 39.76; H, 3.89; N, 38.65. Found: C, 39.65; H, 3.89; N, 38.93.

1-Alkyl-4-(3-cyano-1-triazeno)-1,4-dihydropyridine (Va, b) ——1. From II: Dialkyl sulfate (0.001 mol) in dioxane was added to a solution of II (185 mg, 0.001 mol) in 70% aqueous dioxane (5 ml). The reaction mixture was allowed to stand for 3 hr, then evaporated to dryness under reduced pressure. The residue was extracted with $CHCl_3$, the solvent was removed, and the residue was recrystallized from acetone. 1-Methyl-4-(3-cyano-1-triazeno)-1,4-dihydropyridine (Va): Yield, 60%. mp 148—149° (dec), IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1}: 2180, 2160 (CN). UV $\lambda_{\max}^{95\%\text{EtOH}}$ nm (log ε): 230 (3.80), 245 (3.88), 376 (4.59). NMR (DMSO-d): 7.60 (2H, d, $J=7.0$, ring), 8.55 (2H, d, $J=7.0$, ring), 4.13 (3H, s, CH_3). *Anal.* Calcd. for $C_7H_7N_5$: C, 52.16; H, 4.38; N, 43.46. Found: C, 52.19; H, 4.35; N, 43.24. 1-Ethyl-4-(3-cyano-1-triazeno)pyridine (Vb): Yield, 57%. mp 144—146° (dec.), IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1}: 2160, 2120 (CN). *Anal.* Calcd. for $C_8H_9N_5$: C, 54.84; H, 5.18; N, 39.98. Found: C, 54.67; H, 5.09; N, 40.02.

2. From the Quaternary Salts (VIa, b): The quaternary salts were prepared by mixing equimolar amounts of I and dialkyl sulfate in $CHCl_3$, and allowing the mixture to stand overnight. A solution of potassium cyanide (0.65 g, 0.01 mol) in water (3 ml) was added to a solution of VI (0.01 mol) in 70% aqueous dioxane (10 ml) under ice-cooling. The reaction mixture was allowed to stand for 30 min, and the resulting crystals were filtered off, then recrystallized from acetone. Yield, Va (65%), Vb (51%).

4-Azidopyridine 1-Oxide (VII)——This azide was previously synthesized in 55% yield by treating 4-hydrazinopyridine 1-oxide with nitrous acid and also by treating 4-chloropyridine 1-oxide with sodium azide (10% yield).[7] This time, VII was synthesized directly by the reaction of 4-nitropyridine 1-oxide and sodium azide, giving a better yield, 74%.

A mixture of 4-nitropyridine 1-oxide (1.40 g, 0.01 mol), sodium azide (0.65 g, 0.01 mol) and 50% aqueous ethanol (150 ml), was refluxed on a water bath for 10 hr. The reaction mixture was evaporated to dryness

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[5] Mi. Miyahara, S. Kamiya, M. Nakadate, S. Sueyoshi, M. Tanno, M. Miyahara, I. Suzuki, and S. Odashima, *Eisei Shikensho Hokoku*, 96, 91 (1973).

[6] The following instruments were used to obtain physical data. IR spectra, JASCO IR-S spectrophotometer; UV spectra, Shimadzu UV 210 double-beam spectrophotometer; NMR spectra, Varian 360A and JEOL 60 spectrometers (with tetramethylsilane as an internal standard); mass spectra, JEOL LMS-01 SG-2 spectrometer. All melting points are uncorrected.

[7] T. Itai and S. Kamiya, *Chem. Pharm. Bull.* (Tokyo), 9, 87 (1961).

under reduced pressure, the residue was extracted with $CHCl_3$, and the $CHCl_3$ solution was dried over anhyd. Na_2SO_4. The solvent was evaporated off, and the residue was recrystallized from ethanol to give yellow needles, mp 142—143° (dec.). Yield, 1.0 g (74%).

4-(3-Cyano-1-triazeno)pyridine 1-Oxide Potassium Salt (VIII)——A solution of potassium cyanide (0.65 g, 0.01 mol) in water (3 ml) was added to a solution of VII (1.36 g, 0.01 mol) in 50% aqueous dioxane under ice-cooling, and the reaction mixture was allowed to stand at room temperature for 30 min. The resulting crystals were filtered off and recrystallized from aqueous ethanol to give orange-yellow pillars, mp 238—240° (dec.). UV $\lambda_{max}^{95\%EtOH}$ nm (log ε): 225 (3.83), 255 (3.50), 370 (4.41). IR ν_{max}^{Nujol} cm^{-1}: 2150, 2170 (CN). NMR (DMSO-d_6, δ): 7.15 (2H, d, J=8.0, ring), 8.00 (2H, d, J=8.0, ring). *Anal.* Calcd. for $C_6H_4KN_5O \cdot 2H_2O$: C, 30.37; H, 3.39; N, 29.52. Found: C, 30.63; H, 3.31; N, 29.80.

The free cyanotriazene (IX) was obtained as follows. Hydrochloric acid (10%, 3 ml) was added to a solution of VIII (0.24 g, 0.001 mol) in water (3 ml) under ice-cooling, and the reaction mixture was allowed to stand for 30 min. The crystals that separated were filtered off and washed with ice-water, then with methanol. Brown prisms, mp 139—140° (dec.). Yield, 60 mg (37%). IR ν_{max}^{Nujol} cm^{-1}: 2200 (CN). NMR (DMSO-d_6, δ): 7.45 (2H, d, J=6.5, ring), 8.38 (2H, d, J=6.5, ring). *Anal.* Calcd. for $C_6H_5N_5O$: C, 44.17; H, 3.09; N, 42.93. Found: C, 43.88; H, 3.00, N; 43.26.

4-[3-(N^2-Hydroxyamidino)-1-triazeno]pyridine 1-Oxide (Xa)——A mixture of VIII (0.24 g, 0.001 mol), methanol (10 ml) and hydroxylamine hydrochloride (70 mg, 0.001 mol) was heated at 80° for 20 min. The crystals that separated were filtered off and recrystallized from aqueous methanol to give yellow pillars, mp 180—181° (dec.). Yield, 0.14 g (71%). IR ν_{max}^{Nujol} cm^{-1}; 945 (NOH). NMR (DMSO-d_6, δ): 7.43 (2H, d, J=7.0, ring), 8.13 (2H, d, J=7.0, ring), 6.70 (1H, broad s, NH). *Anal.* Calcd. for $C_6H_8N_6O_2 \cdot 1/2H_2O$: C, 35.61; H, 4.29; N, 41.55. Found: C, 35.49; H, 4.52; N, 41.61.

4-(3-Thiocarbamoyl-1-triazeno)pyridine 1-Oxide (Xb)——Hydrogen sulfide was passed into a mixture of VIII (1.20 g, 0.005 mol), water (15 ml) and 28% ammonia (10 ml) for 1 hr. The resulting crystals were filtered off and recrystallized from methanol to give yellow, fine crystals, mp 145—146° (dec.). Yield, 0.96 g (96%). *Anal.* Calcd. for $C_6H_7N_5OS$: C, 36.54; H, 3.58; N, 35.51. Found: C, 36.54; H, 3.60; N, 35.68.

4-(3-Ethoxycarbonyl-1-triazeno)pyridine 1-Oxide (XI)——Conc. hydrochloric acid (0.3 ml) was added to a solution of VIII (0.72 g, 0.003 mol) in ethanol (300 ml), and the reaction mixture was heated at 55° for 1 hr. The reaction mixture was evaporated to dryness under reduced pressure, the residue was extracted with $CHCl_3$, and the solution was dried over anhyd. Na_2SO_4. The solvent was evaporated off and the residue was recrystallized from ethanol. Colorless plates, mp 193—194° (dec.). Yield, 0.15 g (24%). IR ν_{max}^{Nujol} cm^{-1}: 1760 (CO), 1180 ($COOC_2H_5$). MS *m/e*: 210 (M^+). NMR (DMSO-d_6, δ): 7.50 (2H, d, J=8.0, ring), 8.00 (2H, d, J=8.0, ring), 4.25 (2H, q, J=7.5, $-CH_2-$), 1.30 (3H, t, J=7.5, $-CH_3$), 13.4 (1H, broad s, NH). *Anal.* Calcd. for $C_8H_{10}N_4O_3$: C, 45.71; H, 4.80; N, 26.66. Found: C, 45.76; H, 4.81; N, 26.45.

1-Alkoxy-4-(3-cyano-1-triazeno)-1,4-dihydropyridines (XIIa, XIIb)——1. From VIII: A solution of dialkyl sulfate (0.002 mol) in dioxane (5 ml) was added to a solution of VIII (0.48 g, 0.002 mol) in 70% aqueous dioxane (5 ml), and the reaction mixture was allowed to stand for 3 hr. The reaction mixture was then evaporated to dryness under reduced pressure, the residue was extracted with $CHCl_3$, and the solvent was evaporated off. The residue was recrystallized from acetone to give yellow pillars. 1-Methoxy-4-(3-cyano-1-triazeno)-1,4-dihydropyridine (XIIa): Yield, 60%. mp 152—154° (dec.). IR ν_{max}^{Nujol} cm^{-1}: 2200, 2160 (CN). NMR (DMSO-d_6, δ): 7.46 (2H, d, J=7.5, ring), 8.82 (2H, d, J=7.5, ring), 4.20 (3H, s, OCH_3). *Anal.* Calcd. for $C_7H_7N_5O$: C, 47.45; H, 3.98; N, 39.53. Found: C, 47.15; H, 4.03; N, 39.72. 1-Ethoxy-4-(3-cyano-1-triazeno)-1,4-dihydropyridine (XIIb): Yield, 50%. mp 153—154° (dec.). IR ν_{max}^{Nujol} cm^{-1}: 2180, 2160 (CN). NMR (DMSO-d_6, δ): 7.50 (2H, d, J=7.5, ring), 8.77 (2H, d, J=7.5, ring), 4.45 (2H, q, J=7.5, $-CH_2-$), 1.30 (3H, t, J=7.5, $-CH_3$). *Anal.* Calcd. for $C_8H_9N_5O$: C, 50.25; H, 4.74; N, 36.69. Found: C, 50.21; H, 4.63; N, 37.08.

2. From the Quaternary Salts (XIIIa, XIIIb): The quaternary salts were prepared by mixing equimolar amounts of VII and dialkyl sulfate in $CHCl_3$, and leaving the reaction mixture overnight. The $CHCl_3$ was evaporated off under reduced pressure, and the residue was used without purification. A solution of potassium cyanide (0.65 g, 0.01 mol) in water (10 ml) was added to a solution of XIII (0.01 mol) in 70% aqueous dioxane (10 ml) under ice-cooling. The reaction mixture was allowed to stand for 30 min, the crystals that separated were filtered off and recrystallized from acetone. Yield, XIIa (60%), XIIb (65%).

Formation of Arylazo Compounds (XVa, XVb, XVc) from the Potassium Salt (VIII)——1. With 2-Naphthol: A mixture of VIII (0.24 g, 0.001 mol), 2-naphthol (145 mg, 0.001 mol), 70% aqueous ethanol (10 ml) and conc. hydrochloric acid (0.5 ml) was heated at 90° for 20 min, then the reaction mixture was evaporated to dryness under reduced pressure. The residue was extracted with $CHCl_3$, the $CHCl_3$ solution was dried over anhyd. Na_2SO_4, and the solvent was evaporated off. The residue was dissolved in a mixture of benzene and ethanol (4: 1), then passed through a Florisil column, and eluted with the same solvent. The first fraction gave unreacted 2-naphthol, then the azo compound was eluted. XVa: Reddish-black pillars (from ethanol), mp 229—230° (dec.). Yield, 20 mg (70%). *Anal.* Calcd. for $C_{15}H_{11}N_3O_2 \cdot 1/2H_2O$: C, 65.63; H, 4.37; N, 15.31. Found: C, 66.12; H, 4.13; N, 15.53.

2. With Diphenylamine: A mixture of VIII (0.24 g, 0.001 mol), diphenylamine (0.17 g, 0.001 mol), 70% aqueous ethanol (10 ml) and conc. hydrochloric acid (0.5 ml) was heated at 90° for 20 min. The reaction

mixture was evaporated to dryness under reduced pressure, the residue was extracted with $CHCl_3$, and the $CHCl_3$ solution was dried over anhyd. Na_2SO_4. The solvent was evaporated to dryness, the residue was dissolved in a mixture of benzene and ethanol (4: 1), and the solution was passed through a Florisil column using the same solvent. The first fraction gave unreacted diphenylamine, and the second one gave the azo compound (XVb). The eluate was evaporated to dryness under reduced pressure, and the residue was recrystallized from ethanol. Reddish-purple needles, mp 230—231° (dec.). Yield, 73 mg (25%). MS *m/e*: 290 (M^+). *Anal.* Calcd. for $C_{17}H_{14}N_4O$: C, 70.33; H, 4.86; N, 19.30. Found: C, 69.79; H, 4.87; N, 19.12.

The bis-azo compound (XVc) was synthesized analogously using VIII and diphenylamine in a molar ratio of 2: 1. Black needles (from ethanol), mp 271—273° (dec.). Yield, 0.10 g (23%). *Anal.* Calcd. for $C_{22}H_{17}N_7O_2 \cdot H_2O$: C, 61.48; H, 4.42; N, 22.82. Found: C, 61.31; H, 4.48; N, 22.53.

1-Methyl-4-[3-(N^2-hydroxyamidino)-1-triazeno]-1,4-dihydropyridine (XVI)——A mixture of Va (0.16 g, 0.001 mol), methanol (30 ml) and hydroxylamine hydrochloride (70 mg, 0.001 mol) was heated at 70° for 2 hr. The resulting crystals were filtered off and recrystallized from water to give yellow needles, mp 194—196° (dec.). Yield, 0.15 g (66%). *Anal.* Calcd. for $C_7H_{10}N_6O \cdot HCl \cdot H_2O$: C, 33.78; H, 5.23; N, 33.78. Found: C, 33.83; H, 5.09; N, 33.76.

1-Methoxy-4-[3-(N^2-hydroxyamidino)-1-triazeno]-1,4-dihydropyridine (XVII)——A mixture of XIIa (0.18 g, 0.001 mol), methanol (30 ml) and hydroxylamine hydrochloride (70 mg, 0.001 mol) was heated at 70° for 2 hr. The resulting crystals were filtered off and recrystallized from methanol to give yellow prisms, mp 175—177° (dec.). Yield, 0.19 g (74%). *Anal.* Calcd. for $C_7H_{10}N_6O_2 \cdot HCl$: C, 34.08; H, 4.49; N, 34.07. Found: C, 34.36; H, 4.51; N, 34.34.