$J$ = 7 Hz), 1.4 (t, 3 H, $J$ = 7 Hz); mass spectrum, $m/z$ 285 ($M^+$), 206, 160, 143 (100), 128, 115, 102, 89, 77.

Anal. Calcd for $C_{16}H_{15}NO_2S$: C, 67.35; H, 5.30; N, 4.91. Found: C, 67.34; H, 5.40; N, 4.84.

**2-Propyl-1-(phenylsulfonyl)indole (16b).** The same procedure as described earlier for deoxygenation using borane–*tert*-butylamine complex and $AlCl_3$ with **15b** gave **16b** (75%) after recrystallization from methanol (two crops): mp 111–113 °C; IR (KBr) 1595, 1450, 1360, 1160, 810, 760, 730, 680, 640 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 8.3–7.1 (m, 10 H), 6.4 (s, 1 H), 3.0 (t, 2 H, $J$ = 7 Hz), 2.0–1.5 (m, 2 H), 1.1 (t, 3 H, $J$ = Hz); mass spectrum, $m/z$ 299 ($M^+$), 270, 206, 157, 143, 130 (100), 117, 103, 89, 77.

Anal. Calcd for $C_{17}H_{17}NO_2S$: C, 68.20; H, 5.72; N, 4.68. Found: C, 68.18; H, 5.66; N, 4.66.

**5-Bromo-2-ethyl-1-(phenylsulfonyl)indole (16c). One-Pot Procedure from 14b.** The same procedure as described earlier for acylation–reductive deoxygenation using borane–*tert*-butylamine complex and $AlCl_3$ with **14b** gave **16c** (67%) after flash chromatography using hexanes–$CH_2Cl_2$ (60:40): mp 115–117 °C; IR (KBr) 1445, 1370, 1225, 1200, 1170, 1145, 1095, 1060, 870, 850, 805, 730, 680 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 8.2–7.1 (m, 8 H), 6.4 (s, 1 H), 3.0 (q, 2 H, $J$ = 7 Hz), 1.4 (t, 3 H, $J$ = 7 Hz).

Anal. Calcd for $C_{16}H_{14}NO_2SBr$: C, 52.76; H, 3.87; N, 3.85. Found: C, 52.64; H, 3.78; N, 3.88.

**5-Propionyl-1-(phenylsulfonyl)indoline (18b).** The same procedure as described earlier for Friedel–Crafts acylation but with **17** and propionic anhydride gave **18b** (60%) after recrystallization from methanol (two crops): mp 115–120 °C; IR (KBr) 1670, 1360, 1240, 1170, 1105, 980, 745, 690, 605 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.8–7.2 (m, 8 H), 4.0 (t, 2 H, $J$ = 7.5 Hz), 3.0 (t, 4 H, $J$ = 7.5 Hz, two $CH_2$ groups superimposed), 1.2 (t, 3 H, $J$ = 7.5 Hz); mass spectrum, $m/z$ 315 ($M^+$), 286 (100), 174, 145, 117, 89, 77.

Anal. Calcd for $C_{17}H_{17}NO_3S$: C, 64.74; H, 5.43; N, 4.44. Found: C, 64.92; H, 5.44; N, 4.49.

**5-Ethyl-1-(phenylsulfonyl)indoline (19a).** The same procedure as described earlier for deoxygenation using borane–*tert*-butylamine complex and $AlCl_3$ with **18a** gave **19a** (94%): mp 70–71 °C (lit.[33] mp 70–71 °C); IR (KBr) 1485, 1445, 1350, 1165, 980, 840, 690, 620 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.8–6.9 (m, 8 H), 3.9 (t, 2 H, $J$ = 8 Hz), 2.8 (t, 2 H, $J$ = 8 Hz), 2.5 (q, 2 H, $J$ = 7.5 Hz), 1.2 (t, 2 H, $J$ = 7.5 Hz); $^{13}C$ NMR ($CDCl_3$) $\delta$ 140.0, 139.6, 137.0, 132.9, 131.9, 128.7, 127.2, 127.0, 124.5, 114.9, 50.1, 28.2, 27.8, 15.6; mass spectrum, $m/z$ 287 ($M^+$), 272, 146 (100), 141, 130, 118, 103, 91, 77. This sample was identical (mp, IR, $^1H$ NMR) with a sample previously prepared from **18a** and $NaBH_4$/TFA.

Anal. Calcd for $C_{16}H_{17}NO_2S$: C, 66.87; H, 5.96; N, 4.87. Found: C, 66.95; H, 6.09; N, 4.90.

**5-Propyl-1-(phenylsulfonyl)indoline (19b).** The same procedure as described earlier for deoxygenation using borane–*tert*-butylamine complex and $AlCl_3$ with **18b** gave **19b** (90%). Recrystallization from methanol afforded the analytical sample: mp 72–74 °C; IR (KBr) 2960, 1490, 1350, 1160, 1090, 1050, 975, 820, 670 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.9–6.9 (m, 8 H), 3.9 (t, 2 H, $J$ = 8 Hz), 3.0–2.2 (m, 4 H), 1.8–1.4 (m, 2 H), 0.9 (t, 3 H, $J$ = 7 Hz); mass spectrum, $m/z$ 301 ($M^+$), 272, 160, 130, 118 (100), 105, 91, 77.

Anal. Calcd for $C_{17}H_{19}NO_2S$: C, 67.75; H, 6.35; N, 4.65. Found: C, 67.71; H, 6.23; N, 4.63.

**5-Propyl-1-(phenylsulfonyl)indole (20b).** To a magnetically stirred suspension of manganese(III) acetate dihydrate (0.60 g, 2.2 mmol) in acetic acid (10 mL) at 110 °C was added **19b** (0.17 g, 0.56 mmol). The mixture was stirred for 6 h, allowed to cool to room temperature, and filtered. The solid precipitate (presumably Mn(II) acetate) was washed with acetone, and the combined filtrate and washings were evaporated in vacuo and submitted to flash chromatography using hexanes–$CH_2Cl_2$ (60:40) to afford 0.10 g (60%) of **20b** as a colorless oil: IR (neat) 2960, 2930, 2870, 1560, 1462, 1390, 1265, 1225, 1095, 995, 725 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 8.0–7.0 (m, 10 H), 6.7 (d, 1 H, $J$ = 3 Hz), 2.7 (t, 2 H, $J$ = 7 Hz), 1.6 (m, 2 H), 0.9 (t, 3 H, $J$ = 7 Hz); mass spectrum, $m/z$ 299 ($M^+$), 270, 158, 143, 129, 116, 102, 77 (100).

Anal. Calcd for $C_{17}H_{17}NO_2S$: C, 68.20; H, 5.72; N, 4.68. Found: C, 68.28; H, 5.63; N, 4.61.

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# Substituent-Dependent Competition between 1,5- and 1,5′-Cyclization of Vinyl Azides. 1,2,3-Triazoles and 4,5-Dihydro-1*H*-tetrazol-5-ylidenes from Methyl 3,3-Diazido-2-cyanoacrylate with Amines[1]

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Reaction of methyl 3,3-diazido-2-cyanoacrylate (1) with amines **2** leads to vinyl azides **4a–g**, with **4a–d** being remarkably stable. Among these, the *di*alkylamino-substituted vinyl azides **4a,b** undergo 1,5 ring closure and give via 4*H*-1,2,3-triazoles **5a,b** 2-(methoxycarbonyl)-1,2,3-triazoles **6a,b**. On the contrary, vinyl azides **4c,d** with *mono*alkylamino substituents in the 4-position in the presence of equivalent amounts of triethylamine undergo 1,5′ ring closure to afford tetrazolyl triethylammonium salts **7c,d**. Treatment of **7c,d** with hydrochloric acid yields 4,5-dihydro-1*H*-tetrazol-5-ylidenes **8c,d**. The vinyl azides **4e–g** in situ generated from 1 and primary/tertiary diamines **2e–g** undergo self-induced 1,5′ ring closure to give tetrazolyl ammonium betaines **9e–g**. Reaction of vinyl diazide 1 with bis primary 1,$\omega$-diamines **10** yields crystalline bis vinyl azides **11**. Triethylamine-induced 1,5′ ring closure of **11** produces the bis tetrazolyl ammonium salts **12**.

Acyl azides exist exclusively in the open-chain azide form,[2,3] whereas thioacyl azides cyclize to give 1,2,3,4-thiatriazoles.[2,4]

In the case of imino azides, electron-accepting substit-

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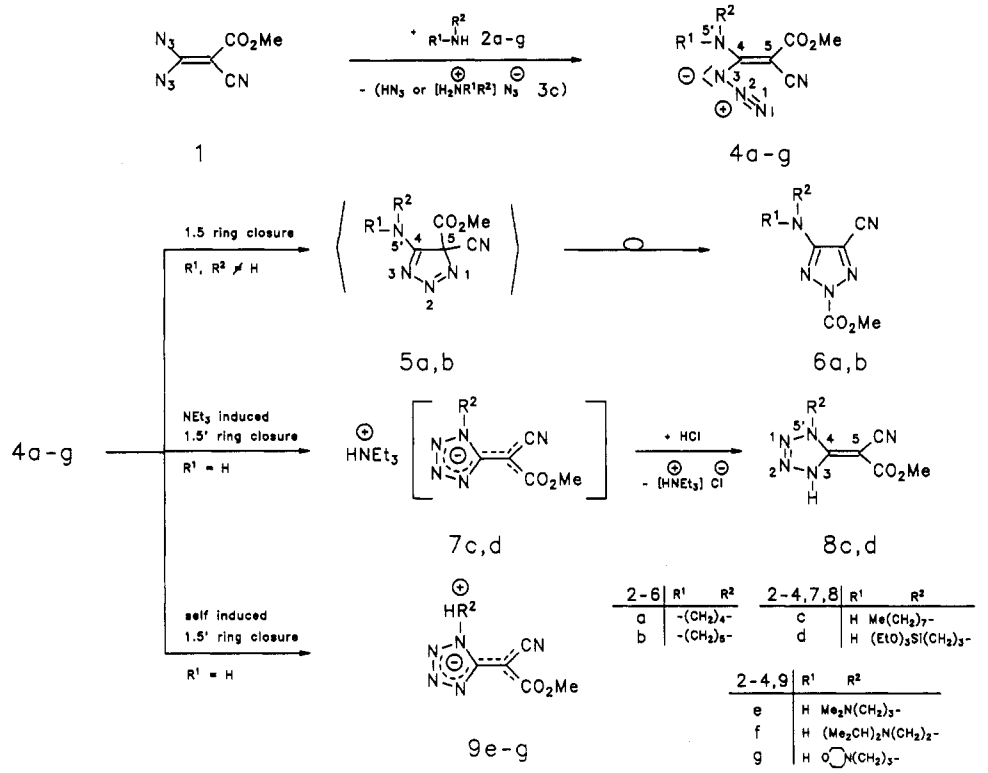
**Scheme I**




uents are capable of stabilizing the azide form, tetrazoles being obtained otherwise.[2,5] The thermal transformation of vinyl azides, with alkyl and aryl substituents only, leads exclusively to 2*H*-azirines. As the reaction mechanism, a 3,5 ring closure of the vinyl azide with concurrent elimination of nitrogen is favored over a pathway involving a free nitrene or one involving a 1,5 ring closure to give 4*H*-1,2,3-triazoles followed by elimination of nitrogen.[2a,6] Whereas the imino azide–tetrazole isomerization[7] is well documented, there have been only a few reports on the vinyl azide–4*H*-triazole isomerization.[8] Donor/acceptor-substituted vinyl azides can cyclize by three different mechanisms undergoing 1,5-, 1,5′-, or 3,5 ring-closure reactions.[8a,9]

Depending on the substituents and the reaction conditions, either stable 1,2,3-triazoles are formed via 4*H*-1,2,3-triazoles, 4,5-dihydro-1*H*-tetrazol-5-ylidenes are generated, or 2*H*-azirines are formed with elimination of nitrogen.

## Results and Discussion

As has been shown earlier for aromatic amines and hydrazine and hydroxylamine derivatives,[9] reaction of methyl 3,3-diazido-2-cyanoacrylate (1) (Scheme I) with primary and secondary amines **2** initially leads to donor/acceptor-substituted vinyl azides **4**,[10] among which **4a–d** are remarkably stable. In the case of amine **2c**, the hydrazoic acid being generated during this reaction is trapped by a second mole of **2c** to give the corresponding ammonium azide **3c**.

The IR spectra of the vinyl azides **4a–d** show two characteristic absorptions for the CN and $N_3$ groups respectively in the range 2140–2205 $cm^{-1}$.

A detailed investigation of the vinyl azides **4** revealed that those having *di*alkylamino substituents in the 4-position, as **4a,b**, undergo 1,5 ring closure to give primarily 4*H*-1,2,3-triazoles **5a,b**,[10] which spontaneously isomerize to yield the stable fluorescent 2-(methoxycarbonyl)-1,2,3-triazoles **6a,b**.[11] In order to avoid trans methoxy carbo-

(1) (a) This paper is no. 8 in the series Geminal Vinyl Diazides. For a preceding report in this series, see: Saalfrank, R. W.; Wirth, U. *Chem. Ber.* **1989**, *122*, 969. (b) This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

(2) Reviews: (a) Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 947. (b) Tisler, M. *Synthesis* **1973**, 123. (c) Butler, R. N. *Adv. Heterocycl. Chem.* **1977**, *21*, 323.

(3) Lieber, E.; Minnis, R. L., Jr.; Rao, C. N. R. *Chem. Rev.* **1965**, *65*, 377.

(4) Holm, A. *Adv. Heterocycl. Chem.* **1976**, *20*, 145. Lieber, E.; Pillai, C. N. *J. Org. Chem.* **1957**, *22*, 1054. Lieber, E.; Ramachandran, J. *Can. J. Chem.* **1959**, *37*, 101.

(5) Von Philipsborn, W.; Müller, R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 383. Hull, W. E.; Künstlinger, M.; Breitmaier, E. *Ibid.* **1980**, *19*, 924. Neidlein, R.; Heukelbach, E. *Ibid.* **1966**, *5*, 520. Huisgen, R. *Angew. Chem.* **1960**, *72*, 359.

(6) Bock, H.; Dammel, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 504. Bock, H.; Dammel, R.; Aygen, S. *J. Am. Chem. Soc.* **1983**, *105*, 7681. Bock, H.; Dammel, R. *Z. Naturforsch.* **1987**, *B42*, 301. Bock, H.; Dammel, R. *Inorg. Chem.* **1985**, *24*, 4427. Hassner, A.; Wiegand, N. H.; Gottlieb, H. E. *J. Org. Chem.* **1986**, *51*, 3176. Yamabe, T.; Kaminoyama, M.; Minato, T.; Hori, K.; Isomura, K.; Taniguchi, H. *Tetrahedron* **1984**, *40*, 2095. Burke, L. A.; Leroy, G.; Nguyen, M. T.; Sana, M. *J. Am. Chem. Soc.* **1978**, *100*, 3668. L'abbé, G. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 775.

(7) Used instead of the term "azido/tetrazolo isomerization".[2b]

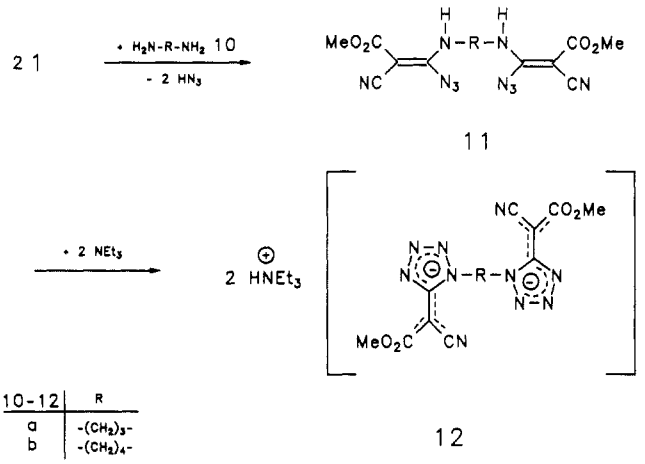
(8) (a) Saalfrank, R. W.; Ackermann, E.; Fischer, M.; Wirth, U. *Chem. Ber.* **1987**, *120*, 2003. (b) Henriet, M.; Hountekie, M.; Techy, B.; Touillaux, R.; Ghosez, L. *Tetrahedron Lett.* **1980**, *21*, 223. Bernard, C.; Ghosez, L. *J. Chem. Soc., Chem. Commun.* **1980**, 940.

(9) (a) Saalfrank, R. W.; Fischer, M.; Wirth, U.; Zimmermann, H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1160. (b) Zimmermann, H.; Gomm, M.; Wirth, U.; Fischer, M.; Saalfrank, R. W. *Acta Crystallogr.*, in press. (c) Saalfrank, R. W.; Wirth, U. *Chem. Ber.* **1989**, *122*, 519. (d) Saalfrank, R. W.; Wirth, U. *Chem. Ber.* **1989**, *122*, 969. (e) Saalfrank, R. W.; Ackermann, E.; Fischer, M.; Wirth, U.; Zimmermann, H. *Chem. Ber.*, in press.

(10) The (unsystematic) numbering of the compounds **4**, **5**, and **8** assists in discussing the substituent effects and in assigning the ring-closure reactions.

(11) Mechanistic aspects of this isomerization currently are under investigation. For rearrangements of 1,2,3-triazoles, see: Jones, J. H.; Wyatt, P. B. *J. Chem. Res., Synop.* **1987**, 396.

**Scheme II**




nylation resulting in the formation of 1,2,3-triazole-4-carbonitriles,[8a] an excess of the amines **2a,b** and the presence of moisture must be strongly prohibited. Strict adherence to the procedures given (see Experimental Section) avoids the formation of mixtures and obviates the need for tedious chromatographic separations.

On the other hand, the vinyl azides **4c–d** with *mono*-alkylamino substituents in the 4-position, in the presence of equivalent amounts of triethylamine in dichloromethane, undergo a 1,5′ ring-closure reaction to afford the corresponding tetrazolyl triethylammonium salts **7c,d**.

Treatment of the ammonium salts **7c–d** with hydrochloric acid yields the methyl (*E*)-2-(1-alkyl-4,5-dihydro-1*H*-tetrazol-5-ylidene)-2-cyanoacetates **8c,d**.[10] The *E* configuration for compounds **8** follows from an X-ray structure analysis carried out for methyl (*E*)-2-(1-phenyl-4,5-dihydro-1*H*-tetrazol-5-ylidene)-2-cyanoacetate.[9a,b,12]

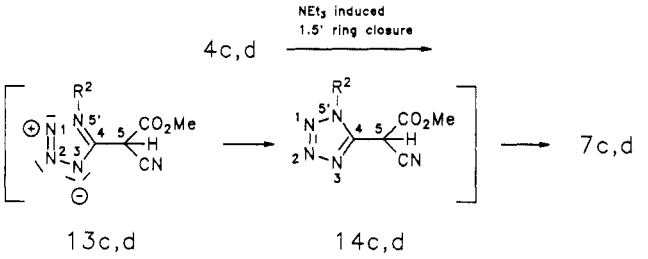
Interestingly, in the case of the vinyl azide intermediates **4e–g**, generated from bisazide **1** and the primary/tertiary diamines **2e–g**, no external base is necessary in order to induce the 1,5′ ring closure. The extra tertiary amino function in the azides **4e–g** acts as an internal base, resulting in tetrazolyl ammonium betaines **9e–g**.

Reaction of the geminal vinyl diazide **1**, at −30 °C in dichloromethane, with the bis primary 1,ω-diamines **10a,b** leads to the corresponding crystalline bis vinyl azides **11a,b** (Scheme II). Since the diamines **10** are known to cleave bis vinyl azides **11**, generating the corresponding vinyl azides, which then spontaneously undergo 1,5′ ring closure to give tetrazolyl ammonium betaines of type **9**,[9d] an excess of **10** must be avoided.

However, triethylamine-induced 1,5′ cyclization of **11a,b** allows the generation of the bis tetrazolyl ammonium salts **12a,b** without the formation of cleavage products.

Mechanistically the triethylamine-induced 1,5′ ring-closure reaction of the vinyl azides **4c,d** with $R^2NH$ groups in the 4-position consists of three successive steps: vinyl azide–imino azide tautomerism (**4c,d** → **13c,d**), imino azide–tetrazole isomerization (**13c,d** → **14c,d**),[9c,d,13] and deprotonation (**14c,d** → **7c,d**). Triethylamine promotes the tautomerization step (currently an anionic pathway cannot be excluded) and thus induces the 1,5′ ring-closure reaction of the vinyl azides **4c,d** to tetrazolyl triethylammonium salts **7c,d** (Scheme III).

**Scheme III**




In the case of **4e–g**, the extra tertiary amino function initiates the 1,5′ ring-closure reaction to give the betaines **9e–g**.

For **4a,b** (with $R^1/R^2 \neq H$) there is no possibility to tautomerize. The vinyl azides **4a,b** with dialkylamino substituents in the 4-position therefore undergo a 1,5 rather than a 1,5′ ring-closure reaction and give the 4*H*-1,2,3-triazole intermediates **5a,b**.

## Experimental Section

The reported melting points are uncorrected (melting point apparatus, Monoskop VS, Fa. Bock, Frankfurt/Main). Elemental analyses were performed on a Hereus CHN-Mikroautomat instrument. The infrared absorption spectra were determined on a Beckman IR-5 and Acculab 3 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. $^{13}C$ 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. All experimental procedures were performed under an atmosphere of dry nitrogen.

**A. Preparation of Vinyl Azides 4. General Procedure.** To a stirred solution of 1.00 g (5.18 mmol) of methyl 3,3-diazido-2-cyanoacrylate (**1**) in 80 mL of dichloromethane at −20 °C was added a solution containing 5.18 mmol of amine **2** in 40 mL of dichloromethane. After stirring for 16 h at −20 °C and filtration, the solvent was removed under reduced pressure. The residue was recrystallized from dichloromethane/ether. For azides **4a** and **4b**, see ref 8a.

**Methyl 3-Azido-2-cyano-3-(octylamino)acrylate (4c).** In this case, 8.86 mmol of amine **2c** is necessary: yield 0.96 g (66.2%); mp 37 °C dec; IR (KBr) $\nu$ 2205 (CN), 2140 ($N_3$), 1660 $cm^{-1}$ (C=O); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 0.89 (m, 3 H, $CH_3$), 1.28 (m, 10 H, 5 $CH_2$), 1.58 (m, 2 H, $CH_2$), 3.36 (q, 2 H, $NCH_2$), 3.77 (s, 3 H, $OCH_3$), 9.47 (br s, 1 H, NH); $^{13}C$ NMR (100.5 MHz, $CDCl_3$) $\delta$ 13.98 ($CH_3$), 22.51, 26.52, 28.96, 29.08, 29.44, 31.63 (6 $CH_2$), 43.08 ($NCH_2$), 51.76 ($OCH_3$), 63.95 (=C), 115.75 (CN), 160.20 (=C), 168.96 (C=O); MS (70 eV), *m/e* 279 ($M^+$). Anal. Calcd for $C_{13}H_{21}N_5O_2$: C, 55.89; H, 7.58; N, 25.07. Found: C, 55.66; H, 7.43; N, 24.78.

**Methyl 3-Azido-2-cyano-3-[[3-(triethoxysilyl)propyl]-amino]acrylate (4d):** yield 1.87 g (97.1%); green oil: IR (100%) $\nu$ 2205 (CN), 2140 ($N_3$), 1660 $cm^{-1}$ (C=O), $^1H$ NMR ($CDCl_3$) $\delta$ 0.60 (t, 2 H, $CH_2Si$), 1.25 (t, 9 H, 3 $CH_3$), 1.70 (m, 2 H, $CH_2$), 3.38 (q, 2 H, $CH_2N$), 3.80 (s, 3 H, $OCH_3$), 3.87 (q, 6 H, 3 $OCH_2$), 9.50 (br s, 1 H, NH); $^{13}C$ NMR (100.5 MHz, $CDCl_3$) $\delta$ 6.97 ($CH_2Si$), 18.07 (3 $CH_3$), 23.05 ($CH_2$), 45.10 ($CH_2N$), 51.81 ($OCH_3$), 58.26 (3 $OCH_2$), 63.41 (=C), 116.05 (CN), 159.73 (=C), 168.67 (C=O); MS (70 eV), *m/e* 371 ($M^+$). Anal. Calcd for $C_{14}H_{25}N_5O_5Si$: C, 45.27; H, 6.78; N, 18.85. Found: C, 45.28; H, 6.83; N, 18.52.

**B. Preparation of *N*-Octylammonium Azide (3c).** See A. After stirring for 16 h, the insoluble crystals were filtered and washed with dichloromethane: yield 0.42 g (83.8%); mp 134 °C; IR (KBr) $\nu$ 2920 ($NH_3^+$), 2020 $cm^{-1}$ ($N_3$); $^1H$ NMR ($CDCl_3$) $\delta$ 0.87 (m, 3 H, $CH_3$), 0.97 (m, 12 H, 6 $CH_2$), 2.93 (t, 2 H, $CH_2N$), 7.20 (s, 3 H, $NH_3^+$); $^{13}C$ NMR (100.5 MHz, $CDCl_3$) $\delta$ 13.97 ($CH_3$), 22.55, 26.65, 27.83, 29.12, 29.15, 31.72, 40.02 (7 $CH_2$).

**C. Preparation of Methyl 1,2,3-Triazole-2-carboxylates 6. General Procedure.** A catalytic amount of pyrrolidine or piperidine was added at 0 °C to 1.50 mmol of vinyl azide **4a,b**[8a]

(12) The vinyl azides **4** are presumably present as *E* isomers.

(13) Cf. also: Chakrasali, R. T.; Ila, H.; Junjappa, H. *Synthesis* **1988**, 453. Quast, H.; Bieber, L.; Meichsner, G.; Regnat, D. *Chem. Ber.* **1988**, *121*, 1285.

in 50 mL of ether. The reaction was allowed to proceed for 72 h at 0 °C. Then the solvent was removed in vacuo, and the residue was recrystallized from dichloromethane/ether.

**Methyl 5-Cyano-4-pyrrolidino-1,2,3-triazole-2-carboxylate (6a)**: yield 0.30 g (90%); mp 121 °C (fluorescent crystals); IR (KBr) $\nu$ 2240 (CN), 1785 $cm^{-1}$ (C=O); $^1H$ NMR ($CDCl_3$) $\delta$ 2.00 (m, 4 H, 2 $CH_2$), 3.56 (m, 4 H, 2 $NCH_2$), 4.09 (s, 3 H, $OCH_3$); $^{13}C$ NMR ($CDCl_3$) $\delta$ 25.33 ($CH_2$), 48.29 ($NCH_2$), 56.03 ($OCH_3$), 111.94 (CN and C-5), 146.82 (C-4), 154.86 (C=O); MS (70 eV), $m/e$ 221 ($M^+$). Anal. Calcd for $C_9H_{11}N_5O_2$: C, 48.86; H, 5.01; N, 31.66. Found: C, 48.59; H, 4.78; N, 31.42.

**Methyl 5-Cyano-4-piperidino-1,2,3-triazole-2-carboxylate (6b)**: yield 0.24 g (68%); mp 96 °C (fluorescent crystals); IR (KBr) $\nu$ 2243 (CN), 1772 $cm^{-1}$ (C=O); $^1H$ NMR (acetone-$d_6$) $\delta$ 1.67 (m, 6 H, 3 $CH_2$), 3.55 (m, 4 H, 2 $NCH_2$), 4.15 (s, 3 H, $OCH_3$); $^{13}C$ NMR (acetone-$d_6$) $\delta$ 22.66, 23.75 ($CH_2$), 47.23 ($NCH_2$), 54.75 ($OCH_3$), 111.06 and 111.78 (CN or C-5), 145.64 (C-4), 156.41 (C=O); MS (70 eV), $m/e$ 235 ($M^+$). Anal. Calcd for $C_{10}H_{13}N_5O_2$: C, 51.06; H, 5.57; N, 29.77. Found: C, 51.25; H, 5.55; N, 29.90.

**D. Preparation of Triethylammonium Salts 7. General Procedure.** To 2 mmol of vinyl azide 4 in 40 mL of dichloromethane at 25 °C was added 2 mmol of triethylamine. The mixture was stirred for 2 h at 25 °C, and then the solvent was removed under reduced pressure. The oily residue was washed with dry ether.

**Methyl (*E*)-2-(1-Octyl-4,5-dihydro-1*H*-tetrazol-5-ylidene)-2-cyanoacetate Triethylammonium Salt (7c)**: yield 0.72 g (75.8%); yellow oil; IR (100%) $\nu$ 2185 (CN), 1630 $cm^{-1}$ (C=O); $^1H$ NMR ($CDCl_3$) $\delta$ 0.86 (m, 3 H, $CH_3$), 1.27 (t, 9 H, 3 $NCH_2CH_3$), 1.30 (m, 10 H, 5 $CH_2$), 1.90 (m, 2 H, $CH_2CH_2N$), 3.32 (q, 6 H, 3 $NCH_2CH_3$), 3.67 (s, 3 H, $OCH_3$), 4.52 (t, 2 H, $NCH_2$), 9.67 (br s, 1 H, NH); $^{13}C$ NMR (100.5 MHz, $CDCl_3$) $\delta$ 8.27 ($NCH_2CH_3$), 13.92 ($CH_3$), 22.46, 26.18, 28.91, 28.94, 29.26, 31.58 (6 $CH_2$), 44.62 (=C), 45.69 ($NCH_2CH_3$), 47.63 ($NCH_2$), 50.32 ($OCH_3$), 123.39 (CN), 153.08 (=C), 169.24 (C=O). Anal. Calcd for $C_{19}H_{36}N_6O_2$: C, 59.97; H, 9.54; N, 22.09. Found: C, 59.67; H, 9.43; N, 21.86.

**Methyl (*E*)-2-[1-[3-(Triethoxysilyl)propyl]-4,5-dihydro-1*H*-tetrazol-5-ylidene]-2-cyanoacetate Triethylammonium Salt (7d)**: yield 1.11 g (93.9%); yellow oil; IR (100%) $\nu$ 2170 (CN), 1645 $cm^{-1}$ (C=O); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 0.67 (m, 2 H, $CH_2Si$), 1.21 (t, 9 H, 3 $CH_3CH_2O$), 1.29 (t, 9 H, 3 $NCH_2CH_3$), 2.00 (m, 2 H, $CH_2CH_2Si$), 3.32 (q, 6 H, 3 $NCH_2CH_3$), 3.67 (s, 3 H, $OCH_3$), 3.80 (q, 6 H, 3 $CH_3CH_2O$), 4.51 (t, 2 H, $CH_2N$), 11.00 (br s, 1 H, NH); $^{13}C$ NMR (100.5 MHz, $CDCl_3$) $\delta$ 6.92 ($CH_2Si$), 8.20 ($NCH_2CH_3$), 18.03 ($CH_3CH_2O$), 22.88 ($CH_2$), 44.31 (=C), 45.64 ($NCH_2CH_3$), 49.68 ($CH_2N$), 50.09 ($OCH_3$), 58.18 ($CH_3CH_2O$), 123.68 (CN), 153.34 (=C), 169.14 (C=O); MS (FD), $m/e$ 472 ($M^+$). Anal. Calcd for $C_{20}H_{40}N_6O_5Si$: C, 50.82; H, 8.53; N, 17.78. Found: C, 50.48; H, 8.59; N, 17.47.

**E. Preparation of 4,5-Dihydro-1*H*-tetrazol-5-ylidenes 8. General Procedure.** Triethylammonium salt 7 (2 mmol) was dissolved in 25 mL of dichloromethane at 25 °C. To this solution was added dropwise 3 mmol of HCl in 25 mL of water. The reaction was allowed to proceed for 1 h, and after filtration, the dichloromethane phase was dried over magnesium sulfate. Removal of the solvent under reduced pressure left a residue, which was washed with ether.

**Methyl (*E*)-2-(1-Octyl-4,5-dihydro-1*H*-tetrazol-5-ylidene)-2-cyanoacetate (8c)**: yield 0.29 g (52.3%); mp 113 °C; IR (KBr) $\nu$ 2200 (CN), 1645 (C=O), 1573 $cm^{-1}$ (N=N); $^1H$ NMR ($CDCl_3$) $\delta$ 0.87 (m, 3 H, $CH_3$), 1.33 (m, 10 H, 5 $CH_2$), 1.93 (m, 2 H, $CH_2CH_2N$), 3.92 (s, 3 H, $OCH_3$), 4.58 (t, 2 H, $CH_2N$), 14.33 (br s, 1 H, NH); $^{13}C$ NMR (100.5 MHz, $CDCl_3$) $\delta$ 13.96 ($CH_3$), 22.48, 25.85, 28.81, 28.90, 29.32, 31.32 (6 $CH_2$), 48.89 ($NCH_2$), 49.30 (=C), 52.44 ($OCH_3$), 116.75 (CN), 148.45 (=C), 169.27 (C=O); MS (70 eV), $m/e$ 279 ($M^+$). Anal. Calcd for $C_{13}H_{21}N_5O_2$: C, 55.89; H, 7.58; N, 25.07. Found: C, 55.51; H, 7.43; N, 24.83.

**Methyl (*E*)-2-[1-[3-(Triethoxysilyl)propyl]-4,5-dihydro-1*H*-tetrazol-5-ylidene]-2-cyanoacetate (8d)**: yield 0.53 g (71.4%); mp 129 °C; IR (KBr) $\nu$ 2210 (CN), 1660 (C=O), 1585 $cm^{-1}$ (N=N); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 0.70 (m, 2 H, $CH_2Si$), 1.23 (t, 9 H, 3 $CH_3$), 2.06 (m, 2 H, $CH_2$), 3.83 (q, 6 H, 3 $OCH_2$), 3.90 (s, 3 H, $OCH_3$), 4.60 (t, 2 H, $CH_2N$), 11.35 (br s, 1 H, NH); $^{13}C$ NMR (100.5 MHz, $CDCl_3$) $\delta$ 6.83 ($CH_2Si$), 18.15 ($CH_3$), 23.27 ($CH_2$), 49.19 (=C), 50.80 ($CH_2N$), 52.36 ($OCH_3$), 58.47 ($OCH_2$), 116.82 (CN), 148.60 (=C), 169.21 (C=O); MS (70 eV), $m/e$ 372 ($M^+$). Anal. Calcd for $C_{14}H_{25}N_5O_5Si$: C, 45.27; H, 6.78; N, 18.85. Found: C, 44.89; H, 6.80; N, 18.50.

**F. Preparation of 4,5-Dihydro-1*H*-tetrazol-5-ylidene Betaines 9. General Procedure.** To a solution of 0.50 g (2.59 mmol) of methyl 3,3-diazido-2-cyanoacrylate (1) in 50 mL of dichloromethane at −25 °C was added 2.60 mmol of amine 2 in 30 mL of dichloromethane. The mixture was stirred for 14 h at −25 °C and was then filtered. The colorless crystals were washed with dichloromethane.

**Methyl (*E*)-2-[1-[3-(Dimethylamino)propyl]-4,5-dihydro-1*H*-tetrazol-5-ylidene]-2-cyanoacetate Betaine (9e)**: yield 0.54 g (83%); mp 198 °C; IR (KBr) $\nu$ 2720 ($NH^+$), 2150 (CN), 1652 $cm^{-1}$ (C=O); $^1H$ NMR (400 MHz, DMSO-$d_6$) $\delta$ 2.14 (m, 2 H, $CH_2$), 2.80 (s, 6 H, 2 $CH_3$), 3.10 (m, 2 H, $NCH_2$), 3.49 (s, 3 H, $OCH_3$), 4.36 (t, 2 H, $CH_2$-ring), 9.38 (br s, 1 H, NH); $^{13}C$ NMR (100.5 MHz, DMSO-$d_6$) $\delta$ 23.78 ($CH_2$), 41.90 (=C), 42.38 (2 $NCH_3$), 44.57 ($CH_2$-ring), 49.41 ($OCH_3$), 54.30 ($NCH_2$), 123.91 (CN), 154.71 (=C), 167.63 (C=O); MS (70 eV), $m/e$ 252 ($M^+$). Anal. Calcd for $C_{10}H_{16}N_6O_2$: C, 47.61; H, 6.39; N, 33.31. Found: C, 47.39; H, 6.35; N, 33.12.

**Methyl (*E*)-2-[1-[2-(Diisopropylamino)ethyl]-4,5-dihydro-1*H*-tetrazol-5-ylidene]-2-cyanoacetate Betaine (9f)**: yield 0.58 g (76%); mp 177 °C; IR (KBr) $\nu$ 2685 ($NH^+$), 2180 (CN), 1600 $cm^{-1}$ (C=O); $^1H$ NMR (DMSO-$d_6$) $\delta$ 1.25 (d, 12 H, 4 $CH_3$), 3.57 (s, 3 H, $OCH_3$), 3.73 (m, 2 H, $CH_2$), 7.63 (t, 2 H, $CH_2$-ring), 9.23 (br s, 1 H, NH); $^{13}C$ NMR (100.5 MHz, DMSO-$d_6$) $\delta$ 16.41, 17.79 (4 $CH_3$, coalescence), 42.46 (=C), 44.74, 45.57 (2 $CH_2$), 49.91 ($OCH_3$), 54.86 (2 CH), 122.85 (CN), 155.07 (=C), 168.73 (C=O); MS (70 eV), $m/e$ 294 ($M^+$). Anal. Calcd for $C_{13}H_{22}N_6O_2$: C, 53.05; H, 7.53; N, 28.55. Found: C, 52.78; H, 7.24; N, 28.23.

**Methyl (*E*)-2-[1-(3-Morpholinopropyl)-4,5-dihydro-1*H*-tetrazol-5-ylidene]-2-cyanoacetate Betaine (9g)**: yield 0.43 g (56.3%); mp 207 °C dec; IR (KBr) $\nu$ 2940 ($NH^+$), 2160 (CN), 1645 $cm^{-1}$ (C=O); $^1H$ NMR (400 MHz, DMSO-$d_6$) $\delta$ 2.22 (m, 2 H, $CH_2$), 3.15 (m, 2 H, $CH_2$-morpholine), 3.31 (m, 4 H, 2 $NCH_2$), 3.50 (s, 3 H, $OCH_3$), 3.78 (m, 4 H, 2 $OCH_2$), 4.36 (t, 2 H, $CH_2N$), 9.55 (br s, 1 H, NH); $^{13}C$ NMR (100.5 MHz, DMSO-$d_6$) $\delta$ 22.97 ($CH_2$), 42.00 (=C), 44.48 ($CH_2$-morpholine), 49.42 ($OCH_3$), 51.29 (2 $NCH_2$), 53.46 ($CH_2N$), 63.40 (2 $OCH_2$), 123.72 (CN), 154.54 (=C), 167.65 (C=O); MS (70 eV), $m/e$ 294 ($M^+$). Anal. Calcd for $C_{12}H_{18}N_6O_3$: C, 48.97; H, 6.16; N, 28.56. Found: C, 48.65; H, 6.39; N, 28.26.

**G. Preparation of Bis Tetrazolyl Triethylammonium Salts 12.** To a solution of 1 g of bis vinyl azide 11[9c] in 50 mL of toluene/hexane (3:1) was added an equimolar amount of triethylamine at 25 °C. After stirring for 20 min, the solvent was removed under reduced pressure. The residue was recrystallized from dichloromethane/ether.

**Dimethyl (*E*)-2,2′-[Trimethylene-1,1′-bis(4,5-dihydro-1*H*-tetrazol-5-ylidene)]bis(2-cyanoacetate) Bis(triethylammonium salt) (12a)**: yield 1.29 g (86.1%); mp 94 °C; IR (KBr) $\nu$ 2156, 2169 (CN), 1645 $cm^{-1}$ (C=O); $^1H$ NMR ($CDCl_3$) $\delta$ 1.31 (t, 18 H, 6 $CH_3$), 2.50 (m, 2 H, $CH_2$), 3.34 (q, 12 H, 6 $NCH_2$), 3.68 (s, 6 H, 2 $OCH_3$), 4.63 (t, 4 H, 2 $CH_2N$-ring), 10.00 (br s, 2 H, 2 NH); $^{13}C$ NMR (100.5 MHz, $CDCl_3$) $\delta$ 8.25 ($CH_3$), 28.19 ($CH_2$), 44.35 (=C), 44.81 ($CH_2N$-ring), 45.72 ($NCH_2$), 50.19 ($OCH_3$), 123.65 (CN), 153.46 (=C), 168.91 (C=O). Anal. Calcd for $C_{25}H_{44}N_{12}O_4$: C, 52.07; H, 7.69; N, 29.15. Found: C, 51.83; H, 7.69; N, 28.92.

**Dimethyl (*E*)-2,2′-[Tetramethylene-1,1′-bis(4,5-dihydro-1*H*-tetrazol-5-ylidene)]bis(2-cyanoacetate) Bis(triethylammonium salt) (12b)**: yield 1.25 g (81.8%); mp 128 °C; IR (KBr) $\nu$ 2160 (CN), 1635 $cm^{-1}$ (C=O); $^1H$ NMR ($CDCl_3$) $\delta$ 1.33 (t, 18 H, 6 $CH_3$), 1.97 (m, 4 H, 2 $CH_2$), 3.32 (q, 12 H, 6 $NCH_2$), 3.67 (s, 6 H, 2 $OCH_3$), 4.55 (m, 4 H, 2 $CH_2N$-ring), 8.83 (br s, 2 H, 2 NH); $^{13}C$ NMR (100.5 MHz, $CDCl_3$) $\delta$ 8.28 ($CH_3$), 26.04 ($CH_2$), 44.26 (=C), 45.73 ($NCH_2$), 46.75 ($CH_2N$-ring), 50.16 ($OCH_3$), 123.86 (CN), 153.46 (=C), 169.06 (C=O). Anal. Calcd for $C_{26}H_{46}N_{12}O_4$: C, 52.86; H, 7.85; N, 28.45. Found: C, 52.67; H, 7.65; N, 28.21.