The Parent of 2-(4,5-Dihydro-1*H*-tetrazol-5-ylidene)-2-cyanoacetate: Synthesis and Reactivity X-Ray Structure of (*E*)-2-[1-(2,2-Dimethylpropyl)-4,5-dihydro-1*H*-tetrazol-5-ylidene]-2-cyanoacetate [1]

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Dedicated to Professor Dr. Paul Binger on occasion of his 60th birthday.

Reaction of 3,3-diazido-2-cyanoacrylate **5** with four moles of ammonia gives tetrazolyl-bisammonium salt **7**. The key-intermediate is the amino-vinyl azide **6** which spontaneously undergoes a 1,5' ring-closure reaction followed by double deprotonation. Treatment of **7** with hydrochloric acid yields the parent of 2-(4,5-dihydro-1*H*-tetrazol-5-ylidene)-2-cyanoacetate **9** (R = Me, Et) as the only tautomer. Regiospecific monoalkylation of bisammonium salt **7a** with dimethyl sulfate and reaction of ammonium salt **12** with hydrochloric acid gives (*E*)-2-(1-methyl-4,5-dihydro-1*H*-tetrazol-5-ylidene)-2-cyanoacetate (**13**) (X-ray structure of derivative **14**). Compound **13** can also be obtained from vinyl azide **10** and methylamine. This experiment as well as AM1 calculations of **9a**, **23** and **24** strongly favour tautomer **9a**.

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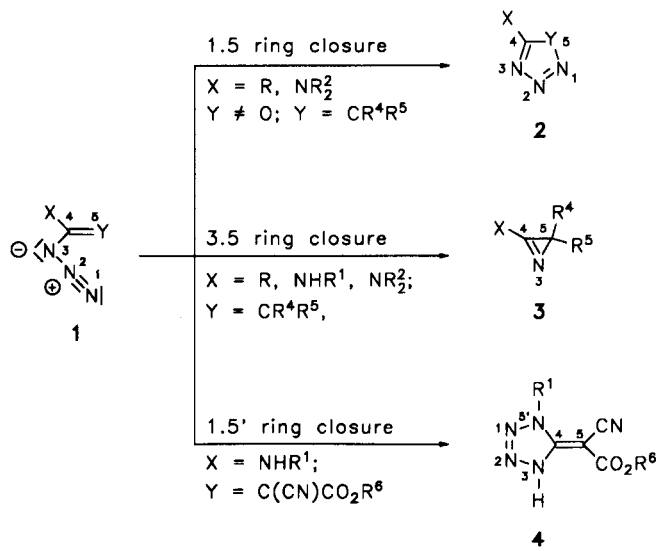
Acyl azides **1** (Y = O) [2,3] normally do not cyclize, whereas thioacyl azides **1** (Y = S) [2,4], imino azides **1** (Y = NR^3) [2,5,6] or vinyl azides **1** (X = NR_2^2, with $R^2 \neq H$, Y = CR^4R^5, with $R^4 = CO_2R^6$ and R^5 = CN, alkyl, aryl) [7] undergo a 1,5 ring-closure reaction [8] to give the corresponding isomeric 1,2,3,4-thiatriazoles **2** (Y = S), tetrazoles **2** (Y = NR^3) and 4*H*-1,2,3-triazoles **2** (X = NR_2^2, Y = CR^4R^5) respectively. The thermal transformation of vinyl azides **1** (X = R, Y = CR^4R^5, with R, R^4, R^5 = H, alkyl, aryl) leads exclusively to alkyl/aryl-substituted 2*H*-aziridines **3**. As the reaction mechanism, a 3,5 ring-closure reaction [8] of **1** with concurrent elimination of nitrogen is favoured over a pathway involving a free nitrene or one involving a 1,5 ring-closure reaction [8] to give 4*H*-1,2,3-triazoles **2** followed by elimination of nitrogen [2].

Among the thermal or photochemical transformation of the vinyl azides **1** (X = NR_2^2, Y = CR^4R^5, with $R^4 = CO_2R^6$ and R^5 = CN, alkyl, aryl) the 1,5 ring-closure reaction [8] competes with the 3,5 ring-closure reaction [8] which leads *via* elimination of nitrogen to the 2*H*-azirines **3** (X = NR_2^2, $R^4 = CO_2R^6$ and R^5 = CN, alkyl, aryl) [2a,9].

Correspondingly, 2*H*-azirine intermediates **3** (X = NHR^1, R^4 = CN, $R^5 = CO_2R^6$) can also be generated from 3-alkyl/aryl-amino-3-azido-2-cyanoacrylates **1** (X = NHR^1, Y = $C(CN)CO_2R^6$) [7,10c].

However, 3-alkyl/arylamino-3-azido-2-cyanoacrylates **1** (X = NHR^1, Y = $C(CN)CO_2R^6$) undergo a novel, base catalyzed 1,5', rather than a 1,5 ring-closure reaction [8], to give 2-(4,5-dihydro-1*H*-tetrazol-5-ylidene)-2-cyanoacetates **4** [1,10].

Scheme I



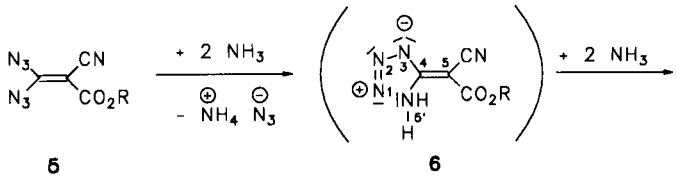
X = R, NHR^1, NR_2^2
Y = O, S, NR^3, CR^4R^5, $C(CN)CO_2R^6$
$R^4 = CO_2R^6$; R^5 = CN, alkyl, aryl

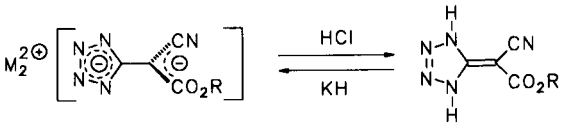
Results and Discussion.

Interestingly, we now succeeded in preparing the parent

of 2-(4,5-dihydro-1*H*-tetrazol-5-ylidene)-2-cyanoacetate **9** [= **4** with R^1 = H, R^6 = Me, Et] starting from 3,3-diazido-2-cyanoacrylate **5** and ammonia. Reaction of **5** with ammonia initially leads to 3-amino-3-azido-2-cyanoacrylate **6** [= **1** with X = NH_2, Y = $C(CN)CO_2R^6$, R^6 = Me, Et]. The hydrazoic acid being generated during this step is trapped by a second mole of ammonia to give ammonium azide. Key-intermediate **6**, in the presence of two equivalents of ammonia, undergoes a base induced 1,5′ ring-closure reaction [8], followed by double deprotonation to afford the corresponding bisammonium salt **7**. By analogy with the structure of tetrakis(dimethylamino)ethylene dication [11] we expect the two carbanion units of **7** to be twisted similarly. Treatment of **7** with hydrochloric acid yields the parent of 2-(4,5-dihydro-1*H*-tetrazol-5-ylidene)-2-cyanoacetate **9** (R = Me, Et). Compound **9a** was converted back into potassium salt **8a** by reaction with potassium hydride.

Scheme II





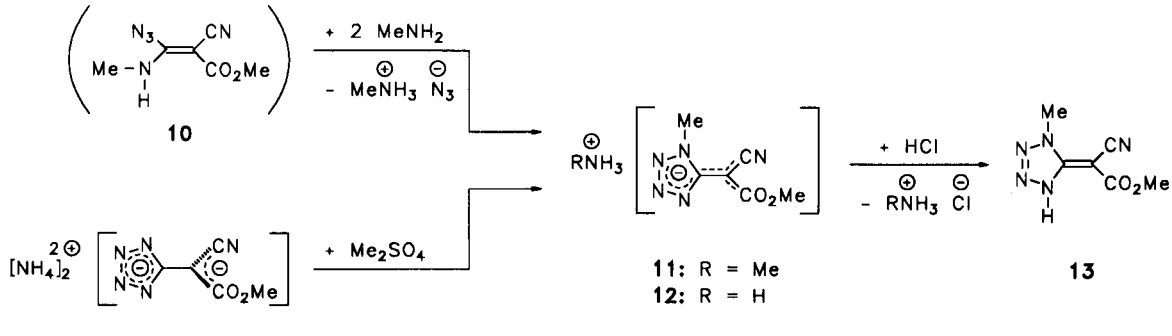
5-9	a	b
R	Me	Et

As has been shown earlier [10a-c], reaction of methyl 3,3-diazido-2-cyanoacrylate (**5a**) with a primary amine, such as methylamine, initially leads to methylamino substituted vinyl azide **10** [= **1** with X = NHMe, Y = $C(CN)CO_2Me$]. In the presence of excess methylamine, vinyl azide **10** spontaneously undergoes a 1,5′ ring-closure reaction [8], to afford the corresponding tetrazolyl methylammonium salt **11**. Treatment of **11** with hydrochloric acid finally yields the corresponding methyl (*E*)-2-(1-methyl-4,5-dihydro-1*H*-tetrazol-5-ylidene)-2-cyanoacetate (**13**) [= **4** with R^1 = R^6 = Me] [12]. Similarly, **13** can also be obtained starting from bisammonium salt **7a**. Regiospecific monoalkylation of the dianion of **7a** with dimethyl sulfate first yields ammonium salt **12**, which is transferred on treatment with hydrochloric acid into **13**. Since **13** is accessible from **7a**, the formation of **13** strongly supports structure **9** for the product formed starting from vinyl bisazide **5** and ammonia. There is no spectroscopic evidence however for the existence of any other possible tautomer of **9** (see also AM1 calculations). The ^1H and ^{13}C nmr spectra of the heterocycles **4** (including **13**) do not unambiguously establish the structure of these compounds. Therefore, we chose to carry out a X-ray structure analysis of **14** [13] (Figure 1).

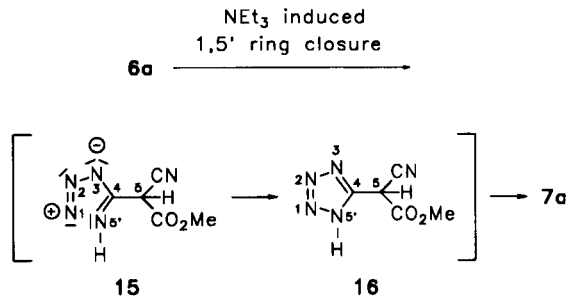
Mechanistically the ammonia-induced 1,5′ ring-closure reaction of vinyl azide **6a** with an amino group in the 4-position consists of three successive steps: vinyl azide - imino azide tautomerism (**6a** → **15**), imino azide - tetrazole isomerization (**15** → **16**) [10a-c] and double deprotonation (**16** → **7a**). Excess ammonia promotes the tautomerization and deprotonation steps (the experimental results can also be interpreted on the basis of an anionic pathway) and thus induces the 1,5′ ring-closure reaction of vinyl azide **6a** to tetrazolyl bisammonium salt **7a**.

Since there is no possibility to tautomerize for vinyl azides with dialkylamino substituents in the 4-position these compounds therefore undergo a 1,5 - rather than a 1,5′ ring-closure reaction.

Scheme III

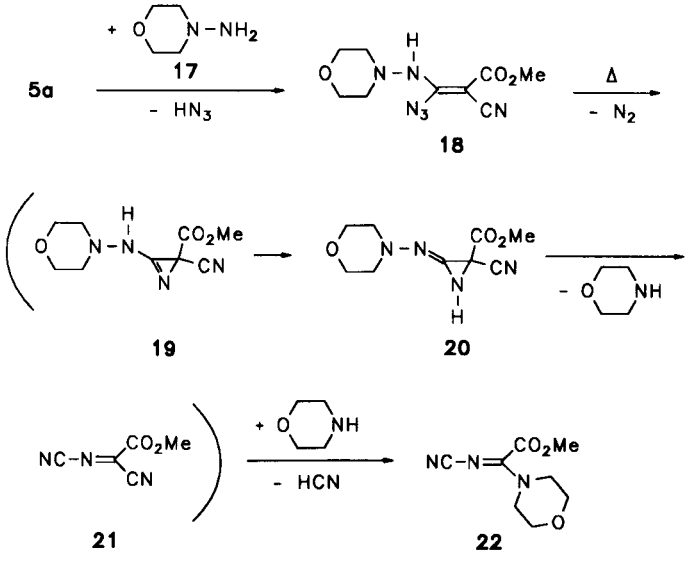


Scheme IV



Compared with the vinyl azides **1** (Y = NHR[1], Y = C(CN)CO_2R^6) reported [10a-c], methyl 3-azido-2-cyano-3-(*N*-morpholinamino)acrylate (**18**) shows completely different chemistry. Compound **18** is generated from methyl 3,3-diazido-2-cyanoacrylate (**5a**) and *N*-aminomorpholine (**17**) and while heated in toluene to 110° yields methyl *N*-cyanomorpholinooxalamidinate (**22**). The profound rearrangement of azide **18** starts with a 3,5 ring-closure reaction. The thus formed aziridine **19** tautomerizes to give iminoaziridine **20**. Ring cleavage and elimination of morpholine from **20** affords methyl cyano(cyanimino)acetate (**21**). Readdition of morpholine to **21** and elimination of cyanic acid affords oxalamidinate **22** [1].

Scheme V



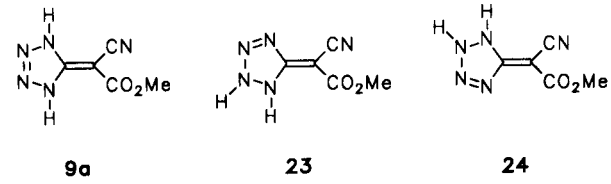
AM1 Calculations.

AM1 calculations carried out on the tetrazolyl model systems **9a**, **23** and **24** strongly support the formation of only one tautomer **9a**, which is 13.98 kcal/mol more stable than **23** and 17.14 kcal/mol more than **24** respectively.

The formation of a hydrogen bridge between the NH proton and the oxygen of the ester carbonyl function leads to an additional stabilisation of the tautomers **9a** and **23**. Moreover **9a** is nearly planar and highly conjugated.

Table 1

With AM1 Calculated Heats of Formation of 9a, 23 and 24



	9a	23	24	23-9a	24-9a
Heat of formation [kcal/mol]	60.78	74.76	77.92	13.98	17.14

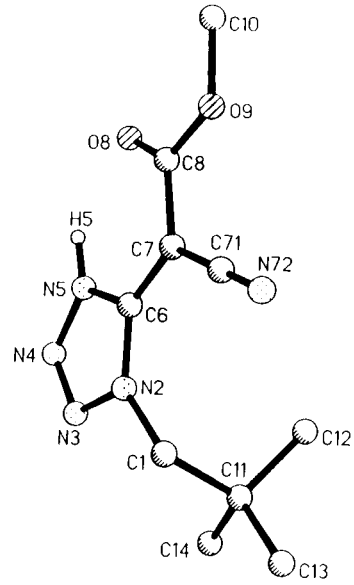


Figure 1. Computer-generated perspective drawing (ORTEP) of methyl (*E*)-2-[1-(2,2-dimethylpropyl)-4,5-dihydro-1*H*-tetrazol-5-ylidene]-2-cyanoacetate (**14**) (oxygen atoms hatched, nitrogen atoms dotted). Hydrogen atoms are omitted for purpose of clarity.

EXPERIMENTAL

The reported melting points are uncorrected (melting point apparatus, Monoskop VS, Fa. Bock, Frankfurt/Main). Elemental analyses were performed on a Hereus CHN-Mikroautomat. The infrared absorption spectra were determined on a Beckman Acculab 1, 3 and 5 spectrometer. Proton magnetic resonance spectra were recorded at 60 or 400 MHz with a JEOL C-60 HL or JNM-GX-400 spectrometer, with tetramethylsilane as internal standard. The ^{13}C magnetic resonance spectra were recorded at 25 or 100.5 MHz on either a JEOL JNM-PS-100 or JNM-GX-400 spectrometer with tetramethylsilane as internal standard. Mass spectra were obtained by direct insertion using a Varian-MAT

CH-48 at 70 eV. The uv spectra were determined on a Beckman spectrophotometer DU-64. All experimental procedures were performed under an atmosphere of dry nitrogen.

Table 2

Atomic Parameters of **14** [x 10^4] with e.s.d.'s in Parentheses and Equivalent Isotropic Displacement Parameters [pm^2 x 10^{-1}] for C, N, and O Atoms ($U_{eq} = 1/3\ \Sigma_i\Sigma_j\ U_{ij}a_i^*a_j^*\alpha_i\alpha_j$)

	x	y	z	U(eq)
C(1)	13932(2)	955(2)	5608(5)	51(1)
N(2)	13151(2)	568(1)	3843(4)	52(1)
N(3)	13569(2)	101(2)	2290(5)	70(1)
N(4)	12773(2)	-151(2)	865(5)	75(1)
N(5)	11827(2)	135(1)	1503(4)	59(1)
C(6)	12029(2)	594(2)	3364(5)	48(1)
C(7)	11247(2)	964(2)	4507(5)	48(1)
C(8)	10097(2)	895(2)	3551(5)	52(1)
O(8)	9752(2)	538(1)	1831(4)	69(1)
O(9)	9436(1)	1274(1)	4809(3)	65(1)
C(10)	8270(2)	1268(2)	3956(6)	74(1)
C(11)	14518(2)	1644(2)	4699(5)	59(1)
C(12)	13677(3)	2232(2)	3623(6)	93(2)
C(13)	15210(3)	2000(2)	6804(5)	74(1)
C(14)	15264(3)	1406(2)	2939(6)	92(2)
C(71)	11540(2)	1386(2)	6561(5)	58(1)
N(72)	11778(2)	1715(2)	8236(5)	88(1)

Table 3

Selected Bond Lengths [pm] and Bond Angles [°] of **14** with e.s.d.s' in Parentheses

C(1)-N(2)	147.0(3)	C(1)-C(11)	153.4(4)
N(2)-N(3)	136.8(4)	N(2)-C(6)	136.1(3)
N(3)-N(4)	126.9(3)	N(4)-N(5)	135.7(4)
N(5)-H(5)	97.3(2)	N(5)-C(6)	134.5(4)
C(6)-C(7)	139.4(4)	C(7)-C(8)	144.3(3)
C(7)-C(71)	141.1(4)	C(8)-O(8)	120.7(3)
C(8)-O(9)	133.8(4)	O(9)-C(10)	144.3(3)
C(11)-C(12)	152.7(4)	C(11)-C(13)	152.6(4)
C(11)-C(14)	151.8(5)	C(71)-N(72)	113.6(4)
N(2)-C(1)-C(11)	114.3(2)	C(1)-N(2)-N(3)	118.2(2)
C(1)-N(2)-C(6)	131.9(2)	N(3)-N(2)-C(6)	109.9(2)
N(2)-N(3)-N(4)	108.6(2)	N(3)-N(4)-N(5)	107.3(2)
N(4)-N(5)-H(5)	121.7(2)	N(4)-N(5)-C(6)	111.8(2)
H(5)-N(5)-C(6)	126.2(2)	N(2)-C(6)-N(5)	102.5(2)
N(2)-C(6)-C(7)	130.7(2)	N(5)-C(6)-C(7)	126.8(2)
C(6)-C(7)-C(8)	118.0(2)	C(6)-C(7)-C(71)	122.4(2)
C(8)-C(7)-C(71)	119.5(2)	C(7)-C(8)-O(8)	125.2(3)
C(7)-C(8)-O(9)	112.0(2)	O(8)-C(8)-O(9)	122.8(2)
C(8)-O(9)-C(10)	116.6(2)	C(1)-C(11)-C(12)	110.7(2)
C(1)-C(11)-C(13)	106.2(2)	C(12)-C(11)-C(13)	108.8(2)
C(1)-C(11)-C(14)	111.4(3)	C(12)-C(11)-C(14)	109.9(3)
C(13)-C(11)-C(14)	109.7(2)	C(7)-C(71)-N(72)	178.8(3)

A. Preparation of 4,5-Dihydro-1*H*-tetrazol-5-ylidene Dianions **7**. General Procedure.

A slow stream of ammonia gas was introduced into a stirred solution of 5.18 mmoles of alkyl 3,3-diazido-2-cyanoacrylate **5** in 100 ml of dichloromethane at -40° for 3 hours. After stirring for 16 hours, the reaction mixture was allowed to warm to 25°. Excess ammonia gas evaporated. The reaction mixture was filtered, the solvent removed under reduced pressure and the residue stirred with 15 ml of cold ethanol. Evaporation under reduced pressure of the filtrate left a residue, which was sublimed (50°/0.05 Torr) and recrystallized from ethanol to give the pure products.

Methyl 2-(4,5-Dihydro-1*H*-tetrazol-5-ylidene)-2-cyanoacetate Diammonium Salt (**7a**).

This compound was obtained in a yield of 0.87 g (84%), colorless crystals, mp 208° dec; ir (potassium bromide): ν 3220, 3160 (NH_4^+), 2950, 2850 (CH), 2180 (CN), 1615 (C=O), 1570 cm^{-1} (N=N); ^1H nmr (400 MHz, perdeuteriomethanol/DMSO-d_6): δ 3.66 (s, 3 H, OCH_3), 4.61 (br s, 8 H, 2 NH_4^+); ^{13}C nmr (100.5 MHz, perdeuteriomethanol/DMSO-d_6): δ 46.88 (=CC_2), 50.87 (OCH_3), 124.24 (CN), 157.17 (N_2C=), 171.06 (C=O); uv (methanol): λ max (log ϵ) 291.5 nm (2.79); ms: FD. m/e 201 (M^+).

Anal. Calcd. for $C_5H_{11}N_7O_2$: C, 29.85; H, 5.51; N, 48.74. Found: C, 29.66; H, 5.50; N, 48.47.

Ethyl 2-(4,5-Dihydro-1*H*-tetrazol-5-ylidene)-2-cyanoacetate Diammonium Salt (**7b**).

This compound was obtained in a yield of 0.81 g (72%), pale yellow crystals, mp 195° dec; ir (potassium bromide): ν 3230, 3170 (NH_4^+), 2980 (CH), 2180 (CN), 1610 (C=O), 1560 cm^{-1} (N=N); ^1H nmr (acetone-d_6/perdeuteriomethanol): δ 1.27 (t, 3 H, O-CH_2-CH_3), 4.17 (q, 2 H, O-CH_2-CH_3), 4.97 (br s, 8 H, 2 NH_4^+); ^{13}C nmr (100.5 MHz, acetone-d_6/perdeuteriomethanol): δ 15.09 (O-CH_2-CH_3), 47.00 (=CC_2), 59.45 (O-CH_2-CH_3), 123.83 (CN), 157.11 (N_2C=), 170.81 (C=O).

Anal. Calcd. for $C_6H_{13}N_7O_2$: C, 33.49; H, 6.09; N, 45.56. Found: C, 33.67; H, 6.07; N, 45.49.

B. Preparation of Methyl 2-(4,5-Dihydro-1*H*-tetrazol-5-ylidene)-2-cyanoacetate Dipotassium Salt (**8a**).

To a suspension of 0.42 g (2.5 mmoles) of methyl 2-(4,5-dihydro-1*H*-tetrazol-5-ylidene)-2-cyanoacetate (**9a**) in 50 ml of tetrahydrofuran was added 0.20 g (5 mmoles) of potassium hydride with violent stirring. After 24 hours the solvent was removed *in vacuo*, and the residue recrystallized from 14% methanolic potassium hydroxide, yield 0.61 g (100%), colorless crystals, mp 270° dec; ir (potassium bromide): ν 2960 (CH), 2170 (CN), 1625 (C=O), 1565 cm^{-1} (N=N); ^1H nmr (12% potassium perdeuteroxide in perdeuteriomethanol/deuterium oxide, 1:1): δ 3.70 (s, OCH_3); ^{13}C nmr (12% potassium perdeuteroxide in perdeuteriomethanol/deuterium oxide, 1:1): δ 47.41 (=CC_2), 51.37 (OCH_3), 130.94 (CN), 163.15 (N_2C=), 171.89 (C=O).

Anal. Calcd. for $C_5H_3K_2N_5O_2$: C, 24.68; H, 1.24; N, 28.78. Found: C, 24.45; H, 1.04; N, 28.76.

C. Preparation of 4,5-Dihydro-1*H*-tetrazol-5-ylidene Parent Compounds **9**. General Procedure.

Compound **7** (3 mmoles) was suspended in 8 ml of methanol and 0.5 ml of water. DMSO was added until the suspension was just dissolved. Then the solution was reduced to half of its original volume under reduced pressure and 0.75 ml of concentrated

hydrochloric acid was added dropwise. The precipitating crystals were collected on a Buchner funnel and washed with diethyl ether.

Methyl 2-(4,5-Dihydro-1*H*-tetrazol-5-ylidene)-2-cyanoacetate (**9a**).

This compound was obtained in a yield of 0.31 g (61%), colorless crystals, mp 177° dec; ir (potassium bromide): ν 3005 (CH), 2180 (CN), 1620 (C=O), 1560 cm^{-1} (N=N); ^1H nmr (DMSO-d_6): δ 3.60 (s, 3 H, OCH_3), 7.27 (br s, 2 H, 2 NH); ^{13}C nmr (100.5 MHz, DMSO-d_6): δ 45.42 (=CC_2), 49.64 (OCH_3), 122.77 (CN), 155.50 (N_2C=), 168.69 (C=O); uv (methanol): λ max (log ϵ) 290 nm (2.74); ms: (70 eV), m/e 167 (M^+).

Ethyl 2-(4,5-Dihydro-1*H*-tetrazol-5-ylidene)-2-cyanoacetate (**9b**).

This compound was obtained in a yield of 0.54 g (99%), colorless crystals, mp 241° dec; ir (potassium bromide): ν 2980, 2940, 2880 (CH), 2200 (CN), 1640 (C=O), 1625 cm^{-1} (N=N). ^1H nmr (DMSO-d_6): δ 1.12 (t, 3 H, O-CH_2-CH_3), 4.03 (q, 2 H, O-CH_2-CH_3), 13.87 (br s, 2 H, 2 NH); ^{13}C nmr (100.5 MHz, DMSO-d_6): δ 14.74 (O-CH_2-CH_3), 46.98 (=CC_2), 59.32 (O-CH_2-CH_3), 118.60 (CN), 151.05 (N_2C=), 166.22 (C=O); ms: (70 eV), m/e 181 (M^+).

Anal. Calcd. for $C_6H_7N_5O_2$: C, 39.78; H, 3.90; N, 38.66. Found: C, 39.89; H, 3,96; N, 38.62.

D. Preparation of Methyl (*E*)-2-[1-(2-Methyl)-4,5-dihydro-1*H*-tetrazol-5-ylidene]-2-cyanoacetate (**13**).

Route A.

Methyl (*E*)-2-[1-(2-Methyl)-4,5-dihydro-1*H*-tetrazol-5-ylidene]-2-cyanoacetate Methylammonium Salt (**11**).

To a stirred solution of 1.00 g (5.18 mmoles) of methyl 3,3-diazido-2-cyanoacrylate (**5a**) in 100 ml of dichloromethane was added 20 ml of methylamine at -30°. After 16 hours the temperature was raised to 25° (excess methylamine evaporated), and the filtrate was concentrated under reduced pressure. The remaining residue was purified by chromatography (acetone/silica gel 0.063-0.200) and recrystallized from methanol/diethyl ether, yield 0.95 g (86%), pale yellow crystals, mp 156°; ir (potassium bromide): ν 2950 (CH), 2175 (CN), 1625 (C=O), 1520 cm^{-1} (N=N); ^1H nmr (400 MHz, acetone-d_6): δ 2.10 (s, 3 H, CH_3-NH_3^+), 3.65 (br s, 6 H, NH_3^+ and OCH_3), 4.04 (s, 3 H, N-CH_3); ^1H nmr (400 MHz, DMSO-d_6): δ 2.41 (s, 3 H, CH_3-NH_3^+), 3.49 (s, 3 H, OCH_3), 3.82 (s, 3 H, CH_3-N), 7.59 (br s, 3 H, NH_3^+); ^{13}C nmr (100.5 MHz, acetone-d_6): δ 30.56 (CH_3-NH_3^+), 34.93 (CH_3-N), 47.26 (=CC_2), 51.34 (OCH_3), 121.69 (CN), 154.42 (N_2C=), 171.66 (C=O); ^{13}C nmr (100.5 MHz, DMSO-d_6): δ 24.56 (CH_3-NH_3^+), 34.61 (CH_3-N), 41.37 (=CC_2), 49.35 (OCH_3), 124.14 (CN), 155.12 (N_2C=), 167.49 (C=O).

Anal. Calcd. for $C_7H_{12}N_6O_2$: C, 39.62; H, 5.70; N, 39.60. Found: C, 39.53; H, 5.63; N, 39.57.

Compound **11** (0.64 g, 3.0 mmoles) was suspended in 5 ml of methanol and 0.5 ml of water. DMSO was added until the suspension was just dissolved. To this solution 0.50 ml of concentrated hydrochloric acid was added dropwise. The precipitating crystals of **13** were collected on a Buchner funnel and washed with diethyl ether. Compound **13** was also obtained starting from **12** (see route B), yield 0.46 g (85%), colorless crystals, mp 189° dec; ir (potassium bromide): ν 2970, 2930, 2860 (CH), 2200 (CN), 1660 (C=O), 1580 cm^{-1} (N=N); ^1H nmr (400 MHz, DMSO-d_6): δ 3.69 (s, 3 H, OCH_3), 4.06 (s, 3 H, CH_3-N), 13.07 (br s, 1 H, NH); ^{13}C nmr (100.5 MHz, DMSO-d_6): δ 35.58 (CH_3-N), 47.14 (=CC_2), 51.08 (OCH_3), 118.28 (CN), 148.73 (N_2C=), 166.69 (C=O); ms: (70 eV) m/e 181 (M^+).

Anal. Calcd. for $C_6H_7N_5O_2$: C, 39.78; H, 3.90; N, 38.66. Found: C, 39.92; H, 3.92; N, 38.67.

Route B.

Methyl (*E*)-2-[1-(2-Methyl)-4,5-dihydro-1*H*-tetrazol-5-ylidene]-2-cyanoacetate Ammonium Salt (**12**).

To a suspension of 0.60 g (3.0 mmoles) of methyl 2-(4,5-dihydro-1*H*-tetrazol-5-ylidene)-2-cyanoacetate diammonium salt **7a** was added 0.89 g (7.0 mmoles) of dimethyl sulfate. The mixture was heated to reflux for 5 days. Subsequently 30 ml of water was added and the solution was stirred for another 10 hours. The dichloromethane phase was dried over magnesium sulfate and the residue was recrystallized from methanol/diethyl ether, yield 0.29 g (49%), pale yellow crystals, mp 173° dec; ir (potassium bromide): ν 2960 (CH), 2170 (CN), 1615 (C=O), 1555 cm^{-1} (N=N); ^1H nmr (400 MHz, pyridine-d_5): δ 3.75 (s, 3 H, OCH_3), 4.10 (s, 3 H, CH_3-N), 8.73 (br s, 4 H, NH_4^+); ^{13}C nmr (100.5 MHz, pyridine-d_5): δ 35.16 (CH_3-N), 44.25 (=CC_2), 50.25 (OCH_3), 125.34 (CN), 156.14 (N_2C=), 169.51 (C=O).

Anal. Calcd. for $C_6H_{10}N_6O_2$: C, 36.36; H, 5.09; N, 42.41. Found: C, 36.37; H, 5.28; N, 42.30.

Reaction of **12** with concentrated hydrochloric acid gave **13**, see data from the preparation of **13** from **11** (Route A).

D. Single-Crystal X-ray Diffraction Analysis of Methyl (*E*)-2-[1-(2,2-Dimethylpropyl)-4,5-dihydro-1*H*-tetrazol-5-ylidene]-2-cyanoacetate (**14**) [1a,13].

A suitable transparent colorless crystal (0.3 x 1.4 x 0.1 mm) was grown through slow crystallization from dichloromethane/*n*-hexane. Data were collected on a Siemens R3m/V four circle diffractometer at room temperature using graphite monochromated MoKα radiation. The unit cell dimensions were obtained by a least-squares fit of 20 centered reflections. Intensity data were collected by using a scan type in the range of $3.5° < 2\theta < 55°$. The structure was solved, and all non-hydrogen atoms were found by using results of SHELXTL PLUS [14]. The positions of hydrogen atoms were located by using a Driding model and included in the final refinement with isotropic thermal parameters. Refinement proceeded to converge by minimizing the function Σ w ($|F_O| - |F_c|$)^2, where the weight, w, is $1/\sigma^2$(F). The discrepancy indices $R = \Sigma \| F_O| - |F_c \| / \Sigma |F_O|$, and $R_w = [\Sigma w (|F_O| - |F_c|)^2 / \Sigma w (|F_O|)^2]^{1/2}$ are presented below.

Crystallographic Data.

$C_{10}H_{15}N_5O_2$, M_r = 237.26, space group $P2_1/n$, monoclinic, a = 1220.7(4) pm, b = 1753.5(6) pm, c = 581.8(2) pm, V = 1234.1(8) x 10^6 pm^3, Z = 4, D_x = 1.227 g x cm^{-3}, (MoKα) = 0.71073 Å, μ = 0.09 mm^{-1}. Final R = 6.8%, R_w = 6.2% for 2093 unique reflections with $F \geq 3\sigma(F)$.

E. Preparation of Methyl *N*-Cyano(morpholino)oxalamidinate (**22**).

Methyl 3-Azido-2-cyano-3-(*N*-morpholinylamino)acrylate (**18**).

To a stirred solution of 1.00 g (5.18 mmoles) of methyl 3,3-diazido-2-cyanoacrylate (**5a**) in 80 ml of dichloromethane at -25° was added a solution containing 0.50 ml (5.18 mmoles) of *N*-

aminomorpholine (**17**) in 40 ml of dichloromethane. After stirring for 16 hours at -25° and filtration, the solvent was removed under reduced pressure. The residue was recrystallized from dichloromethane/diethyl ether, yield 1.07 g (82%), pale yellow crystals, mp 84° dec; ir (potassium bromide): ν 2200 (CN), 2140 (N_3), 1670 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 2.93 (t, 4 H, 2 NH_2C), 3.78 (s, 3 H, OCH_3), 3.83 (t, 4 H, 2 OCH_2), 10.30 (br s, 1 H, NH); ^{13}C nmr (deuteriochloroform): δ 51.84 (OCH_3), 56.45 (NCH_2), 64.28 (=CC_2), 65.59 (OCH_2), 115.72 (CN), 161.20 (N_2C=), 168.38 (C=O); ms: (70 eV), m/e 252 (M^+).

Anal. Calcd. for $C_9H_{12}N_6O_3$: C, 42.86; H, 4.80; N, 33.32. Found: C, 43.10; H, 4.85; N, 33.03.

One g (3.97 mmoles) of methyl 3-azido-2-cyano-3-(*N*-morpholinylamino)acrylate (**18**) was dissolved in 50 ml of toluene and heated to reflux until the evolution of nitrogen ended. Removal of the solvent under reduced pressure left a residue, which was recrystallized from dichloromethane/diethyl ether to give **22**, yield 0.61 g (78%), colorless crystals, mp 107°; ir (potassium bromide): ν 2180 (CN), 1743 (C=O), 1595 cm^{-1} (C=N); ^1H nmr (deuteriochloroform): δ 3.47 and 3.73 (2 m, 8 H, 2 NCH_2 and 2 OCH_2), 4.02 (s, 3 H, OCH_3); ^{13}C nmr (DMSO-d_6): δ 44.17, 48.63 (2 NCH_2), 54.08 (OCH_3), 65.08, 65.89 (2 OCH_2), 115.34 (CN), 159.94, 161.76 (=C and C=O); ms (70 eV), m/e 197 (M^+).

Anal. Calcd. for $C_8H_{11}N_3O_3$: C, 48.73; H, 5.62; N, 21.31. Found: C, 48.49; H, 5.87; N, 21.18.

REFERENCES AND NOTES

[1a] This paper is No. **11** in the series Geminal Vinyl Diazides. For a preceding report in this series, see: R. W. Saalfrank, C.-J. Lurz, J. Hassa, D. Danion and L. Toupet, *Chem. Ber.*, **124**, 595 (1991); [b] This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

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[12] The vinyl azides **10** and **18** are presumably present as (*E*) isomers. In the case of methyl 3-azido-2-cyano-3-(anilino)acrylate, ^{15}N nmr data favour the (*E*) configuration (hydrogen bridge between the NH proton and the oxygen of the ester carbonyl function).

[13] Further details on the structure determination may be obtained from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Informationen mbH, 7514 Eggenstein-Leopoldshafen 2, quoting the depository number CSD-55117, the authors and the reference.

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